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INTERIM REPORT

# PROPERTIES OF THORIUM OXIDE CERAMICS

C. E. Curtis
J. R. Johnson

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METALLURGY DIVISION

INTERIM REPORT

# PROPERTIES OF THORIUM OXIDE CERAMICS

C. E. Curtis and J. R. Johnson

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INTERIM REPORT
PROPERTIES OF THORIUM OXIDE CERAMICS

C. E. Curtis, J. R. Johnson

Metallurgy Division

ABSTRACT

Included in this report are data concerning the strength, density and porosity that may be expected of thoria ceramics formed by dry pressing and isostatic pressing and fired at 1400, 1600 and 1800° C. By dry pressing and firing at 1400° C, a density of 60% of theoretical (10.05) may be obtained; at 1800° C the density increased to 73% of theoretical. By isostatic pressing a density of 86% of theoretical was obtained at 1800° C.

A study of densification of thoria ceramics by small additions of other inorganic materials showed the very marked effect of CaO (or $CaF_2$) in proportions of 0.5 to 3%. In proportions of 0.5 to 1.0%, CaO additions produced densities of 97% of theoretical at 1800° C. Experimental results intended to explain this phenomenon tended to substantiate the theory that it is due to formation of holes by substitutional solid solution and migration of ions in the altered structure.

Thoria ceramics in the form of six inch rods and of small (0.1") pellets with CaO additions were obtained in densities up to 97% of theoretical; evaluation of the abrasion resistance and strength are given.

Other thoria ceramics were produced in which the density was decreased (by addition of volatile material) to 50 or 60% of theoretical.

Tests of the solubility of thoria ceramics showed that water at 250° C or dilute uranyl sulfate solution had no effect. Ready dissolution was obtained by the normal dissolving process for fuel recovery which makes use of nitric acid with hydrofluoric acid as a catalyst.

## Introduction

Thorium in its application as the fertile material in reactors of the converter or breeder type may be present as the metal or in the form of compounds. Among the latter, the oxide is of particular interest, both because of its present availability and because of its chemical stability. Current consideration is being given mainly to its use in the form of suspensions or slurries. However, thorium oxide can be readily formed by well known ceramic techniques into a variety of shapes of widely varying strengths and porosities and these offer some interesting advantages in reactor applications.

Among these advantages are: sufficient strength for materials of construction, resistance to abrasion, oxidation, hot water, most acids, and dilute salt solutions and the ability to withstand extremely high temperatures (2000° C or above) without softening. In addition, there are in operation industrial plants which are equipped for and experienced in the production of such ceramics.

Specific data pertaining to many of the properties of thoria ceramics that are of particular interest in reactor applications are lacking in the literature. In order to fill the gaps in the data, the Ceramic Group of the Metallurgy Division of ORNL is engaged in a study of certain phases of the technology of thorium oxide ceramics. A report of progress and findings up to the present time are included in the following report.

## Raw Materials

In the forming of ceramics, thorium oxide in the powdered form is desirable. When the material is in the form of the carbonate it can be decomposed to the oxide by a heat treatment of 3-5 hours at 1420° C to 1500° C and the calcined product is readily broken down to 200 mesh size in a pulverizer. For finer grain sizing, ball milling for 4-6 hours in an iron mill with iron balls is usually sufficient. Iron mills are used in preference to ceramic mills in this case because of contamination with porcelain whereas iron is readily leached out by treatment with 1/10 N HCl and decantation.

Thorium oxide employed in the studies to be described was prepared thus and contained impurities as shown in Table 1. The particle size of this lot of $ThO_2$ was 1 micron or less and the material in water suspension was practically neutral (pH = 6.8).

## Forming Thoria Ceramics by Dry Pressing Methods

Various procedures that are available for the forming of thoria ceramics have been described in the literature. Of these various methods those mainly employed for the present report can be classed as "dry pressing"; included in this category is "isostatic" pressing.

In dry pressing in general a mixture of powdered thoria is usually blended with a small amount of binder, dextrin for example, to produce dry strength for handling and with 5 to 7 percent of water or other liquid, and then is compacted into the desired shape under pressure. For the purposes of this report, the following provisions were observed in dry pressing:

Thoria - as described above.
Water content - 3-7%.
Binder - 2% dextrin.
Molds - tool steel. Opening 3" long x 1/2 or 3/8" wide.
Direction of pressure application - from top and bottom.
Type of press - hydraulic, hand operated; pressure - 25,400 psi on the test piece.
Test pieces - bars 3" long 3/8 to 1/2" wide, 1/8 to 1/2" thick.

By dry pressing, test pieces of this size are obtained with sharp corners and uniform dimensions without further finishing operations; a variation in density between successive test pieces of not over 2 to 3% was usual. There was apt to be variation in compaction throughout a given test piece, particularly in the direction of pressure application and especially in sections over 1/8" thick. In the case of thoria bars prepared thus and fired for 2 hours at 1800° C, densities of 77 to 80% of theoretical (10.05) were obtained.

Further data concerning results obtained by this type of pressing are presented under the subject of "Densification" and "Pelletizing" later in this report.

Thoria Ceramics by the Isostatic or Hydrostatic Pressing Method

Isostatic pressing is a type of dry pressing but differs from that described above in that pressure is applied to the powdered mixture equally from all directions. More uniform density within the test piece as compared with ordinary dry pressing is then possible. In isostatic pressing the powdered mixture is enclosed in a flexible container of rubber or plastic of approximately the shape desired; this container is immersed in a liquid, usually oil, to which the pressure is applied.

