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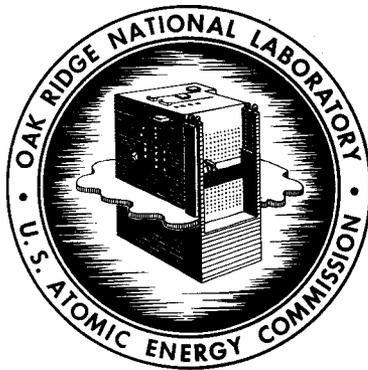
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SUMMARY OF THE KILOROD PROJECT - A  
SEMIREMOTE 10-KG/DAY DEMONSTRATION OF  
 $^{233}\text{UO}_2\text{-ThO}_2$  FUEL-ELEMENT FABRICATION BY THE  
ORNL SOL-GEL VIBRATORY-COMPACTION METHOD

C. C. Haws  
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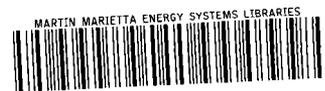
CHEMICAL TECHNOLOGY DIVISION  
METALS AND CERAMICS DIVISION

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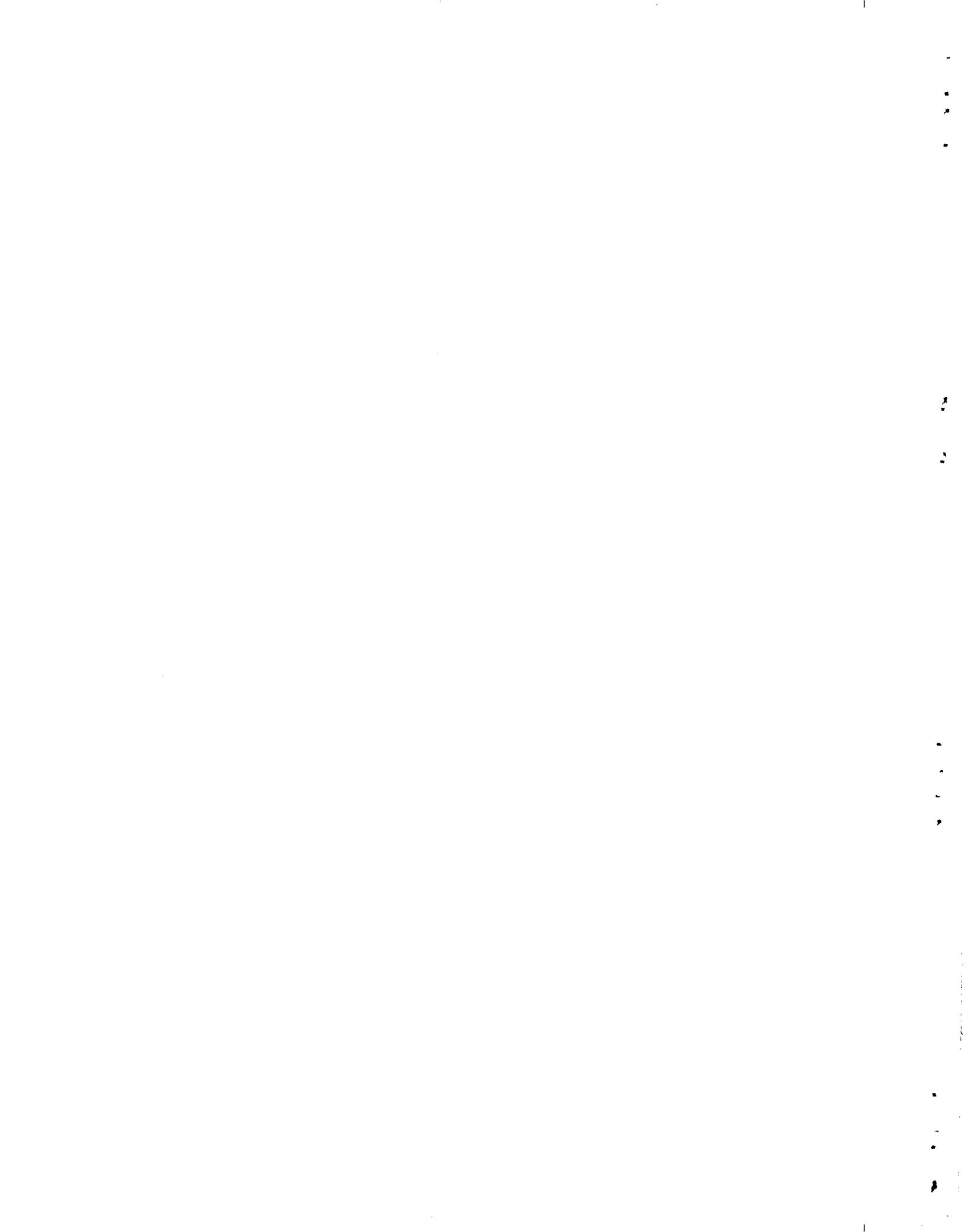
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AUGUST 1965

OAK RIDGE NATIONAL LABORATORY  
Oak Ridge, Tennessee  
operated by  
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SUMMARY OF THE KILOROD PROJECT - A SEMIREMOTE  
10-KG/DAY DEMONSTRATION OF  $^{233}\text{UO}_2\text{-ThO}_2$  FUEL-ELEMENT  
FABRICATION BY THE ORNL SOL-GEL VIBRATORY-COMPACTION METHOD

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1. ABSTRACT

Heretofore, the development of a reactor fuel cycle based on thorium and  $^{233}\text{U}$  had been hindered by radioactivity resulting from the  $^{232}\text{U}$  decay daughter products normally present in  $^{233}\text{U}$ . Because of this associated activity, an economical thorium- $^{233}\text{U}$  fuel cycle requires rapid, simple chemical and mechanical processes easily adaptable by nature to remote operation. The ORNL-developed sol-gel process for preparing granular, mixed oxides of thorium and uranium uniquely meets this requirement. A complete system for making fuel elements is obtained by coupling the sol-gel process with vibratory-compaction loading of fuel tubes. During the past year an intermediate-scale demonstration (10 kg a day) showed the feasibility of this combination of sol-gel and vibratory compaction. During this demonstration, more than 1 metric ton of 3%  $^{233}\text{UO}_2$  - 97%  $\text{ThO}_2$  solids were prepared. Approximately 1000 fuel rods (hence the name Kilorod Program) were fabricated from the solids to fill a request of the Brookhaven National Laboratory.

The Kilorod Operation was made up of three straightforward steps: (1) preparation of feed materials, (2) the sol-gel process, and (3) fuel-rod fabrication. In the preparation of feed materials, the  $^{232}\text{U}$  daughter products were removed from the  $^{233}\text{U}$  by a single-cycle solvent extraction process, and thorium nitrate crystals were converted to a dispersible  $\text{ThO}_2$  under a superheated steam atmosphere at 450 to 500°C. In the sol-gel process,  $\text{UO}_2(\text{NO}_3)_2$  and  $\text{ThO}_2$  feed stocks are blended at 80°C to form a stable sol (3%  $^{233}\text{UO}_2$  - 97%  $\text{ThO}_2$ ). The sol is dried to a gel at 80°C and then calcined and reduced at 1150°C to produce a sintered, fragmented  $\text{UO}_2\text{-ThO}_2$  product. Fuel rods are then fabricated by crushing the sintered solids and screening the solids through a 6-mesh onto a 16-mesh screen. The remainder of the solids are ball-milled to a powder of "smeared" size distribution. These powders are then blended in proper proportions, loaded into Zircaloy tubes by vibratory compaction, and the rod end-fixture is welded into place. The completed fuel rod is then inspected to ensure concentricity, straightness, weld integrity; finally it is decontaminated.

All mechanical and chemical processes of the Kilorod Program behaved as expected. After the startup period,

equipment-repair frequency was low. Both feed-preparation operations realized 100% on-stream efficiency. On-stream efficiency was 90% for the sol-gel operation for the entire operating period and 80% for the rod-fabrication equipment after startup. The latter two are particularly good for directly maintained high-level radiochemical operations.

Fifty kilograms of  $^{233}\text{U}$  (containing 38 ppm  $^{232}\text{U}$ ) were purified by a new solvent extraction system (2-1/2% di-sec-butyl phenyl phosphonate in diethylbenzene). The extracted product met desired chemical specifications for removal of  $^{232}\text{U}$  daughter products.

More than 1200 kg of  $\text{ThO}_2$  suitable for use in the sol-gel part of the process were prepared by hydrothermal denitration. Over 1 metric ton of  $^{233}\text{UO}_2\text{-ThO}_2$  meeting established chemical specifications was prepared by the sol-gel process during the program.

Nine hundred rods, each containing 890 g of mixed oxide, and 200 rods, each containing 310 g of the same mixed oxide were prepared. The fuel column in these rods averaged 89.6% of theoretical density, and variations of density were held to within  $\pm 2\%$  of a median value along the active length of the fuel column. The entire process may readily be scaled to larger operations.

Experience was obtained in the handling of large quantities of  $^{233}\text{U}$ , and radiation data necessary for the design of larger facilities and higher activity levels were collected. Radiation exposure to workers in routine operations was limited to a tenth of the permissible levels. Indeed, a single batch, approximately 100 times more radioactive than the routine Kilorod batch, was prepared to measure exposures to workers at extreme levels of activity. In this safety test, aged  $^{233}\text{U}$  was used to simulate 14-day-old feed solution containing 800 ppm of  $^{232}\text{U}$ . The resulting exposures, using normal Kilorod operating procedures, were at worst eight times higher than when the customary Kilorod  $^{233}\text{U}$  feed solutions had been used. Thus, the present equipment, procedures, and working areas can provide radiological safety at much higher concentrations of  $^{232}\text{U}$  than that used in the present program.

---

## 2. INTRODUCTION

This summary report describes a successful engineering demonstration of the sol-gel, vibratory-compaction process developed here, and its application to the production of 1100 fuel rods loaded with ceramic-grade thoria-urania for use at Brookhaven National Laboratory. This demonstration, conducted in the Kilorod Facility, represents the first

remote fabrication of ceramic-oxide fuels. The facility was shielded to protect the operators from the gamma radiation associated with  $^{232}\text{U}$  and  $^{228}\text{Th}$ , the contaminants in  $^{233}\text{U}$  fuels.

The sol-gel portion of the process, while developed primarily for recycling thorium reactor fuels, promises to become an almost universal method for preparing ceramic fuels because of its simplicity and flexibility. In recycling  $^{233}\text{U}$  and thorium fuels by the sol-gel process, workers can be more easily protected from the gamma rays emitted by the decay products of  $^{232}\text{U}$  and  $^{228}\text{Th}$ . Conventional methods, besides being more complex and less versatile, require much higher calcination temperatures to densify the product and are not so adaptable to remote operation in a shielded facility.

The Babcock and Wilcox Company has installed the sol-gel portion of the process in their pilot plant at Lynchburg, Virginia, for producing  $^{233}\text{U}$ -Th recycle fuels. They will use this process along with vibratory packing for recycling such fuels to the Spectral-Shift-Control Reactor, for example.

Since about a thousand fuel rods were to be made, the program was called the "Kilorod Program." The facility contained equipment to:

1. purify  $^{233}\text{U}$  by solvent extraction,
2. prepare a mixed thorium-uranium dioxide by the sol-gel process,
3. size the powdered oxide,
4. load it into tubes by vibratory compaction,
5. weld the end plugs, and inspect the finished rods.

This summary report on the engineering-scale demonstration of the sol-gel and rod-fabrication processes includes the following: description of the pilot plant and procedures, operating experience, radiation experience, conclusions and recommendations, plus an Appendix, where certain detailed information can be found.

### 3. DESCRIPTION OF THE KILOROD PILOT PLANT

The flowsheet for the Kilorod complex is shown in Fig. 1. Except for the denitration operation, which is located in a separate building

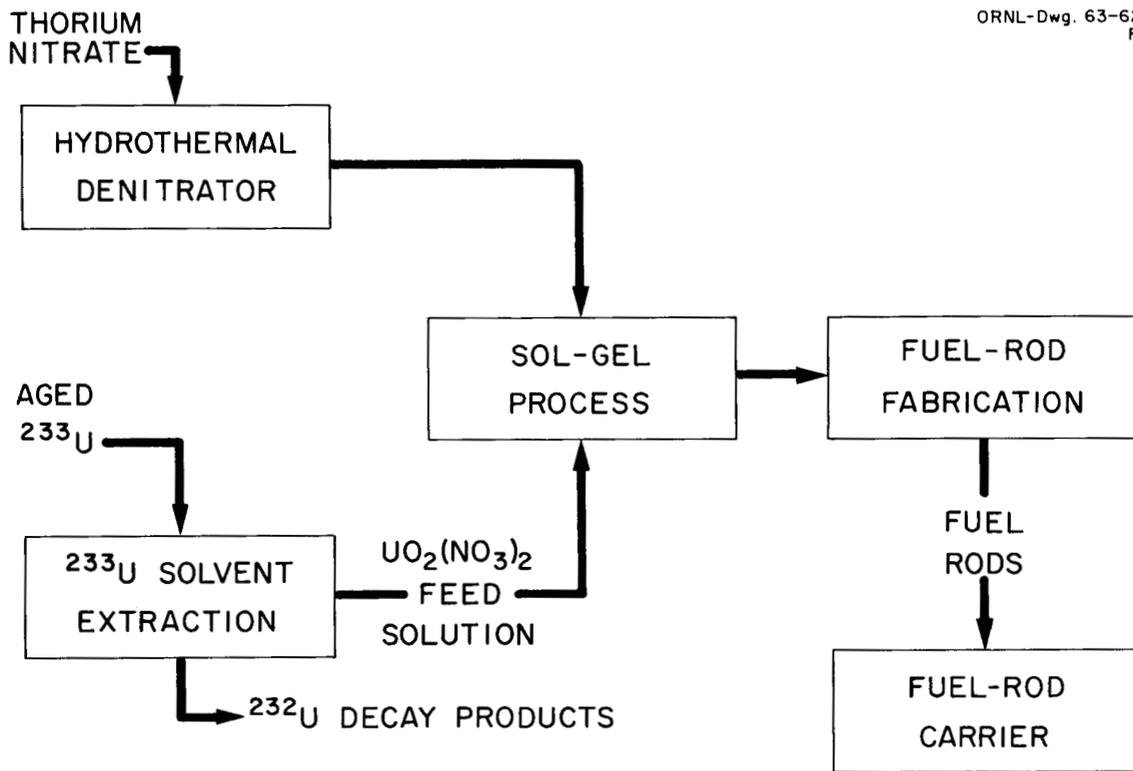


Fig. 1. Flowsheet for Kilorod Facility.

(4501), all other units are located in the 3019 Building of the Laboratory. To simplify discussion, the facility will be visualized as being composed of three parts, as shown on the flowsheet. These are:

1. Feed preparation: hydrothermal denitration and solvent extraction.
2. The sol-gel process: preparation of the sintered solids.
3. The rod-fabrication operation: powder preparation and rod fabrication.

### 3.1 General Flowsheets and Descriptions of Process and Equipment

#### 3.1.1 Floor Plan and Design Features of the Sol-Gel and Rod-Fabrication Units

##### 3.1.1.1 Radiation-Control Factors and Their Effects on Design. -

Several factors concerning adequate radiological protection for the workers were considered in selecting a design for the Kilorod Facility. Since  $^{233}\text{U}$  is a copious alpha emitter, containment requirements for  $^{233}\text{U}$  are essentially the same as for plutonium. Additionally,  $^{232}\text{U}$  is always produced in the preparation of  $^{233}\text{U}$ , and the penetrating gamma emissions of the daughters of  $^{232}\text{U}$  present a further hazard (Fig. 2).<sup>1</sup> The daughters can be removed by solvent extraction but grow back in; thus, the gamma-emission rate increases rapidly from the time of purification, making time a factor in processing. Last, a weekly dose of 1500 millirems to the hands and arms was permitted, much higher than can be tolerated (100 millirems) for whole-body exposures.<sup>2</sup>

Models incorporating the above design criteria were studied, and the present design selected.<sup>3</sup> The resulting facility is best described as a shielded glove-box operation. In this operation, higher doses are taken by intent on the hands and arms than on the body. A 20-day time limitation from solvent extraction to preparation of the last sol-gel batch of a given processing campaign appeared reasonable from the aforementioned calculations.<sup>4</sup> Experience showed that this design and this time limitation were conservative, as will be seen.

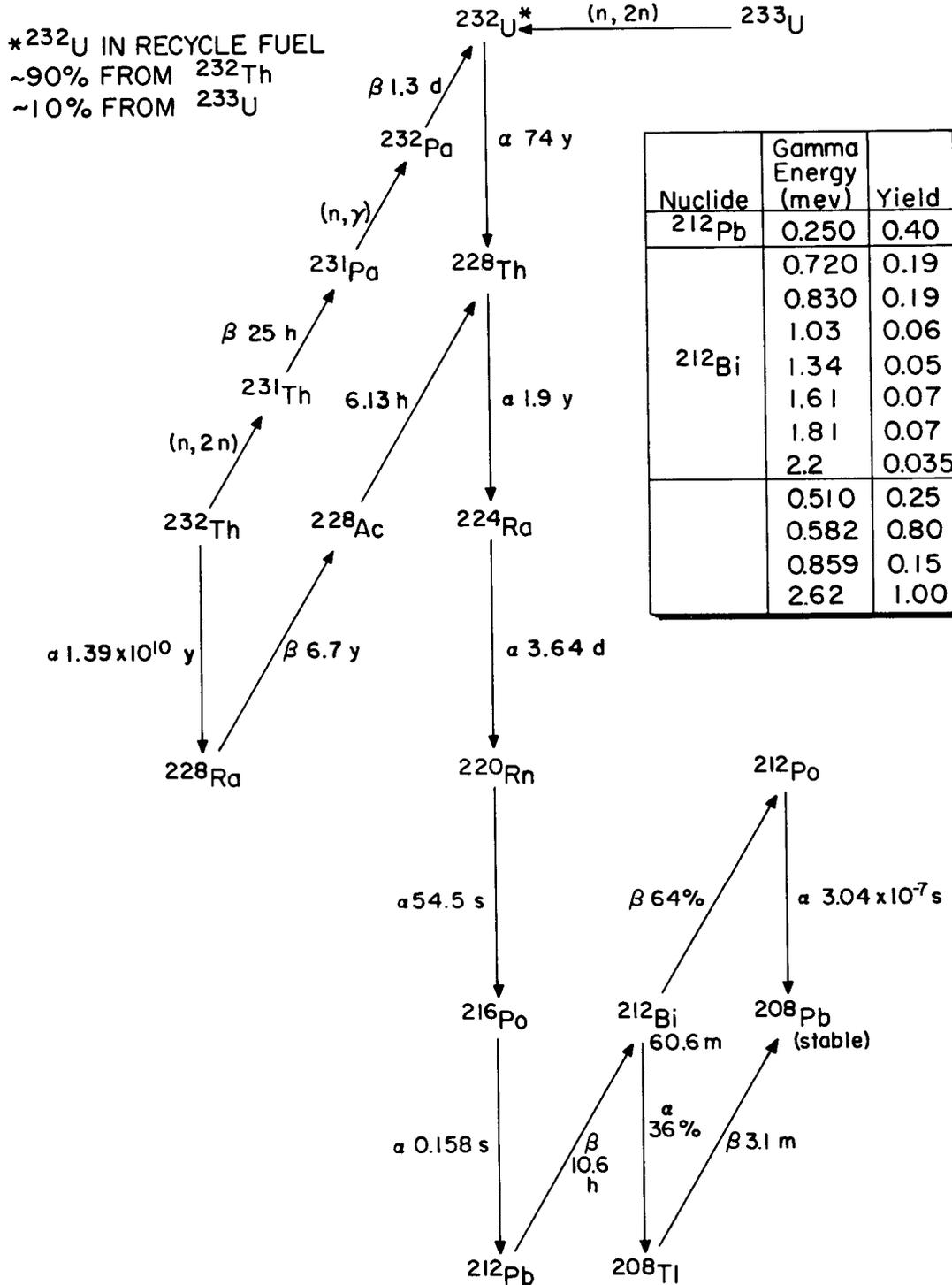


Fig. 2. Decay Chain and Gamma Activity in ThO<sub>2</sub>-<sup>233</sup>UO<sub>2</sub> Fuels.

3.1.1.2 The Kilorod Design and Radiation-Control Policy. - A single cell (No. 4) of Building 3019 was renovated to receive the pilot plant equipment. Two balconies were erected, and processing cubicles were built on each balcony and the main floor (Fig. 3). All the high-level alpha-gamma work was done in these cubicles. Alpha containment is effected by lining the inside of all processing cubicles with 1/8-in. mild-steel sheet. Shielding from the gamma rays is provided by either 4-1/2-in. steel plate, or 8-in. barytes concrete block. Gloved hands or Castle-type manipulators are used for all operations. High-density glass windows were provided for observing operations at all work (glove) stations. Conventional "bag-out" stations were installed for introducing or removing materials from the cubicles. Retractable lead shields were provided for closing glove-port openings when gloves were not in use. Fire shields were also provided to protect the gloves during periods when work was not underway. These shields were set in place on the inside surface of the alpha membrane as the glove was removed from the hand.

In the design and location of the equipment for this high-level alpha-gamma operation, attention was given to the repair of equipment considered susceptible to mechanical failure. Accordingly, equipment considered susceptible is located near a glove and/or bag-out station, or such a station is provided. In this way, replacement parts could be "bagged" into the contaminated area, and replacement or repair can be carried out without making entry into the cubicle. The design time required for this was well spent since minor maintenance (replacement of pH electrodes, thermocouples, lights, or adjustment of limit switches) could be done promptly and as needed without requiring a plant shutdown.

### 3.1.2 Preparation of Feed Materials Entering the Sol-Gel Process

In essence, preparing the feed material consists of two processes:  $\text{ThO}_2$  powder is prepared by the hydrothermal denitration of thorium nitrate crystals, and  $^{233}\text{U}$  as a nitrate solution is freed of  $^{232}\text{U}$  daughter products by solvent extraction.

3.1.2.1 Thorium Oxide Feed Preparation: An Integral Part of the Sol-Gel Process and the First Step Toward Preparing the Mixed Oxides ( $\text{ThO}_2\text{-UO}_2$ ) Needed for Vibratory-Compaction Feed. - The thorium oxide feed is prepared by hydrothermal denitration of thorium nitrate tetrahydrate (TNT) in a horizontal rotary denitrator. The calciner shell in which the

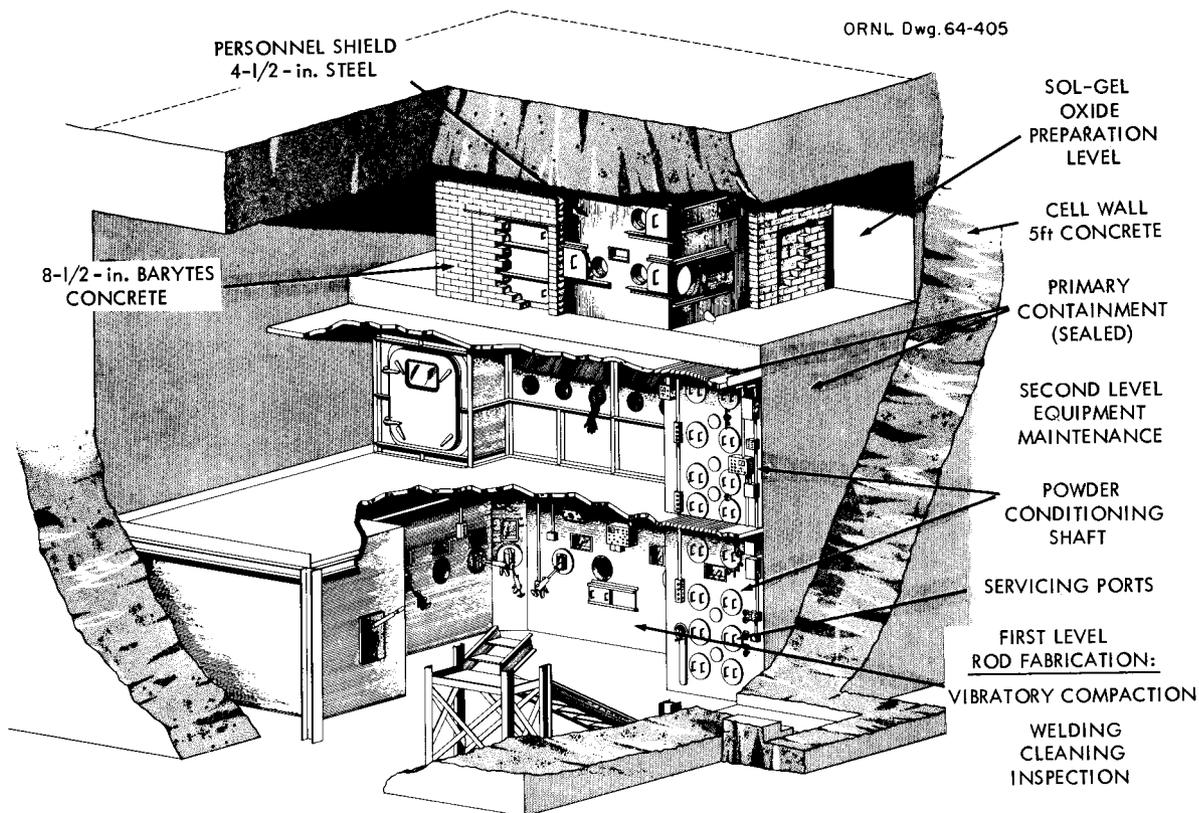


Fig. 3. Kilorod Solids-Preparation and Rod-Fabrication Facility. The process flow begins at the top left with sol blending, flows to the right where the solids are fired, passes down the vertical shaft as the powder is prepared, and across the bottom as the rods are loaded and tested.

denitration takes place, with its clamshell heaters, is shown before assembly (Fig. 4). The heaters and the calciner shell are shown in final assembly (Fig. 5). Note that the calciner is shown tilted to the unloading position. The TNT charge (30 kg) is loaded, and the 13.5 kg of  $\text{ThO}_2$  product is discharged through the same end of the calciner. While operating, the shell turns on the trunnions at the end of the shell. Denitration is accomplished in 5-1/2 hr at 450-500°C by superheated steam.<sup>a</sup> The product is a free-flowing, off-white powder, containing about 95%  $\text{ThO}_2$ . The remainder is water and nitric acid. Since this unit was scaled up from a smaller (2.5-kg) one without difficulty, further scaleup could probably be accomplished with similar ease.

Great care was required to meet the U/Th ratio specification (see Sec 3.1.5.3 for definition). Thus, a batch blender was installed to provide large quantities of powder having uniform properties, thereby facilitating control of the U/Th ratio. The blender was simply a baffled rotating-drum that accepted a 70-kg charge of  $\text{ThO}_2$ . This charge was made up of about five denitrator batches of about 13.5 kg each.

After blending, the powder is sampled and weighed into seven 10-kg (+10 g) batches. These batches are bagged individually into the sol-gel cubicle as one of the two feed materials.

In the forthcoming discussion, the term "sol-gel" will frequently be used as though the entire sol-gel process were conducted within the high-level alpha cubicle alone. It is re-emphasized that denitration is an integral step of the sol-gel process, although it was done in another area.

3.1.2.2 Purification of  $^{233}\text{U}$  Feed Stocks by Solvent Extraction: Daughter Products of  $^{232}\text{U}$  Must be Removed to Permit Gloved Operation of the Kilorod Equipment. - Unlike the denitration operation, the solvent extraction system (SX) is not in the strictest sense a portion of the sol-gel process; however, it was a vital auxiliary. The facility for the purification of the  $^{233}\text{U}$  was provided by minor modification of the Thorex Pilot Plant in cells 5, 6, and 7 of Building 3019.

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<sup>a</sup>This is an "indicated" temperature obtained by thermocouple located between clamshell heaters and calciner shell. Temperature inside of calciner shell is estimated to be 75°C lower.

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Fig. 4. Denitrator Shell and Clamshell Heaters.

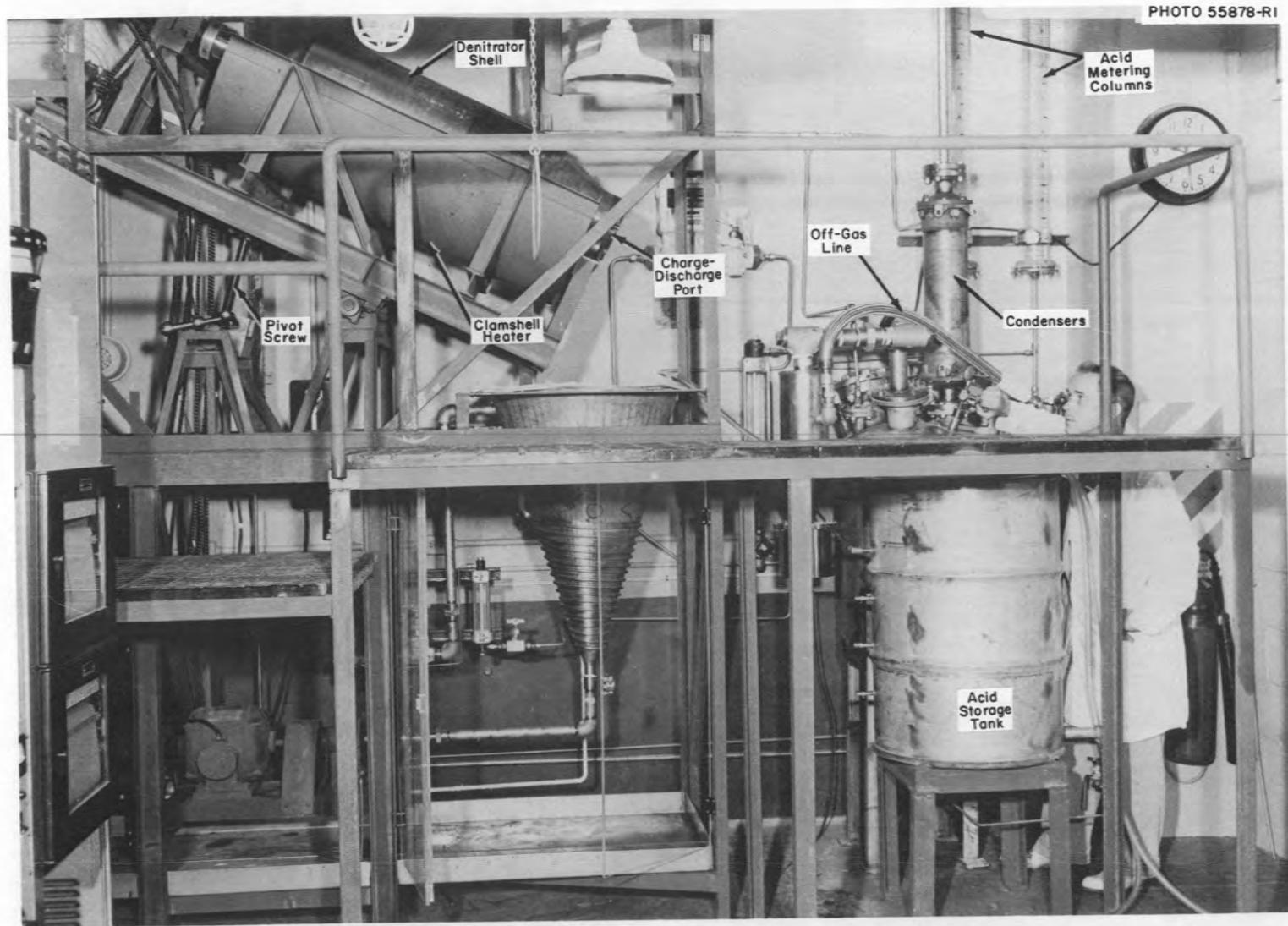


Fig. 5. Rotary Denitrator in the Unloading Position.

The  $^{233}\text{U}$  used in this program was produced under reactor conditions that produced 38 ppm of  $^{232}\text{U}$ . As this  $^{233}\text{U}$  had been stored for a number of years, the  $^{232}\text{U}$  decay products had built up to significant levels, and intense gamma activity was associated with the material. It was therefore necessary to remove these gamma emitters by solvent extraction before the  $^{233}\text{U}$  could be processed in gloved operations.

The impure  $^{233}\text{U}$  used as SX feed came from nitrate solutions of varying concentrations, and from metal fragments. The fragments were dissolved in a boiling mixture of 1.4 M thorium nitrate solution containing 4 moles of free nitric acid per liter (Fig. 6). Four kilograms of  $^{233}\text{U}$  metal were charged to the dissolver vessel each time. Criticality control in the geometrically unsafe tank was ensured by:

1. the presence of thorium, which provided a  $^{233}\text{U}/\text{Th}$  ratio of 0.025, and by
2. maintaining the volume in the dissolver vessel such that the "eversafe" concentration of  $^{233}\text{U}$  in light water could never be exceeded.

The resulting solution was then adjusted to terminal feed conditions by diluting with water. The procedure employing uranyl nitrate solution feed material consisted in the blending of this solution, in small increments, with thorium nitrate solution whose concentration was 400 g/liter.

The uranium purification system utilized a battery of two pulsed columns placed in series (Fig. 7). Feed from the adjustment tank is pumped into the middle of a 38-ft by 5-in.-diam pulsed column (19 ft each of scrub and extraction sections). The extractant, containing 2.5% di-sec-butyl phenyl phosphonate (DSBPP) in a diethylbenzene (DEB) diluent, extracts the uranium into the organic phase. The extract is then scrubbed in the upper section of the column with a 0.8 M  $\text{Al}(\text{NO}_3)_3$  solution, acid deficient ( $-0.4 \text{ M H}^+$ ) to remove entrained thorium and ionic contamination. The scrubbed organic is then routed to a strip column where the uranium is removed from the organic phase with demineralized water. The strip column is a 5-in.-diam column, 20 ft high. The uranium product solution, containing 10 g/liter  $^{233}\text{U}$  is then transferred through a static-diluent wash column to remove trace quantities of organic prior to solution buildown.

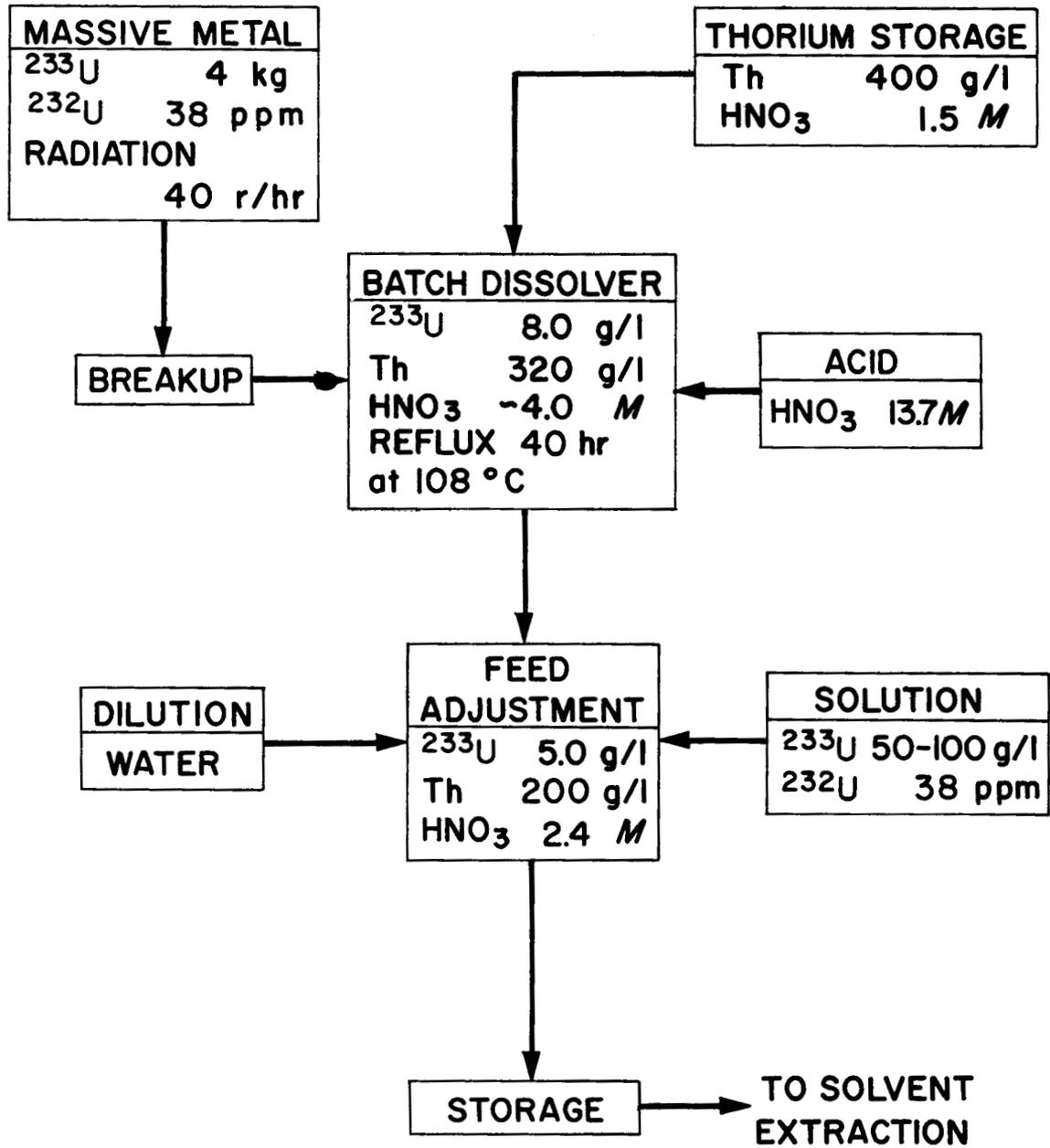


Fig. 6. Flowsheet for Preparing Feed for the Solvent Extraction System.

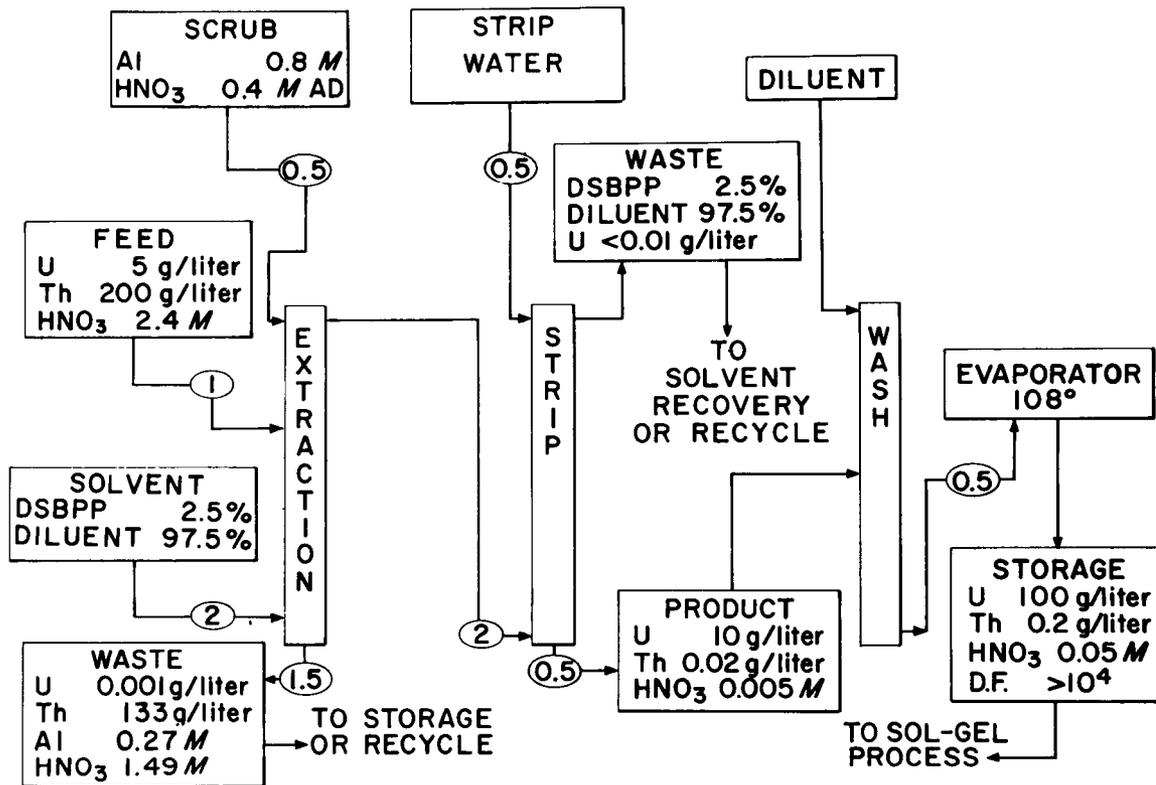


Fig. 7. Flowsheet for Purifying <sup>233</sup>U.

Final concentration to 100 g/liter is done in a criticality-proof evaporator. The tail-end product is then stored in the evaporator-product storage tank (R35) and withdrawn as needed in the sol-gel process. Spent solvent leaving the process is collected batchwise, treated with 0.2 M  $\text{Na}_2\text{CO}_3$ , and reused.

The majority of the vessels used for chemical processing are not of criticality-safe configuration; consequently, several important operational and equipment modifications were made. The total mass of uranium within the facility was limited to 8.5 kg. Solutions were maintained below the  $^{233}\text{U}$  ever-safe concentration of less than 10 g/liter by flowrate adjustments for aqueous streams and by chemical saturation for organic streams. The only stream that exceeded this value was the final-product stream (100 g/liter), which was boiled down in a criticality-proof evaporator - 5-in.-diam pipe surrounded by a 6-in.-diam steam jacket.

In addition to mass and concentration control, the feed extraction column and raffinate catch-tanks contained sufficient thorium to yield a  $^{233}\text{U}/\text{Th}$  ratio of 0.025. The thorium also served as a salting agent for the extraction.

As a final safety device, Pyrex glass rings containing 4% B were placed in important process vessels. Nuclear hazards exist in the expanded 8-to 16-in. sections of the disengaging sections of the pulsed columns and in large-diameter vessels. These sections and vessels were packed with rings, and an x-ray procedure was developed to ascertain their location and condition.

### 3.1.3 Sol-Gel Process Equipment and Operating Procedure

Three operations of the sol-gel process were conducted in the high-level alpha-gamma containment area. These are:

1. blending of the sol,
2. evaporating (or drying) the sol to a gel, and
3. calcining-reducing-sintering the gel to the final product.

The equipment described here was installed within this 7-ft by 10-ft by 8-ft-high containment area as shown in Fig. 8.

