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PREPARATION OF OXIDE FUELS FOR VIBRATORY COMPACTION
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ABSTRACT

This paper describes the sol-gel process for preparing thorium oxide containing uranium oxide for vibratory compaction loading of fuel elements. The sol-gel route for oxide preparation offers the advantage of producing coarse, dense particles of either ThO_2 or $\text{ThO}_2\text{-UO}_2$ while employing a calcination temperature of only 1150°C . This process is uniquely suited for remotely preparing oxide fuel containing U-233.

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This paper presents a description of the sol-gel process and of the mixed $\text{ThO}_2\text{-UO}_2$ made by this method. The process is being developed as a simple method of preparing dense particles of thorium oxide containing U-233 for fuel element fabrication by vibratory compaction. The handling of U-233 fuel is greatly complicated by the presence of U-232 and Th-228 in recycled fuel and fertile material because of the high-energy gamma radiation emitted by members of this decay chain. The amount of U-232 contained in U-233 recycled from thermal reactors will probably fall in the range from 400 to >1000 ppm of U-233. Considerable shielding, about 30 in. of concrete, is necessary for routinely handling recycled U-233 containing this level of U-232 on a production scale. For this reason it is desirable to develop processes for fuel preparation and fuel element fabrication that are readily adaptable to remote operation behind shielding. The alternative, remote operation of present procedures behind heavy shielding, would probably make the U-233 fuel cycle prohibitively expensive.

Vibratory compaction appears feasible as a method of loading oxide powders into fuel tubes and is readily adaptable to remote operation. To attain high fuel densities by vibratory compaction, it is necessary to use a powder with the proper particle size distribution and a particle density near theoretical. The sol-gel process is a simple, low-temperature method for making dense particles of ThO_2 containing UO_2 and the process is readily adaptable to remote operation.

Sol-Gel Process Description

The sol-gel process (Fig. 1) consists of four steps: denitration of thorium nitrate to prepare ThO_2 , dispersion of the thoria to a nitrate-stabilized sol in water, evaporation of the sol to form a gel, and calcination at 1150°C to form large, dense particles of oxide. The process is based on the fact that careful evaporation of a thoria sol and calcination of the resulting gel at the relatively low temperature of 1150°C produces large particles of dense ThO_2 . Satisfactory