Usually the piece formed by isostatic pressing is somewhat irregular in shape and must be machined to size, preferably after it has acquired sufficient strength in a firing operation. This operation may consist of either one or two cycles. Experience has shown that isostatically pressed thoria pieces fired at 1400° C for 2 hours have sufficient strength for the machining operation; in this case, the machined pieces were fired again at a higher temperature (1800° C for 2 hours) to produce the desired strength and density.

For example, a cylindrical thoria bar 8" long and 1" in diameter was pressed at 50 T. per square inch; it was fired to 1400° C and then machined to a predetermined size such that after a second firing at 1800° C it was 4.3" long x 0.7" in diameter; its fired density (apparent) was 8.69, (about 87% of theoretical).

Subsequent experience showed that the procedure can be shortened by employing a single firing at 1800° C followed by machining to size; this is possible because thoria ceramics are easily machined in spite of the high degree of sintering at 1800° C.

Densification of Thoria Ceramics

It is possible that certain reactor applications may require denser thoria ceramics than those produced by sintering at temperatures that are feasible industrially, (1800-1900° C), this limit being fixed by the softening temperatures of furnace linings available commercially.

It is known that sintering of an oxide is sometimes enhanced by small additions of other metallic ions. This possibility existed in the case of thoria but there was little specific data in the literature. An investigation was therefore initiated, the search being confined to materials of low neutron cross-section; included were aluminum oxide, beryllium oxide, calcium oxide, calcium fluoride, magnesium oxide, sodium oxide, zinc oxide, silicon dioxide and zirconium oxide. These were added only in small proportions since they might be considered poisons in a reactor.

Mixtures of thorium oxide with 0.5, 1 and 3 weight percent of each of these materials were dry pressed as described above to form bars 1/8" thick. The results of firing each combination at 1400, 1600 and 1800° C for 2 hour periods were then determined in terms of apparent density.

A summary of preliminary results obtained with some of these additions in proportions of one weight percent is shown graphically in Fig. 1 in terms of density; the effect of the Ca ion in proportions of 0.5 to 1 weight percent of CaO or $CaF_2$ was notable in all cases. Of the other oxides, MgO and $Al_2O_3$ had a much smaller effect that CaO while the action of $Na_2O$, ZnO and $ZrO_2$ were negligible.

A more detailed search of the $ThO_2$-CaO reaction was made, employing 3 proportions of CaO - 0.5, 1 and 3 weight percent - and three firing temperatures - 1400, 1600 and 1800° C, for 2 hour periods. The results were evaluated in terms of density (apparent), porosity (apparent) (ratio of volume of open pores to total volume of the piece), and shrinkage; strength was evaluated in terms of modulus of elasticity and of modulus of rupture. Pertinent results are given in Table 2.

A portion of the results in the case of straight thoria and of thoria plus one percent CaO are shown photographically in Fig. 2 in which is included with each of the three firing groups (1400, 1600 and 1800° C) an unfired bar of the original size to show the amount of shrinkage and any color changes occurring at each temperature.

From the data given it is apparent that pure thorium oxide was not very dense even when fired at 1900° C. With 0.5 CaO present, however, practically complete elimination of porosity and a density close to theoretical was found at 1800° C. This densification was accompanied by a color change from the original white to olive green. A firing temperature above 1800° C did not seem justified.

Note: R. F. Geller observed this effect of CaO in small proportions on the shrinkage of $ThO_2$ in 1944. Apparently the phenomenon was not investigated extensively, however, at that time.(1)

X-Ray Analysis

A determination was made of the X-ray structure of a bar consisting of $ThO_2$ + 1% CaO fired at 1800° C. No trace of CaO was visible in the

X-ray pattern and the cubic structure and size of the unit cell of $ThO_2$ ($a_o$ = 5.5977 Å) was unaffected by the CaO despite the large increase in densification obtained. This same result was obtained with additions up to 25 mol percent CaO.

Petrographic Examination

The chief difference between the $ThO_2$ and the densified $ThO_2$ (fired at 1800° C) visible in either powdered or thin sectioned samples was an increase in grain size by a factor of approximately 15 (from an average of 4 microns to an average of 60) accompanying densification; this crystal growth penetrated and filled most of the voids in the test piece so that pores visible in the undensified thoria were notably lacking in the densified body. A decrease in index of refraction accompanying CaO additions indicated solid solution.

Thermal Expansion

Between room temperature and 1230° C, the thermal expansion rates of $ThO_2$ and of the densified type (1% CaO addition) were similar and showed no variations that would indicate phase changes. The respective linear coefficients were as follows:

Pure $ThO_2$ (fired at 1800° C), 100 to 1230° C = $9.67 \times 10^{-6}$/° C.
$ThO_2$ + 1% CaO (fired 1800° C), 100 to 1230° C= $9.93 \times 10^{-6}$/° C.

Differential Thermal Analysis

The curves were similar, no change in heat absorption from room temperature to 1200° C being indicated by this technique in either pure thoria or the densified type (with addition of 1% CaO) to indicate a phase change.

Thermoluminescence

Thoria fired to 1800° C showed no thermoluminescence to 350° C. After irradiation at 520 roentgens, it had peaks of thermoluminescence at 95° C and 210° C and a smaller peak at 230° C. In densified $ThO_2$ (0.5 wt. % CaO) after irradiation the 95° peak had been eliminated and the high temperature peak had been considerably reduced. It was concluded that the number of electron traps stable at low temperature is greatly reduced and the number at high temperature is considerably reduced by the presence of $CaO^2$. Interpretation of these effects is difficult from these data but they indicate that some change in the structure of $ThO_2$ has been effected by the densification process.

