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PILOT PLANT PREPARATION OF $U^{233}-ThO_2$ SHARDS
BY THE SOL-GEL METHOD, PREPARATORY TO
PRODUCING POWDERS FOR VIBRATORY
PACKING INTO FUEL TUBES*

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1. ABSTRACT

Progress for the first five months of sol-gel pilot plant operation is reported. During this period 500 kg of 3% $U^{233}O_2$ -97% ThO_2 (solid solution) was prepared in the form of shards that had a density 99% of the theoretical. A sustained throughput of 10 kg/day was demonstrated, and all product met expected chemical standards.

The sol-gel process is a unique method for preparing feed materials suitable for vibratory-compaction fabrication of reactor fuel elements. The process upon which the present work was done consisted in the following steps:

1. Preparation of a ThO_2 powder suitable for dispersion in weak nitric acid. The powder is prepared by hydrothermal denitration of thorium nitrate crystals at 500°C.
2. Removal of U^{232} daughter products from U^{233} feed stocks by solvent extraction. This operation permits use of the lightly shielded glove-box type facility built for this work.
3. Blending at 80°C of the ThO_2 powder and U^{233} solution from steps 1 and 2 to form a stable sol.
4. Drying of the sol to a gel state at 80°C.
5. Calcination and reduction of the dried gel at 1150°C under an argon-hydrogen atmosphere to produce shards which are then transferred to the rod-loading facility.

The U/Th ratio,* defined as $\frac{100 \times U^{233}}{U^{233} + Th}$, was controlled to within 3.00 ± 0.05 following the start-up period. Gas-release values to 1200°C were ≤ 0.03 std. cc/gm for the calcined product, and ≤ 0.5 cc/gm for the crushed-sized powder as loaded into the fuel elements. The principal gases released by the product were H_2 , CO_2 , water, and CO(or N_2).

Exposure of workers to radiation was satisfactorily low. Hand-forearm doses did not exceed 200 millirems/wk as contrasted to a 1500 per week permissible dose.

Pilot plant operation will continue until 1000 kg of product has been produced.

*Also called weight percent U^{233} .

2. INTRODUCTION

The sol-gel process is a unique recent advancement in the preparation of ceramic nuclear fuels. This process yields a fragmentary, or shard-type, product having a density of 99% of theoretical. These shards are an ideal starting material for fuel element fabrication by vibratory compaction. Since June, a pilot plant comprised of a sol-gel-process complex and a vibratory-compaction rod-loading unit has prepared 10 kg per day of 3% $U^{233}O_2$ -- 97% ThO_2 . This pilot plant was built to prepare 1000 fuel rods for the Brookhaven National Laboratory; hence, it is called the Kilorod Facility. Basically the operation of the pilot plant includes preparing a ThO_2 powder by hydrothermal denitration of thorium nitrate crystals, blending of a sol using the ThO_2 powder and a U^{233} solution which has been purified by solvent extraction, drying of the sol to a gel, and calcination-reduction of the gel to the glass-like product (or shards). To date, about 500 kg of solids has been produced, representing about half of the program commitment. All material produced has met specifications and has been loaded into reactor fuel tubes.

This paper will first describe briefly the entire Kilorod Facility and discuss in detail only the sol-gel portion of the operation. The next speaker will discuss the operation of the fuel-element fabrication portion of the Facility. After the Kilorod Facility has been described, the sol-gel process will be discussed, and the following topics will be covered:

1. the source and importance of radiation to the design and operation of the process,
2. the floor plan of the facility,
3. the procedure and the sol-gel equipment, and
4. accumulated process control and personnel exposure data.

At the conclusion, the applicability of the sol-gel process to the preparation of a variety of ceramic nuclear materials will be shown.

