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# PREPARATION AND FABRICATION OF $ThO_2$ FUELS

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## ABSTRACT

Dense particles of $ThO_2$-$UO_2$ were prepared by a sol-gel process and vibratorily compacted into metal tubes to a density approaching 9.0 g/cc. The steps in this method are all simple and can be carried out behind shielding, which is necessary for refabricating uranium-233 fuels. The sol-gel process consists of preparing a hydrous thoria sol, adding the uranium-233 as nitrate solution, evaporating to a gel, and finally calcining to almost theoretically dense oxide particles at only 1150°C. The sol-gel-prepared oxide, after being sized, was compacted with a simple, inexpensive pneumatic vibrator.

# DISCLAIMER

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## 1.0 INTRODUCTION

This paper describes the preparation of dense particles of $ThO_2$ and $ThO_2$-$UO_2$ by a sol-gel process, with subsequent vibratory compaction into metal tubes. The process steps are simple and can be carried out behind shielding, which is necessary in processing of recycled fuel materials because of the presence of U-232 decay products. The sol-gel-prepared oxides have the very high density required for vibratory compaction into tubes with a bulk density approaching 90% of theoretical. This fuel density is probably adequate for most reactor fuel elements.

Of several possible ceramic fabrication processes (1), cold pressing and sintering is usually used to produce nuclear fuels containing $ThO_2$ (2,3). Pellets of any of several simple geometric shapes with bulk densities as high as 98% of theoretical can be prepared by this process. Right-circular cylindrical pellets suitable for loading into metal tubes can be produced with a length/diameter ratio of 1 or slightly greater, and to within ± 0.001 in. of a specified diameter. Pellet fabrication by pressing and sintering may be simple and straightforward or difficult and complex, depending on the condition of the starting powder. If the powder is of such a physical character that it is amenable to an automatic pressing scheme, only three steps—granulation, pressing, and sintering—are required. Otherwise, as many as five or six additional steps may be necessary to condition the material for a given fabrication scheme. Even in its simplest form, this fabrication route is not readily adaptable for remote handling.

Arc-melted and crushed $UO_2$ has been compacted by vibration in long, thin metal tubes to bulk densities 90% of theoretical (4). A similar procedure for $ThO_2$-$UO_2$ fuels appears attractive. However, the radiation hazards associated with recycling of U-233 fuels, as discussed in this paper, indicate that some simpler method than fusion or pelletizing may be desirable for making dense, granular materials for heterogeneous nuclear reactors.

The work reported in this paper is a status report on experiments still in progress. It was performed by many people at Oak Ridge National Laboratory, and the authors acknowledge, in particular, W. O. Harms and K. H. McCorkle for help in preparing this paper.*

## 2.0 RADIOACTIVITY OF RECYCLED U-233 AND THORIUM FROM POWER REACTORS

### 2.1 Radioactivity Associated with U-233 from Power Reactors

The chief source of radioactivity in U-233 after Thorex processing of fuel from power reactors will be the decay products of U-232. This

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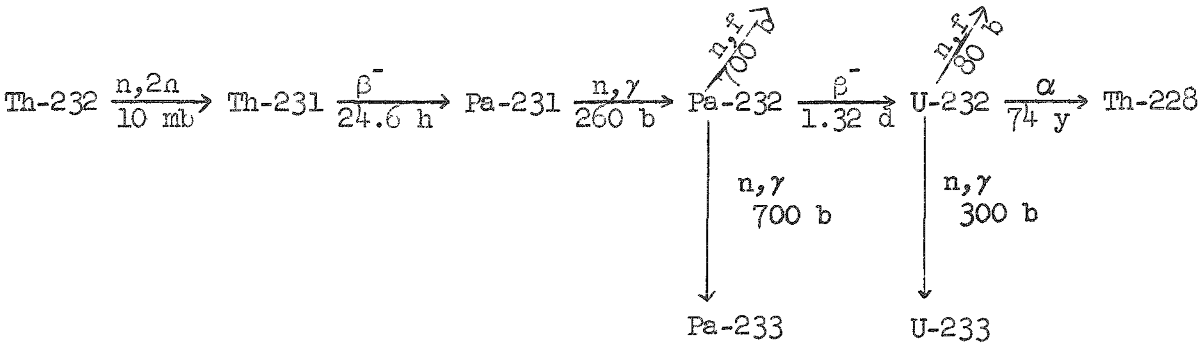
decay chain will contribute both very energetic gamma rays and neutrons from ($\alpha$,n) reactions with any light elements associated with the uranium. The main production of U-232 in a thorium reactor is initiated by an (n, 2n) reaction on thorium:



The ratio of U-232 to U-233 produced increases with increasing neutron flux and irradiation time and is highly dependent on the neutron energy distribution in the reactor, since only neutrons with energies $> 6.37$ Mev produce the (n,2n) reaction. For instance, the effective (n,2n) cross-section, based on thermal neutron flux, is of the order of $10^{-2}$ barn for a well moderated reactor with separate fuel and blanket regions, but in reactors such as the Consolidated Edison Indian Point, with mixed $ThO_2$-$UO_2$ fuel and relatively poor neutron moderation, a cross-section of about $5 \times 10^{-2}$ barn is expected. In this case about 1000 parts of U-232 per million parts of U-233 is expected in the first cycle after 18,000 Mwd/ton irradiation, corresponding to 200 parts of U-232 per million of total uranium. After several cycles the U-232 will reach about 850 ppm based on total uranium, giving about 2500 parts of U-232 per million parts of U-233.

For decay times of interest in fuel fabrication, Th-228 with a half-life of 1.91 years controls the buildup of activity from U-232 daughters, with the growth of $\gamma$ activity into freshly purified U-233 containing U-232 following closely the amount of Th-228 present. The $\gamma$ activities of primary concern are the 2.6-Mev $\gamma$ from Tl-208 and the 2.2-Mev $\gamma$ from Bi-212. Calculation of the neutrons produced by ($\alpha$,n) reactions in U-233 aqueous solutions and the oxide indicates that neutrons will not contribute more than a few percent to the total activity.

In addition to the activity of the U-232 decay chain, the $\gamma$ activity of U-233 itself and of residual fission products must be considered. The penetrating radiation from U-233 is $\gamma$ rays in the 40- to 96-kv region and therefore is easily shielded. The residual fission product content of U-233 can be decreased to almost any desired level by decontamination beyond that obtained in the Thorex process. However, a practical goal seems to be about $1 \times 10^6$ d/m/g U-233 that produce 0.5- to 1.0-Mev $\gamma$ rays. This is about the minimum residual fission product activity to be expected in the Thorex process product.

## 2.2 Radioactivity Associated with Thorium

The chief sources of penetrating radiation from recycled thorium are the Th-228 decay chain, Th-234—Pa-234 from neutron capture by Th-233, and residual fission products. The Th-228 chain activity will be controlling since Th-234—Pa-234 activity can be decreased to insignificant levels by a decay time of 400 days, and that from fission products can probably be decreased to about 1 x $10^{8}$ d/m/kg Th by the Thorex process. About 12 years would be required for the Th-228 in recycled thorium from power reactors to decay to a level sufficiently low that direct fuel preparation and fabrication are safe. For instance, the thorium from the Consolidated Edison reactor after 18,000 Mwd/ton irradiation will contain 50-100 (5) times the amount of Th-228 in natural thorium in equilibrium with its daughters. This can be decreased to twice the level of natural thorium in a decay time of about 12 years. Processing to remove the Ra-228 daughter of Th-232 and additional decay for about 3 years is required to decrease the Th-228 to a level below that in natural thorium.