3.1.3.1 Description of Sol-Gel Process Equipment and Process Materials. - The pilot plant equipment and some of the process intermediates are:

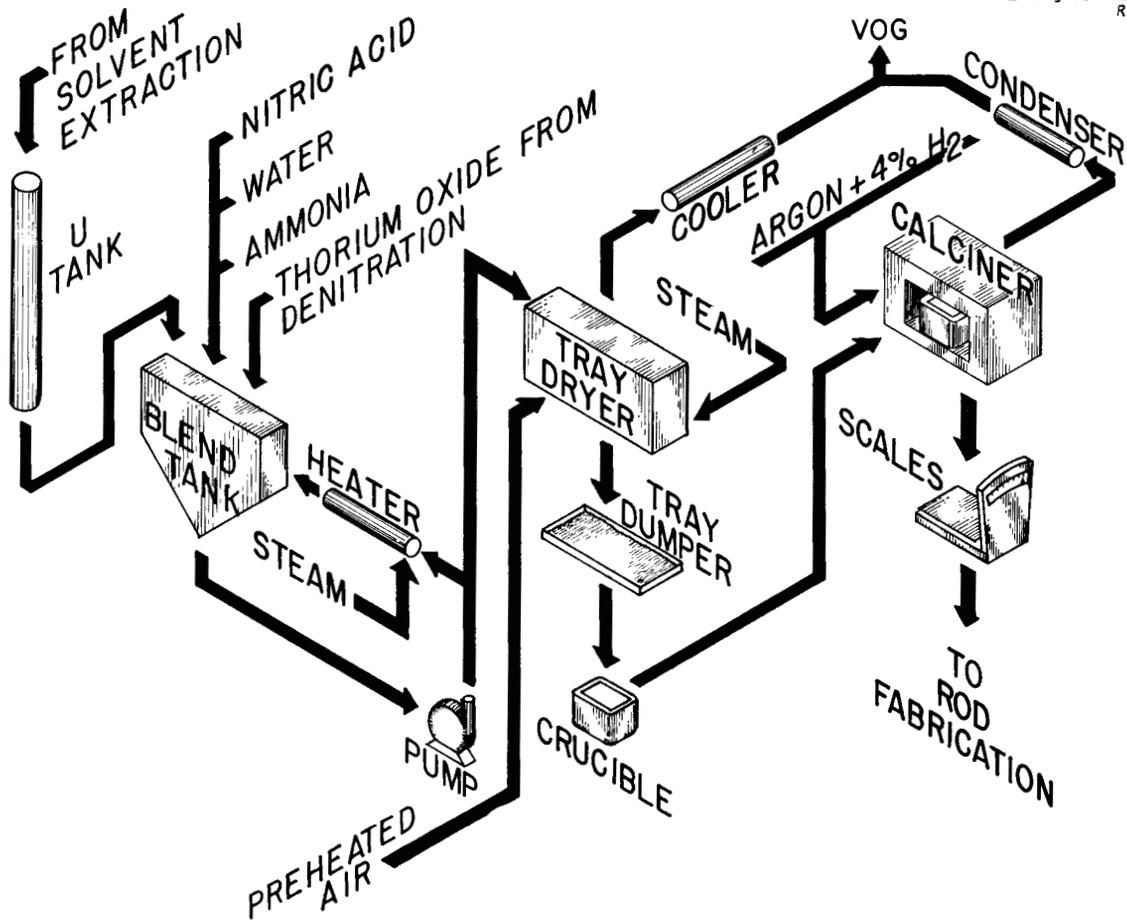


Fig. 8. Sol-Gel Process.

1. The criticality-safe, slab-type blend tank used in prepilot-plant work is shown in Fig. 9. The tank was built with a plate-glass wall to permit viewing of the mixing and possible buildup of material above the water line. The recirculating-mixing-heating of the sol is well illustrated in this figure. At the time the picture was taken, the uranyl nitrate solution had just been added to the tank and the pump started. The pump is mounted on a tight, external, closed pipe loop and provides for recirculation and agitation. Thoria is added through the funnel (partially shown at the top of the figure) in the next step of the blending operation.

2. The pilot-plant blend tank is shown in Fig. 10. It is identical in major features to the tank just shown, except for the plate-glass window. Gage glasses are used instead, and internal lighting is provided. Note the relative size and location of the funnel for charging the powdered thoria. Note also that the blend-tank pump suction connects to the bottom flange on the blend tank and that the return stream from the pump re-enters the tank at a nozzle on the straight side. The blend tank is heated by steam jacketing a section of this pump loop.

3. The tray dryer is shown on Fig. 11. Figure 12 shows a tray of dried gel being removed from the tray dryer. The dried gel has broken into fragments no more than 1/2 in. in the greatest dimension.

4. The calciner used in the pilot plant is shown in Fig. 13. This furnace is a commercial unit used in heat-treating small tools, altered to a minor extent to permit operation within the process cubicle. The heating element is Kanthal A-1. A sample of typical fired product is shown in Fig. 14.

A water-cooling jacket is provided on the top, bottom and two sides. This cooling is provided to lower the quantity of heat escaping to the cubicle, thereby helping to hold the cubicle temperature to a level permitting comfortable use of the rubber gloves. A cooling circuit, with air as the coolant, was also specified in the purchase of the calciner, being provided to remove heat from within the massive brickwork of the furnace. This circuit is necessary if the 24-hr time cycle originally specified, and a 100°C (max.) product withdrawal temperature, are to be met. The circuit was not properly designed and did not perform as specified. Thus, the

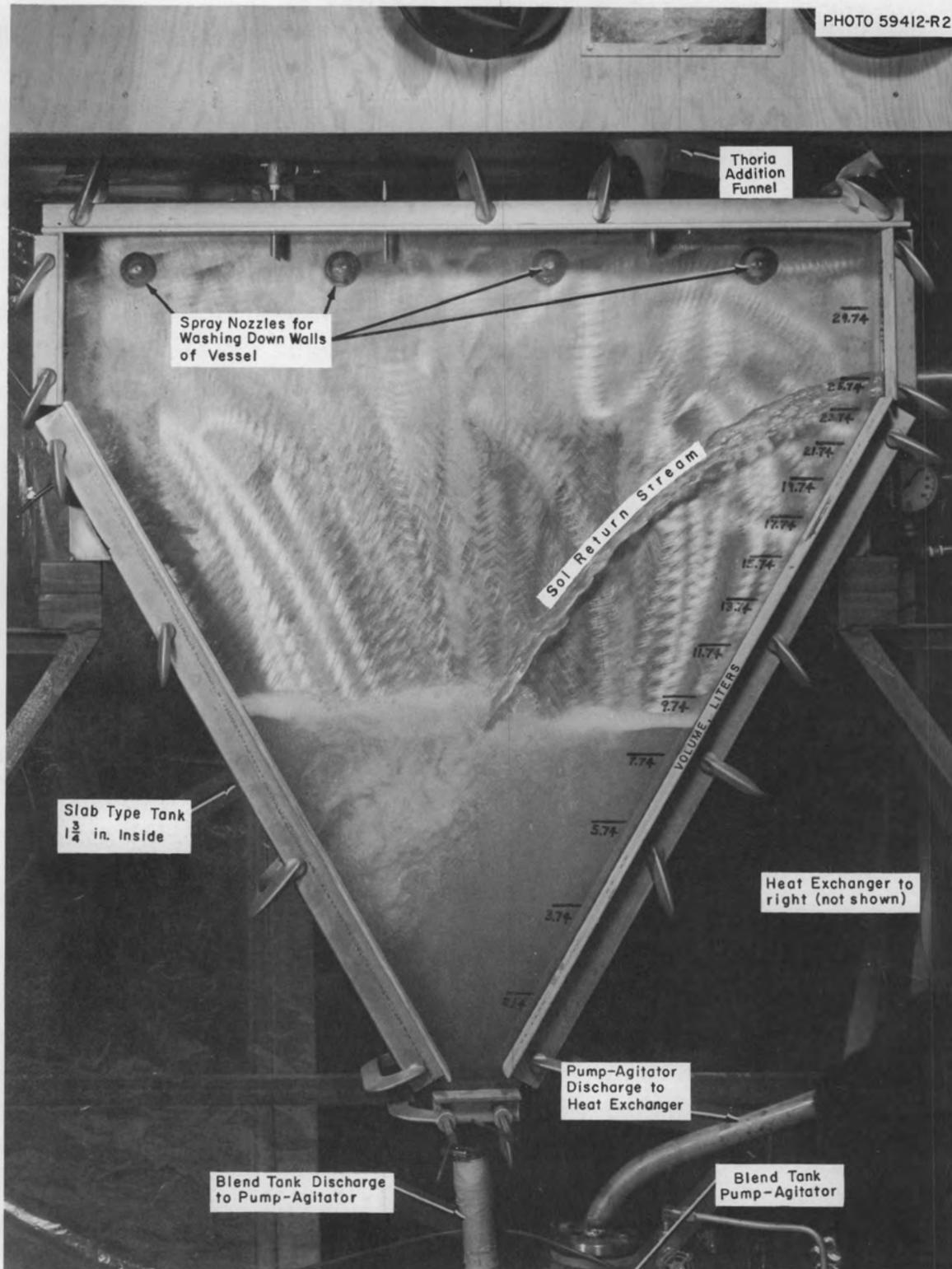


Fig. 9. Cold-Testing Blend Tank for Unit Operations Work.  
 At this point in the sol preparation, the uranyl nitrate solution is in the tank and being heated, ready for thoria addition.

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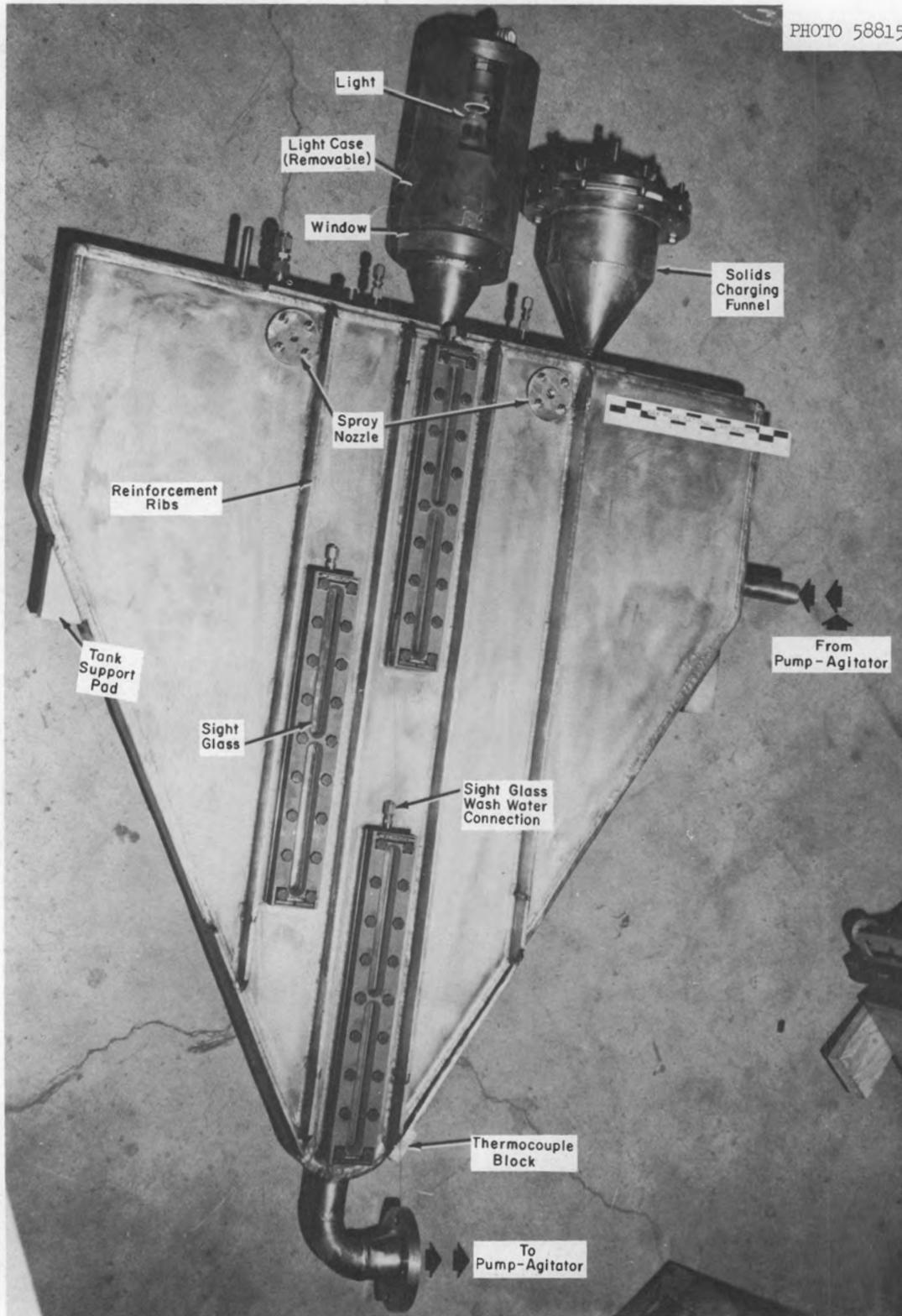


Fig. 10. Pilot Plant Blend Tank.

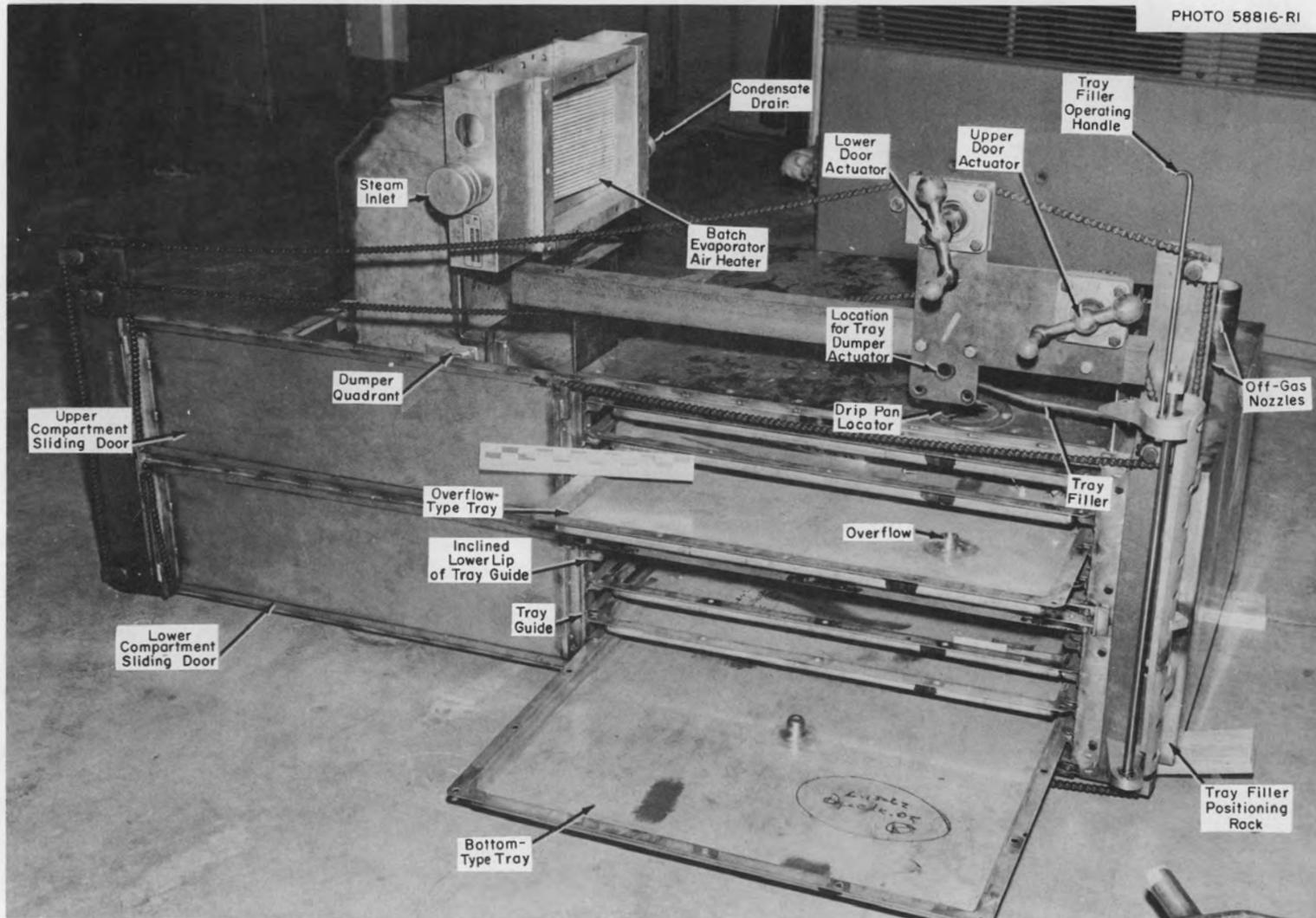


Fig. 11. Batch Evaporator with Trays Partially Pulled.

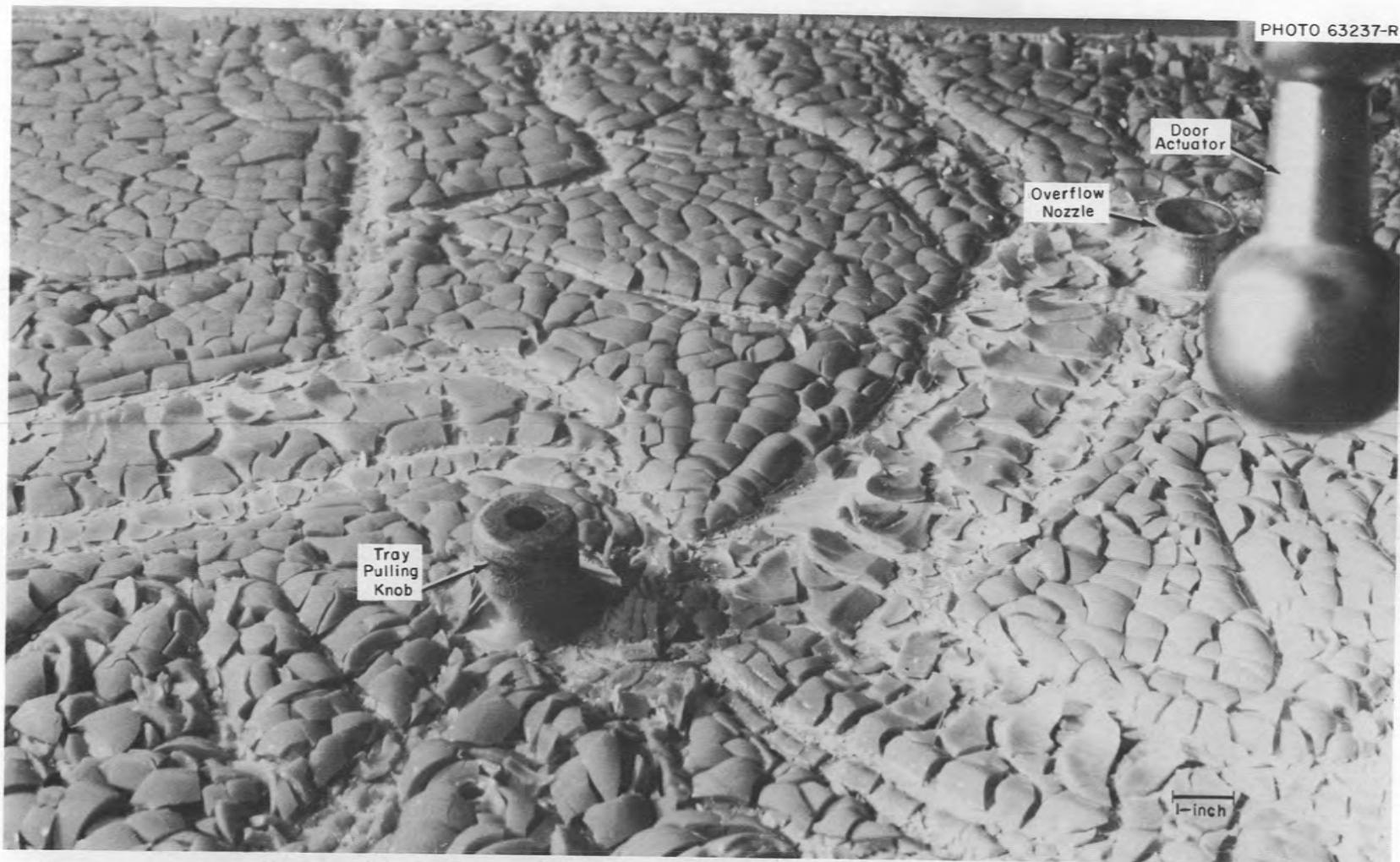


Fig. 12. Evaporator Tray Containing Dried Gel, as Seen Through Cubicle-Shielding Window.

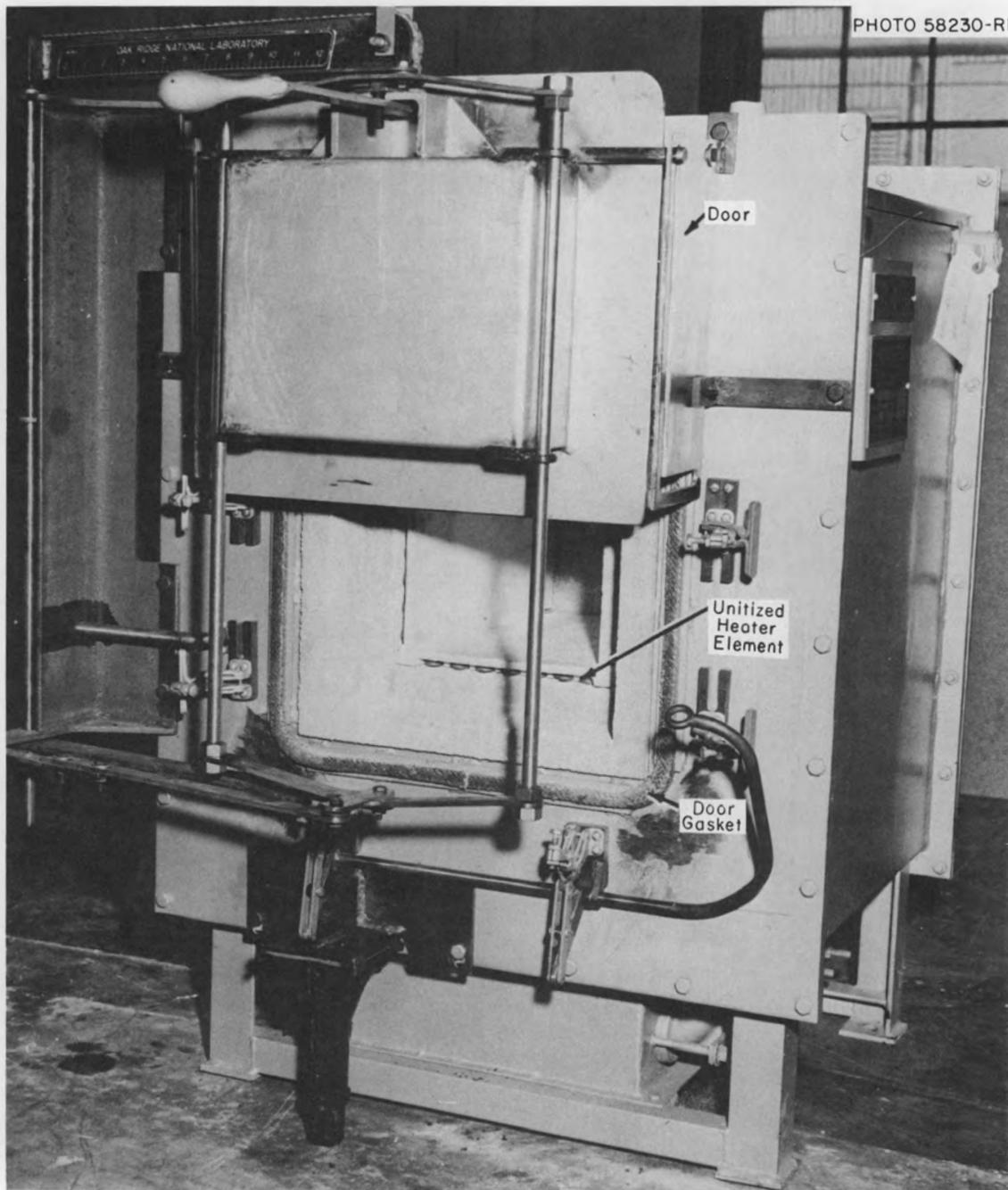


Fig. 13. Batch Calciner, with Door Raised. Door mounting and latches permit operation by one gloved hand.

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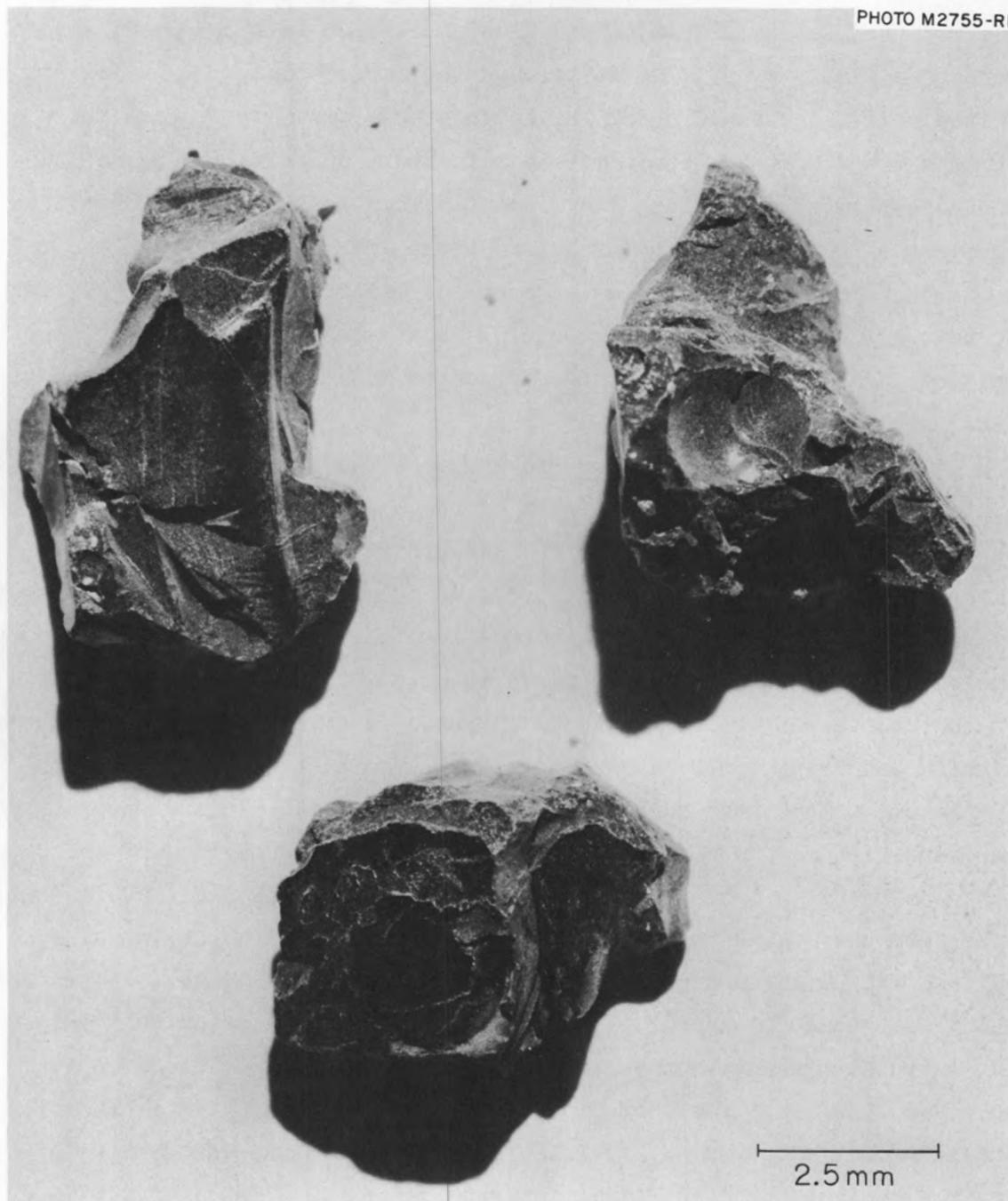


Fig. 14. Sintered Sol-Gel Product. Shown here are typical shapes of calciner product.

furnace charge had to be removed at 350°C instead of the 100°C originally desired (see Sec 4.1.2.2.2). The heating element is a one-piece assembly, removable simply by pulling it through the furnace door. This feature worked well; one could enter the cubicle and remove or replace the element in less than 10 min. Repair of the refractory opposite the burned out area was necessary after pulling the element. This repair took 1-2 hr; thus, a complete element replacement required about 2 hr of exposure in the cubicle.

Minor revisions were also made at the Laboratory to permit the furnace to be operated in the sol-gel cubicle. For example, the door was counter-balanced, and the suspension was revised to make manipulation by one gloved hand possible.

3.1.3.2 Sol-Gel Operation Procedure. - The flowsheet given as Fig. 15 lists operating conditions for each of the high-level alpha steps, as well as the operating conditions for the denitrator.

Before blending the batch of sol, an accurately weighed 10-kg batch of denitrator product ( $\text{ThO}_2$ ) is bagged into the sol-gel cubicle. Accurately analyzed  $^{233}\text{U}$  feed solution is piped into the cubicle, and a calculated volume equivalent to the desired U/Th ratio is carefully measured in the uranium measuring, or U, tank (Fig. 16). A vernier-equipped telescope (cathetometer) mounted outside the cubicle is used to locate accurately the meniscus of the  $^{233}\text{U}$  feed solution in the calibrated section of the U tank.

The blending operation is started by transferring the  $^{233}\text{U}$  feed solution from the U tank to the blend tank. The blend-tank pump is started to agitate the batch, and steam is admitted to the steam heater. Nitrate (as  $\text{HNO}_3$ ) must then "be added" in such quantity that the "added  $\text{NO}_3^-$ " plus the  $\text{NO}_3^-$  already present in the uranyl nitrate (UNH) feed solution is equivalent to a  $\text{NO}_3^-/\text{ThO}_2$  mole ratio of 0.077<sup>(ref. 5)</sup>. At the U/Th ratio specified for the Kilorod product, a  $\text{NO}_3^-/\text{U}$  mole ratio of 2.5 in the UNH feed solution is roughly equivalent to an "added" nitrate ratio ( $\text{NO}_3^-/\text{ThO}_2$ ) of 0.077, and no  $\text{HNO}_3$  is added; thus the  $\leq 2.5 \text{ NO}_3^-/\text{U}$  ratio was established for SX product.

When the blend-tank temperature reaches 60°C, the thoria powder is added to the blend tank through the funnel at the top of the tank. During this addition, the batch temperature continues to rise until it reaches 80°C, where it is held. The batch is mixed for 30 min at 80°C after the

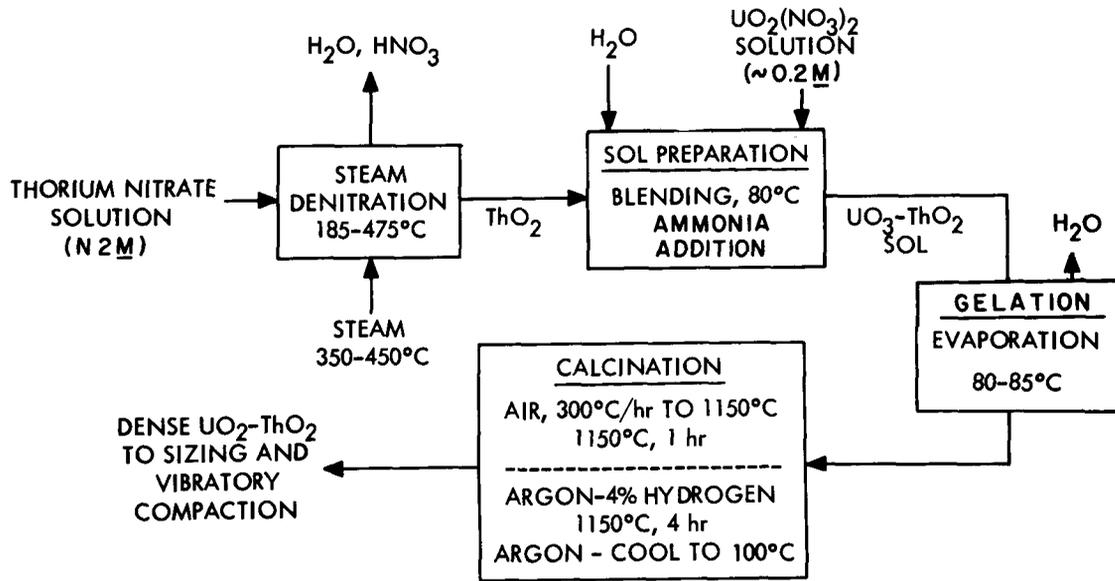


Fig. 15. Flowsheet for the Sol-Gel Process.

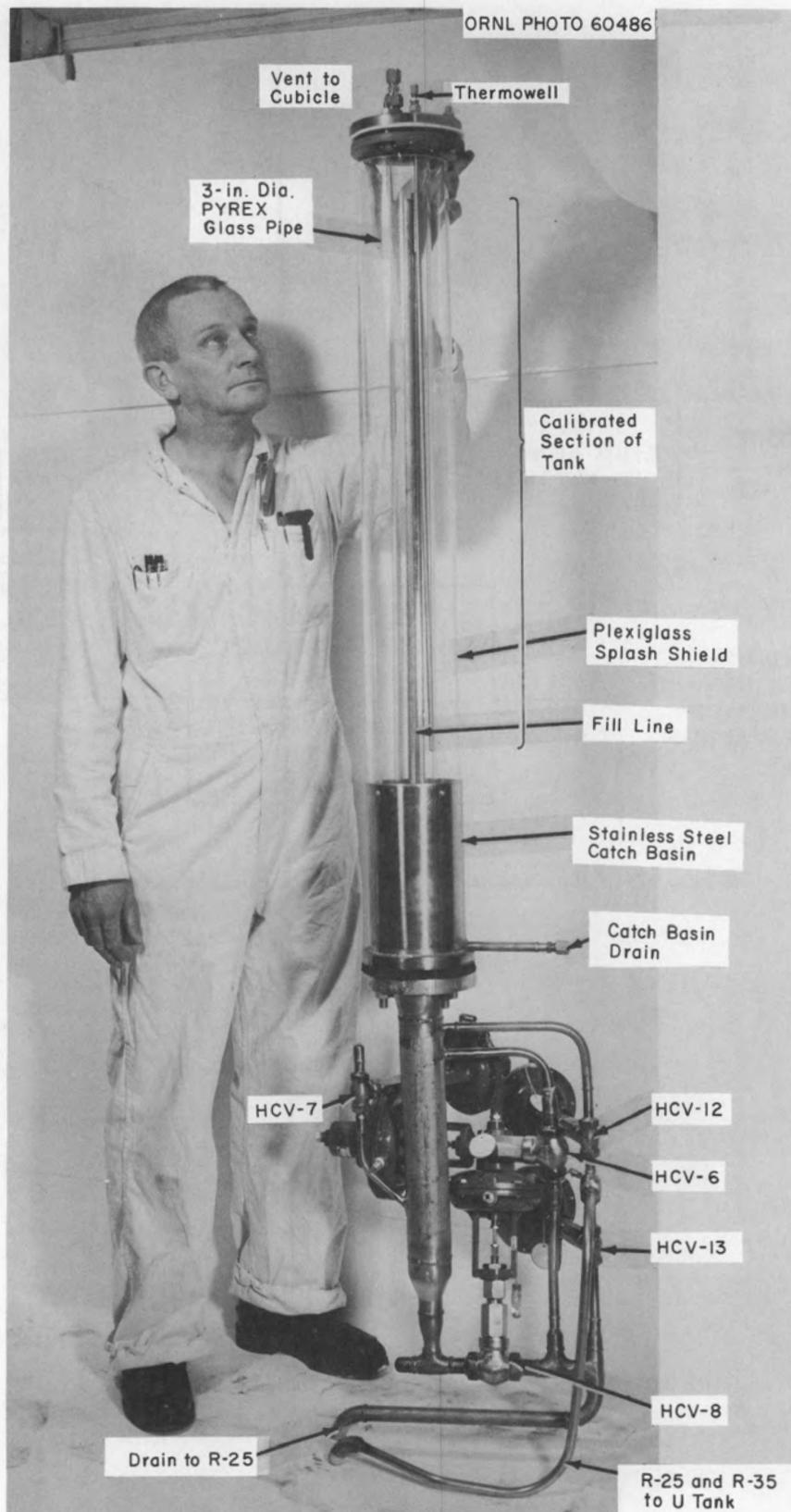


Fig. 16. Uranium-Measuring Tank.

thoria addition. Ammonium hydroxide is then added in an amount equivalent to 0.017 g-mole of  $\text{NH}_3$  per g-mole of  $\text{ThO}_2$ . After circulation is continued at 80°C for another 30 min, the batch is ready for sampling and transfer to the tray dryer.

The inherent latitude of all sol-gel operations is well illustrated by the nitric acid and ammonia additions just mentioned. First, in nitrate addition, no consideration need be given to the quantity of nitrate in the  $\text{ThO}_2$  feed. The  $\text{ThO}_2$  is sufficiently uniform, and process control sufficiently insensitive that the variation in nitrate concentration of the  $\text{ThO}_2$  may be ignored. The back-adjustment with ammonia need not be controlled precisely, either. For example, this adjustment is satisfactory over the  $\text{NH}_3/\text{ThO}_2$  mole ratio of 0.013 to 0.022, with 0.017 selected as a "middle-of-the-road" value. This broad control range actually allows some control of the crushing and grinding characteristics of the calciner product, because resistance to crushing and ball-milling increase with the amount of ammonia added.

The sol is dried at 80 to 95°C, using a 3/4-in. sol depth in the dryer trays. The drying time averages 30 hr. After drying, the batch is dumped into alumina saggars and loaded into the calciner.

The calciner may be charged at any temperature up to 350°C. After charging, the temperature is raised from room temperature to 1150°C in 4-1/2 hr. Air is purged through the calciner during this time. When the temperature reaches 1150°C, the calciner is flushed with argon for 30 min, and then the 4%  $\text{H}_2$  - 96% Ar atmosphere is established for reduction of the  $\text{U}_3\text{O}_8$  to  $\text{UO}_2$ . Four hours are required for reduction and sintering, after which the atmosphere is switched to pure argon, and the furnace power is turned off. The temperature of the furnace falls to 350°C under the argon blanket, and the crucibles are removed and immediately placed under an argon blanket until room temperature is reached. The next batch is loaded into the calciner immediately. The entire operating sequence of the furnace is accomplished by a program controller.

After being calcined, the batch is weighed and transferred to the rod-fabrication portion of the facility.

#### 3.1.4 Rod-Fabrication Facility, Equipment, and Process

The rod-fabrication portion of the facility occupies the lower two levels of the three-level Kilorod Facility (Fig. 17). Here, the three

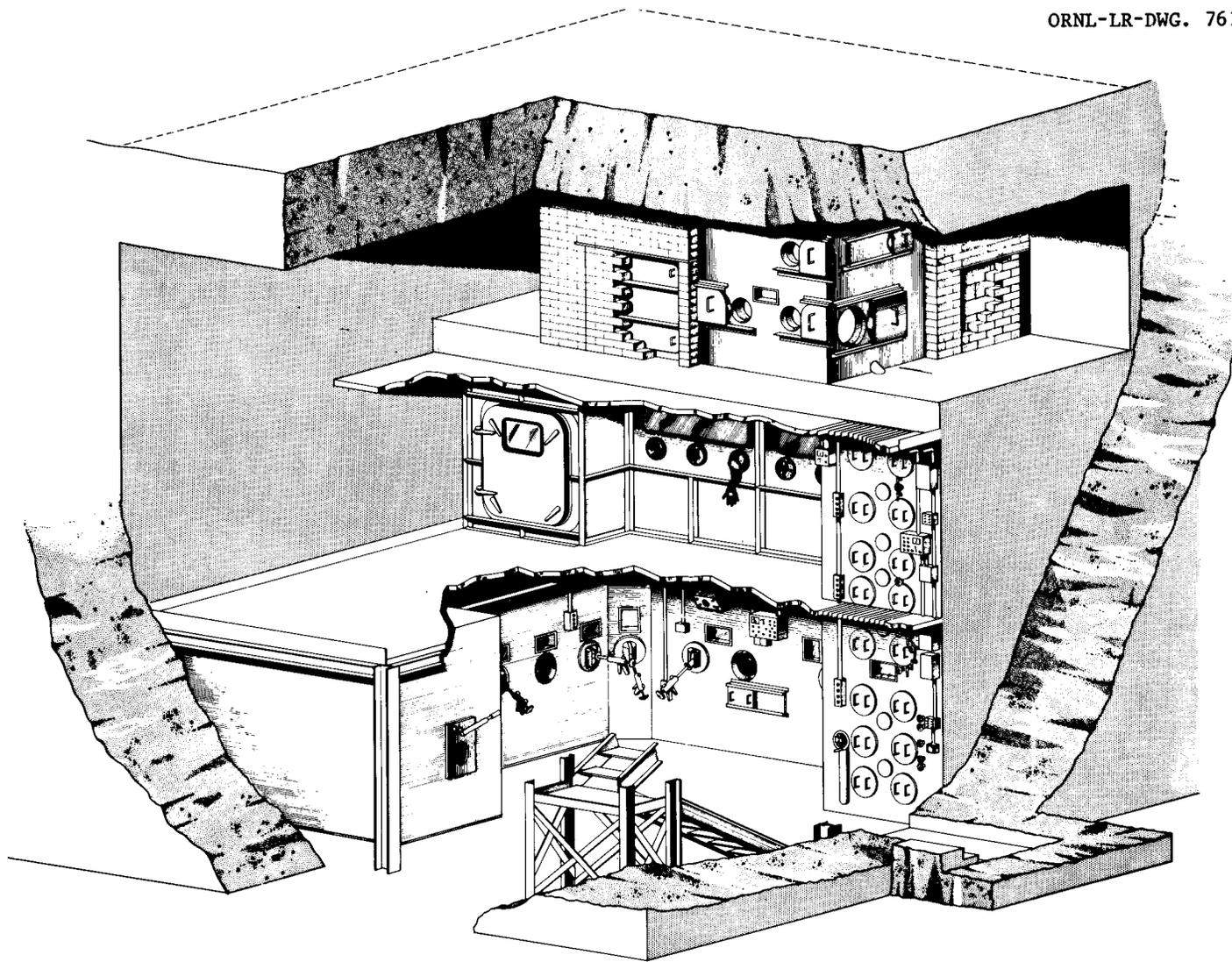


Fig. 17. Kilorod Facility.

major operations necessary to fabricate fuel rods from the bulk oxide were conducted, consisting in:

1. preparing the powder,
2. packing it into the rods and welding the end closures, and
3. cleaning and inspecting the finished rods.

3.1.4.1 Description of Process Equipment and Flowsheet. - The detailed design, mockup testing, and a portion of the operating history of the facility are available in several publications;<sup>6, 7</sup> so only a general description of the equipment is provided below, with more attention given to the flowsheet.

The rod-fabrication process starts with the delivery of the calcined sol-gel oxide to the powder-preparation equipment (Fig. 18). The oxide is first crushed in a jaw crusher and separated by a continuous screen classifier into three mesh-size fractions: +6, -6 +16, and -16. Through recycling of the +6 fraction and judicious charging of the ball mill with the -6 +16 and -16 mesh powders, sufficient amounts of coarse and fine powders consisting of 55% -6 +16 and 45% unclassified fines are produced. The development of equipment for making the fine fraction will be discussed under "cold startup" operations (Sec 4.1.3). The two fractions are then separately weighed on an automatic batch weigher and blended in a "V" blender. A vibrating feeder feeds the powder into the rods and densifies it by means of an air-driven vibratory compactor during feeding. The powder is further densified after the rod is filled by use of a weighted rider rod resting on top of the fuel column. The end cap, spacer, and spring are then placed in the rod, and the end-closure weld is made. Next, the rod is ultrasonically cleaned and gamma scanned to determine the density fluctuations along the long axis. The welds are then helium leak checked, and the rod is "smeared" to ascertain that contamination level is a safe one. Finally, the rod is loaded into the carrier for shipment.

