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ARGONNE NATIONAL LABORATORY
P. O. Box 299
Lemont, Illinois

MANUFACTURE OF THE ThO_2-UO_2 CERAMIC FUEL PELLETS FOR BORAX-IV

by
J. H. Handwerk, C. L. Hoenig, and R. C. Lied

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MANUFACTURE OF THE ThO_2-UO_2 CERAMIC FUEL PELLETS FOR BORAX-IV

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ABSTRACT

Preliminary investigation indicated that it was possible to prepare thoria-urania solid solutions by sintering in air a mixture of ThO_2 and U_3O_8. The U_3O_8 on heating in air was found to disassociate, and when heated with ThO_2, the resultant body was essentially a ThO_2-UO_2 solid solution.

The methods used in preparing and granulating the ThO_2 and U_3O_8 for the BORAX-IV loading are discussed in detail. This material was dry pressed using pressures from 13,000 to 15,000 psi. The pressed pellets were loaded into alumina crucibles and fired to a peak temperature of 1700°C to 1750°C. The fired ware was found to have an average apparent density of 9.8 g/cc.

The pellets were loaded into aluminum-1 w/o Ni tube plates and the annulus between the pellet and the tube was filled with lead. After closing the open end of the tube plates, the plates were spot welded into a subassembly.

INTRODUCTION

Thorium as a source material for U^{233} is of importance in the field of power reactors. Through the Th-U^{233} cycle, thorium can be converted to a fissionable material.

Both thorium and uranium metal are susceptible to corrosion by water, and these metals must be carefully clad with a corrosion resistant material when used in water cooled reactors. The oxides of these metals are resistant to corrosion by water, and these materials when fabricated would appear to be more suitable for nuclear fuels in power reactors.

The work of Corwin and Eyerly[1] had shown that UO_2 and ThO_2 could be fabricated by conventional ceramic methods, and that these materials are suitable for use as refractories in melting metals such as uranium. Ware formed from UO_2 must be sintered in a vacuum or in a protective atmosphere to prevent the oxidation of UO_2 to U_3O_8. This oxidation is accompanied by an increase in volume, which results in rupturing the ware. ThO_2, unlike UO_2,

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forms no higher oxide, and may be sintered in air. Both UO_2 and ThO_2 have face centered cubic or fluorite type structures and as shown by Lambertson[2] and others, they form a complete series of solid solutions. This stability of ThO_2 as well as its conversion to U^{233} would indicate the possibility of a reactor fuel composed primarily of ThO_2 spiked with sufficient UO_2 to cause the reactor to be critical.

PRELIMINARY CONSIDERATIONS

Thoria-Urania Mixtures

The work of Warde[3] and Hoekstra[4] indicates that U_3O_8 is stable in oxidizing atmosphere up to approximately 1150°C. With prolonged heating above this temperature range U_3O_8 decomposes to a lower oxide, and, eventually to UO_2. In order to eliminate the use of a protective atmosphere in sintering UO_2, and in order to avoid the disruptive volume change of UO_2 to U_3O_8, which occurs when UO_2 is heated in air, ThO_2-UO_2 solid solutions were prepared with UO_2 added as an equivalent amount of U_3O_8.[5]

Mixtures of ThO_2 and U_3O_8 containing up to 30 w/o UO_2 (added as an equivalent amount of U_3O_8) were dry pressed into small right cylinders 1/4" in diameter by 1/2" in length. These compositions were fired to 1700° to 1750°C in air. The resultant ware appeared to be free of cracks or other visible defects. Compositions containing up to 25 w/o UO_2 underwent no visible changes when reheated to 1750°-1850°C in air, and compositions containing up to 30 w/o UO_2 did not appear to change when reheated in air to 1400°C for periods as long as 96 hours. The average apparent densities of these samples ranged from 7.85 g/cc for compositions containing 97 ½ w/o ThO_2 and 2 ½ w/o UO_2 to 7.00 g/cc for compositions containing 70 w/o ThO_2 and 30 w/o UO_2.

X-ray diffraction analyses of compositions containing up to 60 w/o UO_2 (added as U_3O_8) indicated that UO_2-ThO_2 solid solutions were formed. For compositions containing 60 w/o or more UO_2 there was considerable line broadening of the x-ray patterns with evidence of an additional phase. These observations parallel the work of Hund[6] who observed the formation of a fluorite-type phase from compositions containing up to 56.5 mol percent U_3O_8 and ThO_2 with the appearance of excess U_3O_8 during the firing of compositions containing more than 56.5 mol percent U_3O_8. X-ray diffraction analyses for compositions containing up to 30 w/o UO_2 showed characteristic patterns of the fluorite-type. No extraneous lines were observed even though a careful search was made for any U_3O_8 lines. However, there was evidence that all the U_3O_8 was not reduced to UO_2, but probably to some oxide with a metal to oxygen ratio of 1 to 2.3 ($UO_{2.3}$).