Limits of Interaction between $ThO_2$ and CaO at 1800° C

A series of mixtures were made up in which the CaO content (in mol percent) was 0, 3, 6.25, 12.5, 25, 37.5, 50, 62.5 and 75%. These mixtures in powder form and also in pressed bars were fired at 1800° C for 2 hours. The following results were noted:

a. The shrinkage rate reached a maximum with 3% CaO present, little further shrinkage occurring with larger additions (Fig. 3).

b. Debye-Scherrer X-ray photographs showed no change in lattice dimensions throughout the series to 37-1/2% CaO and within the limits of accuracy of the apparatus. No CaO was visible in these compositions.

c. The presence of free CaO in compositions containing 25% and over of this oxide was shown by their disintegration in boiling water (Fig. 3).

No free lime was found petrographically in the 12-1/2% sample by Dr. T. N. McVay, employing a technique which makes use of the growth of crystals on a microscope slide when free CaO is present[3]. Compositions containing 0.5, 1.0 and 3.0 percent CaO were unchanged after 6 hours in boiling water and the pH of the water was likewise unchanged. These results further indicate that CaO is taken into solid solution in $ThO_2$ up to at least 12-1/2 mol percent.

Relation of Ion Size to Densifying Effect

The fact that the ionic radius of Ca (0.99 Å)[4] is close to that of Th (1.02 Å)[4] is thought to have a bearing on the effect of CaO. As a test of this relationship, advantage was taken of the fact that the strontium ion (radius = 1.13 Å) is of similar size. Strontium oxide (1 weight percent) was added to $ThO_2$ and the mixture in pressed bars was fired for 2 hours at 1800° C in an oxidizing atmosphere. The resulting density (8.9) was closer to that obtained with the Ca ion than had been obtained with the oxides previously tested (compare Fig. 1) at this temperature.

Equilibrium in $ThO_2$-CaO Solid Solution at 1800° C

In order to determine whether the densifying effect of CaO is complete in one firing operation at 1800° C, the $ThO_2$ + 1% CaO composition previously tested was reground to 200 mesh, repressed and refired at 1800° C for 2 hours in an oxidizing atmosphere. The results were as shown in Table 3. The reground bars were less dense indicating a dynamic effect in the process.

Effect of Furnace Atmosphere on Densification

All of the above densification results were obtained in an oxidizing atmosphere with oxyacetylene or propane as a heat source.

Pressed bars (prepared as before) of thoria, of thoria plus 5 mol percent of CaO and also of thoria plus 5 mol percent of SrO were fired in an atmosphere of helium at 1750° C for 1-1/4 hours; others were fired in hydrogen under the same conditions. After the properties of the fired compositions had been determined, those fired in hydrogen were refired in air to determine whether any additional changes could be effected.

The results are given in Table 4 and indicate that:

1. Vitrification of pure $ThO_2$ is not dependent on the atmosphere since approximately the same density was obtained in all atmospheres.

2. Densification of $ThO_2$ by CaO or SrO is not affected by the absence of oxygen in the furnace atmosphere, for instance, by a helium atmosphere (Column B); however, the CaO reaction is definitely prevented by a reducing atmosphere (hydrogen) (Column C) and the densifying effect is not restored by a subsequent firing in air (Column D).

A survey of the progress of densification of $ThO_2$ produced by 1/2 weight percent of CaO at 1700° C was made by firing dry pressed bars of this composition for various intervals and determining the densities obtained. The shape of the curve of density versus time (Fig. 4) is such as to indicate that a diffusion rate process is involved.

Conclusions, Densification of Thoria by CaO

The $Ca^{++}$ ion has about the same ionic radius as $Th^{++++}$ so that the observed solid solution is expected. Substitution of divalent calcium for quadrivalent thorium in this case will create oxygen ion deficiencies. It is known that vacancy structures such as this permit rapid diffusion of the structural ions. Both surface and solid diffusion are undoubtedly mechanisms for material transport in the sintering of $ThO_2$. It is to be expected that even though the movement of material on the surfaces is the process involved in filling the pores or crystal growth, the controlling feature may well be the rate of supply of material to the surfaces by solid diffusion. Thus rapid diffusion of $Ca^{++}$, $Th^{++++}$ and $O^{--}$ through the vacancy structure will increase the sintering rate.

It should be noted, however, that the dynamic action between CaO and $ThO_2$ grains is involved in the phenomenon. Sintering of calcined grains where solid solution is completed is less rapid. Further, when the

thoria-calcia mix is sintered in hydrogen, sintering is not accelerated over the rate observed for pure $ThO_2$. Apparently, the hydrogen readily supplies electrons to the system, inhibiting the formation of anion vacancies on the surfaces.

Fig. 4 shows a rather massive rod which was pressed isostatically as described above, sintered at 1800° C, then machined. Its density is 97% of the theoretical $ThO_2$ density or 99.5% of the density theoretically possible if the 1/2 weight percent CaO added and the oxygen ion vacancies are taken into account.

By correlation of these data with those of future studies, including diffusion investigations using radioactive $Ca^{45}$ as a tracer, and effects of other gaseous atmospheres, it is hoped that it will be possible to define the mechanisms involved more specifically.

## Pelletized Thoria Ceramics

Thoria in the form of pellets is considered of possible application in "live" breeder blankets, hence some study has been given to the production of such pellets by ceramic techniques.

### Spherical Pellets

Spherical pellets in 1/8", 1/4" and 1/2" sizes (made by the Norton Company, Worcester, Massachusetts), were tested for physical properties as given in Table 5. Rounded pellets in various sizes have been produced in this laboratory by a "snowball" method; in this procedure powdered thoria and a water mist were introduced alternately into a revolving cylinder; globules of powder begin to roll and grow as their moist surfaces pick up layers of powder. In order to give these pellets dry strength, 2% of dextrin is dissolved in the tempering water. Theoretically, pellets in a wide variety of sizes can be made by this method. Properties of spheres made in this way are included in Table 5.