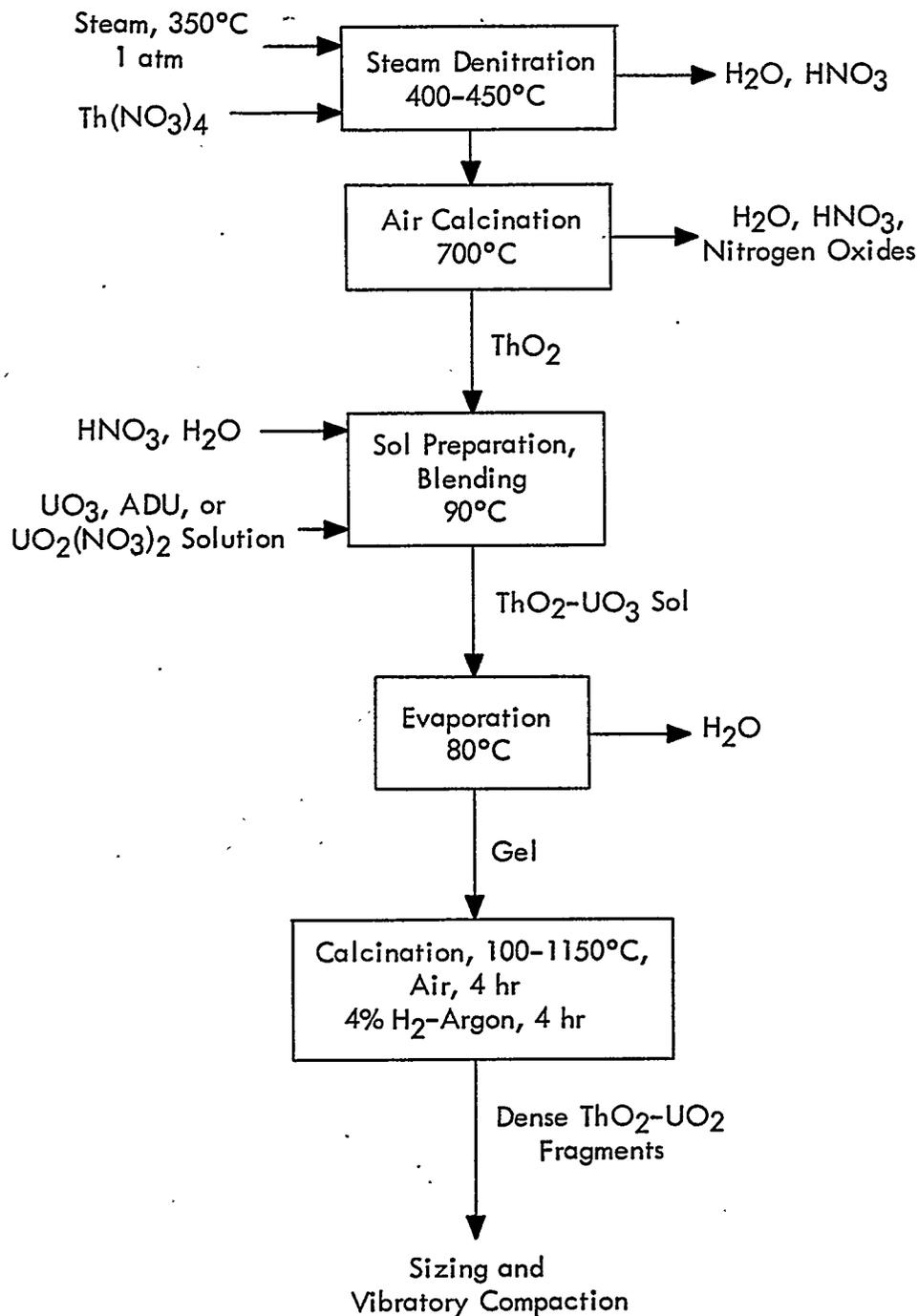


Fig. 1. Sol-gel process for preparation of dense thorium-uranium oxide.

ThO₂ for sol preparation may be made in several ways (1), but the simplest procedure is the hydrothermal denitration of the thorium nitrate. This step has been accomplished in a rotary calciner operated as indicated in the flowsheet. Steam is admitted to the calciner at 350°C and the temperature raised to 400-450°C. At the end of ~3 hr denitration, a granular, free-flowing thorium oxide is obtained which contains residual nitrate to the extent of 0.08 NO₃/ThO₂ (a N/Th ratio of 0.08). This oxide can be used without further treatment for sol preparation. However, if uranium is to be added as uranyl nitrate solution, it is expeditious to further calcine this oxide in air at 700°C for ~1 hr to remove the residual nitrate.

Thorium oxide made in this way is easily suspended in dilute HNO₃ or UO₂(NO₃)₂-HNO₃ solution by the shearing action of a centrifugal pump which breaks up the loose agglomerates of oxide to form the sol. The optimum concentration of nitrate for sol dispersion varies from a N/Th of 0.13 for a steam denitrated oxide to a N/Th of 0.10 for a 700°C air-fired oxide. These concentrations produce a pH of 3.0-3.5, which appears to be optimum for the correct dispersion.

The sol is next evaporated to dryness in shallow trays. A sol depth of 3/4 in. appears best with a drying temperature of 80°C. It is important not to boil the sol after it has become plastic, since this produces a porous gel. Upon setting to a gel, the material will fragment with a characteristic particle size which depends primarily on the nitrate content. The nitrate concentrations given in the flowsheet produce large, centimeter size, particles.

At the gel stage the particles have a density of 5-6 g/cc and still contain water and nitrate. These gel fragments may be calcined rapidly without further fragmentation. After 4 hr at 1150°C in air the contained uranium can be converted to UO₂ by changing to an atmosphere of argon containing 4% hydrogen for an additional 4 hr. The oxide is cooled to room temperature in pure argon to avoid adsorption of reactive gases and is then ready for sizing and vibratory compaction.

Denitration of Thorium Nitrate

Denitration of hydrated thorium nitrate starts at about 200°C in the presence of either air or steam and is essentially complete at 520°C (Fig. 2). The advantage of steam denitration over denitration in air is twofold: the nitrate is removed as easily condensable HNO₃ instead of oxides of nitrogen, and the resulting oxide is more easily dispersed in water.

On a laboratory scale, it was found that reaction temperature was the major controlling variable on the final nitrate content of hydrothermally denitrated thorium nitrate (2). The reaction was essentially complete in 1 hr at all temperatures tested between 370 and 450°C. In this temperature range the residual nitrate content decreased as the temperature increased (Fig. 3). Extrapolation of this plot and independent thermogravimetric studies indicate that the nitrate is essentially removed at about 520°C. However, even at this temperature chemically bound water is still present in the ThO₂ to the extent of about 1.5 g H₂O/100 g of ThO₂.

In scale-up studies, denitration was successfully carried out in an agitated trough calciner on a 5-kg-batch scale. This device had the disadvantage that ThO₂ carryover with the steam was >10% because of the method of agitation. However, a reproducible oxide was prepared (Table 1).

