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SLIP CASTING OF RARE EARTH OXIDES

BY

H. T. FULLAM
CHEMICAL RESEARCH SECTION
CHEMISTRY DEPARTMENT

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SLIP CASTING OF RARE OXIDES

INTRODUCTION

As part of the promethium development program at the Pacific Northwest Laboratory (Battelle-Northwest) various methods of compacting promethium sesquioxide into useful shapes of high density have been evaluated. Fabrication techniques scouted include: cold pressing and sintering[1], hot pressing,[2] slip casting, fusion casting, and pneumatic impaction. This report summarizes a very brief study on the use of slip casting as a compaction method.

Since the availability of promethium sesquioxide was limited and because large amounts of oxide were required in the slip casting studies, the sesquioxides of samarium and neodymium were used as standins for Pm_2O_3 in this work. The results of other compaction studies[2] have shown that data obtained with Sm_2O_3 and Nd_2O_3 are generally applicable to Pm_2O_3. It is felt, therefore, that the slip casting results obtained with standins are applicable to promethium sesquioxide.

Time available for this work was limited and it was impossible to study all the variables involved in slip casting the rare earth oxides. The work was carried only to the point where an evaluation of its potential could be made. For this reason many of the observations and conclusions stated are qualitative in nature rather than quantitative.

SUMMARY

The sesquioxides of samarium and neodymium can be slip cast (solid casting) in plaster molds very readily. Slip preparation is simple and under optimum conditions the cast shape is easily removed from the mold. Green cast shapes having densities greater than 5 gm/cc were prepared using Sm_2O_3. The only major problem encountered was the tendency of the cast shape to crack on firing. Green shapes of low initial density always cracked or spalled badly

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[1] *H. T. Fullam and L. J. Kirby, Cold Pressing and Sintering of Rare Earth Oxides, BNWL-386, May, 1967.*

[2] *H. T. Fullam, Hot Pressing of Rare Earth Oxides, BNWL-448, June 1967.*

on firing. The problem was not as severe with green shapes of high density, and by using very slow heating and cooling rates, it was possible to produce fired shapes that were essentially free of flaws.

By firing the green cast shapes at temperatures of 1500°C and higher, it was possible to produce Sm_2O_3 bodies having densities in excess of 7.2 gm/cc (theoretical density is 7.74 gm/cc). Very little sintering and compaction occurred when the shapes were fired at temperatures below 1200°C. Green shapes of high initial density showed relatively even shrinkage and little distortion on firing. Low-density green shapes, however, showed very irregular shrinkage on firing in addition to cracking.

The over-all potential of slip casting as a method for fabricating promethium sesquioxide into useful shapes depends primarily on the dimensional control required. In those cases where a high degree of dimensional control is required, slip casting does not appear to be practical since dimensional variations of 2-3% often result on firing the cast shapes. If some dimensional variations can be accommodated, however, slip casting appears to be a suitable method for producing Pm_2O_3 shapes of moderately high density (90-95% of theoretical).

Because of radiation exposure problems, any large-scale repetitive production operation would have to be carried out in a remotely operated facility. A limited number of casts could be prepared in a gloved box, however, without excessive operator exposure.

PROCESS OBJECTIVES

In fabricating promethium sesquioxide into useful shapes, there are three basic objectives which the fabrication process should meet:

- The final oxide shape should have a high density and the density should be uniform.

- The final fired shape should have good physical strength.
- Dimensional control of the shape should be good so that source encapsulation is simplified.

In addition there are certain operational requirements which the process should fulfill:

- Physical operations of the process should be simple so they can be easily carried out in a remotely operated facility (such as a hot cell) or a shielded glove box.
- If the work is done in a shielded glove box, the operations should be such that handling requirements are small and operator exposure reduced to a minimum.
- Physical containment of the oxide within the box should be good so that background radiation levels in the glove box are low and box cleanup times reduced to a minimum.

Over-all evaluation of the slip casting process as a means of compacting promethium sesquioxide into useful shapes will be based on all of the above requirements.

SLIP CASTING PROCESS

Slip casting of rare earth oxides can be carried out using standard ceramic techniques (in this work, slip casting refers to solid casting as opposed to drain casting). The process breaks down into three basic operations:

- Preparation of the aqueous slip.
- Casting of the slip in a plaster mold.
- Firing of the cast shape.

