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FUEL CYCLE DEVELOPMENT:

SEMIANNUAL PROGRESS REPORT

FOR PERIOD ENDING MARCH 31, 1961

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CHEMICAL TECHNOLOGY DIVISION
METALLURGY DIVISION
REACTOR CHEMISTRY DIVISION

FUEL CYCLE DEVELOPMENT: SEMIANNUAL PROGRESS REPORT

For Period Ending March 31, 1961

D. E. Ferguson
Project Leader

DATE ISSUED

JUL 18 1961

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ABSTRACT

Flowsheet conditions for the sol-gel process were further optimized to improve the quality of the product and simplify the process. Using the improved procedure, a mixed oxide containing enriched uranium was prepared which consistently vibratorily compacted to 8.7 g/cc in short 0.25-in.-dia tubes. Eight such tubes were inserted in the NRX reactor where they are now under irradiation at an estimated heat flux of 370,000 Btu/hr·ft^2. The rate of fission gas release from sol-gel mixed thorium-uranium oxide was measured. For this oxide the rate of xenon release was diffusion controlled up to about 2200°C, where sublimation appears to start. This change in mechanism of release occurs at about 1800°C for UO_2; otherwise the release rates appear qualitatively the same for both oxides.

Increasing the time of vibratory compaction from 10 min to 1 hr resulted in an increase of only 1% in final packed density. Adding a 0.4-lb load to the top of the oxide in the tube increased the final compacted density by another 1.5%. Studies of mixed oxide samples were made to determine the number of phases present, the O/U ratio, unit cell sizes, refraction index, and homogeneity. An apparatus was constructed and calibrated to determine the area of stability for the fluorite phase by measuring dissociation pressures of the solid solutions of ThO_2 and UO_2.

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1.0 INTRODUCTION

The purpose of the Fuel Cycle Program is to develop an economic method of recycling uranium-233 and thorium to heterogeneous reactors. In the irradiation of thorium, U-232 is formed which cannot be chemically separated from the U-233. The U-232 decays to daughter products that emit high-energy γ rays. In any practical refabrication scheme, operations must be carried out remotely behind shielding. In order to make remote operation economically feasible, the process used must be simple. For this reason, vibratory compaction was chosen as a means of filling fuel tubes which was readily adaptable to remote operation. The sol-gel process is being developed as a simple low-temperature method for preparing mixed thorium-uranium oxide particles suitable for vibratory compaction.

Reported here are the thorium fuel cycle studies for the period September 30, 1960, to March 31, 1961. Earlier work is reported in ORNL CF's 60-5-41, 60-11-56, and ORNL-2965.

Acknowledgment is made to the Analytical Groups of W. R. Laing, G. R. Wilson, C. Feldman, and P. A. Thomason, and to C. W. Greene, whose services have made this work possible.

2.0 PREPARATION OF DENSE ThO_2 and UO_2-ThO_2

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J. W. Snider

About 40 kg of ThO_2 and 1.5 kg of mixed oxide were prepared in the laboratory rotary calciner (Fig. 2.1) by batch steam denitration. Approximately 10 kg of the ThO_2 was converted to dense 3.9-5% uranium-thorium oxide fragments for vibratory compaction tests and the remainder to dense ThO_2 fragments. From 1 kg of mixed oxide, containing 4.39% of 93% enriched uranium, six 0.25-in.-i.d. by 10-in. test capsules were fabricated by vibratory compaction for irradiation in the NRX reactor. A similar batch prepared from another ThO_2 material by the sol-gel process (1) was also fabricated into fuel test specimens. All 12 specimens were vibrated to a bulk density of 8.7 g/cc $\pm$ 1%. Eight of the 12 specimens are now under irradiation in the NRX.

As a result of the experiments the previous flowsheet (1) for the sol-gel process was modified to further optimize the process variables (Fig. 2.2). In the new flowsheet an N/Th atom ratio of 0.13-0.15 is recommended for the precursor oxide, the sol is aged, the ThO_2 concentration is specified in sol preparation, uranium is added to the aged sol as ammonium diuranate,* uranium oxide, or uranyl nitrate solution, the firing temperature is lower, and the hydrogen-fired fragments are cooled in argon instead of hydrogen.

*ADU.

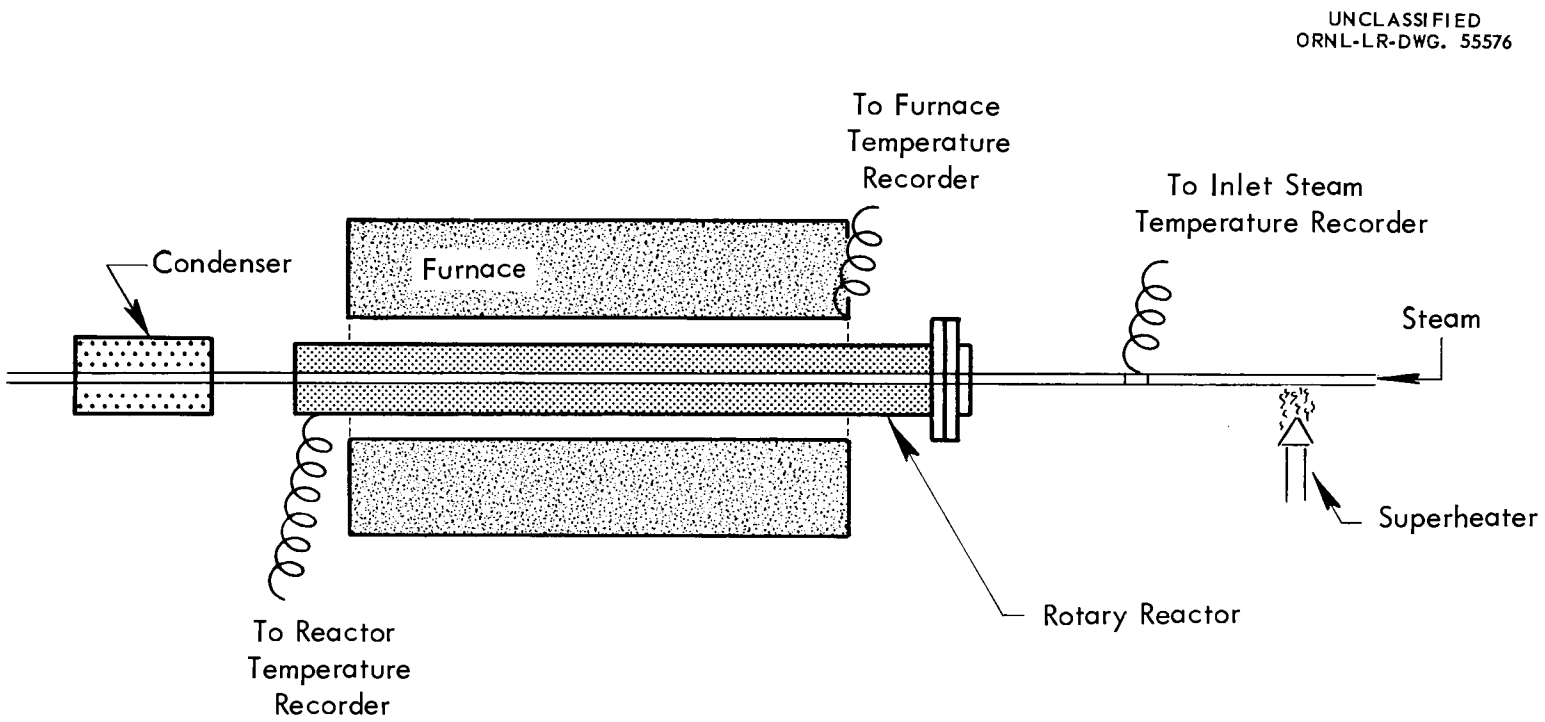

Fig. 2.1. Apparatus for laboratory scale thorium nitrate denitration.

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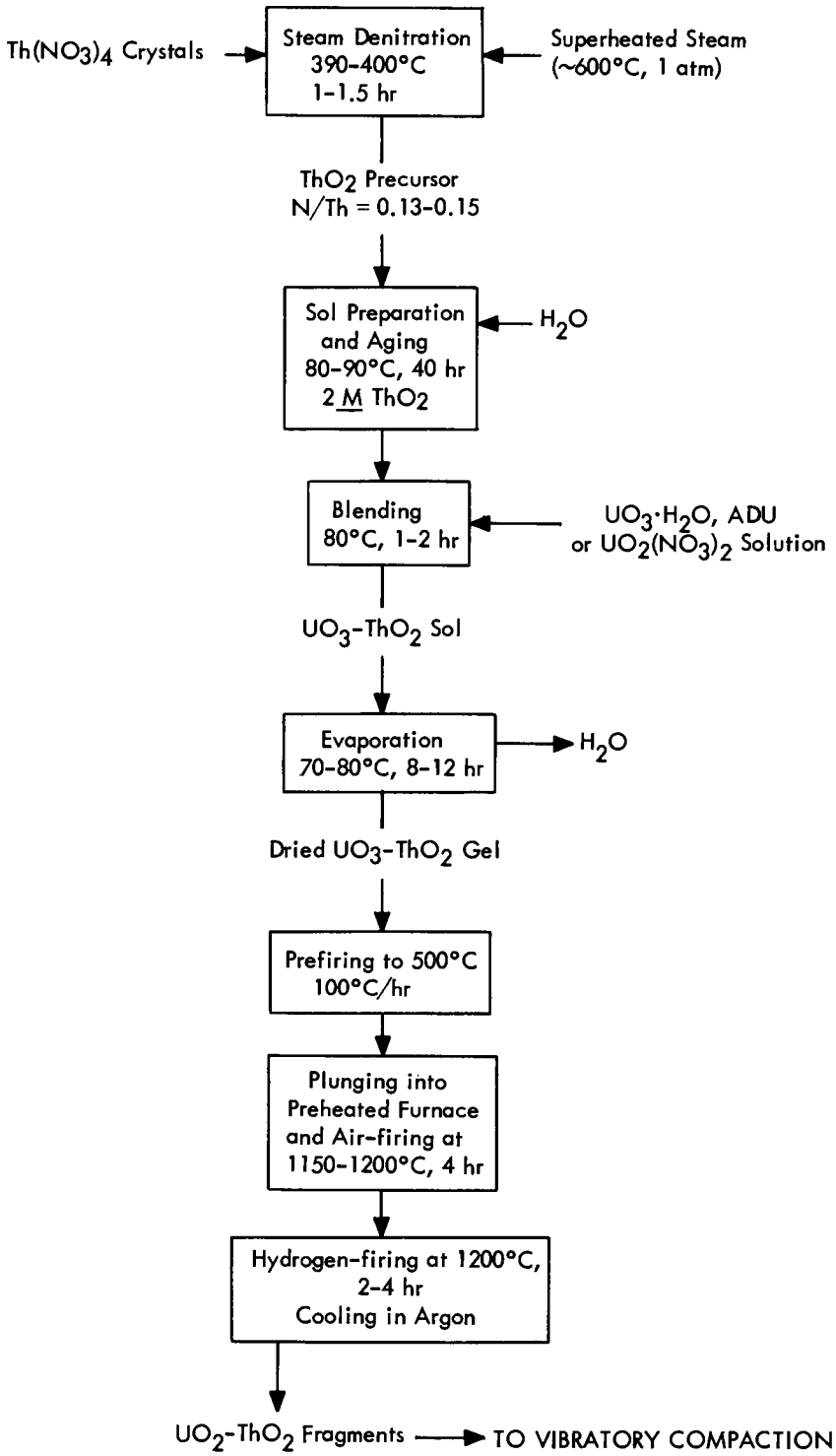