The powder-preparation equipment located in the powder preparation shaft, uses gravity to transport the fuel through pipes from one equipment unit to the next. All the equipment in the powder-preparation shaft is remotely controlled either electrically or by flexible shafts. Minor

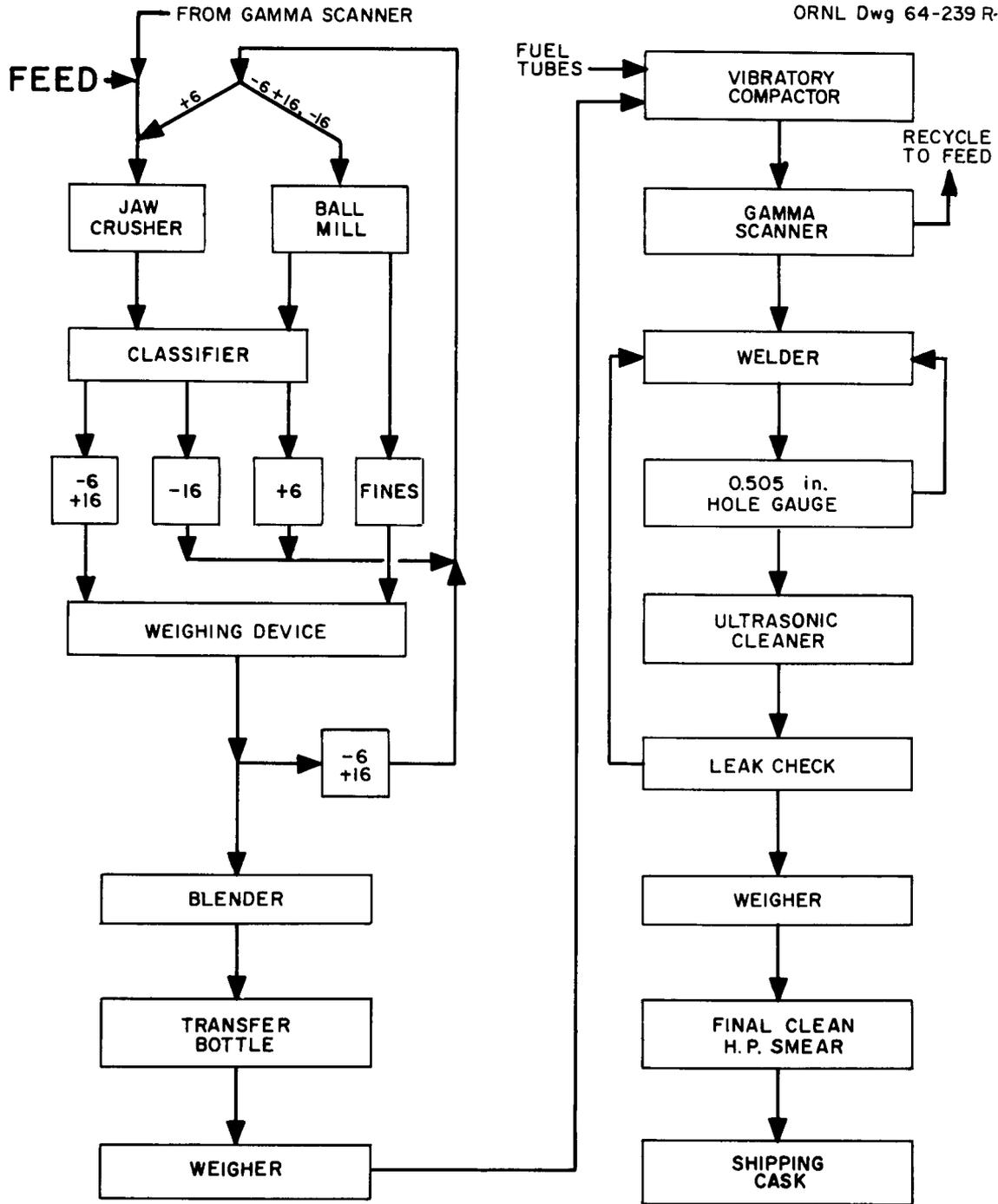


Fig. 18. Flowsheet for Fuel-Rod Fabrication.

repairs are made in-place through glove-access ports. To facilitate major repair, the equipment is mounted on movable racks. In normal operation, the rack-mounted equipment occupies the front half of the shaft. Defective pieces of equipment can be removed by pushing the proper equipment rack to the rear and lifting the piece to the repair area with a hoist.

The vibratory packer is shown in Fig. 19. An air-driven hammer is used as the compactor.

The end-cap welding machine (Fig. 20) evacuates the rod, backfills it with helium, seats the end plug, and makes the fusion end-closure weld.

The ultrasonic cleaning device with its power supply is shown in Fig. 21. This unit fills with water, ultrasonically cleans the rod, drains, sprays the rod with fresh water, and dries the rod in a current of warm air, all controlled from a console in the operating area.

The gamma-ray densitometer is shown in Fig. 22. The variation in packed-fuel density is measured by the attenuation of the  $^{60}\text{Co}$  gamma rays as they pass through the fuel. The beam is collimated by a  $1/8 \times 3/8$ -in. slot between the source and fuel rod.

### 3.1.5 Chemical and Physical Specifications for Process Intermediates and the Fuel Rods

Preliminary criteria were set for all process intermediates and for the fuel rods, based on prior development data. Ability to meet these specifications was tested in cold startup operations. After cold startup, the specifications were revised and extended. The final ones are given below.

3.1.5.1 Specifications for Uranium Feed Product by Solvent Extraction. - The principal specification for the uranium feed is that the nitrate-to-uranium ratio be  $< 2.5$ .

Other specifications imposed on the solvent extraction process by the nature of the feed and accountability requirements are:

Gross gamma decontamination factor	$> 100$
Thorium decontamination factor	$> 10^3$
$^{233}\text{U}$ recovered, %	$> 99.0$
Material balance, %	$99.0$

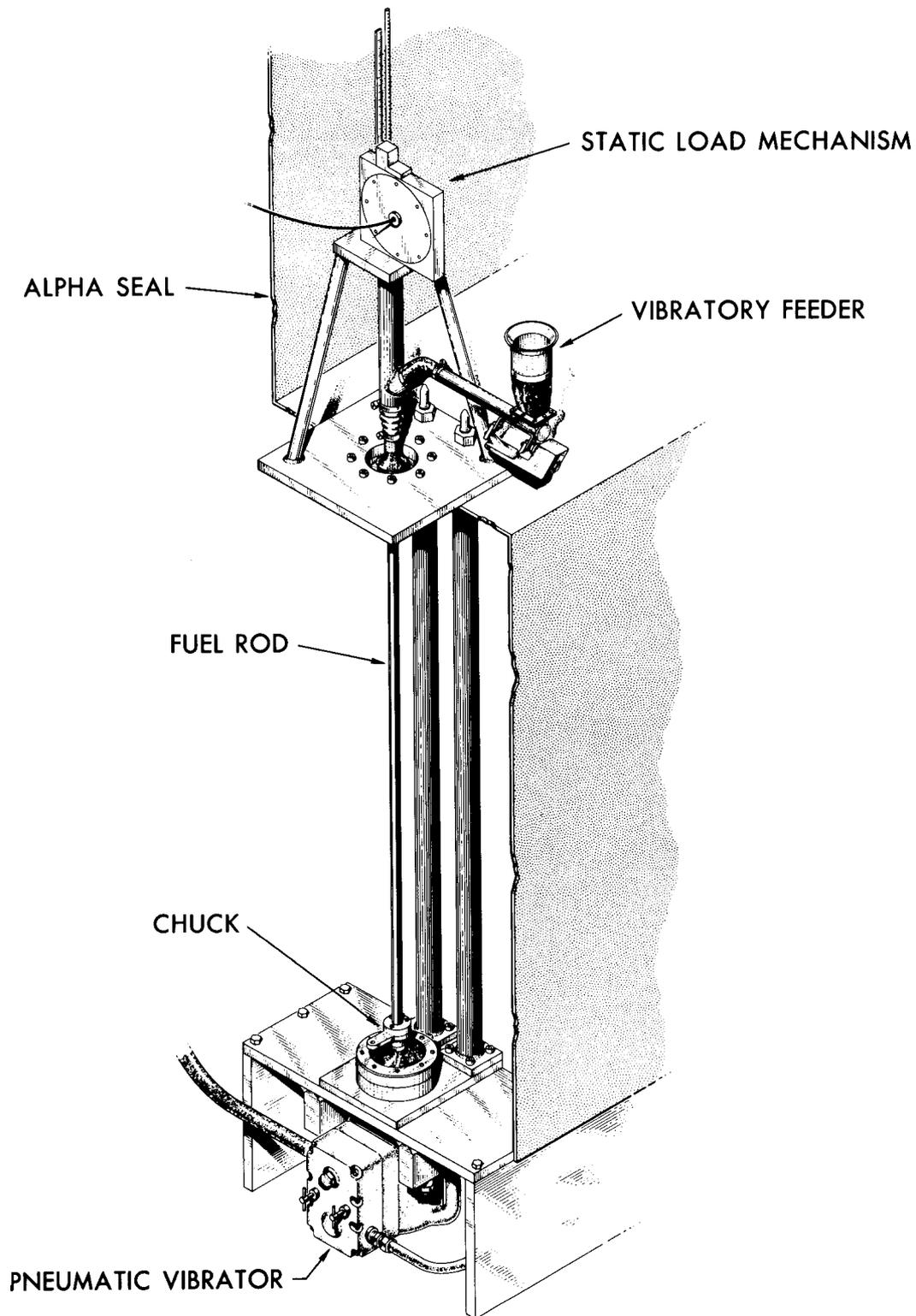


Fig. 19. Vibratory-Compaction Apparatus.

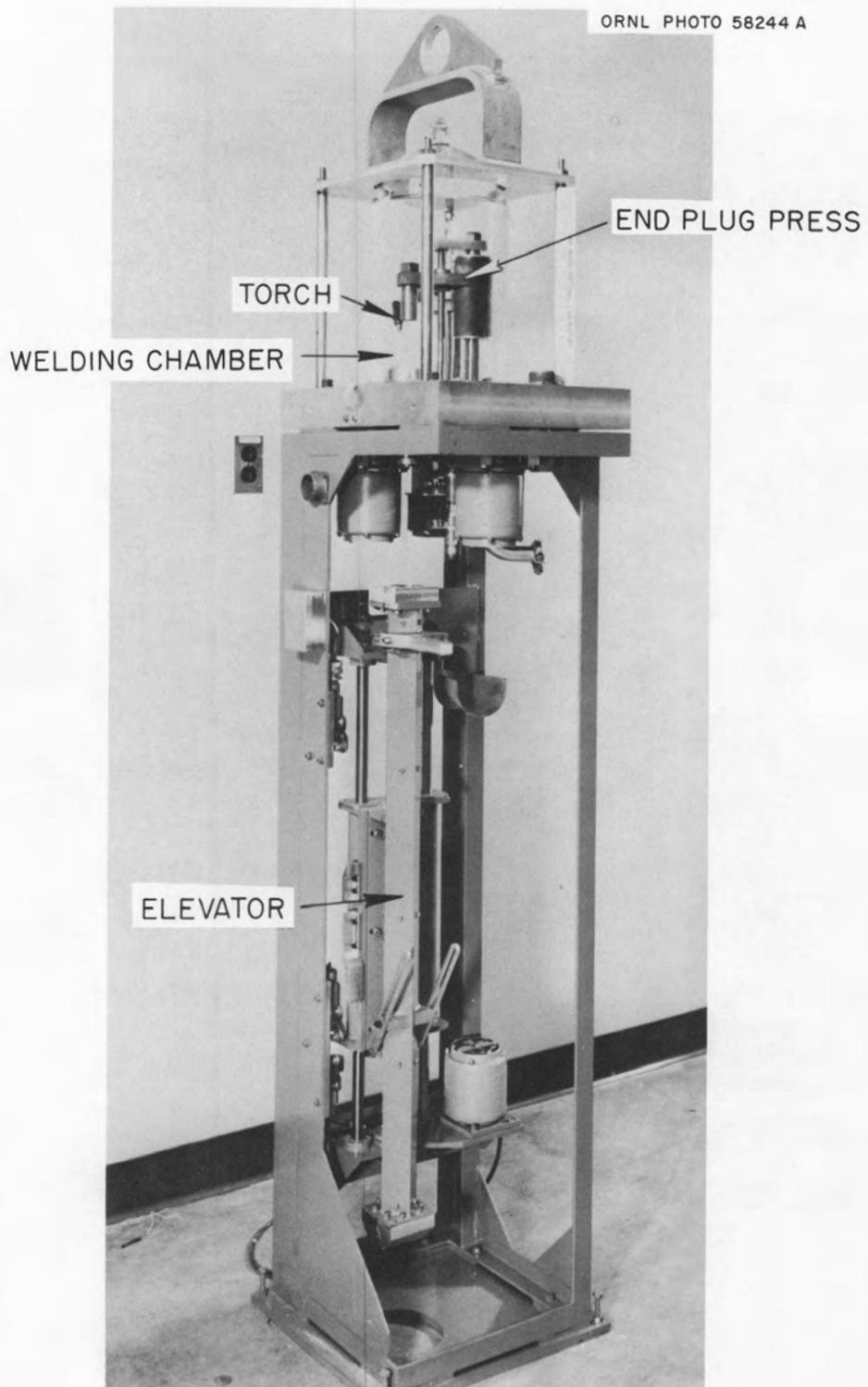


Fig. 20. End-Cap Welding Machine.

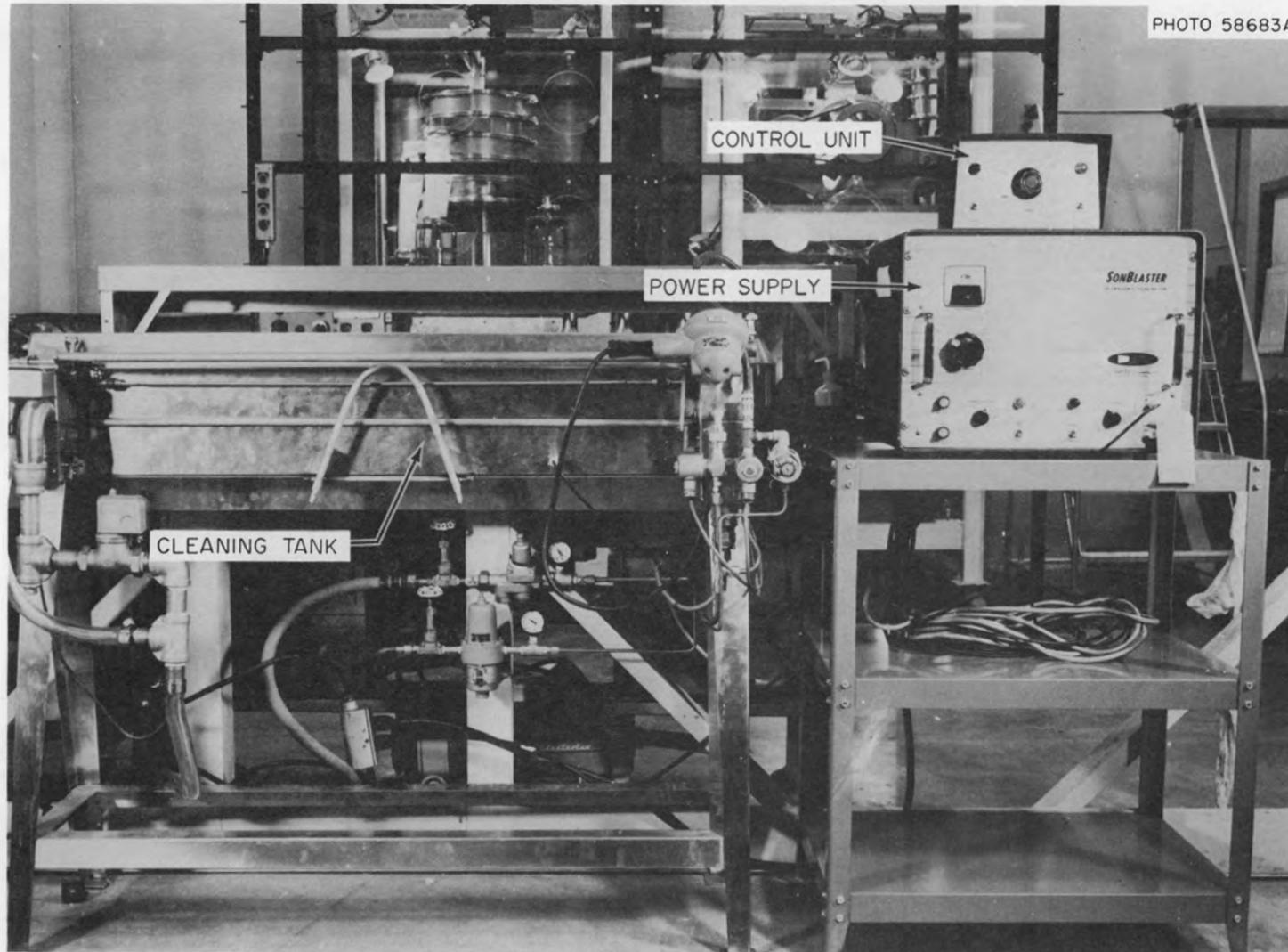


Fig. 21. Ultrasonic Cleaner.

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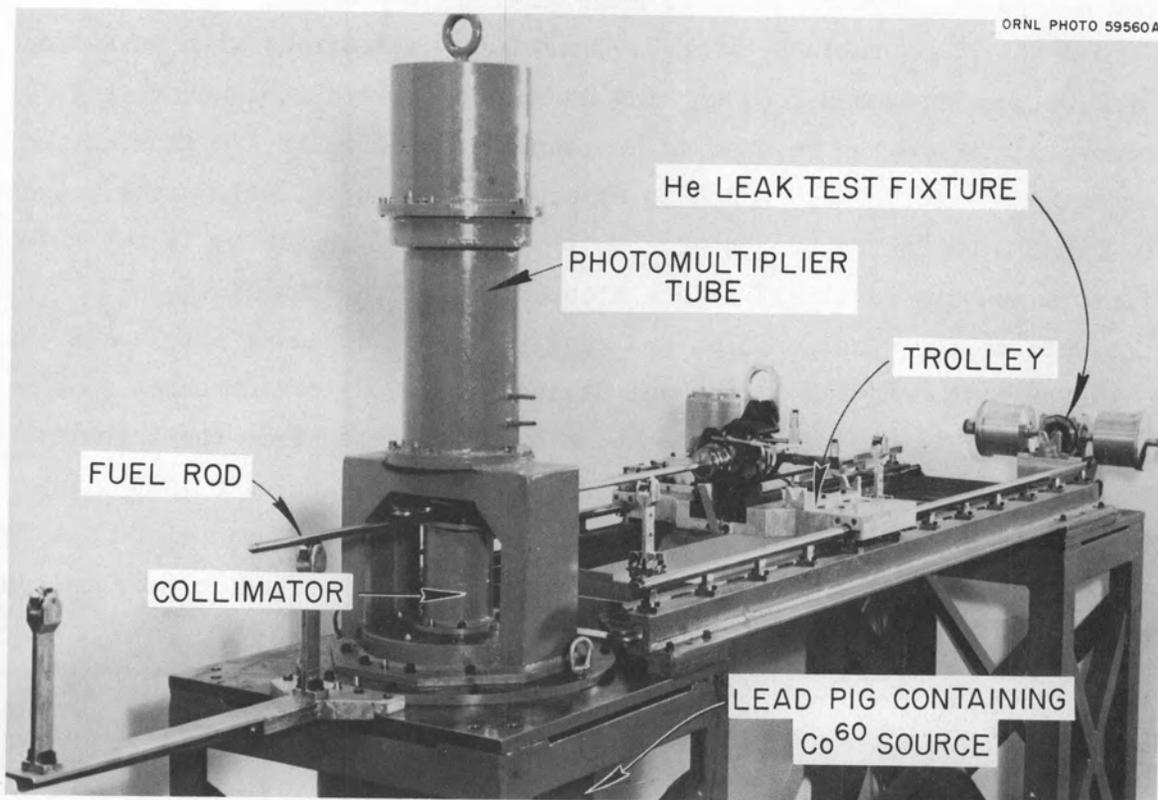


Fig. 22. Gamma Scanner.

3.1.5.2 Denitrator Specifications. - As in much of sol-gel work, the tabulation of a rigorous set of specifications for the  $\text{ThO}_2$  powder is not possible. No tests have yet predicted whether a batch of dry powder will disperse properly. The operation is performed by recipe, and a "cook's judgment" must be made on the acceptability of each batch.

A  $\text{NO}_3^-/\text{ThO}_2$  ratio between 0.03 and 0.06 is desired, with an average of 0.04 accepted as a good working number; however, batches above and below this range can be used if appropriate adjustments are made in the quantity of nitric acid added to effect dispersion. Thus, ratios between 0.02 and 0.08 can be processed. Still, the  $\text{NO}_3^-/\text{ThO}_2$  ratio is not a satisfactory measure in itself, since frequently the results of the  $\text{NO}_3^-$  analysis may be questionable, and easily learned art must supplement it.

The best acceptance test yet devised for a denitrator batch is the result of a dispersion test made with a small sample from the batch of  $\text{ThO}_2$ . Here, about 50 g of  $\text{ThO}_2$  is dispersed in 100 cc of 0.14 N nitric acid. The  $\text{ThO}_2$  disperses to a sol upon stirring for 30 min at 80°C. The sol sample is then poured into a sample bottle and stored for several days before continuing the test.

After several days, the characteristics of the sol are visually examined. The sample bottle is inverted; after gentle shaking, no more than an extremely thin film of very fine sediment should be found on the bottom of the bottle. This may be easily resuspended into the sol by continued gentle shaking. The sample bottle is then shaken vigorously to make the sol wet the bottle better. In a good sol, the film wets the glass uniformly. This wetting is as complete and uniform as though light machine oil were in the bottle. There are no chalky streaks nor a chalky-looking film on the sides of the bottle. The sol is blue-white, not chalky white. The intense blue of the sol becomes more noticeable as the film drains thinner and thinner down the wall of the bottle. These are the visible characteristics of a good sol, and hence, a useful batch of  $\text{ThO}_2$ .

This dispersion test is qualitative; however, with experience one can learn to accept or reject a batch of  $\text{ThO}_2$  powder. Judgment, along with the  $\text{NO}_3^-/\text{ThO}_2$  ratio and the dispersion test, so far must suffice as acceptance tests.

3.1.5.3 Specifications for Sol-Gel Process Intermediates and Calcined Product. - Specifications for sol-gel process materials were not formally established at the start of the program; in fact, such criteria and/or analytical procedures were continually developed throughout the demonstration. However, preliminary but incomplete specifications were proposed, based on Unit Operations experience.

Following cold startup in the pilot plant, a more formal set of specifications, and their interpretations, were worked out with the customer (BNL). These specifications are shown in Table 1.

Table 1. Specifications for Process Intermediates  
and the Product of the Sol-Gel Process

Property Measured	Specification (s) or Desired Value (d)	
	Preliminary	Final
U/Th ratio <sup>a</sup>	3.00 ± 0.03 <sup>b</sup> (s)	3.00 ± 0.05 <sup>c</sup> (s)
O/U ratio	2.01 max.	Deleted
Gas-release values		
Calciner product	0.01 std cc/gm (max) (d)	0.05 std cc/gm (d)
Crushed oxide	0.3 std cc/gm (max) (d)	0.3 std cc/gm (d)
Particle density	9.91 to 9.94 gm/cc <sup>b</sup> (s)	Deleted

<sup>a</sup>U/Th ratio is defined as  $100 \times \frac{^{233}\text{U}}{^{233}\text{U} + \text{Th}}$ . This ratio ignores presence of other U isotopes and is based only on the weights of these two metals.

<sup>b</sup>These preliminary values were suggested in ORNL-CF-61-4-76.

<sup>c</sup>Any powders falling within the 3.00 ± 0.10 range could be blended with other powders to obtain a 3.00 ± .05 ratio for the blend.

The difference between a specification and a "desired value" should be explained. The only rigid specification in the sol-gel operation required that the sol batch meet the U/Th ratio ranges given above. A desired value was the maximum value expected from routine operations and hence were values not expected to be exceeded. The customer's end-use of the product was not vitally affected by exceeding these desired values, and therefore no batches would be rejected if they did not stay below the desired maxima. Extreme variations, of course, could justify rejection

of a batch by the customer; none were rejected. The customer's needs were satisfied when complete analyses were furnished and the values were within or reasonably near the ranges specified. Control data for the entire program were furnished BNL.

The initial specification for gas-release determinations required a gas-release test on pea-sized chunks from each batch of calciner product. This test was made throughout the program. Additionally, a powder control sample was to be taken from the rod-loading operation following preparation of every tenth rod;<sup>a</sup> it was to have been tested for gas release and the composition of the released gas determined. It would have been expensive to do this, so BNL agreed to composited powder samples for each carrier shipment, the composite to be made from the powder-control samples already mentioned. The composite was to be weighed in proportion to the amount of material entering the carrier from any given ten-rod lot of product. By lowering the number of samples processed, this permitted more careful analytical work and gave better results.

The <sup>233</sup>U and Th content were to be determined for both the coarse and fine powder fractions of the composite as well as the composite itself. From earlier Unit Operations work, U/Th ratios for these fractions could not be expected to have better agreement than  $3.00 \pm 0.06$ . Occasional "flyers" outside this range could be expected, and sampling difficulties were the suggested source of error.<sup>8</sup>

The O/U and particle-density specifications were deleted from the final specifications because the method was not accurate. Density-determination procedures were being developed at the time the original specifications were proposed, and a satisfactory procedure for routine "hot" analysis was expected. However, no satisfactory method appeared in time for use.

The O/U specification was also dropped because there was no analytical method sensitive enough to determine the oxygen present at such low uranium concentrations. Initially this specification was based on common  $UO_2$

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<sup>a</sup>Since the rods contained almost 10 kg of powder, this sampling interval corresponded roughly to each batch of sol-gel oxide.

specifications. Since only 3%  $UO_2$  is in the sol-gel product, present analytical methods can detect oxygen down to the  $UO_{2.04}$  level only. Further, the 2.04 value is subject at best to an error of  $\pm 0.02$ , thus the O/U-ratio within the range in question is not an oxygen determination but a method for detecting oxygen.

3.1.5.4 Specifications for the Fuel Rod. - The configuration of the reference fuel rod for the BNL critical experiments is shown in Fig. 23. The BNL experiments required 900 of these rods and 200 identical in design except that they are 18 in. long instead of 46-1/16.

The nominal packed density was not specified by BNL but was to be established from the average density of all rods fabricated. It was specified that the rods should have a fuel density within  $\pm 2\%$  of this average density and that the density variation along any fuel rod should be within  $\pm 2\%$  of the average for the rod. The specifications to which the rods were fabricated are presented in Table 2.

Table 2. Fuel-Rod Specifications

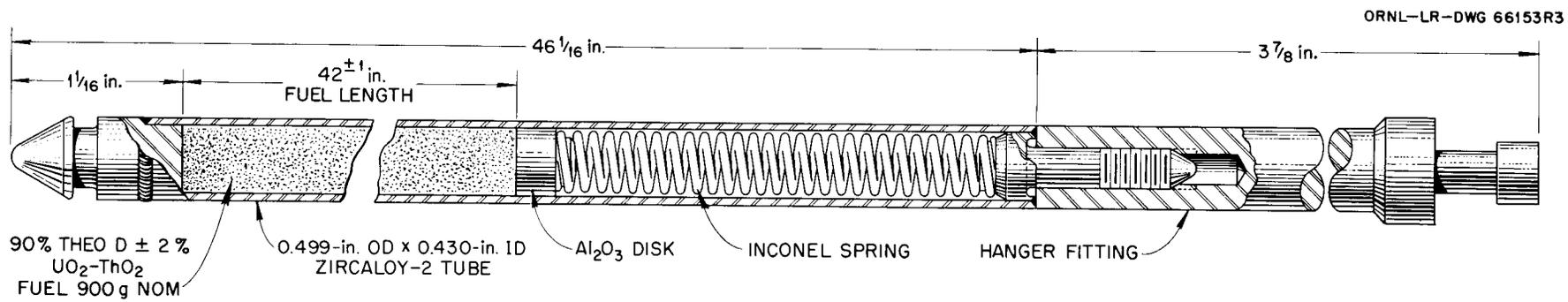
	Height of Fuel Bed (in.)	Density Variation from Rod to Rod	Density Variation Within the Rod	Average <sup>b</sup> Packed Density <sup>c</sup>
46-in. rod <sup>a</sup>	42 $\pm$ 1	$\pm 2\%$	$\pm 2\%$	9.0
19-in. rod <sup>a</sup>	14-1/2 $\pm$ 1/2	$\pm 2\%$	$\pm 2\%$	9.0

<sup>a</sup>Tube length, including bottom end plug.

<sup>b</sup>Determined from operation with depleted (U, Th) $O_2$ .

<sup>c</sup>Unit: g/cc.

The cone-shaped Zircaloy-2 bottom fitting, used for directing the rod into position in the reactor lattice, is welded onto the tube in an inert-gas tungsten-arc welding operation outside the facility. The annular groove in the bottom plug is used as a handling aid during fabrication. In the facility, the top plug, ceramic spacer, and spring are inserted as a unit into the fuel tube after compaction. The ceramic spacer and spring are used in the void area at the top of the fuel rod to prevent the redistribution of the fuel during handling. The Zircaloy-2 top end plug,



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Fig. 23. Design Features of the Brookhaven National Laboratory Fuel Rod.

joined onto the fuel tube by a fusion edge weld in the facility, is threaded to accommodate the stainless-steel hanger fitting. This fitting is used to facilitate handling of the fuel rod in the reactor lattice.

### 3.2 Alterations to Equipment or Installation During Cold Startup Period

#### 3.2.1 Solvent Extraction Pilot Plant

The solvent extraction process always worked well, and the equipment reliability was exceptionally good. However, during the first hot campaign, the uranium concentration of the solvent extraction product varied widely, as indicated by the analyses of samples from the product storage tank (R-25). Accurate analyses and stable concentrations are absolutely necessary at this point to meet the exacting specification for the U/Th ratio.

The difficulty with concentration of the SX product in the storage tank arose this way: The 18-in.-diam product tank (R-25, Fig. 24) was packed with 4% glass Raschig rings (neutron poison). It was also equipped with an air sparger and air-purged liquid-level and density probes. Samples taken immediately after purification of the uranium for the first campaign indicated a  $^{233}\text{U}$  concentration of 119 g/liter. Samples after one week (only about 4 hr of sparging for agitation occurred during the interim) indicated a concentration of 129 g/liter, and in a few days (no further air sparging) a further increase to 137 g/liter. Material balances verified the accuracy of the analyses and indicated that the varying concentration was due primarily to the solution being concentrated by the dry air introduced by the instrument probes and, to a lesser extent possibly, by sparging during sampling.

To correct the difficulty it was necessary to install another product storage tank. The new tank (R-35, Fig. 24) is 5 in. in diameter, thus eliminating the borated-glass Raschig rings used as neutron poison. In practice, the purified product is transferred to R-35, where it is sampled before it enters the sol-gel process.

#### 3.2.2 Alterations to Sol-Gel Equipment Immediately Before or During the Cold Startup Testing

Three pieces of equipment were altered significantly from the original design during the construction-startup period. They were the U tank

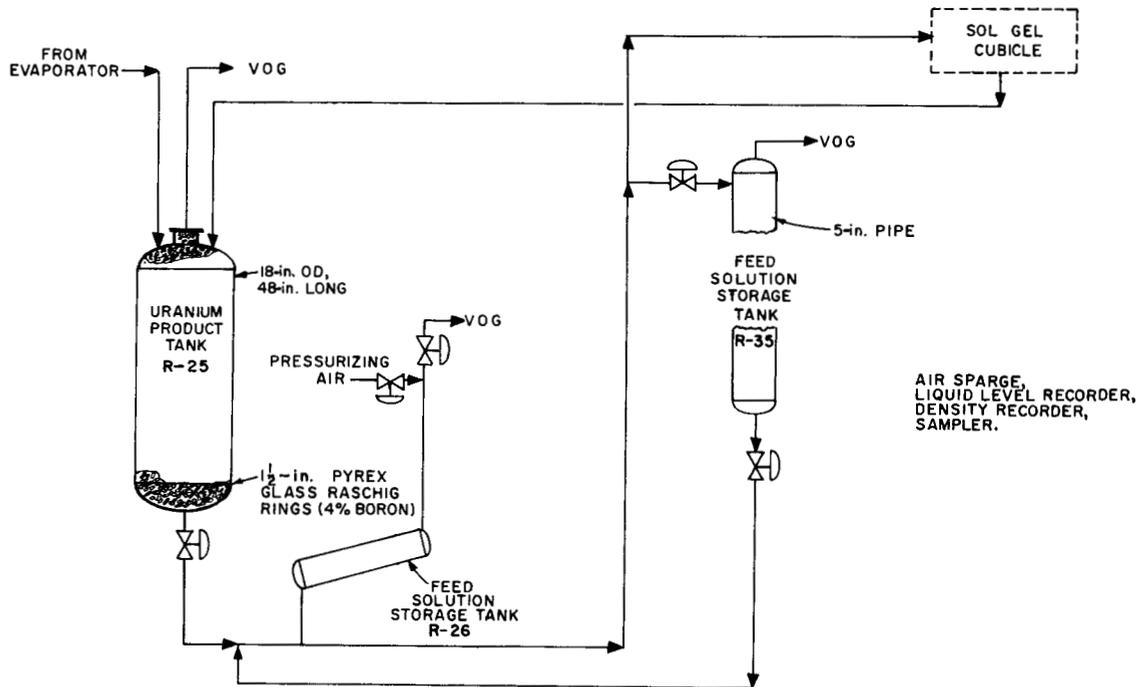


Fig. 24. Solvent Extraction Uranium Storage and Transfer System.

(used for measuring the uranyl nitrate feed solutions), the tray dryer, and the calciner.

3.2.2.1 Redesign of the Uranium Tank. - Initially the uranium tank was made from a 4-ft length of 3-in. Pyrex glass pipe, of precise bore. The solution level in the tank and hence the volume in the tank, was to be read with a vernier-equipped cathetometer located on the outside wall of the cubicle. A lead-glass window was provided through which the meniscus could be seen. The 3-in. glass pipe of the main body of the tank was reduced to 1/2-in. at the bottom. During the construction period, the design of this tank was reconsidered, and one of improved design was built (Fig. 25). The improved features of the later design were:

1. Rigid piping enters the tank through the stainless steel bottom section only, allowing the glass section to stand unconstrained. Only a thermocouple lead and a vent made of flexible plastic tubing enter through the top of the column.

2. A large cross-section (equivalent to the 3-in. glass-pipe size) is maintained throughout the glass portion of the tank, offering considerably more strength than the minimum 1/2-in. glass-pipe cross section presented in the original column. The desirability of this change was underscored by the fact that this column, even with a 3-in. straight pipe section, was broken twice during construction.

3. Only one valve must be absolutely leak tight (HCV-8) for this assembly to meet operating requirements. All other valves could leak slowly without affecting operation.

4. A combination splash-shield and catch basin was provided in case the column broke. The drain from the annular volume of this basin led to a stainless steel beaker on the floor of the cubicle beneath the bottom of the uranium tank.

5. Accuracy of solution delivery was significantly improved by locating the U tank end of the solution delivery line at the smallest cross-sectional area available within the tank. Accuracy of delivery was less than  $\pm 15$  cc, an error of about 0.5%, when the 2700-cc batch volume is considered.

3.2.2.2 Alterations to the Tray Dryer. - The original tray dryer and its accessories were assembled in a toroidal arrangement. An enclosed, propeller-type fan forced the air across a heating coil, over the sol

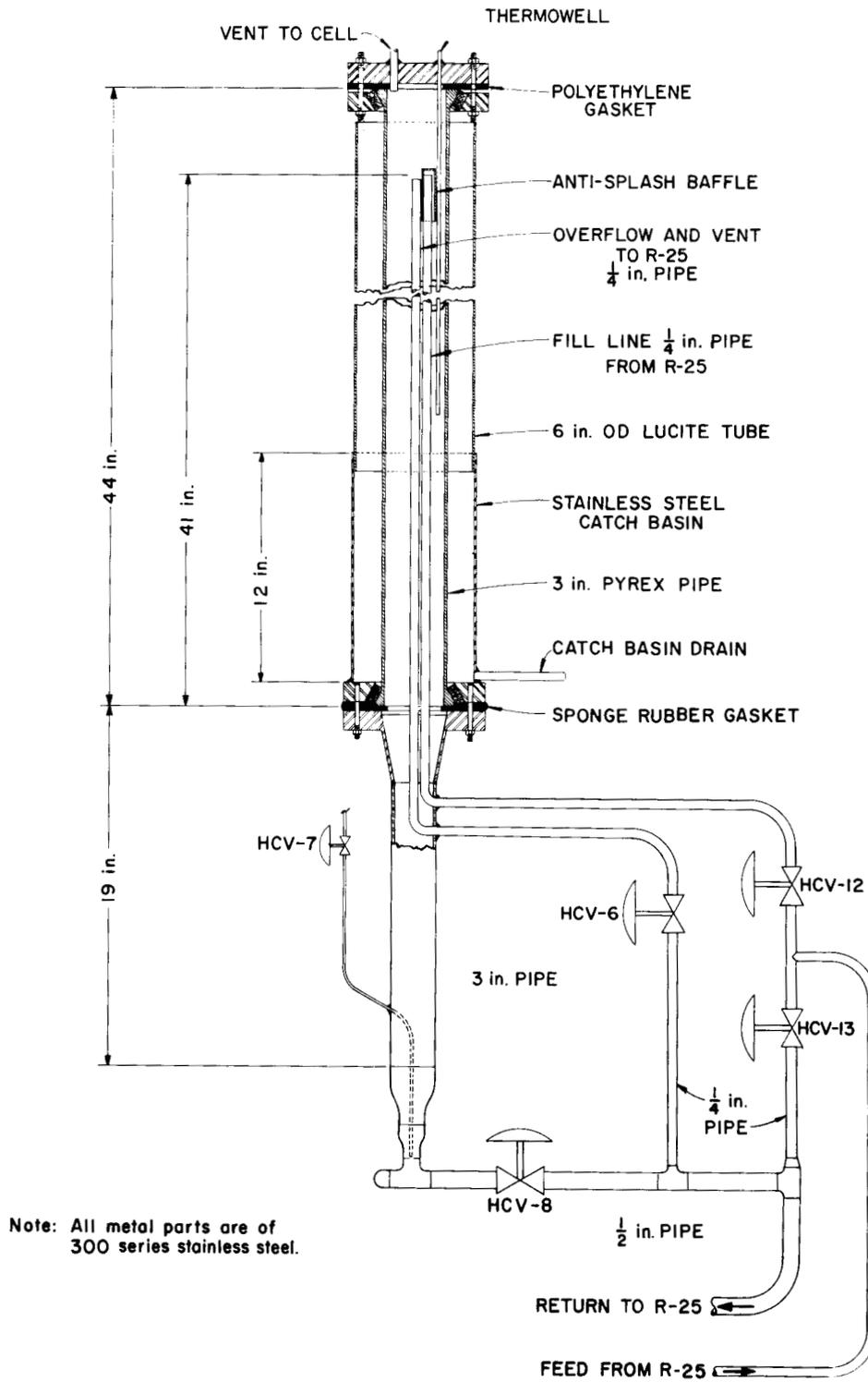


Fig. 25. Details of Uranium Measuring Tank.

(or gel) in the trays, and thence through a cooler (condenser) for removing the water picked up from the sol. The fan intake was coupled directly with the cooler outlet. A steady stream of air was to be withdrawn from the assembly to the hot off-gas system to maintain a flow of air into the equipment. The design of the dryer was altered in the following respects and for the reasons indicated:

1. There was considerable uncertainty about the service life of the fan bearings, since nitric acid vapor would contact it.
2. Should the fan break down, it would be almost impossible to repair it under the conditions obtaining, because the bulky fan-cooler-heater combination would have occupied so much of the working space inside the process cubicle. This allowed only enough working room for one man in an air suit at any one time; further, some portions of the assembly were simply inaccessible. Any minor breakdown would have resulted in an extended plant shutdown. It was imperative that more space be obtained for servicing and/or accessibility should trouble develop in the dryer.

In altering the dryer, the fan and the cooler were removed and the air heater fitted directly to the end of the tray chamber by sheet metal adaptors. The exhaust from the dryer was connected directly to the hot off-gas system. Thus air could be drawn from the cubicle through the air heater and across the trays and thence into the hot off-gas system. Booster heating plates were made by welding 1/2-in. stainless steel tubing in a serpentine arrangement onto 1/4 x 24 x 24 in. stainless steel sheets. One drying tray was removed from the upper compartment and one from the lower compartment of the dryer. With removal of these trays, sufficient space within each dryer cavity was obtained for installation of these booster heating plates. One booster heating plate was installed at the top and at the bottom of the upper and lower dryer compartments.

A working dryer, considerably less trouble-prone, much less difficult to service should the need arise, and leaving much more space for servicing other equipment, was obtained.

3.2.2.3 Modifications to the Calciner and its Control Circuit. - Except for incidental changes, the calciner and the control circuit installed for the Kilorod operation were the same as those used in Unit

Operations work. However, the total mass charged to the earlier calciner was about 20 kg, while it exceeded 40 kg with the Kilorod furnace. Herein lay the primary trouble in the startup of the Kilorod calciner. This extra charge weight led to extreme lag of the charge temperature behind the element temperature during the heat-up portion of the calciner cycle. This led to overheating of the furnace heating element (Kanthal Al) and subsequent premature burnout of the elements. Unit-Operations testing showed that a heating-element life of about 30 cycles could be expected. Kilorod experience in cold startup showed only two to four cycles could be expected.

To correct the intolerably short service-life of the Kilorod elements, the following changes were made to the design of the furnace as received from the manufacturer:

1. The atmosphere entry pipe was moved from the rear of the furnace to the front. In its original position, the entering gases blew directly on the thermocouple used for sensing the temperature of the crucibles. This aggravated the aforementioned problem.

2. Entering through the rear of the furnace, an open-ended tube was installed directly beneath and terminating near the geometric center of the bottom surface of the Kanthal heating element. Two bare thermocouples (Pt, Pt-10% Rh) were inserted into the furnace through this tube. The bare junctions were pushed on through the open tube end (see Fig. 26) so that they could "see" the heating element directly.

3. Two other similar bare thermocouples were inserted through the rear of the furnace and into the furnace cavity on about 2-in. centers. These thermocouples were placed with their junctions about 1/16 in. away from the rear of the crucibles.

4. Each of the thermocouples of (2) was connected to temperature-limit switches. One of these was set to limit the element temperature to 1250°C. This instrument also served as a recorder. The second, simply a limiting device, was set to limit the temperature to 1290°C. These temperatures were selected to allow the fast heatup rate desired in the calciner and yet low enough to protect the Kanthal element. Thermocouple burnout protection was provided in both instruments.

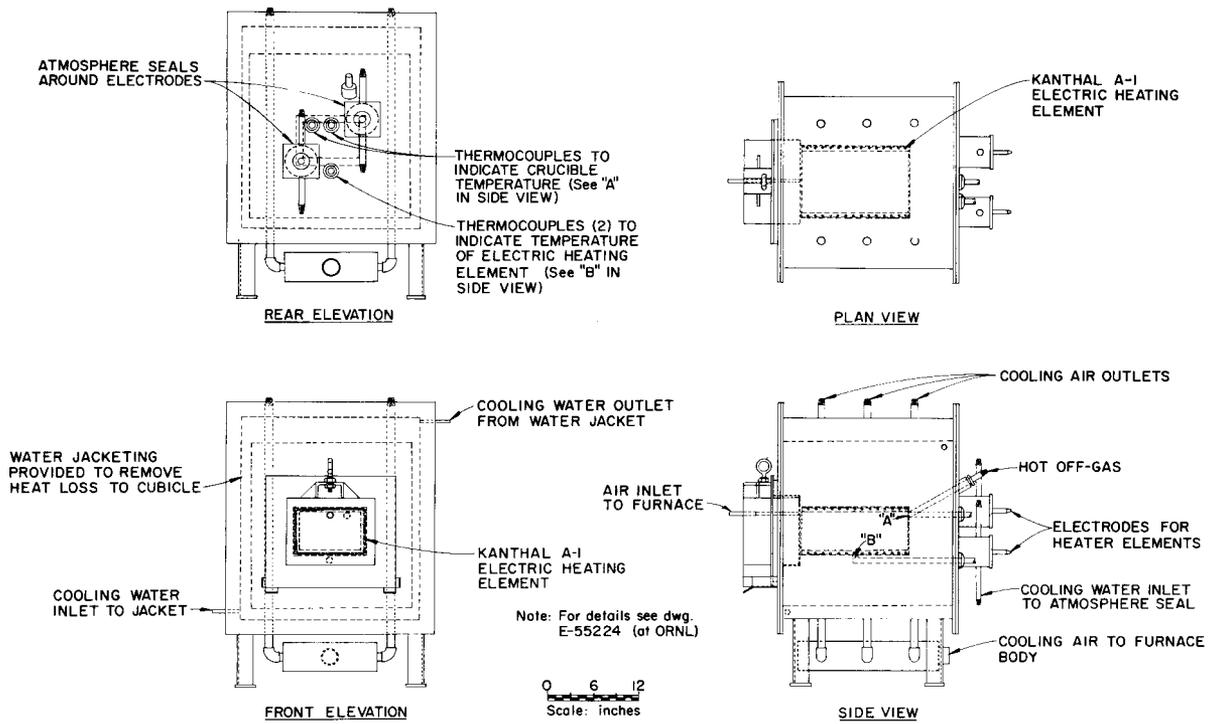


Fig. 26. General Arrangement of Calciner.