Each of the three steps as they apply to the slip casting of samarium and neodymium sesquioxides are discussed briefly in the following sections.

Slip Preparation

Aqueous slips of rare earth oxides are prepared by combining a weighed amount of oxide with a deflocculating agent, adding a known volume of water, and mixing the resulting slurry until a fluid slip is obtained. The deflocculating agent used in this work was Daxad 23, supplied by Dr. R. S. Rosenfels of Isochem, Inc. Milling of the slip is carried out in a porcelain ball mill using alumina balls. Normally about one hour's milling produces a slip of minimum viscosity.

Casting Operation

After the slip is milled, it is removed from the ball mill and poured into a plaster-of-paris mold. As water is adsorbed by the mold, additional slip is added until the mold is filled. Once the mold is filled, it is allowed to set until the adsorption of water is complete and the cast shape is firm. The cast shape is then removed from the mold and its physical dimensions and weight determined. It normally takes 30-60 minutes for the cast to set up to the point where it can be removed from the mold. All of the shapes cast in this work were right circular cylinders.

Firing

The green cast shape when removed from the mold normally contains about 10% water. Most of this water is removed by drying the cast in a flowing stream of air at ambient temperature. The air-dried shape (containing 0.5 - 1.0% H_2O) is then heated to approximately 80°C and held for one hour. The temperature is then slowly increased to the final firing temperature. A typical firing curve for Sm_2O_3 is shown in Figure 1-B. Also included is the drying curve for the cast shape (1-A).

CHARACTERIZATION OF RARE EARTH OXIDE SLIPS

Samarium and neodymium slips can be prepared very readily. The fluidity of the slip depends on its water content and milling time. A deflocculating agent is required to reduce slip viscosity to a useable level.

Rheological Properties

From an operational viewpoint, the viscosity of the slip is the most important variable to be considered. In this work slip viscosities were measured with a Brookfield Model RVT viscometer. It was difficult to get an