Fig. 2.2. Schematic flowsheet for the sol-gel process.

2.1 Steam-denitration Tests

Thorium oxide was prepared in 14 runs and mixed oxide in 3 to determine optimum operating variables (Table 2.1). In the laboratory calciner, optimum conditions for producing products with N/Th ratios from 0.13 to 0.15 were ~1000 g of thorium nitrate, 40 g/min of steam entering at 600°C for ~1 hr (temperature inside reactor 110-330°C), followed by cutting the steam flow to ~10 g/min for an additional hour at 390°C. To prevent "burning" the oxide the reactor wall should not exceed 330°C until after the reactor temperature exceeds 330°C, and it should never exceed 450°C. If a lower (0.07-0.09) N/Th ratio is desired, the final reactor temperature can be raised to 450°C.

Five runs in the rotary calciner were analyzed in detail by determination of acid, nitrate, and thorium in the off-gas (see Figs. 2.3 and 2.4 for typical runs 60 and 61). In run 60 a significant fraction of the heat that decomposed the nitrate was furnished by the furnace, whereas in run 61 heat of decomposition was furnished by the steam, the furnace acting only as a thermal guard. In both runs significant decomposition began at 280°C and was about 80% complete at 330°C. Considerable brown fuming was noted in run 60 at 60 min (310°C), indicating that the decomposition reaction changed from the mechanism of displacement of nitrate to thermal destruction of the nitrate ion. Such decomposition leads to the production of a difficultly dispersible fraction of product and is generally to be avoided. While the denitration in run 60 stopped at 180 min as compared to 230 min in run 61, the residual nitrate value in run 61 was lower, which is important in making good-quality fragments. Because thoria entrainment is greatest after the reactor reaches its maximum temperature, time and steam flow are minimized at this stage.

2.1.1 Control of Residual N/Th Atom Ratio in Steam-denitrated Thoria Products. The results of vibratory compaction tests indicated that the best particles are made from thoria preparations with a N/Th atom ratio of 0.13-0.15. At 550°C, the residual volatile material in steam-denitrated thorium oxide is ~1.5 g/100 g ThO_2. An inflectional point at this temperature in the curves of weight loss on heating vs temperature in 20 preparations (see Fig. 2.5 for three of them) indicates a change in the decomposition mechanism at this temperature, and extrapolation to the intercept N/Th = 0 suggests that the nitrogen may have been totally removed at 550°C and that the 1.5% volatile residue is water. Curves for oxides prepared at different temperatures and times differed only in the lower temperature regions. All samples showed a pseudostability range with a midpoint at 300°C, and plots of the values for residual volatile matter at these midpoints vs the N/Th atom ratio and the grams of nitrate per 100 g of ThO_2 were straight lines (Fig. 2.6).

Table 2.1. Batch Steam Denitration of Thorium Nitrate

Reactor: 4-in.-i.d. 12-in.-long stainless steel rotary calciner; gas-fired steam superheater; reactor walls thermally guarded by a 5-in.-dia tube furnace

	Conditions of Denitration						Properties of ThO_2 Product			
	Temp, °C		Time, min							
Run No.	Final Reactor Steam[a]	Highest Furnace Wall	From Introduction of Steam	At Max. Temp	Thorium Nitrate Charge,[b] g	Average Condensate Rate, ml/min	Wt, g	ThO_2 Entrainment, %	N/Th Atom Ratio	Chemically Bound Volatile Matter,[c] g/100 g ThO_2
20	390	150	168	68	979	52	404	15	0.183	5.14
22	390	415	120	68	978	51	443	6.4	0.142	4.21
23	380	405	183	93	1030	23	464	7.5	0.150	4.30
24	390	400	153	93	1050	23	470	5.9	0.136	4.02
25	370	395	153	93	1060	23	481.5	5.0	0.166	4.80
26	405	410	148	93	1003	39	446.0	7.5	0.104	3.52
27	380	410	133	93	979	40	450.5	6.0	0.156	4.62
33	450	475	110	10	1000	43	433.5	9.6	0.074	2.55
48	390	465	480	405	1034	33	444.5	10.0	0.104	3.45
55	395	340	480	94	1470	19	692	2.7	0.215	-
56	390	320	475	60	1517	19	721	2.0	0.221	-
60	390	445	215	90	1027	19.6	484.5	0.75	0.179	-
61	395	430	230	110	1172	20.2	524	2.8	0.155	-
63	320	330	240	120	1134	21.6	507.5	9.5	0.268	-
41[f]	395	440	130	60	1035	25	497	1.03	0.118	4.40
42[g]	405	450	143	60	1028	26	491	1.64	0.117	3.45
43[h]	420	465	130	60	1141	27	551	0.67	0.095	3.00

[a]Temperature taken from thermocouple probe at center of reactor.

[b]Average determinations: 46.3% ThO_2; 42.55% NO_3^-; balance H_2O.

[c]Determined by thermogravimetric analyses between "stability ranges" at 300 and 1000°C.

[d]About 20% of the product adhered to the calciner walls at the end.

[e]80% of product free flowing.

[f]4.26% uranium added to calciner as 2 M $UO_2(NO_3)_2$ solution.

[g]4.06% uranium added to calciner as 2 M $UO_2(NO_3)_2$ solution.

[h]4.29% uranium added to calciner as 2 M $UO_2(NO_3)_2$ solution.

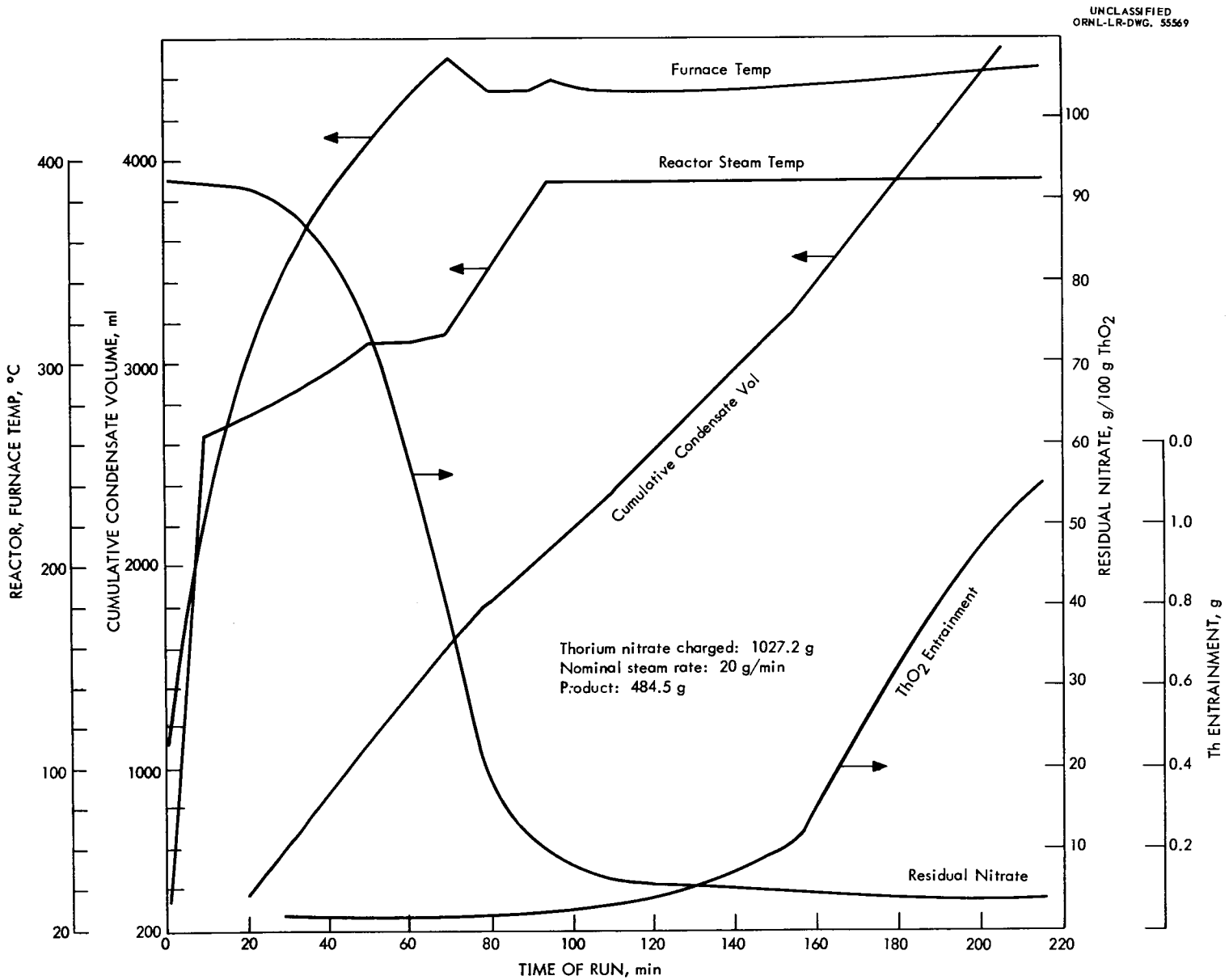

Fig. 2.3 Steam denitration of thorium nitrate, run 60.