### Cylindrical Pellets of Thorium Oxide

Cylindrical thoria pellets were needed for obtaining abrasion data in view of the possible application of thorium oxide in this form. In order to expedite production of the pellets, use was made of the personnel and equipment of the American Lava Corporation in Chattanooga. The cylindrical shape desired in these pellets permitted the use of a punch press by means of which very uniform pellets can be produced at a rapid rate.

The thorium oxide was granulated before pressing to enable it to flow freely into the die. Granulation consisted in pressing a mixture of thoria powder with dextrin and water (5%) and breaking the resulting brick to plus 80 mesh size.

Pelletizing by this method is a dry pressing operation; in this case a toggle type punch press was used which produced 7 pellets per stroke or about 200 per minute. Sleeve or washer type pellets containing a 1/16 inch longitudinal hole were also produced on the same machine with a slight change in the die.

The pressed pellets were given a prefiring operation at 1650° C in air to burn out the dextrin and to produce strength for handling. This was followed by a high firing at 1800° C for 2 hours. Experience indicated that the prefiring operation might be dispensed with. The solid pellets were 0.1" long and 0.1" in diameter after firing. Some were made of pure thoria; the remainder were densified with 0.5 mol percent of CaO. Pellets of the washer type were all of the densified type.

Some of the properties of these pellets are given in Table 6. The only strength tests possible with pieces of this size were crushing resistance and abrasion rate. (Results of tests of their abrasion in moving water are given in ORNL 54-3-44, Secret.)

It is probable that pellets with greater strength and density and better resistance to abrasion can be produced by using the experience gained in these operations.

## Forms of Thorium Oxide Ceramics

In Fig. 6 are shown some of the forms in which thoria ceramics have been produced: From left to right: two types of dry pressed cylindrical pellets, washer and solid; three sizes of hand rolled spheres, a dry pressed 1 cm. cube; a dry pressed disc and a strip, both 1/32 inch in thickness. An isostatically pressed rod was previously shown in Fig. 4. Many other shapes and sizes are possible, of course.

## Light Weight Thoria Ceramics

Fired thoria of low density may also be of interest in certain reactor applications. Low density products were obtained by adding to the thoria various proportions of a fine grained material, which is volatile or combustible or both, then pressing bars 3 x 1/4" x 1/8" from the mixture and firing these for 2 hours at 1800° C. One of the combustibles used in this case was naphthalene.

Results are given in Table 7 and indicate that with increasing proportions of naphthalene, density is decreased but shrinkage seemed to be unaffected by the additions. Strength of the ceramics decreased with increasing porosity so that for practical purposes 16% of naphthalene is about the limit that should be used.

## Corrosion of Thoria Ceramics

Resistance of thoria ceramics to hot water, to uranium salt solutions and to molten metals is of interest in reactor applications. The few data concerning corrosion in the literature are seldom correlated with the densities and porosities of the specimens and is therefore apt to be of limited value. Some tests have been made to meet this need as detailed below and more tests are in prospect.

## Corrosion in High Temperature Water

Thoria dry pressed bars (fired at 1700° C) and thoria spheres 1/8" and 1/4" in diameter (Norton Company) also fired at 1700° C were sealed in Pyrex glass tubes containing water. Some of the spheres were free to roll the length of the tube but most were fixed in place. The Pyrex tubes were placed in autoclaves of the rocking type and heated at 250° C (590 psi) for 50 hours.

It is apparent from the data in Table 8 that these thoria ceramics were practically unaffected by high temperature water even though they were porous. The densified, non-porous thoria previously described should be even more resistant.

## Corrosion of Thoria Ceramics in Uranyl Sulfate

In cases where fired thorium oxide ceramics are exposed to a fuel solution of dilute uranyl sulfate it was of interest to know how much corrosion would occur. Thoria pellets similar to those in Table 8 after 50 hours' exposure to a dilute solution of the fuel at 300° C in an autoclave were unaffected.

## Solution of Thoria Ceramics in Nitrate Solution

In the recovery of $U^{233}$ from irradiated thorium oxide, it is necessary to dissolve the ceramic material. Nitric acid with a small addition of HF is suitable as a solvent. It was of interest to know whether the solution rate of thoria ceramics is comparable with that of thorium or uranium metal in the usual slug form in this solvent and how the rate of solution is affected by the firing temperature to which the ceramics have been subjected.

A test of the solution time in nitric acid (4.5 mols $HNO_3$ to 1 mol $ThO_2$ + 0.075 mols $F^-$) was carried out on three samples of $ThO_2$ in the form of small cylinders which had been calcined at temperatures of 700, 1200 and 1630° C respectively. The time required for 100% dissolution was 1-1/2 hours, 2.6 and 5 to 5.5 hours respectively.

In another case thoria spheres 1/8 x 1/4" in diameter (porosity 2-9%) fired at 1200° C in excess $HNO_3$ + 1/10 molar HF were 75% dissolved in 12 hours.

For comparison, an ordinary type of uranium slug 6" long by 1-1/2" in diameter reportedly requires approximately 30 hours for solution.

It should be pointed out in the case of the thoria ceramics that the solution time is not excessive under these conditions and doubtless it could be decreased further by simply crushing the material, an operation which is rather easily performed because of the brittle nature of the ceramic.

References:

1. Geller, R. F., Chief of Pottery Section, U. S. Bureau of Standards, personal communication.

2. Daniels, Farrington, Chairman of Department of Chemistry, University of Wisconsin, December 11, 1953, personal communication.