Table 1. Reproducibility of the N/Th Ratio for Fixed Run Times Using 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 |

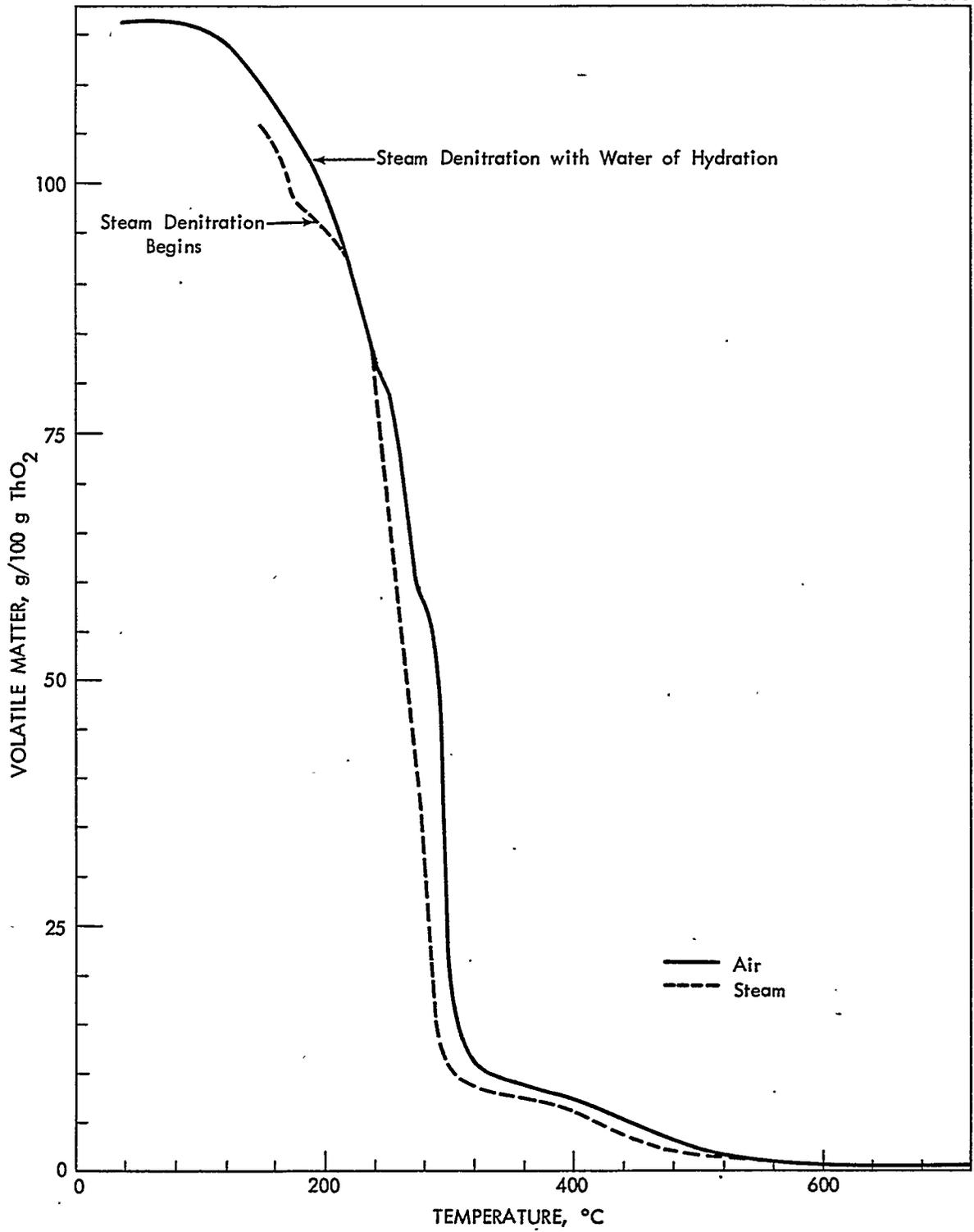


Fig. 2. Thermogravimetric analysis of $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ at $6^\circ\text{C}/\text{min}$ rise rate in steam and air.