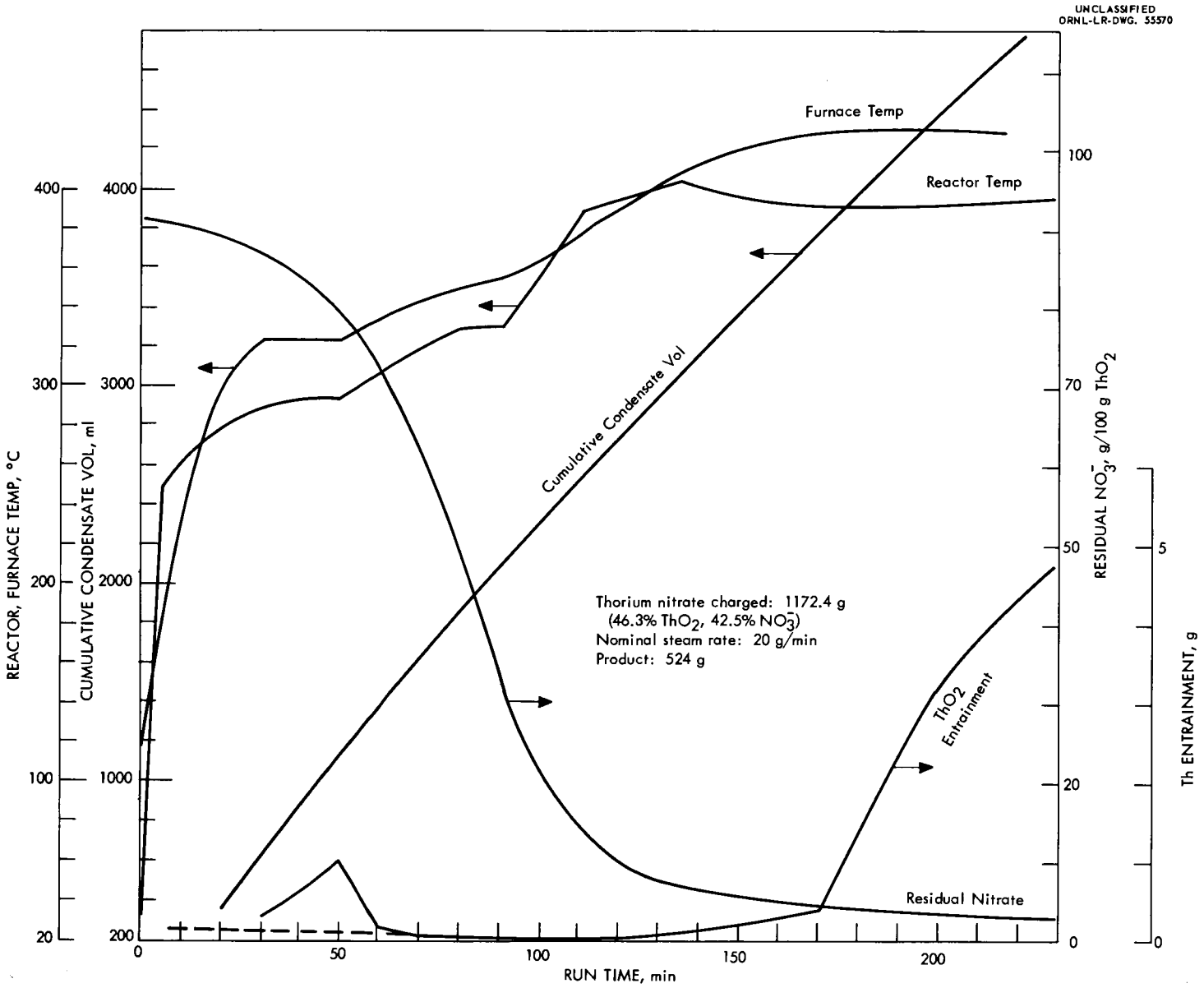

Fig. 2.4 Steam denitration of thorium nitrate, run 61.

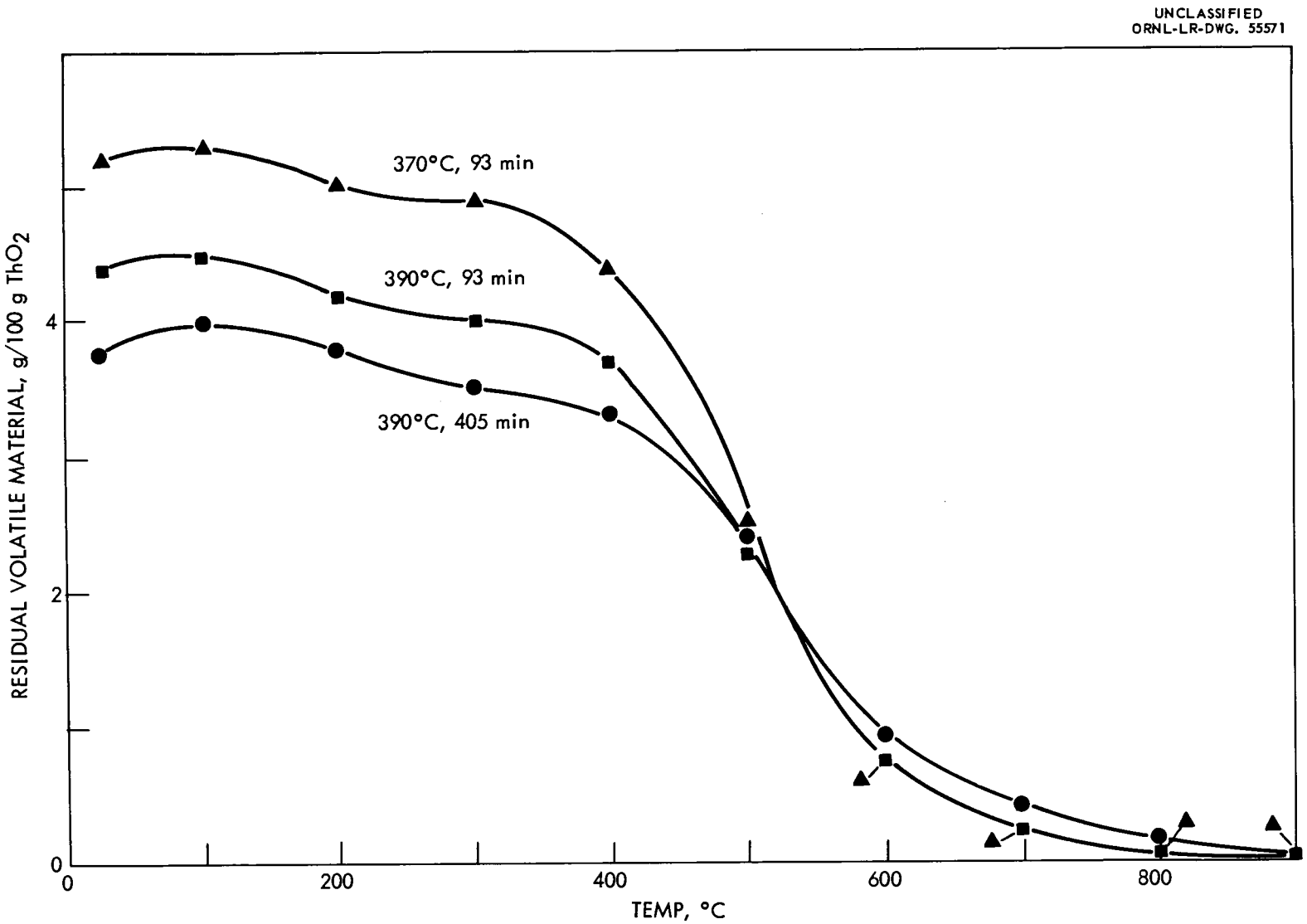

Fig. 2.5. Residual volatile matter in steam-denitrated thorium oxide preparation as a function of temperature to which the preparation is heated. Temperature rise rate 1°C/min.