Specimens of two thoria-urania bodies were irradiated in both the MTR and the CP-5 reactors. The first body was composed of 97 ½ w/o ThO_2

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and $2\frac{1}{2}$ w/o UO_2 while the second body was composed of 90 w/o ThO_2 and 10 w/o UO_2. The UO_2 content of these bodies was above 90% enrichment and was added as an equivalent amount of U_3O_8. The sample preparation and irradiation tests made in the MTR reactor are reported by Kittel and Handwerk.(7) Postirradiation examination revealed that specimens of the two bodies did develop some cracks and that some fragmentation had occurred. However, in general the condition of the slugs appeared to be good. A typical irradiated specimen of the 90 w/o ThO_2 - 10 w/o UO_2 body is shown in Figure 1. This specimen was encased in aluminum - 1 w/o nickel with the annulus between the pellet and can filled with a welding gas having the approximate composition of 80% He and 20% A. The pellet was irradiated to a burnup of 0.64 a/o of the metal.

The results of the irradiation tests on the two bodies made in the CP-5 reactor have been reported (Granacki et al(8,9,&10)). Postirradiation examination of specimens of the $97\frac{1}{2}$ w/o ThO_2 - $2\frac{1}{2}$ w/o UO_2 body indicated that the fission products were apparently quite well contained within the capsules.(8) After opening the capsules the pellets were found to be intact, however, microscopic examination revealed that the pellets were cracked. Postirradiation examination of the 90 w/o ThO_2 - 10 w/o UO_2 specimens revealed that the aluminum - 1 w/o nickel cans were coated with a heavy deposit of iron oxide.(10) Noticeable distortion had occurred in the jackets, and in some cases the lead which was used to fill the annulus was visible in the ruptured wall of the can. Examination of the pellets was accomplished by partial dissolution of the jackets. Some of the pellets had remained intact with only a minimum of end spalling while other pellets were found to be fragmented.

FUEL FABRICATION

The preliminary tests indicated that a thoria-urania solid solution fuel would be feasible, and that these solid solutions could be formed by sintering a mixture of ThO_2 and U_3O_8. The low thermal conductivity of the ceramic indicated a high central metal temperature, and in order to minimize this high central temperature, the fuel design was suggested as a rod or pin with as small a diameter as could be fabricated. This diameter for the ceramic fuel rods was established at 1/4", for this size was considered the minimum size pellet which could be easily dry pressed.

The reactor was designed to contain 72 subassemblies. Each subassembly was composed of six tube plates, and each tube plate contained eight tubes. The length of the fuel in each tube was set at 24". On the basis of a 72 subassembly reactor with each subassembly composed of 48 fuel rods 24" in length, approximately 83,000" of fuel would be required, or on basis of pellets 1/2" in length approximately 166,000 pellets would be required. In addition to the 72 fuel subassemblies, 10 other, loaded with thoria,

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were needed. These subassemblies were estimated to require 23,000 pellets of thoria. Several automatic presses were available, but these presses were not suitable for enclosure in the glove boxes situated in the ceramic laboratory. Total enclosure was considered necessary because of the toxic nature of the materials involved, and because of the strict accountability of the material. As commercial presses were deemed unsuitable for enclosure in the existing laboratory glove boxes, a small automatic press was designed and built[11] as shown in Figure 2. This press was installed in one of the glove boxes in the ceramic laboratory, and then equipped with a conveyor (Figure 3) for transporting the pressed ware from the vicinity of the press to an adjoining glove box where it could be inspected.

Both the ThO_2 and U_3O_8 were received as -325 mesh material. The thoria was supplied by the National Lead Company, and a spectrographic analysis of this material is shown in Table 1. The U_3O_8 was supplied by the Oak Ridge National Laboratory. This material was manufactured by steam oxidizing uranium metal chips, and the "as received" material was in the form of a fine black powder. No analyses were made on this material. Prior experience had shown that the pressing characteristics of the thoria were improved by calcining overnight at 1000°C, and so all thoria was calcined at 1000°C before mixing. As calcining at 1000°C did not appear to affect the U_3O_8, this material was used as received.