## 2.3 Calculated Activity Level for a Typical Fuel Fabrication Situation

The total activity from the various sources in recycled thorium and U-233 makes it desirable to use shielding and remote operation in preparing the fuel material and fabricating fuel elements for the thorium fuel cycle. For calculation purposes (6), a typical process situation may be visualized as a sphere of thorium oxide-uranium oxide with a density of 4.5 g/cc and containing 33 kg of thorium and 1 kg of U-233. The contribution of the U-232 decay products and unirradiated thorium to total penetrating radiation 10 cm from this sphere as a function of decay time after processing is shown in Fig. 2.1a. Three cases are considered: (1) complete removal of all U-232 decay products at zero time, (2) complete removal (TBP solvent extraction) of all decay products except 1% of the Th-228 which will have grown in during 2 months' storage and shipping, and (3) removal of 90% of the Th-228 (cation exchange) but none of the other decay products produced by 2 months' decay. The values were calculated for a mixture of U-233 containing only 50 ppm of U-232 (material currently on hand at ORNL), and unirradiated thorium containing only 1/3 the equilibrium concentration of Th-228 in normal thorium, with no residual fission product activity. Even for this very conservative situation, about 5 cm of lead (Fig. 2.1b) would be required to decrease the radiation level to 1 mr/hr at 10 cm 5 days after isolation of the U-233, and it is difficult to visualize fuel preparation and fabrication being completed in < 5 days.

Calculated radiation intensities for a more realistic situation to be encountered in the thorium fuel cycle for power reactors as a function of time (Table 2.1), again with conservative assumptions, indicate that about 8 cm of lead is required for safe handling. For the calculations the U-232 content in the U-233 was assumed to be 200 ppm, the minimum expected for recycled power reactor fuels. The residual Th-228 content of the thorium was assumed to be the equilibrium amount in normal thorium, which could be attained only after 10-15 years' decay. The holdup of

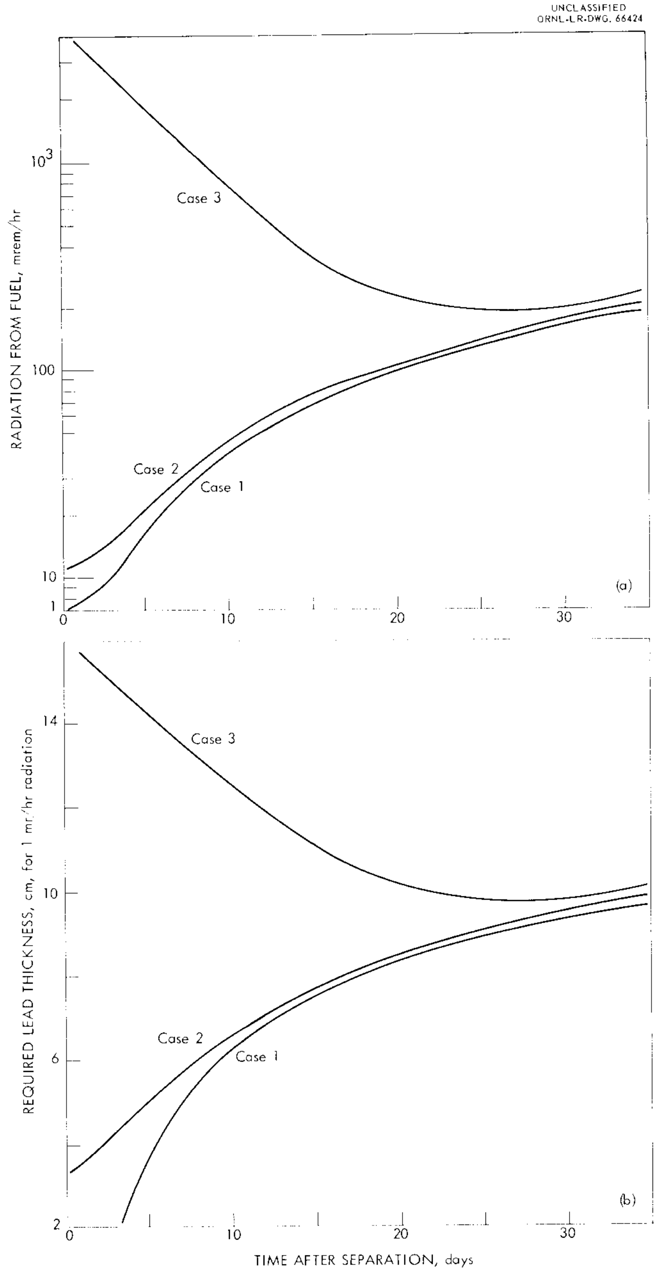


Fig. 2.1. (a) Radiation from recycled $ThO_2$-$UO_2$ and (b) lead shielding requirements as a function of time after processing. Case 1, removal of U-232 daughters at time zero; case 2, removal of 99% of U-232 daughters; case 3, removal of 90% of Th-228 only.

Time since Thorex processing: 2 months
Radiation source: 12.2-cm-radius sphere of 1 kg U-233 in 33 kg $ThO_2$, 4.5 g/cc, 50 parts U-232 per $10^6$ U-233
Radiation measured 10 cm from surface of sphere
Radiation rate proportional to concentration of U-232 and to amount of U-233 in sphere

older material containing U-232 was assumed to be only 1% of the equipment capacity with a complete cleanup every two months, and the amount of residual fission products was based on two complete cycles of Thorex processing of irradiated fuel decayed 400 days before processing.

Table 2.1. Gamma Activity of Sphere Containing 33 kg of Thorium and 1 kg of U-233 as Oxide

Density: 4.5 g/cc
U-233 containing 200 ppm of U-232

| Time Since Final U Separation, days | Residual Activity at 10 cm, mrad/hr | | | | |
|---|---|---|---|---|---|
| | U-232 Daughters[a] | Residual Th Activity[b] | Equipment Contamination[c] | Fission Products[d] | Total |
| 1 | 15 | 20 | 15 | 5 | 55 |
| 3 | 30 | 20 | 15 | 5 | 70 |
| 7 | 90 | 20 | 15 | 5 | 130 |
| 12 | 200 | 20 | 15 | 5 | 240 |
| 20 | 380 | 20 | 15 | 5 | 420 |
| 30 | 640 | 20 | 15 | 5 | 680 |

[a] Based on 99% removal of U-232 decay products at zero time.

[b] Based on Th containing an equilibrium concentration of Th-228.

[c] Residual contamination of process equipment assumed to be 1% of equipment inventory and aged an average of 2 months.

[d] Fission products based on $1 \times 10^8$ d/m/kg Th and $1 \times 10^9$ d/m/kg of U-233 of 0.5- to 1.0-Mev $\gamma$ rays.

## 3.0 SOL-GEL PROCESS FOR PREPARING $ThO_2$ AND $ThO_2$-$UO_2$

In the sol-gel process (7) (Fig. 3.1) a $ThO_2$ hydrosol is carefully evaporated to a gel, from which glassy millimeter-size $ThO_2$ particles of density > 99% of theoretical are produced by calcination to only 1150°C. The process consists of simple steps which can be easily operated behind shielding. The $ThO_2$ feed may be prepared by denitration of the $Th(NO_3)_4$ product of the Thorex process. When uranium oxide is added to the sol and the product calcined in an atmosphere containing hydrogen, a homogeneous solid solution of $UO_2$ in $ThO_2$ is produced, as shown by x-ray and metallographic study.