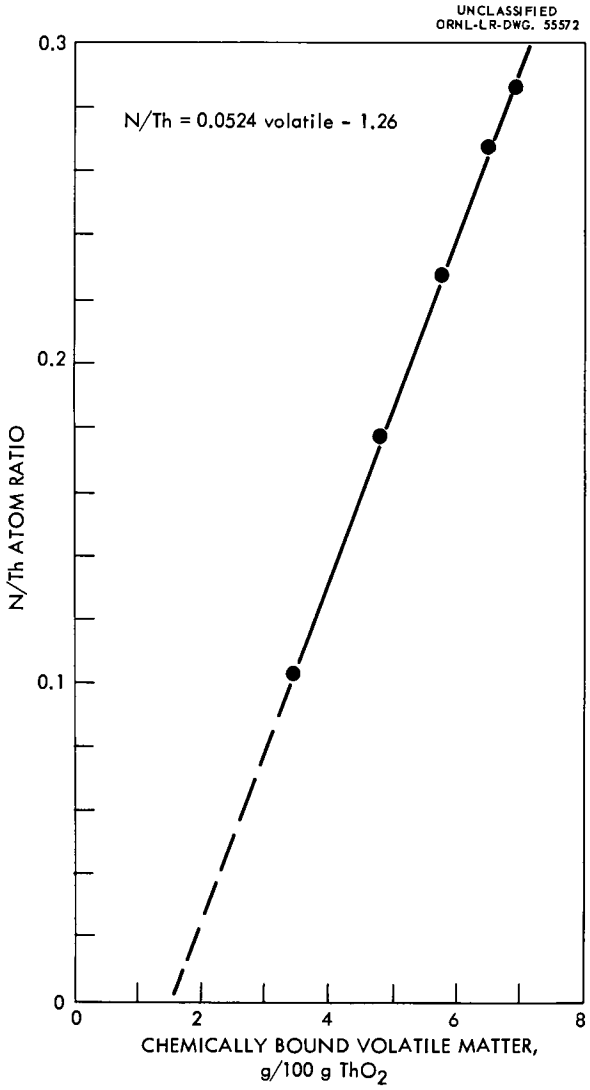

Fig. 2.6. Nitrogen content of steam-denitrated ThO_2 as a function of chemically bound volatile matter.

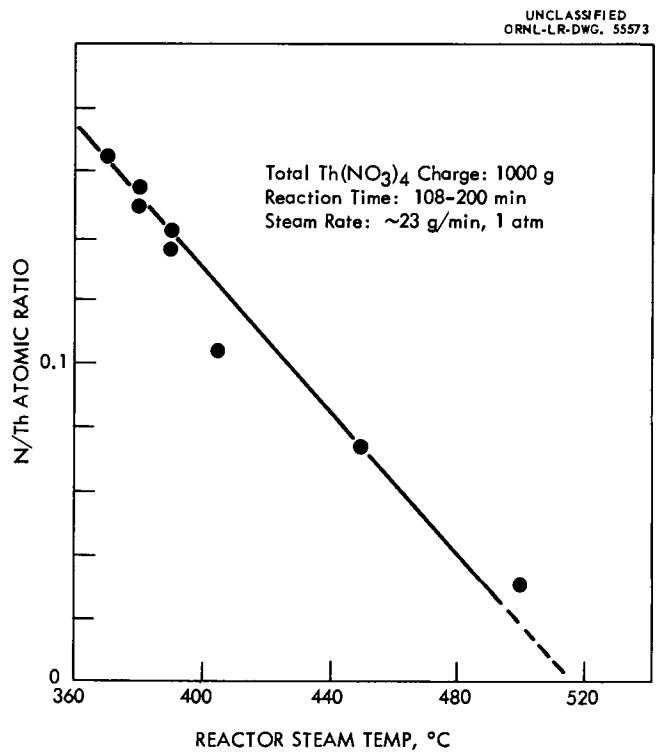

Fig. 2.7. Effect of reaction temperature on residual nitrogen in denitration of thorium nitrate.

A reasonably accurate analytical method for small amounts of nitrogen in large amounts of thoria has only recently been established, and further work is needed to increase its reliability. If the above correlation between residual volatile matter and the N/Th ratio proves accurate, determination of the residual volatile matter at 300°C will provide an easy method of detecting the nitrogen content of the denitration products.

2.1.2 Variables Affecting the Residual Nitrogen Content of Steam-denitrated Products.

Temperature. The temperature had the greatest effect of any variable on the rate of nitrogen removal. From a few runs in which bed depth, reaction time, and steam rates were similar, a straight-line correlation of residual nitrogen content with reaction temperature was shown (Fig. 2.7). One run conducted at an approximately doubled steam rate gave a point below the line at 405°C. The 100°C range from 360 to 460°C, where most of the runs were made, was the most interesting, since only sols prepared from oxides from this temperature range gave fired gels of desired characteristics. The temperature--residual nitrogen relation in the 360-460°C range was linear, and if it remained so for ~100°C higher, nitrogen would be completely eliminated by steam calcination at 500-550°C, 1 atm. This is also supported by thermogravimetric studies of steam denitrated material (1) which indicated that the residual volatile matter at 500-550°C is 1.4 to 1.5 g/100 g ThO_2.

Steam Rate. In general, doubling the steam rate (increasing from 20 to 40 g/min) increased the rate of nitrogen removal 10 to 20% in the 360-460°C temperature range. However, in the rotary calciner used, this increase in steam rate, particularly after maximum run temperature had been reached, seriously increased entrainment of thoria although the use of high steam rates at the lower temperatures used in the earlier runs did not increase them (Sect. 2.1).

Bed Size. At 390°C, 20 g/min steam flow, and 200 min reaction time, increasing the thorium nitrate charge from 1000 to 1500 g increased the residual N/Th ratio from 0.14 to 0.22. It is not known whether or not increased steam flow in the temperature range from 110 to 330°C could offset this change.

Reaction Time. For the apparatus used and for a 1000 g thorium nitrate charge, time beyond 60 min at 390°C appeared to produce negligible further denitration. The optimum time to produce an N/Th ratio of 0.13-0.15 in the temperature range 110 to 330°C varied from 60 to 90 min as the steam flow rate varied from 40 to 20 g/min.

2.2 Preparation of ThO_2 and UO_3-ThO_2 Sols

The addition to water of thoria with a N/Th ratio of 0.13 to 0.15, prepared by steam denitration, produces a stable sol from which little solid material settles. Addition of water

to thoria caused a "gummy" layer to be deposited on larger particles which hindered homogenization and required considerably more agitation for satisfactory dispersion. When thoria containing a lower N/Th ratio was used, a chalky deposit was observed which could be dispersed easily in very dilute nitric acid if it had been denitrated below 400°C in steam or only with difficulty in 2-4 M HNO_3 if its denitration temperature was >425°C in steam or any temperature >350°C in air. Oxide particles made from sols containing chalky deposits gave fragments inhomogeneous with respect to U/Th ratio and density. When thoria having too high an N/Th ratio was dispersed in water, a soft, flocculent precipitate was formed, which was easily dispersed by dilution in water. Evaporation and firing sols which contained this material gave a glassy, cracked product (Fig. 2.8). The crevices could not be filled by fine solids used in vibratory compaction.

The optimum range of nitric acid concentration in the solution phase for peptization of thoria particles is 10^{-4} to 10^{-2} M (2,3,4). At 10^{-2} M, thoria dissolved slowly, and at $\sim 10^{-4}$ M flocculation occurred. When a sol initially 2 M in ThO_2 is evaporated to a gel with a density of 6 g/cc, the concentration factor is ~10, and in order to maintain a dispersed ThO_2 system the concentration of HNO_3 in the initial liquid with all ThO_2 surface sites saturated with NO_3^- should be between 10^{-3} and 10^{-4} M; this corresponds to a pH of 3 to 4. Evaporation of a thoria sol at this pH gave blocky, porcelain-like particles (Fig. 2.9).

2.2.1 Properties of ThO_2 Sols. Sols with N/Th ratios in the neighborhood of 0.1 were difficult to clarify by centrifugation. Three sols, with N/Th ratios of 0.35, 0.143, and 0.104 were supercentrifuged in a field of ~45,000 G (Table 2.2). Separation of supernatant solution from solid cake gave a clear solution in the first case, but the other two showed Tyndall-cone effects. The middle N sol, when hydrogen-fired to an oxide gel, was vibrated to 86-87% of theoretical density. The high N sol precipitated flocculent material, and the low N sol, granular material. The uptake of nitrate by the solids at room temperature approached a N/Th ratio of ~0.13 when sufficient nitrate was available from the solution. Larger particles (low N) did not extract nitrate as completely from solution as the smaller. In other experiments, when large (granular heel) and small particles were present in the same sol, the smaller particles become saturated with nitrate at the expense of the larger. This may explain the coexistence of glassy and powdery dried gels.

2.2.2 pH Measurements. The nitrate to thorium ratios in the supernatants indicated that the pH of the intermicellular liquid is determined by the hydrolysis of the thorium ion. The pH values in the high N supernatant (Table 2.2) are probably nearly correct because there were no detectable ThO_2 particles present. In the other two sols the readings were probably a little too high because of the effect of ThO_2 on the rate of transport of chloride ion from the calomel electrode.

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Fig. 2.8 Undesirable glassy, cracked gels.