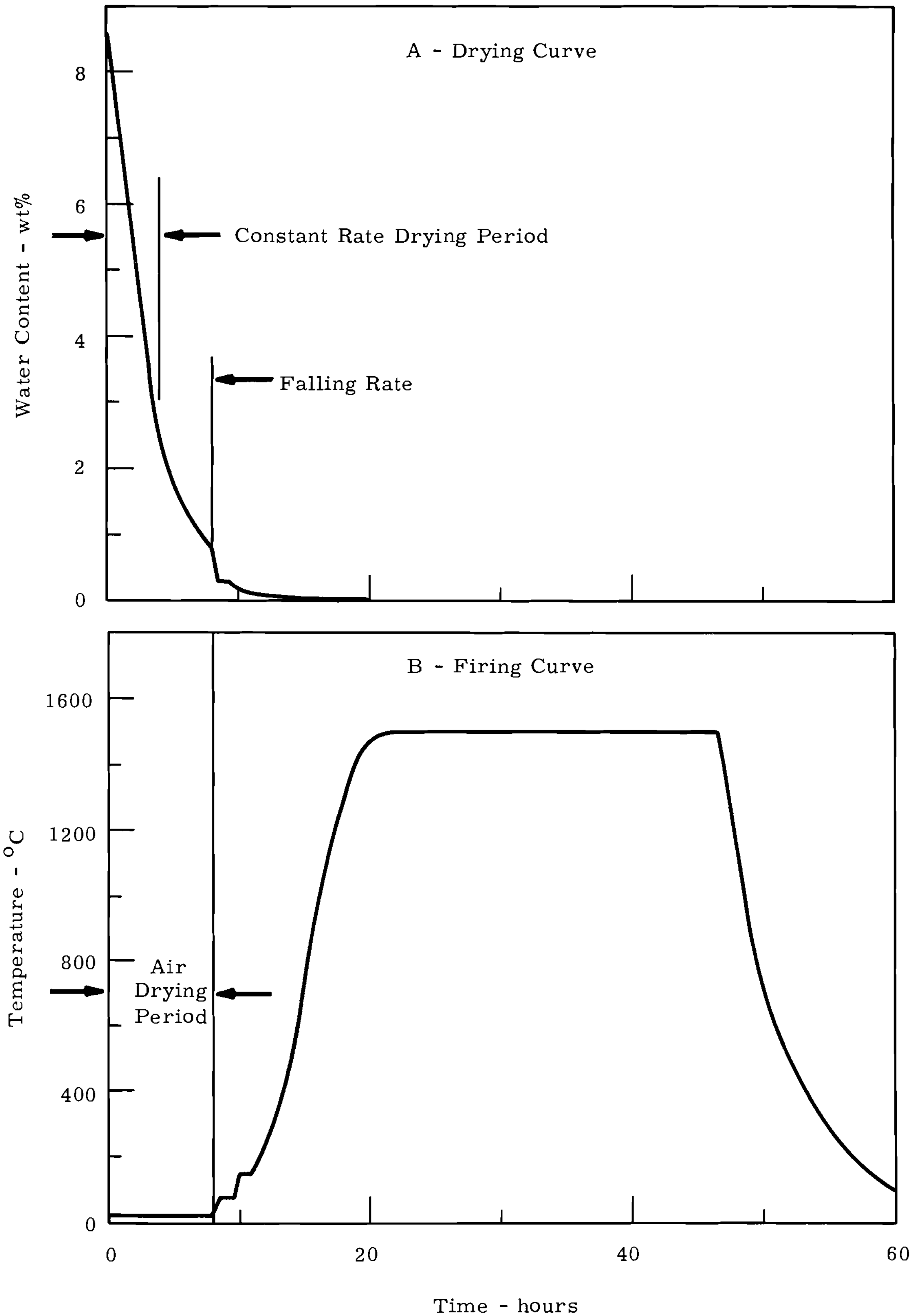

FIGURE 1 - Typical Drying and Firing Curves for Rare Earth Oxide Casts

accurate measure of slip viscosity, however, due to oxide settling, and the viscosity data given have an accuracy of no better than ± 20%. Samarium and neodymium oxide slips appear to be non-Newtonian fluids of the dilatant class and their apparent viscosity increases with increasing shear rate. All viscosity data herein reported were obtained using a number 2 spindle and a speed of 20 RPM.

With samarium and neodymium sesquioxide slips a deflocculating agent is required to reduce slip viscosity to a useful level. When a deflocculating agent such as Dexad 23 is used, a samarium sesquioxide slip containing as low as 11.5 wt.% water is sufficiently fluid to be castable.

In preparing most of the rare earth oxide slips, 0.5 wt.% Dexad 23 was used. Increased amounts of the deflocculating agent did not appear to reduce the viscosity appreciably. It was found that a milling time of about one hour was sufficient to produce a slip of minimum viscosity. With a "dilute" slip additional milling time did not appear to change the viscosity appreciably. With "concentrated" slips, however, the viscosity apparently increased substantially upon prolonged milling (See Table I).

Table I

Variation in Viscosity with Milling Time

Milling Time (hrs)	Viscosity (cps)	
	40 wt.% H_2O 59.5 wt.% Sm_2O_3	16.6 wt.% H_2O 82.9 wt.% Sm_2O_3
1	16	82
2	20	84
8	20	146

The variations in slip viscosity with water content for Sm_2O_3 slips are shown in Figure 2. The oxide used had been calcined at 1100°C prior to slip preparation. The calcination temperature appears to affect slip viscosity but not enough data was obtained to determine the exact relationship. Viscosity