### 3.1 Steam Denitration of Thorium Nitrate

Hydrated thorium nitrate crystals are rapidly denitrated in superheated steam between 180 and 290°C, evolving totally condensable $HNO_3$ and $H_2O$ and producing a solid residue containing about 20% of the original nitrate. The reaction appears to be first order with respect to thorium nitrate and to have an activation energy of 1.25 kcal/mole. Thermogravi-

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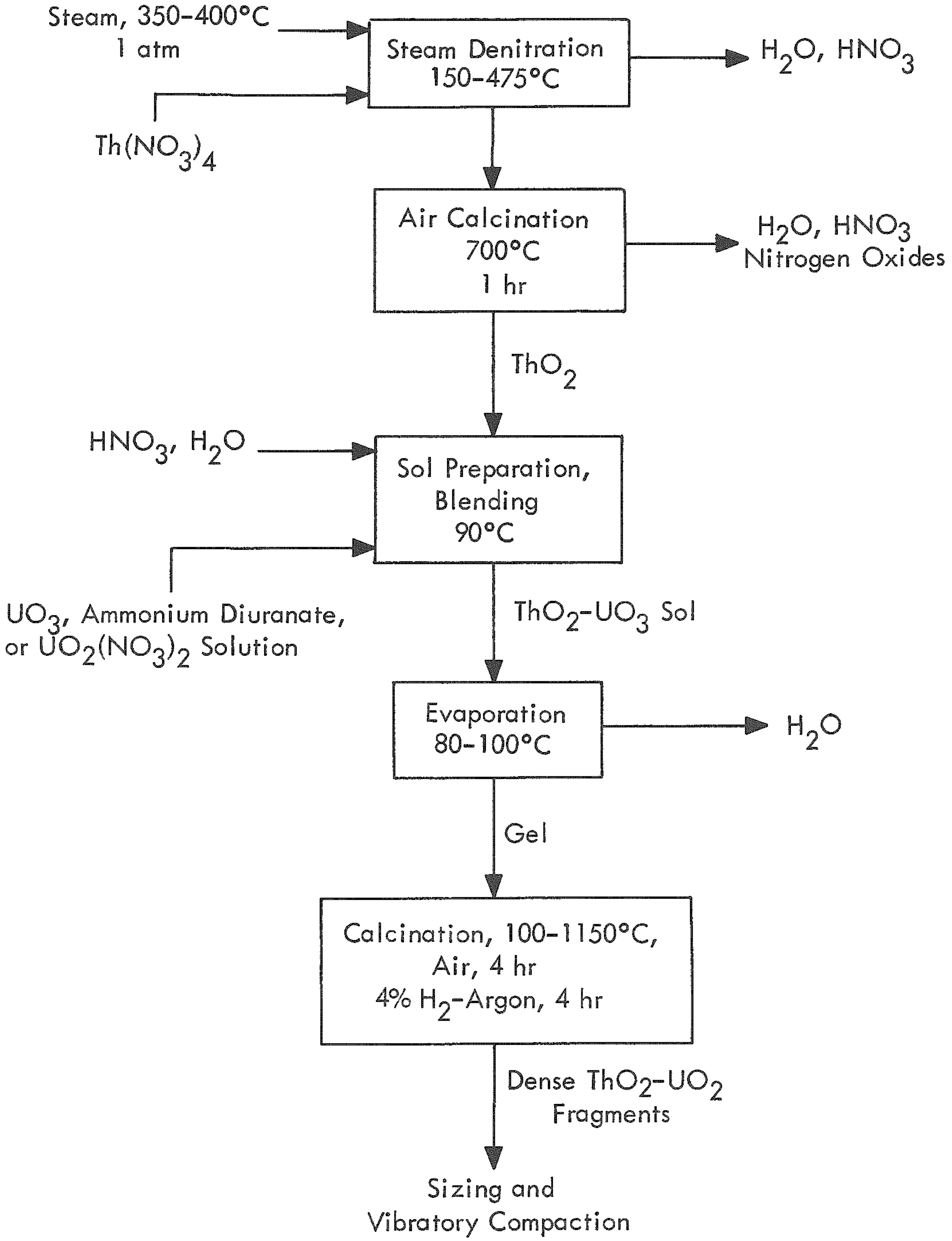

Fig. 3.1. Sol-gel process for preparation of dense thorium-uranium oxide.

metric analysis (Fig. 3.2) showed a second reaction in which the product of the first is further denitrated by steam but more slowly, with evolution of $HNO_3$ and $H_2O$. If a significant amount of the heat is supplied through the reactor walls or if the first step is conducted in air, the products are difficultly condensable brown nitrogen oxides and a solid residue which is only difficultly dispersible in dilute nitric acid.

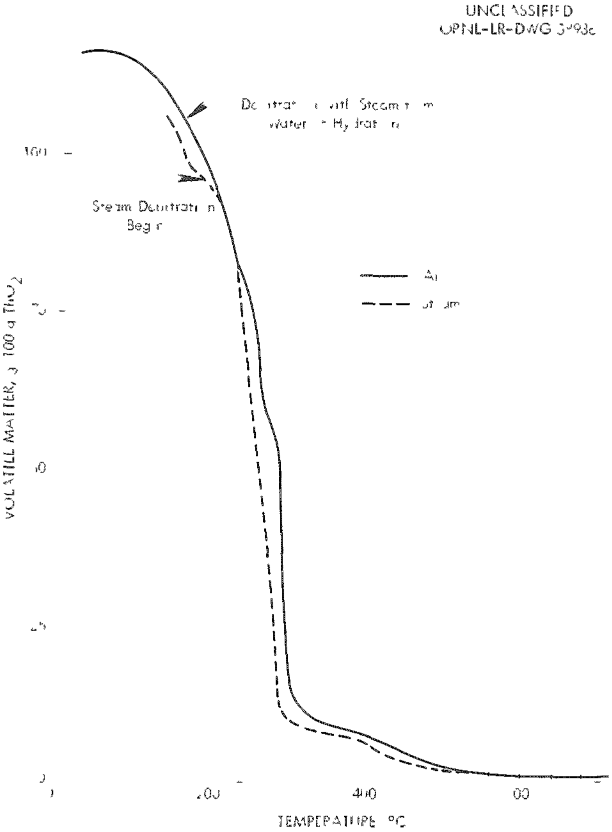

Fig. 3.2. Thermogravimetric analysis of $Th(NO_3)_4 \cdot 5H_2O$ at 6°C/min rise rate in steam and air.

The optimum procedure for batch denitration of thorium nitrate in a kilogram capacity rotary calciner 12 in. long by 4 in. dia was to introduce steam superheated to 350-450°C at 40 g/min while controlling the reactor wall temperature at or below 350°C until the oxide temperature exceeded 350°C. This required about 1 hr, after which the steam flow was decreased to 10 g/min to minimize entrainment loss of solid product, and the reactor wall temperature was increased to the final desired temperature (320-500°C). Temperature was the most effective variable in determining the residual nitrate and chemically bound volatile matter content (Table 3.1), time being of minor significance (Fig. 3.3). Reaction was essentially complete in 1 hr for the temperatures and batch sizes studied. The denitration rate in steam or air was slower for solids with N/Th ratios <0.10, even at temperatures as high as 500°C (Figs. 3.2 and 3.3).

Table 3.1 Steam Denitration of Thorium Nitrate in a Rotary Calciner

Calciner: 4 in. i.d. 12 in. long, stainless steel, rotated at 2 rpm; thermally guarded by exterior furnace

Charge: 1 kg thorium nitrate crystals[a]

Steam: 600°C; flowing at ~40 g/min up to max temp, then decreased to 10 g/min

| | Denitration Conditions | | | | Time, min, at Max. Temp. in Air | Properties of $ThO_2$ Product | |
|---|---|---|---|---|---|---|---|
| | Temp, °C | | Time in Steam, min | | | | |
| Run No. | Final Reaction[b] | Highest Furnace Wall | From Start of Steam | At Max. Temp. | | N/Th Mole Ratio | Chemically Bound[c] Volatile Matter, g/100 g $ThO_2$ |
| 73 | 320 | 390 | 92 | 32 | - | 0.272 | 7.00 |
| 63 | 320 | 330 | 240 | 120 | - | 0.268 | 6.93 |
| 25 | 370 | 395 | 153 | 93 | - | 0.166 | 4.80 |
| 23 | 380 | 405 | 183 | 93 | - | 0.150 | 4.30 |
| 22 | 390 | 415 | 168 | 68 | - | 0.142 | 4.21 |
| 24 | 390 | 400 | 153 | 93 | - | 0.136 | 4.02 |
| 26[d] | 405 | 410 | 148 | 93 | - | 0.104 | 3.52 |
| 33 | 450 | 475 | 110 | 10 | - | 0.074 | 2.55 |
| 85[e] | 485 | 500 | 60 | 8 | 50 | 0.035 | 2.06 |
| 87[e] | 495 | 500 | 70 | 10 | 110 | 0.037 | 2.06 |
| 86[e] | 490 | 505 | 70 | 20 | 55 | 0.020 | 1.70 |
| 88[e] | 505 | 500 | 135 | 55 | 200 | 0.004 | 1.29 |
| 48 | 390 | 465 | 480 | 405 | - | 0.104 | 3.45 |
| 20[d] | 390 | 150 | 168 | 68 | - | 0.183 | 5.14 |

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[a] Average composition: $Th(NO_3)_4 \cdot 4.5\ H_2O$.

