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# SOL-GEL THORIA EXTRUSION

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METALS AND CERAMICS DIVISION

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R. B. Fitts
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SEPTEMBER 1968

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# SOL-GEL THORIA EXTRUSION

R. B. Fitts H. G. Moore[1]
A. R. Olsen J. D. Sease

## ABSTRACT

The sol-gel process, developed at the Oak Ridge National Laboratory, provides a stable colloidal suspension of various ceramic materials. This suspension, or sol, may be concentrated, dried, and fired at low temperatures to form dense ceramic bodies. We use standard ceramic equipment and the concentrated sol, or clay, with powder additions to extrude pure oxide ceramic bodies of various shapes and controlled density. The extrusion blend requires no extraneous binders or plasticizers. We have demonstrated in laboratory-scale work that this process produces high-strength solid and cored extrusions of thoria fired at 1150°C with controlled densities ranging from 70 to 99% of theoretical and with diameters up to 1/2 in. (±0.001 in.) and lengths to 3 in. We have defined the effects of various powder additions and drying conditions on extrusion quality and density. This process, proven in the thoria system, may make improvement and greater economy possible in the fabrication technology for ceramic shapes of zirconia, alumina, and other ceramics amenable to the sol-gel process.

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## INTRODUCTION

The extrusion of ceramic bodies is common industrial practice, but there is little information in the literature on extruding pure oxides.[2] The fact that extrusion is generally adapted to producing ceramic bodies with large length-to-diameter ratios led to investigations[3,4] of

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[1]Now with Los Alamos Scientific Laboratory.

[2]C. Hyde, "Vertical Extrusion of Nonclay Compositions," pp. 107–111 in Ceramic Fabrication Processes, ed. by W. D. Kingery, John Wiley and Sons, Inc., New York (1958).

[3]W. E. Bailey, $UO_2$ Fabrication by Extrusion, CVNA-42 (February 1960).

[4]Final Report, Phase III, Extruded Ceramic Nuclear Fuel Development Programs, ACNP-62550 (June 15, 1962).

standard ceramic extrusion techniques for producing oxide nuclear fuels and to recommendations that commercial production facilities be developed. These recommendations were not followed, probably because the apparent economic advantage did not affect the capital investment needed to replace existing equipment for large-scale pelletization. The recent rapid growth of the nuclear power industry and the coming need for processing recycle fuels mean that new facilities will be needed, and such new facilities could be designed to take advantage of the high production rates of extrusion if a reliable process were to be developed.

The sol-gel process developed at the Oak Ridge National Laboratory (ORNL) produces high-purity oxides of various nuclear fuel materials.[5–8] One product of this process can be a highly concentrated gel that has many characteristics of a natural clay and is therefore ideally suited to extrusion. We have developed a technique based on this product of the high-purity sol-gel process for extruding oxide ceramics[9] into variously shaped ceramic bodies with controllable densities.[10] This particular technique, one of several recent approaches toward developing new fuel

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[5]O. C. Dean et al., "The Sol-Gel Process for Preparation of Thoria-Base Fuels," pp. 519–542 in Proceedings of the Thorium Fuel Cycle Symposium, Gatlinburg, Tennessee, December 5–7, 1962, USAEC Report TID-7650, ORNL and ANS (1963).

[6]J. P. McBride, Preparation of $UO_2$ Microspheres by a Sol-Gel Technique, ORNL-3874 (February 1966).

[7]J. P. McBride (compiler), Laboratory Studies of Sol-Gel Processes at the Oak Ridge National Laboratory, ORNL-TM-1980 (September 1967).

[8]P. A. Haas, C. C. Haws, Jr., F. G. Kitts, and A. D. Ryon, Engineering Development of Sol-Gel Processes at the Oak Ridge National Laboratory, ORNL-TM-1978 (January 1968).

[9]A. B. Meservey, J. D. Sease, and R. B. Fitts, Method of Fabricating Ceramic Nuclear Fuel Product, (to U.S. Atomic Energy Commission). U.S. Patent 3,356,776 (December 5, 1967).

[10]R. B. Fitts, J. D. Sease, and A. L. Lotts, "Preparation of Ceramic Nuclear Fuels by Sol-Gel Extrusion," Chem. Eng. Prog. Symposium Series 63(80), pp. 28–33 (1967).

fabrication techniques for the recycling of ceramic reactor fuels,[11] was developed because of the prospect of economic advantage from applying sol-gel extrusion to fabricating of small-diameter fast-reactor fuels.[10,12]

The investigation as fully reported here was limited to ascertaining the potential of sol-gel extrusion rather than the details of the process. Some details of drying techniques and attainable densities were investigated since drying presents the greatest apparent difficulty and densities are of greatest practical interest.

## MATERIALS

This process utilizes, as do all ceramic extrusion processes, a plastic mass based upon a clay-like material used with or without the addition of powders. The history and characteristics of the starting materials are presented below.

### Sol-Gel Clay

A thoria sol (colloidal dispersion) can be evaporated to a high molar concentrate that resembles, in many ways, a natural clay. This concentrated gel, which we call "sol-gel clay," is the basic ingredient in the extrusion process. We generally made our clays by forming a sol and reducing it to the sol-gel clay in one continuous operation. In the thoria system this clay is produced by the aqueous digestion of steam-denitrated thoria powder with a slight excess of nitric acid over that required to form a sol.[13] The thoria goes

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[11] A. R. Olsen, J. D. Sease, R. B. Fitts, and A. L. Lotts, Fabrication and Irradiation Testing of Sol-Gel Fuels at the Oak Ridge National Laboratory, ORNL-TM-1971 (September 1967).

[12] T. N. Washburn, A. L. Lotts, and F. E. Harrington, Comparative Evaluation of Sol-Gel Fuel Fabrication Costs, ORNL-TM-1979 (September 1967).

[13] D. E. Ferguson (compiler), Status and Progress Report for Thorium Fuel Cycle Development for Period Ending December 31, 1962, ORNL-3885 (October 1963).

through a sol stage and, as evaporation proceeds, coagulates to a finely divided precipitate. This precipitate is the thoria sol-gel clay. The clays we have used are shown in Table 1. A detailed recipe for preparing $ThO_2$ clay is given in Appendix A.

The sol-gel clay may be extruded as it is precipitated or with powder additions. The clay serves as a plasticizer when materials with high powder content are extruded. It is a very unique

Table 1. Sol-Gel Clays Used in Extrusion Development

| Preparation | Composition | |
|---|---|---|
| | $ThO_2$ M | $H_2O$ (wt %) |
| Bow-1 | 7.41 | 29.13 |
| Bow-2 | 10.41 | 20.88 |
| Bow-3 | 7.47 | 28.94 |
| Bow-4 | 10.28 | 21.16 |
| Bow-5 | 10.20 | 20.50 |
| Bow-3A[a] | 11.78 | 18.15 |
| TC-4 | 12.35 | 17.12 |
| Bow-3B[a] | 17.04 | 10.90 |
| M-2 | 11.90 | 17.90 |
| M-1A[a] | 12.79 | 16.40 |
| 1-17-67-1 | 9.09 | 24.06 |
| 1-19-67-1 | 9.50 | 23.00 |
| 1-19-67-2 | 9.42 | 23.19 |
| 1-19-67-3 | 8.92 | 24.50 |
| Th-U | 10.23[b] | 21.30 |
| M-1 | 9.78 | 22.30 |

[a]Partially dried by stirring and evaporation after initial forming.

[b]$ThO_2$ + 8% $UO_2$.

plasticizer, however, in that as it dries it contributes oxide material to the finished body rather than introducing contaminants.

The $(Th,U)O_2$ clay listed in Table 1 was extruded both without powder additions and with different amounts of $ThO_2$ powder added. Results show no large change in the extrusion behavior from small amounts of $UO_2$ in the sol-gel thoria clay. The formation of other mixed clays is possible, but they were not included in this phase of the study.

## Powders

We have used the following types of powders: (1) an "oxalate powder" prepared by precipitation from thorium nitrate solutions as oxalate and subsequently calcined (particle size less than 1 μ), (2) "microspheres" ranging from less than 44 to 210 μ, and (3) dried sols crushed to less than 325 mesh (< 44 μ). We used the dried sol material in four different conditions: (1) "as-dried powder" prepared by crushing sol-gel shards that had been dried at 100°C, (2) "calcined powders" prepared by calcining the "as-dried powder" at temperatures between 400 and 700°C for 1 hr, (3) "fired powder" prepared by sintering "as-dried powder" at 1150°C for 1 hr (a dead-burned powder), and (4) "ball-milled powder" prepared by ball milling "fired powder" in an alumina mill with alumina balls for 65 hr to produce rounded particulates with the following size distribution:

| Particle Size, μ | Distribution, % |
|---|---|
| >.10 | 16 |
| < 5 | 65 |
| < 3 | 55 |
| < 2 | 46 |
| < 1.5 | 34 |
| < 1 | 22 |
| < 0.7 | 13 |
| < 0.5 | 6 |
| < 0.3 | 4 |
| < 0.2 | 3 |
| < 0.1 | 2 |

Note that these are the only materials needed for extrusion. No binders or plasticizers were added to the extrusion mixture. The effects of using these various materials in the extrusion mass will be discussed after a survey of the sol-gel extrusion-forming technique.

## EQUIPMENT AND PROCEDURES

Like all extrusion processes, this one, as may be seen from the flowsheet in Fig. 1, consisted of preparing an extrusion mass, forcing it through a die, drying the formed body, and firing it. The equipment we used in the first two steps is shown in Fig. 2.