5. One of the thermocouples of (3) was connected to a recorder to obtain a record of the crucible temperature. The other was connected to a disk-type time-temperature program controller and controlled the rate of temperature rise within the furnace chamber.

Alterations made as described above were effective in preventing premature burnout of the heating elements. The two independent temperature-limiting circuits may at first seem unnecessary, yet the primary circuit failed twice during the program. The use of these two circuits however did make the time-temperature program controller unnecessary and it was not used in the last half of the program.

### 3.2.3 Rod Fabrication

Most of the equipment operated as originally designed and installed. One item was modified (helium leak test chamber); one was added (balance); and one alteration of the facility (sump jets) was required.

Helium-Leak-Test Chamber. - The helium-leak-detector vacuum chamber originally consisted of a double-O-ring-sealed unit that pumped down only the weld to be inspected. A standard assault-mask filter was placed in the high vacuum line to filter out any particles which may have been entrained in the pumpdown cycle.

The attainment of a satisfactory high-vacuum seal with the O-ring assembly was difficult, requiring precise alignment of the rod with the center axis of the vacuum chamber. In addition, the presence of the filter at a long distance from the pumps, about 15 ft of 1/2-in. copper connecting pipe, would result in an excessively long pumping cycle. It was doubted that 10 rods per day could be examined with this apparatus.

This chamber was replaced with one made of 1-1/2-in. type 304 L stainless steel pipe. The vacuum seal was made by a simple O-ring flange assembly, using the difference in pressure to effect the seal. The chamber was big enough to contain five entire rods, thereby ensuring that this would not be limiting on the production rate. The particle filter was moved so that it was very near the pumps, to take advantage of the higher pumping speeds.

Additional Balance. - A balance, in addition to the one determining the weight of the finished rod, was placed between the blender and powder feeder station. This balance was used to ensure that a full rod charge was delivered from the transfer bottle.

Sump Pumps. - Since the first-level cubicles were located below the hot-drain system, the liquid waste was raised from the sumps to the hot drain by steam-jet pumps. The hot-drain system was thus left directly connected to the cubicle atmosphere through the jets. Because of this fault, it was not possible to attain the required cubicle in-leakage rate. Each delivery line was opened and a valve inserted to correct this condition.

At the end of the cold startup operations all equipment that would contain <sup>233</sup>U was cleaned carefully to remove all traces of the depleted uranium. All portable equipment inside the cubicles and all sappers in which depleted uranium had been fired were discarded. The cubicle and the floors and walls were scrubbed thoroughly. All samples of uranium-bearing solids were removed to another building (the denitrator area), sealed in a large carton and stored.

Nine of the first ten batches prepared were sampled before loading into the fuel rods and submitted for mass assay to ensure that no isotopic dilution had occurred. No perceptible dilution was found.

### 3.3 Utilities and Waste Disposal

#### 3.3.1 Emergency Power and Lighting

Radiation instruments and lights provided within the Kilorod cell are connected to both normal and emergency power supplies. A constantly charged, battery-powered light was also provided in the event that the emergency generator did not start. No other equipment was connected to the emergency power since operator safety was not involved.

#### 3.3.2 Air Flow and Cubicle-Cell Operating Pressures

Air (2400 cfm) entered the cell by way of the normal access stairwell at "Point A" on Fig. 27. Before reaching point A, the air passes through a filter bank, equipped with gravity-operated louvres that act as back-flow preventers. The filter was common, pleated, glass wool. This filter bank-louvre system and the cell proper constitute the outer, or secondary containment for the operation. The operating cubicles and absolute air filters (see below) on the cubicles formed the primary (high-level alpha) containment.

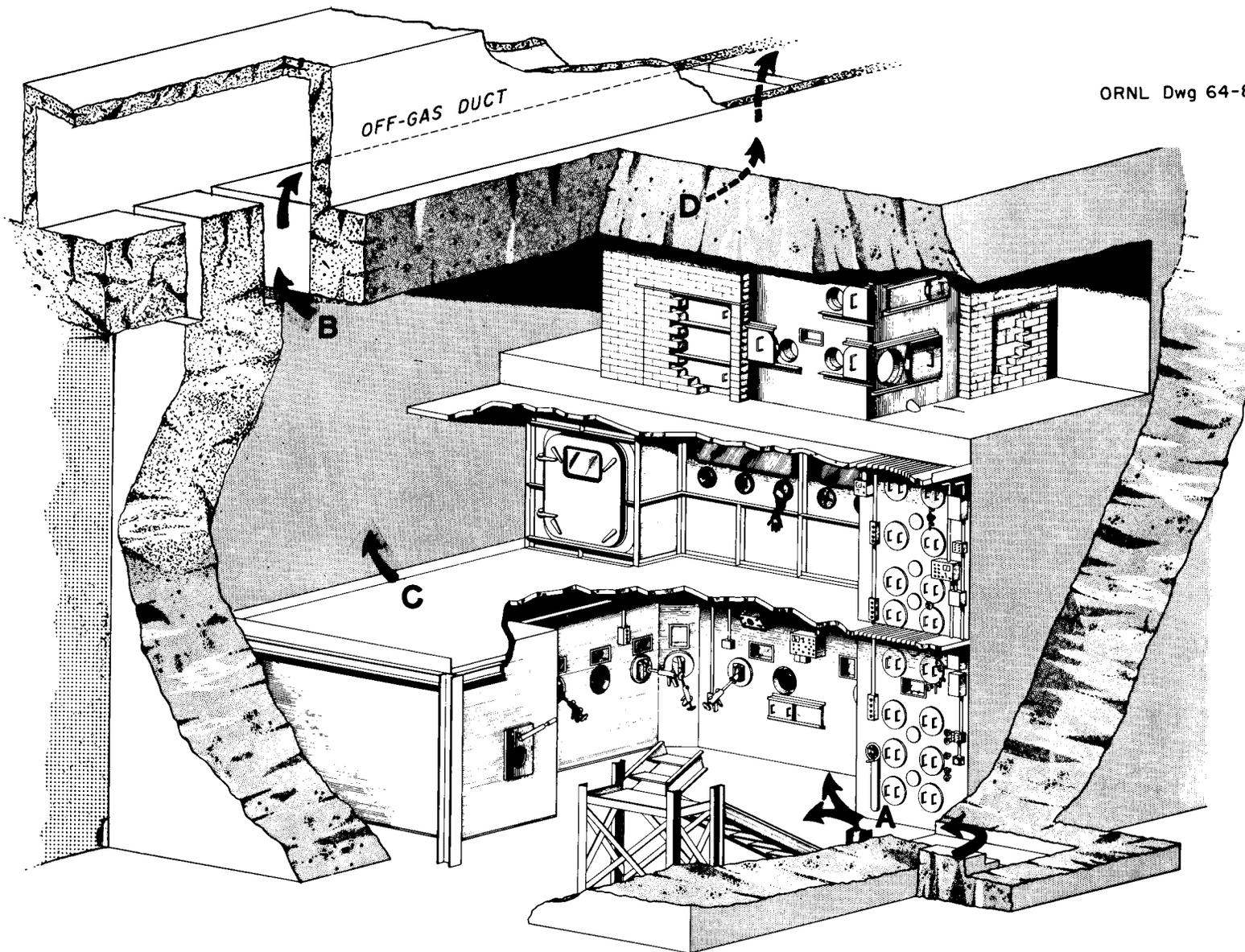


Fig. 27. Air-Flow Pattern in Cell 4.

Within the cell, the air is split into two streams: One supplies air to the working, or occupied, portion of the cell exterior to the process cubicles, while the other supplies air to the processing cubicles. The first of these air streams passes up through the open portion of the cell shaft and exhausts through an absolute filter bank located in the top northwest corner of the cell at "Point B." This filter bank is also equipped with gravity-operated louvres. The discharge leads into the building off-gas duct and thence to the stack (Building 3020). The second air stream enters a bank of absolute filters in the service area of the first balcony ("Point C"). From this bank, ducts equipped with gravity-operated louvres conduct the air into the process cubicles. Leaving the process cubicles, the air passes through lever-operated damper valves at the air exit port of each cubicle and then through a final bank of filters. This bank includes both roughing (Fiberglas, 1 in.) as well as absolute filters. Again, these filters are located on the first balcony service area. From the filter bank, the air passes through the upper, northeast corner of the cell ("Point D"), through gravity-operated louvres into the building off-gas duct and stack. The air passing through the working space was regulated at about 2200 cfm, while the total quantity passed through all process cubicles at about 200 cfm.

The pressure in the occupied areas of the cell was always held at 0.1 in. ( $H_2O$ ) below atmospheric pressure. The pressure within the operating cubicles was held to 0.1 to 0.2 in.  $H_2O$  below the pressure within the cell; thus the operating cubicles were at a pressure 0.2 to 0.3 in. ( $H_2O$ ) below atmospheric. The building off-gas duct provided the pressure drop needed to maintain the negative pressure differences. The flowing air proceeded from relatively uncontaminated to progressively more contaminated ones. For example, on the first floor, air moved from the carrier-loading station through the various cubicles of the fabricating area and was removed at the rod-loading station.

Immediately before the start of cold-testing, each cubicle was made ready, and the air in-leakage rate was determined. All hot working spaces met the  $<0.005$  working space vols/min in-leakage rate (at 1 in.  $H_2O$  negative pressure), required by Laboratory practice.<sup>9</sup> The filter banks were tested with dioctyl phosphate smoke in situ, also as required by Laboratory practice, and found to be  $>99.99\%$  efficient.

### 3.3.3 Disposal of Wastes

Each of the processing cubicles was equipped with a floor drain, or if on the bottom floor, a steam jet to the hot waste system. All these waste lines and the process condensate from the sol-gel operations was piped to the hot waste. Normal steam condensate and cooling water were "tied" to the process waste header.

Each vessel in the sol-gel system was connected to the hot-vessel off-gas system and equipped as well with a water-cooled condenser. An inward sweep of air was maintained on all vessels at all times. Gases pulled through these condensers were piped to the common hot-off gas header, passed through an absolute filter to remove particles, and then into the hot-off-gas disposal system for the plant.

Solid wastes were picked up by vacuum cleaner from the tables and other working surfaces. As the bags were filled, they were replaced, and the full ones bagged out for reprocessing of the material they contained. Other solid wastes (broken crucibles, etc.) were bagged out and buried.

## 4. OPERATING EXPERIENCE

### 4.1 Construction and Cold Startup Operations

The SX equipment was converted by September 1962, and cold testing started in November. The first hot (trace-element) runs were made in January 1963 and the plant placed in operation for the Kilorod Program in March.

Installation of the equipment began in cell 4 in mid-October 1962, and was completed in early March, 1963. Preliminary equipment testing began on February 15 and was completed on May 3. During the period of April 3 to May 3, test results showed that several equipment changes would have to be made in order to meet the throughput rates for which the sol-gel process was designed (see Sec 3.2.2). These changes were completed and final adjustments made by May 10. Necessary equipment changes and cold-testing operations were completed on the rod-fabrication equipment in early June. Hot feed was introduced into the sol-gel cubicle on June 11, 1963.

#### 4.1.1 Preliminary Testing of the Solvent Extraction Equipment and Flowsheet

Upon the completion of the necessary changes to the Thorex Pilot Plant, the solvent extraction plant was operated in four trace-level and two

intermediate-level ( $^{233}\text{U}$  concentration about one-tenth that of full flow-sheet concentration) tests under flowsheet concentrations.

The objectives of the test program were to:

1. evaluate the proposed flowsheet;
2. demonstrate the dissolver-charging procedures;
3. test the sampling procedures, run sheets, data sheets, and accountability requirements;
4. evaluate equipment operability;
5. demonstrate criticality control procedures and safeguards; and
6. acquire operating experience.

The results of the test runs are summarized in Table 3.

Table 3. Summary of Startup Runs in the Kilorod Solvent Extraction Pilot Plant

Run No. <sup>a</sup>	Overall Decontamination Factors		Distribution of U Losses <sup>b</sup> (%)		
	Gross $\gamma$	Thorium	AW	CUW	CW
CT-2	100	1100			
CT-3 <sup>c</sup>	130	$2.5 \times 10^4$			
CT-4	100	3400			
HR-1	500	1700	0.07	0.4 <sup>d</sup>	< 0.005
HR-2		1900	0.05	0.3 <sup>d</sup>	< 0.005

<sup>a</sup>Run CT-2 and CT-3: column pulse amplitude, 0.8 in.; pulse frequency, 50 cpm. Run CT-4; pulse amplitude, 1.0 in.; pulse frequency, 50 cpm. Run HR-1 and HR-2: pulse amplitude, 1.0 in.; pulse frequency, 58 cpm for extraction, 50 cpm for stripping.

<sup>b</sup>Uranium losses during CT runs were not significant.

<sup>c</sup>Three-column operation (separate extraction, scrub, and strip column).

<sup>d</sup>High losses attributed to entrainment in evaporator. CUW losses were < 0.01% in second half of run HR-2 when water reflux was added to evaporator top plate.

All objectives of the test program were met. Satisfactory decontamination factors, uranium recovery, and product quality were assured for the full-level runs.

#### 4.1.2 Sol-Gel Pilot Plant

4.1.2.1 Denitrator Startup and Operating Data. - The rotary, hydro-thermal denitrator was built and operated during the pre-Kilorod (Unit Operations) testing program. As the program was anticipated at that time,

the denitrator was built large enough to supply Kilorod requirements. This earlier work had reduced the operation of this step of the sol-gel process to routine; so the equipment was started up without event and operator training completed during January 1963.

As a precaution, the first 12 batches of rotary denitrator product were analyzed for  $\text{NO}_3^-$  and Th (Table 4). Four later batches were also spot-checked. These analyses were made to ensure that the product was equal to that made in the earlier runs, or otherwise satisfactory for processing. The  $\text{NO}_3^-$  and Th analyses, with two possible exceptions, fell within the desired range; so subsequent denitrator batches were not analyzed.

Table 4. Analytical Data on Individual Batches of Thorium Oxide Prepared During Kilorod Startup

RDP <sup>a</sup> No.	$\text{NO}_3^-$ (%)	Th (%)	$\text{NO}_3^-/\text{ThO}_2$ Mole Ratio	RDP <sup>a</sup> No.	$\text{NO}_3^-$ (%)	Th (%)	$\text{NO}_3^-/\text{ThO}_2$ Mole Ratio
1	0.89	85.94	0.039	9	0.97	86.23	0.042
2	1.06	85.92	0.046	10	0.89	86.30	0.039
3	1.06	85.90	0.046	11	0.97	85.96	0.042
4	0.58	86.40	0.025	12	1.33	85.28	0.058
5	0.49	86.41	0.021	15	0.89	86.23	0.039
6	0.84	85.92	0.037	20	0.84	86.33	0.036
7	0.97	85.97	0.042	21	1.06	85.33	0.047
8	0.80	86.33	0.0347	22	0.97	85.88	0.042

<sup>a</sup>Rotary denitrator product - batch number.

An "optimum"  $\text{NO}_3^-/\text{Th}$  ratio for a  $\text{ThO}_2$  powder is judged to be about 0.04. There is a broad range of  $\text{NO}_3^-/\text{Th}$  ratios, however, over which a powder may be used. Powders with ratios from 0.03 to 0.06 are satisfactory, and there is no practical difference in behavior over this range. Powders with ratios as low as 0.02 may be dispersed but frequently require a higher  $\text{NO}_3^-/\text{Th}$  ratio for complete dispersion.

Two of the rotary denitrator products (RDP's 4 and 5) fell below the 0.03 arbitrarily set as the desirable minimum (Table 1). Their ratios are suspect for several reasons. The standard dispersion test showed that both

batches could be dispersed readily at the standard  $\text{NO}_3^-/\text{Th}$  ratio (see Appendix). Control records gave no reason for the low  $\text{NO}_3^-/\text{Th}$  ratios found in the two questionable batches. The powder was used in startup tests, and no abnormal behavior was noted in sol preparation. Unfortunately, the duplicate samples held on these two batches were used to prepare analytical standards before the discrepancies were noted; so a second analysis could not be made. The  $\text{NO}_3^-$  analysis is not thoroughly reliable and is frequently subject to error (see below). In view of all the above, it is suggested that the fault lay in sampling-analytical methods.

Since most of the  $\text{ThO}_2$  needed in the Kilorod Program was prepared before "hot" operations began in the cell-4 complex, the data collected on the large (nearly 70 kg) batches of blended powder are presented in Table 5. One batch (BB-2) of the 16 prepared was below the desired lower limit. The comments presented in the discussion on the RDP-4 and -5 samples apply here, also. The  $\text{NO}_3^-/\text{ThO}_2$  ratios calculated for BB's 1 and 2 are presented in the footnotes below Table 5 to illustrate the error commonly associated with the  $\text{NO}_3^-$  analysis. The allowable  $\text{NO}_3^-/\text{Th}$  ratio is so broad that a low value is of little concern if the other factors are favorable.

#### 4.1.2.2 Installation and Startup of Equipment in the Sol-Gel Cubicle. -

Objectives of Cold-Testing. - As the equipment had only been operated piece by piece to this point, a sustained five-day cold run (using depleted uranium and thorium) was planned. This sustained operating test was intended to do the following:

1. Show the operability of the sol-gel equipment as an integrated process on the 10-kg/day (design) scale. Operation would cover the normal five-day work week and use the stringent containment and operating restrictions which later high-level alpha work would require.
2. Confirm the estimate that two men could satisfactorily operate the plant.
3. Demonstrate capability of meeting the stringent U/Th ratio specification.
4. Establish the feasibility of operating the calciner on a 24-hr cycle. To meet this time cycle, removal of the crucibles from the furnace at  $350^\circ\text{C}$  would be required. The crucibles would have to be placed

Table 5. Analytical Data on All Blended Powder Batches Prepared for the Kilorod Program

Batch size, about 70 kg ThO<sub>2</sub>

BB <sup>a</sup> No.	NO <sub>3</sub> <sup>-</sup> (%)	Th (%)	NO <sub>3</sub> <sup>-</sup> /Th Mole Ratio	BB <sup>a</sup> No.	NO <sub>3</sub> <sup>-</sup> (%)	Th (%)	NO <sub>3</sub> <sup>-</sup> /Th Mole Ratio
1	0.73	86.01	0.032 <sup>b</sup>	9	1.00	85.93	0.044
2	0.66	86.20	0.029 <sup>c</sup>	10	0.93	85.34	0.041
3	0.73	86.14	0.032 <sup>d</sup>	11	0.84	84.63	0.037
4	0.80	85.94	0.035	12	1.06	85.95	0.046
5	0.88	84.98	0.039	13	0.93	85.41	0.041
6	0.89	85.88	0.039	14	0.84	85.94	0.037
7	0.89	85.29	0.039	15	0.80	85.87	0.035
8	0.80	84.79	0.035	16	0.80	85.57	0.035

<sup>a</sup>(Powder) blender batch number.

<sup>b</sup>Using individual RDP analyses this ratio is calculated to be 0.039.

<sup>c</sup>Using individual RDP analyses this ratio is calculated to be 0.037.

<sup>d</sup>Equivalent data not available for this batch.

immediately under an argon-purged cap, and the calciner recharged with "green" gel. This change in firing procedure involved handling the crucibles (with tools and rubber gloves) while hot, and exposure of the  $UO_2ThO_2$  to air for several minutes while the crucibles were being placed under the argon. Had the furnace cooled in the time stated in the specifications, a 24-hr cycle would have been possible, with crucible removal at 100°C.

5. Prove final operating conditions for the calciner.

Results of Cold Test Operations. - The five-day sustained operating test of the sol-gel cubicle was conducted without event. With all steps of the operation under way, the following facts were established:

1. Two men could prepare 10 kg of product per day on a continuing basis.
2. Ability to meet the primary specification for the U/Th ratio, i.e.,  $3.00 \pm 0.03$  on individual batches, appeared doubtful; therefore permission was obtained from BNL to revise the primary specification for individual batches to  $3.00 \pm 0.05$  (see Table 6). Permission was also obtained to blend powders falling outside the primary specification but within the  $3.00 \pm 0.10$  range. By agreement, this powder blending was to be done so that the U/Th ratio obtained in the blended product fell within the  $3.00 \pm 0.05$  specification; thus, for example, a batch whose U/Th ratio was 3.10 could be blended with a batch analyzing 2.96 to obtain a 3.03 ratio for the blend. The uranium concentration for the second sol batch would be lowered intentionally to accomplish this purpose. In this way the target value for the U/Th ratio would not be 3.00 for every batch during the hot operation, but would be adjusted as necessary to maintain as near a 3.00 ratio as possible for a given campaign or shipment. The success of this control scheme is attested by the data obtained from hot operations (see Sec 4.2.2).
3. Pulling the calcined product at 350°C was practical from an operating standpoint. There was no evidence that the product was oxidized under this handling procedure.
4. An attempt was made to raise the calciner charge from 10 (design capacity) to 12 kg, but this was unsuccessful. In calciner design, two saggars were sized to fill the furnace cavity fully, with each holding

Table 6. U/Th Ratio Control Results  
During Sustained, Cold Operating Test

SGBD <sup>a</sup> No.	apH <sup>b</sup> of Sol	Nominal Batch Wt. (kg)	$\frac{U}{U+Th}$ Ratio	SGBD <sup>a</sup> No.	apH of Sol	Nominal Batch Wt. (kg)	$\frac{U}{U+Th}$ Ratio
1	-	12.4	3.01	7	3.6	10.3	2.96
2	-	12.4	3.04	8	3.5	10.3	2.96
3	3.5	10.3	2.94	9	3.8	10.3	2.96
4	3.6	10.3	2.90	10	3.7	10.3	3.00
5	3.6	10.3	3.04	11	3.5	10.3	2.98
6	3.6	10.3	2.96	12	3.8	10.3	3.01

<sup>a</sup>Sol-gel batch number, cold test series.

<sup>b</sup>"apH" is the apparent pH.

NOTE: The sustained cold operating test included sol preparation and drying for batches 8-12 and calciner batches 6-10.

5 kg of green gel ("bone-dry" basis). Less than 1 in. of freeboard remained. Gel was unavoidably spilled when trying to increase the sagger loading beyond 5 kg under limitation of glove operations. As no spillage could be tolerated, the decision was made to remain at the 10-kg batch size.

5. An air-operated pressure cell was installed to weigh the product before it was dumped to the solids-preparation shaft. This type of cell had given satisfactory performance in previous installations at the Laboratory; however, a poorly designed mounting system prevented proper operation in this service. As the inaccessible location of the pressure-cell installation precluded reworking of the assembly, it was decided not to use this particular device and to go to mechanical scales operated with the gloved hands, and an inexpensive platform-type domestic scales (which could be read to within  $\pm 1$  oz) was purchased for temporary use. A second and more accurate triple-beam balance was ordered for later use. This second balance was capable of weighing 5 kg to within  $\pm 5$  g. The spring balance was available and used for the second hot campaign. The triple-beam balance was installed and ready for use at the start of campaign 3

and was used for the rest of the program. The pressure cell was used for the first hot campaign, but the results are subject to a  $\pm 5\%$  error, and are therefore of little value.

Little data of value were obtained in the first five batches prepared in the cold test operation, because of startup troubles in the various equipment pieces (see Table 6). In the sustained test (batches 6-12), however, everything functioned smoothly, and the data ensured that hot operations could be undertaken with confidence from both equipment operability and product-quality standpoints.

The gas-release values for the calciner product had been expected to be  $\leq 0.03$  std cc/g (see Sec 3.1.5.3). Cold test data showed that this release might be as high as 0.05 std cc/g. Gas release values of  $\leq 0.3$  std cc/g were confirmed for the finely divided powder as loaded into the fuel rods. These values ( $\leq 0.05$  std cc/g for calciner product and  $\leq 0.3$  std cc/g for powdered oxide) were proposed and accepted as product specifications.

Control of the apparent pH of the sol between 3.6 and 3.8 was easily accomplished, and in general the performance of the proposed flowsheet was excellent. The calcined product obtained at these apH values was extremely hard and brittle, both desirable properties (see later discussion on these properties and apH control, Sec 4.2.2). The material also performed satisfactorily in powder preparation, where rods were prepared with this feed consistently met specifications (Sec 4.1.3).

The opportunity was seized during the sustained operating test to optimize operating conditions for the calciner. A 2.04 (max) value for the O/U ratio in the calciner product indicates that complete reduction of the  $U_3O_8$  was obtained. This 2.04 value actually represents the limit of analytical detection for oxygen in the (3% U - 97% Th) $O_2$  product (Sec 3.1.5.3). Complete reduction was therefore obtained in runs 7 and 8 (Table 7). A reduction period of about 4 hr and a tenfold excess of hydrogen was required to complete the reaction.

#### 4.1.3 Rod-Fabrication Pilot Plant

During the initial cold testing of the fabrication equipment, it soon became evident that the powder-conditioning equipment was the area of major concern. Despite efforts to contain dust within the system, an unexpectedly

Table 7. Physical Data on the Sol-Gel Oxides Prepared During  
the Sustained Cold Operating Test

Batch No.	Sample Code <sup>a</sup>	Gas Release (std cc/gm)	O/U Ratio
6	SGOD-	0.045	2.10
	COC-	0.024	
	COF-	0.25	
	COMP.-	0.054	
7	SGOD-	0.035	2.03
	COC-	0.016	
	COF-	0.10	
	COMP.-	0.17	
8	SGOD-	0.033	2.04
	COC-	0.034	
	COF-	0.11	
	COMP.-	0.059	
9	SGOD-	0.036	2.09
10	SGOD-	0.018	--

<sup>a</sup>SGOD is a calciner batch number.  
COC represents a batch of crushed oxide, coarse (6/16) fraction.  
COF represents a batch of crushed oxide, fine (-16/325) fraction.  
COMP represents powder as loaded into the rods, i.e., 55% COC -  
45% COF.

large quantity of oxide dust accumulated on the exterior of the equipment. Obviously, this very abrasive dust can cause excessive wear of bearing- and bearing surfaces. The abrasiveness of the powder caused extensive trouble with the ball mill (Fig. 28). The requirement that the mill be simultaneously rotated about three axes called for several types of bearings. Extensive modifications were essential to obtain a suitable working situation. Even after apparently solving the bearing problem, other modifications were necessary; because of the wearing of bearing surfaces, extraneous material was introduced into the fuel. Before cold testing, there was concern that the classifier screens might block during operation; however, the cold runs showed that some screen blockage would occur but not enough to be of concern. The remainder of the powder-conditioning equipment performed satisfactorily. In the complete system, a material holdup of about 2 kg was observed during the cold runs.

During the operation of the vibrator system, several modifications were necessary. The need to observe the feeding of the fuel into the rod required the elimination of the dust boot over the end of the feeder trough. Although the elimination of the boot increased the dusting, it was felt that adequate feeder control could not be obtained without observing the feeding. The chuck for holding the rod was designed to utilize a slightly modified Swagelok tube coupling. This coupling uses a standard 1/2-in. pipe to 1/2-in. tube male connector with specially machined split ferrule. During the cold operations, failure of the Swagelok chuck was usually observed after 10 to 12 rods; therefore, it is planned to change the Swagelok tube coupling after the compaction of six rods. Also, a number of failures in the other components of the vibrator-chuck assembly are anticipated because of the extremely high levels of acceleration associated with the Branford<sup>a</sup> vibrator (reportedly as high as 20,000 to 100,000 g). Along with daily maintenance checks on all fasteners on the unit, spare components to the entire vibratory compaction assembly are considered absolutely essential.

In operating the vibrator, it was found that the freedom of the anvil, to which the rod to be filled is attached and upon which the pneumatic hammer impinges, is very important. The anvil must be allowed to move a short distance (about 1/16 in.) to obtain the desired compaction. If the

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<sup>a</sup>Manufactured by the Branford Co., New Britain, Conn.

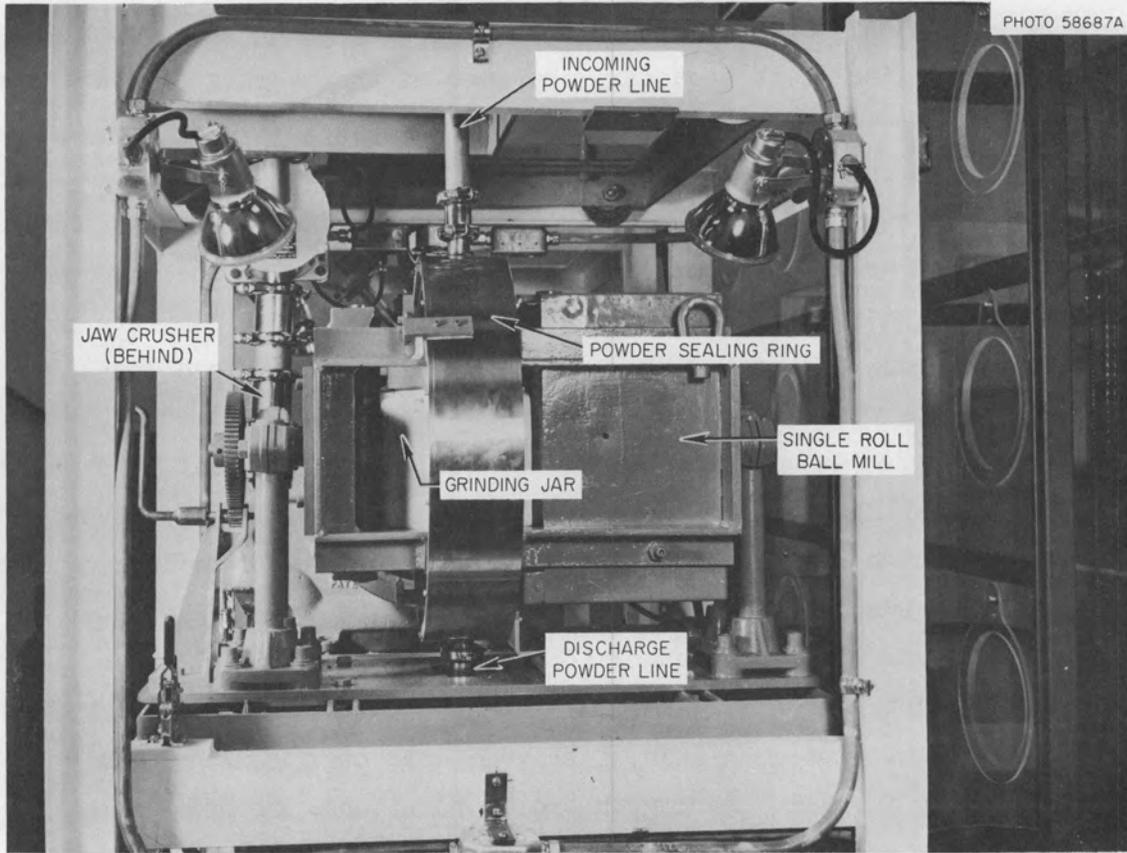


Fig. 28. Original Ball Mill.

anvil is not allowed to reciprocate, a reduction in packed density of 8 to 10% is observed. Some difficulties were experienced with the Branford vibratory due to component failures within the vibrator unit.

After demonstrating the ability of the powder-preparation equipment to produce powders of three size fractions for loading into the fuel tubes, it was decided to modify the system to produce powders of a binary-size distribution. The decision to operate the system with two size fractions was based on two factors: (1) the binary system is equal to the ternary in compaction density that is attainable, and (2) the binary is much easier to operate, especially remotely. During the cold runs, the binary-size distribution was optimized and now consists of a charge of 55% of a classified -6 +16 mesh fraction and 45% of an unclassified ball-mill fraction. The ball-mill fraction is controlled by the weight of charge and the time spent in milling. A set of conditions was determined which would result in the most practical use of the distribution produced by the jaw crusher and which would pack to acceptable densities. The ball-mill fraction has typically the distribution given in Table 8.

Table 8. A Typical Size Distribution for the  
Ball-Milled Fraction

Range of Particle Sizes	Percentage of Particles Within Given Range
-16 +50	20
-50 +140	30
-140 +200	20
-200 +325	25
-325	5

With this distribution, 20 sample rods were packed to an average bulk density of 90% of theoretical, with a deviation from rod to rod of < 1%. The density profile measured with the gamma scanner within these rods was well within the specified  $\pm 2\%$ , with the majority showing a deviation of < 1-1/2%. The results were most gratifying, since they had not been predicted from laboratory experience. Apparently, a wider distribution

range of powders can be utilized with the bottom-actuated pneumatic device mounted similarly or on a beam mount. The greater breakup of powder during compaction with the pneumatic device can account for this observation.

## 4.2 Hot Operation

### 4.2.1 Solvent Extraction Pilot Plant

About 50 kg of  $^{233}\text{U}$  was purified in nine runs during the Kilorod Program. A summary of the significant results of these runs is presented in Table 9. Also presented are the specifications imposed on the  $^{233}\text{U}$  purification by the sol-gel process. Specifications were met in each instance. Detailed results are presented in Appendix Section 8.1.3.

The gross gamma decontamination factors shown in Table 9 were obtained from the gamma activity of the concentrated product. A more significant study of the gamma activity of the product is presented in Fig. 29, which presents the change in gamma activity of dilute stripped product (expressed as gamma counts per min per mg of  $^{233}\text{U}$ ) with time after purification. Radiochemical analyses of the product<sup>25</sup> indicate the removal of more than 99.9% of the longer-lived daughters of  $^{232}\text{U}$  with the exception of about 0.3% of the  $^{212}\text{Pb}$ . Apparently, the  $^{212}\text{Pb}$  resulted from the decay of  $^{220}\text{Rn}$  which was extracted. The high energy gamma activity (primarily  $^{208}\text{Tl}$ ) associated with the product decreased for about four days as the  $^{212}\text{Pb}$  decayed and then began to increase as the  $^{228}\text{Th}$  concentration built up.

Also presented in Fig. 29 for comparison is a curve of data obtained by Rainey in laboratory-scale countercurrent work. Because of shorter contact time less  $^{220}\text{Rn}$  was extracted in the countercurrent work, resulting in lower  $^{212}\text{Pb}$  content and the absence of initial decay as exhibited by the Kilorod product. However, after a few days the activity of the countercurrent product is approximately of the same level as the Kilorod product.

Approximately 13 kg of the material purified in runs DC-2 and DC-3 was used to supply the requirement in another AEC-sponsored program.

To summarize, the solvent extraction process used to purify  $^{233}\text{U}$  produced material which met all specifications imposed by the sol-gel process.

### 4.2.2 Results of Sol-Gel Operations

By the completion of the Kilorod Program more than 1 metric ton (1003 kg) of product had been prepared. This included 993 kg of regular Kilorod

Table 9. Kilorod Program Summary of Solvent Extraction Results

Run No.	<sup>233</sup> U Recovered (g)	Decontamination Factors		NO <sub>3</sub> /U Ratio	Measurable Ionic Impurities (ppm <sup>233</sup> U)			
		Gross $\gamma$	Thorium		Al	Na, Mg	Ca, Li	Total
HJ-1	4622	230	$3.0 \times 10^3$	2.42	2490	2201.86		4744
HJ-2	4527	380	$5.0 \times 10^3$	2.25	52	<360.22		193
HJ-3	3784	416	$3.0 \times 10^3$	2.16	37	220.10		271
DC-1	4358	185	$2.0 \times 10^3$	2.12	28	296.46		310
DC-2	7793	310	$5.50 \times 10^3$	2.12	23	165.05		207
DC-3	7918	258	$5.50 \times 10^3$	2.12	16	75.59		113
DC-4	5030	300	$3.10 \times 10^3$	2.20	26	113.00		155
HJ-4	5034	194	$2.60 \times 10^3$	2.14	12	<234		193
HJ-5	6485	150	$1.96 \times 10^3$	2.19	26	62		162
	Specifications	100	$10^3$	2.5				

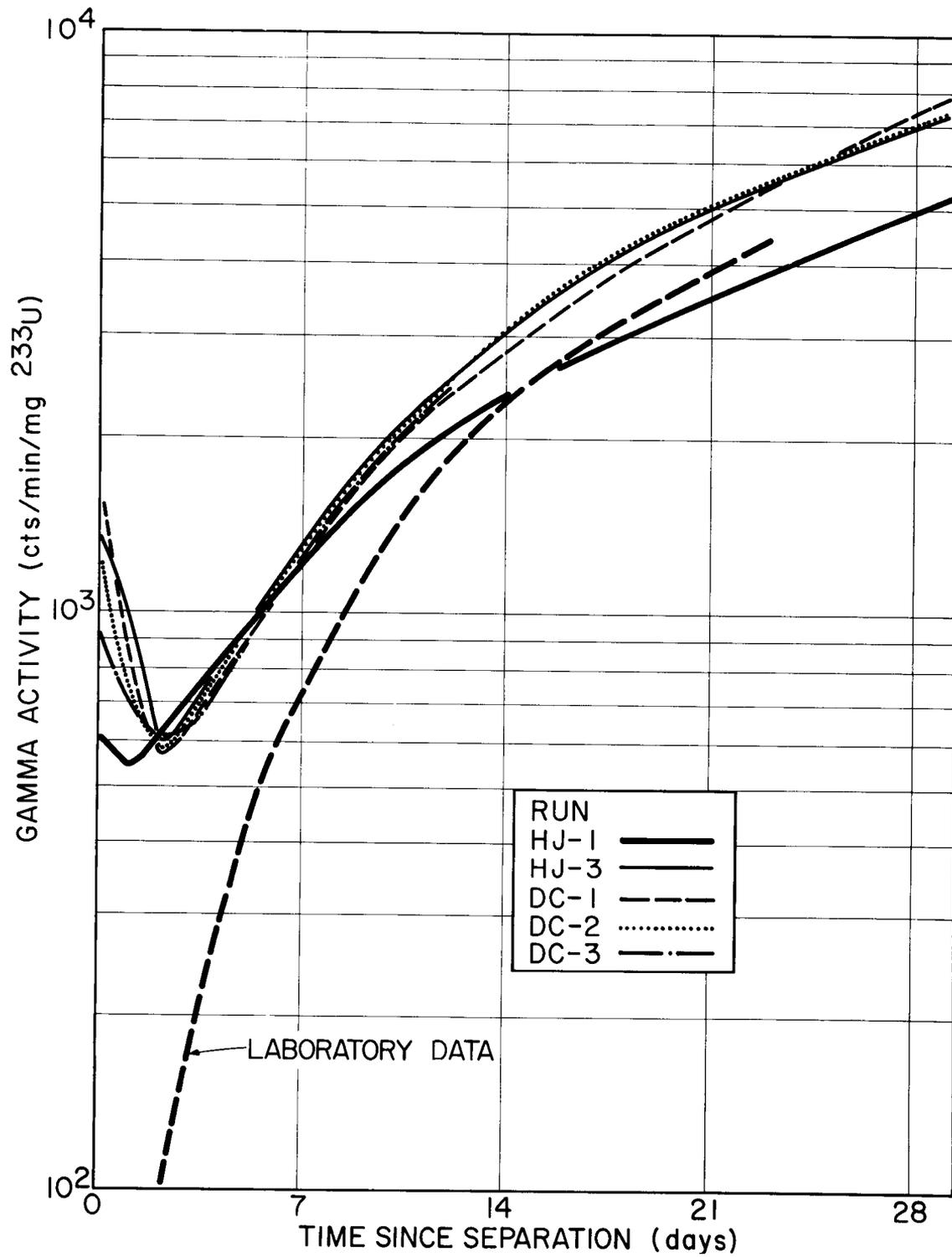


Fig. 29. Growth of Gamma Activity in Purified  $^{233}\text{U}$ .

product and the 9.9 kg prepared in the high-radiation-level test. Except for the first campaign, as noted below, process control and product uniformity were excellent throughout the program.

4.2.2.1 Operational Control of the U/Th Ratio During Hot Startup. - Ratio control for the Kilorod operation must be divided into two operating periods for analysis and discussion. The first period includes the first 12 runs, which comprised the first campaign. The second period includes the rest of the program (campaigns 2-7). Ratio control was poor for the first campaign but excellent for the remainder of the program, as will be discussed.

A campaign scheme of operations was selected for the Kilorod operation. A batch of  $^{233}\text{U}$  was prepared by solvent extraction and placed in the UNH feed solution storage tank. The solids prepared from this batch of UNH feed solution were given a campaign number in passing through the sol-gel and rod-fabrication operations. At the end of each campaign, the SX, sol-gel, and rod-fabrication equipment were cleaned thoroughly, and strict accountability made. This was done for criticality control as well as accountability.

The campaign required storage of feed solutions for several weeks. Proper feed-solution storage demanded an almost invariant uranium concentration over the period of storage. This was necessary if proper control of the U/Th ratio were to be obtained. Analytical costs and the limited number of analysts available were also to be considered.

The original feed-solution storage tank (R-25) was unsatisfactory. The tank, which was filled with boron-glass Raschig rings, could not be agitated properly with the air-spargers provided. Apparently the liquor became entrained by the agitating air up into the packing, lost a considerable amount of water and then dripped back down into the solution in the lower part of the tank. This drain-back would occur for an extended time after agitation and sampling. It was thus difficult to get agreement between duplicate samples. In addition to this drain-back, a current of air passed through the tank from instrument probes. Thus, there was a steady but erratic concentrating of the feed liquor. For example, in a nine-day period the  $^{233}\text{U}$  concentration rose from 116.8 to 133.5 g/liter, obviously intolerable. Therefore, it was decided to stop operations and to

install a new feed solution storage tank (R-35). This new tank would have no packing as it was of critically safe geometry (5-in. IPS, 13-ft high), and, being slender, agitation and sampling would be satisfactory (see Fig. 30). Accordingly, the first campaign was halted after 12 runs, the entire plant cleaned out, and the new feed solution storage tank installed.

The results given in Table 10 show the control problem encountered in the first campaign. A target ratio of 3.00 was selected for each batch, and yet individual sol analyses ranged from 2.88 to 3.19. This was primarily the result of the drift in the feed solution concentration. However, superimposed on this uncertainty was also the analytical-sampling errors, graphically shown in the poor agreement between repetitive samples taken from certain batches (see results 4A, 4B and 4C or 10A, 10B, 10C and 10D). Despite these difficulties and using averages of all analyses received on each batch, only one batch (No. 10) did not fall within the  $3.00 \pm 0.10$  value in which powder blending was permissible. BNL permission was obtained to blend this batch with other powders. Actually blending was practiced with all batches of this campaign as a precautionary measure. For example, batches 4 and 11 were blended, as were batches 8, 10, and 12.