3. McVay, T. N., Consultant to Ceramic Laboratory, Metallurgy Division, ORNL, personal report.

4. Handbook of Chemistry and Physics, 33rd edition (1951-1953), Chemical Rubber Publishing Company (pp. 2820-2822).

TABLE 1

SPECTROGRAPHIC ANALYSIS OF THORIUM OXIDE

(in ppm)

| | | | |
|---|---|---|---|
| Si | 800 | Be | 100 |
| Mg | 500 | Ca | 100 |
| Cd | less than 500 | Zn | less than 100 |
| Co | less than 500 | Al | 30 |
| Cr | less than 500 | Fe | 30 |

TABLE 2

CERAMIC PROPERTIES OF $ThO_2$ AND OF DENSIFIED $ThO_2$ (DRY PRESSED)

| Addition | Firing T. | Density[a] | Porosity (% appar.) | Shrinkage (% total) | Modulus of Elas.[b] (psi) | Modulus of Rupt.[c] (psi) | Crushing Strength[d] (psi) |
|---|---|---|---|---|---|---|---|
| None | 1400 | 5.90 | 46.9 | 1.7 | $7.3 \times 10^6$ | $7 \times 10^2$ | - |
| | 1600 | 6.70 | 27.8 | 6.4 | 12.8 | 9 | $32.5 \times 10^4$ |
| | 1800 | 8.02 | 17.6 | 10.5 | 19.6 | 13 | 21.0 |
| | 1900 | 9.14 | 1.8 | 11.6 | - | - | - |
| 0.5 CaO | 1600 | 8.00 | 17.2 | 12.2 | 20.7 | 9 | 30.4 |
| | 1800 | 9.65 | 0.0 | 17.5 | 20.9 | 19 | 35.5 |
| 1.0 CaO | 1600 | 8.1 | 12.8 | 12.0 | 19.9 | 9 | 32.3 |
| | 1800 | 9.5 | 0.0 | 17.6 | 33.9 | 20 | 40.0 |
| | 1900 | 9.5 | 0.0 | 17.9 | - | - | - |
| 3.0 CaO | 1400 | 6.1 | 35.1 | 7.3 | 10.7 | 7 | - |
| | 1800 | 9.1 | 0.0 | 18.5 | 43.6 | 26 | - |

[a] "Apparent" density from suspended weight method.

[b] Modulus of elasticity by the sonic method, using bars 3" x 1/4" x 1/8".

[c] Modulus of rupture was obtained on bars as in (b); 1-1/2" span. Rate of loading was 7.4 lb/sec.

[d] Employing cubes approximately 1/2" on a side.

TABLE 3

| Treatment | A<br>Fired once at 1800° C | B<br>Product A Reground and Refired |
|---|---|---|
| Density | 9.68 | 7.76 |
| Porosity (Appar.) | 0.0 | 20.9 |
| Shrinkage (Total) | 17.4% | 2.4 |

TABLE 4

EFFECT OF FURNACE ATMOSPHERE ON DENSIFICATION OF PURE $ThO_2$

| | $ThO_2$ | | | |
|---|---|---|---|---|
| | (A) | (B) | (C) | (D) |
| Firing | Original | Original | Original | (C) Refired in |
| Atmosphere | Air | Helium | Hydrogen | Air |
| Time (hours) | 2 | 1-1/4 | 1-1/4 | 1-1/4 |
| Temperature (°C) | 1750 | 1750 | 1750 | 1750 |
| Density | 7.2 | 7.7 | 7.4 | 7.6 |
| Porosity (%)(Appar) | 27.1 | 22.4 | 25.1 | 22.8 |
| Shrinkage (%) (Total) | 8.2 | 9.4 | 8.5 | 9.0 |
| Color | Light tan | White | White | Very light tan |

| | $ThO_2$ + 5 Mol % CaO | | | |
|---|---|---|---|---|
| | (A) | (B) | (C) | (D) |
| Firing cycle | Original | Original | Original | (C) Refired in |
| Atmosphere | Air | Helium | Hydrogen | Air |
| Time (hours) | 2 | 1-1/4 | 1-1/4 | 1-1/4 |
| Temperature (°C) | 1750 | 1750 | 1750 | 1750 |
| Density | 8.7 | 9.0 | 7.75 | 7.8 |
| Porosity (%)(Appar) | 3.1 | 2.7 | 17.2 | 14.9 |
| Shrinkage (%) (Total) | 17.1 | 14.7 | 10.4 | 10.4 |
| Color | greenish yellow | light tan | White | Varies greenish yellow to orange |

| | $ThO_2$ + 5 Mol % SrO | |
|---|---|---|
| Firing | Original | Original |
| Atmosphere | Air | Helium |
| Time (hours) | 2 | 1-1/4 |
| Temperature (°C) | 1800 | 1250 |
| Density | 8.9 | 8.1 |
| Porosity (%)(appar) | 1.6 | 15.8 |
| Shrinkage (%) (Total) | 13.7 | 10.6 |
| Color | Tan | Light Tan |

TABLE 5

PROPERTIES OF TWO TYPES OF THORIA SPHERES

| How Made | Firing Temp(°C) | Density | Porosity | Description |
|---|---|---|---|---|
| By rolling plastic mass in hands | 1700 | 8.71 | 5.6 | Comparatively spherical. Internal cracks present due to forming method. |
| Snowballing | 1800 | 7.51 | 18.7 | Not perfectly spherical, no cracks. |

TABLE 6

PROPERTIES OF PELLETIZED THORIA FROM PUNCH PRESS

| Shape | Composition | Firing T.(°C) | Density | Crushing Strength[a] (psi) | Abrasion Rate[b] (% per hr.) |
|---|---|---|---|---|---|
| Solid | $ThO_2$ | 1800 | 9.59 | $2 \times 10^4$ | 0.20 |
| Solid | $ThO_2$ + 0.5 CaO | 1200 | 7.75 | 0.2 | |
| | | 1650 | 9.29 | 1.7 | 0.18 |
| | | 1800 | 9.71 | 4.6 | 0.17 |
| Washers | $ThO_2$ + 0.5 CaO | 1800 | 9.48 | 4.5 | 0.18 |

[a] Crushed by pressure on individual pellets. Values given are very general as there was considerable variation between similar pieces, due in part to their small area.