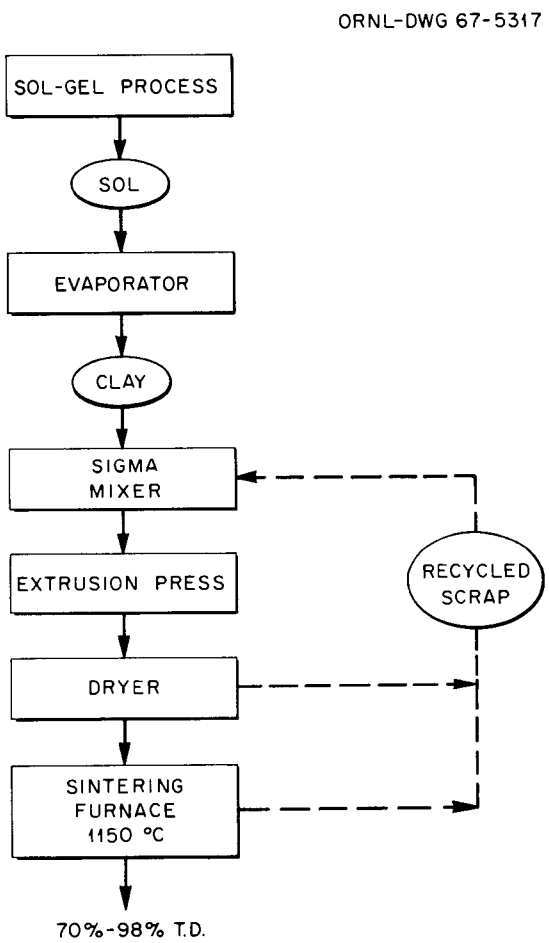


Fig. 1. Flowsheet for Sol-Gel Extrusion Process.

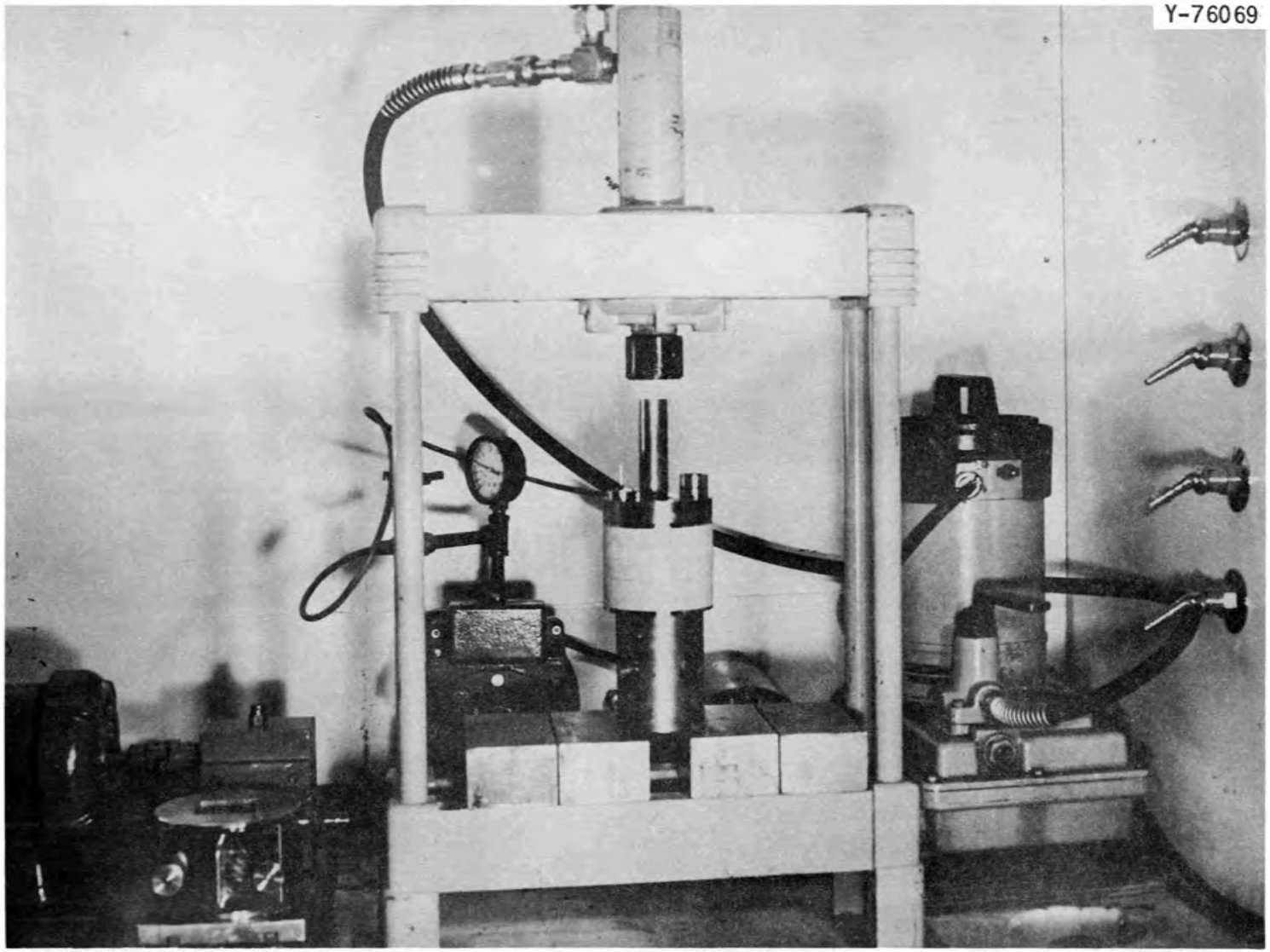


Fig. 2. Extrusion Mixer and Press.

## Preparation of Extrusion Mixture

We used a 10-$cm^3$ capacity sigma mixer, since this type of mixer produced the most uniform distribution of powders in our clays. A Mix Muller had limited success. A Waring Blendor is unsatisfactory for mixtures of pure clay and powder; although this type of blender may be used if liquid is added to the clay-powder mixture to lower its viscosity, the presence and removal of this liquid may have significant effects upon the characteristics of the extrusion mass.

## Extrusion

The extrusion press used in most of our experiments (Fig. 2) is a simple, laboratory-scale, ram press with a 1-in.-diam piston. The larger 2-in.-diam ram press shown in Fig. 3 was used for a limited number of runs of larger batches.

Despite the emphasis upon die design in the literature of extrusion we did not see, under our conditions, that reasonable changes in die dimensions had a very strong effect on the extrusion process. The dimensions of the die used in most of our tests are shown in Fig. 4.

We mixed the extrusion mass, loaded it into the barrel of the extrusion press, and then removed the air from it by creating a vacuum in the press chamber. The problem of removing the air that our quite plastic extrusion mass readily trapped and held was minimized by loading the press very loosely with small chunks of the mixture.

After the air was removed from the extrusion mass, pressure was applied to the ram. We did not determine the extrusion rate and pressure in our work, but the extrusions were formed very rapidly at quite low pressures. The standard gages on the 2-in.-diam commercial extrusion press indicated no pressure during the extrusion of this material. An undefined but minor variation in what is apparently a narrow range of permissible water content changed the plastic extrusion mass into a composition too dry to extrude.

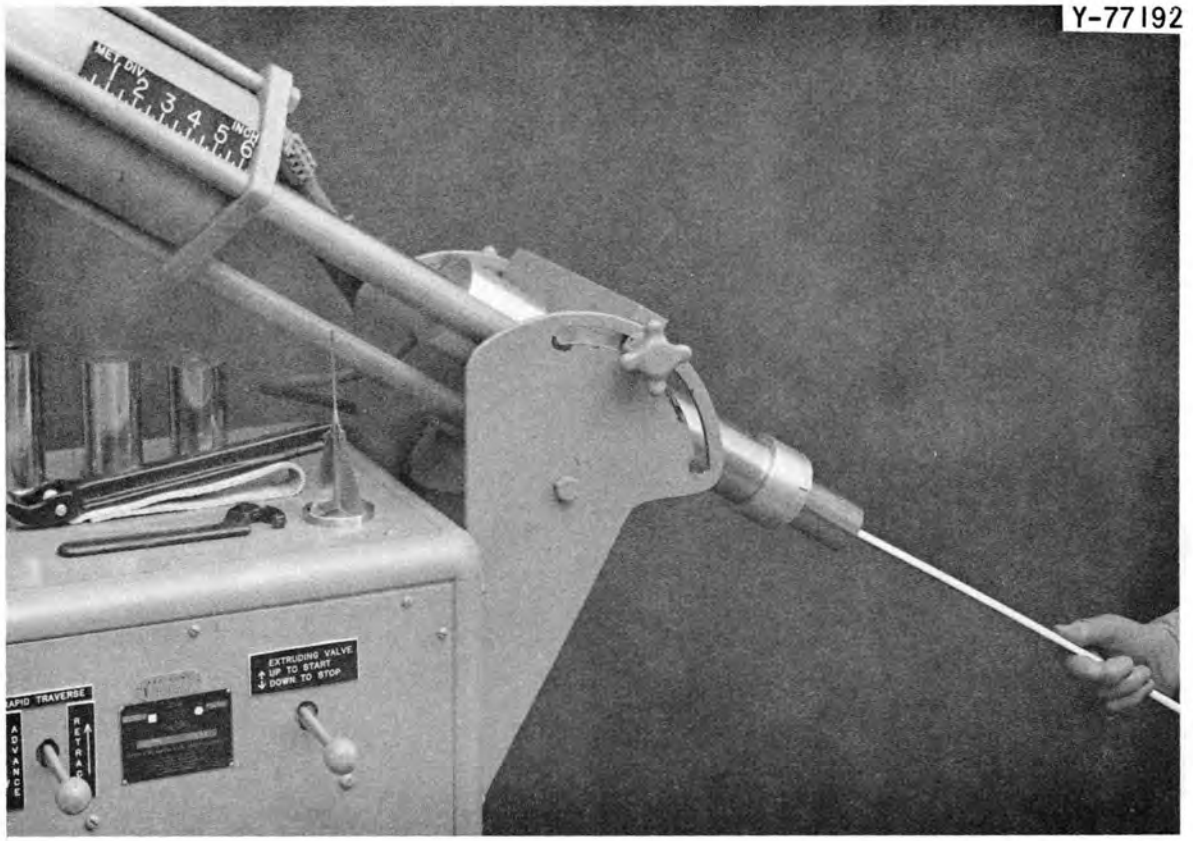


Fig. 3. Large Extrusion Press.