3. DESCRIPTION OF THE KILOROD FACILITY

3.1 Radiation-Control Factors

Several factors concerning personnel protection were considered in selecting a design for the Kilorod Facility. The containment requirements

for U^{233} are essentially the same as for plutonium, since U^{233} also emits alpha particles at a high rate. Additionally, U^{232} is always produced in the preparation of U^{233} , and 38 ppm is present in the U^{233} used for the Kilorod feed (see Fig. 1). The gamma-emitting daughters of U^{232} present a penetrating radiation hazard. The daughters can be removed by solvent extraction, but grow back in; thus, the gamma emission rate increases rapidly from the time of purification, and a time limit is imposed upon processing. A weekly dose of 1500 millirems to the hands and arms is permitted, much higher than can be tolerated (100 millirems) for whole-body exposures.¹

Models incorporating the above design criteria were studied, and the following design was selected. The resulting facility is a shielded glove-box type of operation. In this type of 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. Experience has shown that this design and this time limitation were conservative, as will be shown.

3.2 Process Flowsheet

The flowsheet of the entire Kilorod Facility is shown in Fig. 2. To simplify discussion, the facility will be visualized as being composed of three parts, as shown on the flowsheet. These are:

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

As mentioned above, only the first two subjects are covered in this talk.

3.2.1 Floor Plan of the Sol-Gel and Rod-Fabrication Units

The equipment for the sol-gel process and rod fabrication was installed in one cell at the Laboratory. Figure 3 is an artist's conception of the portion of the facility within this cell. Note that the processing

¹Health Physics Manual, Procedures and Practices for Radiation, Protection, Oak Ridge National Laboratory, Procedure 20.

Fig. 1. Decay Chain and Gamma Activity in $ThO_2-U^{233}O_2$ Fuels.

Fig. 2. Kilorod Facility Flowsheet.

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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.

cubicles are built in a three-level arrangement within the outer (concrete) walls of the cell. All process cubicles are lined with 1/8-in.-thick mild steel, for alpha particle containment. Shielding of workers from gamma rays is provided by either 4-1/2 in. of steel or by 8 in. of dry, stacked barytes block. The sol-gel cubicle (about 7 ft x 10 ft) is located on the third floor, and the rod-fabrication equipment extends from just below the third floor down to and across the first floor.

3.2.2 Location of Feed-Preparation Operations

The solvent extraction plant is located in three adjoining cells within this same building, while denitration is carried out in a separate building.

4. DESCRIPTION OF THE EQUIPMENT AND THE OPERATING PROCEDURE

4.1 Preparation of Feed Materials

In essence, feed material preparation consists of two processes: ThO_2 powder is prepared by the hydrothermal denitration of thorium nitrate crystals, and U^{233} as a nitrate solution is freed by solvent extraction of U^{232} daughter products.

4.1.1 Thorium Oxide Feed Preparation: The First Step Toward Preparing Mixed Oxides ($\text{ThO}_2\text{-UO}_2$) by the Sol-Gel Process

The thorium oxide feed is prepared by hydrothermal denitration of thorium nitrate tetrahydrate (TNT) in a horizontal rotary denitrator (Fig. 4). The calciner shell in which the denitration takes place, with its clamshell heaters, is shown before assembly. The heaters and the calciner shell are shown in final assembly (Fig. 5). The TNT charge (30 kg) is loaded, and the 13.5 kg of ThO_2 product is discharged through this end of the calciner. The calciner is shown tilted to the unloading position. While operating, the shell turns on these trunnions. Denitration is accomplished in 5-1/2 hr at 450°C under a super-heated steam atmosphere. The product obtained is a free-flowing powder, off-white in color, containing about 95% ThO_2 . The balance is water and nitric acid. As this unit was scaled up from a 2.5-kg scale without difficulty, further scale-up could undoubtedly be similarly accomplished.

Fig. 4. Rotary Denitrator in the Unloading Position.

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Fig. 5. Denitrator Shell and Clamshell Heaters.