[b] At thermocouple probe at axis of calciner in early reactor; at reactor wall in new calciner.

[c] From volatile matter lost between 300 and 1000°C.

[d] Steam flow maintained at 40 g/min throughout the run.

[e] Runs in new calciner, completely thermally guarded; temperature of reactor measured at reactor wall.

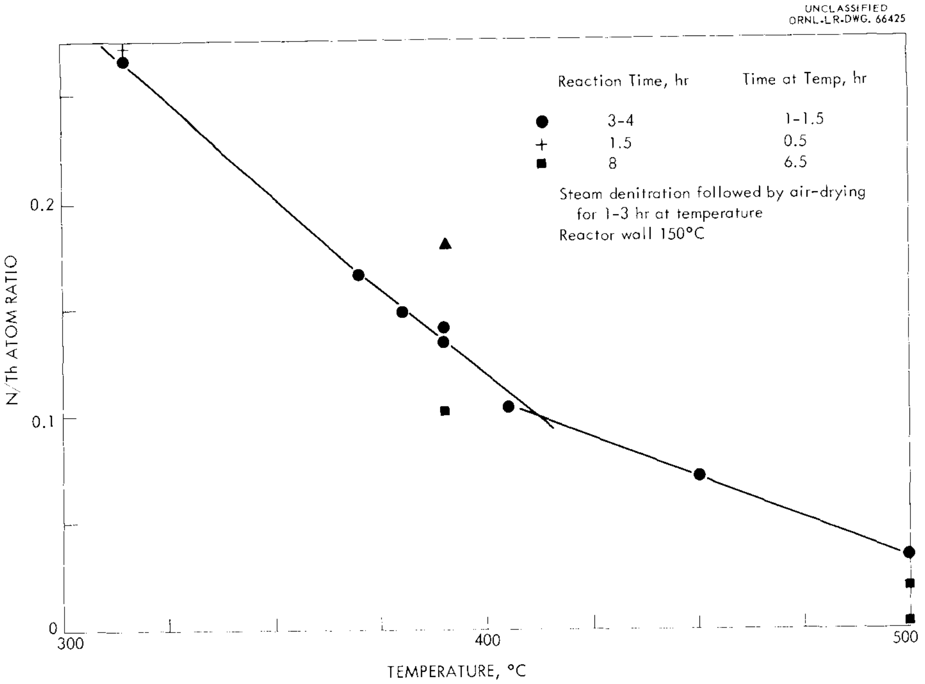

Fig. 3.3. Residual nitrate in steam denitrated $ThO_2$ as a function of temperature of denitration.

Extrapolation of the curve predicts complete removal of the nitrate at a maximum reactor temperature of 550°C. Thermogravimetric studies of thorium oxide products of steam denitration showed a linear relation between the residual volatile matter content after heating at 300°C for 1 hr and the N/Th mole ratio (Fig. 3.4). Extrapolation to zero N/Th gave a residual value of 1.3 g of volatile matter per 100 g of $ThO_2$, which is thought to be water or hydroxide bound directly to thoria.

In scaleup studies, a reproducible oxide was prepared in an agitated trough calciner in 5-kg batches (Table 3.2). Because of the method of agitation, $ThO_2$ carryover with the steam was > 10%

Table 3.2 Reproducibility of the N/Th Ratio for Fixed Run Times in the Agitated Trough Calciner

| Run No. | Run Time, min | Skin Temp, °C | Steam Temp, °C | Off-gas Temp, °C | Steam Rate, lb/hr | LOI (300-1000°C), wt % | N, % | N/Th Atom Ratio |
|---|---|---|---|---|---|---|---|---|
| 31 | 180 | 425 | 425 | 260 | 8 | 3.32 | 0.34 | 0.066 |
| 32 | 180 | 425 | 425 | 260 | 8 | 3.31 | 0.34 | 0.066 |
| 33 | 180 | 425 | 425 | 260 | 8 | 3.29 | 0.34 | 0.066 |
| 34 | 180 | 425 | 425 | 260 | 8 | 3.27 | 0.34 | 0.066 |
| 35 | 180 | 425 | 250 | 260 | 8 | 3.00 | 0.35 | 0.068 |
| 38 | 210 | 425 | 265 | 260 | 8 | 2.88 | 0.33 | 0.064 |

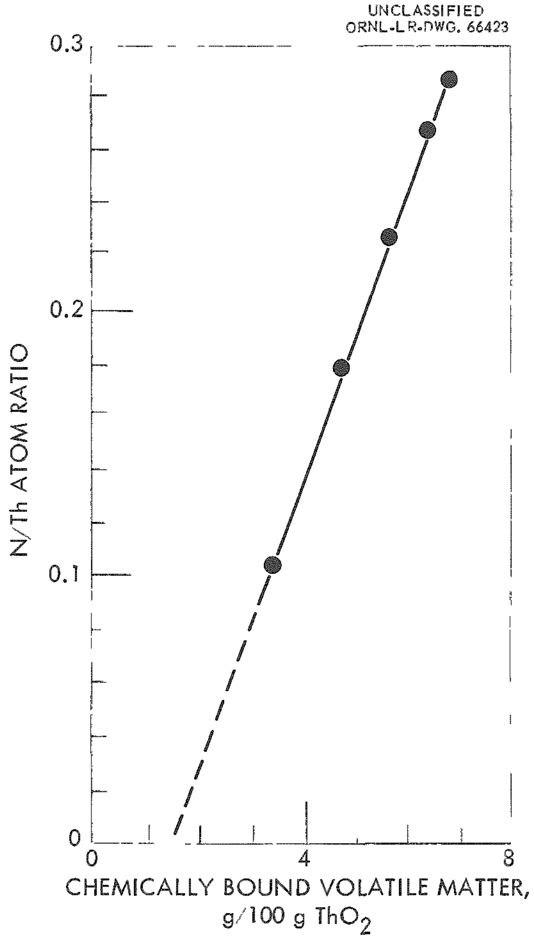

Fig. 3.4. Relationship of nitrate content of steam denitrated $ThO_2$ to the total volatile matter.

## 3.2 Sol Preparation

Thorium oxide is added to water or dilute nitric acid to produce a 2 M $ThO_2$ sol. The most important measurable variable in this step for formation of final particles of good compactability is the pH. This should be between 3 and 4 to keep the nitric acid concentration in the solution phase of the sol in the peptization range during the 10-fold volume reduction of the evaporation step, which is given by an $HNO_3$ concentration of $10^{-4}$-$10^{-2}$ M (9-11). The exact value of the $NO_3^-/ThO_2$ mole ratio required for sol stabilization depends on the surface area of the oxide. $ThO_2$ prepared by steam denitration of thorium nitrate at 400°C has an average crystallite size of 50 A and a surface area of 85-90 $m^2/g$, and required a $NO_3^-/ThO_2$ ratio of 0.13-0.15. If steam denitration at 400°C is followed by air calcination at 700°C for 1 hr, the average crystallite size is 80 A, the surface area 30 $m^2/g$, and the $NO_3^-/ThO_2$ requirement 0.06-0.08. With a higher mole ratio than optimum, two phases of solids are deposited when the sol is evaporated because of flocculation by excess acid (glassy heel). Lower than optimum ratios lead to nondispersion of large agglomerates (chalky heel). Preparations containing such multiphase deposits gave particles that did not densify well on compaction. The most satisfactory sols were prepared by removing all residual nitrate by air calcination of the steam-denitrated product at 700°C for 1 hr and then dispersing in a controlled amount of nitric acid. Fourteen hours' aging of high-surface-area thoria sols ($> 40\ m^2/g\ ThO_2$) was required for uniform distribution of nitrate on the thoria surface.