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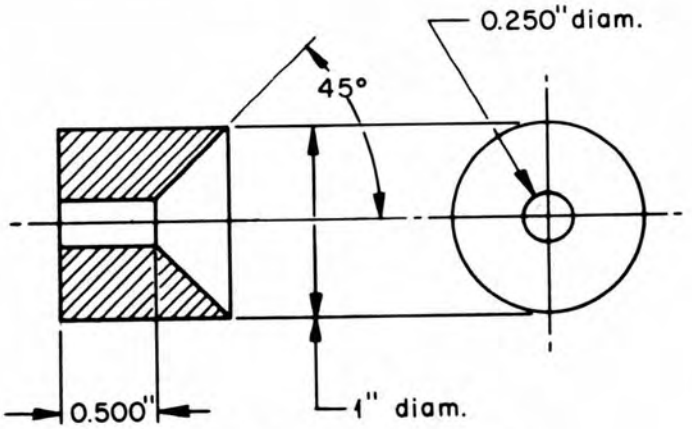


Fig. 4. Extrusion Die.

After the extruded body has been formed it must be caught without introducing deformation. This problem was aggravated by the extreme plasticity of sol-gel extrusions before drying.

## Drying

After the extrusion is formed it must be dried. This is a critical step in the extrusion of ceramics in general, and particularly so for sol-gel extrusion because of the plastic nature of newly formed bodies and the large shrinkages which must be accommodated (see following section on Effects of Powder Additions to Sol-Gel Extrusions).

We investigated various drying atmospheres and ways of supporting the extrusion during drying. The drying behavior of sol-gel clay in normal laboratory air (25°C, 30% humidity) was determined, and a representative result is shown in Fig. 5. The last datum point

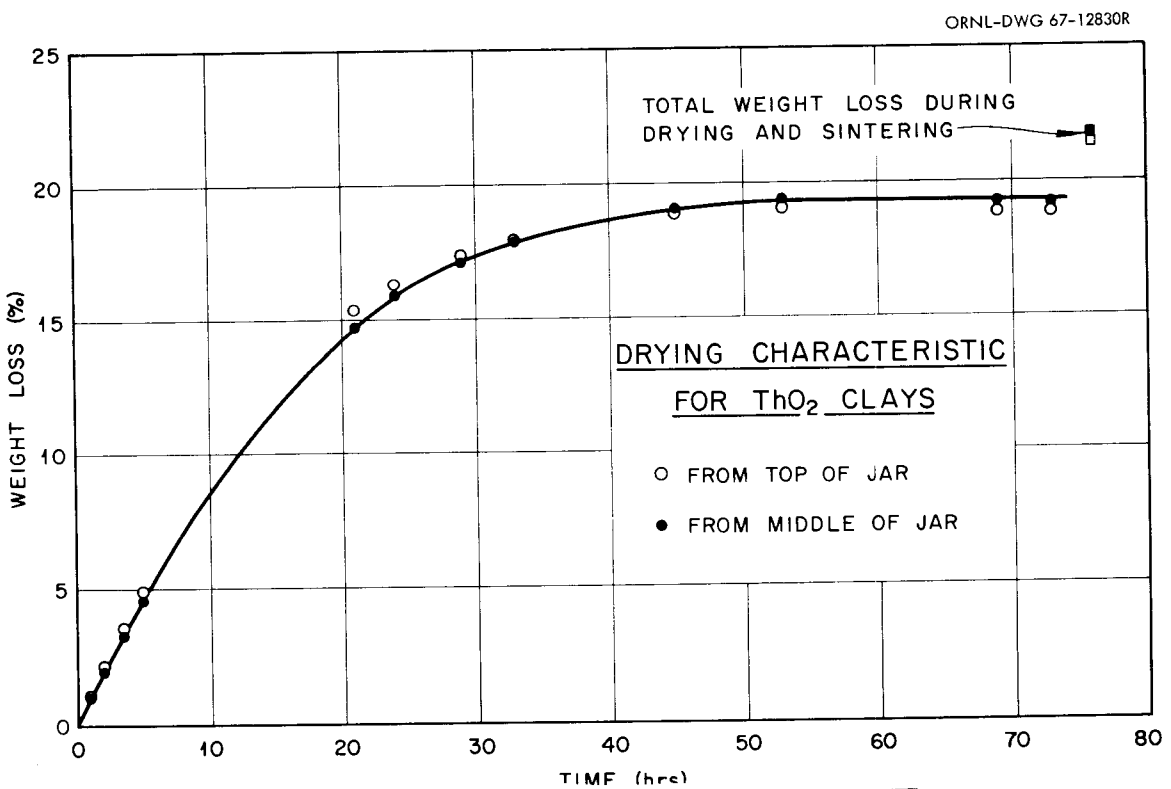


Fig. 5. Drying Weight Loss of Clay.

represents the weight loss after firing at 1150°C. Low-humidity drying atmospheres, such as a 100°C furnace or a desiccator, were unsatisfactory. Extrusions dried in these undergo a surface reaction when returned to a normal atmosphere before sintering. The reaction, probably rehydration of the surface material, causes violent chipping and disintegration of the extrusion within a few minutes. We gave only passing attention to high-moisture atmospheres and controlled, gradual reduction of moisture content by passing a moist air flow through a glass frit supporting an extrusion, but this approach appears to reduce cracking somewhat in larger (approx 1/2 in. diam) samples. Attempts to dry samples in liquids that might affect the rate of water removal have failed. The liquids we have tried are water, toluene, trichloroethylene, acetone, methanol, carbontetrachloride, dicyclohexyl, xylene, and butyl alcohol; all react with unsintered extrusions. In every case, bubbles evolved, and the samples soon disintegrated. This same phenomenon prevented the determination of as-dried densities by immersion techniques. An attempt to affect the drying rate of sol-gel extrusions by adding glycerin to the extrusion mix also failed. The samples containing glycerin (3% glycerin in the mixture) crumbled during firing.

The extrusions invariably curled when dried on pads, trays, or v-blocks. The most beneficial drying effects were obtained with conditions which promoted uniformity of drying. Hang-drying was unsuccessful since the extrusion always broke off near the clamped end. Drying inside a rotating tube was beneficial but not satisfactory because even a small fragment prevents uniform rolling. The use of two parallel synchronized Teflon rollers to turn and support the extrusion during drying in air produced the best results. The dried bodies from this apparatus were straighter and had better surface finish than did those from any other drying technique. (See later section of this report, Effects of Roll Drying on Extrusion Characteristics.)

We have isostatically pressed dried extrusions before sintering in a further attempt to reduce cracking, but we saw no difference in the sintered structure of pressed and unpressed samples.

## Sintering

We fired these extrusions in a laboratory-scale tube furnace in an air atmosphere at 1150°C for 1 hr. This temperature is quite low for the production of fully dense thoria bodies and reflects one of the advantages of sol-gel-derived materials — their very active sintering behavior. Sintering at higher temperatures (up to 1800°C for 1 hr in Ar–4% $H_2$) has no observable effect on microstructure or density, even for densities as low as 70% of theoretical. The rate of temperature rise during firing also appears to be unimportant, for dried extrusions have been placed in a furnace already at the sintering temperature with no adverse effects. A bed of thoria microspheres prevented reaction with alumina or stainless steel supports during firing.

## CHARACTERISTICS OF EXTRUSIONS WITHOUT POWDER ADDITIONS

When thoria clay (about 10 M) was extruded we found a 16% diametral shrinkage from drying and a similar amount from firing, a high fired density (99% of theoretical density),[14] and a good mechanical strength. The structure of a 0.027-in.-thick section is shown in Fig. 6. No grain structure can be seen. The microstructure of samples with diameters over about 80 mils contains a network of fine cracks, as shown in Fig. 7. Adding or evaporating water to obtain 10.9 to 29.1 wt % of water (17.0 to 7.4 M) appeared to have little effect on the final fired structure.

## CHARACTERISTICS OF EXTRUSIONS WITH POWDER ADDITIONS

Since the best way to reduce cracking in extrusions of large diameter (0.08 to 0.5 in.) was the addition of powders, most of our efforts were concentrated on this approach.

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[14]All densities based on physical dimensions and weights, or mercury porosimetry.