The pressing mixture for the BORAX-IV fuel was calculated to be 93.41 w/o ThO_2 and 6.59 w/o U_3O_8. The U_3O_8 used was above 90% enrichment, and for accountability reasons this material was weighed in a dry box. To ease the problem of weighing the U_3O_8, approximately 200 grams of the oxide were transferred to a tared bottle. The accurate weight was determined, and the amount of ThO_2 to be added was calculated and weighed in an open hood. The thoria and urania (approximately 3000 grams) together with 2.5 w/o of the batch of polyvinyl alcohol were charged into a one gallon porcelain lined pebble mill in a glove box. Approximately one kilogram of porcelain pebbles were added, and the mill was closed and wrapped in polyethylene sheeting. The mill was removed from the glove box and transferred to a mill rack, where the ThO_2, U_3O_8 and polyvinyl alcohol were mixed together for three hours. The mill was then removed and returned to the glove box.

The dry oxides were not free flowing, and when charged in the press would bridge over the die cavities. In order to develop free flowing characteristics, the material was granulated. The oxides were transferred from the mill to a small Hobart mixer situated in a glove box, and the powder was dampened with approximately 12 w/o water containing 0.5 w/o aerosol. The moist mixture was forced through a 16 mesh screen to form granules, and the granulated material was then dried at 80°C for four hours. This granulation procedure produced a free flowing powder. Before pressing 30 ml of a mixture of 50 volume percent kerosene and 50 volume percent oleic acid were added as a lubricant. This mixture was then charged into the press hopper shown in Figure 2.

The press is essentially a double acting press with four cavities, and is capable of producing up to eighty pellets per minute. In operation, however, the rate was set at approximately twenty-five pellets per minute, in order to allow sufficient time for handling the pressed ware from the conveyor. The diameter of the pressed pellets was controlled by the die size while the length of the pellets was controlled by the volume of material which dropped in the die cavity. The lengths of the pellets were therefore proportional to amount of material which dropped in the die cavity. This quantity was controlled by the free flowing characteristics of the material. In operation the lengths of the pellets were found to vary from 0.750" to 0.375", and the diameters from 0.267" to 0.270".

The ThO_2-U_3O_8 mixture was pressed at from 13,000 to 15,000 psi. The pressed ware was transferred laterally by means of a conveyor (Figure 3) to an adjoining glove box. The pressed pellets were inspected and those which appeared to be good were randomly loaded into alumina crucibles. Ware which was cracked or chipped was regranulated by forcing the pressed pellets through a 16 mesh screen. This regranulated material was returned to the press.

The crucibles containing the pressed pellets were transferred to an electric furnace, and were heated to 260°C overnight. This calcination removed most of the organic binders. The crucibles containing the calcined pellets were transferred to a gas fired kiln where they were fired in air to 1700° to 1750°C in approximately 16 hours. The peak temperature was held for two hours, the kiln shut off, and the ware was allowed to cool in the furnace to room temperature. The fired ware had a uniform appearance, and the pellets did not appear to sinter either to the crucible or to themselves. Figure 4 is a photograph of one of the crucibles filled with thoria-urania pellets after firing.

The thoria pellets for the ten blanket assemblies were made in a similar manner. Batches of approximately 3000 grams of the calcined thoria were weighed and mixed dry for three hours with 2.5 w/o polyvinyl alcohol. This mixing was accomplished in one gallon porcelain lined pebble mills containing approximately one kilogram of porcelain pebbles. The dry mixture was transferred to a small Hobart mixer where it was mixed with approximately 12 w/o water containing 0.5 aerosol. The damp mixture was forced through a 16 mesh screen and the granulated material thus formed was dried at 80°C for four hours. This material was mixed with a lubricant, (30 ml of a mixture of 50% kerosene and 50% oleic acid) and charged to the press hopper shown in Figure 2 where it was pressed into pellets at 13,000 to 15,000 psi. The pressed pellets were randomly loaded into alumina crucibles and fired in a gas fired kiln to a temperature of 1700° to 1750°C. The peak temperature was held for two hours, the kiln shut off, and the ware allowed to cool to room temperature. These pellets also were of uniform appearance. A crucible filled with fired thoria pellets is shown in Figure 5 while two typical fired thoria pellets are shown in Figure 6.

Rejects in firing due to chips, cracks, or otherwise defective ware averaged less than 4%. A representative sample of each kiln firing was measured and the diameters of the pellets were found to be in the range of 0.229 ± .002". The firing shrinkage was calculated from the average pressed diameter (0.268") and the average fired diameter of (0.229"). This firing shrinkage was found to be 17.0% based on the fired diameter.

The average apparent density determined by water immersion using representative samples from each kiln firing was found to be 9.5 g/cc for the thoria pellets, and 9.8 g/cc for the thoria-urania pellets. The average geometric density of the thoria-urania pellets as calculated from the measured dimensions of the pellets was found to be 8.3 g/cc. This difference between the two methods of measuring density was attributed for the most part to the porosity or open pore structure in the pellets; however, surface imperfections on the pellets would also be a factor due to errors introduced by calculating the volume of the pellet from measured dimensions.