#### 4.2.2.2 Test of Feed Solution Stability in the New R-35 Storage Tank. -

The process-control difficulty arising from the unstable uranium concentration in the R-25 tank, demanded a sampling-analytical study to ensure that adequate control could indeed be accomplished through use of the newly installed R-35 tank. This test was also highly desirable for other reasons. First, the U/Th ratio specification demanded extreme accuracy in the uranium analysis of the feed solution, an accuracy not before met in process control. Anything less than the most accurate analysis was worthless, and the recognized limits of accuracy indicated that the precision of even the most accurate method was marginal. The coulometric method, accepted standard for this determination, had been performed in the past, mostly by specialists.<sup>10</sup> The number of analyses anticipated and the availability of these specialists only during the day made necessary the use of "production" analysts under production conditions. Thus the need was established not only to determine the stability of the solution concentration in the new storage tank but to test the reproducibility of samples

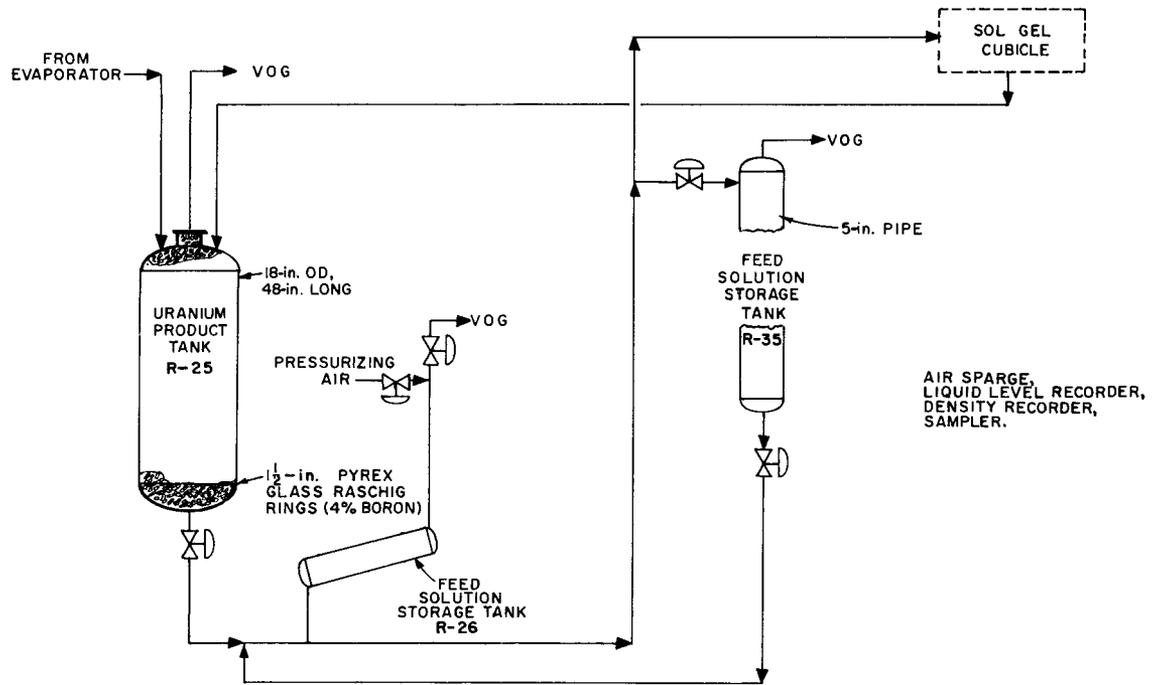


Fig. 30. Solvent Extraction Uranium Storage and Transfer System.

Table 10. Individual U/Th Ratios for the 12 Batches  
Comprising the First Hot Campaign

Sol-Gel Batch No. SGB <sup>a</sup>	Ratio by Laboratory Analysis	Sol-Gel Batch No. SGB	Ratio by Laboratory Analysis
1	2.92	8A	2.88
2A	3.02	B	2.92
B	3.01	C	2.92
3A	2.99	9A	2.99
B	3.01	B	3.00
C	3.01	10A	3.15
4A	3.04	B	3.07
B	3.05	C	3.11
C	3.19	D	3.15
5	2.91	11A	2.93
6	2.94	11B	2.91
7	2.95	12	2.92

<sup>a</sup>When repetitive sampling and analysis was done, average of all values was used to determine the ratios.

taken by the remote sampling device, the inherent accuracy of the method used, and the capabilities of the methods, men, and coulometers under production conditions.

A statistical study was blocked out for this problem. Samples were withdrawn in duplicate (or triplicate) at irregular intervals from the R-35 tank over the period July 21 to September 3 (campaign 2). The "original" analysis (see below) was performed in duplicate on the samples immediately after withdrawal. Determinations were made in duplicate, and all results were reported. The unused portions of these samples were sealed and held for periods ranging from 7 to 17 days and submitted for repeat analysis (see below). These repeat analyses were made in blocks ranging from 2 to 6 in number.

The statistical evaluation of the data is the subject of another report.<sup>11</sup> In this evaluation, the following were established at the 95% confidence level:

1. There is no "drift" with time in the analytical operation.
2. As a result of a t-test, the mean of the original analyses and the repeat analyses are equal.
3. A gradual but small increase in the concentration of the feed solution was found. This amounted to 0.04 gm U/liter/day. As a result of a least-squares plot of the data, the concentration of the feed solution was found to fit the following equation:

$$U(\text{g/liter}) = 108.9 + 0.042\theta,$$

where

$\theta$  is lapsed time in storage tank in days.

4. The precision of the two coulometers assigned to the Kilorod Program was equal. The same was true of the work of the two analysts.
5. The mean of the results obtained on coulometer 1 was different from those for coulometer 2. The mean of the operator's results were also not equal. However, this was to be expected since the first coulometer was used exclusively through the first ten days (13 determinations) of the test. The second one was used throughout the remainder. The same is true of the operator's work, as one performed the first 24 "original" determinations, while the second performed 5 original determinations almost at the end of the program. In this regard, reference is made to the clearly established rise in concentration discussed above.

Several spot checks throughout the test period were also made during the period between the work of the Kilorod analysts and the specialists mentioned. The maximum discrepancy noted in these tests in no case exceeded an acceptable 0.6 g/liter at the 100-g/liter level.

This study clearly showed the adequacy of the R-35 installation. Infrequent analysis of the feed solution (every 10 days) would provide excellent process control. The results of the analysts' work exceeded expectations; the commonly accepted error for the method under the handling of specialists is  $\pm 0.5-0.75$  g/liter at the 100-g/liter level, as opposed to a  $\pm 0.2$  g/liter at the 108-g/liter level obtained by the Kilorod analysts.

#### 4.2.2.3 Control of U/Th Ratio During the Remainder of Hot Operations. -

The installation of R-35 solved the U/Th ratio control problem for the remainder of the Kilorod Program (campaigns 2-7). At the same time, the sampling-analytical problems associated with hot operations were also worked out. Analyses of the individual sol batches of the second campaign show the marked improvement made in the operation by this equipment addition (see Table 11). This control is typical of the remainder of the operation. A standard deviation of 0.038 was maintained between the target value of the U/Th ratio and the ratio by sol analysis over the last 88 batches processed.

Table 11. Individual-Batch U/Th Ratios Based on Sol Analysis  
Second Campaign

SGB No.	Ratio by Sol Analysis	Target Ratio	SGB No.	Ratio by Sol Analysis	Target Ratio
13	2.98	3.00	21A	3.02	2.97
14	3.02	3.02	B	3.01	2.97
15	3.03	3.02	C	2.98	2.97
16	3.03	3.02	22	2.94	2.95
17A	2.94 <sup>a</sup>	3.00	23	2.99	3.00
B	3.01	3.00	24	3.01	3.00
18A	3.00	3.00	25	3.04	3.00
B	3.03	3.00	26A	3.07	3.00
19	3.08	3.05	B	3.03	3.00
20	3.07	3.05	27	3.02	3.00
			28	3.03	3.00

<sup>a</sup>The analyst questioned this result independently and requested resampling.

The U/Th ratio can be determined by three methods. The relative accuracy of those methods is discussed so the U/Th ratio data can be better interpreted.

The first (SS transfer ratio) method is considered the most accurate. In the SS transfer method the  $^{233}\text{U}$  contained in the feed solution and the weight-analysis of the  $\text{ThO}_2$  feed are used. These values and the weight of the product leaving the cubicle are the most accurate data available to sol-gel operations (see Sec 4.3.3).<sup>12</sup>

The second, or sol-analysis method, is the second most accurate method.<sup>13</sup> This ratio is based upon the analysis of the sol. However, the analysis of the two elements in the presence of each other in the sol is not as accurate as in the analysis of the individual metals in the separate feed fractions. Also, the sampling of the sol is not as good as the sampling in the SS transfer method.

The third method (powder-analysis method) includes the preparation of a composite sample representing a large quantity of product (the quantity of product in a carrier). This ratio is the least accurate of the three, undoubtedly the result of sampling error.

The first (SS-transfer ratio) method was adopted as the official ratio and is the ratio upon which SS transfers to BNL were made. The sol-analysis ratio was useful as a confirmatory figure for the SS-transfer ratio. Excellent agreement between these two could be expected over any campaign, and the U/Th ratios actually obtained in the sol-gel campaign represent to some extent a compromise between the two methods.

The objective of each campaign was to achieve an overall average U/Th ratio of  $3.00 \pm .03$ . This objective was easily met in all campaigns, with the possible exception of the startup campaign (Table 12). At the same time, by established practice, no sol-gel product was transferred to rod fabrication which did not have a sol-analysis ratio within the primary specification ( $3.00 \pm .05$ ) range. This was accomplished as follows: Any batch whose sol analysis fell outside this range was placed in temporary storage after calcining. A second batch was prepared with a "target" ratio selected to offset the error apparent from the sol analysis of the earlier batch. The batches of calciner product thus "paired" were thoroughly mixed before transferring to the rod-fabrication

Table 12. Summary of the  $100x \frac{^{233}\text{U}}{^{233}\text{U}+^{232}\text{Th}}$   
 Ratios for the Product of Each Campaign

Campaign No.	Number of Batches	SS-Transfer Ratio	Sol-Analysis Ratio	Range of Sol Analyses
1	12	2.96	2.97	2.91 - 3.12
2	16	3.01	3.02	2.94 - 3.08
3	12	3.00	3.00	2.95 - 3.06
4	13	3.02	3.00	2.94 - 3.07
5	23	3.00	2.99	2.91 - 3.05
6	17	3.02	2.98	2.93 - 3.04
7	7	3.03	2.99	2.95 - 3.06

train. "Target" ratios in all cases were held within the specification range to avoid unnecessarily large variations in the product ratios. In one case (campaign 1), three batches were blended to obtain the desired ratio before dumping.

The above batch-blending scheme favored the SS transfer data but resulted in a reasonable compromise between that method and the sol analysis. The agreement obtained between the two methods is excellent (Table 13). A somewhat larger variation is noted when comparing the results of either of these two methods with the powder analysis but still falls within the  $\pm 2\%$  error ( $3.00 \pm 0.06$ ) predicted in the earlier work.<sup>12</sup>

The practice of withholding batches outside the primary specification until a "paired" batch was available yielded distinct benefits. In this way, it was not possible to load a single rod with powder which did not meet the ratio specification. A considerable amount of powder (15 kg) was withheld from campaign 1 for this reason and later blended with material from campaign 3 (see Appendix). Product from campaigns 1 and 2 was also blended to complete the first carrier shipment. Note that the carrier-product ratios were held very close to 3.00 by this procedure for the first three carriers, while variations in the ratios for the three corresponding campaigns varied.

The apparent wide range of sol-analysis ratios which occurred in each of the campaigns should not be of concern in an overall process control

Table 13. Summary of the  $100x^{233}\text{U}/^{233}\text{U+Th}$   
Ratios for the Fuel in Carrier Shipments by the Three  
Customary Methods

Carrier Shipment No.	SS-Transfer <sup>a</sup> Ratio	Sol-Analysis Ratio	Powder-Analysis Ratio
1	2.99	2.99	2.99
2	3.00	3.00	3.04
3	2.99	3.00	3.03
4	3.02	3.00	2.96
5	3.00	2.98	3.00
6	3.00	3.01	2.95
7	2.99	2.99	3.02
8	3.01	2.97	3.03
9	3.03	3.00	2.94

<sup>a</sup>Best values for the  $^{233}\text{U} \times 100 / ^{233}\text{U+Th}$  ratio.

sense, because generally only one of the extreme ratios shown represents a batch outside the primary specification range. The batch at the other limit of the range is simply the "paired" batch.

4.2.2.4 Gas-Release Values for the Kilorod Product. - The gas release of each batch of calciner product was determined throughout the program (Table 14). Gas release for each of the nine carrier composite samples was determined by crushing the entire sample to -100 mesh before out-gassing. This departure from the procedure upon which the gas-release specification was written will be discussed later.

The gas-release data for the calciner product fell well within the limits expected from the limited Unit Operations and cold startup work. In the more extensive Kilorod work, 94 batches were made under standard operating procedure. Four of these exceeded the expected maximum of 0.05 std cc/g. The maximum of these exceptions was 0.057 and thus not significantly in excess of the expected maximum.

Toward the end of the program, it was decided to test the hot off-gas from the calciner for activity. Up to this time no activity had accumulated in the hot off-gas line, contrary to expectations. A high gas

Table 14. Gas-Release Values for the Powder  
Loaded into the Fuel Rods for Each Carrier Shipment

Conditions:

1. Carrier composite sample used for this test
2. Sample crushed and passed through 100-mesh screen before checking gas release

Sample Identity	Gas Release (std cc/gm)								
	Carrier Shipment No.								
	1	2	3	4	5	6	7	8	9
Comp. - A	0.48	0.18	0.41	0.29	0.54	0.37	0.19	0.67	0.30
- B	0.52	0.25	0.43	0.32	0.18	0.38	0.26	0.67	0.24

release will be noted ( $\leq 1$  std cc/g - see Appendix) for calciner batches 96, 97 and 98. During these runs, samples were being withdrawn continuously from the calciner off-gas stream, and the operators could not maintain the atmosphere in the calciner. The product was thus higher than normal in this respect, but when blended with material prepared in normal operation the gas release was lowered to normal, that is, 0.27 for the carrier composite containing these calciner products (see carrier shipment No. 9 data in the Appendix).

The gas-release data for the composite powder samples appear high upon first examination. This is not true when the effect of a change in the analytical procedure is considered. In the original specification, the gas-release test was to be done on a composite sample of powder as taken directly from the rod-loading operation. More than 60% of this powder was +100 mesh. This relatively coarse powder has gas-release properties approximately equal to that of the calcined product, or about 0.05 std cc/g. During the progress of the operation, it was noted that a 5-8 fold increase was obtained in the quantity of gas released, if a given sample of coarse material was crushed and ground to -100 mesh before out-gassing.<sup>14</sup> In reality, this is the increase in gas release noted between the "calciner product" and "crushed powder" values of the specification, that is, 0.05 std cc/g and 0.3 std cc/g, although it was not so recognized at the time these values were agreed upon. In such case, the gas released by the coarse powder fraction is not appreciable when compared with the release of the fine powder. Thus, a doubling of the gas-release quantity would be expected as a minimum from this change in the analytical procedure.

The expectation of a doubling of the quantity of gas released by this change in analytical technique is supported by the results. Powder samples removed from the rod-loading station during the loading of the first 150 rods were analyzed individually for gas release. The average for this first 14 samples while using the original procedure was 0.11 std cc/g, while the range was 0.05 to 0.28 std cc/g. These samples in turn were used to prepare the first carrier composite sample from which gas-release values of 0.48, 0.50 and 0.54 were obtained. The results of the most general data (Table 14) give further confirmation with an average of 0.37 std cc/g and extremes of 0.18 to 0.67 std cc/g.

The above change was suggested as an improvement in the analytical procedure since the BNL group was interested in the total gas contained in the product. BNL agreed that the change was worthwhile and the product acceptable on these grounds.

While this change in procedure gave a better value than the original method, it is recognized that it still does not liberate all gases from the solid product. Only an arc-fusion method would do this, and even these results would be subject to inaccuracies arising from oxidation-reduction reactions occurring during the analysis.

4.2.2.5 Analysis of the Gas Released from the Carrier Composite Samples. - In the early part of the Kilorod Program the gas-release apparatus could handle only small (1-g) samples. This sample size was large enough to give accurate gas-release values; therefore early gas-release values are satisfactory. However, the quantity of gas contained in the capsules was frequently too low for mass-spectrometer use. Further, those capsules which apparently contained enough gas for analysis still did not contain enough sample to obtain acceptable accuracy. Duplicate samples frequently had no semblance of agreement.

This problem was recognized, and the analytical gas-release equipment revised so that much larger samples (10 g) could be used. Also the manifold-capsule volume ratio was reduced considerably. Considerably higher capsule pressures could thus be obtained and the accuracy of the gas analysis improved markedly. A sufficient volume of sample was obtained for analysis by both mass spectrometer and gas chromatograph. The gas chromatograph gave separate values for the  $N_2$  and  $CO$ , not available from mass-spectrometer operation alone. In turn, the gas chromatograph gave no values for water present.

Agreement between mass-spectrometric and chromatographic analyses is good, with the exception of the carrier-5 sample (see Table 15). The mass-spectrometer data are presented first, showing the water contained, and then on a "bone dry" basis for direct comparison with the gas-chromatographic values. Note that the agreement between duplicate samples on the water determination is poor. Also note that there is a tenfold variation in water content from one sample to another. This cannot be explained. Analysis is considerably better for the other gases present,

Table 15. Composition of the Gas Released by the Kilorod Product  
(Volume %)

Carrier Composite Sample No.	Anal. <sup>a</sup> Method	H <sub>2</sub> O	H <sub>2</sub>	CH <sub>4</sub>	HC <sup>b</sup>	N <sub>2</sub>	CO	N <sub>2</sub> + CO	O <sub>2</sub>	CO <sub>2</sub>	NO	
1	MS	23.9	21.3	0.4	0.2	--	--	31.5	0.2	19.4	3.1	
		4.1	26.9	0.5	0.3	--	--	41.1	0.1	25.4	1.6	
	GC	--	28.1	0.6	0.3	--	--	42.0	0.2	26.1	2.9	
		--	31.8	0.6	--	5.2	25.6	30.8	2.2	28.7	--	
2	MS	27.7	19.6	0.2	0.2	--	--	28.2	0.9	19.7	3.5	
		22.1	21.2	0.2	0.2	--	--	30.7	0.6	21.9	3.1	
	GC	--	27.2	0.3	0.3	--	--	39.3	1.0	27.8	4.4	
		--	27.1	0.5	--	5.0	32.3	37.3	2.0	25.6	--	
3	MS	10.8	29.3	0.3	0.5	--	--	40.2	<0.01	18.5	0.4	
		35.9	19.7	0.3	0.3	--	--	27.5	0.03	13.0	3.0	
	GC	--	31.8	0.5	0.5	--	--	44.0	0.3	20.5	2.5	
		--	36.9	0.6	--	4.72	30.7	35.4	2.2	21.2	--	
4	MS	2.2	33.7	0.2	0.1	--	--	50.4	--	13.2	0.1	
		9.0	30.6	0.2	0.3	--	--	47.3	0.2	12.2	0.3	
	GC	--	34.1	0.2	0.2	--	--	51.8	0.1	13.5	0.2	
		--	34.8	0.9	--	4.8	33.2	38.0	2.4	19.1	--	
5	MS	17.3 <sup>c</sup>	11.8	0.3	0.3	--	--	36.6	4.2	28.9	0.6	
		--	14.3	0.3	0.4	--	--	44.3	5.1	34.9	0.7	
	GC	--	31.8	0.6	--	12.8	12.9	25.7	5.9	38.3	--	
		--	20.6	28.2	0.2	0.4	--	--	25.3	0.1	24.6	0.6
6	MS	13.8	31.1	0.3	0.3	--	--	27.7	0.1	25.8	0.9	
		--	35.9	0.3	0.4	--	--	32.0	0.1	30.5	0.5	
	GC	--	41.6	0.4	--	7.1	25.2	32.3	3.1	28.0	--	
		--	36.4	0.4	0.5	--	--	37.9	0.1	20.0	1.4	
7	MS	3.3	33.6	0.5	0.4	--	--	37.2	0.1	19.9	1.4	
		6.9	36.8	0.5	0.5	--	--	39.7	0.2	21.0	1.5	
	GC	--	40.6	0.8	--	4.5	29.9	34.4	1.5	21.9	--	
		--	2.02 <sup>c</sup>	27.0	0.2	0.3	--	--	43.3	0.2	26.8	0.2
8	MS	--	27.5	0.2	0.3	--	--	44.2	0.2	27.4	0.2	
		--	29.9	0.6	--	6.0	32.5	38.5	2.74	17.1	--	
	GC	--	3.0	33.8	0.5	0.4	--	--	51.4	<0.05	10.7	0.2
		--	1.2	35.0	0.5	0.5	--	--	52.5	<0.05	10.2	0.1
9	MS	--	35.1	0.5	0.5	--	--	53.1	<0.1	10.7	0.2	
		--	38.3	1.0	--	6.81	49.2	56.0	3.4	7.8	--	

<sup>a</sup>MS - Mass spectrometer. GC - Gas chromatographic.<sup>b</sup>Hydrocarbons.<sup>c</sup>Duplicate sample lost.

with only an infrequent 30% discrepancy between duplicates. For this reason, duplicate values are given only for the water analysis and there only to show the discrepancies encountered.

The product-contained gases are primarily  $H_2$ ,  $H_2O$ ,  $CO$  and  $CO_2$ , present in roughly equal volume percentages. Hydrogen is present in the solids equivalent to  $\approx 3$  ppm by weight. The corrosion of the Zircaloy by the hydrogen is of no concern in the present fuel tubes since zero power experimental use is planned.

The existence of a set of complex equilibria between the gases given above and/or their dissociation products at the  $1200^\circ C$  out-gassing temperature is recognized. The analytical data are presented as received without an attempt to evaluate the effect of these equilibria. Such an evaluation is beyond the scope of this report, and further, the available data are insufficient to support such an analysis.

4.2.2.6 Trace Elements in Feed Materials, In-Process Materials, and in the Powder Loaded Into the Fuel Rods. - Trace-element analyses were made on the  $^{233}U$  and thorium nitrate feed materials, the denitrated thoria powder, and the powdered solids as loaded into the fuel rods.

Trace-Element Contamination in the  $^{233}U$  of the Feed Solutions. - Trace contaminants for a typical  $^{233}U$  feed batch are given in Table 16. Note that an upper limit is given for most of the elements sought, meaning that if the contaminant is present (and it may not be) that its concentration is below the stated limit. This use of limits rather than exact values was imposed upon the analytical procedures by the size of  $^{233}U$  sample that could be handled in the hot cells. A complete tabulation of the trace analyses for all  $^{233}U$  feed-solution batches is given in the Appendix. During the period of the Kilorod operation, a continuing attempt was made to improve the spectrographic procedures. A considerable improvement was made, as shown by examination of the above referenced tabulation. Recall that only 3% of the  $^{233}U$  is present in the final product; thus the contaminants shown are correspondingly lower in concentration in the final product.

Table 16. Results of Trace-Element Analysis of a  
 Typical Uranyl Nitrate Feed, Batch HJ-4  
 Basis: ppm of  $^{233}\text{U}$

Element		Element		Element		Element	
Ag	< 1	Fe	12.7	Nd	< 82	Sm	< 7
Al	12	Ga	< 5	Ni	< 1	Sn	< 13
As	< 66	Gd	< 3	Os	< 33	Sr	< 7
Au	< 13	Ge	< 13	P	< 164	Ta	< 33
B	< 7	Hf	< 7	Pm		Tb	< 33
Ba	< 131	Hg	< 131	Pb	< 13	Tc	< 3
Be	< .01	Ho	< 33	Pd	< 7	Te	< 66
Bi	< 33	In	< 10	Pr	< 33	Th	
Ca	< 75	Ir	< 66	Pt	< 13	Ti	< 1
Cd	< 13	K	< 131	Ra		Tl	< 16
Ce	< 16	La	< 13	Rb	< 66	Tm	< 66
Co	< 13	Li	< 7	Re	< 7	V	< 1
Cr	4.3	Lu	< 13	Rh	< 13	W	< 16
Cs	< 33	Mg	5	Ru	< 7	Y	< 1
Cu	2.9	Mn	< 1	Sb	< 7	Yb	< 3
Dy	< 16	Mo	< 2	Sc	< 3	Zn	< 16
Er	< 66	Na	147	Se		Zr	< 1
Eu	< 3.3	Nb	< 16	Si	9		

Trace-Element Contamination in the Thorium Nitrate Feed Crystals. - A complete trace-element analysis was made on the thorium nitrate feed crystals. Unfortunately, it was not possible to sample the crystals properly in the classical sense. However, in the crystallizer used to prepare the crystals, thorough mixing was unquestionably obtained, and all the crystals used were from the same batch. The concentrations of the trace contaminants present for two grab samples are given in Table 17. The spectrographic values given for sample A are believed to be the best obtainable as they were obtained by using the most precise instrument and the best-trained personnel at the Laboratory. Also, as the thorium nitrate dissolved easily

Table 17. Results of Trace-Element Analysis of Thorium Nitrate  
 Feed Crystals - Rare Earths and Corrosion Products  
 Spectrographic, ppm

Element	Sample Identity		Element	Sample Identity	
	A	B		A	B
Ag	< 0.075	< 0.068	Nd	< 9.4	< 8.5
Al	1.9	0.8	Ni	0.25	< 0.17
As	< 7.8	< 6.8	Os	< 3.8	< 3.4
Au	< 1.5	< 1.4	P	< 15	< 17
B	3.9	< 1.2	Pb	< 1.5	< 1.4
	4.5		Pd	< 0.75	< 0.68
Ba	< 1.5	< 1.4	Pr	< 3.8	< 3.4
Be	< 0.00075	< 0.068	Pt	< 1.5	< 1.4
Bi	< 3.8	< 3.4	Re	< 0.75	< 0.68
Cd	< 1.5	< 1.4	Rh	< 1.5	< 1.4
Ce	6	4.3	Ru	< 0.75	< 0.68
Co	< 1.5	< 1.4	Sb	< 0.75	< 0.68
Cr	1.1	0.31	Sc	< 0.38	< 0.34
Cu	< 0.16	0.41	Si	1.4	< 0.14
Dy	< 1.9	< 1.7	Sm	< 0.75	< 0.68
Er	< 7.5	< 6.8	Sn	< 1.5	< 1.4
Eu	< 0.38	< 0.34	Ta	< 3.8	< 3.4
Fe	9.5	< 2.90	Tb	< 3.8	< 3.4
Ga	< 0.61	< 0.51	Tc	< 0.75	< 0.34
Gd	< 0.38	< 0.34	Te	< 7.5	< 6.8
Ge	< 0.15	< 0.14	Ti	< 0.038	< 0.034
Hf	< 0.75	< 0.68	Tl	< 1.9	< 0.68
Hg	< 15	< 14	Tm	< 0.75	< 1.7
Ho	< 3.8	< 3.4	U	< 1	
In	< 1.1	< 1.0	V	< 0.15	< 0.14
Ir	< 7.5	< 6.8	W	< 1.9	< 1.7
La	2.3	1.2	Y	2	0.68
Lu	< 1.5	1.4	Yb	< 0.38	< 0.34
Mg	< 3.6	0.25	Zn	< 1.9	< 1.7
Mn	< 0.075	0.054	Zr	< 0.15	< 0.14
Mo	< 0.23	< 0.21			
Nb	< 1.9	< 1.7			

in water, there was no error from that source, as would have been encountered in analyzing the product; therefore, this is believed the best boron analysis available. (See further discussion below on dissolution and analysis of product solids.) Note that the boron in sample A was re-determined, since the first value was unexpectedly high. The "B" sample was analyzed with less-precise hot-cell equipment by technicians rather than by thoroughly skilled analysts. Agreement between the two sets of analyses is satisfactory. Except for the discrepancy between the boron values, the differences are of no practical significance.

Trace contaminants that could not be determined spectrographically were determined by other methods and are listed in Table 18.

Table 18. Other Trace Contaminants in  
the Thorium Nitrate Feed Crystals

Element	Concentration (ppm)	Element	Concentration (ppm)
Br <sup>a</sup>	2.2	Li <sup>c</sup>	< 1
Ca <sup>c</sup>	12		< 1
	30	Na <sup>c</sup>	50
Cl <sup>a</sup>	< 4		300
Cl+Br <sup>b</sup>	< 10	Rb <sup>c</sup>	< 1
Cs <sup>c</sup>	< 1		< 1
	< 1	S <sup>b</sup>	28
I <sup>b</sup>	< 10	Sr <sup>c</sup>	< 1
	< 2		< 1
K <sup>c</sup>	< 1	U <sup>b</sup>	< 1

<sup>a</sup>Determined by activation analysis.

<sup>b</sup>Determined by standard analytical procedure; distillation and micro-titration.

<sup>c</sup>Determined by flame spectrophotometry.

Trace-Element Contamination in the Denitrator Product. - The denitrator product was analyzed spectrographically for trace-element contamination. Two composite samples were prepared. Composite A represented the first denitrator batches (13-25), while Composite B represented later batches (26-54). These results showed no detectable contamination from denitrator operation (see Table 19).

Trace-Element Contamination in the Product. - Each of the nine carrier composite samples was analyzed spectrographically for trace contaminants, and the results are presented in the Appendix. Table 20 presents these data for a typical shipment, No. 4. In view of the thorough feed-materials analysis already conducted, and by agreement with BNL, attention in this final analysis was directed primarily toward contaminants that may have been added during processing.

The contamination resulting from normal equipment corrosion and wear (Cr, Cu, Fe, Ni, and Si) was held to a very low level. If we consider spectrographic accuracy and sample-preparation errors, the contamination added by the process may have been negligible. Compare data of Table 19 with those of Tables 15-18. The ranges (ppm) over which these elements were present in the fuel are abstracted from Table 19 and given below:

Cr	< 0.1 - 2.3	Fe	1.7 - 97
Cu	0.1 - 2.1	Ni	< 0.1 - 3.6
	Si	< 0.4 - 0.9	

The product has almost the same contaminant level for Cr, Cu, and Si as the feed materials. The fuel of carrier shipments 2, 3, 4, and 5 were spot-checked for Na, K, and Li, none of which was present to an objectionable level. Some measure of the iron and silica contamination was expected from crusher operation, but, from the data above neither of these contaminants is of concern. The data are contradictory in that some of the "fine" powder has a higher iron content than the corresponding "coarse" powder. (See iron analysis under carrier shipments 2, 3, 4, and 5.)

Nickel is possibly picked up during the processing, and contamination from iron appears to have increased in the later shipments (carrier shipments 6-9). The level of contamination is not high enough to be objectionable for any single element for any of the carrier shipments. This is considered here as excellent contamination control.

Table 19. Results of Trace Analysis of Denitrator  
Product (ThO<sub>2</sub>)  
Results expressed as ppm

Element	Comp. A	Comp. B	Element	Comp. A	Comp. B
Ag	< 0.2	< 0.2	Ni	1.0	1.4
Al	0.09	0.07	Os	< 38	< 38
As	< 7.8	< 7.8	P	< 15	< 15
Au	< 2	< 2	Pb	< 9	< 9
Ba	< 3	< 3	Pd	< 10	< 10
Be	< 0.004	< 0.004	Pt	< 5	< 5
Bi	< 5	< 5	Rb	< 0.05	< 0.05
Ca	26	28	Re	< 10	< 10
Cd	< 4	< 4	Rh	< 10	< 10
Co	< 1.5	< 1.5	Ru	< 2	< 2
Cr	1.3	1.8	Sb	< 2	< 2
Cs	< 0.3	< 0.3	Si	< 1	< 1
Cu	< 2	< 2	Sn	< 3	< 3
Fe	11	13	Sr	1.2	1.5
Ga	< 10	< 10	Ta	< 4	< 4
Gd	< 3.8	< 3.8	Te	< 10	< 10
Ge	< 0.9	< 0.9	Ti	< 0.09	< 0.09
Hf	< 20	< 20	Tl	< 5	< 5
Hg	< 15	< 15	V	< 0.4	< 0.4
In	< 11	< 11	W	< 3	< 3
Ir	< 10	< 10	Zn	< 9	< 9
K	1.1	1.8	Zr	< 0.4	< 0.4
Li	< 0.05	< 0.05			
Mg	10	14			
Mn	0.7	0.8			
Mo	< 0.9	< 0.9			
Na	290	270			
Nb	< 0.9	< 0.9			

Table 20. Trace Element Analysis for Product  
in the Fourth Carrier Shipment

Element	Analysis <sup>a</sup>		Element	Analysis <sup>a</sup>	
	Cof	Coc		Cof	Coc
Ag			Mn	0.7	0.44
Al	4.4	3.9	Mo	< 0.42	< 0.4
Au	< 4.4	< 4.0	Na		21
Be	< 0.002	< 0.001	Nb	< 5.2	< 5
Ca		20	Ni	1.2	3.6
Cd	< 4.4	< 4	Pb	< 4.4	< 4
Co	< 4.4	< 4	Pd	< 2.2	< 2
Cr	1.4	1.2	Si	0.9	< 0.4
Cu	0.34	0.36	Sn	< 4.4	< 4
Fe	15.0	7.8	Ta	< 12	< 10
In	< 3.1	< 3.0	Ti	< 1.2	< 1
Ir	< 21.0	< 20.0	V	< 0.44	< 0.4
K		< 4	W	< 5.5	< 5
Li		< 0.04	Y	0.17	0.065
Mg	0.8	0.45	Zn	< 5.5	< 5

<sup>a</sup>Parts of element per million parts of powder.

Analysis of the carrier composite samples presented the most difficult analytical problem in the program. Work continued on proper analytical techniques on this procedure throughout the operating period, but the problem was never wholly solved. The compromise solution finally adopted yielded no analysis for boron at all and also undoubtedly added some iron contamination. This solution was the best available, and but for these two exceptions gave good results. Because of the analytical delays, all carrier composite samples were held until the end of the program and analyzed nearly at the same time.

The problem arose primarily from the refractoriness of the sol-gel product. For example, the first carrier composite sample was refluxed for 11 days in fuming HNO<sub>3</sub> before the coarse particles finally dissolved.

This was not a practical procedure. Crushing the coarse particles to -100 mesh and treating with nitric acid (0.004 M in HF) readily dissolves them under reflux, but boron was picked up from the glassware. The crushing of the powder also introduced an undetermined amount of iron into the product.

After weighing the problem carefully, it was decided to crush the product and then to dissolve it on a water bath; platinum dishes were used. It took about 24 hr to dissolve the samples. Although the boron was lost (as  $\text{BF}_3$ ), and some iron was introduced, the method was satisfactory. The iron values given in Table 19 are therefore high, and boron was detectable in only the first carrier shipment, where it was reported to be < 2 ppm. The boron analysis suggested for the final product is equivalent to that originally present in the thorium nitrate crystals (see Table 16). This amounts to 8-10 ppm.

There was no appreciable difference between the results of analyses of the crushed (COC) and the crushed and ball-milled (COF) powders, insofar as alumina content is concerned. However, these alumina data are doubtful because the analyst infrequently reported that some of the samples had a white, insoluble floc present.

An attempt was made, beyond the spectrographic analyses reported in Table 19, to determine the pickup of alumina from the ball-milling operation. For this purpose, dissolutions of both the ball-milled (fine) fraction (COF) and the crushed (coarse) fraction (COC) were routinely examined. The sample containing the worst floc was selected by visual inspection, then filtered, ignited, and weighed. The weight of the precipitate was equivalent to 500 ppm based on the original sample weight, but was only 40%  $\text{Al}_2\text{O}_3$  - the balance being  $\text{ThO}_2$ . The maximum alumina in any event could thus not be expected to exceed 200 ppm.

#### 4.2.2.7 Activities Present in Off-Gas from Sol-Gel Operation. —

During the cold startup operations, the gaseous exhaust from the calciner was sampled in an attempt to determine radioactive species released by the calcination. This was done by drawing the entire gas stream through Millipore filter disks ( $0.047\mu$ ) for 5-min sampling periods at 1-hr intervals throughout the calciner operating cycle. The particulate deposit caught in the filter disks was counted for alpha activity on a "Poppy"

at 8% geometry. Counts were repeated on every disk at 1-hr intervals to get a buildup-and-decay curve. As soon as the decay rate had declined sufficiently, a scaler laboratory instrument was used to obtain these counts. The counts were repeated but at ever increasing intervals until the samples either decayed to zero or a steady state.

The cold test indicated that radon was the prime element in the off-gas, as a half-life of about 10 hr was obtained by all samples. Gas release was slow at low calciner temperatures, increased steadily to 1000°C, and then a "burst" of activity was detected at approximately 1150°C. Activity release began to decline shortly after 1150°C was reached. The samples released at low temperatures (less than 1000°C) decayed to zero over a period of days. The samples taken during the "burst" period decayed for a period of days with a slightly greater half-life, but then reached a base level that exhibited an apparent rate of decay of about a few years.

Because of the temperature and the much longer apparent half-life, the burst was postulated to be metallic radium released by sintering. Laboratory study of the burst release however showed that the material released was not the postulated radium.

The same procedure used during startup was repeated toward the end of the Kilorod Program (calciner batches 97 and 98). More complete and better data were obtained than in the early test (see Table 21).

In examining the data, the following facts are noted:

1. The first appreciable activity is noted at 500°C (Sample No. 5). The activity release is erratic, but generally increasing from 500 to 1150°C.
2. The "burst" of activity is first noted with Sample No. 16.
3. Approximately 1 hr after the "burst" is noted, a maximum (Sample No. 18) is reached.
4. From the "burst" a steadily declining rate of release is noted until the furnace is turned off at Sample No. 24.
5. One hour after power off the release rate has fallen to insignificant levels.

The tabulated release rates were single readings taken from the filter disks immediately after removal from the mounting fixture. Periodic counts subsequently taken on the individual disks for a long time show a buildup occurring on each disk after the readings taken for Table 21. Samples were

Table 21. Release of Particles During Calciner Operating Cycle

Sample No.	Elapsed Time <sup>a</sup> to Sample Removal (hr)	Initial Alpha Count on Filter Disk	Temperature of Calciner At Time Sample Taken (°C)
1	0.5	-	60
2	1.0	-	175
3	1.5	-	285
4	2.0	-	385
5	2.5	137,500	500
6	3.0	156,000	600
7	3.5	500,000	700
8	4.0	112,000	790
9	4.5	125,000	865
10	5.0	188,000	950
11	5.5	188,000	1,000
12	6.0	175,000	1,060
13	6.5	156,000	1,095
14	7.0	231,000	1,135
15	7.5	219,000	1,160
16	8.0	$1.13 \times 10^6$	1,155
17	8.5	$3.1 \times 10^6$	1,155
18	9.0	$5.2 \times 10^6$	1,150
19	9.0	$3.2 \times 10^6$	1,150
20	10.0	$2.4 \times 10^6$	1,160
21	10.5	$2.0 \times 10^6$	1,150
22	11.0	$1.5 \times 10^6$	1,150
23	11.5	$1.3 \times 10^6$	1,150
24	12.0	$0.8 \times 10^6$	1,140
25	12.5	269,000	1,100
26	13.5	27,500	975
27	14.5	6,250	860

<sup>a</sup>Zero time assigned as time calciner power was turned on.

selected to show buildup-and-decay curves early in the calciner cycle immediately before the burst, and within the burst period.

Sample 3 illustrated the low gas-release rate and low maximum release rate typical of samples taken early in the calciner operating cycle. The activity decayed sharply with a half-life of 7 hr and decreased to background within a week.

Sample 9 was typical of the samples taken just before the burst period. The decay showed a much higher maximum gas-release rate than for the previously discussed sample. This decay also reached background within a week.

Sample 17 showed a higher release rate and maximum value than did sample 9. Initially sample 17 decayed rapidly but did not return to background for a long time (32 days). This residual activity, postulated in the cold test to be radium, was found to be  $^{233}\text{U}$  (less than 5%) and thorium (more than 95%). This specific particulate material (material that never decayed to background levels) was released by the oxide only during the sintering-reduction portion of the calciner cycle. Samples drawn before or after this part of the cycle decayed to background quickly.

The burst of activity released is undoubtedly analogous, insofar as the radon is concerned, to the burst of fission products observed when  $(\text{U}, \text{Th})\text{O}_2$  fuel particles have undergone a sharp temperature increase. The U-Th-bearing fraction of the activity is postulated to be particles thrown into the sweep gas stream as the result of fracture of the  $(\text{U}, \text{Th})\text{O}_2$  particles. Since this release of particles continued (but at a decreasing rate) throughout the  $1150^\circ\text{C}$  hold period, the fracture is probably the result of reduction-sintering, not thermal shock or relief of strains within the crystal lattice.

The half-lives calculated for all samples in the period of fast decay actually ranged from 6 to 12.5 hr.

#### 4.2.3 Results From the Rod-Fabrication Operation

The operation of the facility with  $^{233}\text{U}$  as the feed material was initiated after the flowsheet had advanced to the point that sustained operation was indicated. The operation was separated into time periods by two schemes: (1) the production of 120 finished rods, and (2) the preparation of about 100 kg of fuel. When 120 rods had been made, a short

interruption was required for assembling and calculating the shipping data. The interruptions that were based on amount of fuel processed were at the convenience of the fuel-production plant and were called "campaigns." During the intercampaign breaks, the system was remotely cleaned, a material balance made, and the operating history critically reviewed. Modifications to the operating procedures were determined during this period and initiated at the startup of the ensuing campaign.

The end product of the Kilorod operation was the production of 1100 fuel rods containing about 880 kg of fuel. It was necessary to pack 1191 rods to obtain 1100 specification-grade rods; 7.6% of the total rod production was recycled from the gamma-scanning step. Both the hardware and the fuel were recovered and reused from a rod not meeting the density specifications. The amount recycled between compaction and gamma-scanning steps during the early campaigns was nearly 20% and ranged to a low of less than 1% (one rod out of 120) in the later campaigns. The summarized data for the rods are presented in Table 22.

Table 22. Fuel-Rod-Loading Data

Shipment Number	Shipment (kg)	Average Density in Shipment (g/cm <sup>3</sup> )	Average Rod Loading (g)
1 (120 rods)	108.8	9.00	906
2 (240 rods)	108.6	8.93	905
3 (360 rods)	108.4	8.91	904
4 (480 rods)	109.2	8.98	908
5 (600 rods)	109.2	8.97	905
6 (720 rods)	108.5	8.94	904
7 (840 rods)	108.7	8.96	906
8 (900 rods)	54.5	8.99	909
9 (1100 rods)	62.6	9.04	313

The sole criterion for recycling a packed rod was excessive variation of the density within the rod, as determined by the gamma scanner. One area of needless concern was in the final end-closure weld, where no difficulty was experienced. However it should be noted that these welds were submitted to a helium leak test only.

The maximum transferable contamination was specified at  $2000 \text{ dis min}^{-1} \text{ cm}^{-2}$ . The rods were routinely cleaned to about  $500 \text{ dis min cm}^2$  to determine the efficiency of methods and cleaning solutions.

A time-and-motion study was performed to establish base-line data for the evaluation of other facilities. The following information has been extracted from that study.<sup>24</sup>

The manpower required to operate the facility was one supervisor and three technicians. A total of 28 subroutines comprised of over 200 elements was divided among these men, and elemental time values were determined for each. Table 23 presents the subroutines and time required for each. Calendar time is the length of time required to do an operation. Work time is the number of minutes required for a man to perform that operation.

In addition to a summary of times required for each subroutine and for each fuel rod, summaries of time required for three production rates (7, 10, and 15 rods per day) are given. All these data were used, after initial operation, to evenly distribute work loads among the operators and to assess the efficiency of the operation.

The operating effectiveness was readily ascertained from data such as that in Fig. 31, which shows that, for an operating force of 3.5 men, the maximum possible production rate is 15.5 rods per operating day. An operating day does not include time that the facility cannot be operated because of equipment breakdown, etc. It is notable that, in calculating the operating effectiveness, an allowance of 108 min was made for reductions in work time caused by personal time, fatigue, and the access limitations imposed by the contamination-control area.

The analysis of the logbook is shown in Table 24. In this discussion the emphasis is placed on that portion of the table occurring below the heading "Total," where the crew and process effectiveness are shown.