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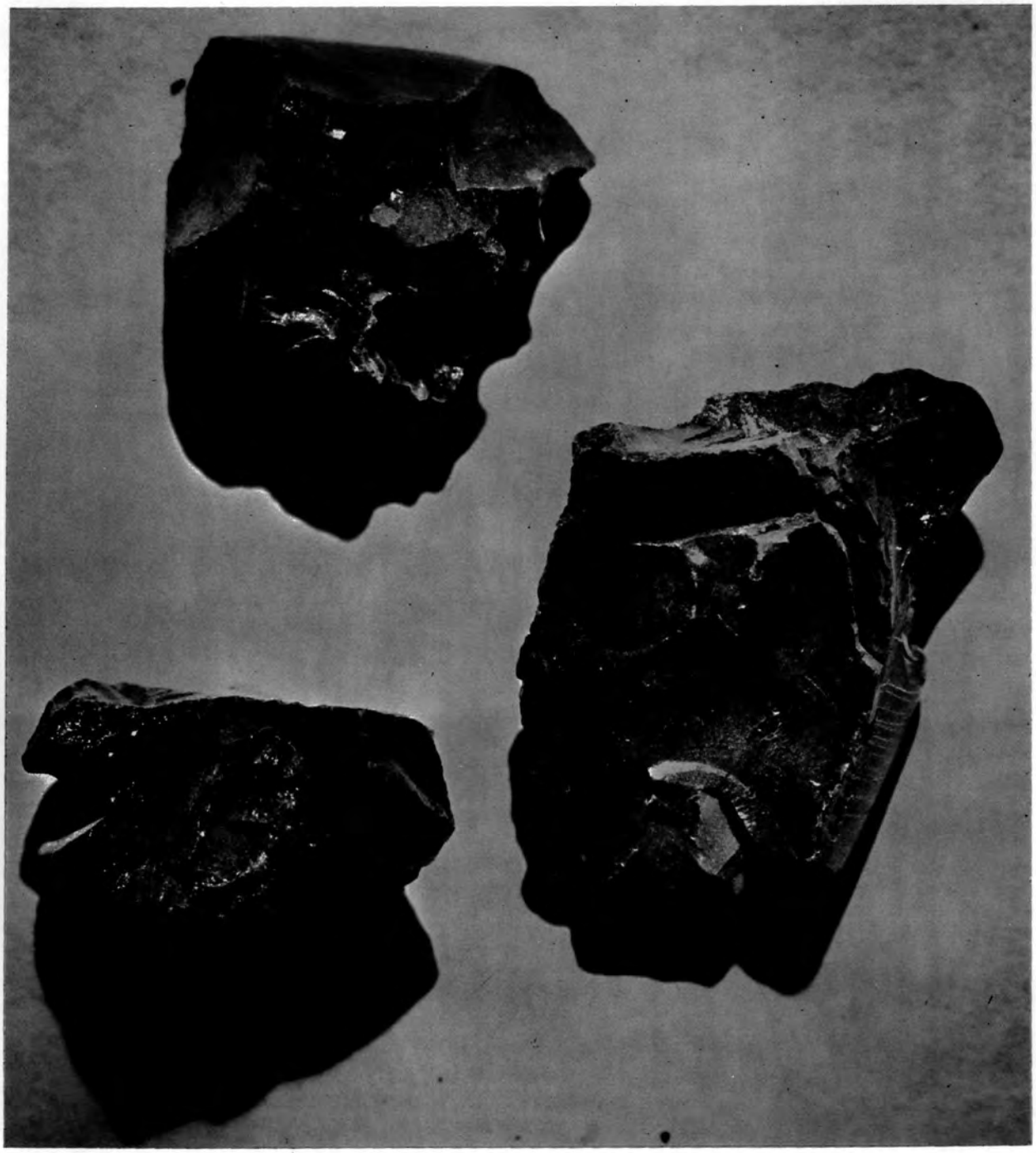

Fig. 2.9 Optimum-shape thorium-uranium oxide particles.

Table 2.2. Separation of Solution from Solids in ThO_2 Sols by Supercentrifugation

Sample	Sol: Solids Conc, g ThO_2/100 ml	Sol: N/Th Atom Ratio	Supernatant: NO_3^-, M	Supernatant: Th Conc, M	Supernatant: pH	Solids: Loss on Ignition,[b] %	Solids: N/Th[a] Atom Ratio
High N	60.8	0.354	0.41	0.111	2.10	6.72	0.13
Middle N	42.7	0.143	0.005	0.56×10^{-4}	3.10	4.56	0.111
Low N	63.9	0.104	0.016	1.2×10^{-4}	3.70	6.26	0.083

[a]Corrected for nitrate in interparticle solution.

[b]Weight at 135°C - weight 1000°C.

Table 2.3. Flocculated and Dispersed States of Sols of Steam-denitrated ThO_2

ThO_2 concentration: 24.8 g/100 ml sol

N/Th Atom Ratio	pH: Filtrate	pH: Unfiltered Sol	State of Ppt
1.16	0.36	0.42	Flocculent and settled
0.43	1.01	1.02	Flocculent and settled
0.19	1.95	1.91	Clear, bluish dispersion
0.12	2.69	3.14	Opaque, polydispersed, little settled
0.098	3.35	4.05	Polydispersed, some settled

In another experiment to relate state of dispersion to nitrate content and pH in ThO_2 sols from steam-denitrated oxides, an oxide, steam-stripped at 450°C to a residual N/Th ratio of 0.089, was spiked with 5 levels of nitrate as HNO_3. The additions were made into sols of 24.8 g ThO_2/100 ml sol and then refluxed ~40 hr. The pH was determined on the sols at room temperature and on supernatants after filtration through a micropore filter, and the state of flocculation was observed visually after one week. Table 2.3 summarizes the results and supports the assumption that dispersion is maximum when the solid has adsorbed a certain fixed amount of nitrate from the solution, and when there is a low residual nitrate concentration present in the solution. For the oxide used in this experiment, the optimum N/Th ratio for dispersion was between 0.12 and 0.19. There is little doubt that if the sol of 0.19 N/Th ratio had been evaporated, flocculation would have occurred before gelation. Again, false readings of pH in sols occurred when surfaces unsaturated with respect to nitrate-absorbed chloride from the calomel electrode.

In another experiment the anion exchange of nitrate and hydroxyl ion on steam-denitrated ThO_2 was demonstrated. Addition of a potassium nitrate solution of pH 6 to a sol of pH 2.92 resulted in an increase of pH to 11 overnight.

2.2.3 Aging. Aging of a sol at ~90°C appeared to homogenize and stabilize a large fraction of particles in a sol. Changes in a sol having an N/Th ratio of 0.16 were studied during aging at room temperature and at 100°C for 185 and 71.5 hr, respectively. Two-milliliter samples were withdrawn periodically and centrifuged at ~1100 G. The supernatant was separated from solids and analyzed for nitrate and acid deficiency. A residue of ~5% of the solids had particles too small to be removed in the centrifugal field used. Since nitrate and acid deficiency increased rapidly in the early stages of aging, the conclusion reached was that there was a progressive transfer of nitrate and soluble thorium from the particles to the solution. There was a rapid increase in the fraction of solids settled from the sol by gravity as flocculent material in 23-40 hr. Centrifugation deposited, roughly, two types of solids, a more flocculent one at the bottom and a finer, more thixotropic one at the top. After 71 hr aging at 100°C, the ratio of these two types of solids was not visually changed. Since the more rapid changes occurred in the first 40 hr, this aging time was chosen as a tentative optimum.

In another experiment, the pH changes of sols at 90-100°C with N/Th atom ratios of 0.179, 0.180, and 0.227 were studied as aging progressed. The pH dropped rapidly for the first 10-14 hr, but was approximately constant for the next 60 hr. Thoria was transferred from sol to a flocculent deposit rapidly in the first 10-14 hr, but the solids concentration remained essentially constant after that. Observation under a microscope of dried particle samples of sol showed a change from sharp and glassy to "blocky" and opaque in the same time interval. The major changes in aging appeared to be nearly complete in ~14 hr.

2.2.4 Addition of Uranium. In preparations reported previously, uranium was added to the ThO_2 sol as uranium trioxide monohydrate. In the successful preparation containing U-235 (Sect. 2.0) uranium was added as ammonium diuranate. The sol was heated for ~2 hr at 90°C until the color changed from light yellow to peach-orange before evaporation.

2.3 Calcination of Dried, Prefired Gels

The effects of final firing temperature and atmosphere on the density, O/U ratio, and crystallite size of calcined, oxalate-derived thoria gels containing 9.6 and 4.2 mole % uranium have been reported (1). The rate of removal of oxygen above an O/U ratio of 2 by hydrogen-firing of the 4.2% urania gels appears to be first order with respect to excess oxygen. This may be described mathematically as

$$\frac{O/U - 2}{O/U_{initial} - 2} = e^{-kt}$$

where t = time and k = rate constant. For hydrogen firings where t = 4 hr, k was calculated for five temperatures (see Table 2.4).

Table 2.4 The Effect of Firing Temperature on the Rate of Removal of Oxygen from Calcined Th-U Oxide

Initial composition: 4.2 mole % $UO_{(2+x)}$ - ThO_2
Atmosphere: H_2
Initial O/U: 3
Firing time: 4 hr

Firing Temp, °C	1/T°K	Final O/U Ratio	k, hr^{-1}
850	8.90×10^{-4}	2.547	0.151
950	8.17×10^{-4}	2.230	0.368
1050	7.55×10^{-4}	2.085	0.617
1150	7.04×10^{-4}	2.005	1.34
1250	6.55×10^{-4}	2.0002[a]	2.15

[a]Accuracy of data questionable at this level.

The linearity of the Arrhenius plot (Fig. 2.10) is evidence for the correctness of the assumption that removal of oxygen from these gels by hydrogen firing is a first order reaction. The activation energy is ~27 kcal per mole of uranium, which agrees well with that determined for self-diffusion of oxygen in urania lattices (5).

2.3.1 Calcination of Thoria Gels. Unexpectedly, the densities of products from hydrogen firing of pure ThO_2 were greater than air firing (Table 2.5). Crystallite growth agreed with this observation. For this study, thoria gels derived from 650°C-fired oxalate-prepared ThO_2, nitrate-dispersed sols were calcined in air and in hydrogen. The gels were prepared as described in an earlier report (1).

Table 2.5 Effects of Atmospheres and Temperature on Density and Crystallite Size for Oxalate-derived Thoria Gels

	Density[a], g/cc		X-ray Crystallite Size, A	
Temp, °C	H-fired	Air-fired	H-fired	Air-fired
825	9.05	9.00	190	160
940	9.50	9.30	670	460
1040	9.50	9.80	1520	1490
1145	9.95	9.85	1930	2170
1255	9.90	9.80	>2500	>2500

[a]Toluene immersion method; not out-gassed by vacuum.