The average density of 9.8 g/cc as determined by water immersion appears to be about 97% of theoretical density for the thoria-urania mixture. This was estimated by first calculating the fired composition by assuming all U_3O_8 was dissociated to UO_2 in the firing process. The fired composition was calculated to be 93.65 w/o ThO_2 and 6.35 w/o UO_2. A plot of the theoretical densities of ThO_2 (10.03)[12] and UO_2 (10.95)[13] was made as shown in Figure 7, and from this the theoretical density of the thoria-urania body was estimated to be 10.09 g/cc.

LOADING OF PELLETS INTO THE TUBE PLATES

The jacketing material for BORAX-IV was aluminum - 1 w/o nickel. This material was fabricated into tube plates[14] (8 tubes per plate) and closed on one end as shown in Figure 8. These plates were leak tested using a helium mass spectrograph, weighed, and placed in the loading fixture shown in Figure 9.

The loading fixture (Figure 9) consisted of a grooved steel plate mounted on a vibrator, in such a manner that the grooves were aligned with the tubes in the tube plate. Thoria-urania fuel pellets and the thoria blanket pellets were loaded by first aligning a column of pellets in a "V" plate. The pellets were then pushed into the grooved plate. Eight columns of pellets 24" to 24-3/16" long were aligned in the grooved plate. These columns were then pushed into the aluminum - 1 w/o nickel tube plate. The tube plate containing the pellets was weighed, an aluminum plug was inserted in each tube, and a crimp made just above the aluminum plug to prevent the charge from falling out during subsequent filling and closing operation.[14]

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The average weight of thoria-urania per 24" length was calculated to be 113.5 grams. Based on a pellet diameter of 0.580 cm (approximately 0.229") the actual average geometric density per tube was calculated to be 7.1 g/cc. This is somewhat lower than the average geometric density as determined from dimensional measurements taken on a representative lot of individual pellets. This difference can be attributed to the uneven seating of the pellets in the tube due to chips or burrs on the ends of the pellets.

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TABLE I

SPECTROGRAPHIC ANALYSIS OF THORIA

Elements Assay 87.2% Th	Concentration
Ag	Less than - 1 ppm
Al	- 70
As	Less than - 10
B	- 1
Ba	Less than - 10
Be	Less than - 5
Bi	Less than - 10
Ca	- 300
Co	Less than - 5
Cr	- 25
Cu	- 30
Fe	- 300
K	Less than - 50
Li	Less than - 1
Mg	- 40
Mn	- 3
Mo	Less than - 20
Na	- 50
Ni	- 20
P	Less than - 50
Pb	- 50
Sb	Less than - 1
Si	- 100
Sn	Less than - 5
Sr	Less than - 200
Ti	Less than - 50
U	Less than - 10
Zn	Less than - 50

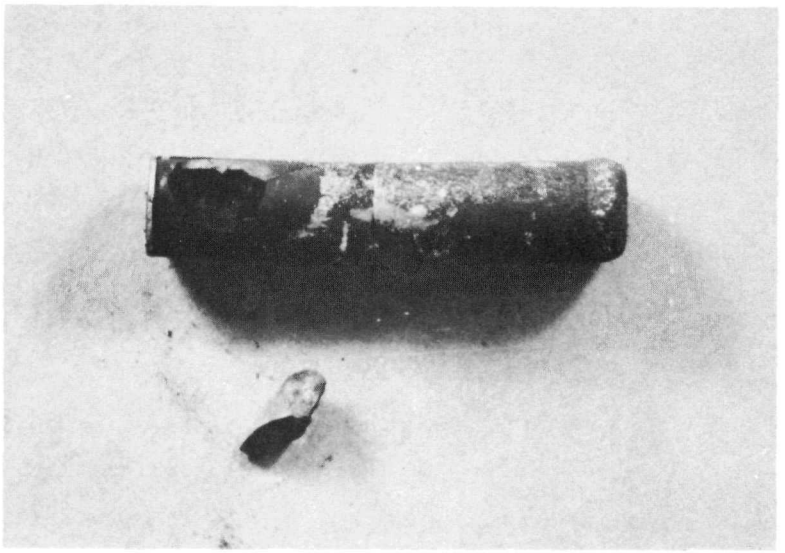

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Figure 1. 90 w/o ThO_2 - 10 w/o UO_2 Specimen After Removal of Al-Ni Cladding