In the Kilorod operation to date, this installation has processed 1000 kg of a total requirement of 1100 kg, without the rejection of a single batch or a significant equipment failure. A simple dispersion test with nitric acid and water, followed by visual examination of the resulting thoria sol, is the only analytical acceptance test needed for the thoria batches. Thoria is a "natural" sol former, and one looks for only two things in this simple test: First the sol must wet the glass of a sample bottle uniformly, i. e., with no "chalky" streaks present. Second, the wetting sol film must have a blue color, recognized easily with experience.

Denitrator operation is typical of sol-gel simplicity, reliability and ease of operation.

4.1.2 Powder Blending

Great care is required to meet the uranium-thorium ratio specification (see Table 3 for definition). A batch blender was installed to provide large, uniform quantities of powder and thereby to assist in ratio control. The blender is a rotating-drum type and accepts a 70 to 80 kg charge. After blending, the powder is sampled and then weighed into 10-kg (± 10 gm) batches. These batches are "bagged" into the sol-gel cubicle as one of the two feed materials for the blending operation.

4.1.3 Purification of U^{233} Feed Solution, An Operation for Removing Gamma-Emitting Daughters from U^{232} in the U^{233}

Unlike the denitration operation, the extraction system in the strictest sense is not a portion of the sol-gel process; however, it is a vital auxiliary. The U^{232} daughter products are gamma-ray emitters and must be removed from the U^{233} in order that the Kilorod equipment may be operated with only gloved hands. The solvent extraction flowsheet used in this operation is shown on Fig. 6. The feed for the extraction plant is made up from aged uranyl nitrate solution or by dissolution of U^{233} metal. Following extraction, the purified uranyl nitrate solution is concentrated by evaporation to U^{233} concentration of about 100 g/liter, and it is then stored until needed in the sol-gel operation.

The results of the extraction operation are given in Table 1. Note that all specifications were met. The NO_3^-/U mol ratio is of significance in sol-gel operations, as will be discussed later. Decontamination

Fig. 6. Kilorod U²³³ Purification Flowsheet.

factors for hard-gamma-emitting isotopes are given in Table 2. These are the U^{232} daughter products previously discussed.

Table 1. Uranium Purification by Solvent Extraction
Exceeds Purity Specifications

Run No.	Uranium Recovered %	Decontamination Factor		UNH Product NO ₃ /U Ratio
		Gross γ	Thorium	
HJ-1	99.8	230	3×10^3	2.42
HJ-2	99.6	380	5×10^3	2.25
HJ-3	99.8	416	3×10^3	2.16
Spec.	99.90	100	10^3	< 2.50

Table 2. Favorable Decontamination Factors
in Solvent Extraction

Gross γ	250
Th ²²⁸	2,500
Ra ²²⁴	5,000
Pb ²¹²	300

4.2 Preparation of Sol-Gel Product Containing ThO₂ and UO₂ in Solid Solution

The process described below provides a sol-derived gel that can be sintered to near theoretical density, and the process is simple and troublefree.

4.2.1 Flowsheet Conditions

Three individual operations make up the portion of the sol-gel process within the shielded facility. These are:

1. blending of the sol,
2. evaporation (or drying) of the sol to a gel, and
3. calcination-reduction-sintering of the gel to the final product.

The flowsheet given as Fig. 7 lists operating conditions for each of these steps, as well as the operating conditions for the denitrator.

4.2.2 Procedure

Preparatory to blending the batch of sol, the 10-kg batch of denitrator product (ThO_2) is bagged into the sol-gel cubicle. Precisely analyzed U^{233} feed solution is piped into the cubicle and a calculated volume carefully measured. This volume is calculated to yield the desired $\text{U}^{233}/\text{U}^{235} + \text{Th}$ ratio.

The U^{233} feed solution is then transferred to the blend tank and a calculated quantity of nitric acid is added. The blending pump, which is installed on a pipe loop outside the blend tank, is started to agitate the batch. Steam is admitted to the steam heater, a jacketed section of the pipe loop. The amount of nitric acid added depends upon the total NO_3^- already present in the uranium solution and the quantity of thorium used. Sufficient nitrate is added to increase the NO_3^- -to-Th ratio by 0.077; if the NO_3^-/Th ratio is 2.5, then no nitric acid is added, and a ratio > 2.5 is not acceptable for processing (see Table 1).