The hydrogen-fired products were purplish-black, while the air-fired samples were off-white. Spectrographic analysis showed no color-producing cationic impurity greater than 2 ppm, and the only cationic impurity of significance was sodium (100 ppm). All samples were previously prefired in air at 500°C. Because of the anomalous behavior, the experiment was repeated with closely duplicated results. Samples fired in hydrogen at 1040°C were lighter and less homogeneous in color than those fired in hydrogen at other temperatures. The only other difference in preparation was that the sample was preheated in argon for a longer time before hydrogen was admitted. As a test, special samples were fired at 1000°C: (a) in air 4 hr, then hydrogen 4 hr; (b) in argon 4 hr, then hydrogen 4 hr; and (c) in hydrogen from room temperature to 1000°C, then at 1000°C 4 hr. Special samples (a) and (b) were lighter gray and mottled, while sample (c) was more uniformly dark than any sample observed previously. Refiring of sample (c) for 4 hr in air at 1200°C produced the off-white thoria usually observed from air-firing. The possibility exists that some of the nitrate is reduced by hydrogen to thorium nitride, which in turn acts as a fluxing agent.

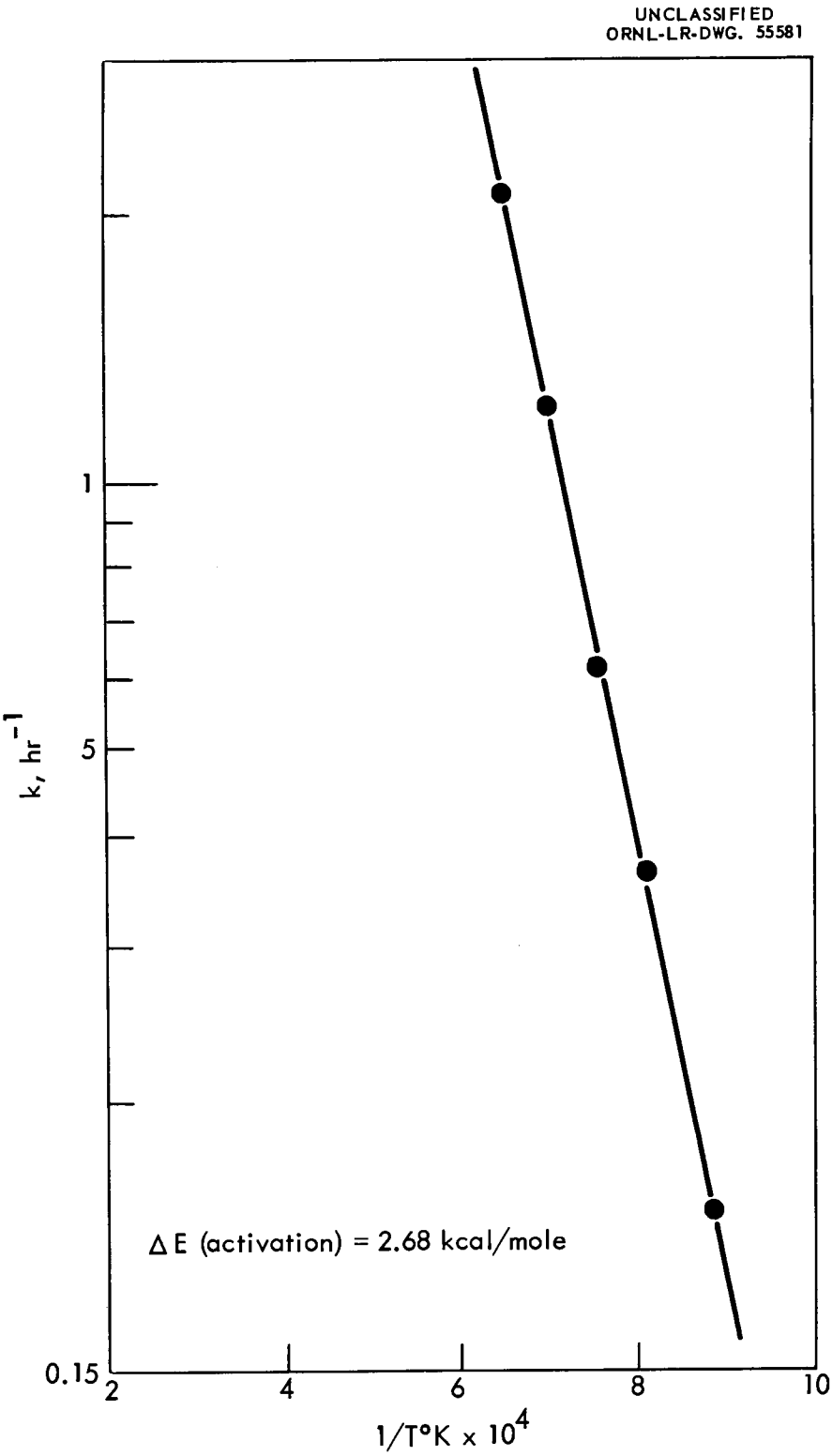

Fig. 2.10. Rate of removal of oxygen from uranium-thorium oxide gels by hydrogen firing.

A slight reduction in density from 1150 to 1250°C was observed consistently for thoria and for urania-containing thoria gels. Lattice parameters for hydrogen-fired thoria samples were 5.5975 A at 1145°C and 5.5971 A at 1255°C. It is therefore concluded that the optimum final firing temperature is 1150°C instead of the previously reported 1250-1300°C.

3.0 FISSION GAS RELEASE

D. F. Toner
J. L. Scott

Several specimens of ThO_2-5 wt % UO_2 (prepared by the sol-gel process) were tested for fission-gas-retention properties in the temperature range 1440 to 2015°C by a neutron-activation technique (11). The amount of gas released increased with increasing temperature (Fig. 3.1). Except for a small initial burst of gas, the mechanism of release was diffusion. This is particularly significant at 2015°C, because in bulk UO_2 at this temperature the most important mechanism of release would be by sublimation. The greater stability of ThO_2-UO_2 over that of UO_2 would be expected as a result of the higher melting point of ThO_2 (3300°C) compared to that of UO_2 (2750°C). From the slope of the curve of log D' where $D' = D/a^2$, D being the diffusion coefficient and a the radius of the uniform sphere (12) vs the reciprocal of the absolute temperature (Fig. 3.2), the activation energy for the 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 UO_2 (13).

For these experiments, individual samples containing 0.2-0.6 mg of U-235 were irradiated to an integrated dose of 6.77×10^{17} nvt in the graphite reactor. The specimens were subsequently heated in an induction furnace in a vacuum of about 10^{-3} mm Hg, and the Xe-133 released was collected in a continuously monitored charcoal bulb. A plot of the fraction of the Xe-133 released at a given temperature as a function of the square root of the time is a straight line for a diffusion mechanism of release.

4.0 VIBRATORY COMPACTION STUDIES

E. S. Bomar W. S. Ernst J. W. Snider
S. D. Clinton P. A. Haas A. W. Seifert

The density attained by vibratory compaction of some earlier oxides prepared by the sol-gel process was only 8.0 to 8.3 g/cc. Microscopic examination of the larger particles of these oxides (Sect. 2.2, Fig. 2.8) showed rough surfaces and cracks which acted as closed pores. Oxides prepared by the modified flowsheet (Fig. 2.1) did not show these bad features and were easily vibrated to a density of 8.7 g/cc.

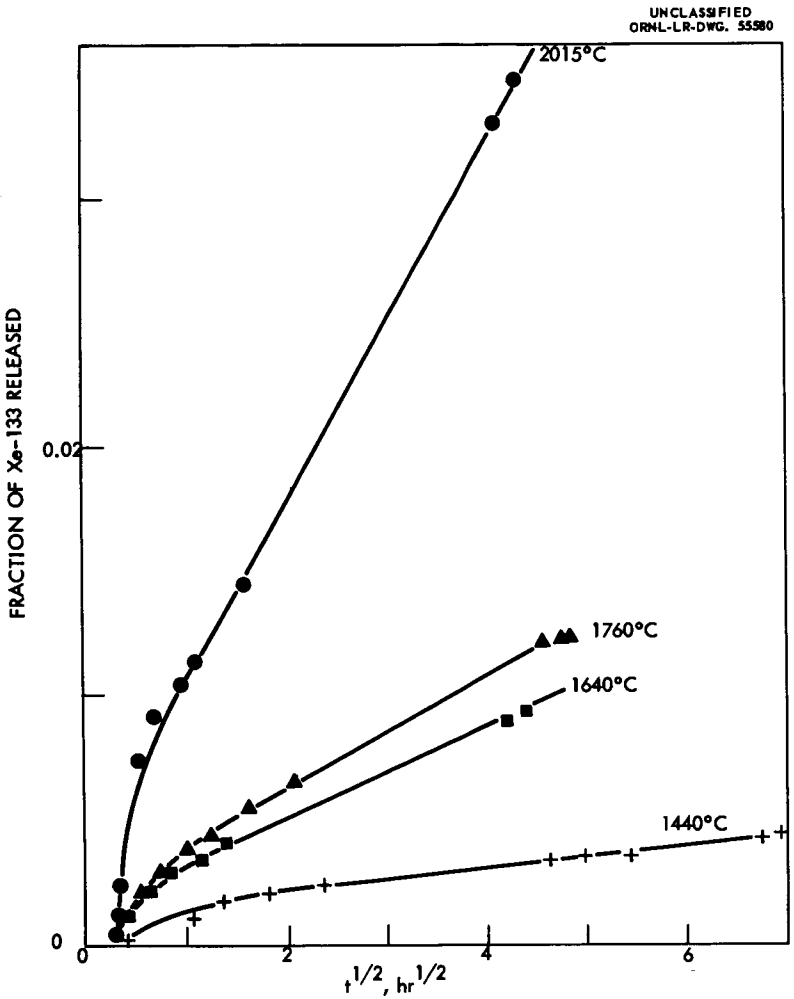

Fig. 3.1. Release of Xe-133 from ThO_2-5 wt % UO_2 prepared by the sol-gel process.