The effectiveness values reflect the percentage of the time actually spent producing 120 rods, taking into account a factor for the recycling

Table 23. Operational Subroutines and Time Values

Subroutine Number	Subroutine	Time in Minutes at 100% Effectiveness										
		Subroutine Cycle				Daily Time (Maximum Routine Included)						
		Number of Rods	Time per Subroutine		Per Rod		7-Rod Schedule		10-Rod Schedule		15-Rod Schedule	
			Calendar	Work	Calendar	Work	Calendar	Work	Calendar	Work	Calendar	Work
0	Energize equipment; pick up liquid nitrogen	D0 <sup>a</sup>	12.	12.	1.71 <sup>b</sup>	1.71 <sup>b</sup>	12.	12.	12.	12.	12.	12.
1	Load in shipping cask - one man	120	12.	12.	.1	.1						
2	- second man	120	9.	9.	.08	.08						
3	Jaw crusher	11	8.45	5.95	.77	.54	8.45	5.95	8.45	5.95	16.9	11.9
4	Recycle	11	21.9	21.9	1.99	1.99	21.9	21.9	21.9	21.9	43.8	43.8
5	<sup>c</sup> Ball mill - 16 fraction into fines	8	145.2	10.2	9.10 <sup>d</sup>	.93			145.2	10.2	145.2	10.2
6	Ball mill - 6/+16 fraction into fines	10	432.1	12.1	.40	.37	13.2	12.1	13.2	12.1	13.2	12.1
7	Blend; transfer bottle loading	1	11.2	8.2	11.2	8.2	78.4	57.4	112.0	82.0	168.	123.
8	Sample (-168-6/+16 fractions)	10	5.	5.	.5	.5	5.	5.	5.0	5.	10.	10.
9	Seal samples	10	1.	1.	.1	.1	1.	1.	1.	1.	2.	2.
10	Dispose of old bag (powder preparation cubicle)	10	2.1	2.1	.21	.21	2.1	2.1	2.1	2.1	4.2	4.2
11	Seal old bag	10	1.	1.	.1	.1	1.	1.	1.	1.	2.	2.
12	Compacting	1	16.7	7.5	16.7	7.5	116.9	52.5	167.	75.	250.5	112.5
13	Transfer plugged rod for scanning	1	.9	.9	.9	.9	6.3	6.3	9.	9.	13.5	13.5
14	Scanner check	1	9.8	4.6	9.8	4.6	68.3	32.2	98.	46.	147.	69.
15	Welding	1	15.5	11.5	15.5	11.5	108.5	80.5	155.	115.	232.5	172.5
16	Ultrasonic cleaning	5	39.45	13.95	7.89	2.79	78.9	27.9	78.9	27.9	118.4	41.9
17	Dry, leak test, and weight	5	18.3	15.5	3.66	3.1	36.6	31.	36.6	31.	54.9	46.5
18	Rod cleaning	10	10.7	10.7	1.07	1.07	10.7	10.7	10.7	10.7	21.4	21.4
19	Smear - smear man	10	8.4	7.8	.84	.78	8.4	7.8	8.4	7.8	16.8	15.6
20	- cubicle man	10	6.2	6.2	.62	.62	6.2	6.2	6.2	6.2	12.4	12.4
21	Assemble hanger and load in carrier - hanger man	10	13.1	8.65	1.31	.87	13.1	8.65	13.1	8.65	26.2	17.3
22	- carrier man	10	13.45	13.	1.35	1.3	13.45	13.	13.45	13.	26.9	26.
23	Mark, weight, and record empty rod	5	15.	15.	3.	3.	30.	30.	30.	30	45.	45.
24	3-piece rod end assembly	20	6.	6.	.3	.3	6.	6.	6.	6.	6.	6.
25	Remove and dispose of cleaning pads	50	10.	10.	.2	.2	10.	10.	10.	10.	10.	10.
26	Load shipping cask - one man	120	12.	12.	.1	.1						
27	- second man	120	9.	9.	.08	.08						
Total Time (excluding routines 1, 2, 26 and 27) =					89.22 <sup>b</sup>	53.18 <sup>b</sup>	656.4	441.2	964.2	549.5	1398.8	840.8

<sup>a</sup>D0 = one day output.<sup>b</sup>Based on 7 rod day.<sup>c</sup>Ball milling done overnight and unattended.<sup>d</sup>Ball milling attended maximum of twice a day (plus one -6/+16 fraction ball milling) to produce fines to meet maximum schedule.

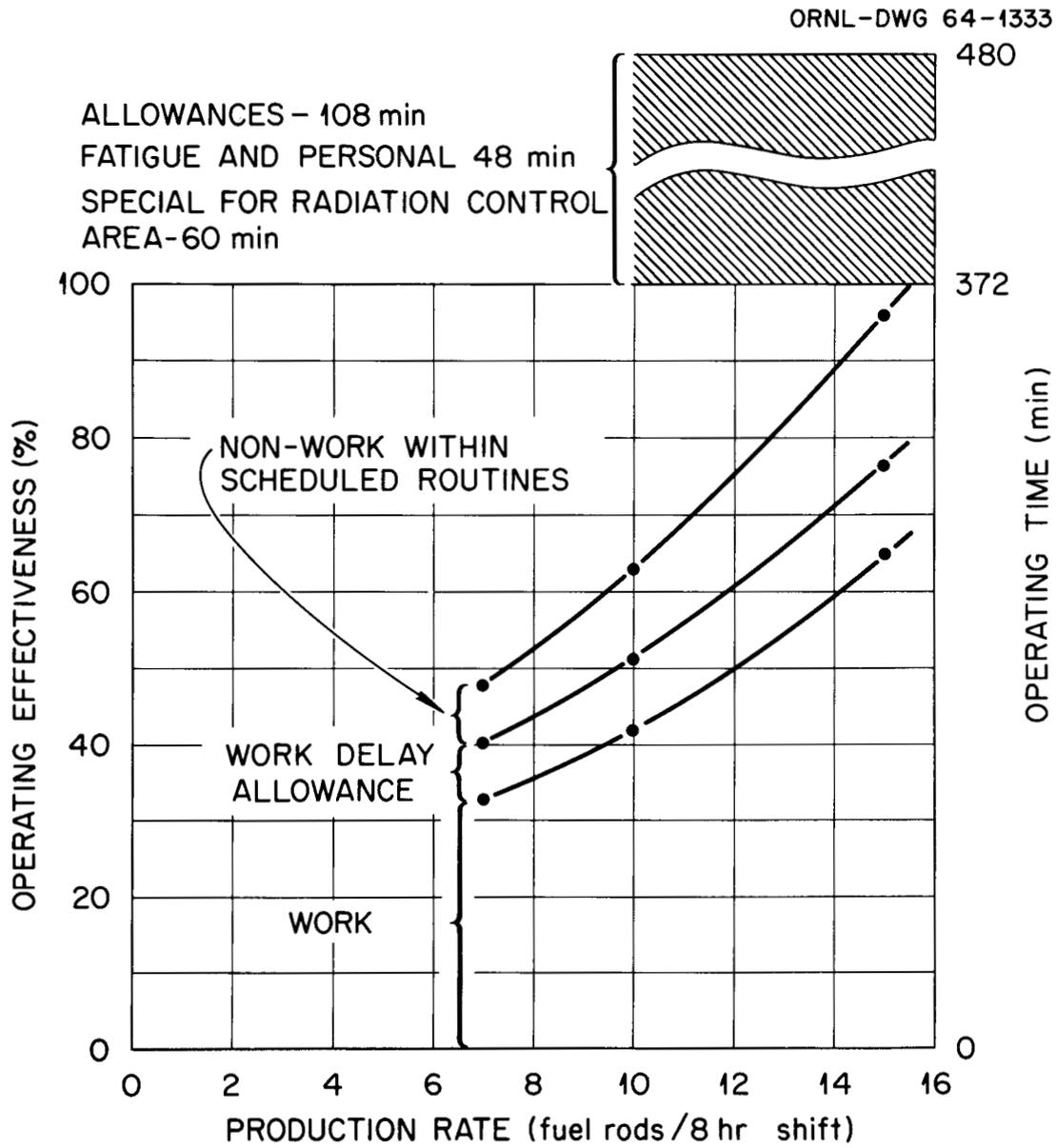


Fig. 31. Operating Effectiveness of Rod-Fabrication Operation.



of rods between the compaction and gamma scanning steps. Several factors contribute to lowering the effectiveness, the major one being the time spent in maintenance or repair. A low effectiveness value does not necessarily reflect poorly on the performance of the crew or process; however, some cause of extended off-stream time should be presented to explain the low value.

The process effectiveness ranged from a low value of 16% in the first shipment to a high value of 76% in the seventh. There were two major contributors to the low value: (1) frequent repair of the ball mill and (2) the large number of recycle rods, 43, required. The high value in the seventh shipment was characterized by a small amount of downtime and few recycle rods.

#### 4.3 Material Balances

In handling fissionable materials, accountability must be exact, and nonrecoverable losses of such materials cannot be tolerated. Errors inherent in process measurements, sampling, and analytical procedures must be recognized. Kilorod experience met all expectations in this important phase of operation. To simplify the discussion of these balances, certain terms used in the following statements on material accountability and material utilization must be defined. Accountability and material balance (termed "SS balance") are used synonymously. Material loss (termed "SS loss") represents a loss of process materials ("book" or otherwise) which cannot be explained. The term process loss means a recoverable waste material which cannot be used again without extensive chemical reprocessing. Thus, for example, any discrepancy between the material charged to an operation and the accounting of materials leaving an operation (waste and otherwise), represents a material ("SS loss") loss. As a second example, the dust produced (and recovered) in denitrator operation is a process loss since the dust can be reclaimed but must be completely reprocessed before the thorium can be used.

##### 4.3.1 Over-All <sup>233</sup>U Material Balance for the Kilorod Program

Table 25 presents a summary of the <sup>233</sup>U material balance data for the entire Kilorod Program. Included in this balance is the <sup>233</sup>U not used in sol-gel but purified for Westinghouse (Bettis).

Table 25. Over-All Kilorod Material Balance

	Total U (g)	<sup>233</sup> U (g)
Input		
From U-60	7,281	7,081
From storage	615	599
From Davison Chemical Company	25,886	25,179
From Jezebel fuel	12,257	12,026
From M. Lloyd	78	76
From bottle 36P	66	64
Total input	46,183	45,035
Output: Shipments		
To BNL	23,744	23,145
To Bettis	13,345	12,989
To M. Lloyd	109	107
To Y-12	146	142
Total shipments	37,344	36,383
Miscellaneous		
Process losses	99	97
To BTC storage	131	127
BPID, April 1964	146	134
	376	350

<u>Final Kilorod Inventory</u>	<u>Total U (g)</u>	<u><sup>233</sup>U (g)</u>
Product tank (R-25)	4,018	3,932
Feed-adjustment tank (S-2)	607	595
In retained mixed oxide	289	282
In retained rods	286	279
In canned ground mixed oxide	2,430	2,370
Oxide in system	81	79
Total inventory	7,711	7,532
Total output + inventory	45,431	44,283
Input-output	752	752
Material balance, %	98.4	98.3

Measurement of feed stock and product values plus measured losses account for 98.3% of the total  $^{233}\text{U}$  handled; the only uncertainty in the balance is the 752 g unaccounted for and accumulated over a nine-month period, after 45.035 kg were processed. This difference between output and input figures may be explained as follows:

1. The content of the final solid inventory is based on weights of material obtained in a rather incomplete cleanout of the rod-fabrication cubicle. Complete cleanout was not practical because subsequent operations were in progress.

2. Part of the difference may be attributable to analytical and volume-measurement uncertainties. The limit of error for the coulometric method of uranium determination has been established as  $\pm 0.5\%$ . Previous statistical studies established a  $\pm 0.7\%$  uncertainty in feed liquid-level measurements, even with dual instruments.

In summary, it is felt that the over-all  $^{233}\text{U}$  material balance obtained is well within the normal engineering-balance standards.

#### 4.3.2 Solvent Extraction Material Balance

Table 26 presents a summary of the solvent extraction  $^{233}\text{U}$  material balance. A total of 99.4% of the material input is accounted for in this balance. The 0.6% of unaccountable loss is well within the established uncertainty for analytical and volume-measurement losses.

Table 26. Kilorod Program Solvent Extraction  
Over-All  $^{233}\text{U}$  Material Balance

	Input	$^{233}\text{U}$ (g)
From U-60		7,081
From storage bottles		599
From Davison Chemical Company		25,179
From Jezebel fuel		12,026
From M. Lloyd		76
From bottle 36P		<u>64</u>
Total input		45,035
	Output	
To sol-gel		26,779
To Bettis		12,989
To M. Lloyd		107
To Y-12		142
To BTC storage		127
Accountable losses		97
Retained in product tank		3,932
Retained in feed tank		<u>595</u>
Total output		44,768
	Unaccountable Losses, g	267
	Material Balance	
		$\frac{44,768}{45,035} \times 100 = 99.4\%$

Table 27 is a summary of the  $^{233}\text{U}$  and thorium material balances obtained in the individual solvent extraction runs. The  $^{233}\text{U}$  material balances varied from 96.81 to 102.66% and averaged 98.98%. The wide variation and relatively inferior balances obtained in several runs is thought to be due to system holdup, an estimate of which is impractical. The satisfactory over-all balances obtained for the entire program is thought to be a more accurate indication of the successful measurement of input and output quantities.

Table 27. Kilorod Solvent Extraction Material Balance

			Runs									
			HJ-1	HJ-2	HJ-3	DC-1	DC-2	DC-3	DC-4	HJ-4	HJ-5	
Input	<sup>233</sup> U	U-60		3279	3452	3970	6784	7259	5235	1570	1327	32,876
	Dissolution	S-2	4056							3871	4026	11,953
	Recycle	S-2	595	1363	197	352	897	680	96	181	929	5,290
	Cold feed	S-4	9	20		4	7	8	4	16	1	69
	Total <sup>233</sup> U input		4660	4662	3649	4326	7688	7947	5335	5638	6283	50,188
Output	<sup>233</sup> U											
	Product (R-25)		4028	4407	3430	4109	7426	7634	4972	4767	6158	46,931
	Recycle (R-2)		441	352	314	96	123	95	217	847	103	2,588
	Feed tank heel	S-4	20		4	7	10	4	16	1		62
	Process losses		10	16	8	7	10	20	8	6	10	95
	Samples to laboratory		24	11	36	19	18	15	19	10	10	162
	Total <sup>233</sup> U output		4523	4786	3792	4238	7587	7768	5232	5634	6281	49,675
					- 116 <sup>a</sup>	- 50 <sup>b</sup>						
					3676	4188						
	Material balance <sup>233</sup> U		97.06%	102.66%	100.73%	96.81%	98.69%	97.71%	98.07%	99.93%	99.97%	
Input	Thorium											
	Cold feed		303,380	222,825	249,985	273,000	221,900	203,232	230,826	301,741	258,075	2,264,964
	Hot feed		229,461	279,169	261,030	178,796	316,139	337,016	226,883	223,865	350,590	2,402,949
	Total thorium input		532,841	501,994	511,015	451,796	538,039	540,248	457,709	525,606	608,665	4,667,913
Output	HAWC recovery		564,693	539,638	534,302	452,175	556,342	543,870	462,822	573,775	634,110	4,861,727
	Material balance (Thorium), %		100.60	107.50	104.56	100.08	103.40	100.67	101.12	109.16	104.18	104.15

<sup>a</sup>Retained in R-2 at end of HJ-2.

<sup>b</sup>Material returned to R-25 from R-35.

### 4.3.3 Material Balances Over the Sol-Gel Operation

4.3.3.1 Material Balance Over Cold Startup. - Several methods of accountability were proposed for the sol-gel operation. Data permitting the study of all these methods were taken during the cold startup. A subsequent analysis of the data showed that the most accurate accountability could be maintained as follows.<sup>14</sup>

1. Uranium would be charged by calculation against the system from the uranium tank values.

2. Thorium would be debited to the process as calculated from the  $\text{ThO}_2$  analysis and the batch weight.

The largest errors expected in these debits were those from the coulometric uranium analysis, subject to a maximum error of  $-0.50\%$ <sup>14</sup> and the thorium analysis, subject to about the same error. Other errors were insignificant.

3. Both uranium and thorium would be credited to the sol-gel cubicle on the basis of the product-weight dumped to the powder-preparation shaft.

4. A rigorous accounting of all analytical samples and waste materials leaving the cubicle was made.

Material balances of  $100 \pm < 1\%$  could be expected in hot operations using the procedure described, thus meeting all accountability requirements for this type of operation.

The material balance made across the sol-gel cubicle during the cold testing is given in Table 28 and is the method used for the hot campaign.

4.3.3.2 Material Balances Across the Entire Hot Sol-Gel Operation. - Material accountability was rigidly maintained across the denitrator and the sol-gel cubicle.

4.3.3.3 Material Balance: Denitrator Operation. - A calculated total of 1116 kg of thorium metal (as nitrate) was fed to the denitrator during the Kilorod Program. The useful  $\text{ThO}_2$  product prepared from this quantity of nitrate crystals was equivalent to 1094 kg of thorium metal (see Table 29). Process losses amounted to 19 kg of thorium. This includes analytical samples and dust recovered from the off-gas condensate. This dust loss represents less than 1% of the material processed. Thorium oxide was consumed at a high rate in analytical testing during the startup - 5 kg in the first 20 runs. After assurance that operation was satisfactory, the

Table 28. Kilorod Sol-Gel Operation: Over-All  
Material Balance During Cold Startup Tests

## Conditions:

1. Coulometric U analysis of UNH feed solution
2. Volume UNH measured in U tank
3. Thorium analysis by ignition
4. Thorium feed material and all product materials weighed to +0.1%

	Weight (g)	Percent of Total
Feed Materials - In		
ThO <sub>2</sub>	121,540	97.01
UO <sub>2</sub>	<u>3,740</u>	<u>2.99</u>
	125,280	100.00
Product Materials - Out		
Product, ThO <sub>2</sub>	97,622	80.31
Product, UO <sub>2</sub>	2,988	
Sample of sol	60	0.05
Heel of B-tank, ThO <sub>2</sub>	1,834	
Heel of B-tank, UO <sub>2</sub>	76	1.52
Operating loss of dried gel	780 (est.)	0.62
Operating loss of oxides	190	0.15
Dried-gel sample to laboratory	1,310	1.04
Dried-gel (No. 11, No. 12)	<u>20,000</u>	<u>15.98</u>
Total material accounted for	124,860	99.67
Unaccountable losses	420	
Over-all U/Th ratio for this campaign = 2.99		

Table 29. Denitrator Operations Material Balance  
Metal Basis

Material Description	Product Quality Material (kg)	Process Losses (kg)	Thorium Accountability Totals (kg)
Feed Materials In:			
2,802 kg TNT x 0.398 g Th/g TNT	1,116	--	1,116
Product and Waste Materials Out:			
Product weighed out	1,093.509	--	--
Analytical samples	0.797	--	--
Process Losses:			
Powder consumed in analytical procedures	--	8.002	--
Powder recovered from off-gas condensate	--	11.000	--
Subtotal	1,094.306	19.002	--
Total			1,113
		Discrepancy (SS Loss) = 3 kg	
Material balance: 99.8%			

sample size was reduced to 66 g per 13.5 kg batch. Thus, in a sustained operation the analytical (process) losses would be considerably less than that experienced here. The discrepancy (SS loss) of 3 kg is small.

4.3.3.4 Material Balance: Sol-Gel Cubicle. - The quantities of  $(^{233}\text{U}, \text{Th})\text{O}_2$  prepared in each campaign, SS balances (expressed as percentage of individual incoming feed metals), and the apparent discrepancies in SS accountability are given in Table 30. Material balances for  $^{233}\text{U}$  and Th over the sol-gel operation are presented in Table 31.

The product weight data are poor for campaign 1, as already discussed (see Sec 4.1.2). The table, therefore, is incomplete for campaign 1.

The campaign-2 balance was calculated using weights given by the domestic balance already described. This balance is considerably more accurate than the balance used in campaign 1, but even so is not highly accurate. This is suggested as the reason for the presence of a larger error in campaign-2 accounting than in the succeeding ones using the metric balance.

With the single exception of campaign 1, these data gratifyingly met accountability expectations. Complete details and calculations of these material balances are given in the Appendix.

Table 30. Sol-Gel Over-All Material Balances

Conditions:

1. Spring-operated domestic balance used for weighing product of campaign 2; subject to  $\pm 1$ -oz. error
2. Metric balance, capable of weighing to within  $\pm 5$  g, was used for campaigns 3 through 7

Camp. No.	Metallic Oxide Accountability (kg)			Thorium Metal Accountability (%)	$^{233}\text{U}$ Metal Accountability (%)
	Feed Material In	Product Weight Out	SS Loss (kg)		
1	122.8 <sup>a</sup>	118.6	4.2	--	--
2	159.6	160.9	(1.3)	(100.74)	(101.16)
3	118.7	118.5	0.2	99.82	99.90
4	128.6	128.7	(0.1)	(100.09)	(100.05)
5	227.3	226.8	0.5	99.76	99.73
6	167.1	166.7	0.4	99.79	99.78
7	<u>68.6</u>	<u>68.6</u>	<u>0.002</u>	<u>100.00</u>	<u>100.02</u>
Totals:	869.9	870.2	(0.3)avg.	100.03	100.11

<sup>a</sup>Campaign-1 values were not used in preparing totals.

Table 31. Material Balance by Campaigns for  
 $^{233}\text{U}$  and Thorium Over the Sol-Gel Process  
 $^{233}\text{U}$  Recovery = 99.93%  
 Th Recovery = 99.83%

Campaign No.	$^{233}\text{U}$ Input (g)	Th Input (g)	$^{233}\text{U}$ Output (g)	Th Output (g)
1 <sup>a</sup>	3,196.18	104,693	2,748.56	89,992
2	4,255.80	137,159	4,481.04	143,661
3	3,164.60	102,468	3,344.39	108,334
4	3,449.95	110,724	3,490.01	112,070
5	6,052.96	195,530	6,040.80	195,195
6	4,520.85	145,182	4,513.94	144,974
7	1,873.93	59,972	1,881.52	60,204
Hot run	<u>265.07</u>	<u>8,570</u>	<u>259.96</u>	<u>8,419</u>
Total	26,779.34	864,298	26,760.22	862,849

<sup>a</sup>Output weights subject to errors as discussed in text.

#### 4.3.4 Material Balance Over the Rod-Fabrication Operation

The material balance data are presented in Table 32. The process losses represent the material that leaked out of the system or spilled during transfer in the compaction operations. This material was removed from the cubicles during postoperation cleanout and dissolved for subsequent recovery of the uranium and thorium.

The SS loss represents the amount of material that remained unaccounted for at the end of each and also the final campaign. The system was remotely cleaned after each campaign, using a vacuum cleaner; but even after cleaning, some powder was still present on various surfaces and in inaccessible places.

The utilization of the powder in the comminution process was 100%, as no off-size material was produced. The over-all utilization of the powder was 94.25%. Of this, 89.51% was loaded into the rods and 4.7% was removed as analytical samples. The unused analytical samples do not represent a

Table 32. Fuel-Utilization Data

Campaign No.	Fuel in Rods	Analytical Samples	Process Loss	Process Hold Over	SS Loss	Total <sup>a</sup> Material in Campaign
Weight (kg)						
1 and 2	208.4	12.0	16.5	31.4	--	268.3
2 and 3	130.2	6.5	7.6	7.4	--	151.7
3 and 4	116.5	6.0	4.4	10.7	--	137.6
4 and 5	197.7	11.0	8.2	20.2	--	237.1
5 and 6	163.3	9.0	3.0	11.9	--	187.2
6 and 7	61.8	2.0	13.5	--	3.2	80.5
Total	877.9	46.5	53.2	81.6	3.2	1062.4
Percentages						
Fuel Utilization <sup>b</sup>	89.51	4.74	5.42	--	0.33	--

<sup>a</sup>Total material charged to system = total material in campaign - process hold over; that is, for the total program, material charged to system = 1062.4 - 81.6 = 980.8 kg.

<sup>b</sup>Based on material charged to system (980.8 kg).

process loss since they could be used in the present state for rod loading. However, since they remained unused after all phases of the program were completed, all must be reprocessed to recover the uranium and thorium.

#### 4.4 Waste Materials Generated: Efficiency in Using Process Materials

##### 4.4.1 Waste Materials from Sol-Gel Operations

Sol-gel operations were unusually efficient in holding the quantities of operational wastes to a minimum. Operational problems, resulting in preparation of off-specification batches, were also held to acceptable levels.

4.4.1.1 Denitrator Operation: Waste Materials. - At the conclusion of the Kilorod denitrator operation, 95 batches of product-quality ThO<sub>2</sub> (1277 kg) had been prepared in the denitrator. During this same period,

five batches, amounting to 67.5 kg ThO<sub>2</sub>, were rejected. These rejections, combined with dust and analytical losses of 22 kg, give a total process loss of 89.5 kg ThO<sub>2</sub> (see Table 29). A feed-to-product efficiency in material usage of 93% was therefore obtained.

#### 4.4.2 Sol-Gel Operations: Waste Material

The disposition of all materials that entered the sol-gel cubicle during campaigns 2 through 7 is given in Table 33. Almost 99% of all the product entering the cubicle was transferred to the rod-fabrication portion of the facility as finished product. Not a single batch was rejected during the entire program.

Table 33. Efficiency of Process Materials Usage in  
the Sol-Gel Cubicle

Conditions:

Includes campaigns 2 through 7

All figures given on metal basis

Percentage of product oxides used = 99.1%

Process losses = 0.8%

Known accountability losses = 0.1%

	Product Weighed Out (g)	Process Losses (g)	SS Losses (g)
Number of batches rejected	0		
Net product produced	771,131		
Miscellaneous wastes:			
Spilled process materials		4	54
Powder losses (recovered with vacuum cleaner)		1,141	
Blend-tank heels		5,311	
Analytical wastes	3,686 <sup>a</sup>		793
Totals	774,817	6,456	847

<sup>a</sup>Unused portions of analytical samples returned directly to operation.

The largest single process loss, amounting to 82% of the total loss, was the material held up in the bottom of the blend tank at the end of each campaign. This process loss could have been eliminated entirely by one of several means. The heel could simply have been left in the tank and mixed into the first batch of the next campaign. This was feasible insofar as the process was concerned, but a sharp intercampaign cut-off was desired to obtain the precise material balances that have already been discussed; so this system was not used. Another method would have been to thoroughly rinse the blend tank immediately after making the last batch in each campaign. This was not convenient, although it could have been done. Another method would have been to reroute the pump loop at the discharge of the tank so that it would drain completely. This would have required a shutdown and some construction work, deemed undesirable at the time. Eliminating the blend-tank heels would have raised the product usage up to 99.8%. The problem was not believed significant, so the practice of pumping the heels to recoverable waste was continued throughout the program.

#### 4.5 Equipment Reliability and Maintenance Experience

Equipment reliability was high for the Kilorod Program as a whole, when the protracted plant outage so common to equipment breakdown in other directly maintained radioactive operations is considered. The prime indicator of equipment reliability in this program lies in the number of cubicle entries required, because a cubicle entry<sup>a</sup> necessitated plant down time and an unavoidable interruption of operations. Records were kept on cubicle entries (major repairs) for all equipment throughout the program.

The on-stream efficiencies given below represent the actual time lost as a percentage of the total scheduled operating time in the program.

##### 4.5.1 Solvent-Extraction-Equipment Service Record

The only difficulty encountered in the entire SX operation was the variable concentration of the feed solution in the feed storage tank (R-25), which has already been discussed. The installation of the separate feed-storage tanks was completed during an intercampaign shutdown; therefore no operating time was lost. Routine instrument and electrical

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<sup>a</sup>A cubicle entry is defined as any occasion which required stopping operation and entry of a man in an air suit into the high-activity area in the cubicle.

servicing were required, but no down time resulted from any of these repairs. On-stream time is considered to be 100%.

#### 4.5.2 Denitrator Service Record

At the start of the Kilorod Program, the denitrator had been operated to produce about 40 batches of  $\text{ThO}_2$ . During this pre-Kilorod work, several heaters and thermocouples failed. The slip joint at the discharge of the denitrator shell started to leak and drip acid condensate. Since the equipment continued to operate and produce satisfactory product despite these failures, no time was taken to repair the equipment before startup.

During the operating period, the equipment was operated an additional 99 cycles for Kilorod use and 8 cycles for other customers. One or two heating elements and/or thermocouples failed, but sufficient electrical capacity and temperature control still existed to permit continuation of the operation.

In November, without prior warning, the steam was turned off to the process building, which caused the steam superheater to burn out. As more than enough material had been produced by this time to meet Kilorod needs (1272 kg, while about 1000 kg were needed), the operation was shut down.

Up to this point, 100% on-stream efficiency had been obtained, a period even longer than that covered by the Kilorod operation.

After the shutdown from the Kilorod Program, the electrical heaters that were suspected to have burned out were examined. It was found that none of the heaters had actually burned out, but that the crimp-on type lugs used to connect the wires to the heaters had burned off. This was surprising, since 750°F, steel-sheathed, strip heaters had been used, and these elements had been operating (intermittently) above 500°C for about two years. Had hard-soldered joints been made from the leads to heater terminals it is doubtful that any failures would have occurred.

#### 4.5.3 Maintenance in the Sol-Gel Cubicle

Most maintenance items in the sol-gel cubicle were corrected with gloved hands. In this fashion, thermocouples, pH electrodes, and sagger-support racks were readily replaced. Repair and adjustment in this manner did not affect the on-stream time.

Major repairs within the sol-gel cubicle included the replacement of three burned-out calciner heating elements and the re-trimming of two control valves. Only three shutdowns were made, however, as the valve repairs were delayed until calciner repair was necessary.

Service life of the calciner heating elements averaged 33 cycles, exceeding expectations derived from Unit Operations work, where the average element life was 20 cycles.

As the calciner was designed to allow disconnecting services by gloved hands, cubicle entry was necessary only to remove the burned-out element, repair the refractory, and to push the new element into place. The heating element was box-like, which permitted its removal by simply pulling the element through the open doorway. This repair scheme sharply limited the amount of time spent in the cubicle for calciner repairs. Each burned out element caused a two-day shutdown. The defective element was removed, and the refractory was repaired on the first day, and the new element was installed the second. The maximum time spent in the cubicle by any worker for any day was 2 hr. The maximum daily whole-body dose received by any worker during calciner repair was 70 millirems.

The triple-beam-balance support was built so that it could be introduced into the cubicle through a bag-out station, re-assembled inside the cubicle, and mounted on the elevator without entering the cubicle. This was done without difficulty or error, between operating campaigns.

The miniature pH-electrode assembly, installed during construction, never worked properly. It consistently gave lower readings, usually about 0.5 unit, than the more precise laboratory pH meter. Several unsuccessful attempts were made to service the electrodes and the instrument, but the idea was dropped because the use of this instrument was not mandatory. Instead, sol samples sent to the laboratory for sol analysis were routinely checked for pH.

Aside from the minor exceptions noted above, all equipment performed as designed and without event.

A total of seven days of delay was encountered in all the major repairs mentioned above, out of the 100 days scheduled for operation, resulting in an on-stream efficiency of better than 90%. This is an excellent maintenance record for a high-level alpha facility directly serviced.

#### 4.5.4 Maintenance in the Rod-Fabrication System

The major portion of the equipment alterations was performed during the cold startup described in Sec 4.1; however, continuous maintenance and modification were required throughout the operation. The remote ball mill (Fig. 28) performed unsatisfactorily, requiring repair fourteen times during the first two months of operation. The remote mill was eventually replaced with one of much simpler design and operable with gloved hands. The cause of the malfunctioning of the remote mill was the escape of powder from the system, causing excessive bearing wear. The remainder of the powder-preparation equipment operated only with periodic maintenance.

A number of alterations, adjustments, and repairs on the vibratory compaction equipment (Fig. 19) were also required. The major cause of these difficulties was the extremely high level of acceleration (20,000 to 100,000 g) imparted by the Branford<sup>a</sup> pneumatic-compaction device.

The rod-chucking mechanism, which was used to attach the rods to the compactor, was particularly susceptible to damage and required careful attention to the design of all components to eliminate stress risers. The static-load mechanism, which rides on top of the fuel column during packing also required periodic repairs. The vibrator units required maintenance at an average frequency of once per 100 rods.

The end-cap welding machine (Fig. 20) operated satisfactorily, requiring only replacement of the tungsten tip. The tip was replaced after each 200 welds.

The gamma-ray densitometer (Fig. 22) performed adequately, but not to design expectations. An integrator circuit was provided by the design to measure the bulk density of the fuel column. The output of the detector tube, however, was unstable over a period of time, thus precluding the establishment of a long-term baseline for measurement. Because of this, it was necessary to run a set of standards with each rod and compare the results from these standards with those from the rod. Two typical scans are presented in Fig. 32. The separation between the standards is used to determine the number of chart divisions over which the fuel-column scan can range and still meet the specification of  $\pm 2\%$  of the bulk-density variation within a rod.

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<sup>a</sup>Manufactured by the Branford Company, New Britain, Conn.

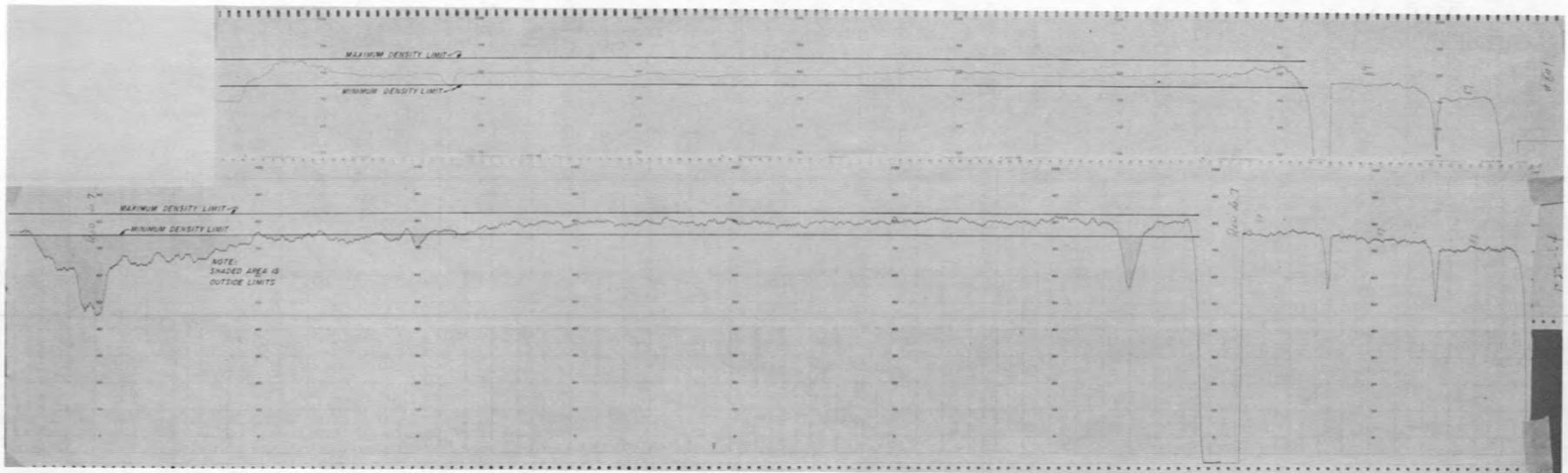


Fig. 32. Typical Gamma-Ray Scans of Fuel Rods.

The complete maintenance history is summarized in Table 23, divided into shipments of 120 rods. The items covered are not those which were performed on a regular schedule. Considerable repair work was necessary during the production of the first shipment, totaling 51 jobs. As mentioned previously, the remote ball mill was very troublesome and required repair 14 times during this period and averaged 10 man-hours per job. This item was replaced during the later part of the period, and ball-mill maintenance does not reappear until the eighth shipment, when 4 hr were required for repair.

The other bit of important data garnered from Table 23 is the realization that the more frequently repaired items indicate the need for further design improvements. The most frequently repaired item was the compactor, which was expected, due to the high stresses caused by the vibrators. This entire assembly is presently being redesigned, including the vibrator itself.

## 5. RADIATION EXPERIENCE

The radiation monitoring in the Kilorod Program may be divided into (1) routine radiation monitoring during the production of the BNL fuel rods using  $^{233}\text{U}$  containing 38 ppm  $^{232}\text{U}$  and (2) radiation monitoring during a special run using  $^{233}\text{U}$  containing an estimated 800 ppm  $^{232}\text{U}$ .

In each of these phases, the primary objective was to ensure that radiation doses to personnel remained below maximum permissible levels. In addition, radiation data were obtained for use in the design of future facilities.

### 5.1 Monitoring Procedures

#### 5.1.1 Personnel Exposure Monitoring

Total body, hand, and arm exposures were used in the personnel exposure monitoring program.

A. Total-Body-Exposure Monitoring - Total-body exposures were determined by ORNL film badges, pocket ionization chambers, recording dosimeters, personal radiation monitors, monitrons, and whole body counters.

Urine and feces were also analyzed. Mostly, the ORNL film badge and the pocket ionization chamber (pocket meter) were used. The film badge was processed quarterly, and the pocket meters daily. The film badge was used for obtaining quarterly exposure data and the pocket meters for daily and weekly exposures. The quarterly film-badge figure is much superior to the presumably equivalent figure obtained by adding the daily values of the pocket meters. The error is especially large when using low, daily, pocket-meter figures because of the rounding-off done in reporting those data. Adding such rounded-off values results in a high cumulative error.

The recommended total body exposure limit was 100 millirems per week<sup>15</sup> and three rems per quarter.<sup>16</sup> If necessary, these values would have been superseded by data from the age-proration formulas,  $5(N-18)$  and  $30(N-18)$ , respectively.

The shielded cubicles provide little shielding for the shoulder area. Since the pocket meters were customarily worn in one of the breast pockets, with the film badge hanging from the collar, higher readings were obtained. This fact makes the exposures presented higher than those actually received. However, design data based on such exposures will be conservative.

In some cases (for example, for cubicle entries), total-body exposures for special jobs were determined with recording dosimeters. The advantage of these instruments over the pocket meter was that the exposure received could be read directly from the instrument. Film badges and pocket meters were also worn to determine quarterly and daily exposures.

B. Hand and Arm Exposure Monitoring - Hand and arm exposures were measured principally with the hand-exposure meter (film ring). The recommended weekly exposure limit was 1.5 rems. If necessary, this value would have been superseded by the quarterly limit of 25 rems.<sup>17</sup>

Three film readings were obtained: (1) open window (W); (2) plastic ( $P_L$ ); and, (3) cadmium (Cd). To determine the exposure in rems, these three values were substituted into the equation:  $D_s = 2.5(W - P_L) + Cd$ .

Film data were reported weekly by the Health Physics Division and were rounded off to the nearest 0.1 rem. In this report, however, the values are given to the nearest 5 millirems. This was done to reduce the cumulative error in the sums of the film ring data.

Film rings were used in two ways: (1) by individuals and (2) at work stations. A personal film ring was worn by an operator in performing all his work for a calendar week and processed. A station film-ring was used at each selected work station during a calendar week and then processed. Such a ring was worn every time work was done at that station and was kept in a lead container the remainder of the time. Station film rings were used only in the sol-gel cubicle. They could not practically be used in the rod-fabrication because of the repeated short-time uses of the gloves. Also, the rings are mechanically weak, and repeated glove entries broke them.

To obtain exposures to hands and arms in the rod-fabrication cubicles, station film packs instead of film rings were used. A film pack was taped onto the inside of one glove so as to contact the back of the hand, left there for a week, and then processed. When not in use the glove hung outside the shield. The values obtained by this procedure were 2 or 3 times greater than those obtained by the use of the film pack, probably due to additional exposure of the film pack while the glove hung outside the cubicle.

For the 800-ppm  $^{232}\text{U}$  run, immediate exposures to the hands and arms were obtained by recording dosimeters. The exposures so obtained were about a third to a fifth of corresponding film-ring data, apparently because of the shielding in the recording dosimeters. However, conservative use of the recording-dosimeter data and its immediate availability prevented over-exposure of personnel.

C. Exposure by Inhalation - Exposure by inhalation was monitored by a Q-2340 continuous alpha monitor.

The maximum permissible amount of alpha radioactivity in the air was  $2 \times 10^{-12}$   $\mu\text{c}/\text{cc}$ , the mpc value for soluble  $^{232}\text{Th}$ .<sup>18</sup> More than this requires that the operators wear a respirator. The concentration of  $^{232}\text{Th}$  was chosen as the tolerance because of the high percentage (97%) of  $^{232}\text{ThO}_2$  in the mixed oxides prepared in this program.

#### 5.1.2 Radiation-Background Measurements

Radiation-background measurements were obtained with film packs, G-M survey meters, ionization chambers, and "cutie pies." Film packs and G-M survey meters were used for most of the work. Ionization chambers and cutie pies were used less frequently, and those used were the standard ORNL instruments.

Three readings were obtained from the film packs: (1) window (W); (2) plastic ( $P_L$ ); and shielded (Cd). The data usually reported here are the window readings - to correspond to both the hard and soft radiation received by the hands and arms. A sensitive film (du Pont type 555) was used for exposures from about 20 to  $10^4$  millirads and an insensitive film (du Pont type 834) for exposures from  $10^4$  millirads.<sup>19</sup>

The G-M survey meter used was model Q-2092A-IRI, with a 0-20 millirads/hr range. The meters were calibrated every six weeks by the use of radium gamma rays of an average energy of about 1 Mev, with the shield closed and the batteries being charged continuously.<sup>20</sup> Although the readings were energy dependent, this instrument was used extensively because the design of its probe made it comparatively easy to obtain incubicle data. Its accuracy should be within  $\pm 7\%$  of full scale.<sup>21</sup> The probes were usually unshielded, thus the readings corresponded to both soft and hard radiations.

The frequency of obtaining radiation data during the BNL work depended on the need for the data and the means of obtaining it. The frequency of obtaining operator exposures were discussed above, except for cubicle entry data which were taken for each entry. The frequency of obtaining design background radiation data was based on the processing campaign. Each campaign lasted three to six weeks, and such data were obtained during five periods as follows:

- Period 1: After cleaning out waste material from the preceding campaign and before any new material was charged.
- Period 2: During the startup of the campaign.
- Period 3: During the middle of the campaign.
- Period 4: Near the end of the campaign.
- Period 5: After all processed material was removed but before cleaning out waste material.

## 5.2 Routine Radiation Monitoring Program

### 5.2.1 Total-Body Exposure

The total-body exposures of all Kilorod personnel are summarized in Table 34.

Table 34. Summary of Total Body Exposure of All Kilorod Personnel

Personnel Identification	Total Body Exposure, (millirems)																	
	3rd Quarter 1963						4th Quarter 1963						1st Quarter 1964					
	Film Badge		Pocket Meter				Film Badge		Pocket Meter				Film Badge		Pocket Meter			
	Dc		Average	Range of	Maximum	Dc		Average	Range of	Maximum	Dc		Average	Range of	Maximum			
Total	Weekly	Daily Values	Weekly	Weekly	Total	Weekly	Daily Values	Weekly	Weekly	Total	Weekly	Daily Values	Weekly	Weekly				
Denitrator Operators																		
A	100 <sup>a</sup>	15	0-25	35	340 <sup>b</sup>	26	0-15	30	--	--	--	--	--	--				
Sol-Gel Operators																		
B	220	17	0-100 <sup>d</sup>	120 <sup>d</sup>	240	18	0-20	30	310	24	0-40	100						
A	100	15	0-25	35	See Denitrator Above				270	21	0-90 <sup>d</sup>	130 <sup>d</sup>						
C	10	0.8	0-20	35	120	9	0-20	20	160	12	0-30	55						
Rod-Fab. Operators																		
D	150	12	0-20	40	250	19	0-10	30	350	27	0-30	55						
E	230	18	0-60	60	290	22	0-15	45	270	21	0-30	75						
F	310	24	0-25	55	200	15	0-20	35	220	17	0-30	60						
G	170	13	0-30	50	120	9	0-10	35	160	17	0-15	30						
Supervisors																		
R	70	5	0-15	25	50	4	0-10	20	60	5	0-20	30						
S	140 <sup>c</sup>	11	0-20	35	20	7	0-5	5	60	5	0-15	25						
T	--	--	0-40	40	80	6	0-15	75	70	5	0-20	20						

<sup>a</sup>Worked first half of quarter in cell 4 and last half at denitrator.

<sup>b</sup>Worked seven weeks at denitrator and six in cell 4.

<sup>c</sup>Assigned to another project for the first four weeks in the quarter.

<sup>d</sup>This high value believed to be result of dropping of meters. Operator did no unusual task during this week.

The data indicates that no employee received a quarterly dose to the critical organs greater than 350 millirems - a value much less than the maximum permissible quarterly exposure of 3 rems. The highest average weekly dose was 27 millirems.

Also presented in Table 34 are selected pocket-meter data. The recommended permissible dose for either a day or a week was not equaled or exceeded. The apparent weekly overexposure by operator B in the third quarter of 1963, and by operator A in the first quarter of 1964, were both believed to have been caused by dropping the pocket meters. Both reported exposures would have been highly improbable because the background reading at the sol-gel cubicle face was usually less than 1 millirad, and no unusual occurrence was recorded in the operating logbook in either instance.

These data also indicate that the denitrator operator received as much exposure during periods of denitrator operation as he (or the regular sol-gel operator) received in the sol-gel work. It is also indicated that somewhat higher weekly total body exposures were received in rod-fabrication than in sol-gel work.