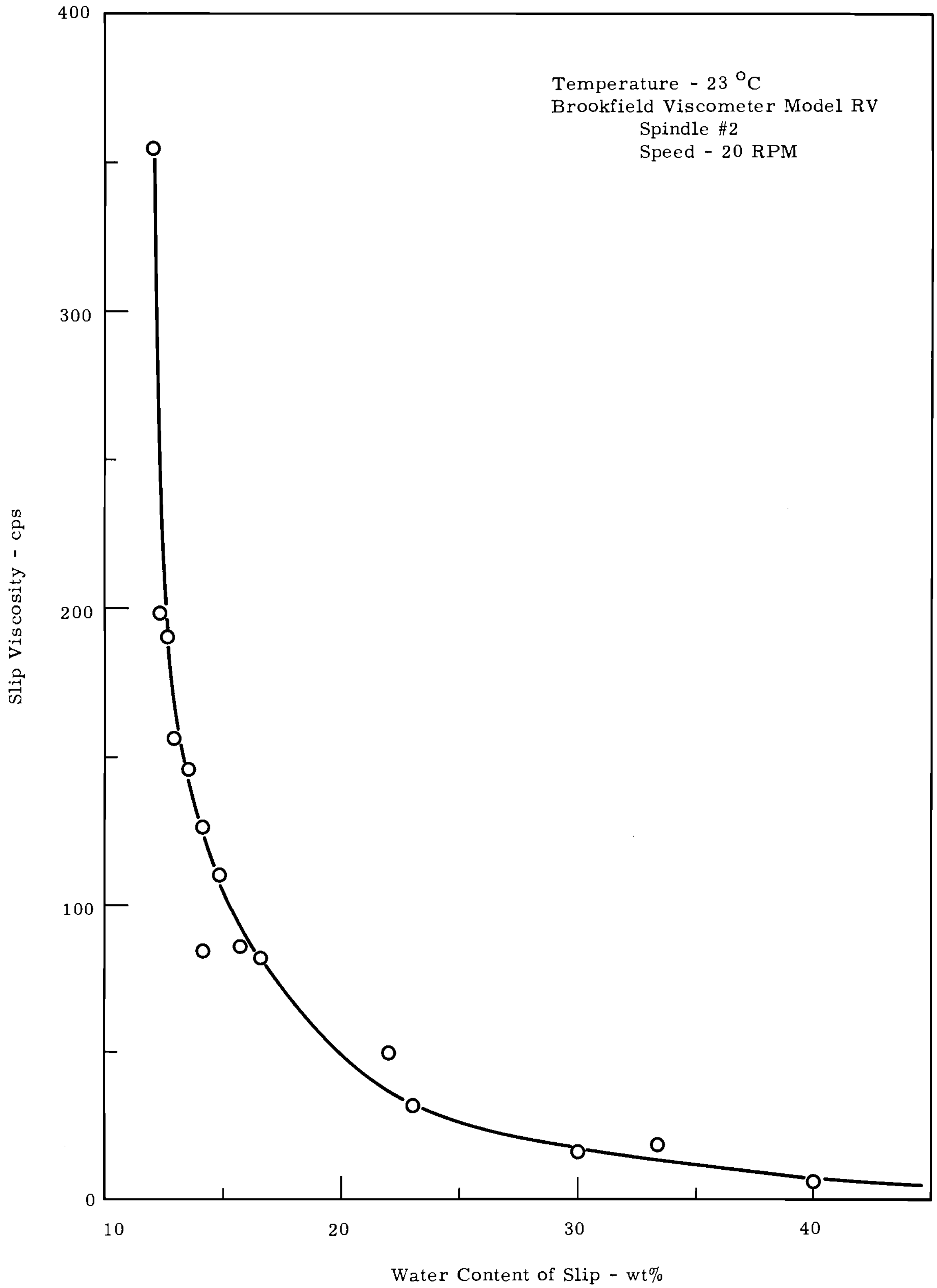

FIGURE 2 - Viscosity of Sm_2O_3 Slips as a Function of Water Content

remains fairly low as the water content of the slip is reduced from 40 wt.% to about 20 wt.%. At lower water contents, however, the viscosity increases very rapidly and it was not found possible to prepare a fluid slip having a water content of less than 11 wt.%.

Slip Density

The densities of Sm_2O_3 and Nd_2O_3 slips depend primarily on the water content of the slips and on the temperature at which the oxide is calcined prior to use. The effect of water content is shown in Figure 3 for oxides calcined at 1100°C. The variation in slip density with oxide calcination temperature was only partially evaluated and the results available are shown in Table II.

Table II

Variation in Slip Density with Oxide Calcination Temperature

Oxide	Calcination Temp., °C	Water Content Wt. %	Slip Density gm/cc
Lindsay Sm_2O_3*	Unknown	22.3	2.95
Sm_2O_3	1100	22.3	3.02
Sm_2O_3	1500	22.2	3.51

*Samarium sesquioxide as received from Lindsay Chemical has a cubic structure whereas oxide calcined at 800°C and above has a monoclinic structure.