When the blend-tank temperature reaches 60°C , the thorium powder is added to the blend tank through a funnel at the top of the tank. During addition, the batch temperature continues to rise until it reaches 80°C , where it is controlled. The batch is allowed to agitate for 30 min at 80°C after the thorium addition. Ammonium hydroxide is then added in an amount equivalent to 0.017 g-mole of NH_4OH per g-atom weight of thorium. Circulation is continued for another 30 min; the batch is sampled; and it is then ready for transfer to the tray dryer.

The inherent latitude of all sol-gel operations is well illustrated by the nitric acid and ammonia addition just mentioned. First, note that in nitrate addition no consideration was given to the quantity of nitrate in the ThO_2 feed. The ThO_2 is sufficiently uniform, and process control limits are so broad that the variation in nitrate concentration in the ThO_2 is not significant. The back adjustment with ammonia need not be controlled precisely, either. This adjustment is satisfactory over the NH_4/Th mole ratio of 0.013 to 0.022. This broad control range actually allows some control of the crushing and grinding characteristics of the calciner product as toughness increases with the amount of ammonia added.

Fig. 7. Sol-Gel Process Flowsheet.

Drying is carried out at 80 to 95°C, over a 30-hr period. After drying, the batch is dumped into Alundum crucibles and loaded into the calciner.

The calciner temperature is raised from room temperature to 1150°C in 4-1/2 hr. Air is purged through the calciner during this period. When the temperature reaches 1150°C, the purge gas is changed to 4% H₂ -- 96% argon for reduction of the U₃O₈ to UO₂. Four hours are required for reduction. At the end of this time, the atmosphere is switched to pure argon, and the furnace power is turned off. When the temperature of the furnace falls to 350°C, the crucibles are removed and placed under an argon blanket until the crucibles reach room temperature. The next calciner batch is loaded immediately. The entire operating sequence of the furnace is accomplished by a program controller. By pulling the charge and reloading the furnace while hot (300 to 350°C), an overall time cycle of 24 hr is possible.

Following calcination, the batch is weighed and transferred to the rod-fabrication portion of the Facility.

4.2.3 Description of Sol-Gel Process Equipment

The pilot plant equipment and some of the process intermediates are shown as follows:

1. The blend tank used in prepilot-plant work is shown on Fig. 8. This tank was built with a plate-glass wall to observe mixing and holdup of material above the water line. The uranyl nitrate solution has been added and circulation (agitation) has just started. Thoria will be added through the funnel partially shown here.

2. The pilot-plant blend tank is shown on Fig. 9. It is identical to the tank just shown except for the plate-glass window. Gage glasses were used instead.

3. The tray dryer is shown on Fig. 10. Figure 11 shows a tray of dried gel being removed from the tray dryer. The dried gel is broken to fragments no more than 1/2 in. in the greatest dimension.

4. The calciner used in the pilot plant is next shown in Fig. 12. This furnace is a commercial tool-treating furnace. Minor revisions were made at the Laboratory to permit operation within the sol-gel cubicle. For example, the door was counter-balanced, and the suspension was

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Fig. 8. Cold-Testing Blend Tank. 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. 9. Blend Tank.

Fig. 10. Batch Evaporator with Trays Partially Pulled

Fig. 11. Evaporator Tray Containing Dried Gel, as Seen Through Cubicle-Shielding Window.

Fig. 12. Batch Calciner, with Door Raised. Door mounting and latches permit operation by one gloved hand.

revised to make manipulation easier. The heating element is Kanthal A-1. A sample of typical fired product is shown in Fig. 13.