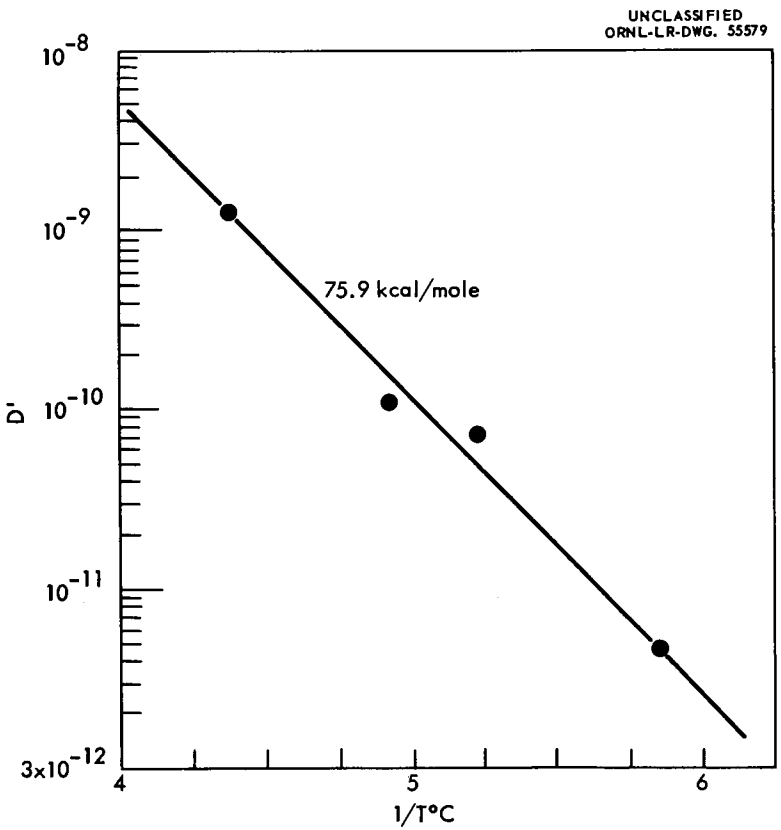

Fig. 3.2. Log D' vs 1/T for ThO_2-5 wt % UO_2 prepared by the sol-gel process.

4.1 Effect of Compaction Time and Compressive Load on Product Density

After 60 min compaction, the density was only 1% greater than that at 10 min (Fig. 4.1). A 0.4-lb compressive load placed on the oxide after 2 hr compacting increased the density another 1.5%. When a 0.4-lb load was placed on the oxide after the initial 10 min, the maximum density was reached at 40 min.

For these experiments fused, ground ThO_2—3.4 wt % UO_2 was compacted into tubes 4 ft long by 0.5 in. o.d. Tubing of 0.020 and 0.035 in. thickness was used. No effect of wall thickness on bulk density was found.

4.2 Preparation of Irradiation Capsules

Irradiation of mixed ThO_2-UO_2 prepared from highly enriched uranium by the sol-gel process (Sect. 2.0) is under way in the NRX. A set of eight 11-1/4-in.-long x 0.025-in.-wall capsules made of type 304 stainless steel was prepared and loaded with mechanically conditioned and sized granules by shaking with a pneumatic vibrator to densities of 8.7 g/cc.

The samples are being exposed in a thermal neutron flux of about 5.5×10^{13}, resulting in an expected heat flux of 370,000 Btu/hr·ft^2. The residence time in the reactor has not been fixed. Postirradiation inspection will include a survey of the intensity of γ-ray emission along the tube lengths, a measure of fission-gas release, and possibly preparation of sections for metallographic examination.

4.3 Optimum Size Fractions in Blended Oxides

While densities as a function of size fractions have been determined experimentally for mixtures containing three sizes of particles of ThO_2-UO_2, less tedious methods are needed for estimating the packed densities of various compositions. Studies with glass beads are being made to determine the maximum density of two- and three-size systems. The data have been studied with a reciprocal fractional volume model (6) (Fig. 4.2). An additive fractional volume model (7) has been proposed which appears more satisfactory for the data obtained. Studies at Nuclear Materials and Equipment Corporation (8) with steel shot also indicate that the additive fractional volume model is best. The reciprocal fractional model assumes an infinite diameter ratio between the two sizes although a proposed (9) modification allows for finite diameter ratios and predicts fairly accurately the region in which maximum densities lie.

4.3.1 Two-size Blends. At present no satisfactory model is available that will predict the effect of particle shape on compacted density, and in the final analysis one must resort to experimental procedures. Spherical glass beads did not compact so well as arc-fused oxides, i.e., the ratio of density obtained to maximum predicted density is higher for the arc-fused oxides (Table 4.1). This was attributed to the fact that the arc-fused oxide particles were irregular in shape. The densities of the glass

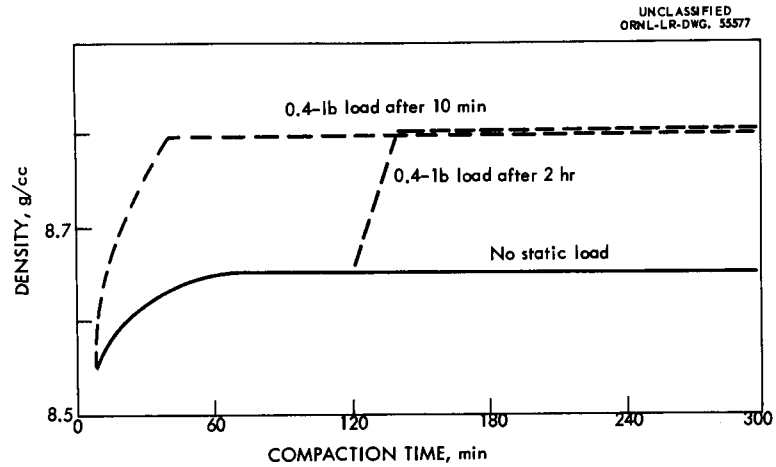

Fig. 4.1. Effect of compaction time and small load on bulk density. Solid lines indicate no load; dashed line indicates 0.4-lb load.

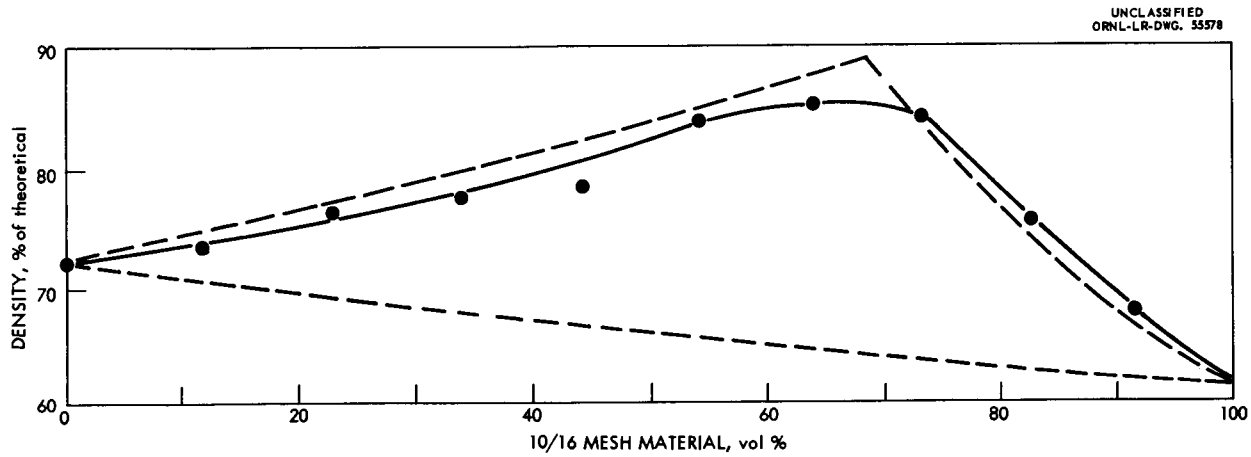

Fig. 4.2. Density as a function of volume percent of large-grain oxide in a mixture of 10/16 and -200 mesh grains of arc-fused ThO_2-UO_2 (3.4 wt % UO_2). ---regions of possible densities predicted from the reciprocal fractional volume model.

Table 4.1 Maximum Densities and Their Corresponding Compositions for Two-size Systems

Composition, %, by Grain Size[a]				Density[b]		
wt % of 10/16	wt % of 70/100	wt % of -200		Observed % of Theor.	Predicted % of Theor.	Ratio, Observed to Predicted
				Fused ThO_2		
65	-	35		84.0	87.5	0.960
-	60	40		77.5	87.5	0.886
70	30	-		78.5	84.0	0.935
				Fused ThO_2-UO_2		
65	-	35		86.5	89.0	0.972
-	60	40		80.0	88.0	0.908
70	30	-		78.5	85.0	0.925
wt % of No. 4[c]	wt % of No. 15[c]	wt % of No. 20[c]	wt % of No. 19[c]		Glass Beads	
70	-	30	-	75	80	0.938
67	-	-	33	79	84	0.940
-	74	26	-	70	81	0.864
-	67	-	33	68	85	0.800
55	45	-	-	73	87	0.840

[a]Composition that gave the maximum density of any mixture of the two size fractions it contained.

[b]Predicted for the case of infinite diameter ratios for reciprocal fractional volumes additive.

[c]See Fig. 2.3 for size distributions.

beads are tap densities, but those of the arc-fused materials were obtained by vibratory compaction into a 3/8-in.-o.d. stainless steel tube with 35-mil walls. (A few cursory experiments in which glass beads were vibrated in the same tube under similar conditions gave no apparent increase in density over that obtained from tap density.) The effect of shape was also evident when by replacing the small size fraction in an oxide mixture with ThO_2 spheres a packed density reduction occurred.