## 3.3 Uranium Addition

Up to 10 mole % uranium may be added to the $ThO_2$ sol as $UO_3$, ammonium diuranate, or $UO_2(NO_3)_2$ solution. If the nitrate is used, its content must be adjusted to compensate for that added with the uranium, which is difficult for uranium concentrations $> 2\%$. A 2-hr digestion at 90°C after uranium addition appears adequate to ensure a product homogeneous with respect to the U/Th ratio.

## 3.4 Sol Drying

The $ThO_2$ sol is converted to a glassy gel by careful evaporation, the primary requirement being not to boil the sol. This was done in the laboratory on a 1-kg scale by surface evaporation at 80-90°C and in engineering-scale tests with a steam-heated vacuum tray dryer. The equipment and operating procedure for this step are being studied in more detail.

## 3.5 Calcination

The recommended calcination procedure is to raise the temperature of the gel to 1150°C, at a rate not exceeding 300°C per hour up to 500°C, and calcine in air for 4 hr. Limiting the temperature rise rate to 300°C per hour up to 500°C, at which temperature most of the nitrate and volatile material were gone, gave minimum decrepitation and maximum-strength particles. The rate from 500 to 1150°C had no significant effects on final particle density, and was limited only by the resistance of furnace ceramic liners to thermal shock. If uranium has been added, an additional 4-hr calcination in an argon atmosphere containing 4% hydrogen is needed to reduce the uranium to $UO_2$.

Maximum-density thorium oxide was obtained at 1150°C (Fig. 3.5) in both air and hydrogen. Calcination in air gave consistently higher density, more than 99% of theoretical, of oxides containing uranium. However, calcination in hydrogen produced a denser pure $ThO_2$.

With final calcination temperatures above 1050°C in air, the O/U mole ratio for a 4.2 mole % uranium-thorium oxide reached a constant value (Fig. 3.6), but in hydrogen the value was consistent with an oxygen-diffusion rate-limiting step with an activation energy of 27 kcal/mole. The log of the rate constant vs reciprocal temperature, assuming first-order kinetics, was linear (Fig. 3.7).

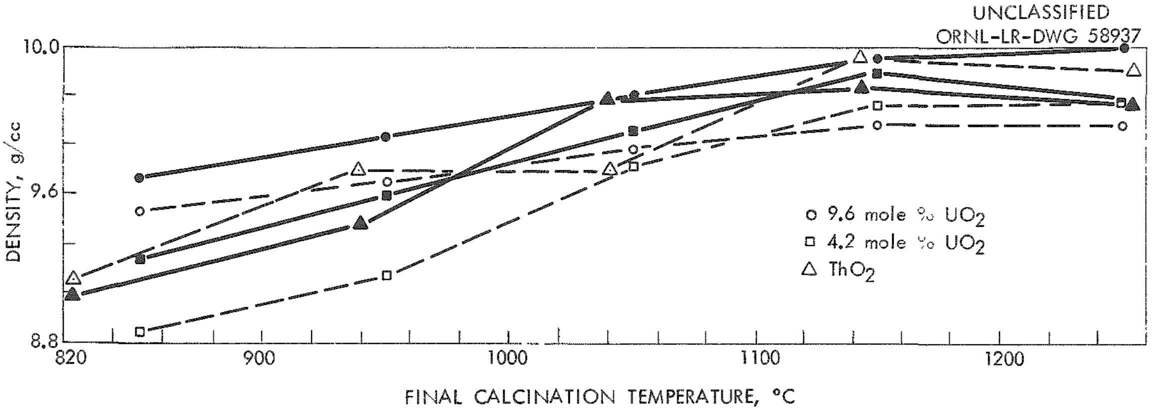

Fig. 3.5. Effect of final calcination temperature on density of mixed uranium and thorium oxides fired in air (solid lines) and hydrogen (dashed lines).

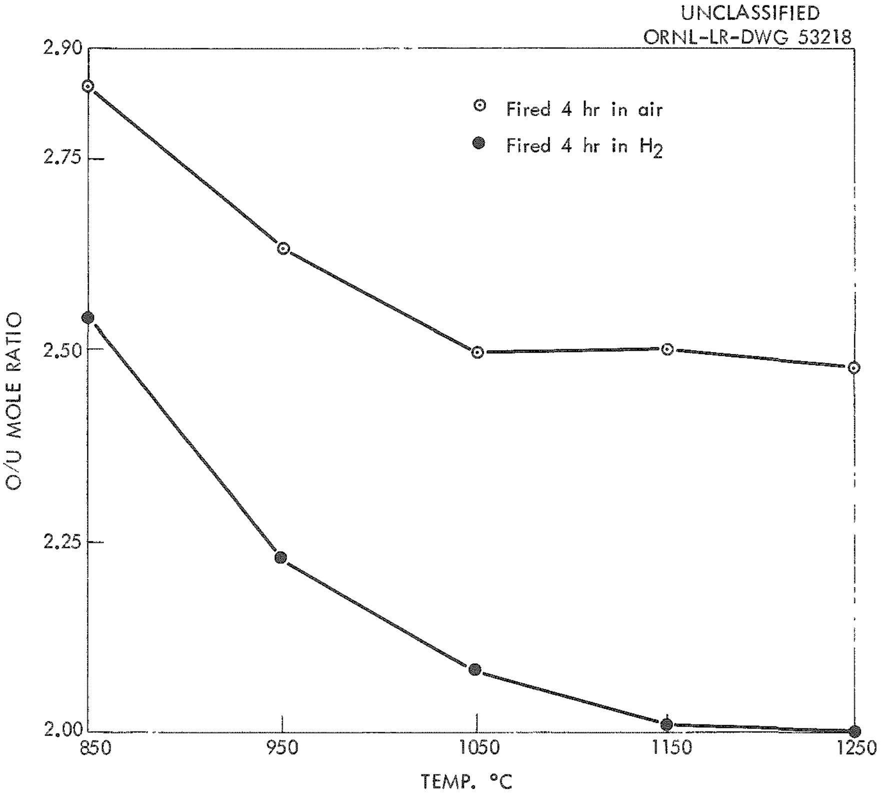

Fig. 3.6. Effect of final calcination temperature on O/U ratio; oxide composition: 4.2 mole % $UO_{2.x}$ - 95.8% $ThO_2$.

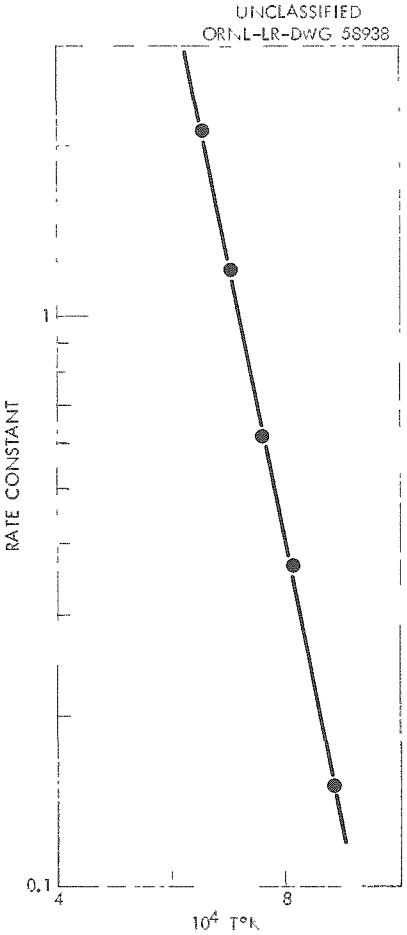

Fig. 3.7. Rate constant for the reduction of 4.2 mole % uranium-thorium oxide in $H_2$, assuming first order kinetics.

## 3.6 Properties of Final Calcined Gel Fragments

The chief improvements over earlier products in properties of calcined oxides prepared for irradiation tests by the flowsheet shown in Fig. 3.1, including 700°C air calcination of $ThO_2$ prior to sol preparation, D and E vs A, B, and C (7) were a lower O/U ratio, less gas release at 1200°C, and lower surface area (Table 3.3). Photomicrographs failed to show phase discontinuity.