5. RESULTS OF THE SOL-GEL OPERATIONS

As of November 1, 1963, the sol-gel operation had produced 500 kg of $U^{233}O_2-ThO_2$ meeting chemical specifications. Within the period covered in processing the first 12 "hot" batches (about 120 kg), some difficulty was encountered in holding the weight percent U^{233} within the $3.00 \pm 0.05\%$ specified. This difficulty lay entirely in our inability to agitate and sample the U^{233} feed tank properly. This difficulty was corrected by a new feed tank. Actually, all material prepared during this early period was usable since it met all other specifications and since blending of the various batches to obtain the desired percentage of U^{233} was permitted by the customer. Only one instance of equipment repair has been experienced in the sol-gel cubicle to date. This item was minor, delaying operations less than an hour. No cubicle entries, the indicator of major equipment repair, have been required.

Kilorod specifications and analytical results obtained thus far are summarized on the following table:

Table 3. Operating Results of the Sol-Gel Kilorod Program

Property Measured	Specification or Desired Max. Value	Summary of Analytical Data	
		Average Value	Range of Values
$\frac{U^{233}}{U^{233} + Th} \times 100$	$3.00\% \pm 0.05^a$	3.01	2.96-3.05
Gas Release:			
Calcined Product	0.05 cc/g max.	0.022	0.004-0.05
Crushed Oxide	0.3 cc/g max.	0.11	0.05-0.28

^a Powders falling within the 2.9-3.1 may be blended to yield the desired concentration.

Note that control of the percentage of U^{233} in the product has been excellent and, in fact, is well within recognized limits of analytical error. The results of the first 12 runs, incidentally, are not included in this figure, because they are not representative of the control

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Fig. 13. Sintered Sol-Gel Product. Shown here are typical shapes of calciner product.

capability of the process as already discussed. Gas-release data for both the calcined product and the crushed oxide also show average and maximum values within the desired ranges. Actual O/U ratios have not been determined for the "hot" product since proper facilities are not available. However, the actual oxygen present in stoichiometric excess is known to be low. Cold operations experience shows that a gas release for this product of $\lesssim 0.03$ cc/gm is $\lesssim \text{UO}_{2.04}$. This $\text{UO}_{2.04}$ is actually the lower analytical limit of detection for this uranium concentration. Some pickup of gases is noted and expected in the preparation of the powder. No attempt is made to control this pickup because the powder is prepared in contact with the atmosphere.

The composition of the gases released was also as expected. Hydrogen, the gas of greatest interest, was not expected to exceed 50 vol % (see Table 4). The highest value thus far was 33%. The scatter and the uncertainties encountered in collection of the data make interpretation exceedingly difficult.

Table 4. Quantity and Composition of Gases Released^a by Solid Products

Gas	Calcined Product ^b		Crushed Oxide ^c	
	Average	Range	Average	Range
Quantity of gases released: (std cc/gm)	0.022	0.004-0.06	0.11	0.05-0.28
Analysis of gases released: (vol %)				
H ₂	7.6	0.7-16	21	4-33
CH ₄	1.5	0.7-2	0.5	0.3-1
H ₂ O	7.8	0.4-25	2.7	0.1-18
N ₂ or CO	36.9	0.7-71	39	7-59
O ₂	12.7	0.3-56	0.6	0.1-3
A	0.4	0.2-0.7	0.1	0.1-0.2
CO ₂	41.8	0.15-73	40	6-83

^aObtained by heating to 1200°C under vacuum.

^bResults represent first 28 calciner batches.

^cResults represent first 150 rods.

6. KILOROD PROGRAM RADIATION DATA

Compilation of radiation data from each of the sol-gel manipulations is an important objective of the Kilorod Program. These data are necessary for the design of future facilities and the handling of higher U^{232} concentrations. At the conclusion of the Kilorod program, the U^{232} content of a batch will be increased to the equivalent of about 1000 ppm for radiation control data of interest to power reactor recycle work.