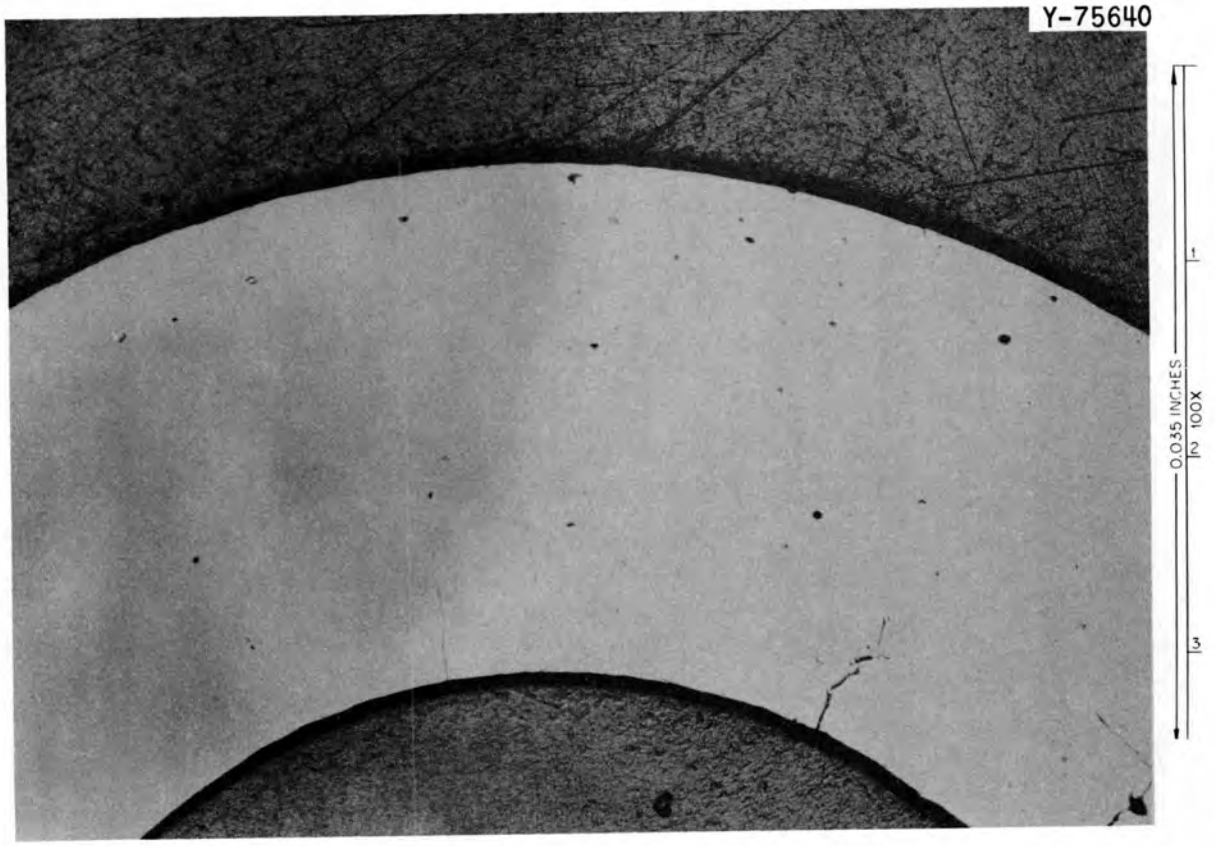



Fig. 6. Fully Dense Plain Clay Extrusion.

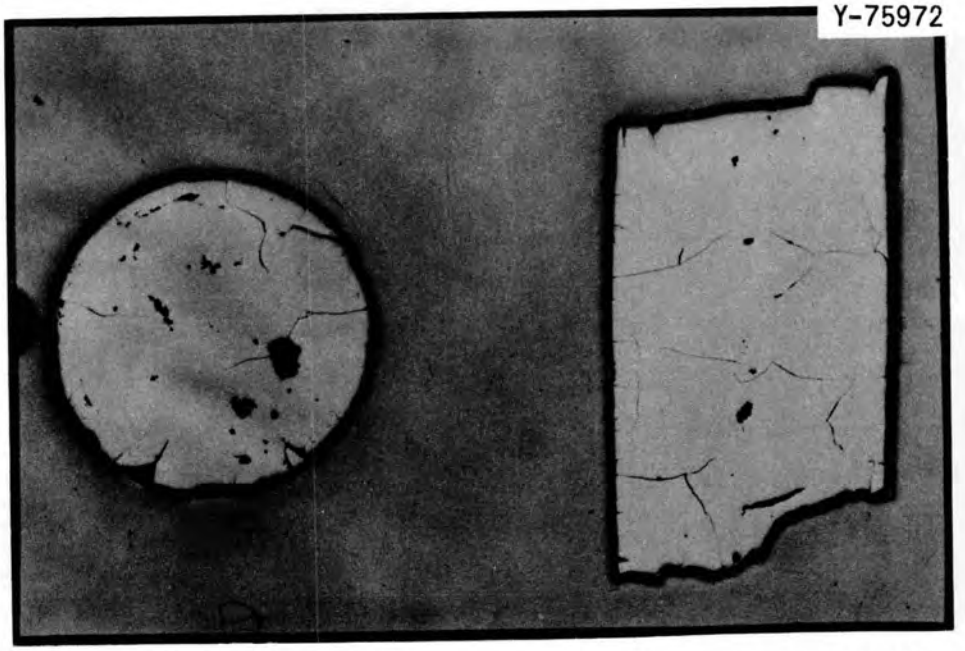
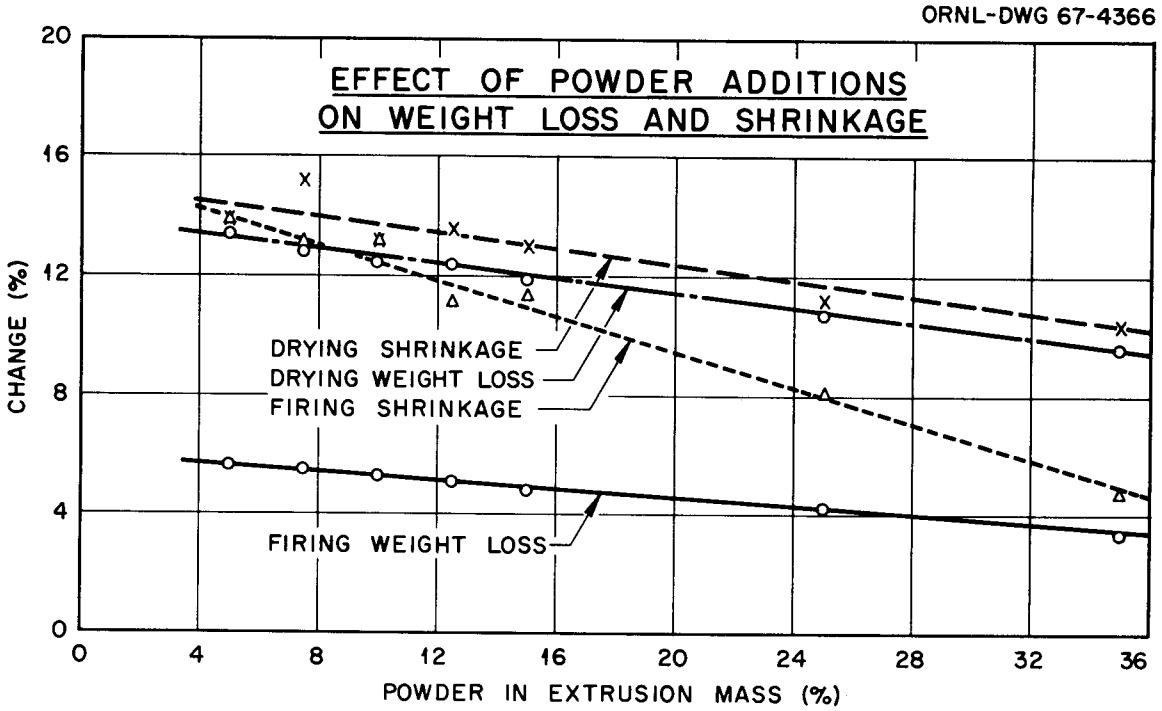



Fig. 7. Pure Clay Fired Extrusion. 17X. Reduced 43.5%.

We have used the powders described above to stabilize the extrusions and to adjust their final fired density. The "oxalate" powder behaved similarly to the fired powder discussed below. The "microspheres," in small sizes, behaved much as did fired powders. The larger sizes of microspheres produced surface roughening and very low strength in the fired extrusions.

In most of our work we used the powders derived from dried sols. These were all less than 325 mesh (< 44 μ) particle size, since larger particles tend to promote surface roughening. The "as-dried" powder (dried at 100°C) in amounts of over 5 to 10% of the total extrusion mass led to a clay-powder mixture too dry to extrude. The lightly "calcined" powder (calcined at 400 to 700°C), when mixed with the clay at between 22 and 35 wt %, produced a very plastic mixture which could be deformed after extrusion without cracking. This plasticity helps stop cracking, probably by enhanced stress relaxation in the extruded body during drying.