Fragments of 10 to 16 mesh pure thoria (Fig 3.8a) and 1/4-in. fragments of 95% $ThO_2$-5% $UO_{2.375}$ (Fig. 3.8b) showed a polycrystalline structure. An electron photomicrograph of a fracture surface replica taken from a 1250°C hydrogen-fired 5% $UO_2$ mixed oxide (Fig. 3.9) indicates an average grain size of about 5000 A, which is larger than the x-ray crystallite size measured by line broadening. One possible explanation for the discrepancy is the possibility of strain broadening of the x-ray pattern. Extremely close packing of the crystallites is indicated by the high particle density and low nitrogen surface area.

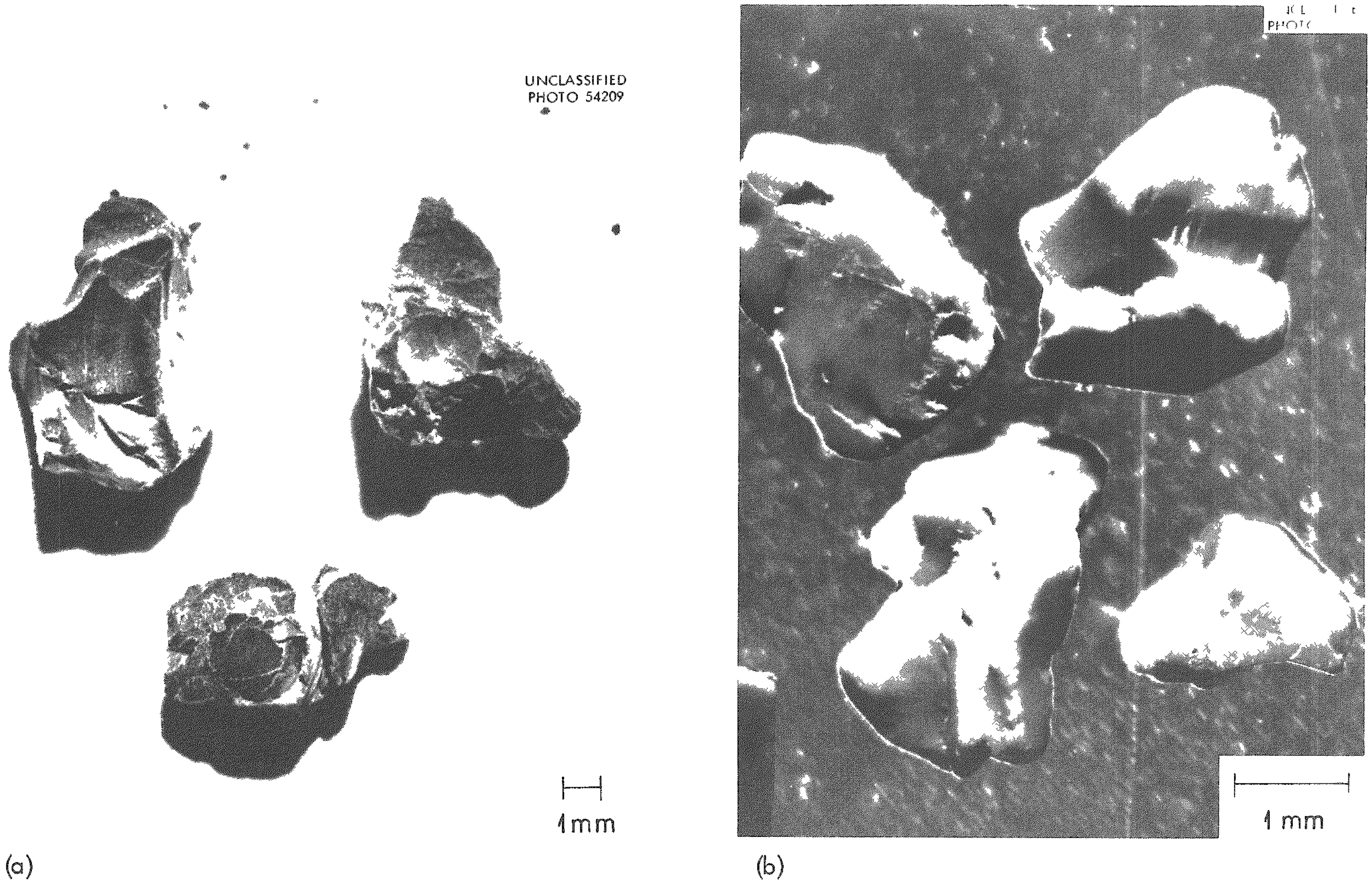

Fig. 3.8. (a) Calcined 94.8% $ThO_2$-5.2% $UO_{2.375}$, of 1/4-in. size fraction and (b) calcined $ThO_2$ gel, 10-16 mesh size fraction.

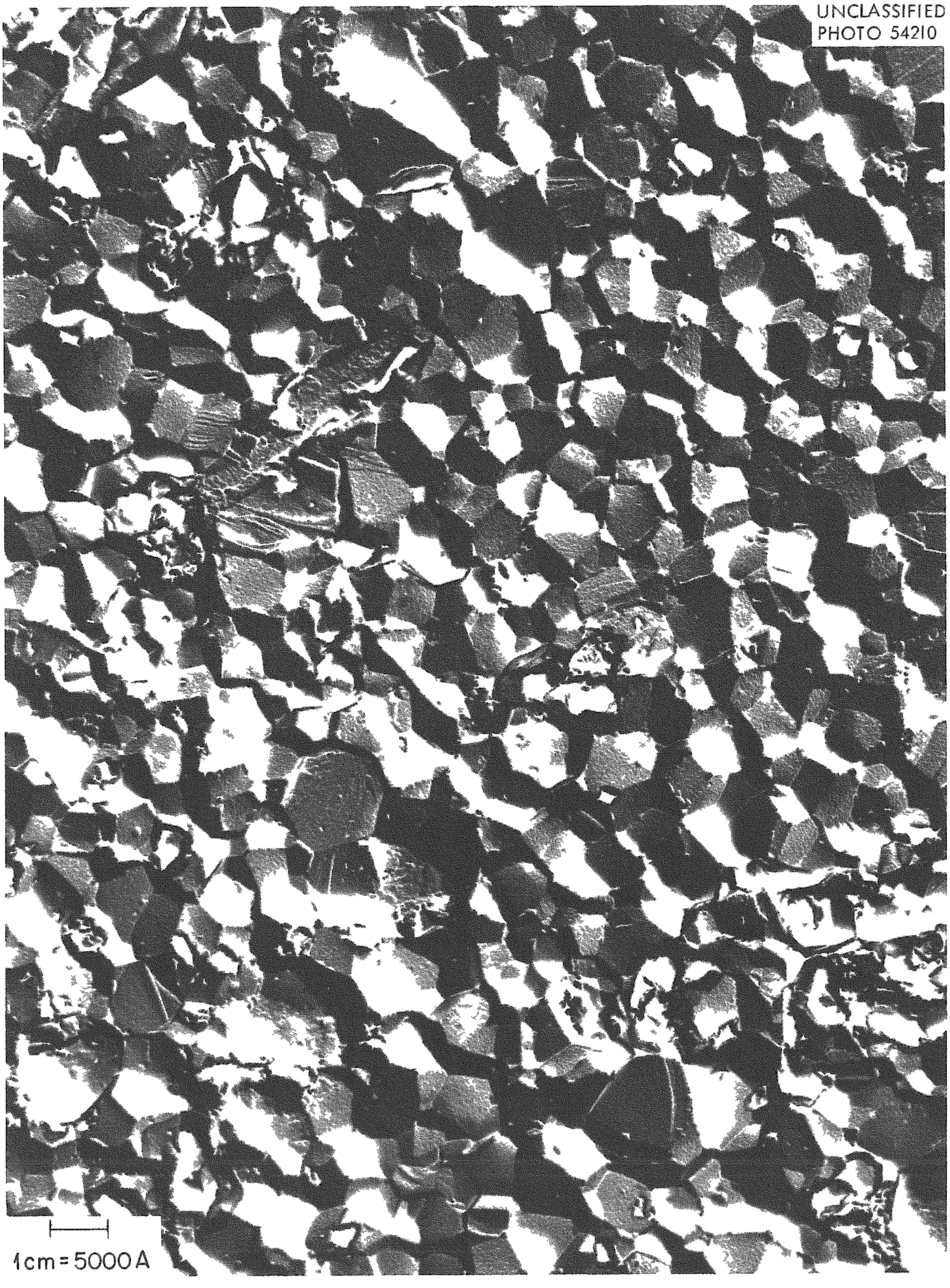

Fig. 3.9. Surface replica of hydrogen-calcined 95% $ThO_2$-5% $UO_2$ gel oxide.