In all cases, analyses of urine and fecal samples indicated exposures of less than one-fourth of the maximum permissible quarterly dose.<sup>22</sup>

Comparisons of whole-body counts of workers before and after the BNL work indicated no significant differences in body burdens.<sup>23</sup> Radiochemical species in these comparisons were the daughter products of  $^{232}\text{Th}$  and  $^{232}\text{U}$ .

#### 5.2.2 Hand and Arm Exposure

Table 35 presents a summary of the hand and arm exposure received by Kilorod personnel in campaigns 1 and 3 through 7. No data was taken in campaign 2.

The data shows that no employee received a weekly hand and arm exposure greater than the maximum permissible value of 1500 millirems. The greatest weekly dose received by an individual was 1055 millirems, during Health Physics week 13, 1964. This occurred in the rod-fabrication cubicle during cleanout after completion of the BNL program. The largest weekly dose during normal operation was 840 millirems, during HP week 52, 1963, also in the rod-fabrication cubicle. Since the other weekly exposures

Table 35. Radiation Exposure to Hands and Arms for All Kilorod Personnel  
(Millirems), as Measured by Film Rings

Process	Campaign											
	1		3		4		5		6		7	
	Range	Average	Range	Average	Range	Average	Range	Average	Range	Average	Range	Average
Sol-Gel	0-75	27	75-170	137	40-190	127	0-95	54	0-160	49	0-510	95
Rod Fabrication	0-100	34	45-180	141	0-210	72	0-840	139	0-365	82	0-1055	125

were so much lower than the two values cited above, it follows that the quarterly exposure for an individual did not approach the maximum permissible value of 25 rems.

### 5.2.3 Radiation Backgrounds of Operating Areas and Equipment

Table 36 presents a summary of the radiation background in operating areas and equipment for the BNL program in the range of 5 to 30 days after purification of the  $^{233}\text{U}$ . Two sets of data are presented: (1) film-pack open-window data and (2) data obtained by unshielded G-M survey-meters. Both sets of data correspond to dosages which would be received on the hands and arms by personnel working in the cubicles. The film-pack data indicate that the radiation background increased somewhat during campaigns 4 through 7. A comparison of the campaign-7 data obtained by these two methods indicates the film-pack values are higher, sometimes by a factor of 2 to 3.

Table 37 presents period-1 and period-5 radiation-background data obtained with film packs at seven work stations for campaigns 3-6.

The fact that the radiation backgrounds for period 1 at the blend tank (BOS-1) and at the crucible table did not change significantly during campaigns 4-7 indicates that cleanout was effective during these campaigns. This fact also shows that the waste that accumulated in each campaign at these stations was new waste. It is also apparent that some old waste remained after each campaign, because the period-5 reading was usually higher than the period-1 value.

Cleanout was less effective at BOS-2, the ball mill, the powder blender, and the rod-loading stations. The radiation backgrounds from period 1 in campaign 4 to period 1 in campaign 7 almost doubled. This increase probably represented small oxide particles and dust which could not be cleaned out easily. This waste apparently collected generally during each campaign.

### 5.2.4 Radiation Exposures by Operation

A detailed analysis was made of the total-body and hand and arm exposures obtained during the BNL program to obtain the exposure by operation. The procedure used in this analysis is presented in detail in the Appendix. Briefly, it involves assigning the exposures received to a particular operation according to the time spent on that operation as indicated by a time-and-motion study made by J. J. Varagona.<sup>24</sup>

Table 36. Radiation Backgrounds at Various Locations in the Sol-Gel  
and Rod-Fabrication Cubicles During the BNL Program

Conditions: All film pack data were taken in period 2 of each campaign, between 5 and 20 days after extraction; G-M survey meter readings were taken in period 3, between 20 and 30 days after extraction

Location	Radiation Background (millirads/hr)					G-M Survey Meter (Unshielded) Campaign 7
	Film Pack (Window)					
	Campaign					
	4	5	6	7	Average	
<b>A. Sol-Gel Cubicle</b>						
WS-1 (Blend tank)	7.0	10.0	15.4	11.7	11.0	7
WS-1 (outside cubicle face)	Not available	-----	-----	-----	-----	< 1
WS-2 (No. 1 bagout station)	5.6	8.8	15.4	14.3	11.0	7
WS-3 (Crucible station)	10.4	9.2	22.9	7.6	12.5	10
WS-3 (outside cubicle face, max.)	Not available	-----	-----	-----	-----	< 2
WS-4 (No. 2 bagout station)	12.5	13.3	35.8	20.9	20.6	10
WS-13 (top of crucible of green gel)	880.0	230.0	200.0	400.0	428.0	200
WS-14 (tray of green gel)	Not available	170.0	270.0	240.0	227.0	200
WS-23 (top of crucible of fired oxide)	1320.0 <sup>a</sup>	300.0	480.0	Not available	390.0	200
<b>B. Rod-Fabrication Cubicle</b>						
WS-5 (Ball mill)	20.0	32.5	34.6	20.4	26.9	8
WS-6 (Blender)	11.3	17.5	26.3	26.0	20.3	10
WS-6 (outside cubicle face, max.)	Not available	-----	-----	-----	-----	
WS-7 (Rod loading)	14.6	17.9	17.5	26.0	19.0	15
WS-7 (outside cubicle face, max.)	Not available	-----	-----	-----	-----	

<sup>a</sup>Not included in average.

Table 37. Radiation Background Data for Selected Work Stations in Campaigns 3-6.

	Radiation Background (millirads/hr)							
	Campaign		Campaign 5		Campaign 6		Campaign 7	
	Period 1	Period 5	Period 1	Period 5	Period 1	Period 5	Period 1	Period 5
Blend tank	10.7	10.2	18.8	N.A.	8.8	11.8	11.4	17.1
BOS-1	10.0	18.4	11.3	N.A. <sup>a</sup>	7.5	8.3	11.4	14.6
Crucible table	4.5	5.4	5.4	3.9	3.9	5.0	5.0	20.8
BOS-2	2.9	10.8	10.8	6.1	6.1	9.2	9.2	15.0
Ball mill	13.3	N.A. <sup>a</sup>	31.7	20.0	17.1	23.1	22.6	53.3
Powder blender	14.2	N.A. <sup>a</sup>	7.9 <sup>b</sup>	32.1	17.6	26.2	23.5	30.0
Rod loading	10.4	N.A. <sup>a</sup>	16.3	23.7	20.6	26.2	27.8	30.4

<sup>a</sup>Not available.

<sup>b</sup>Questionable.

A. Total-Body Exposure - Table 38 presents the total-body exposure obtained by operation. Values are given for the three HP quarters in which the BNL program was conducted. Averages of the three quarter values are also given. The average values indicate the following:

1. The sum of the total body exposures in the rod-fabrication process was nearly twice the sum of the exposures in the sol-gel or denitration processes. This is understandable because only the oxide powder is handled in the rod-fabrication phase of the process, and the operating time was greater than that for either of the other two phases. At any rate the exposure in rod-fabrication was less than the weekly tolerance of 100 millirems, and therefore one man could have performed the operation without overexposure.

2. The highest exposure in the sol-gel process was received while performing the operations at the crucible table while handling oxide.

3. The highest exposure in the rod-fabrication process was obtained in the compacting operation.

B. Hand and Arm Exposure - The hand and arm exposure per operation is presented in Table 39. These data indicate:

1. Hand and arm exposure in the rod-fabrication process was about three times that for the sol-gel process. The exposure for either was considerably less than the weekly tolerance of 1500 millirems, again indicating that one operator could have performed all phases of the sol-gel or the rod-fabrication process without overexposure.

2. The maximum hand and arm exposure in the sol-gel process was received in the crucible-table operations, while that in the rod-fabrication process was received in compacting and powder blending.

#### 5.2.5 Radiation Monitoring of Fuel Rods

During the Kilorod Program, four fuel rods were selected at random and periodically monitored with a G-M survey meter to determine the variation of radiation activity with time since  $^{232}\text{U}$  activity removal or age of the fuel mixture. A similar study was made with film packs; however, the resulting data showed no apparent correlation with age, whereas the G-M survey-meter values, which are presented in Fig. 35, increased steadily with age, as would be expected, because of growth of  $^{232}\text{U}$  daughter growth.

Table 38. Total-Body Radiation Exposures per Operation  
for the Kilorod Program

Source: Dc Values from film badges. See Appendix for methods

Process	Operation	Total Body Exposure (millirems/week)			Average
		3rd Quarter (1963)	4th Quarter (1963)	1st Quarter (1964)	
Denitration	All operations	15	24 <sup>a</sup> (7 weeks' operation)	Shutdown	20
	Blending operations at crucible table	22 <u>29</u> 51	9 <sup>a</sup> <u>12<sup>a</sup></u> 21	20 <u>25</u> 45	17 <u>22</u> 39
Rod Fabrication	Jaw crushing and sampling	3.2	5.1	7.3	5.1
	Ball milling	2.1	3.2	4.6	3.2
	Blending (powder)	5.3	8.4	12.0	8.4
	Compacting	16.0	20.0	19.0	18.0
	Scanning (transferring rod for scanning)	4.8 0.5	3.0 0.4	3.4 0.5	3.4 0.4
	Welding	6.5	4.5	6.0	5.5
	Ultrasonic cleaning	2.2	1.6	2.1	1.9
	Leak testing and weighing	2.5	1.7	2.3	2.1
	Turco cleaning; smearing and loading into carrier	4.4	5.4	6.5	5.4
	Supervising	19.0	12.0	14.0	14.0
	Total	67.0	66.0	78.0	67.0

<sup>a</sup>From sum of pocket-meter values.

Table 39. Hand- and Arm-Radiation Exposure per  
Operation for the Kilorod Program

Source: Film-ring data. See Appendix for methods.

		Hands and Arms Exposure, millirem/week				
Process	Operation	4th Quarter (1963)	No. of Weeks	1st Quarter (1964)	No. of Weeks	Weighted Average
Denitration	All operations					
Sol-Gel	Blending Operations at crucible table	55 70 <u>125</u>	10 (one operator)	53 68 <u>121</u>	12 (one operator), 9 (other operator)	54 69 <u>123</u>
Rod Fabrication	Jaw crushing and sampling	44	9	63		54
	Ball milling	28		40	11	35
	Blending (powder)	72		103		89
	Compacting	125	11	70	11	98
	Scanning	27	11	15	8	22
	Transferring rod for scanning	1		1		1
	Welding	18	10	15	12	16
	Ultrasonic cleaning	6		5		6
	Leak testing and weighing	7		6		6
	Turco cleaning; smearing and loading into carrier	36	9-11	39	11-12	38
	Supervising	105 <u>469</u>	11	59 <u>416</u>	8	86 <u>451</u>

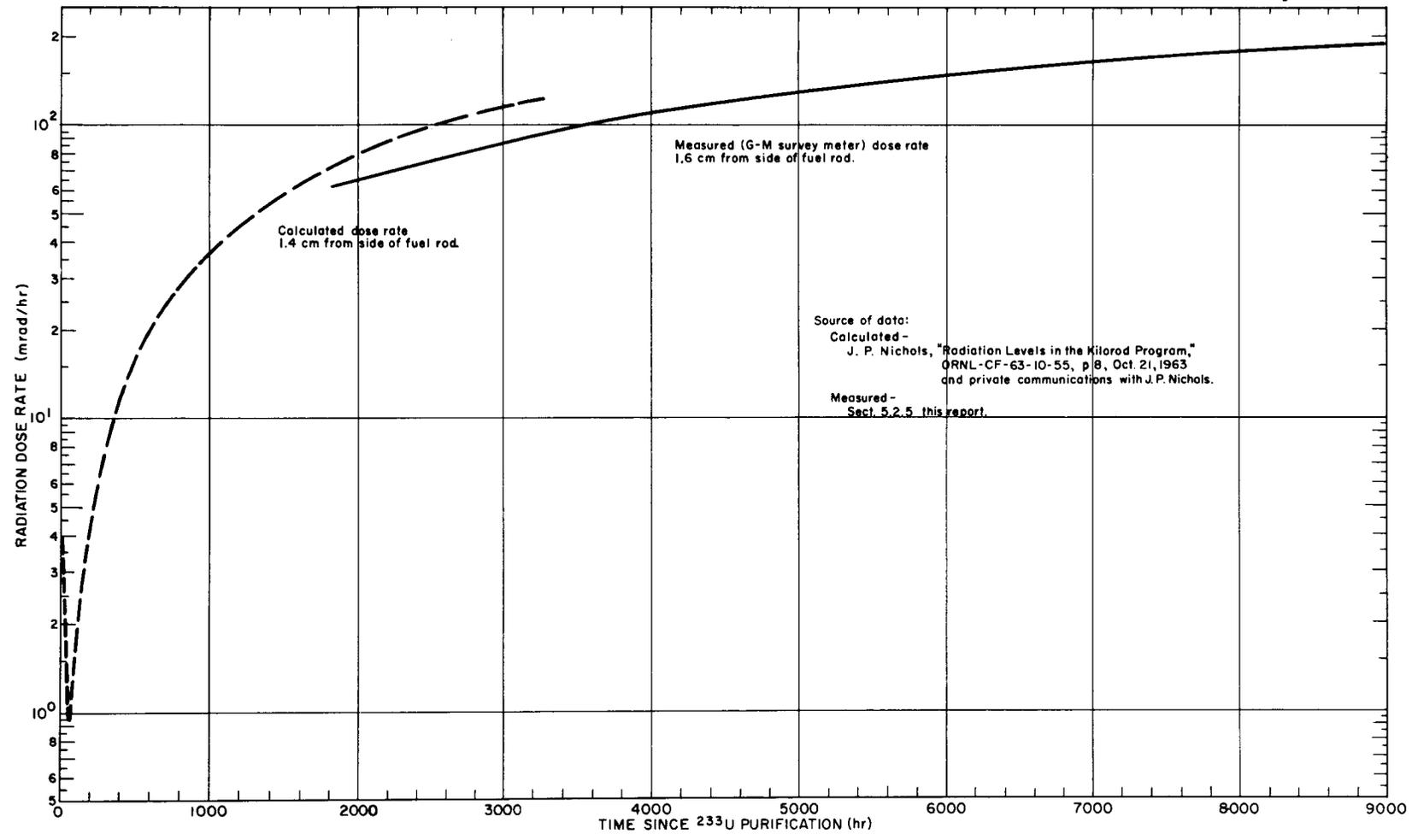


Fig. 33. Variation in Dose Rate of a Kilorod Fuel Rod With Time Since  $^{233}\text{U}$  Purification.

Also included in Fig. 35 is a plot of data predicted by J. P. Nichols,<sup>25</sup> using a dose point of 1.4 in. as compared with an estimated dose point of 1.6 in. for the measured values. The measured data compares very favorably with the predicted values in the overlapping region of the curves. As would be expected, the predicted values are higher because of the closer dose point. However, the variation is the same as would be expected from the inverse-square law. The agreement between the two sets of data is better than would be expected because no correction was made for the energy dependence of the G-M survey-meter data.

#### 5.2.6 Radiation Exposures During Maintenance

Two types of maintenance on operating equipment were performed:

(1) that done without entering the cubicles and (2) that done by entering the cubicles. When possible, maintenance was performed externally, with the radiation exposure received not being monitored separately from that received while operating. A radiation work permit was issued for in-cubicle maintenance. The radiation exposure received was monitored separately with a recording dosimeter as well as with the film badge and pocket meters. During the program, only three maintenance jobs were done in which an individual received a daily total-body exposure of more than 20 millirems:

1. repairing ball mill on Aug. 8, 1963, during which one operator received 60 millirems and a second operator 10;
2. moving blender to maintenance area on Sept. 27, 1963, during which an operator received 30 millirems;
3. replacing furnace element on Oct. 29, 1963, during which an operator received 70 millirems.

### 5.3 High <sup>232</sup>U Content Monitoring Program

#### 5.3.1 Objective

Upon completion of the BNL fuel-rod commitment, a special run was made with aged <sup>233</sup>UNH to simulate operation with high <sup>232</sup>U content feed. In this run, <sup>233</sup>UNH containing 38 ppm of <sup>232</sup>U, which had been purified approximately six years before, was blended with recently purified material to obtain a daughter in-growth equivalent to that of feed containing an estimated 800 ppm of <sup>232</sup>U which was only 14 days old. The principal

objective was to obtain radiation data for use in scaling up the process for working with higher levels of  $^{232}\text{U}$  than that encountered in the Kilorod Program. It should be recognized that since only one 10-kg batch of high-radiation-level oxide was prepared, the radiation background and exposure data was extremely conservative since inventory equilibrium was not attained.

### 5.3.2 Radiation Background of Operating Areas and Equipment

Table 40 presents the radiation background in operating areas or equipment during the 800-ppm  $^{232}\text{U}$  content run. These data indicate that the radiation backgrounds were two or three-times higher in the 800-ppm than in the 38-ppm work.

### 5.3.3 Radiation Exposure

Table 41 presents a summary of the radiation exposure experienced during the 800-ppm run.

When the exposures resulting from 800-ppm and 38-ppm batches are put on the same basis (millirems per 10-kg batch), it is indicated that the total body exposure for the 800-ppm run was about 3 times greater (117 millirems, compared with 35). The hand and arm data for the 800-ppm run was about 5 times greater (950 millirems, compared with 190). Variation in the individual operations were about the same as the variation of the total.

As previously mentioned, because of the limited amount of high-level material processed, "steady-state" background levels were not attained, and the radiation exposures attained are conservative. It is estimated that with continuous operation, the Kilorod facility could process material having a  $^{232}\text{U}$  content of about 500 ppm.

## 5.4 Application of Radiation Experience to Design Scaleup

Table 42 presents the results of a study by J. P. Nichols, R. E. Brooksbank, and D. E. Ferguson to estimate the radiation dose rates to operating personnel as a function of shielding and  $^{232}\text{U}$  content.

It is estimated that with weekly chemical purification, the average elapsed time during sol-gel and rod-fabrication work can be reduced to about 7.5 and 12 days, respectively. If this time reduction were obtained,

Table 40. Radiation Backgrounds at Various Locations in the Sol-Gel and Rod-Fabrication Cubicles During the 800-ppm <sup>232</sup>U Content Run

Location	Radiation Background (millirads/hr)	
	Film Pack (Window)	G-M Survey Meter (Unshielded)
Sol-Gel Cubicle		
WS-1 (Blend tank)	16.8	8
WS-1 (outside cubicle face, max.) (At work table above blend tank)	Not available	~6 <sup>a</sup>
WS-2 (No. 1 bagout station)	27.9	<10
WS-3 (Crucible station)	36.3	7
WS-3 (outside cubicle face, max.)	0.8	3 <sup>a</sup>
(Bottom of tray dumper outside cubicle face, shields closed, loaded crucibles on table, max.)	Not available	60-65
WS-4 (No. 2 bagout station)	34.8	8
Tray of dried gel, near contact	3,200	2,500 <sup>b</sup>
Crucible of fired oxide, near contact	6,400	4,000 <sup>b</sup>
Rod-Fabrication Cubicle		
WS-5 (Ball mill)	84.3	44
WS-5 (outside cubicle, face, max.)	12.6	1.8
WS-6 (Blender)	52.9	40
WS-6 (outside cubicle, face, max.)	5.6	2.0
Against ball mill while in use	Not available	~600 <sup>b</sup>
Against jaw crusher while in use	Not available	120
Against classifier while in use	Not available	180
WS-7 (Rod loading)	91.3	250
WS-7 (outside cubicle face, max.)	1.3	1.4
Rod (at contact, 18 in. from threaded end)	600.0	~600 <sup>b</sup>
Rod (at contact, 24 in. from threaded end)	600.0	~600 <sup>b</sup>
Rod (at contact, 30 in. from threaded end)	657.0	~550 <sup>b</sup>

<sup>a</sup>Shield closed.

<sup>b</sup>Cutie pie was used because of the 200 mr/hr limit on G-M survey meter.

Table 41. Radiation Exposure During 800 ppm  $^{232}\text{U}$   
Content Run (millirems per Operator)

Basis: One batch weighing 10 kg, producing 10 fuel rods

	Total Body Exposure		Hand and Arm Exposure	
	Shoulder Dosimeter	Pocket Meter	Sleeve Dosimeter	Film Ring
Sol-Gel Process				
Blending	<11	10	27	95
Crucible-table operation	< 7	20	53	155
Total	<18	30	80	250
Rod Fabrication				
Crushing	4		11	
Ball milling	6		18	
Blending	10		30	
Compacting	8		40	
Scanning	3		15	
Welding	5		20	
Clearing	2		5	
Leak testing and weighing	2		10	
Smearing	3		15	
Supervision	4		10	
Total	47	87	174	700(+30% <sup>a</sup> )

<sup>a</sup>Estimated.

Table 42. Estimated Radiation Dose Rates to Operating Personnel  
 As a Function of Shielding and  $^{232}\text{U}$  Content for Fuel Element Manufacture  
 Glove-Box Line Producing 97%  $\text{ThO}_2$  - 3%  $^{233}\text{UO}_2$  by Sol-Gel and Vibratory  
 Compaction;  $^{233}\text{U}$  Purified by Solvent Extraction

Type of Operation	Scale (kg oxide/day)	Shielding as Equivalent of Lead of Shadow Shield	Average Post Purification Time in Sol-Gel Process Average (days)	Average Post Purification Time in Rod Fabrication (days)	Weekly Radiation Dose Rate to Operators (millirems)		$^{232}\text{U}$ Content (ppm in $^{233}\text{U}$ )
					Hands	Body	
Kilorod facility	10	2	15	19	100	20	40
Batch facility	10	2	15	19	500	100	200
	10	2	7.5	12	500	100	500
	10	0	7.5	12	50	100	50
Semicontinuous facility	100	2	4.5	6	500	100	600
	100	0	4.5	6	50	100	50

the use of 2 in. of lead shielding would permit operation with  $^{233}\text{U}$  that contains 500 ppm of  $^{232}\text{U}$ . Further,  $^{233}\text{U}$  containing 50 ppm of  $^{232}\text{U}$  could be processed with no shielding other than the walls of the vessels and glove boxes and from self-shielding in the fuel material.

By designing a plant to operate semicontinuously to minimize holdup times in all steps, the average elapsed time in sol-gel work can be reduced to 4.5 days, and in rod-fabrication work to 6 days. Such a design becomes reasonable for a plant considerably larger than the Kilorod facility. Much of the equipment in such a plant would be automated to minimize attendance by personnel, and an automatic conveyor belt tray-dryer and a gravity-fed tube furnace would be used. Under these assumed conditions, at a rate of 100 kg of total oxide per day,  $^{233}\text{U}$  containing 600 ppm of  $^{232}\text{U}$  can be processed with 2 in. of lead shielding, and that containing 50 ppm with only the shielding offered by the vessels and fuel.

In general, shadow shielding is required for working with a mixed-oxide fuel containing 3% uranium-233 if the uranium contains more than about 50 ppm of  $^{232}\text{U}$  unless the glove box is well designed and extreme care is taken in its use. With 2-in. lead-equivalent shadow shields for the major pieces of process equipment,  $^{232}\text{U}$  concentrations of about 500 ppm can be handled safely on a batch basis at a scale of about 10 kg of mixed-oxide per day. At the larger scale of 100 kg of total oxide per day, a semicontinuous process is reasonable, and  $^{233}\text{U}$  containing 500 ppm of  $^{232}\text{U}$  can be handled safely with shadow shields. Operation with higher levels of  $^{232}\text{U}$  will require complete shielding and remote operation.

In the Kilorod Program, the solids-handling equipment and cubicles were decontaminated effectively with a vacuum cleaner; chemical treatment was not needed. This is contrary to previous experiments with ceramic-grade  $\text{ThO}_2$  powders, which were difficult to remove from surfaces. The dissimilarity apparently is attributable to the refractoriness of the sol-gel oxide. This experiment indicates that equipment can be maintained in unshielded or lightly shielded glove boxes following relatively effortless decontamination.

In the above discussion, operation with weekly radiation exposure to operators of 100 millirems per week has been assumed. However, routine operation at a level of 40 millirems per week is recommended; therefore, the permissible  $^{232}\text{U}$  content levels suggested in Table 41 should be reduced 60%.

## 6. CONCLUSIONS AND RECOMMENDATIONS

The Kilorod Program was an unqualified success, meeting every objective. The 10-kg-per day design rate for the sol-gel operation was sustained, as scheduled, over long operating periods. The longest of these was fourteen consecutive days in the November-December period. All equipment except the calciner could produce at least double the production design rate. Rod-fabrication operations were similarly successful, with an average sustained production rate of 13 rods having been demonstrated over a period of 10 scheduled operating days. A maximum of 21 rods was fabricated in a single working day, once during the program. All chemical and fabrication specifications were met or exceeded.

From the Kilorod experience, the following conclusions are reached:

1. The sol-gel process for preparing a 3%  $UO_2$  - 97% product is now a practical, working process. This process can be scaled up directly to any immediately foreseeable production rate.
2. A sol-gel, rod-fabrication combination is also a practical, working process that can be scaled up directly to any immediately foreseeable production rate.
3. Specifications requiring both high product purity and fuel element uniformity can be met routinely in a combined sol-gel, vibratory-compaction, fuel-rod-preparation plant.
4. Batch rejection and internal recycle of materials (as wastes) are almost nil in a sol-gel, vibratory-compaction operation as represented by the Kilorod installation.
5. Both sol-gel and rod-fabrication operations are amenable to rigid analytical control, as evidenced by the process control during this program.
6. Exposure of workers to radiation at the 38-ppm  $^{232}U$  level was far below permissible limits.
7. Considerably higher  $^{232}U$  concentrations can be handled safely in the present equipment by current operating procedures.
8. Loss of process materials in all operations can be held to extremely low if not insignificant values.

9. Aged  $^{233}\text{U}$  (38 ppm  $^{232}\text{U}$ ) can be satisfactorily purified for use in the sol-gel process by a solvent extraction process based on extraction by di-sec-butyl phenyl phosphonate.

From Kilorod experience the following recommendations are made:

1. The problems associated with the gases contained in the final sol-gel product should be studied. Unfortunately, it was impossible to study them in conjunction with the normal operation.

2. Consideration should be given to the design, construction and startup of a continuous denitrator. The present unit, even though completely dependable in all respects, is a high-labor-cost operation. Any future, large-scale thorium processing plant must necessarily include a complete and continuous conversion of a thorium nitrate solution to a powder (or sol). In this innovation lies probably the largest single cost-reduction item now apparent and is also probably the one requiring the least effort (or money).

3. The cost of gases (Ar, Ar--4%  $\text{H}_2$ ) was excessive and must be reduced. Other gases, quantity purchase and storage, and error-proof mixing system should be considered.

The success of the Kilorod Program represents a significant breakthrough in the fabrication of ceramic fuel elements. The sol-gel, vibratory-compaction combination offers advantages in simplicity, reliability, and ease of process control available in no other fabrication scheme.

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## 8. APPENDIX

## 8.1 Detailed Information on the Solvent Extraction Operation

8.1.1 Description of Facility

The Thorex Pilot Plant in cells 5, 6, and 7 of Building 3019 was modified to provide a facility for purification of the  $^{233}\text{U}$  feed stocks for the program. A schematic equipment flowsheet is presented in Fig. 1A.

The  $^{232}\text{U}$  content and age of the  $^{233}\text{U}$  available, together with the planned semiremote method of fabrication, indicate that a gross gamma decontamination factor of only 100 was required. In addition, the sol-gel process requires that the  $^{233}\text{U}$  feed should not have a nitrate to uranium ratio above 2.5 if a satisfactory gel is to be obtained. This requirement necessitates a thorium decontamination factor of at least 1000.

Extensive experimental work by Ryon indicates that the use of a solvent containing 2.5% (di-sec-butyl phenyl phosphonate), also in diethylbenzene, provides gross gamma and thorium decontamination factors as much as 4 times greater than that offered by a similar system employing tributyl phosphate. While it is true that the decontamination-factor requirement is relatively low, it was decided to use the newer DSBPP solvent to obtain pilot plant experience.

In the DSBPP flowsheet, the adjusted feed is introduced into the extraction column where it is contacted with the extractant. The uranium is extracted into the organic phase, which is then scrubbed with a 0.8 M aluminum nitrate solution which is 0.4 M acid deficient to remove entrained thorium and ionic contamination. The aqueous raffinate from the extraction column is routed to storage. The scrubbed organic then cascades to a strip column where the uranium is removed from the organic phase with water. The resultant uranium solution is then transferred through a static diluent wash column for the removal of trace quantities of organic prior to concentration. Spent solvent is collected batchwise, treated with 0.2 M  $\text{Na}_2\text{CO}_3$  and reused.

To provide a facility for the  $^{233}\text{U}$  purification the Building 3019 solvent extraction facility was extensively reconditioned and modified. Extracting and scrubbing were done in the original 5-in.-diam, 38-ft-high



pulsed column (N-1). Laboratory results indicate that at least four extraction and three scrub stages will be required. When operating at a pulse amplitude of 1 in. and a frequency of 58 cpm, the required stages are obtained when introducing the feed at a point to obtain 15 ft of extraction and 17 ft of scrub. If necessary, additional scrub stages could be obtained by operating with an additional 5-in.-diam column providing 12 ft of pulse plates (P-1).

The organic stripping was performed in an existing 5-in.-diam, 20-ft-high column (R-1). Ryon's results indicate that when operated at 1.0-in. amplitude and 50 cpm the required two stages will be obtained.

A new 2-in.-diam column packed with 1/2-in. Raschig rings (stainless steel) for the static diluent-wash column, and a new 5-in.-diam product evaporator and product storage tank, were installed.

The majority of the vessels to be used are not of critically safe geometry; consequently, several important operational and equipment modifications have been made. The total mass of uranium within the facility did not exceed 8 kg. Solutions were maintained below the  $^{233}\text{U}$  maximum "eversafe" value of 10 g/liter by flowrate adjustments for aqueous streams and chemical saturation for organic streams. The only stream which exceeded this value was the final product stream (100 g/liter), which was boiled down in a 5-in.-diam evaporator critically safe to a concentration of 200 g/liter.

In addition to mass and concentration control, the feed extraction column and raffinate catch tank contained sufficient thorium to yield a  $^{233}\text{U}/\text{Th}$  ratio of  $<0.025$ .

As a final safety device, Pyrex Raschig rings containing 4% B were placed in critical process vessels, notably in the expanded sections of the columns, waste tanks, solvent tanks, and product tanks.

The product evaporator is made of 5-in. pipe, with a jacketed section providing  $4.5 \text{ ft}^2$  of heating surface. Three perforated plates are provided for vapor de-entrainment, and the feed is introduced between the bottom two plates. Cold tests before installation indicated that at 25 liter/hr boilup, entrainment was negligible when operated with no reflux; however, in the intermediate-level runs, operation without reflux resulted in overhead losses as high as 0.5%. The use of 3 liter/hr water reflux introduced 2 ft above the feed reduced the loss to  $<0.01\%$  during the latter part of the intermediate level run and was negligible throughout the hot operation.

As previously mentioned, satisfactory sol-gel product is dependent on strict control of the nitrate ion concentration in the sol. This establishes an upper limit on the nitrate-to-uranium ratio in the solvent extraction product. (In the Kilorod process this ratio is 2.5.)

Product from the solvent extraction system normally contains a constant concentration of excess nitrate ion (nitrate from sources other than uranyl nitrate). As a result, the nitrate-to-uranium ratio is high at the beginning and end of a solvent extraction run since the uranium concentration is low at these times. Consequently, off-specification product is obtained for a period at the beginning and at the end of each run.

During operations, a product cut is collected as feed to the evaporator. The nitrate-to-uranium ratio is controlled by diversion of product between the product tank and recycle tank.

#### 8.1.2 Detailed Discussion of Operating Procedures

Operation of the Kilorod sol-gel and rod-fabrication facility at the design capacity required about 265 g of  $^{233}\text{U}$  per day and a program total of nearly 28 kg. The capacity of the solvent extraction facility at equilibrium flowsheet conditions is 250 g/hr. Although the capacity of the solvent extraction facility is such that it would be possible to purify the entire  $^{233}\text{U}$  requirement in about 112 hr of equilibrium operation,  $^{232}\text{U}$  daughter growth necessitates intermittent operation. Initial prediction of this growth and criticality safety considerations led to the decision to accumulate no more than a three weeks' supply or to process the uranium in batches of about 5 kg.

Each purification batch involved the following operations:

1. cold feed and scrub makeup,
2. metal dissolution and/or hot feed makeup,
3. solvent extraction,
4. solvent treatment, and
5. reworking of "off-spec" solutions.

These operations were conducted with two operators per 8-hr shift, following detailed operating sheets. Operations involving significant quantities (more than 500 g) of  $^{233}\text{U}$  were supervised by technical personnel. The run sheet for the solvent extraction operation is presented as an example of the procedures used.

Rev: 3-12-63

KILOROD  
Solvent Extraction Column  
Startup and Operation Run Sheet

Run number \_\_\_\_\_

## 1.0 Equipment check:

<u>Time</u>	<u>Date</u>	<u>By</u>	
_____	_____	_____	1.1 Check that the following tanks are empty: N4 _____, N2 _____, N8 _____, N16 _____, N7 _____, R2 _____, R3 _____, T10 _____.
_____	_____	_____	1.2 Check that the following tanks contain nuclear poison and level of each remains constant: P3 _____, P4 _____, P70 _____, R9 _____, S5 _____, T5 _____, T20 _____, T25 _____.
_____	_____	_____	1.3 Check that P69 contains _____ liters of clean solvent and that sample results indicate 2.5 wt % DSBPP is within speci- fications.
_____	_____	_____	1.4 Check that M18 contains HAS solution with sample results within specifications. Record results of sample: H <sup>+</sup> _____, AL _____.
_____	_____	_____	1.5 K2 and K3 made up and sample results indicate HCX within specifications. H <sup>+</sup> _____.

2.0 Complete containment check-out run sheet before continuing further.

\_\_\_\_\_ Approved to proceed to step 3.0 by \_\_\_\_\_.

## 3.0 Diluent wash column.

_____	_____	_____	3.1 Wash column empty _____.
_____	_____	_____	3.2 R28 empty _____.

<u>Time</u>	<u>Date</u>	<u>By</u>	
_____	_____	_____	3.3 Measure (5) five liters of water and transfer to diluent addition tank C-19.
_____	_____	_____	3.4 Open drain valve under C19 and drain contents of C19 to R20.
_____	_____	_____	3.5 When C19 is empty close valve and add (5) five liters of diluent (DEB) to C19.
_____	_____	_____	3.6 Set PlHC-R-21 to 18 inches water pressure.
_____	_____	_____	3.7 Drain contents of C19 to R20. Then close C19 drain valve.
_____	_____	_____	3.8 Set Fl-R27 to 60% of scale.
			4.0 Column startup
			4.1 R-1 column
_____	_____	_____	Close jet suction valve (TOG _____).
_____	_____	_____	Close steam to bottom jet (TOG _____).
_____	_____	_____	Close steam to interface jet (TOG _____).
_____	_____	_____	Set FRC-HCX to control on automatic at ____%.
			(25 liters/hr).
_____	_____	_____	Open K2PS recirculation valve.
_____	_____	_____	Open K2 to K20s suction valve.
_____	_____	_____	Open K2P discharge valves to FR-HCS.
_____	_____	_____	Open K2P discharge valves to FR-HCX.
_____	_____	_____	Start K2PS.
_____	_____	_____	When Li-R1 indicates rise in liquid level in column, open R1P transmission valve and start R1P. Bleed air from pulse transmission line.
_____	_____	_____	Set R1P as follows:
			_____ amplitude
			_____ frequency
_____	_____	_____	Set LiRC-R1 to control on automatic at ____%.
_____	_____	_____	Set FI-RIP to 10% of scale.
			4.2 P-1 column
_____	_____	_____	Close jet suction valve (TOG _____).
_____	_____	_____	Close steam to bottom jet (TOG _____).

<u>Time</u>	<u>Date</u>	<u>By</u>	
_____	_____	_____	Close steam to interface jet (TOG _____).
_____	_____	_____	Close P11 to R11 valve.
_____	_____	_____	Open P11 to P1 valve.
_____	_____	_____	Open M18 to M18P valve.
_____	_____	_____	Open M18P to P14 valve.
_____	_____	_____	Open P14 to P1.
_____	_____	_____	Start M18P and adjust rate to 25 liters/hr.

NOTE: Watch P1 Li closely and do not allow P1 to overflow to R11.

_____	_____	_____	When L1-P1 indicates buildup in P1, open P-1 P transmission valve and P1P transmission line bleed until the line is free of air.
_____	_____	_____	Start P1P and set:
_____	_____	_____	Amplitude at _____.
_____	_____	_____	Frequency at _____.
_____	_____	_____	Set L1RC-P1 at 33%.
_____	_____	_____	Set P26-LRC at 25%.
_____	_____	_____	When P26 liquid level reaches 10%, start P26.

4.3 N-1 Column

_____	_____	_____	Set L1RC-N1 on manual control with "0" output.
_____	_____	_____	When flow to N4 is established, open valve in pulse transmission line.
_____	_____	_____	Start N1P and bleed air from pulse transmission line.
_____	_____	_____	Set amplitude at _____.
_____	_____	_____	Set frequency at _____.
_____	_____	_____	Set L1RC-N1 to control on automatic at _____%.

Approved to proceed to step 5.0 by \_\_\_\_\_.

Date \_\_\_\_\_.

5.0 Establishing organic flow through system.

_____	_____	_____	Close T5P to T4 _____.
_____	_____	_____	Open P69 to T5P _____.
_____	_____	_____	Close FR-HAX by pass _____.
_____	_____	_____	Open T5P manual valves _____.

<u>Time</u>	<u>Date</u>	<u>By</u>	
_____	_____	_____	Set FRC-HAX at _____% on automatic control.
_____	_____	_____	Start T5P.
_____	_____	_____	Set F1-P1P organic purge at 6 liters/hr. (Approximately 20% on rotometer).

6.0 Start recording data requested.

Approved to proceed to step 7.0 by \_\_\_\_\_.  
Date \_\_\_\_\_.

7.0 Synthetic feed.

_____	_____	_____	S4 should contain _____ liters of synthetic feed.
_____	_____	_____	Open N9 to N1 (TOG _____).
_____	_____	_____	Open S4P to N9 (TOG _____ and TOG _____).
_____	_____	_____	Close valve and cap S4P flush line.
_____	_____	_____	When column operation is satisfactory and material balance indicates proper column operation, start S4P. Adjust feed rate to _____ liters/hr.

8.0 Hot feed operation.

_____	_____	_____	When S4 1R has depleted to _____%, prepare to jet feed in S2 to S4.
-------	-------	-------	---

Transfer approved by \_\_\_\_\_.

_____	_____	_____	Record:
			L.L.                  Sp. G.                  Vol. Temp.
			S2                  _____
			S4                  _____

_____	_____	_____	Open block valve _____.
_____	_____	_____	Open TOG _____. Jetting contents of S2 to S4. When S4 ceases to build up shut-off TOG _____ and close block valve _____.
_____	_____	_____	Jet N4 to N2 and sample

_____	_____	_____	Record:
			L.L.                  Sp. G.                  Temp.                  Vol.
			S2                  _____
			S4                  _____

<u>Time</u>	<u>Date</u>	<u>By</u>	
_____	_____	_____	Adjust feed rate to _____ liters/hr.
_____	_____	_____	After _____ hr on hot feed, open valve rotating HCU stream to R3.
_____	_____	_____	Comply with sampling schedule.
_____	_____	_____	When results on N2 sample are known, jet N2 to N8.
_____	_____	_____	When N4 volume reaches 300 liters, jet N4 to N2 and sample.
_____	_____	_____	Jet contents of N2 to N8.
_____	_____	_____	Cut N8 to N7. Watch closely for indication of organic in N8 on D1-N8.
_____	_____	_____	Dispose of N8 and N7 as directed.
_____	_____	_____	9.0 Cold feed shutdown.
_____	_____	_____	Sparge S2 for 1 hr.
_____	_____	_____	Jet S2 to S4 when approved.
_____	_____	_____	Transfer approved by _____.
_____	_____	_____	Record:
			L.L.      Sp. G.      Temp.      Vol.
			S2      _____
			S4      _____
_____	_____	_____	When transfer from S2 to S4 is complete, record:
			L.L.      Sp. G.      Temp.      Vol.
			S2      _____
			S4      _____
_____	_____	_____	Switch HCU flow to R2 after _____ hr.
_____	_____	_____	Sparge S4 for 1 hr.
_____	_____	_____	Time start _____; time finish _____.
_____	_____	_____	Start sampling HCU flowing stream every _____ hr.
_____	_____	_____	When sample of HCU indicates $^{233}\text{U} \alpha < 10^5$ cts/min/ml, proceed to step 10.0

10.0 Column shutdown.

<u>Time</u>	<u>Date</u>	<u>By</u>	
_____	_____	_____	Close organic purge valve to PIP.
_____	_____	_____	Set FRC-HAX on manual control with "0" output.
_____	_____	_____	Shut off T5P.
_____	_____	_____	Close P69 to T5P.
_____	_____	_____	Set LIRC-N1 to 95%.
_____	_____	_____	When LIRC-N1 indicates all aqueous, shut off S4P. Close (TOG _____).
NOTE: Watch level in N4; level may start to increase before N1 is all aqueous. If so, shut off S4P and finish filling column with scrub.			
_____	_____	_____	When N1 is all aqueous, set LIRC-P1 at 95% and shut off P26.
_____	_____	_____	When P1 is all aqueous, shut down M-18P and close suction and discharge valves.
_____	_____	_____	Set LIRC-R1 to 66%.
_____	_____	_____	When LIRC-R1 indicates all aqueous, shut-off K2PS.
_____	_____	_____	Set FRC-HC4 to "0" with no output to valve.
_____	_____	_____	Close K2PS suction valve _____.
_____	_____	_____	Close K2PS discharge valve _____.
_____	_____	_____	Close K2PS recirculation valve _____.
_____	_____	_____	Shut off FI-R-1P purge.
_____	_____	_____	Shut off R1P.
_____	_____	_____	Close R1P transmission valve.
_____	_____	_____	Jet N4 to N2.
_____	_____	_____	Sample P69 code _____.
_____	_____	_____	N2 code _____.
_____	_____	_____	R2 code _____.
_____	_____	_____	Shut-off N1P.
_____	_____	_____	Close N1P transmission valve.
_____	_____	_____	Shut-off P1P.
_____	_____	_____	Close P1P transmission valve.
_____	_____	_____	Set LIRC-R1 100 c/o.

8.1.3 Detailed Dissolution Data

Three dissolution runs were made during the Kilorod Program using the procedure described in Sec 3.1.2. Typical data obtained in dissolution HJ-1 are presented in Table 1A.