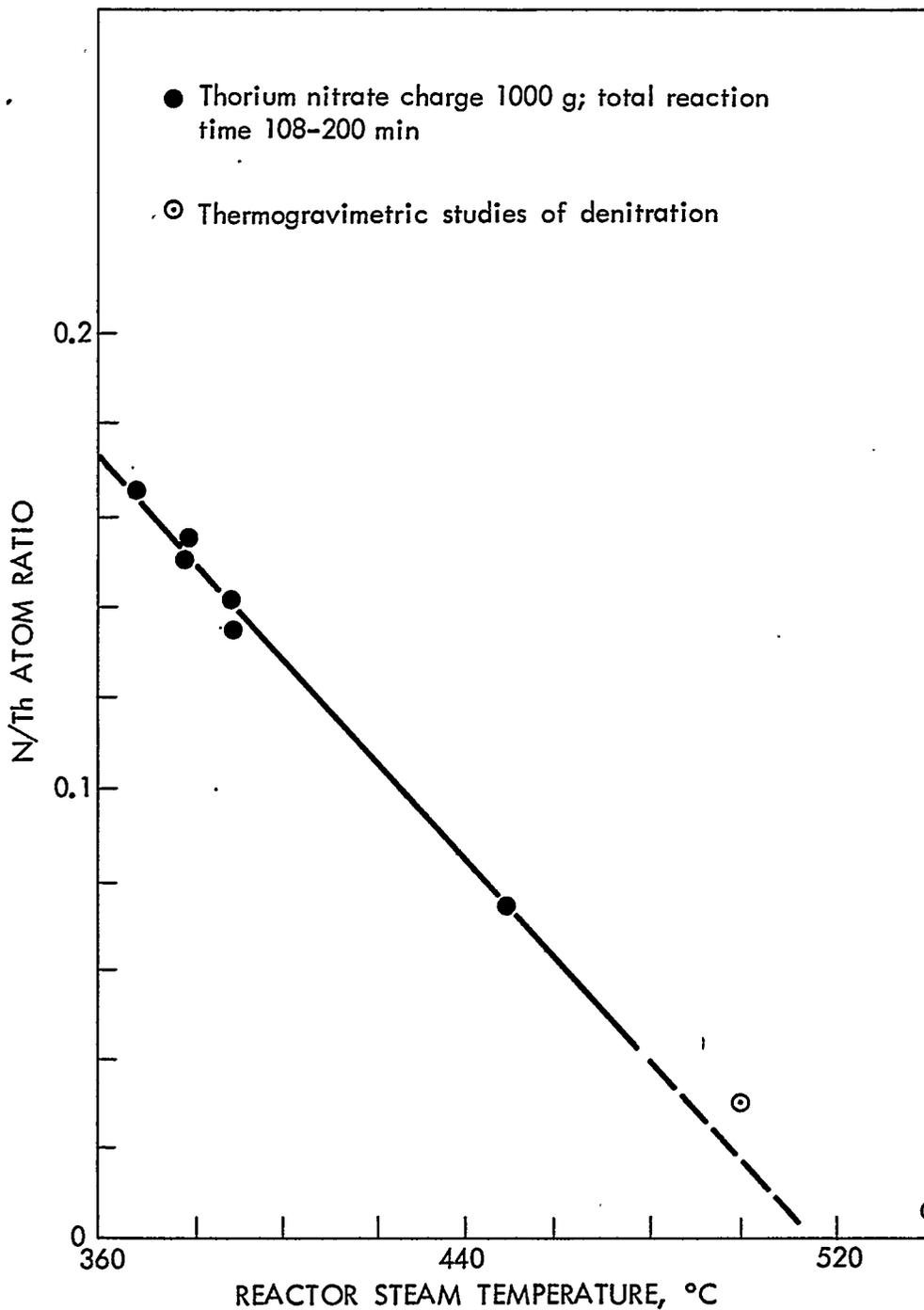


Fig. 3. Effect of reaction temperature on residual nitrogen in denitration of thorium nitrate.

The denitration was also carried out in a rotary calciner on a 15-kg-batch scale. The thorium nitrate was charged as $\text{Th}(\text{NO}_3)_4 \cdot 4.5\text{H}_2\text{O}$ crystals, but could as easily be added as a concentrated thorium nitrate solution from a Thorex plant. Steam at a flow rate of 40 lb/hr is superheated to 350°C with an electric superheater and the calciner is mounted in an electric furnace for temperature control. About 8 hr is required for a batch, of which 3 hr is actual denitration time. The final temperature reached was 425°C , which produced an oxide containing a residual nitrate content of 0.08 N/Th.

Sol Preparation

The most important single factor that determines whether a water- HNO_3 suspension of ThO_2 is dispersed or flocculated is the hydrogen ion concentration in the solution phase, the optimum range being 10^{-4} to 10^{-2} M H^+ (3,4,5). At 10^{-2} M H^+ , ThO_2 dissolves slowly and at $\sim 10^{-4}$ M H^+ , flocculation occurs. To keep the solution phase of a sol in this range during evaporation from a 2 M ThO_2 sol to a gel requires that the starting H^+ concentration be in the range 10^{-3} to 10^{-4} M (pH 3 to 4). In practice the optimum pH was found to be 3.0-3.5. A sol of ThO_2 made from oxide denitrated at 450°C , with a final N/Th ratio of 0.13-0.15, has a pH in this range after aging for 12 hr at 100°C . For an oxide air fired to 700°C after steam denitration, less nitrate, a N/Th ratio of ~ 0.10 produces this pH and aging is not necessary.