Table 3.3 Summary of Properties of Sol-Gel-Prepared Uranium-Thorium Oxides Used in Fabrication of Irradiation Specimens

Final calcination temperature 1200°C; atmosphere air, then $H_2$

| | Prep. A | Prep. B | Prep. $C^c$ | Prep. $D^c$ | Prep. $E^c$ |
|---|---|---|---|---|---|
| Total U, wt % | 4.31 | .39 | 4.01 | 2.43 | 4.21 |
| U enrichment, % | 93 | 93 | 93 | 93 | 93 |
| Carbon, wt % | 0.011 | 0.010 | 0.006 | 0.004 | 0.013 |
| Nitrogen, ppm | 22 | 21 | 55 | 29 | 31 |
| Iron, wt % | 0.01 | 0.605 | 0.0265 | 0.014 | 0.016 |
| Silicon, ppm | 600 | 500 | 20 | <10 | <10 |
| $N_2$ surface area, $m^2/g$ | 0.20 | 0.26 | 0.03 | 0.008 | 0.011 |
| O/U ratio | 2.005 | 2.005 | 2.035 | <2.01 | <2.01 |
| Volatile matter released in vacuum at 1200°C, cc/g | 0.125 | 0.151 | 0.055 | 0.012 | 0.027 |
| Lattice parameter, A | 5.59121 | 5.59189 | 5.59263 | - | 5.59300 |
| Crystallite size, A | 2400 | 1700 | 2200 | - | - |
| Particle density, g/cc[a] | 9.94 | 9.92 | 9.76 | 9.97 | 9.92 |
| Packed density, g/cc[b] | 8.69±.03 | 8.69±.03 | 8.36 | 8.74 | 8.84 |

[a] Toluene intrusion, pycnometric method. Theoretical density: 10.03 to 10.04 g/cc.

[b] Navco air vibrator, 1.25 in.; 5/16 x 11 in. stainless steel tube.

[c] Cooled in pure argon after calcination in hydrogen.

### 3.7 Fission Gas Release

Several specimens of $ThO_2$-5 wt % $UO_2$ prepared by the sol-gel process were tested for retention of fission gas in the temperature range 1·40 to 2015°C. The amount of gas released increased with increasing temperature (Fig. 3.10). A plot of the fraction of gas released at a given temperature as a function of the square root of time is a straight line for a diffusion mechanism and release, and, except for a small initial burst of gas, the mechanism of Xe-133 release from this oxide was diffusion. This fact is particularly significant at 2015°C, because in bulk $UO_2$ at temperatures above 1800°C the most important release mechanism would be sublimation. Greater stability of $ThO_2$-$UO_2$ compared to $UO_2$ would be expected as a result of the higher melting point, 3300°C, for $ThO_2$ compared to 2750°C to the melting point for $UO_2$. From the slope of the curve of the log of the ratio of the diffusion coefficient to the square of the radius of the uniform sphere (13), vs the reciprocal of the absolute temperature (Fig. 3.11), the activation energy for diffusion of Xe-133 from $ThO_2$-$UO_2$ was calculated to be 75.9 kcal/mole. This compares to 70-80 kcal/mole reported for diffusion of xenon from $UO_2$ (14).

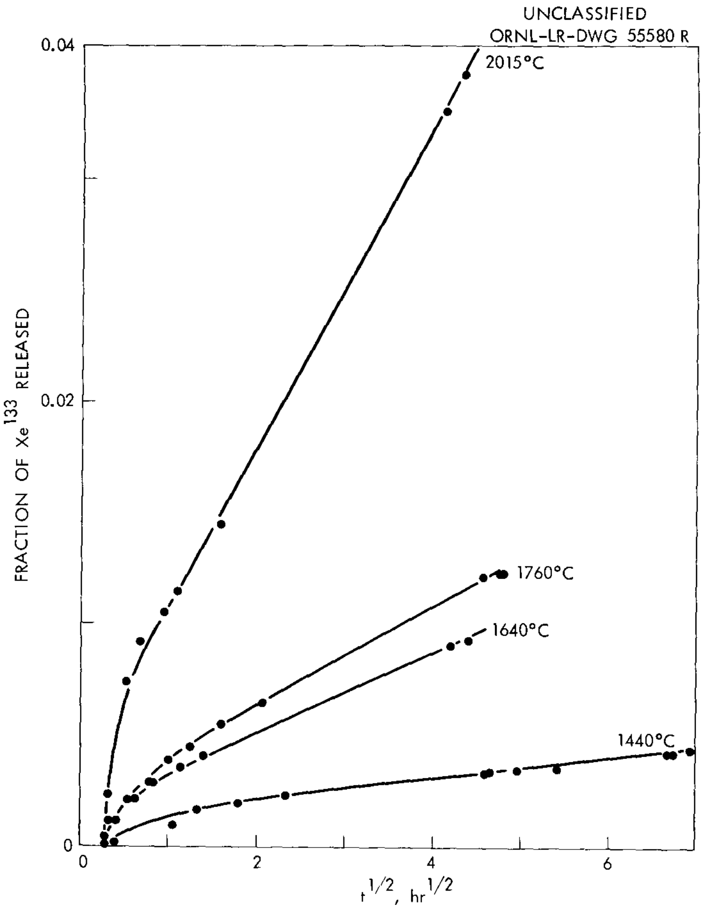

Fig. 3.10. Release of Xe-133 from $ThO_2$-5 wt % $UO_2$ prepared by the sol-gel process. Results obtained by neutron-activation technique.

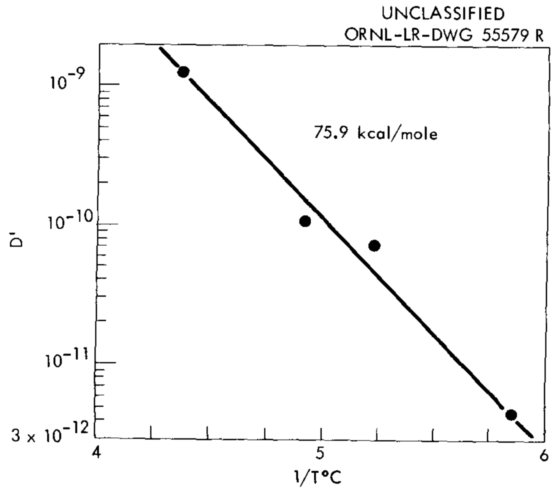

Fig. 3.11. Log D' vs 1/T for $ThO_2$-5 wt % $UO_2$ prepared by sol-gel process. $D' = D/a^2$ where D = diffusion coefficient and a = radius of the uniform sphere.

A neutron activation technique (12) was used for these experiments. Individual samples containing 0.2-0.6 mg of U-235 were irradiated to an integrated dose of $6.77 \times 10^{17}$ nvt in the graphite reactor and then heated in an induction furnace in a vacuum of about $10^{-3}$ mm Hg. The Xe-133 released was collected in a continuously monitored charcoal bulb.

## 4.0 VIBRATORY COMPACTION

Vibratory compaction is a relatively simple process for fabricating granular oxide fuel rods. Because of its simplicity, this fabrication technique is economically attractive for first-cycle $UO_2$ fuels and lends itself to remote operation in the recycling of Th-U-233 oxide fuels. Oak Ridge National Laboratory has been primarily interested in developing a simple vibratory compaction process capable of using the $ThO_2$-$UO_2$ fuels made by the sol-gel process. Other laboratories in the United States, e.g. Hanford, Savannah River, Combustion Engineering, General Electric (San Jose), and Babcock and Wilcox, have been interested primarily in developing vibratory compaction for arc-melted $UO_2$ fuels.