4.3.2 Three-size System. For a three-size system (Fig. 4.3) it becomes even more desirable to have a mathematical model for predicting optimum composition and density, as the amount of experimental data required to study such a system increases tremendously. No literature reviewed to date offers any type of model that would predict the curved maximum peak and the second isolated one seen in Fig. 4.3. However, an effective empirical procedure has been found to decrease the amount of experimental data required to locate the optimum composition: (1) apply the method outlined by Westman and Hugill (10) to locate the region of maximum density; (2) choose various proportions of coarse and medium grains and then add fines in incremental steps until the bed appears saturated with fines, blending the bed carefully after each incremental loading followed by tapping; (3) continue to add fines until the bed is supersaturated with fines. The region of maximum density lies between these limits, and several well chosen mixtures will outline the area of interest.

This method was applied to the first arc-fused material received. In one afternoon a blend, 58 wt % coarse, 15 wt % medium, and 27 wt % fines, was chosen which, to date, has not been improved for pneumatically vibrated tubes for the diameters of interest. During the past 15 months other blends have been studied that are as good but none have made any significant improvement in packed density. Blends reported by other investigators were compared with the above composition with no density improvement for pneumatic vibrator compaction.

A series of studies is in progress with a larger fine fraction, beads No. 19 replacing beads No. 20 (Fig. 4.4) but with the same coarse and medium fractions. Preliminary data indicate that the area of maximum density is broadened considerably. This type of mixture is highly desirable for vibratory compaction since various lots of material of the same grains vary somewhat in size distribution.

5.0 BASIC CHEMISTRY OF MIXED OXIDES

R. E. Thoma
H. A. Friedman

5.1 The System UO_2-ThO_2-O_2

Phase equilibria in the system UO_2-ThO_2-O_2 are being studied by two approaches: (1) determination of the oxygen content and phases present in UO_{2+x}-ThO_2 samples of

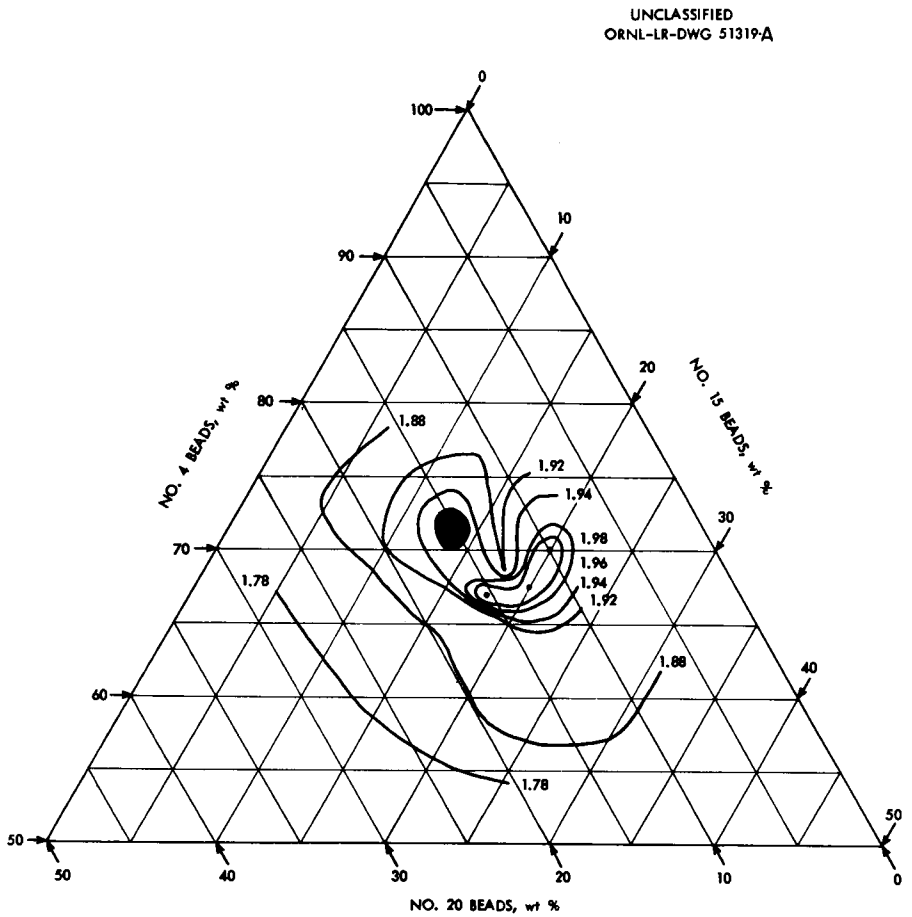

Fig. 4.3. Three-phase diagram of a system of glass beads of three different sizes. Isorithmic lines of constant density are in grams per cubic centimeter. Solid dots (·) are points of 2.0 g/cc.

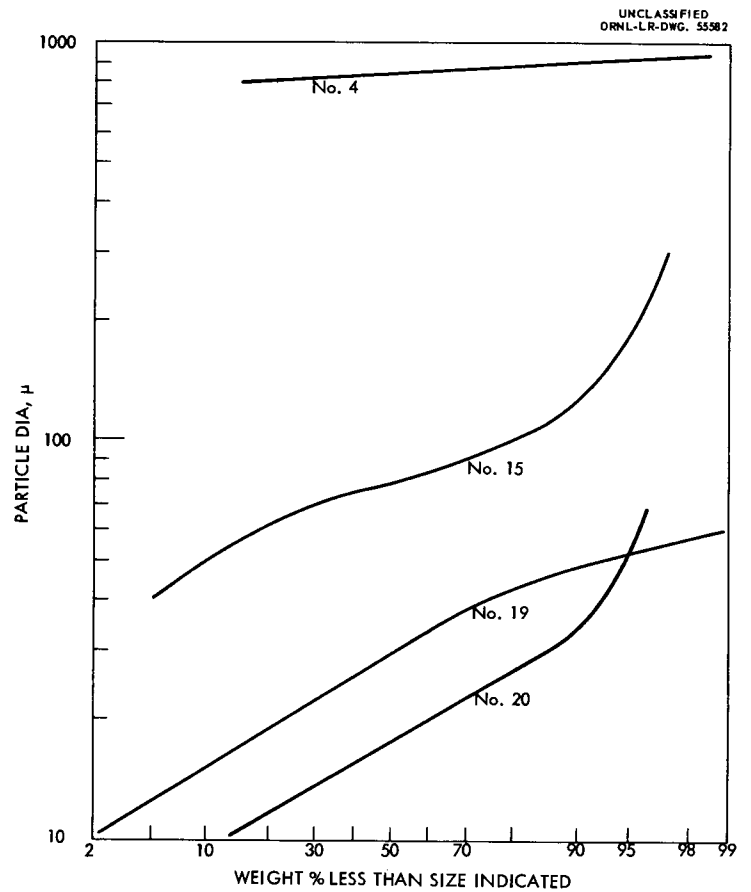

Fig. 4.4. Particle size distribution of glass beads used in two- and three-component studies.

various uranium-thorium ratios in air up to 1000°C, with correlation of the fluorite phase unit cell size with the uranium-thorium ratio and oxygen content, and (2) determination of the limiting area of the fluorite phase field by plotting measured dissociation pressure values of the solid solutions as a function of the composition in the temperature range 400-1000°C.

A horizontal thermal gradient furnace was constructed for the study of UO_{2+x}-ThO_2 mixtures equilibrated in air. A boat-like sample holder, positioned in the furnace, is separated into 27 platinum compartments. This arrangement allows temperature and composition to be varied simultaneously. Rapid cooling after annealing preserves the equilibrium phases present at high temperatures, and phase compositions are identified by chemical, optical, and x-ray diffraction methods. On 9 samples of the mixed oxides annealed at 1500°C for 9 to 15 hr and quick-cooled, determinations are being made of (1) the number of phases present, (2) O/U ratio, (3) unit cell sizes of the fluorite phase, (4) refractive index of the solid solution, and (5) sample homogeneity.

Modified apparatus for the study of equilibrium dissociation pressures of oxygen over UO_{2+x}-ThO_2 solid solutions as a function of temperature includes a quartz heating chamber 12 in. long, 3/4 in. o.d. The system can be evacuated to 8×10^{-7} mm, measured on an ion gauge, with the mercury pressure measuring device shut off. Gas pressure above samples can be measured to temperatures as high as 1000°C, the softening point of quartz. The tube can be closed and removed from the furnace to cool the sample rapidly, and to permit transfer of the sample in an oxygen-free atmosphere. In order to expose samples to a gas stream at high temperatures, the closed tube is replaced with an 18-in. long quartz tube open at both ends. Gaseous reactants can be introduced into the system and circulated by a Toepler pump. This arrangement is used to introduce carbon monoxide in the system to reduce uranium oxide. The resultant carbon dioxide can be caught in a cold trap, warmed, and then collected in U-tube samplers.

P-V-T calibrations of the closed tube system were made for its use in determining the amount of oxygen released by heated UO_{2+x}-ThO_2 samples. The volume was determined by measuring the pressure resulting from the addition of a known amount of air to the evacuated system. Pressures as low as 5 mm were measured on a mercury manometer and lower pressures by a McLeod gauge. The pressure effects caused by temperature changes in the system were determined for several different quantities of contained oxygen gas. A calibration chart was constructed from these data which shows the standard volume of gas evolved from heated samples as a function of equilibrium pressure. The evolution of enough oxygen from a 2-g sample of mixed oxides to cause a 1-mm pressure change at constant temperature represents approximately 0.01 atomic weight of oxygen evolved per mole of sample.

Preliminary measurements of UO_{2+x}-ThO_2 dissociation pressures were started with 60-40 and 80-20 mole % ThO_2-UO_{2+x} samples.

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