The use of "fired" powder produced by sintering the "as-dried" powder caused the greatest reduction in drying and firing shrinkage and also simulated the addition of recycle scrap to the extrusion mix. Direct recycle of fabrication scrap is economically desirable. The drying and firing shrinkages and weight losses for a set of samples of this type of extrusion are shown in Fig. 8 as a function of powder content. The drying shrinkage and weight loss and the firing weight loss are reduced with increased powder or decreased water content as might be expected. The firing shrinkage is reduced even more markedly, since the fully dense powder stabilizes the dried structure. In Fig. 9 the dried and sintered densities of these extrusions are shown as a function of powder content. The green density (density after drying) is increased with powder addition and is comparable to that obtained by standard pelletizing techniques. The sintered density covers a wide range and approaches the green density at high powder contents. The reduced shrinkage and higher dried density of the high powder content extrusions indicate that we should be able to obtain good dimensional control by this technique, especially at lower



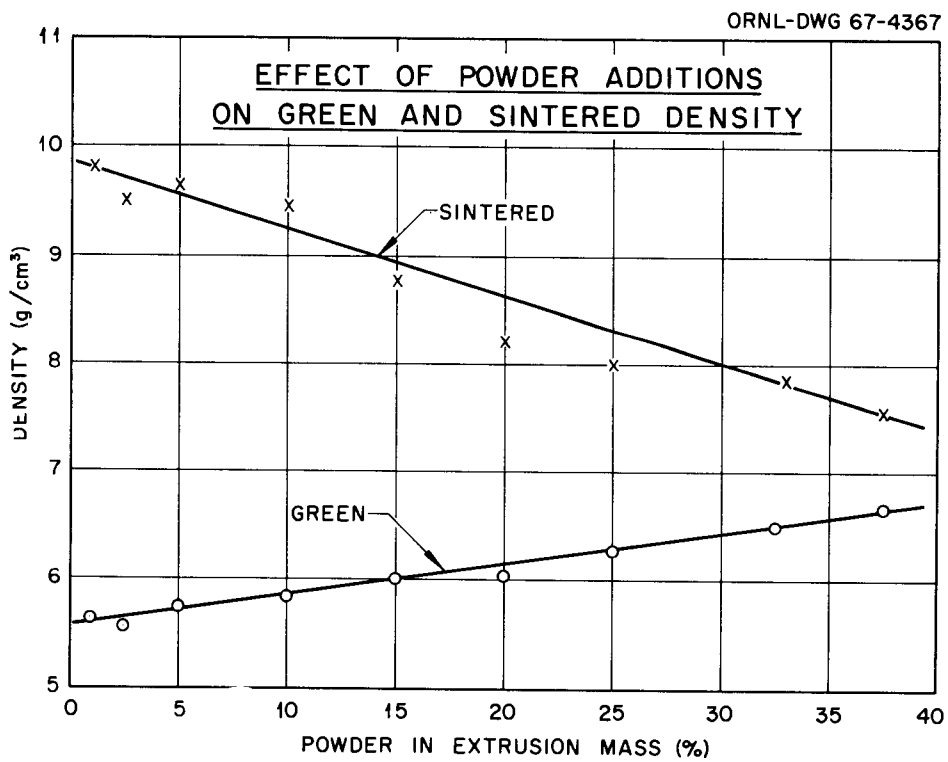




Fig. 9. Dried and Fired Density of Clay Containing Fired Powder.

densities. We have not made large-scale tests of dimensional reproducibility but we have produced several small batches of extruded, 1/4-in.-long insulators with diameters of 0.228 ± 0.001 in. at about 30 wt % powder.

The density is not solely a function of powder content. We prepared a series of samples from two different clays, both prepared by the technique described in Appendix A, with fired powder additions ranging from about 1 to about 37 wt %. One of these clays at 9.5 M contained 23 wt % water, and the other at 10.2 M contained 20 wt % water. We found, as shown in Fig. 10, that although both produced extrusions of about the same green density, the fired density was slightly higher for the lower molarity clay. This is further illustrated by the diametral

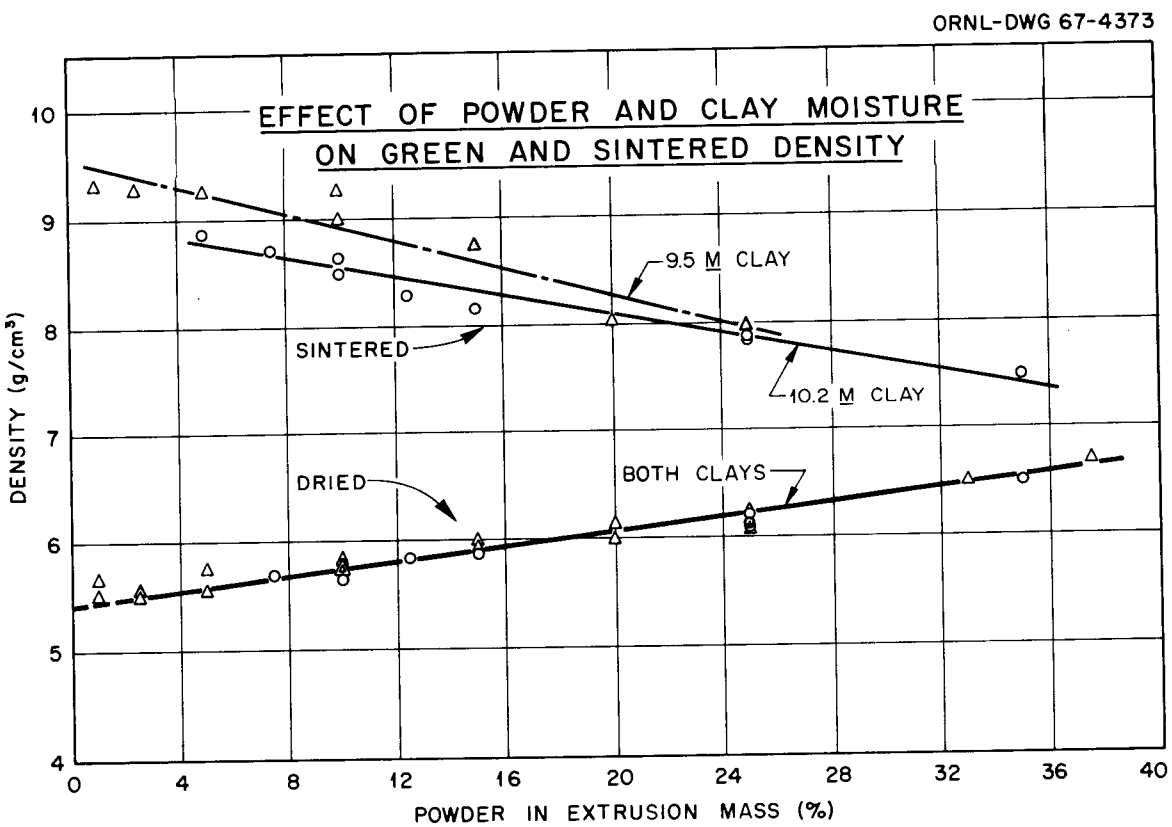



Fig. 10. Dried and Fired Density of Two Different Clays Containing Fired Powder.

shrinkages and weight losses. Figure 11 shows the drying shrinkage and total shrinkage obtained with these two clays. The firing shrinkage was about the same for each, as may be seen in Fig. 12. But a greater weight loss occurred during drying of the wetter clay, as shown in Fig 13. Thus the removal of water and consequent shrinkage during drying were apparently more effective in promoting densification with the clay of higher water content than with the drier clay.

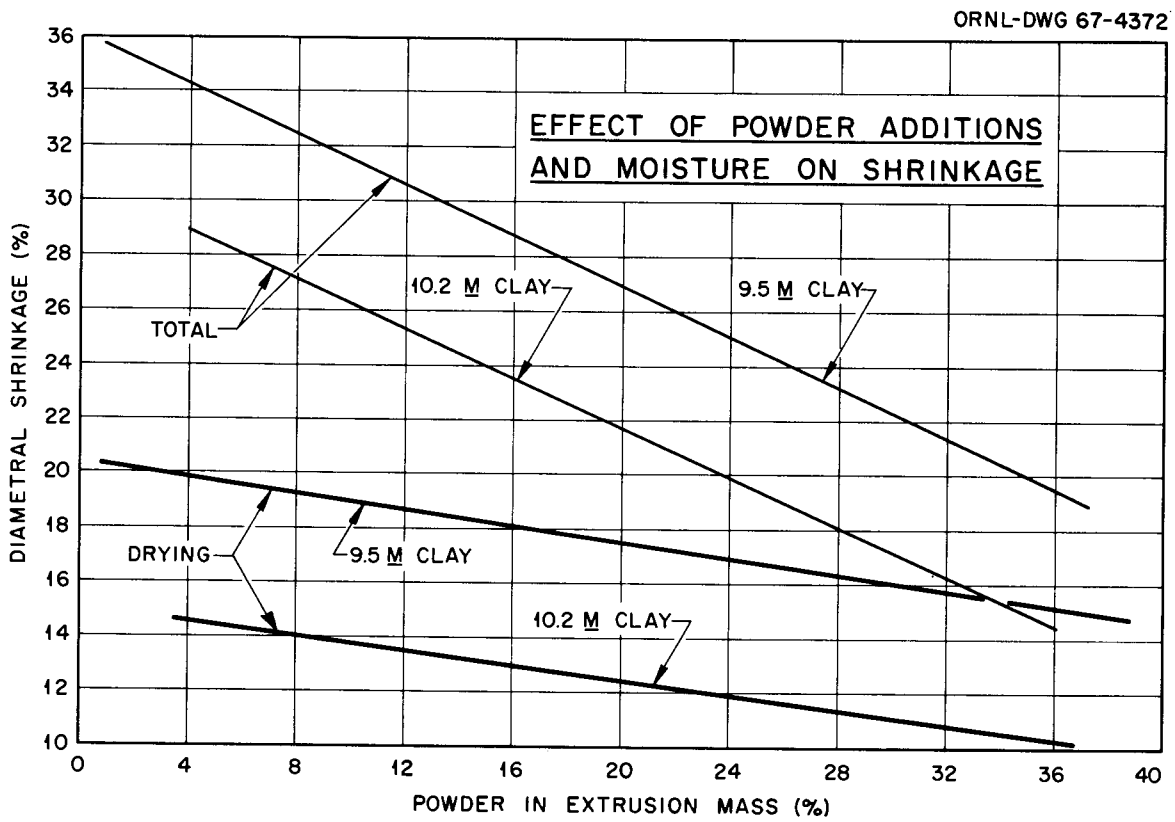



Fig. 11. Shrinkage of Two Different Clays Containing Fired Powder.