When ThO_2 containing the optimum nitrate concentration is added to water, a stable sol of about 2 M ThO_2 can be produced. Conversely, addition of water to the oxide produces a gummy mass which is difficult to disperse. When oxide containing significantly less nitrate is used, dispersion is incomplete and a rapidly settling oxide heel remains. When ThO_2 with significantly more nitrate is used, a soft flocculent precipitate forms which can be dispersed by addition of water. However, oxide particles made from such sols were glassy with many cracks and were unsuitable for vibratory compaction.

On an engineering scale, 7.5-kg batches of ThO_2 were successfully dispersed by a centrifugal pump which provided agitation and broke up the loose ThO_2 agglomerates. The pump takes its suction from the bottom of a cone-shaped tank and discharges back into the top of the tank. As soon as the ThO_2 is dispersed, uranium, if desired, can be added directly to the same tank.

Uranium Addition

Up to 10 mole % uranium may be added to the ThO_2 sol as UO_3 or ammonium diuranate. A solution of uranyl nitrate may also be used, provided that the nitrate content of the original ThO_2 is adjusted to compensate for that added with the uranium. This becomes difficult for uranium concentration above 3%, but has been accomplished at that level with several samples by 700°C air calcination of the ThO_2 before suspension. A 2 hr digestion at 90°C after uranium addition appears adequate to ensure a homogeneous product with respect to the U/Th ratio.

Sol Drying

The sol is converted to a glassy gel by careful evaporation, the primary requirement being not to boil the sol. With a 2 M ThO_2 sol, the optimum depth in the drying trays is $3/4$ in. and the optimum temperature $80-90^\circ\text{C}$. In the tray dryer used in these studies a production rate of 1500 g/day per square foot of drying surface was easily attained.

Calcination

Studies of the calcination of ThO_2 and mixed $\text{ThO}_2\text{-UO}_3$ gels in both air and hydrogen indicate maximum densification at 1150°C (Fig. 4). For oxides containing uranium, calcination in air gave consistently higher density, $>99\%$ of the theoretical 10.0 g/cc. However, strangely, calcination in hydrogen produced a more dense pure ThO_2 .

The rate of temperature rise during the calcination step does not appear to be a critical variable. Raising the temperature to 500°C in as short a time as 2 hr does not break up the gel particles, and the rate of temperature rise