Burnup 0.64% Total Metal

Gas Bond 80% He - 20% A

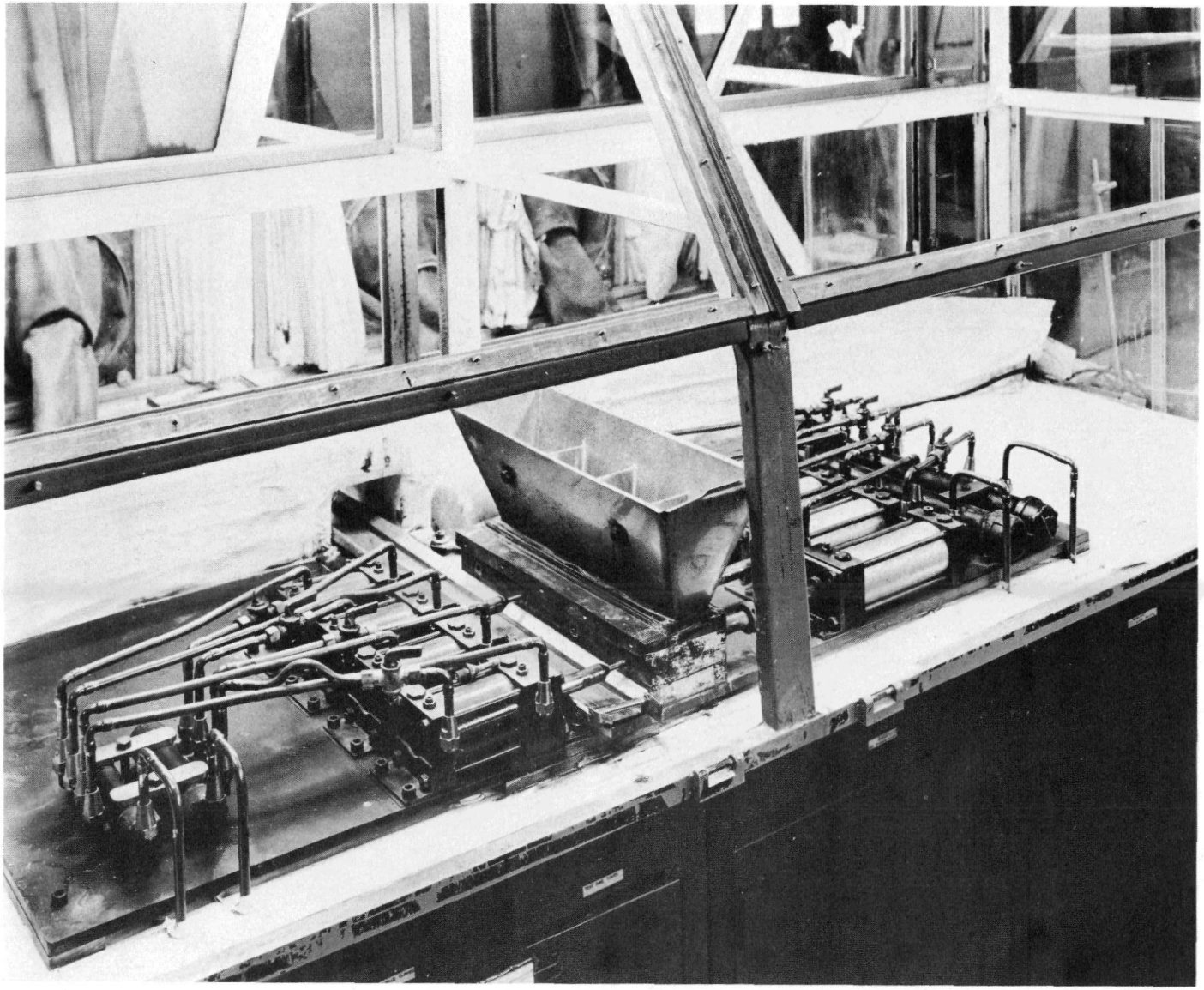

Figure 2. View of Press in Glove Box[11]