CASTING CHARACTERISTICS

In the casting operation the important considerations are:

- Transfer of the slip from the ball mill to the mold.
- Removal of the cast from the mold.
- The green density of the cast shape.

The first two factors are important in as far as they effect the radiation exposure of the personnel. The third is important because of its effect on the firing characteristics of the cast shapes.

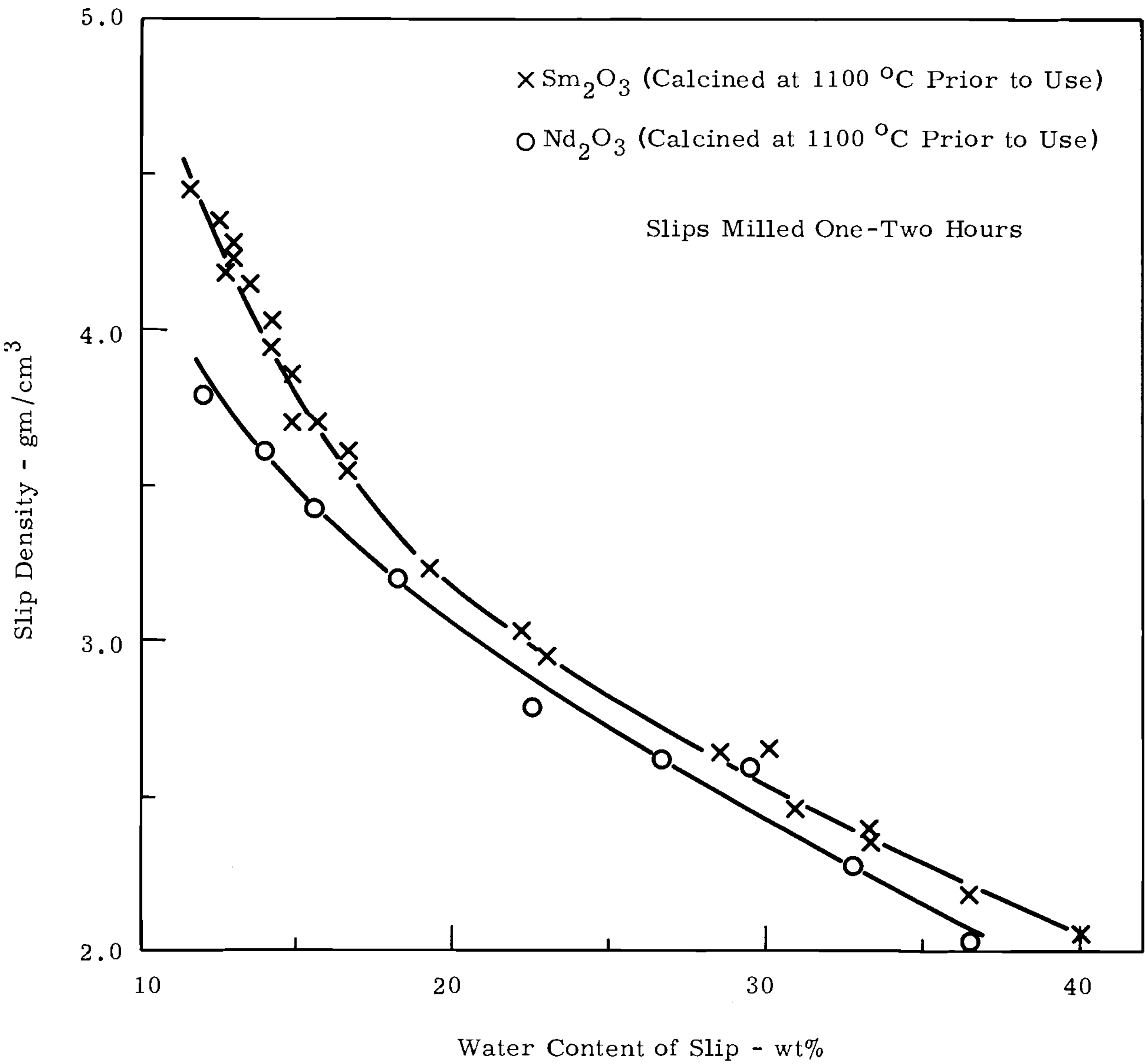

FIGURE 3 - Slip Density as a Function of Water Content for Sm_2O_3 and Nd_2O_3 Slips