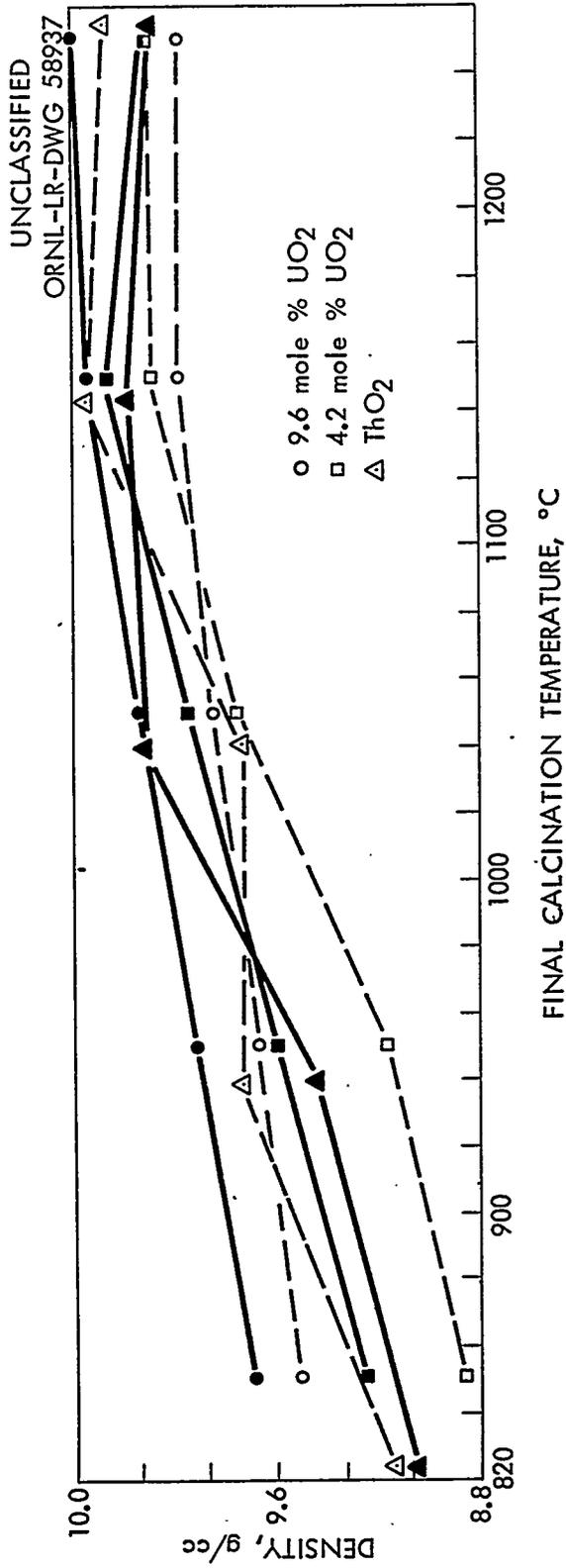


Fig. 4. Effect of final calcination temperature on density of mixed uranium and thorium oxides fired in air (solid lines) and hydrogen (dashed lines).

between 500 and 1150°C is immaterial. A calcination time of 4 hr at 1150°C was adequate to produce maximum densification.

Following the 4 hr calcination in air, an additional 4 hr at 1150°C in a mixture of 96% argon-4% hydrogen (a nonexplosive gas when mixed with air) is required to reduce the uranium from U_3O_8 to UO_2 . Oxygen/uranium ratios of <2.01 were obtained with this procedure. After the uranium reduction step, the furnace should be purged with pure argon and the oxide cooled to room temperature in an argon atmosphere to avoid absorption of oxygen or hydrogen.

Properties of Oxide Prepared by the Sol-Gel Process

Some typical properties of mixed ThO_2-UO_2 made by the sol-gel process on a laboratory scale are given in Table 2. All the preparations were intended for in-pile irradiation testing and contain enriched uranium. All except sample C were loaded into the small irradiation capsules to a bulk density of 8.7 g/cc or greater by vibratory compaction (6). Sample C, which was compacted to only 8.4 g/cc, was prepared from a ThO_2 containing excess nitrate. The excess nitrate was destroyed at the sol step by reaction with formic acid, but the density was only 9.76 g/cc, and the material was exceptionally tough and difficult to size for vibratory compaction.

Samples A and B were prepared early in the laboratory studies by slightly different procedures; samples D and E were prepared by the procedure described in this paper. The major improvements effected by the changes in procedure were decreased surface area and lowered volatile matter content of the product.

It should be noted that the material prepared by this method is polycrystalline with a crystallite size of about 2000 Å as measured by x-ray diffraction line broadening. These crystallites, however, must be very tightly packed together to attain the very high density, $>99\%$ of theoretical, and the low nitrogen surface areas, 0.01 m²/g.

Table 2. Summary of Properties of Sol-Gel-Prepared Uranium-Thorium Oxides Used in Fabrication of Irradiation Specimens

| | A | B | C | D | E |
|---|---------|---------|---------|-------|---------|
| Total U, wt % | 4.31 | 4.39 | 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 |
| Lattice parameter, Å | 5.59121 | 5.59189 | 5.59263 | - | 5.59300 |
| Crystallite size | 2400 | 1700 | 2200 | - | - |
| Particle density, g/cc | 9.94 | 9.92 | 9.76 | 9.97 | 9.92 |
| Chromium, wt % | 0.00034 | 0.00054 | - | - | - |
| Nickel, wt % | 0.0023 | 0.013 | - | - | - |
| Chloride, ppm | <5 | <5 | <10 | - | - |
| Volatile matter released in vacuum at 1200°C, cc/g | 0.305 | 0.373 | 0.055 | 0.012 | 0.027 |

A photograph of a mixed $\text{ThO}_2\text{-UO}_2$ sample at low magnification is shown in Fig. 5 and an electron photomicrograph of a fracture surface replica at high magnification in Fig. 6. The apparent grain size in the photomicrograph is about 5000 \AA , which is larger than the crystallite size determined by x-ray diffraction line broadening. This discrepancy may be due to strain broadening of the x-ray pattern.

With the range of parameters covered in these studies, small variations in process conditions did not affect the usefulness of the product for vibratory compaction (Table 3). Some of the products made without air calcination compacted well; however, more consistently good results were obtained from air-calcined ThO_2 . The last run in Table 3 illustrates the effect of excess nitrate in the sol.

A standard powder sizing and vibratory compaction technic was used on these materials. This technic, which is described in "Vibratory Compaction Studies at ORNL," by W. S. Ernst, Jr. in this symposium, is also under development and the results given here may be significantly changed by additional vibratory compaction development.

Oxide prepared by the sol-gel process has been studied for fission gas release. Results of these studies and the irradiation testing of sol-gel oxides are given in "Nonsintered Fuel Irradiations," by W. C. Thurber in this symposium.