Figure 3. View of Conveyor Discharge

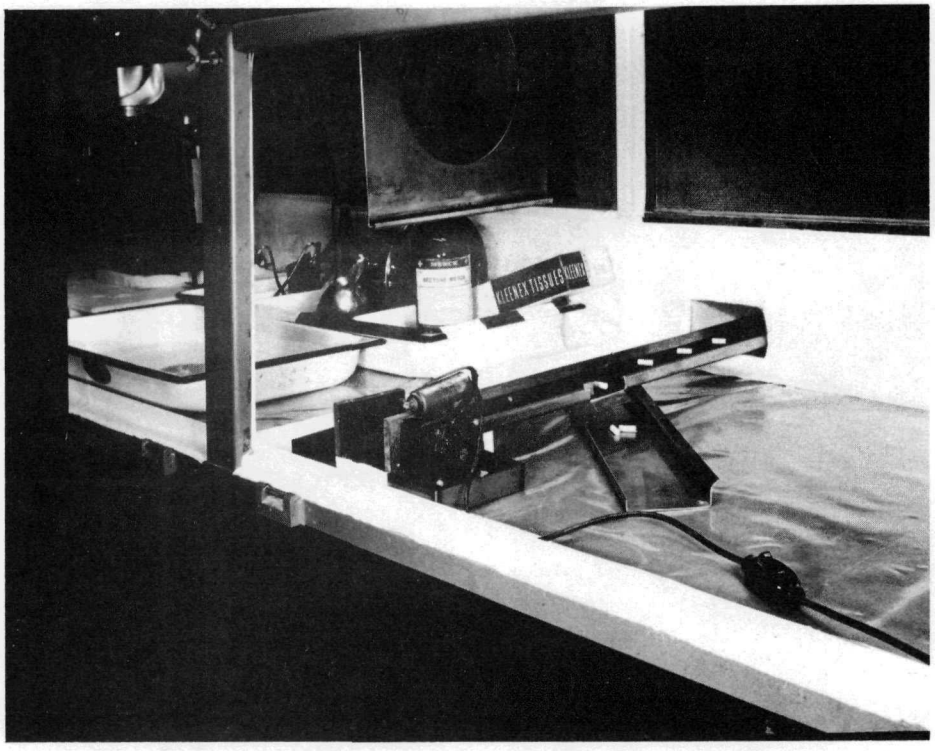

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Figure 4. Crucible Containing Fired Thoria-Urania Pellets

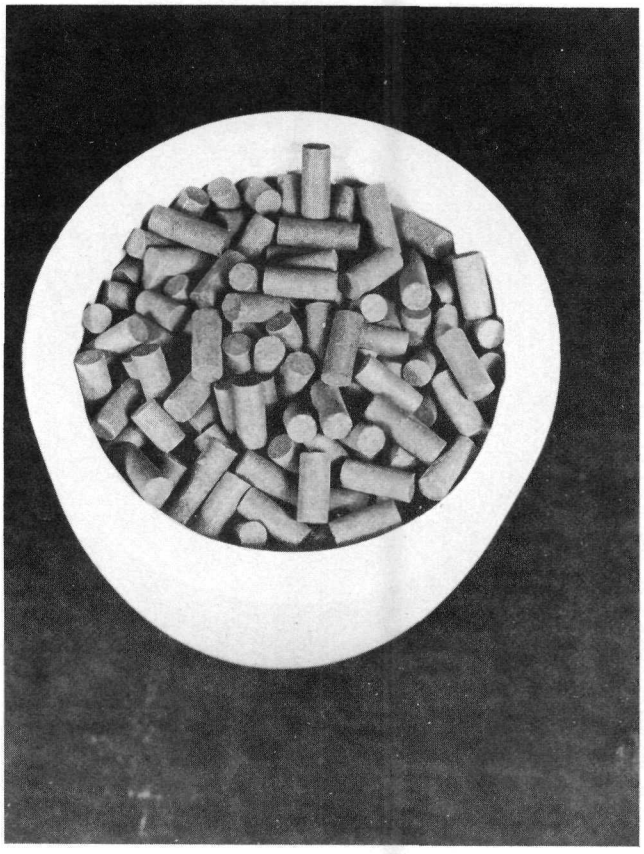

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Figure 5. Crucible Containing Fired Thoria Pellets