[b] Tumbled dry in 200 g. batches in an iron mill 5-1/4" in diameter, revolving at 68 rpm. Rate of travel of pellets was approximately 1.9 ft./sec.

TABLE 7

LIGHT WEIGHT THORIA CERAMICS

| Composition of Body | Naphthalene (wt-%) | Density | Porosity (% Appar.) | Shrinkage (Total)(%) |
|---|---|---|---|---|
| $ThO_2$ | 0 | 8.0 | 17.6 | 10.5 |
| | 3 | 7.1 | 25.6 | 10.0 |
| | 8 | 6.0 | 39.4 | 10.0 |
| | 12 | 5.3 | 46.6 | 9.8 |
| | 16 | 5.3 | 45.5 | 10.0 |
| $ThO_2$ + 1% Wt CaO | 0 | 9.7 | 0 | 17.4 |
| | 12 | 6.4 | 34.3 | 18.7 |
| | 16 | 6.3 | 34.6 | 18.2 |

TABLE 8

CORROSION TESTS OF THORIUM OXIDE IN WATER AT 250° C (50 hrs.)

| Shape | Firing Temp. (°C) | Density | Porosity (%) | Loss in 50 hrs. |
|---|---|---|---|---|
| 1/4" spheres | 1700° | 8.8 | 2.1 | (Rolling)* -0.08 to 1.5%<br>(Stationary)- nil |
| Dry pressed Bar | 1400° | 5.9 | 41.9 | (Stationary)- nil |
| | 1600° | 6.6 | 34.0 | (Stationary)- nil |

* Loss was mainly by abrasion, not by solution. These tests were made by D. Ferguson's group, Homogeneous Reactor, Chemical Processing.

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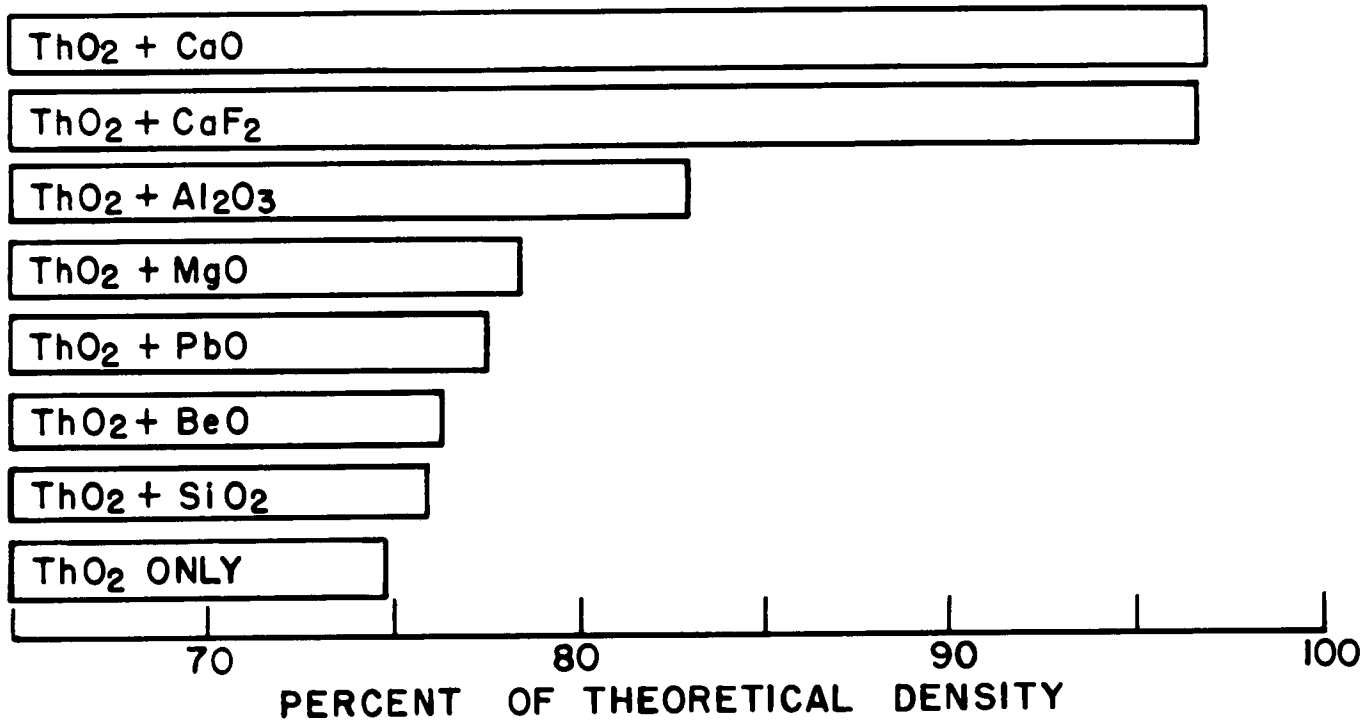


FIGURE 1. CHANGES IN DENSITY OF THORIUM OXIDE CERAMICS EFFECTED BY ONE wt. PERCENT OF VARIOUS ADDITIONS (FIRING TEMP. = 1800°C.)