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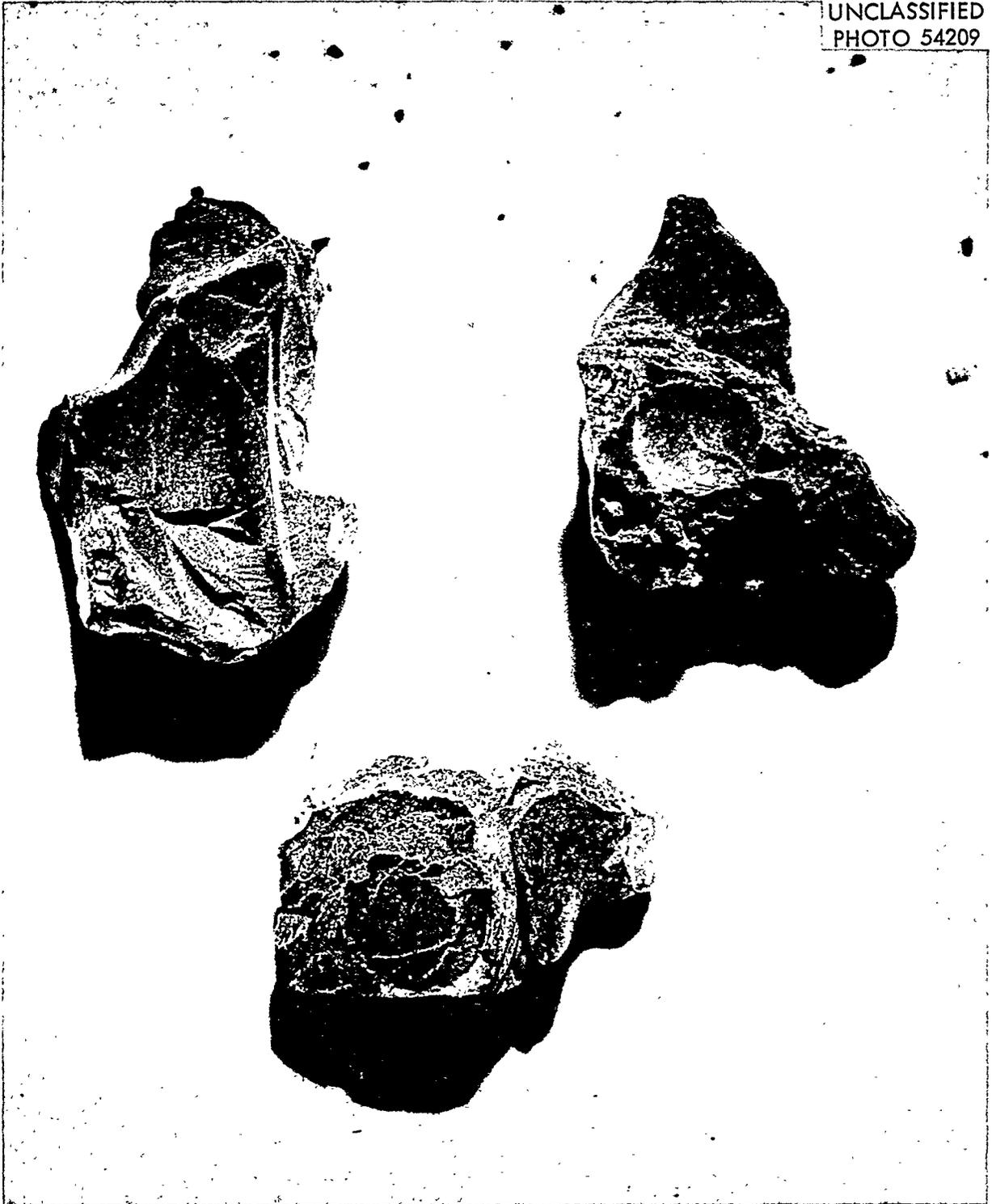


Fig. 5. ThO₂-5% UO₂ particles prepared by sol-gel process (12X).