Table 1A. Dissolution Data for Run HJ-1

Time at Boiling Point (105°C hr)	Analysis of Solution ( $\alpha$ counts min <sup>-1</sup> ml)	Total U in Solution (g)	Dissolution Rate Over Internal (g of U/hr)
~6	$1.93 \times 10^7$	1000	165
13	$3.82 \times 10^7$	2100	160
19.5	$5.2 \times 10^7$	3000	140
25.5	$6.19 \times 10^7$	3600	100
32	$6.50 \times 10^7$	3800	30
37	$6.70 \times 10^7$	3900	20
44.5	$6.9 \times 10^7$	~4050	20
52	$6.5 \times 10^7$	--	--
56	$6.7 \times 10^7$	--	--

Table 2A

	Run Numbers									
	HJ-1	HJ-2	HJ-3	DC-1	DC-2	DC-3	DC-4	HJ-4	HJ-5	
<u>Feed</u>										
<u>Composition</u>										
$^{233}\text{U}$ , g/liter	4.66	3.75	3.34	5.22	5.74	5.17	5.18	5.32	3.81	
Th, g/liter	230.00	225.50	224.00	220.50	245.45	213.00	220.50	214.50	212.35	
$\text{HNO}_3$ , M	2.60	2.73	2.61	2.78	2.75	2.43	2.82	2.71	2.57	
<u>Average Flowrate</u>										
Liters/hr	43.57	44.70	43.56	39.50	45.44	51.26	47.85	52.69	51.83	
% of Flowsheet	87.14	89.40	87.12	79.00	90.88	102.52	95.71	105.38	103.66	
<u>Solvent (HAX)</u>										
<u>Composition</u>										
% DSBPP	2.74	2.5 to 3.5 <sup>a</sup>	2.45	2.59	2.68	2.65	2.75	2.74	2.74	
<u>Average Flowrate</u>										
Liters/hr	99.91	101.50	101.60	104.40	103.20	103.90	102.69	99.20	108.00	
% of Flowsheet	99.91	101.50	101.60	104.40	103.20	103.90	102.69	99.20	108.00	
<u>Scrub (HSS)</u>										
<u>Composition</u>										
Al (M)	0.84	0.91	0.80	0.80	0.80	0.95	0.83	0.83	0.75	
Acid Deficiency (M)	0.42	0.37	0.41	0.46	0.45	0.38	0.45	0.45	0.39	
<u>Average Flowrate</u>										
Liters/hr	26.37	29.55	27.90	26.00	27.09	25.30	30.80	30.00	26.70	
% of Flowsheet	105.48	118.20	111.60	104.00	108.36	101.20	123.20	120.00	106.80	
<u>Strip (HCX)</u>										
<u>Average Flowrate</u>										
Liters/hr	27.70	27.00	30.10	28.20	28.48	27.30	27.70	30.00	28.58	
% of Flowsheet	110.80	108.00	120.40	112.80	113.92	109.20	114.80	120.00	114.32	
<u>Results</u>										
Product, g ( $^{233}\text{U}$ )	4028	4407	3430	4109	7426	7634	4972	4767	6158	
Proc. Losses, %	0.21	0.34	0.22	0.16	0.13	0.25	0.15	0.11	0.16	
Mat'l Bal, %	97.06	102.66	100.73	96.81	98.69	97.71	98.07	99.93	99.97	
<u>Product Quality</u>										
$^{233}\text{U}$ /liter	114.42	125.68	114.35	113.42	129.73	128.78	114.32	121.13	126.71	
$\text{NO}_3/\text{U}$ ratio	2.42	2.25	2.16	2.12	2.12	2.12	2.20	2.14	2.19	
Al, ppm	2490	52	37	28	23	16	26	12	26	
Th g/liter	3.76	1.62 <sup>h</sup>	3.04	2.55	1.01	0.98	1.58	1.93	1.43	
$\gamma$ counts $\text{min}^{-1}$ ml	$6.09 \times 10^4$	$7.44 \times 10^4$	$7.17 \times 10^4$	$1.38 \times 10^5$	$8.79 \times 10^4$	$9.11 \times 10^4$	$7.47 \times 10^4$	$8.15 \times 10^4$	$1.17 \times 10^5$	
$\gamma$ DF	230	380	416	185	310	258	301	194	150	
Th DF	$3.0 \times 10^3$	$4.6 \times 10^3$	$2.55 \times 10^3$	$2.04 \times 10^3$	$5.5 \times 10^3$	$5.5 \times 10^3$	$3.1 \times 10^3$	$2.6 \times 10^3$	$1.96 \times 10^3$	

<sup>a</sup>See Sec 8.1.5, Plant Performance for Run HJ-2.

### 8.1.5 Summary of Solvent Extraction Plant Performance

Run HJ-1. - The solvent extraction columns, product evaporator, and all auxiliary equipment functioned well. Equilibrium was attained in the columns faster than expected (4 hr after hot feed, compared with 6 hr expected), and depletion of uranium from the system was also fast, being nearly complete 12 hr after exhaustion of hot feed (20 hr anticipated).

Run HJ-2. - The solvent extraction columns, product evaporator, and all auxiliary equipment functioned well. The 0.39% HAW loss was partly attributed to a periodic, low extractant content in the recycled solvent (diluent was periodically added in the solvent recycle tank to reduce the extractant content, and mixing may have been poor). An increase in the strip column pulsed frequency from 50 to 58 cpm did not significantly decrease the uranium recycle in the solvent below the 1.3% of run HJ-1. An unexplained increase in the extractant (di-sec-butyl phenyl phosphonate) content from 2.5 to 3.5% in the diethylbenzene diluent occurred during the run. A critically safe (5-in.-diam, cadmium-lined) product tank (R-35) was installed before the run to minimize product analysis variations experienced in the glass-Raschig-ring-filled tank (R-25).

Run HJ-3. - The solvent extraction columns, product evaporator, and all auxiliary equipment functioned satisfactorily. An increase in the strip column pulse frequency from 50 cpm to 58 decreased the uranium recycle in the solvent from 1.3% (run HJ-1) to 0.31%. Analyses of feed and strip column product streams indicated a DF for <sup>224</sup>Ra of at least 5,000. The DSBPP content of the solvent remained constant at 2.45% during run HJ-3.

Run DC-1. - The solvent extraction column and auxiliary equipment functioned satisfactorily. The product evaporator was operated with the steam coil processing approximately 30 liters/hr of HCU feed, compared with about 20 liters/hr in the previous run when operating with the steam jacket. The strip column was operated with a pulse amplitude of 58 cpm, in an average flowing stream HCU loss of 0.12%.

Run DC-2. - Solvent extraction column and auxiliary equipment functioned satisfactorily.

Run DC-3. - Solvent extraction column and auxiliary equipment functioned satisfactorily.

Run DC-4. - Solvent extraction column and auxiliary equipment functioned satisfactorily.

Run HJ-4. - Solvent extraction column and auxiliary equipment functioned satisfactorily. A power failure about 5 hr after start of hot operation caused a complete shutdown. However, after re-establishment of power, operations were resumed without abnormal losses to extraction column raffinate or stripped solvent. The incident resulted in abnormally high entrainment of  $^{233}\text{U}$  to the product evaporator condensate. This material, containing 8 g  $^{233}\text{U}$ , was concentrated and recycled to the next run. No significant reduction was noted in the ionic contaminant content of the product by the treatment of the strip solution with a mixed resin exchange column.

Run HJ-5. - Equipment performance was excellent.

## 8.2 Detailed Tabulations of the Data Collected During the Sol-Gel Operation

Table 3A. Isotopic Analysis of Uranium in Carrier  
Shipments (at. %)

Conditions:

All values are average of two readings

All analyses calculated to total 100%

Carrier Shipment No.	1	2	3	4	5	6	7	8	9
Isotope:									
$^{233}\text{U}$	97.665	97.395	97.235	97.270	97.295	97.240	97.855	97.950	97.840
$^{234}\text{U}$	1.335	1.475	1.505	1.565	1.550	1.560	1.265	1.200	1.350
$^{235}\text{U}$	0.025	0.005	--	--	--	--	--	--	0.015
$^{238}\text{U}$	0.975	1.125	1.260	1.165	1.155	1.200	0.880	0.850	0.795

Table 4A. Composition of Gases Released by the Powder-Loaded  
into the Fuel Rods (vol %)

Conditions:

Gas sample obtained by heating 100-mesh powder to 1200°C in vacuum

Gas analysis by mass spectrometry

Shipment No.	1		2		3		4		5	
	A+B <sup>a</sup>	A	B	A	B	A <sup>b</sup>	B	A	B	
Element:										
H <sub>2</sub>	14.4	1.8	23.9	30.7	34.4		27.4	24.4	1.4	
CH <sub>4</sub>	--	--	--	--	--		1.1	0.4	--	
H <sub>2</sub> O	3.0	6.6	4.2	8.0	2.1		5.9	8.4	0.9	
HC	--	--	--	--	--		0.8	0.4	--	
N <sub>2</sub> +CO	71.1	72.9	65.5	57.7	59.3		60.0	43.2	68.9	
O <sub>2</sub>	8.1	16.5	0.3	0.7	0.7		0.3	0.1	8.9	
A	0.4	0.7	0.2	--	--		--	--	0.6	
CO <sub>2</sub>	3.0	1.5	5.9	2.9	3.5		4.5	23.1	19.3	
NO	--	--	--	--	--		--	--	--	

Shipment No.	6		7		8		9	
	A	B	A	B	A	B	A	B
Element:								
H <sub>2</sub>	23.9	31.2	36.4	33.6	2.5	27.0	33.8	35.0
CH <sub>4</sub>	0.3	<0.1	0.4	0.5	<0.05	0.2	0.5	0.5
H <sub>2</sub> O	2.2	0.6	3.3	6.9	0.8	2.0	3.0	1.2
HC	--	--	0.5	0.4	<0.05	0.3	0.4	0.5
N <sub>2</sub> +CO	62.3	59.1	37.9	37.2	74.6	43.3	51.4	52.5
O <sub>2</sub>	1.2	<0.1	0.1	0.1	18.4	0.2	<0.05	<0.05
A	0.3	<0.1	--	--	0.8	--	--	--
CO <sub>2</sub>	9.8	9.1	20.0	19.9	2.9	26.8	10.7	10.2
NO	--	--	1.4	1.4	--	0.2	0.2	0.1

<sup>a</sup>Samples A and B combined.

<sup>b</sup>Duplicate sample lost.

Table 5A. U/Th Ratios and Gas-Release Values for the Powder Loaded into the Fuel Rods

Carrier Shipment No.	1		2		3		4		5	
Sample Identity	Ratio by Analysis	Gas Release (std. cc/g)	Ratio by Analysis	Gas Release (std. cc/g)	Ratio by Analysis	Gas Release (std. cc/g)	Ratio by Analysis	Gas Release (std. cc/g)	Ratio by Analysis	
Coarse A	2.96		3.08		3.02		3.01		3.00	
B			2.91		2.94		2.96		2.89	
Fine A	3.06		2.96		2.99		2.99		2.99	
B			2.99		3.00		3.03		2.98	
Comp <sup>a</sup> A		0.48, 0.50	3.04	0.18	3.01	0.41	2.90	0.29	2.99	
B		and 0.54	3.04	0.25	3.04	0.43	3.01	0.32	3.01	
Powder Ratio:	2.99		3.04		3.03		2.96		3.00	

Carrier Shipment No.	5		6		7		8		9	
Sample Identity	Gas Release (std. cc/g)	Ratio by Analysis	Gas Release (std. cc/g)	Ratio by Analysis	Gas Release (std. cc/g)	Ratio by Analysis	Gas Release (std. cc/g)	Ratio by Analysis	Gas Release (std. cc/g)	
Coarse A		2.99		3.01		2.94		2.97		
B		2.98		3.14		2.94		2.99		
Fine A		3.03		2.99		3.06		2.96		
B		3.06		3.01		2.98		2.86		
Comp <sup>a</sup> A	0.54	3.01	0.37	2.98	0.19	3.00	0.67	2.97	0.30	
B	0.18	2.89	0.38	3.06	0.26	3.05	0.67	2.91	0.24	
Powder Ratio:		2.95		3.02		3.03		2.94		

<sup>a</sup>Average of two composite values used in preparing U/Th powder ratios.

Table 7A. Detailed Calculation of SS Transfer Ratios

Sol-Gel Batch No. (SGB)	<sup>233</sup> U (g)	Th (g)	<sup>233</sup> U + Th (g)	Sol-Gel Batch No. (SGB)	<sup>233</sup> U (g)	Th (g)	<sup>233</sup> U + Th (g)
Carrier Shipment No. 1							
1	88.16	2,925	3,013.66	10	269.37	8,623	8,892.37
2	261.53	8,629	8,890.53	11	266.70	8,623	8,889.70
3	261.24	8,619	8,880.24	12	266.70	8,623	8,889.70
4	261.61	8,632	8,893.61	13	265.16	8,573	8,838.16
5	92.95	3,060	3,152.95	14	267.65	8,573	8,840.65
6	273.56	9,026	9,299.56	15	267.24	8,582	8,849.24
7	273.56	9,026	9,299.56	16	266.96	8,573	8,839.96
8	261.34	8,623	8,884.34	17	267.26	8,582	8,849.26
9	266.92	8,623	8,889.92	18	269.71	8,573	8,842.71
Total:					4,448.12	144,448	148,936.12
Sample calculation: $\frac{233\text{U}}{233\text{U} + \text{Th}} \times 100 = \frac{4,448.12}{148,936.12} \times 100 = 2.99$							
SS Weight Ratio = 2.99							
Carrier Shipment No. 2							
19	2.69.71	8,573	8,842.71	25	265.04	8,569	8,834.04
20	269.71	8,573	8,842.71	26	265.04	8,569	8,834.04
21	262.42	8,573	8,835.42	27	265.04	8,569	8,834.04
22	260.44	8,570	8,830.44	28	265.04	8,569	8,834.04
23	265.04	8,569	8,834.04	29	265.15	8,573	8,838.15
Total:					2,917.67	94,276	97,193.67
SS Weight Ratio = 3.00							
Carrier Shipment No. 3							
30	265.15	8,573	8,838.15	36	263.76	8,528	8,791.76
31	264.68	8,558	8,822.68	37	263.76	8,528	8,791.76
32	259.15	8,528	8,787.15	38	263.76	8,528	8,791.76
33	264.15	8,540	8,804.15	39	263.76	8,528	8,791.76
34	263.76	8,528	8,791.76	1 and 5 <sup>a</sup>	156.05	5,188	5,344.05
35	263.76	8,528	8,791.76	8, 10, 12 <sup>a</sup>	289.83	9,471	9,760.83
Total:					3,081.67	100,026	103,107.67
SS Weight Ratio = 2.99							

<sup>a</sup>Product from earlier campaigns.

Table 7A (continued)

Sol-Gel Batch No. (SGB)	<sup>233</sup> U (g)	Th (g)	<sup>233</sup> U + Th (g)	Sol-Gel Batch No. (SGB)	<sup>233</sup> U (g)	Th (g)	<sup>233</sup> U + Th (g)
Carrier Shipment No. 4							
40	263.76	8,528	8,791.76	46	265.13	8,484	8,749.13
41	262.41	8,484	8,746.41	47	265.84	8,450	8,715.84
42	266.91	8,484	8,750.91	48	265.94	8,598	8,863.94
43	266.91	8,484	8,750.91	49	265.94	8,598	8,863.94
44	265.13	8,484	8,749.13	50	268.69	8,598	8,866.69
45	265.98	8,484	8,749.98	53	259.19	8,380	8,639.19
Total:					3,181.83	102,056	105,237.83
SS Weight Ratio = 3.02							
Carrier Shipment No. 5							
51	265.94	8,598	8,863.94	58	263.94	8,534	8,797.94
52	265.94	8,598	8,863.94	59	263.95	8,534	8,797.95
54	265.83	8,595	8,860.83	60	265.75	8,534	8,799.75
55	258.05	8,343	8,601.05	61	261.32	8,449	8,710.32
56	258.05	8,343	8,601.05	62	263.96	8,534	8,797.96
57	258.04	8,343	8,601.04	63	261.76	8,463	8,724.76
Total:					3,152.53	101,868	105,020.53
SS Weight Ratio = 3.00							
Carrier Shipment No. 6							
64	261.76	8,463	8,724.76	71	265.84	8,595	8,860.84
65	263.54	8,463	8,726.54	72	265.84	8,595	8,860.84
66	263.54	8,463	8,726.54	73	265.84	8,595	8,860.84
67	261.76	8,463	8,724.76	74	264.04	8,595	8,859.04
68	263.54	8,463	8,726.54	75	264.04	8,595	8,859.04
69	262.22	8,421	8,683.22	76	88.17	2,851	2,939.17
Total:					3,255.97	105,157	108,412.97
SS Weight Ratio = 3.00							
Carrier Shipment No. 7							
76	176.34	5,701	5,877.34	82	264.15	8,541	8,805.15
77	258.71	8,541	8,799.71	83	256.90	8,541	8,797.90
78	263.25	8,541	8,804.25	84	262.14	8,594	8,856.14
79	259.62	8,541	8,800.62	85	268.53	8,594	8,862.53
80	265.97	8,541	8,806.97	86	263.97	8,594	8,857.97
81	267.79	8,541	8,808.79	87	129.58	4,147	4,276.58
Total:					2,936.95	95,417	98,353.95
SS Weight Ratio = 2.99							
Carrier Shipment No. 8							
87	128.26	4,147	4,275.26	90	267.40	8,587	8,854.40
88	265.81	8,594	8,859.81	91	267.40	8,587	8,854.40
89	265.81	8,594	8,859.81	92	267.40	8,587	8,854.40
Total:					1,462.08	47,096	48,558.08
SS Weight Ratio = 3.01							
Carrier Shipment No. 9							
93	263.35	8,371	8,634.35	97	266.46	8,557	8,823.46
94	265.60	8,587	8,852.60	98	269.20	8,557	8,826.20
95	267.40	8,585	8,854.40	99	269.20	8,557	8,826.20
96	266.46	8,557	8,823.46	100	75.49	2,400	2,475.49
Total:					1,943.16	62,173	64,116.16
SS Weight Ratio = 3.03							

Table 8A. U/Th Ratios and Gas-Release Values Obtained for Every  
Sol-Gel Batch Prepared During Kilorod Program

Sol-Gel Batch No. (SGB-1)	$^{233}\text{U}/^{233}\text{U} + \text{Th}$ Ratio by Analysis	Gas <sup>a</sup> Released (std cc/g)	Sol-Gel Batch No. (SGB)	$^{233}\text{U}/^{233}\text{U} + \text{Th}$ Ratio by Analysis	Gas Released (std cc/g)
Campaign 1					
1 A	2.92	0.018	8 A	2.88	0.038
2 A	3.02	0.013	B	2.92	-
B	3.01	-	C	2.92	-
3 A	2.99	0.013	9 A	2.99	0.015
B	3.01	-	B	3.00	-
C	3.01	-	10 A	3.15	0.034
4 A	3.04	0.004	B	3.07	-
B	3.05	-	C	3.11	-
C	3.19	-	D	3.15	-
5 A	2.91	-	11 A	2.93	0.031
6 A	2.94	0.013	B	2.91	-
B	-	0.018	12 A	2.92	0.038
7 A	2.95	0.005			
Campaign 2					
13 A	2.98	0.050	21 A	3.02	0.021
14 A	3.02	0.019	B	3.01	0.022
15 A	3.03	0.038	22 A	2.94	0.043
16 A	3.03	0.054	23 A	2.99	0.026
17 A	2.94	0.016	24 A	3.01	0.013
B	3.01	0.018	25 A	3.04	0.008
18 A	3.00	0.005	26 A	3.07	0.022
B	3.03	-	B	3.03	-
19 A	3.08	0.010	27 A	3.02	0.010
20 A	3.07	0.036	28 A	3.03	0.033
Campaign 3					
29 A	3.00	0.013	35 A	3.00	0.013
30 A	3.05	0.017	36 A	3.01	0.015
31 A	3.10	0.016	37 A	2.96	0.011
B	3.02	-	38 A	2.98	0.014
32 A	2.95	0.025	39 A	3.07	0.007
33 A	3.01	0.013	B	3.06	-
34 A	2.99	0.020	40 A	3.00	0.012
Campaign 5					
41 A	2.94	0.010	47 A	3.01	0.011
B	2.94	-	48 A	2.96	0.031
42 A	3.01	0.012	49 A	3.05	0.015
43 A	3.02	0.018	50 A	2.99	0.042
44 A	2.97	0.019	51 A	3.02	0.040
44 B	2.98	-	52 A	2.98	-
45 A	3.02	0.010	53 A	3.09	0.039
B	3.00	-	B	3.05	-
46 A	2.95	0.015			
Campaign 6					
54 A	3.02	0.030	65 A	3.00	0.015
55 A	2.95	0.053	66 A	3.00	0.018
56 A	2.96	0.025	67 A	2.96	0.014
57 A	2.99	0.009	68 A	3.00	0.004
58 A	3.00	0.018	69 A	3.01	0.016
59 A	3.01	0.057	70 A	3.00	0.006
60 A	2.99	0.048	71 A	3.05	0.057
61 A	3.01	0.012	72 A	3.02	0.008
62 A	2.87	0.056	73 A	3.04	0.006
B	2.95	-	74 A	2.99	0.004
63 A	2.96	0.004	75 A	3.04	0.010
64 A	2.97	0.035	76 A	3.00	0.011
Campaign 7					
77 A	2.93	0.007	92 A	2.95	0.008
B	2.94	-	93 A	3.04	0.010
78 A	2.99	0.005	94 A	3.05	0.034
79 A	2.95	0.015	B	2.96	-
80 A	3.02	0.005	C	2.94	-
81 A	3.04	0.019	D	2.97	-
82 A	3.00	0.009	95 A	2.95	0.027
83 A	2.93	0.022	B	3.00	-
B	2.92	-	C	2.98	-
84 A	2.97	Sample Lost	D	2.98	-
B	2.94	-	96 A	2.97	0.071 <sup>b</sup>
85 A	3.03	0.008	B	2.96	-
86 A	2.98	0.007	97 A	2.95	0.103 <sup>b</sup>
87 A	3.03	0.003	B	2.93	-
88 A	2.98	0.006	98 A	2.98	0.075 <sup>b</sup>
89 A	2.97	0.004	99 A	3.01	0.025
90 A	2.96	0.020	100 A	3.06	0.020
91 A	2.95	0.004	B	3.06	-

<sup>a</sup>Obtained by heating sample to 1200°C in vacuum.  
<sup>b</sup>Off-gas upset due to furnace test.

Table 9A. Gas-Release Composition for the First  
Twenty-eight Sol-Gel Calciner Products, Before Crushing

Sol-Gel Batch No. (SGB)	Composition of Released Gas (vol %)						
	H <sub>2</sub>	CH <sub>4</sub>	H <sub>2</sub> O	HC	N <sub>2</sub> + CO	O <sub>2</sub>	CO <sub>2</sub>
1	—	1.2	5.1	1.2	43.7	1.6	47.2
2	0.7	1.0	0.7	2.3	47.8	0.3	47.2
3	1.3	—	9.5	0.7	15.7	25.5	47.0
4	6.4	—	3.5	—	47.6	1.4	40.4
7	—	—	—	—	15.0	9.0	76.0
8	—	—	2.9	—	8.0	47.4	41.7
9	3.5	—	14.3	—	14.1	1.0	66.9
10	—	—	3.5	—	7.4	56.3	32.8
11	—	—	2.5	—	13.8	51.3	32.5
12	—	0.7	10.4	—	12.6	3.7	72.6
13	16.1	2.3	1.1	—	59.2	0.9	20.3
14	—	—	17.1	1.6	26.7	2.0	52.2
15	—	—	25.5	1.3	23.5	—	49.7
16	4.7	2.0	0.4	—	40.2	—	52.7
17	—	—	5.4	—	13.4	28.1	53.1
18	—	—	15.8	—	42.1	—	42.1
19	—	—	13.0	—	43.5	—	43.5
20	6.7	1.5	1.0	—	70.8	4.1	15.6
21	10.3	2.2	—	—	53.7	0.7	33.1
22	10.4	0.8	0.4	—	60.5	2.5	25.3
23	—	—	1.1	—	54.0	1.1	43.7
24	3.6	—	—	—	41.7	—	54.8
25	5.4	—	6.5	—	48.9	—	39.1
26	9.5	—	15.5	—	53.6	—	21.4
27	14.8	—	7.4	—	59.3	3.7	14.8
28	13.8	2.3	17.4	3.4	42.6	0.3	20.1

NOTE: Gas analysis data contained in this table is presented for record only, as it is less accurate than similar data obtained later in program (see text).

Table 10A. Gas-Release and Gas-Analysis Data for the  
First 15 Powder Samples Removed from the Rod-Loading Station

CO Batch No.	Gas Released <sup>a</sup> (std cc/g)	Composition of Released Gas						
		H <sub>2</sub>	CH <sub>4</sub>	H <sub>2</sub> O	HC	N <sub>2</sub> + CO	O <sub>2</sub>	CO <sub>2</sub>
1	0.054		0.5	2.3		21.4	0.3	75.5
2	0.045			3.0		14.0	<1.0	83.0
3	0.092	c						
4	0.11	3.9	0.5	4.3		10.5	0.4	80.4
5	0.14	14.7	0.4	1.3		47.0		36.6
6	0.54 <sup>b</sup>	32.0	1.0	0.2	1.6	57.2	0.1	7.8
7	0.18	16.9	0.3	0.8	0.6	57.9		23.4
8	0.11	7.4		0.9		44.0		47.7
9	c	32.1	0.4	0.2		59.2		8.1
10	0.18	c						
11	0.05	33.0	0.9	0.1	1.4	55.5	2.8	6.2
12	0.12	13.9	0.5	2.2	0.6	36.1	0.07	46.6
13	0.22	30.2		0.6		50.6	0.2	18.4
14 <sup>c</sup>								
15	0.17	30.9	0.3	0.6		53.5	0.5	14.2

<sup>a</sup>Obtained by heating sample to 1200°C under vacuum.

<sup>b</sup>Analyst reported sample to be contaminated with wax.

<sup>c</sup>Not measured.

NOTES:

Argon content, <0.5 percent.

CO designates crushed oxide sample removed from the feed to the rod-loading station. Gas-analysis data contained in this table is presented for record only as it is less accurate than similar data obtained later in program (see text).

Table 11A. Kilorod Program: Trace Analysis of Uranyl Nitrate Feed Batches Prepared in Solvent Extraction Pilot Plant  
Parts of Element Per Million Parts <sup>233</sup>U

Element	Solvent Extraction Batch Numbers								Element	Solvent Extraction Batch Numbers							
	HJ-1 (1)	HJ-2 (2)	HJ-3 (3)	DC-1 (4)	DC-3 (5)	DC-4 (6)	HJ-4 (7)	HJ-5 (8)		HJ-1 (1)	HJ-2 (2)	HJ-3 (3)	DC-1 (4)	DC-3 (5)	DC-4 (6)	HJ-4 (7)	HJ-5 (8)
Ag	<3	<3	<1	<1	<1	<1	<.1	<.6	Ni	<83	5	<17	3	<2	4	<1	3
Al	2490	52	37	28	16	26	12	26	Os	<66	<83	<14	<14	<31	<35	<33	<32
As	<332	<166	<70	<72	<62	<70	<66	<63	P	<830	<830	<174	<180	<155	<175	<164	<158
Au	<66	<68	<14	<14	<12	<14	<13	<13	Pb	<66	<332	<14	<14	<12	<14	<13	<13
B	<33	<17	<7	<7	<6	<7	<7	49	Pd	<33	<332	<70	<7	<6	<7	<7	<6
Ba	<664	<33	<139	<144	<124	<140	<131	<126	Pr	<166	<166	<35	<36	<31	<35	<33	<32
Be	<1	<1	<1	<1	<1	<1	<.01	<.01	Pt	<66	<166	<14	<14	<12	<14	<13	<13
Bi	<166	<83	<35	<36	<31	<35	<33	<32	Rb					<62	<70	<66	<63
Ca	<166	<8	<35	147	31	16	<75	34	Re	<33	<166	<7	<7	<6	<7	<7	<6
Cd	<66	<83	<14	<14	<12	<14	<13	<13	Rh	<66	<166	<14	<14	<12	<14	<13	<13
Ce	<83	<166	<17	<18	<16	<18	<16	<16	Ru	<33		<7	<7	<6	<7	<7	<6
Co	<66	<83	<14	<14	<12	<14	<13	<13	Sb	<33	<17	<7	<7	<6	<7	<7	<6
Cr	<75	5	23	<9	5	<1	4.3	5	Sc	<17	<8	<3	<4	<3	<4	<3	<3
Cs					<31	<35	<33	<32	Si	<7	9	<1	<6	<1	<1	9	8
Cu	<7	9	<1	4	2	9	2.9	1	Sm	<33	<42	<7	<7	<6	<7	<7	<6
Dy	<83	<42	<17	<18	<16	<18	<16	<16	Sn	<66	<166	<14	<14	<12	<14	<13	<13
Er	<332	<42	<70	<72	<62	<70	<66	<63	Sr	<33		<7	<7	<7	<7	<7	<6
Eu	<17	<8	<3	<4	<3	<4	<3.3	<3	Ta	<166	<208	<35	<36	<31	<35	<33	<32
Fe	246	113	36	5	16	19	12.7	14	Tb	<166	<83	<35	<36	<31	<35	<33	<32
Ga	<25	<17	<5	<5	<5	<5	<5	<5	Tc	<17	<8	<3	<4	<3	<4	<3	<3
Gd	<17	<17	<3	<4	<3	<4	<3	<3	Te	<332	<166	<70	<72	<62	<70	<66	<63
Ge	<7	<3	<1	<1	<1	<1	<1.3	<1	Ti	<2	<2	<1	<1	<1	<1	<1	<0.3
Hf	<33	<66	<7	<1	<6	<7	<7	<6	Tl	<83	<42	<17	<18	<16	<18	<16	<16
Hg	<664	<830	<139	<144	<124	<140	<131	<126	Tm	<33	<17	<7	<7	<6	<7	<66	<6
Ho	<166	<8	<35	<36	<31	<35	<33	<32	V	<7	<66	<1	<1	<1	<1	<1	<1
In	<50	<25	<10	<11	<9	<11	<10	<9	W	<83	<664	<17	<18	<16	<18	<16	<16
Ir	<332	<166	<70	<72	<62	<70	<66	<63	Y	<7	<3	<1	<1	<1	<1	<1	<1
K	<664		<139	<97	<123	<140	<131	<126	Yb	<17	<8	<3	<4	<3	<4	<3	<3
La	<66	<17	<14	<14	<12	<14	<13	<13	Zn	<83	<83	<17	<18	<16	<18	<16	<16
Li	<27	<17	<3	<27	<6	<7	<7	<6	Zr	<7	<7	<1	<1	<1	<1	<1	<1
Lu	<66	<166	<14	<14	<12	<14	<13	<13									
Mg	<1	<3	<7	1	4	36	5	7									
Mn	<3	<3	<1	1	<1	<1	<1	<1									
Mo	<10	<10	<2	<2	<2	<2	<2	<2									
Na	2009	<332	176	122	40	61	147	15									
Nb	<83	<166	<17	<18	<16	<18	<16	<16									
Nd	<415	<208	<87	<90	<78	<88	<82	<79									

Table 12A. Trace Elements Present With Powder Loaded into the BNL  
Fuel Rods for Carrier Shipments 1-9

Element <sup>a</sup>	Carrier Shipment No.						
	1		2		3		4
	Comp. <sup>b</sup>	Fine <sup>c</sup>	Coarse <sup>d</sup>	Fine	Coarse	Fine	Coarse
Ag	<.2	--	--	--	--	--	--
Al	0.2	0.75	0.53	4.8	0.45	4.4	3.9
Au	<4	<.4	<4	<3.9	<4.0	<4.4	<4.0
B	<2	--	--	--	--	--	--
Be	<1	<0.001	<0.001	<0.002	<0.001	<0.002	<0.001
Ca	--	0.4	1.2	--	1.2	--	20.0
Cd	<4	<4	<4	<3.9	<4.0	<4.4	<4.0
Co	<4	<4	<4	<3.9	<4.0	<4.4	<4.0
Cr	<0.1	<0.14	<0.14	1.6	<0.14	1.4	1.2
Cu	0.1	0.099	0.34	1.5	0.1	0.34	0.36
Fe	5	1.7	8.1	28.0	5.2	15.0	7.8
In	<3	<3	<3	<3.0	<3.0	<3.1	<3.0
Ir	<20	<20	<20	<20.0	<20.0	<21.0	<20.0
K	--	<4	<4	--	<4.0	--	<4.0
Li	--	<0.04	<0.04	--	<0.04	--	<0.04
Mg	0.1	0.099	0.11	--	0.17	0.8	0.45
Mn	<0.2	<0.04	<0.04	0.63	<0.04	0.7	0.44
Mo	--	<0.4	<0.4	<0.58	<0.4	<0.42	<0.4
Na	--	2.9	3.8	--	6.0	--	21.0
Nb	<5	<5	<5	<4.7	<5.0	<5.2	<5.0
Ni	<0.1	<0.14	<0.14	0.99	<0.14	1.2	3.6
Pb	<4	<4	<4	<3.9	<4.0	<4.4	<4.0
Pd	<2	<2	<2	<2.0	<2.0	<2.2	<2.0
Si	<0.4	<0.4	<0.4	<0.39	<0.4	0.9	<0.4
Sn	<4	<4	<4	<3.9	<4.0	<4.4	<4.0
Ta	<10	<10	<10	<96.0	<10.0	<12.0	<10.0
Ti	<1	<1	<1	<0.96	<0.1	<1.2	<1.0
V	<0.4	<0.4	<0.4	<0.39	<0.4	<0.44	<0.4
W	<5	<5	<5	<2.8	<5.0	<5.5	<5.0
Y	--	--	--	0.21	0.06	0.17	0.065
Zn	<5	<5	<5	<2.8	<5.0	<5.5	<5.0
Zr	<5	--	--	--	--	--	--

Table 12A (continued)

Element	Carrier Shipment No.					
	5	6	7	8	9	
	Fine <sup>c</sup>	Coarse <sup>d</sup>	Comp. <sup>b</sup>	Comp. <sup>b</sup>	Comp. <sup>b</sup>	Comp. <sup>b</sup>
Al	6.0	5.4	8.5	9.3	2.8	4.2
Au	<4.0	<3.8	<4.0	<4.0	<4.0	<4.0
Be	<0.001	<0.002	<0.002	<0.002	<0.002	<0.002
Cd	<4.0	<3.7	<4.0	<4.0	<4.0	<4.0
Co	<4.0	<3.7	<4.0	<4.0	<4.0	<4.0
Cr	1.6	1.1	2.3	1.1	1.4	1.9
Cu	0.94	1.1	2.1	0.9	0.5	0.88
Fe	11.0	39.0	97.0	56.0	40.0	57.0
In	<2.0	<2.9	<3.0	<3.0	<3.0	<3.0
Ir	<20.0	<19.0	<20.0	<20.0	<20.0	<20.0
Mg	0.58	--	--	--	--	--
Mn	1.4	<0.39	1.4	1.1	0.6	0.86
Mo	<0.4	<0.57	<0.6	<0.6	<0.6	<0.6
Nb	<5.0	<4.6	<5.0	<5.0	<5.0	<5.0
Ni	1.5	1.1	2.4	1.4	1.1	1.7
Pb	<4.0	<3.8	<4.0	<4.0	<4.0	<4.0
Pd	<2.0	<1.9	<2.0	<2.0	<2.0	<2.0
Si	<0.4	<0.38	<0.4	<0.4	<0.4	<0.4
Sn	<4.0	<3.8	<4.0	<4.0	<4.0	<4.0
Ta	<10.0	<95.0	<10.0	<10.0	<10.0	<10.0
Ti	<1.0	<0.95	<0.1	<0.1	<0.1	<0.1
V	<0.4	<0.38	<0.4	<0.4	<0.4	<0.4
W	<5.0	<2.7	<2.5	<2.5	<2.5	<2.5
Y	0.07	0.15	0.4	0.4	0.2	3.4
Zn	<5.0	<2.7	<2.5	<2.5	<2.5	<2.5

<sup>a</sup>Values given denote parts of element per million parts of powder.

<sup>b</sup>"Comp." denotes a composited sample prepared by mixed 55 wt % of a coarse fraction and 45 wt % of a fine fraction.

<sup>c</sup>The fine fraction results from the ball-milling operation.

<sup>d</sup>The coarse fraction is screened through a 6-mesh onto a 16-mesh screen.

Table 13A. Mass Assays for the First Batches  
of ( $^{233}\text{U-Th}$ ) $\text{O}_2$  Prepared in the Kilorod Program

Isotope	$^{233}\text{U}$ Feed Batch No.		Mass Assays of the Uranium in the Powder Sampler Loaded into First Fuel Rods
	HJ-1 <sup>a</sup>	HJ-2 <sup>a</sup>	Range of Values <sup>b</sup>
$^{233}\text{U}$	97.88	97.36	97.17 - 97.87
$^{234}\text{U}$	1.29	1.50	1.28 - 1.47
$^{238}\text{U}$	0.83	1.11	0.84 - 1.31
$^{235}\text{U}$	--	0.03	0.01 - 0.05

<sup>a</sup>Average of two readings.

<sup>b</sup>The first ten powder batches were sampled; however, the sample from batch No. 9 was lost in the laboratory.

Table 14A. Composition of Argon-Hydrogen Mixtures  
Used in Kilorod Program (vol %)  
Five Cylinders, random solution

$\text{H}_2$	4.217	4.249	4.937	5.326	4.654
$\text{CH}_4$	0.005	0.0006	0.0006	0.0005	0.0005
$\text{H}_2\text{O}$	0.0013	0.0024	0.0026	0.0021	0.0023
$\text{N}_2 + \text{CO}$	0.0033	0.0035	0.0032	0.0028	0.0032
$\text{O}_2$	0.0064	0.0068	0.0067	0.0063	0.0070
A	95.771	95.737	95.050	94.662	95.333
$\text{CO}_2$	0.002	0.0002	0.0001	0.0001	0.0001

### 8.3 Method Used to Obtain Radiation Exposure per Operation

NOTE: The following method was used to calculate the data in Tables 38, 39, and 41.

#### A. Denitration Process (one operator)

1. Obtain the sum of the pocket-meter data during a given Health Physics (HP) quarter for the denitrator operator from Table 34, Sec 5.2.1. (Note: Film rings were not worn at the denitrator; therefore, exposures to the hands and arms were not determined.
2. Divide the value in step 1 by the number of weeks the denitrator was operated during that HP quarter to obtain the average weekly exposure.

#### B. Sol-Gel Process (two operators)

1. List the operating steps in the sol-gel process:
  - a. Blending
  - b. Loading evaporator
  - c. Unloading evaporator
  - d. Loading furnace
  - e. Unloading furnace
  - f. Sampling and dumping fired oxide
2. Combine steps a and b and term the aggregate operation "blending;" combine the other four steps and call the aggregate operation "operations at the crucible table."
3. Base the radiation exposure to the total body and to the hands and arms on the station film ring data for campaigns 4-7 at the blend tank (WS-1) and crucible table (WS-3). The calculations are as follows:
  - a. List the campaign data for radiation exposure and number of weeks film rings used and determine totals as follows:

## Exposure to the Hands and Arms at:

Campaign No.	WS-1		WS-3	
	Campaign Total (millirems)	No. of Weeks Rings Used	Campaign Total (millirems)	No. of Weeks Rings Used
4	200	4	350	4
5	100	2	305	4
6	190	3	300	6
7	390	6	550	6
Total for four campaigns	880	15	1505	20

- b. Divide the total exposure for the four campaigns by the number of weeks that data were taken to obtain the overall weekly average exposure.

WS-1: Overall weekly average exposure =  $880/15 = 58.6$  millirems/week.

WS-3: Overall weekly average exposure =  $1505/20 = 75.3$  millirems/week.

- c. Determine the percentage of exposure received during each aggregate operation as follows:

(1) Blending =  $58.6/58.6 + 75.3 \times 100 = 43.8$  or 44%.

(2) Operations at the crucible table =  $75.3/58.6 + 75.3 \times 100 = 56.2$  or 56%.

4. For the two operators, add together the average weekly exposure for each HP quarter to obtain a total average weekly exposure for that HP quarter. The sources of the exposure were:

Type of Exposure	<u>3rd Qtr. 1963</u>	<u>4th Qtr. 1963</u>	<u>1st Qtr. 1964</u>
Total body	ORNL film badges	Pocket meters	ORNL film badges
Hands and arms	Not available	Film rings	Film rings

Pocket-meter data were used for total-body exposures in the 4th quarter of 1963 because of the many changes of personnel. Film-ring data were used throughout for exposure to the hands and arms.

5. Distribute the total average weekly exposure for each HP quarter between "blending" (44%) and "operations at the crucible table" (56%).

C. Rod Fabrication (three operators and one supervisor)

1. Obtain the sum of the pocket meter or film ring data for a given campaign for each rod-fabrication worker.
2. Divide the value in step 1 for each worker by the number of weeks in that campaign.
3. Using the seven-rod-per-day schedule, list the work times for the 28 subroutines (SR's) as given below:<sup>24</sup>

<u>SR No.</u>	<u>Assignment</u>	<u>Subroutine</u>	<u>Work Time (min)</u>
0	G	Energize equipment; pick up liquid nitrogen	12.0
1	DEG	Load in shipping cask - one man	< 1.0
2	DEG	Load in shipping cask - other man	< 1.0
3	D	Jaw crusher	5.95
4	D	Recycle	21.9
5	D	Ball Mill - 16 fraction into fines	10.2
6	D	Ball Mill - 6 + 16 fraction into fines	12.1
7	D	Blend; transfer bottle loading	57.4
8	D	Sample (-16 and -6 +16 fractions)	5.0
9	DEG	Seal samples	1.0
10	D	Dispose of old bag (powder preparation cubicle)	2.1
11	DEG	Seal old bag	1.0
12	E	Compacting	140.0 <sup>a</sup>
13	G	Transfer plugged rod for scanning	6.3
14	F	Scanner check	32.2
15	G	Welding	80.5

<u>SR No.</u>	<u>Assignment</u>	<u>Subroutine</u>	<u>Work Time (min)</u>
16	G	Ultrasonic cleaning	27.9
17	G	Leak test and weigh	31.0
18	DEG	Turco cleaning	10.7
19	DEG	Smear - one man	7.8
20	DEG	Smear - one man	6.2
21	DEG	Assemble hanger and load into carrier	8.65
22	DEG	Assemble hanger and load into carrier	13.0
23	B	Mark, weigh, and record empty rod	30.0
24	G	Three-piece rod-end assembly	6.0
25	DEG	Remove and dispose of kleenex	10.0
26	DEG	Load shipping cask - one man	< 1.0
27	DEG	Load shipping cask - other man	< 1.0

<sup>a</sup>Varagona's figure of 52.5 min was revised to 20 min per rod, based on later experience.

4. Eliminate subroutines in which negligible radiation exposures were received and also subroutines requiring less than 2 min.
5. Combine subroutines 18-22, which were done jointly (as designated by "DEG" in the assignment column).

<u>SR No.</u>	<u>Work Time (min)</u>
18	10.7
19	7.8
20	6.2
21	8.65
22	<u>13.0</u>
Total	46.35

6. Assign one-third of the aggregate time for subroutines 18-22 (46.35 min divided by 3 = 15.4 min) to each of the three operators: D, E, and G
7. Determine the percentage of each worker's time spent on each operation, as follows:

D

<u>Column 1</u> <u>SR No.</u>	<u>Column 2</u> <u>Subroutine</u>	<u>Column 3</u> <u>Work Time</u> <u>(min)</u>	<u>Column 4</u> <u>Percentage of</u> <u>Work Time per</u> <u>Operation</u>
3, 4, 8, and 10	Jaw crushing and sampling	35.0	26.9
5 and 6	Ball milling	22.3	17.1
7	Blending	57.4	44.1
18-22	Turco cleaning, smearing, and loading into carrier (one-third)	<u>15.4</u>	<u>11.9</u>
Total		130.1	100.0

E

<u>Column 1</u> <u>SR No.</u>	<u>Column 2</u> <u>Subroutine</u>	<u>Column 3</u> <u>Work Time</u> <u>(min)</u>	<u>Column 4</u> <u>Percentage of</u> <u>Work Time per</u> <u>Operation</u>
12	Compacting	140.0	90.1
18-22	Turco cleaning, smearing, and loading into carrier (one-third)	<u>15.4</u>	<u>9.9</u>
Total		155.4	100.0

F

<u>Column 1</u> <u>SR No.</u>	<u>Column 2</u> <u>Subroutine</u>	<u>Column 3</u> <u>Work Time</u> <u>(min)</u>	<u>Column 4</u> <u>Percentage of</u> <u>Work Time per</u> <u>Operation</u>
14	Scanning check	32.2	20.1
None	Supervising	<u>127.8</u>	<u>79.9</u>
Total		160.0	100.0

G

<u>Column 1</u> <u>SR No.</u>	<u>Column 2</u> <u>Subroutine</u>	<u>Column 3</u> <u>Work Time</u> <u>(min)</u>	<u>Column 4</u> <u>Percentage of</u> <u>Work Time per</u> <u>Operation</u>
13	Transferring rod for scanning	6.3	3.9
15	Welding	80.5	49.9
16	Ultrasonic cleaning	27.9	17.3
17	Leak test and weigh	31.0	19.3
18-22	Turco cleaning, smearing, and loading into carrier (one-third)	<u>15.4</u>	<u>9.6</u>
Total		161.1	100.0

8. To obtain the radiation exposure for a given operation in a given campaign, multiply the value from step 2 for the appropriate operator for that campaign by the percentage value in column 4 for that operation.

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