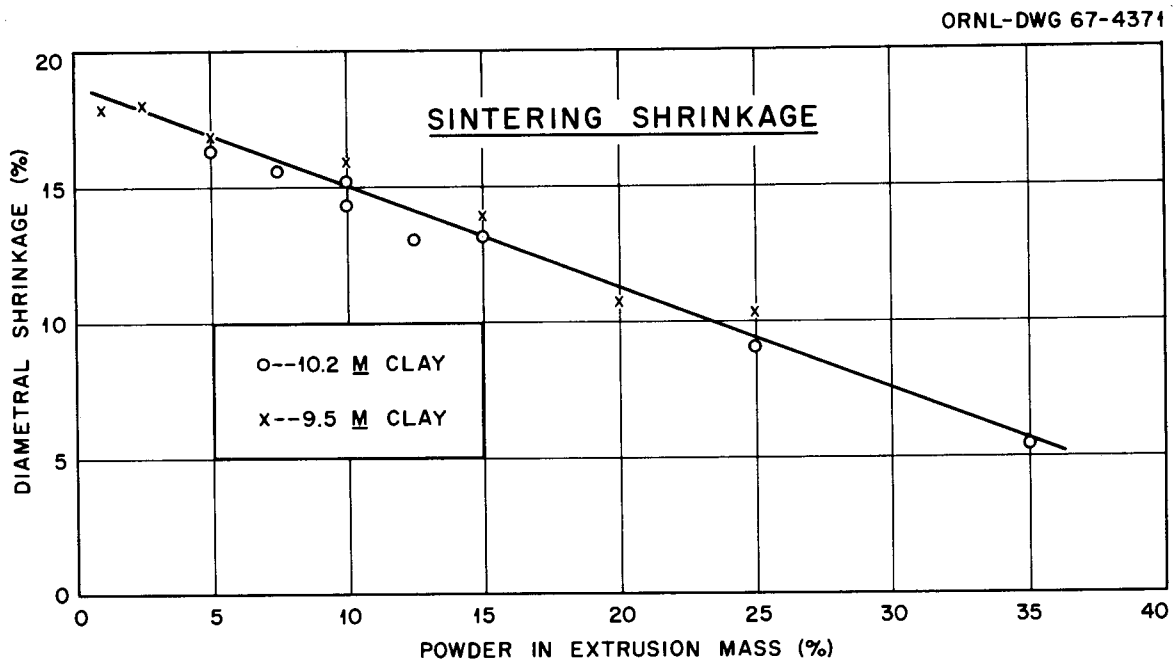



Fig. 12. Firing Shrinkage of Two Different Clays Containing Fired Powder.

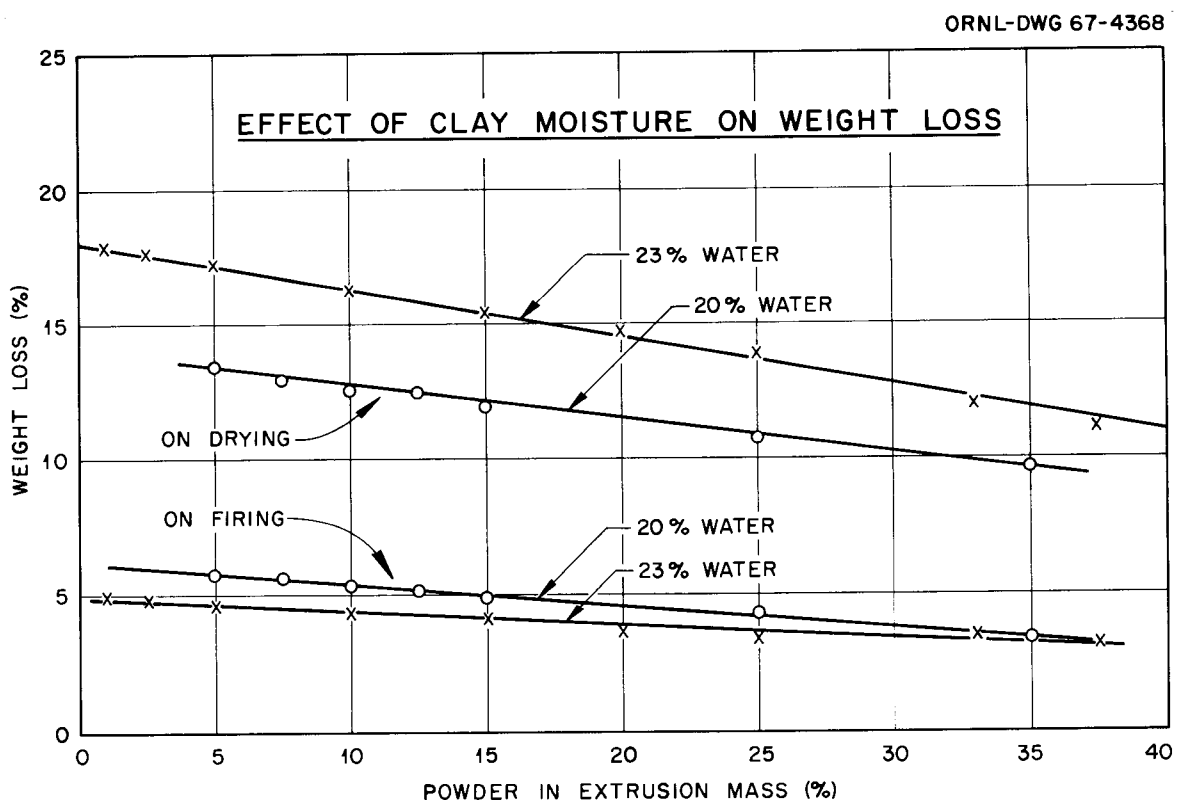



Fig. 13. Weight Loss for Two Different Clays Containing Fired Powder.

The structure of these extrusions is illustrated in Figs. 14 and 15. Figure 14 shows an extrusion with a density 72% of theoretical. In the structure are high-density areas composed of the fired powder joined by bridges of high-density material formed from the mixture of clay and calcined powder. These extrusions appear to have high mechanical integrity and resistance to chalking even at low densities. The bridged structure appears to explain that observation since it is a strong, yet open, structure. The structure obtained at lower powder content and higher density is shown in Fig. 15. Here the clay, present in larger amounts, is dried into larger blocks separated by very angular porosity. The material in the pores is mounting material, which points out the fact, supported by mercury porosimetry, that essentially all of the porosity in these samples is surface-connected.

One set of samples containing fired powder was tested for crushing strength. These data, which are based upon too few samples to be anything more than an indication of the strength, are shown in Table 2.

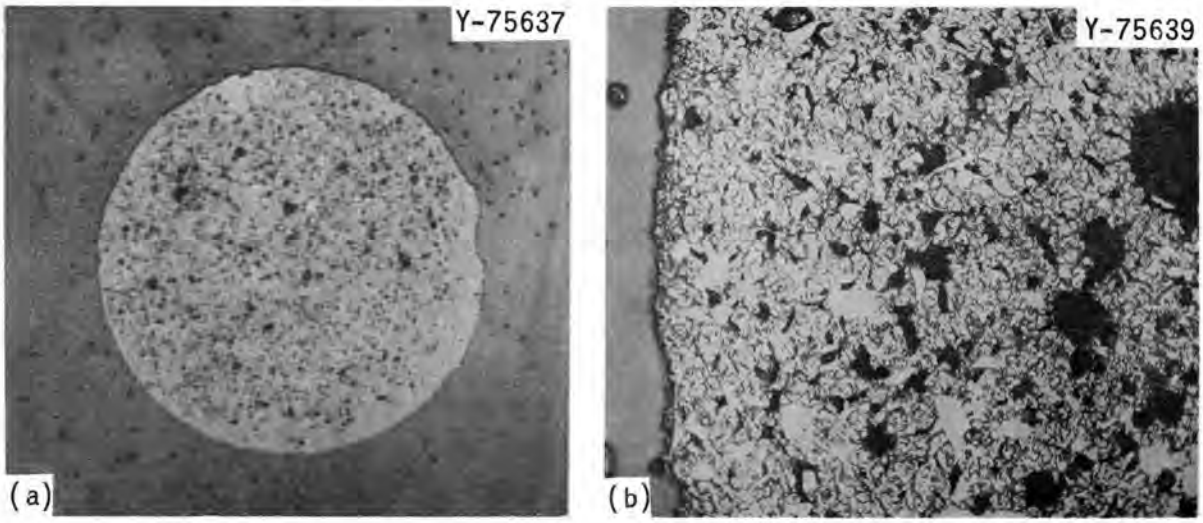



Fig. 14. Insulator at 72% of Theoretical Density. Made of 45% clay + 15% calcined powder + 40% fired powder. (a) 14x. (b) 100x. Reduced 22.5%.