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| FIRING TEMP. (°C) | UN-FIRED | 1400 | 1400 | UN-FIRED | 1600 | 1600 | UN-FIRED | 1800 | 1800 |
| CaO ADDN. (Wt. %) | 0 | 0 | 1 | 0 | 0 | 1 | 0 | 0 | 1 |
| DENSITY (Fired) | | 5.9 | 7.1 | | 6.4 | 8.1 | | 8.0 | 9.7 |

FIG. 2. THORIA – EFFECT OF FIRING TEMPERATURE AND CaO ON DENSITY AND FIRING SHRINKAGE.

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| umber | 201A | 201B | 201C | 201D | 201E | 201F |
|---|---|---|---|---|---|---|
| aO addn. | 0 | 3.0 | 6.25 | 12.5 | 25.0 | 37.5 |
| hrinkage | 17.1 | 18.4 | 21.2 | 24.0 | 25.3 | 23.4 |

FIG. 3. THORIUM OXIDE – DRY PRESSED, FIRED 2 HOURS AT 1800°C.
NOS. 201E AND 201F SHOW EFFECT OF BOILING WATER.

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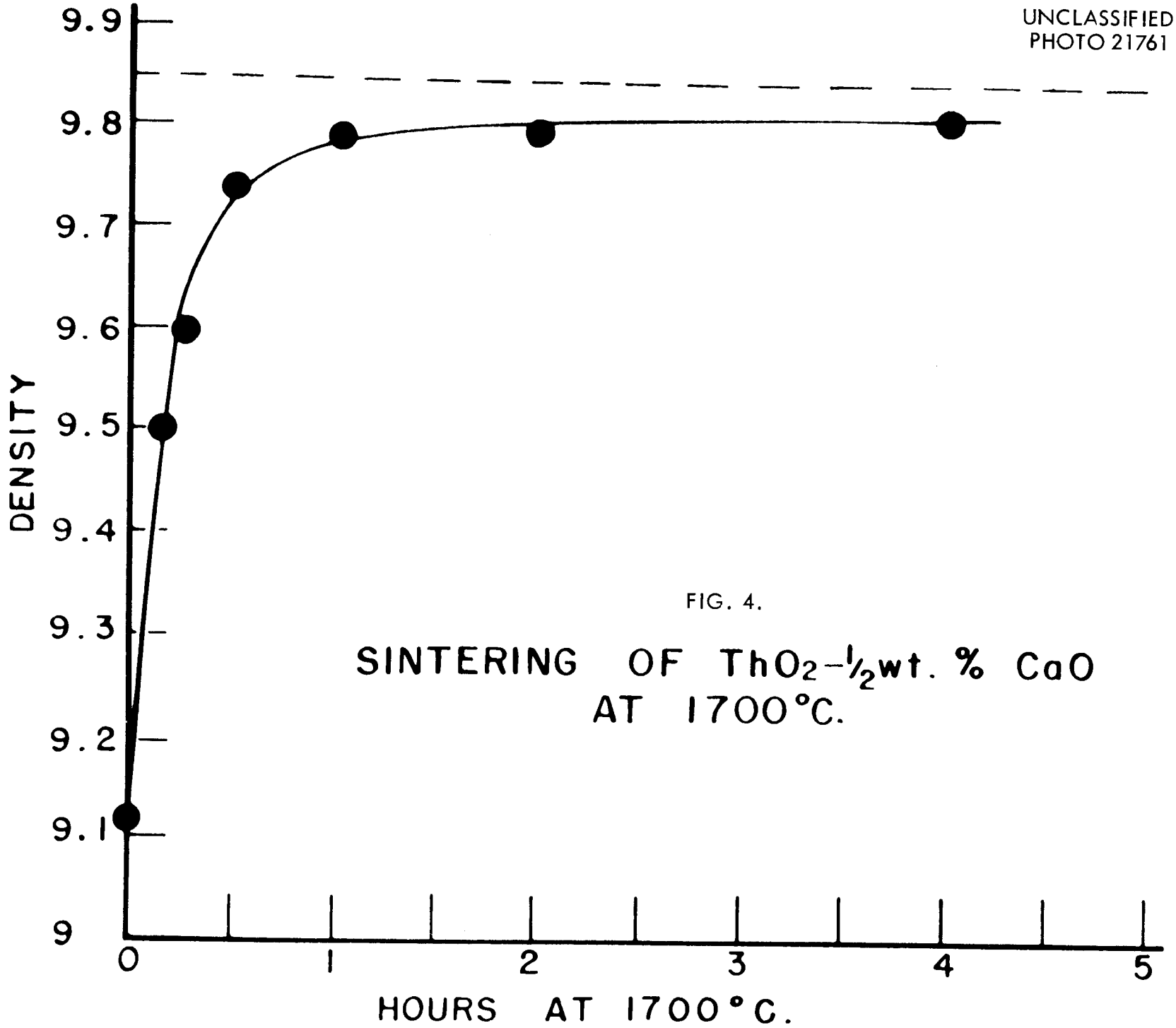


FIG. 4.

SINTERING OF $ThO_2$-½wt. % CaO AT 1700°C.