The fuel elements of a large number of heterogeneous reactors are composed of long cylindrical tubes which can be loaded in a vertical position by pouring in the granular oxide. Vibration of the tube during the pouring and for some time afterwards results in oxide bulk densities $> 90\%$ of theoretical (7,8,15). Of the many types of vibration energy sources available, only two have been used extensively, pneumatic vibrators of the reciprocating piston design and electrodynamic equipment. The two types give about the same results but represent extremes in cost, complexity, and flexibility. The pneumatic vibrator, which costs about $100 installed, is a simple air-driven piston in a cylindrical cavity with a restricted frequency range (approximately 100 cycles/sec), thrust range, and wave form. The electrodynamic vibrator, which costs upward of $20,000 installed, consists basically of a complex high-power audio-amplifier driving an electromechanical transducer. It has a wide frequency range, 50-5000 cycles/sec, and thrust range, and the wave form is limited only by the ability of the transducer to reproduce an electric signal. Because of its flexibility, it is a useful research tool in defining the vibration energy characteristics. Very little is known of the effects of such characteristics on the bulk density obtainable in fuel rods, but they appear to be of secondary importance (16,17) since results with the simple pneumatic vibrator and the electronic one operated under widely different conditions were comparable.

The primary factor that controls the bulk density of vibrated material is the particle size distribution, particularly where densities approaching 90% of theoretical are sought. Mixtures of coarse, medium, and fine size fractions of fused and ground $ThO_2$—3.4% $UO_2$ were pneumatically vibrated to a bulk density of $> 9.0$ g/cc. There is a small range of compositions (8) that will yield densities $> 8.80$ g/cc, the limits being 65 and 50% coarse (-10/+16), 35 and 10% medium (-70/+100), and 30 and 15% fine (-200). Ten minutes' pneumatic vibration of 55-25-20 $ThO_2$-3.4 wt % $UO_2$ gave a higher density product than did 15 min with size distributions used in electronic vibration of $UO_2$ (Table 4.1). Because of its greater thrust, a 1-5/8-in. vibrator gave a higher density product than a 1-1/4-in. vibrator with the same composition.

A mixture of only the coarse and fine fractions gave a product of 8.7 g/cc density, which is of interest because the expensive medium fraction is eliminated. For maximum economy, continuous particle size distributions offer the possibilities of decreasing the number of operations in the process and of completely using all the crude starting material. Continuous distributions prepared by selective grinding only, and using all the starting material, were compacted to bulk densities ranging from 8.5 to 8.7 g/cc.

While densities vs size fraction compositions have been determined experimentally, less tedious methods are desirable for estimating the density obtainable from a given particle size distribution. No satisfactory mathematical model is available that will accurately relate the composition and density of a mixture containing only two size fractions when shape is introduced as a variable, and irregular particles are desirable. However, an empirical procedure found which significantly decreases the number of experimental data required to determine the optimum composition (16, 17) consists in using a range of ratios of coarse to medium size grains and to each mixture adding fines, with vibration, until the bed appears saturated with fines. Several well chosen mixtures will define the area of interest for more detailed study.

The rod-to-rod reproducibility of bulk densities obtained by vibratory compaction is considered good (Table 4.2). Although there were variations from set to set, each run of a set was compacted under identical conditions. Among the sets the maximum deviation varied from ± 0.4 to ± 1.4% of the average density, while the average deviation varied from only ± 0.2 to ± 0.6%.

Granular $ThO_2$-$UO_2$ prepared by the sol-gel process with a 60-15-25 particle distribution was vibratorily compacted in capsules prepared for the NRX and OR reactors to bulk densities (Table 4.3) slightly less than those obtained with fused material (Table 4.1). The OR capsules contain an axial molybdenum thermocouple well and are very fragile. They were therefore vibrated for only 25-50% of the time usually used and only enough to yield the minimum bulk density required, 8.50 g/cc. The same lot (C) vibrated normally in the NRX capsule had a density of 8.70 g/cc. For vibration of lot D an OR capsule without a thermocouple well was used, giving a density of 8.77 g/cc.

Table 4.1 Bulk Densities Obtained with Various Particle Size Distributions of Fused $ThO_2$-3.4 wt % $UO_2$

Vibrations in type 304 stainless steel tubes nominally 19 in. long, NAVCO BH-1-1/4 in. pneumatic vibrator used in runs 1-6; a 1-5/8 in. one used in run 7; 10 min vibration in run 5, 15 min in other runs

| Run No.[a] | Composition, wt % of various particle size fractions[b] -6 +8 | -6 +10 | -8 +10 | -10 +16 | -10 +20 | -12 +20 | -16 +20 | -20 +30 | -30 +60 | -35 +70 | -70 +100 | -60 +200 | -200 | -325 | 2 to 4 µ | No. of Runs | Average Bulk Density, g/cc |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 40 | | 11 | | | 13 | | 7 | 4 | | | 2 | 23 | | | 4 | 8.71 |
| 2 | | 56 | | | | | | | | 24 | | | | 16 | 4 | 2 | 8.80 |
| 3 | | 48 | | | | | 4 | | | 24 | | | | 20 | 4 | 2 | 8.81 |
| 4 | | 50 | | | 12.5 | | | | | 17.5 | | | 20 | | | 4 | 8.77 |
| 5 | | | | 55 | | | | | | | 25 | | 20 | | | 1 | 8.94 |
| 6 | | | | 60 | | | | | | | 15 | | 25 | | | 5 | 8.85 |
| 7 | | | | 60 | | | | | | | 15 | | 25 | | | 5 | 9.02 |

[a] Distribution for runs 1-4 were the same as those used by other laboratories with fused $UO_2$

[b] Weight percent passing through (-) screen and retained on (+) screen (U.S. Standard Sieve Series).

### Table 4.2 Reproducibility of Bulk Density of Vibratorily Compacted $ThO_2$-$UO_2$

Tube material: type 304 stainless steel in sets A and C-F; aluminum alloy 1100 H14 in set B

Fuel material: fused $ThO_2$-3.4 wt % $UO_2$ in sets A-E; sol-gel prepared $ThO_2$-5 wt % $UO_2$ in set F

| | Nominal Tube Dimensions | | | | | | |
|---|---|---|---|---|---|---|---|
| Set | Length, ft | O.D., in. | Wall Thickness, in. | Runs Per Set | Bulk Density (arithmetic avg), g/cc | Avg Deviation (arithmetic), g/cc | Max Deviation, g/cc |
| A | 8 | 3/8 | 0.035 | 10 | 8.61 | ± 0.02 | ± 0.03 |
| B | 8 | 3/8 | 0.035 | 9 | 8.49 | ± 0.05 | ± 0.12 |
| C | 4 | 1/2 | 0.035 | 11 | 8.57 | ± 0.03 | ± 0.09 |
| D | 4 | 1/2 | 0.020 | 6 | 8.57 | ± 0.03 | ± 0.05 |
| E | 2 | 3/8 | 0.035 | 5 | 8.86 | ± 0.05 | ± 0.10 |
| F | ~1 | 5/16 | 0.025 | 8 | 8.69 | ± 0.03 | ± 0.04 |

### Table 4.3 Results of Vibratory Compaction of Sol-Gel-Prepared $ThO_2$-$UO_2$ in NRX and OR Reactor Fuel Tubes

| | | Nominal Tube Dimensions | | | |
|---|---|---|---|---|---|
| Lot | $UO_2$[a], wt % | Length, in. | O.D., in. | Wall Thickness, in. | Bulk Density, g/cc |
| A | 4.3 | 11 | 5/16 | 0.025 | 8.70 |
| B | 4.4 | 11 | 5/16 | 0.025 | 8.67 |
| C | 2.6 | 11 | 5/16 | 0.025 | 8.70 |
| | | 7 | 5/8 | 0.020 | 8.55 |
| D | 3.8 | 11 | 5/16 | 0.025 | 8.65 |
| | | 7 | 1/2 | 0.020 | 8.77 |

[a] Fully enriched in U-235.

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