Cast Preparation

As previously stated, samarium and neodymium oxide slips containing as little as 11.5 wt.% water can be successfully cast in plaster molds. The water content (and thus the viscosity) of the slip, however, has a pronounced effect on the ease of the casting operation. High viscosity slips are difficult to remove from the mill and large amounts of the slips are always left behind. Low viscosity slips are easily removed from the mill but require longer casting times. (The casting time is herein defined as the time required to fill the mold, but does not include the time required for the cast to set up so that it can be removed from the mold.) The data shows that the casting time varies with the water content of the slip assuming constant milling time (Table III).

Table III

Effect of Water Content on Casting Time

Oxide	Milling Time Hr.	Water Content Wt. %	Casting Time (min.)
Sm_2O_3	1	11.5	5
Sm_2O_3	1	22.3	12
Sm_2O_3	1	40.0	20

In addition, it was found that the longer the casting time the longer the setting up period before the cast could be removed from the mold. However, shapes made from low viscosity slips, after setting up, were much easier to remove from the molds than were those shapes prepared from high viscosity slips.

If the slips were milled for long periods of time (>two hours) the casting times became excessive. For example, a Sm_2O_3 slip containing 30% water, which had been milled for one hour, had a casting time of about 15 minutes to produce a one inch diameter by four inches long cylinder. A similar slip milled for eight hours had a casting time of eight hours. A Nd_2O_3 slip (25.5% H_2O) milled for 60 hours had a casting time in excess of 24 hours. Therefore, the shortest milling time which gives a fluid slip is desired from a casting standpoint.

The green strength of rare earth oxide casts is good and they can be handled readily without physical damage. They are not as strong, however, as cold pressed pellets.

Green Cast Density

The green density of rare earth oxide casts depends primarily on the density of the slip (which in turn is dependent on the water content). This relationship is shown in Figure 4 for Sm_2O_3. The data given are for slips which were milled about one hour. If the slips are milled for longer periods of time (>4 hours), the slip density is not affected but the green cast density is greatly increased as shown by the following numbers (Table IV).

Table IV

Effect of Milling Time on Green Cast Density of Sm_2O_3

Water Content (Wt. %)	Milling Time (Hrs.)	Slip Density gm/cc	Green Cast Density gm/cc
22.3	2	3.02	3.92
22.2	8	3.02	4.65
30	1	2.68	3.51
30	8	2.65	4.57

The advantages of increasing green density by additional milling, however, are offset by the long casting times required.

The density of the green cast can also be increased by calcining the rare earth oxide at higher temperatures prior to slip preparation. The exact relationship has not been established but the following numbers indicate the over-all trend.