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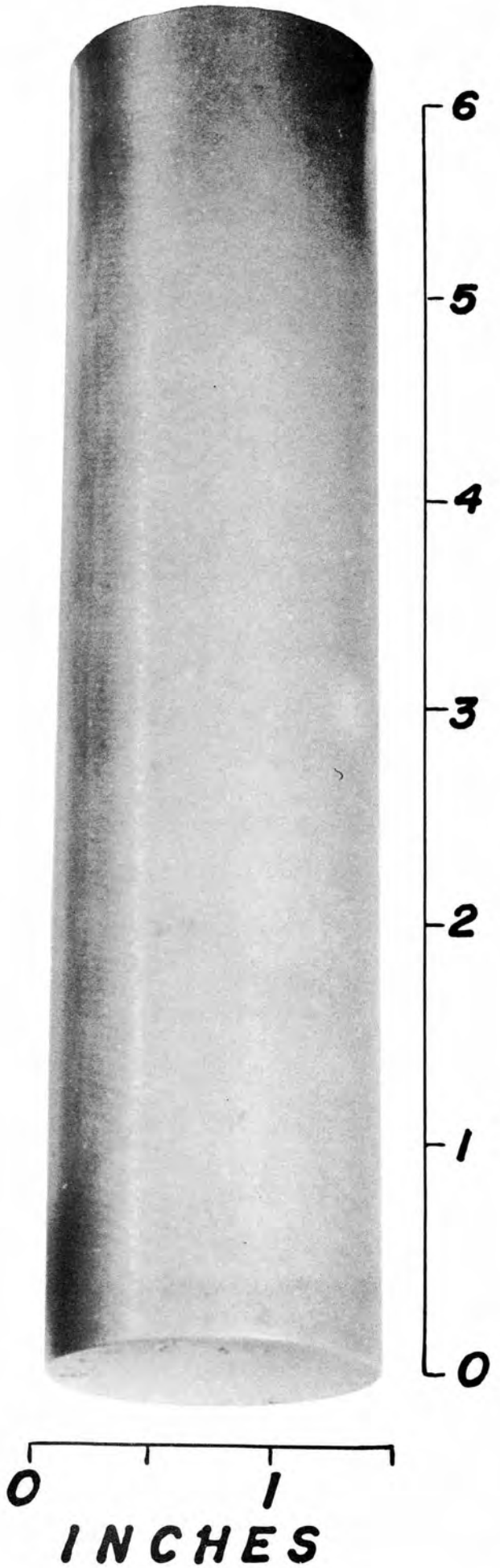


FIG. 5

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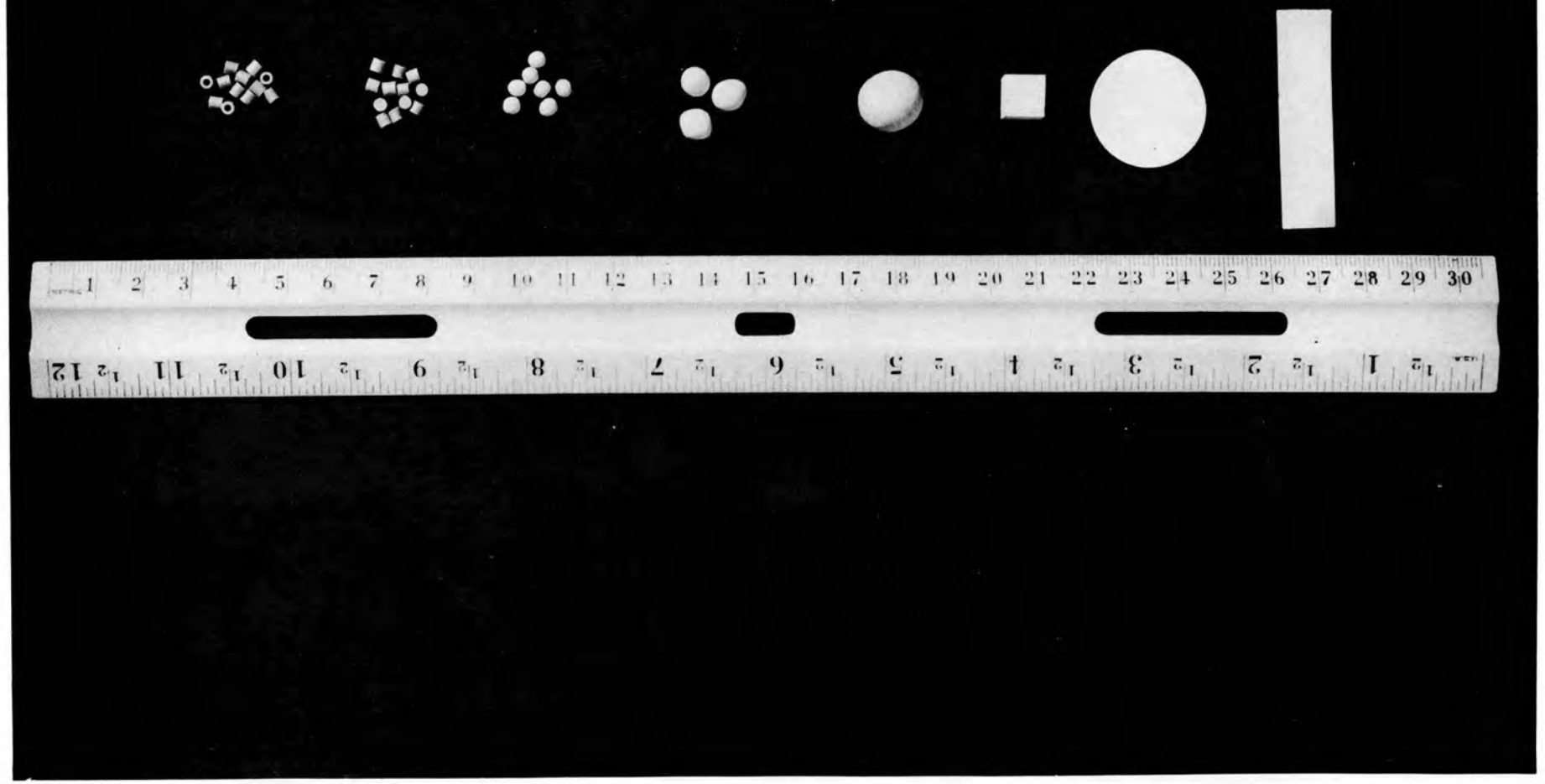
FIG. 6

THORIUM OXIDE CERAMICS