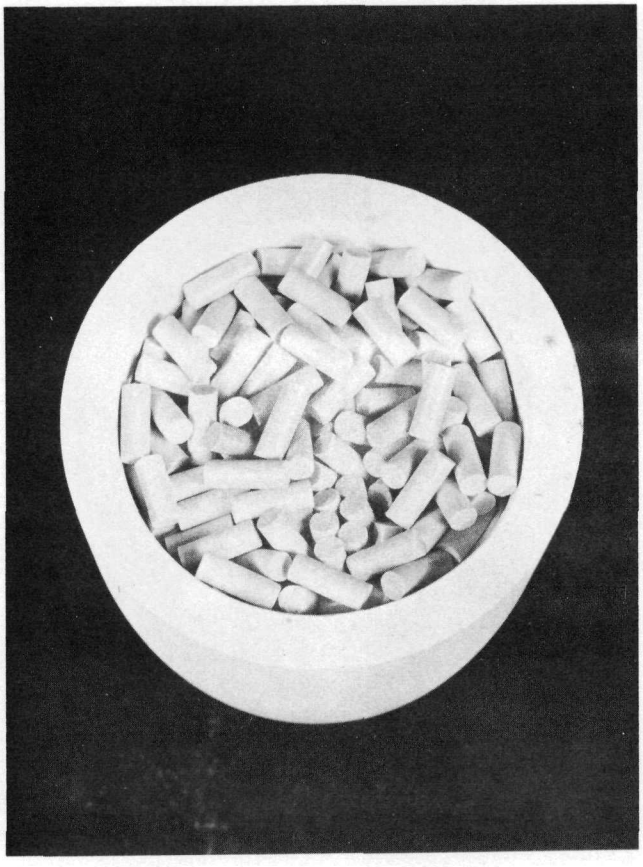

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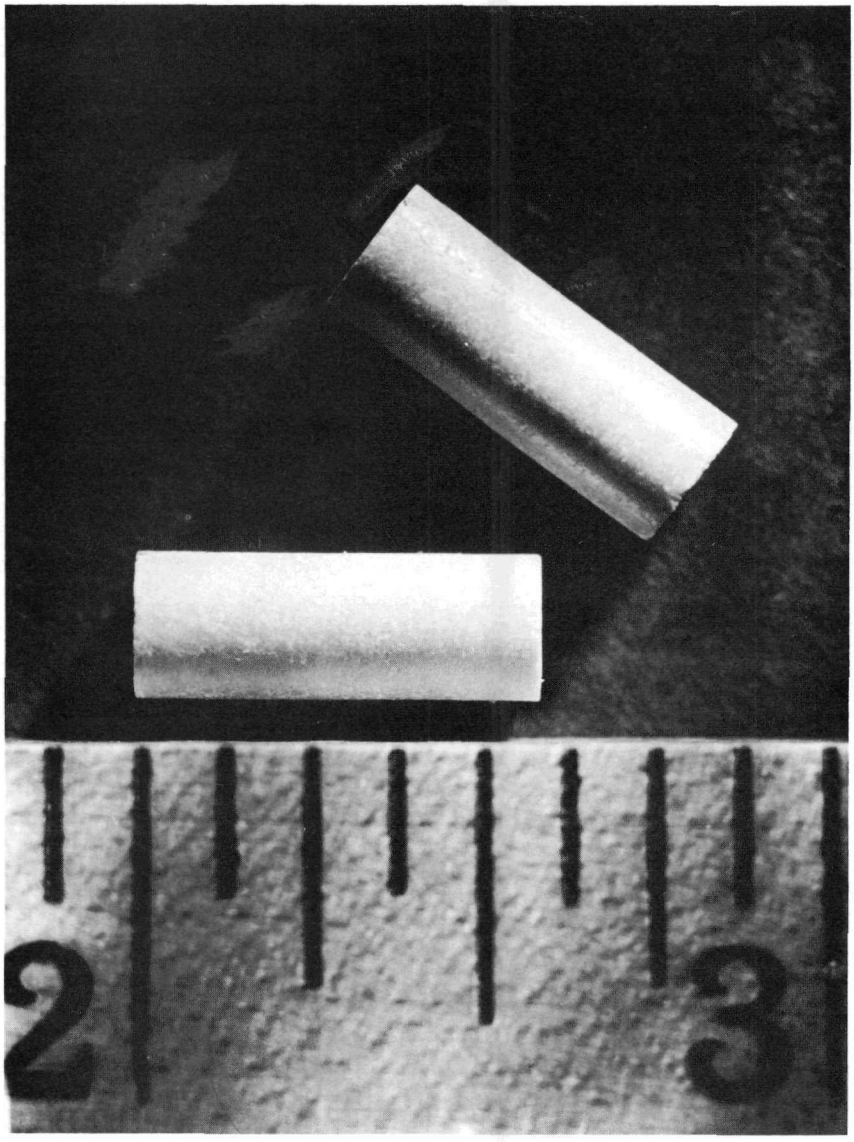
Figure 6. Fired Thoria Pellets