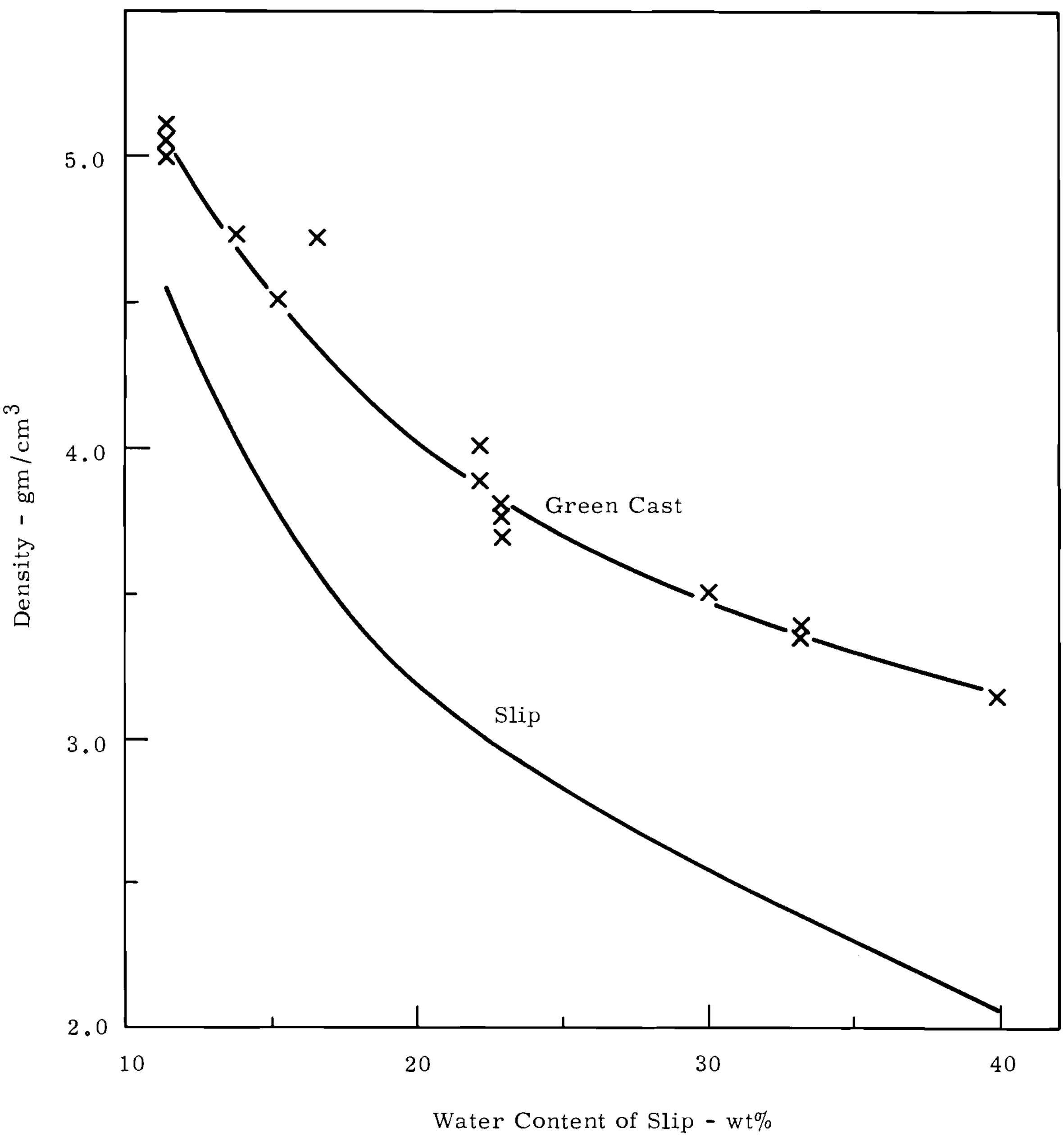

FIGURE 4 - Green Cast Density as a Function of Slip Composition for Sm_2O_3

Table V

Effect of Oxide Calcination Temperature on Green Cast Density

Oxide	Calcination Temp., °C	Water Content of Slip - wt. %	Slip Density gm/cc	Green Cast Density-gm/cc
Sm_2O_3	1100	22.3	3.02	3.92
Sm_2O_3	1500	22.2	3.51	4.58

FIRING CHARACTERISTICS

The objectives of the firing operation are to increase the physical strength and density of the cast shape. In addition, uneven shrinkage and dimensional variations should be reduced to a minimum.

Density of Fired Shapes

For a given firing temperature and time, the density of the fired shape is related directly to the green density and, therefore, to the water content of the slip, the milling time, and the oxide calcination temperature. Figure 5 shows the variation in density of Sm_2O_3 fired shapes with the water content of the slip (Sm_2O_3 calcined at 1100°C, milled 1-2 hours and fired at 1300 or 1500°C). It can be seen that a low water content and high slip density are required to give a high fired density.

When the slip cast shapes were fired at temperatures of 1100°C or less, no increase in density was achieved. Some sintering did occur but the decrease in shape volume was offset by the loss of moisture and the final density of the fired shape was approximately the same as the initial green density. The variations in fired density with firing temperature for Sm_2O_3 shapes of varying green densities are summarized in Figure 6. Figure 7 shows typical Sm_2O_3 shapes in the various stages of the firing process.