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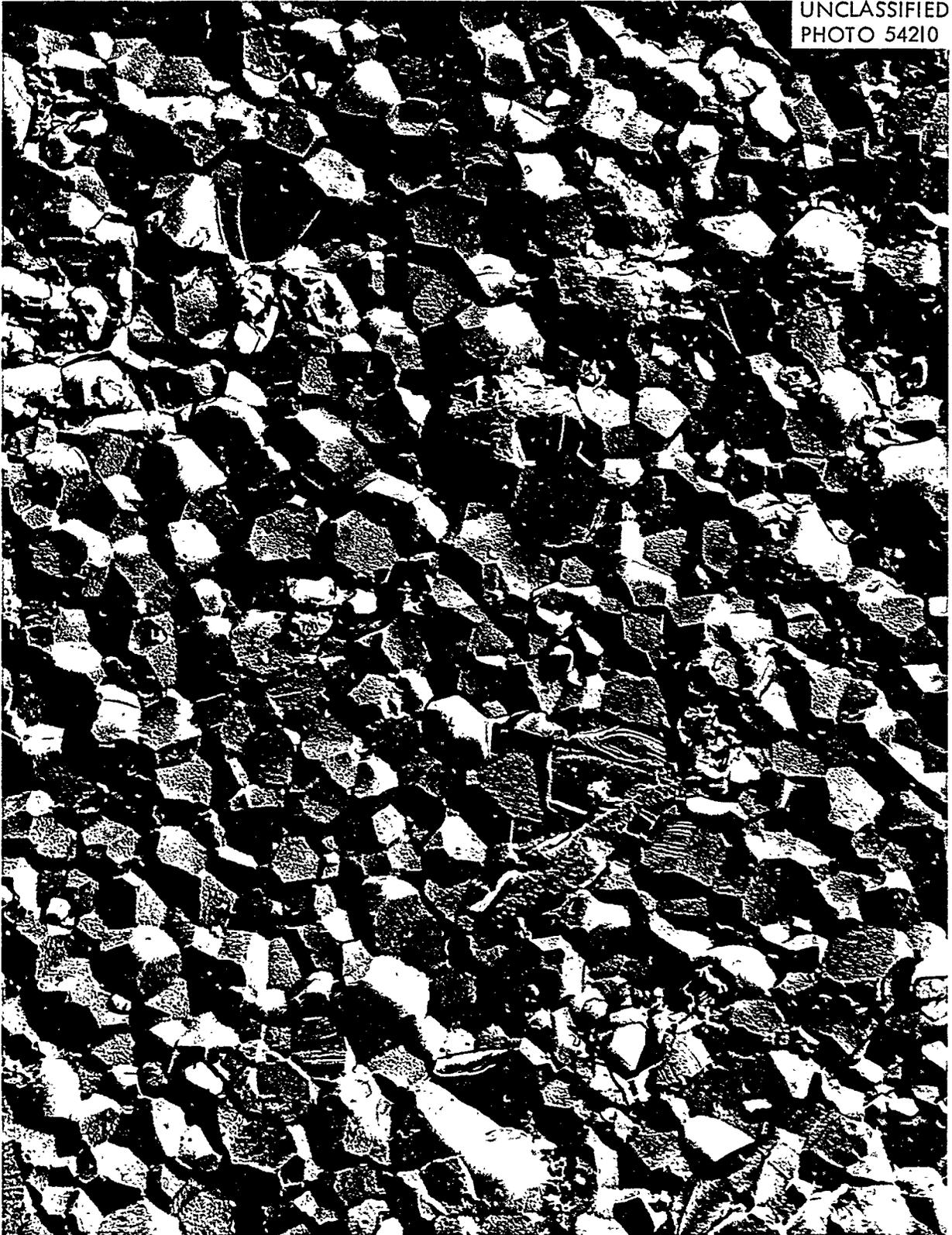


Fig. 6. Surface replica of ThO₂-5% UO₂ sol-gel oxide (20,000X).

Table 3. Results of Vibratory Compaction of Oxide Prepared by Sol-Gel Process

Thoria prepared in agitated trough denitrator on 5-kg scale; 3.8 wt % uranium added as ammonium diuranate; oxide sintered at 1150°C before H₂ reduction

| Final Steam Denitration Temp, °C | Air Calcination Temp, °C | N/Th Ratio of ThO ₂ | N/Th Ratio of Sol | Sol Drying Depth, in. | Batch Size, kg | Bulk Density after Vibration, g/cc | |
|----------------------------------|--------------------------|--------------------------------|-------------------|-----------------------|----------------|------------------------------------|------------------|
| | | | | | | 5/16-in.-dia Tube | 1/2-in.-dia Tube |
| 400 | None | 0.09 | 0.13 | 1 | 1.5 | 8.4 | 8.6 |
| | | | | 1.5 | 1.0 | 8.6 | - |
| | | | | 2 | 0.8 | 8.7 | - |
| 425 | None | 0.06 | 0.13 | 2 | 5.5 | 8.3 | - |
| 425 | 450 | 0.04 | 0.13 | 0.75 | 0.4 | 8.6 | - |
| | | | | 1.0 | 0.8 | 8.8 | - |
| | | | | 2 | 0.6 | 8.5 | 8.5 |
| 425 | 700 | ~0 | 0.09 | 2 | 0.9 | 8.7 | - |
| 425 | 700 | ~0 | 0.09 | 2 | 0.9 | 8.7 | - |
| 425 | 700 | ~0 | 0.13 | 1 | 2.0 | 8.4 | - |
| | | | | 2 | 2.9 | 8.4 | - |

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