Personnel exposures have been consistently well below permissible levels, and the accumulation of activity by the equipment has also been low (Table 5). Individual hand and forearm exposures will average about 100 millirems per week, as opposed to the 1500 permissible value. The highest rate recorded in surveying any equipment piece to date is 50 mr, found inside the calcining chamber.

Radiation levels of process materials have been monitored, and the highest levels obtained are given in Table 6. Detailed data, in addition, have been fitted to the calculated buildup curve, as shown in Fig. 14.

Table 5. Personnel Radiation Exposures and Accumulated Activity in Equipment: Less than Maximum Permissible¹

Operation	Max. Accumulated Weekly Exposure ^a (millirems)	Present Background ^c (millirems)
Blending	7	6(a)
Dryer	7	7(a)
Calciner	15	50(b)
Total Exposure to Individual	< 200 ^b	

^aExposure taken by a finger ring which is used only at the given work station.

^bThis reading taken from individual finger ring which accumulates individual dose for all duties.

^cReadings taken with G-M survey meter (a) and ion chamber (b). About 1/3 of program had been completed and all equipment given normal cleaning.

Fig. 14. Tl²⁰⁸ Activity as a Function of Time Since Purification.

Table 6. Radiation Levels of Process Materials

Material	Max. Readings Taken (millirems/hr)	Days Since Extraction
Crucible of dried gel (5 kg) ^a	< 200	50
Crucible of fired particles (5 kg) ^a	< 200	50
Finished rods ^b	77	78
	96	98
	118	121

^aG-M survey meter used. Probe held in contact with and across top of crucible.

^bG-M survey meter used. Probe held in contact with rod and with axis of rod and probe parallel.

7. FUTURE SOL-GEL WORK

The variety of ceramic nuclear fuels which can be prepared by the sol-gel technique has already been mentioned. The materials already prepared on a laboratory scale by using variations of this procedure are given on Fig. 15. Note that uranium, plutonium, and thorium have been prepared in combination. Plutonium dioxide has also been prepared. Note that preparation of certain carbides has also been demonstrated. Further, since the preparation of this slide, the ThO₂-ZrO₂ combination has been made. The future of pilot plant work lies within the products shown.

An interesting variation, one yielding an unpowdered product, is used to illustrate the flexibility of the sol-gel process. Figure 16 shows microspheres of ThO₂ prepared by a sol-gel procedure. These microspheres are about 100 μ in diameter.

These same microspheres coated with pyrolytic carbon are shown on the following figure (Fig. 17). A microradiograph of these carbon-coated spheres is shown next on Fig. 18a and polished sections on 18b. The primary application for fuel in microsphere form lies in the preparation of dispersion fuels.

Fig. 15. Examples of Flexibility of Sol-Gel Process. This flowsheet illustrates the many types of thorium based reactor fuels already prepared in the laboratory by Sol-Gel techniques.

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Fig. 16. Sol-Gel Microspheres.

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Fig. 17. Sol-Gel ThO_2 Microspheres Coated with Pyrolytic Carbon Coating.

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Y-52668

a. Autoradiograph

PHOTO
Y-52802

b. Sections

Fig. 18. Sol-Gel Thorium Oxide Microspheres. Notice in Fig. 18b that the coating (in cross section) is the same as shown in Fig. 17 and Fig. 18a.

8. CONCLUSIONS

The Kilorod Program has reached the half-way point, and the following conclusions have been reached:

1. The sol-gel process has been demonstrated at the 10 kg/day scale and has met chemical specifications.
2. Personnel exposures have in all cases been well below established limits.
3. Materials exhibiting considerably higher levels of radiation may be processed in the existing facility.

The process represents a significant breakthrough in the preparation of ceramic reactor fuel materials. Kilorod operating results to date show that the sol-gel process offers advantages in simplicity, reliability, and ease of control. The flexibility of the sol-gel approach in preparing a variety of materials has now been demonstrated in laboratory tests. These other materials obviously can and will be made by this process.

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