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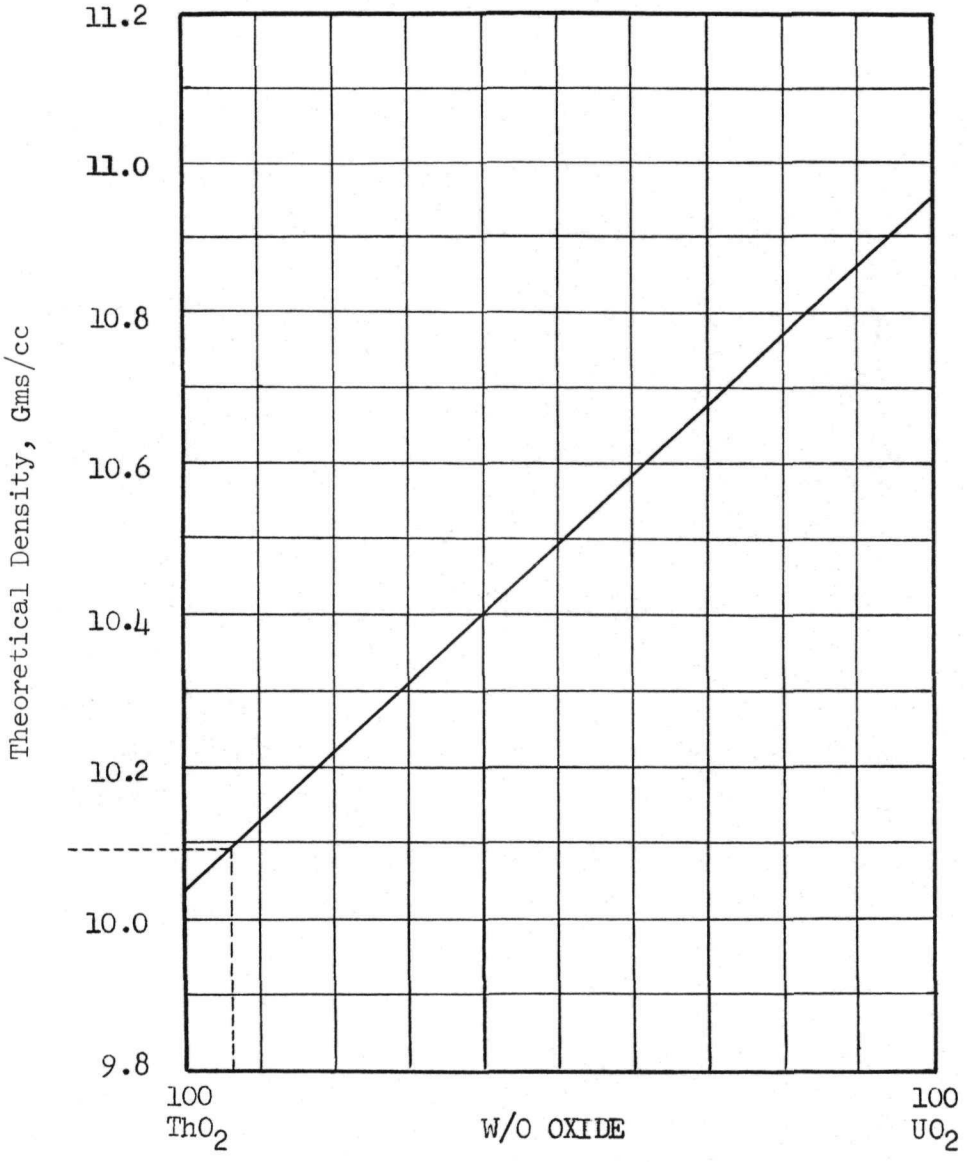

Figure 7. Plot of Theoretical Density of Thoria-Urania

Figure 8. Tube Plate Closed on One End

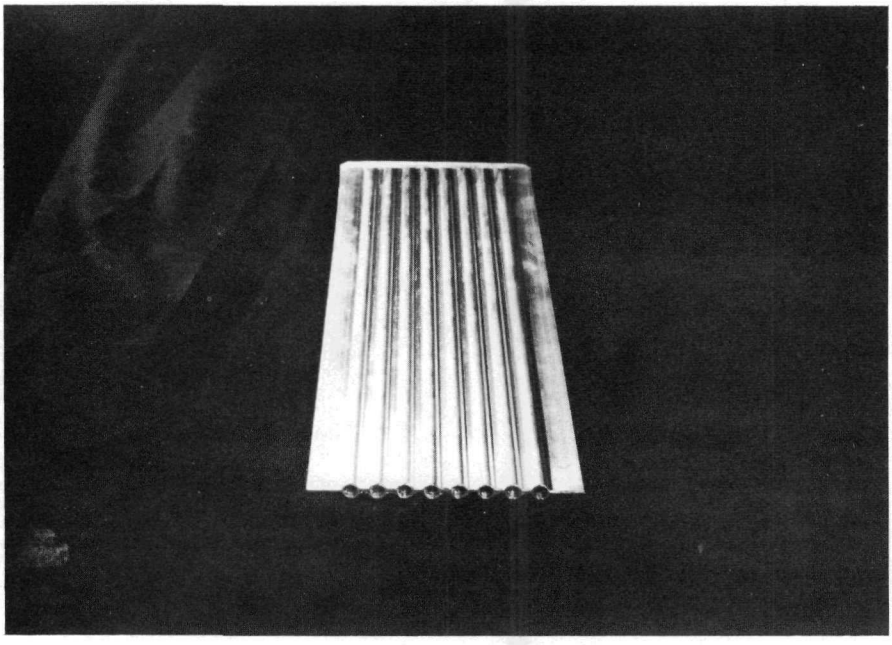

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Figure 9. Fixture for Loading Fuel Pellets