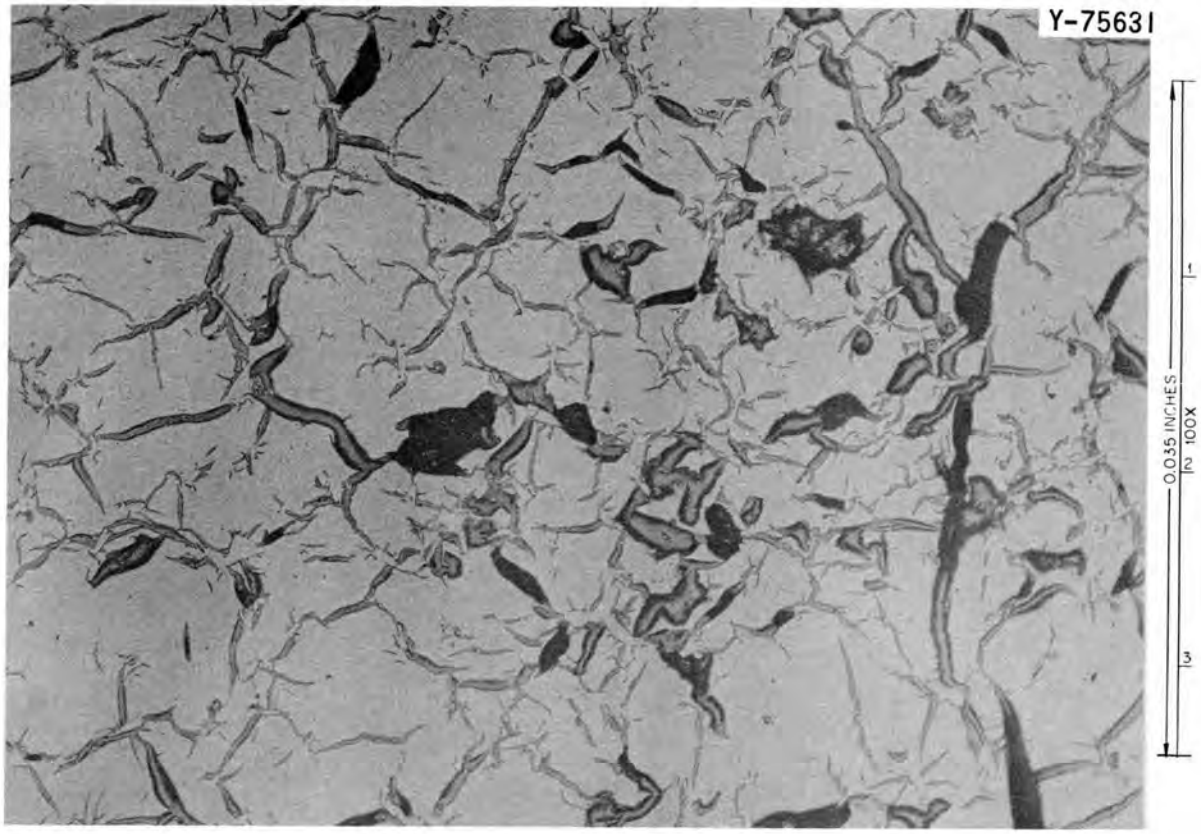



Fig. 15. Extrusion Structure at 83.4% of Theoretical Density. Made of 85% clay + 15% fired powder.

Table 2. Room-Temperature Crushing Strength of Thoria Extrusions

| Density (% of theoretical) | Strength[a] (psi) |
|---|---|
| | $\times 10^3$ |
| 97.7 | 33.3 |
| 97.3 | 40.7 |
| 96.7 | 37.5 |
| 93.8 | 50.4 |
| 82.6 | 32.4 |
| 74.8 | 26.9[b] |
| 69.2 | 13.0[b] |

[a]Based upon one sample at each density sintered in air at 1150°C.

[b]Based upon two samples.

The strength of this material is below that reported for pressed and sintered thoria pellets, but is still adequate for many applications. The strength is probably lowered in these samples by microcracking in the high-density material. It may also be affected by the porosity distribution. The porosity tends to be axially aligned by the flow of material during extrusion, whereas it is radially aligned during uniaxial pressing of pellets.

The other type of powder we used, the "ball-milled" powder, is not as effective in reducing shrinkage as is the angular fired powder. This ball-milled material, however, reduces cracking almost as well as does the angular powder. The densities obtained in samples with various percentages of ball-milled powder are given in Table 3, along with the results from some samples containing angular fired powder in the same percentages. The increased density from ball-milled powder was obtained at the expense of greater shrinkage.

Table 3. Comparison of Ball-Milled and Crushed Powder

| Percent Powder[a] | Ball-Milled Powder Samples | | | Crushed Powder Samples | | |
|---|---|---|---|---|---|---|
| | Density, $g/cm^3$ | | Diametral Shrinkage (%) | Density, $g/cm^3$ | | Diametral Shrinkage (%) |
| | Green[b] | Fired | | Green[b] | Fired | |
| 5 | 5.70 | 9.87 | 30.2 | 5.63 | 8.34 | 27.2 |
| 10 | 5.78 | 9.89 | 29.0 | 5.72 | 7.85 | 24.8 |
| 25 | 5.62 | 9.60 | 25.6 | 5.85 | 6.97 | 21.4 |

[a]By weight in mixture with 10 M clay.

[b]After tray drying.

## EFFECTS OF ROLL-DRYING ON EXTRUSION CHARACTERISTICS

The effect of roll-drying, which we have mentioned previously as being beneficial, is illustrated for extrusions containing angular crushed powder in Fig. 16. Here we see the increased density obtained with 9.5 M clay when it is roll-dried. Note that this effect does

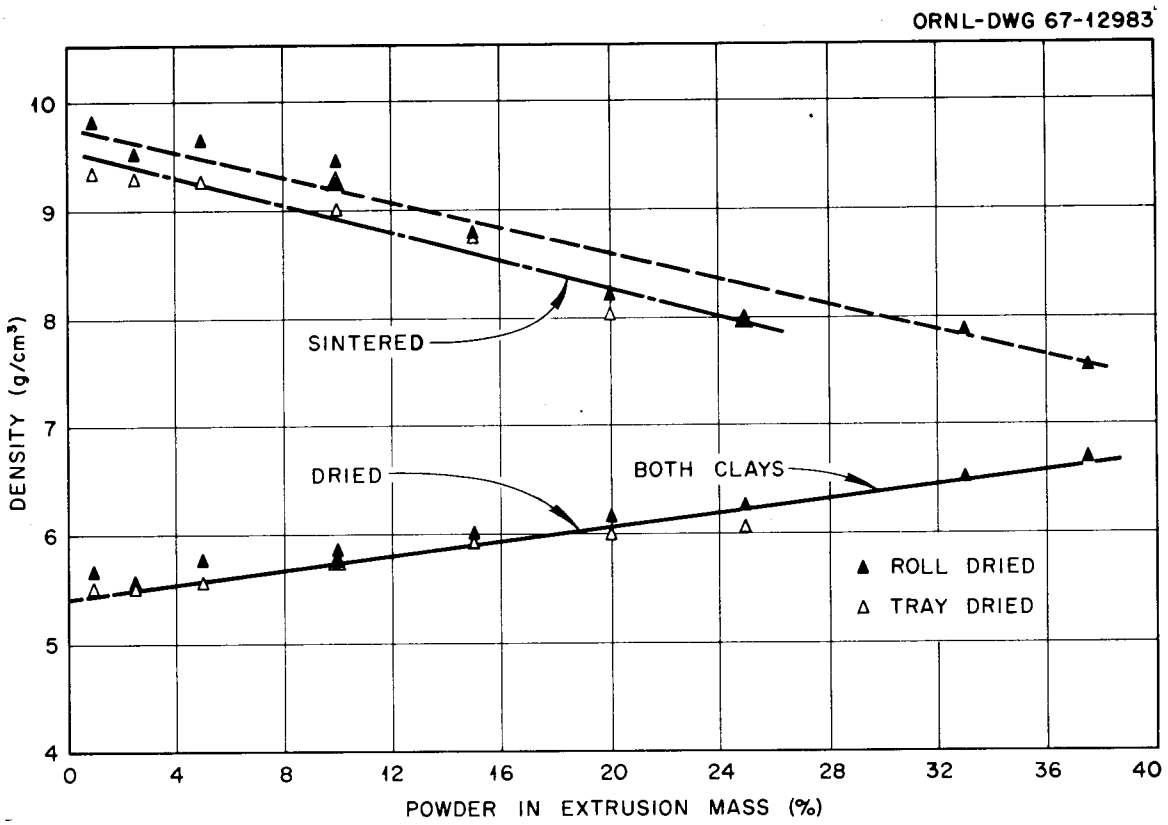



Fig. 16. Effect of Powder and Drying Technique on Dried and Sintered Density.

not appear as strongly in the dried density as it does in the sintered density. In Fig. 17 we see two pairs of sintered extrusions. The top two extrusions are 96% of theoretical density, and the bottom two are 80% of theoretical density. Of these pairs, the top one in each case was roll-dried and the bottom one tray-dried. The top sample in each case exhibits none of the bowing observed in the tray-dried samples and also has an improved surface finish. In addition, although it does not show in this figure, we found that roll-drying allowed the production of slightly longer samples than did tray-drying because there was less cracking in the roll-dried material.

## ITEMS PRODUCED BY SOL-GEL EXTRUSION

In Fig. 18 we show some examples of useful products we have made by sol-gel extrusion. In the center is a 96% dense rod. It might be useful as blanket material in a breeder reactor, or, with a small

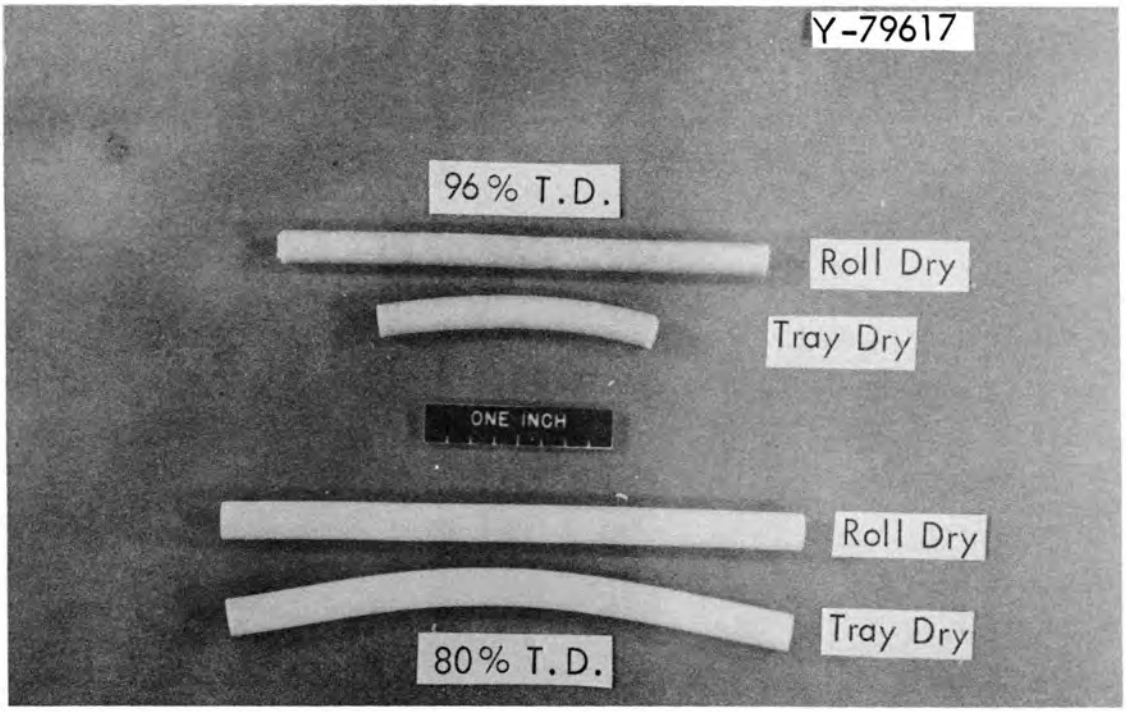



Fig. 17. Roll-Dried and Tray-Dried Sintered Extrustions.

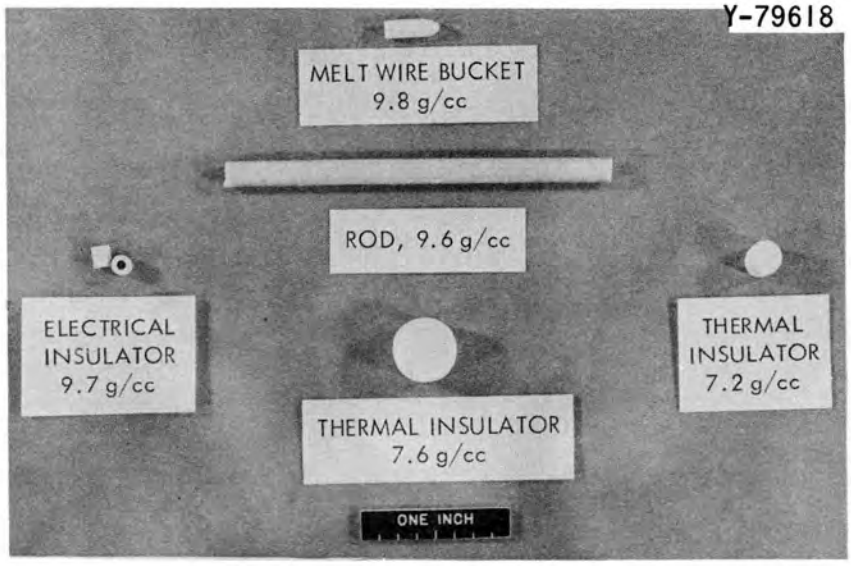



Fig. 18. Products Made by Sol-Gel Extrusion.

amount of uranium dioxide it would make a good thermal converter reactor fuel. On the left is a pair of insulators made by extruding a cored cylinder to 1/8 in. in diameter with a 30-mil wall. These high-density electrical insulators have been used successfully at temperatures up to 2000°C in a severe thermal gradient. At the top is a melt wire bucket made to hold wires in an irradiation experiment. The melting of these wires gives an indication of the temperatures reached in the experiment. The bucket was made from a clay containing calcined powder for plasticity and ball-milled powder for stability. A hollow cylinder was extruded, then broken to length, and finally pinched shut at the bottom before drying. Most of the buckets were fired without any cracking at the bottom where they were deformed. The remaining two items are insulators, for use in irradiation experiments, formed at 0.228- and 0.438-in. diameters.

## SUMMARY AND DISCUSSION

Our work has shown that thoria and thoria-urania sol clays can be extruded to produce high-purity, high-density, small-diameter bodies. Extrusion of clays with diameters above approximately 80 mils produces high-density bodies containing some fine cracking. These same clays with powder additions will produce high-density and low-density fuels with limited internal cracking. Although we have studied principally density and structure, making little effort to control diameter and bow, we have produced 3-in.-long, 80% dense, 0.230-in.-diam extrusions which vary less than 0.0005 in. in diameter from end to end.

Further work on thoria sol-gel extrusion should probably start with a systematic look at variations in the clay-forming process. The effects of crystallite size and morphology on the clay properties should be investigated. This would eliminate what is probably a major source of variation in the present work and permit the study of the items of major commercial concern — large-scale dimensional and density control.

The extension of the sol-gel extrusion technique to other materials appears desirable. Experimental application of the technique has been attempted only in the thoria and thoria-urania systems described here

and in the pure urania system. Application to the urania system has been complicated because the technique employed for forming clay in the thoria system is not directly transferrable to the urania system; inert atmospheres may be required to prevent oxidation of the urania sols, and urania sol behavior in general is not as well understood as is that of thoria sols. An extrudable urania clay has been formed,[15] but the quality of the extrusions made from this material is not as high as that obtained in the thoria system. This technique should be evaluated in other areas of apparent commercial application where colloids of the materials of interest are available. One such application might be the production of ferrites utilizing the iron colloids.

The characteristics associated with the sol-gel process (such as low sintering temperature, micron-scale homogeneity in mixed-sol systems, and applicability to a wide range of materials) when combined with those associated with the extrusion-forming technique (such as the ability to fabricate a variety of shapes in high length-to-diameter ratios) and those unique to the process (such as production of controlled-density bodies over a wide density range and with high mechanical integrity at low density) lead to the conclusion that the sol-gel extrusion technique offers a high potential for application to a variety of materials.

## ACKNOWLEDGMENTS

We gratefully would like to acknowledge the technical assistance and encouragement provided by A. L. Lotts and A. B. Meservey in the pursuit of this work. The work was done under the direction of A. L. Lotts. A. B. Meservey developed the technique for formation of high-molarity sol-gel clays. We also appreciate the support of numerous other personnel of the Metals and Ceramics Division of ORNL who contributed to this effort.

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[15] J. G. Stradley, R. L. Hamner, and J. M. Robbins, pp. 124–25 in Metals and Ceramics Div. Ann. Progr. Rept. June 30, 1967, ORNL-4170.

# APPENDIX A

## RECIPE FOR THORIA SOL-GEL CLAY

1. Pour 2500 ± 50 ml distilled water and 82 ± 2 ml concentrated $HNO_3$ (15.4 M) into a 4-liter stainless steel beaker equipped with a strong stirrer.
2. Heat to 95 to 100°C.
3. With stirring, add through the course of about 5 min, 8 moles of steam-denitrated $ThO_2$ powder (2112 g as pure $ThO_2$). The suspension should remain fluid. If thickening occurs, add $HNO_3$, 5 ml at a time, until thin and fluid.
4. Stir the suspension at 95 to 100°C for 4 to 5 hr, with the beaker loosely covered to contain spatter and retard evaporation. Every half hour, stir up any caked sediment with a spatula. The material should gain a creamy consistency.
5. Evaporation should reduce the volume to about 1.5 liters in 3 to 5 hr. If evaporation is faster than this, add water from time to time.
6. At the proper stage of cooking and concentrating, which may differ slightly between thoria raw material batches, the suspension changes from a creamy sol-like consistency to a thinner suspension, which separates on standing to a heavy but not sticky sludge and a waterwhite supernate. This is the stage for filtering.
7. Transfer the material to a suction filter, using no water. The filtrate or supernate should be used as a rinse for the beaker to aid in the transfer. If water is used, the filterable precipitate will become granular and unfilterable.
8. Filter to a firm cake, sealing cracks with a spatula as necessary. Keep suction on until dripping has virtually ceased, but do not allow the cake to become dried out and hardened. Place the cake in sealed containers to prevent drying to stoney hardness. A typical preparation is about 10 M in $ThO_2$ and contains about 20% $H_2O$.

9. There are indications that the particle size of the clay can be controlled. Small particle sizes, slow to separate by decantation or filtration, are produced by "cooling" at 80 to 90°C, or by cooking at higher temperatures for shorter times than optimum, or by having as little as 10% too much water in the mixture when filtering is attempted.
10. It is possible to produce mixed thoria-urania clay by the above method when part of the $HNO_3$ additive is replaced by uranyl nitrate. This clay is orange in color.
11. Mixing a little water with the filtered cake, which is a rather stiff nonsticky clay, converts it to a very sticky clay, more colloidal in character. The added water can vary from 35 to 100 ml/kg, depending on the consistency desired. Conversely, a drier clay can be made from the filtered cake by breaking it up and spreading it in trays for partial drying at room temperature. The clay will become very hard if allowed to dry completely, however.

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