Structural Stability

Slip-cast Sm_2O_3 and Nd_2O_3 shapes which had been fired at temperatures of 1100°C and above had good physical strength. However, those shapes which had low green densities always cracked and spalled very badly when air dried and fired. Most of the cracking occurred during the air drying period or when the shapes were heated from ambient to 200°C. The most prevalent type of failure was the development of surface cracks and subsequent spallation.

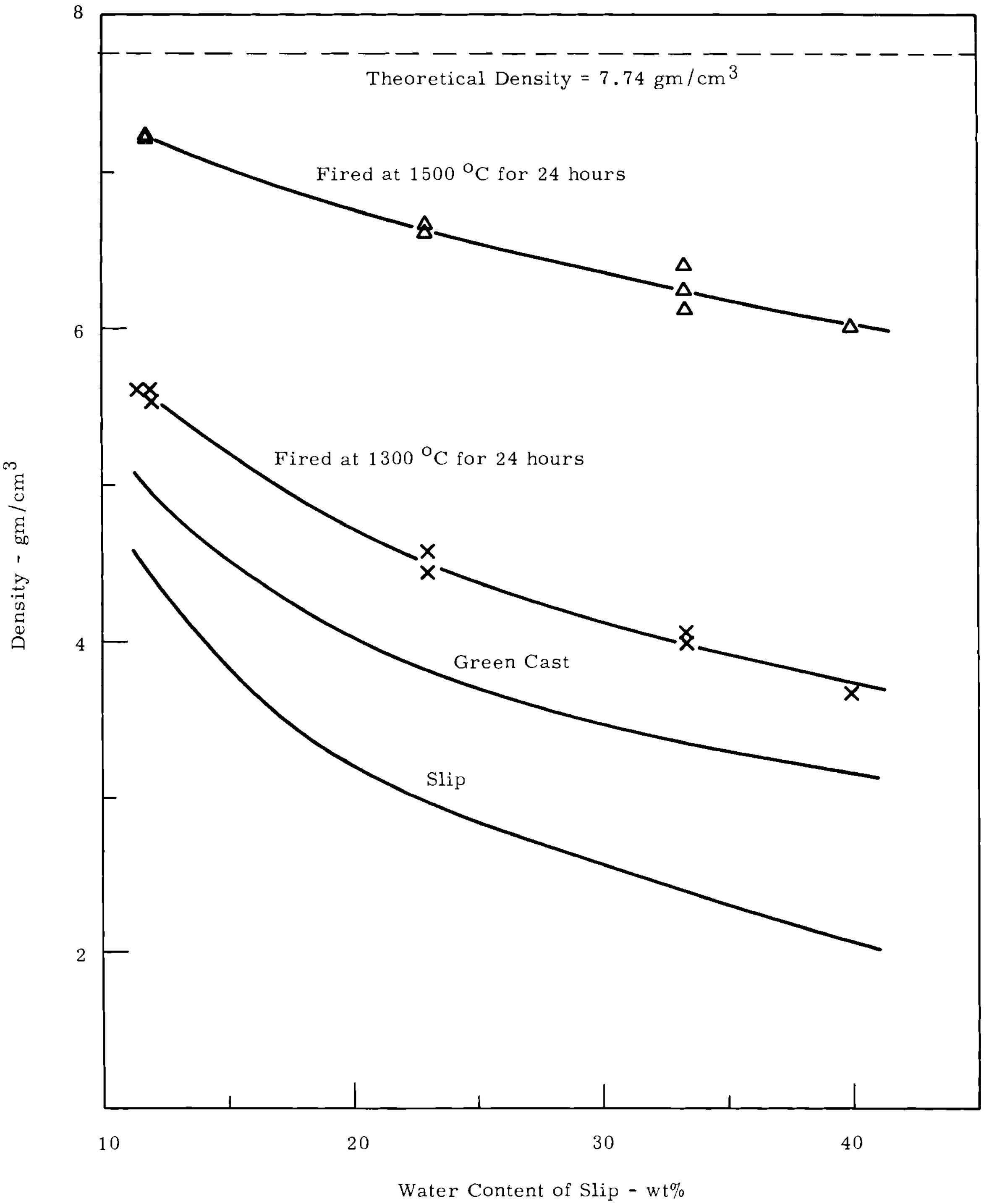

FIGURE 5 - Variation in Fired Density with Slip Composition for Sm_2O_3

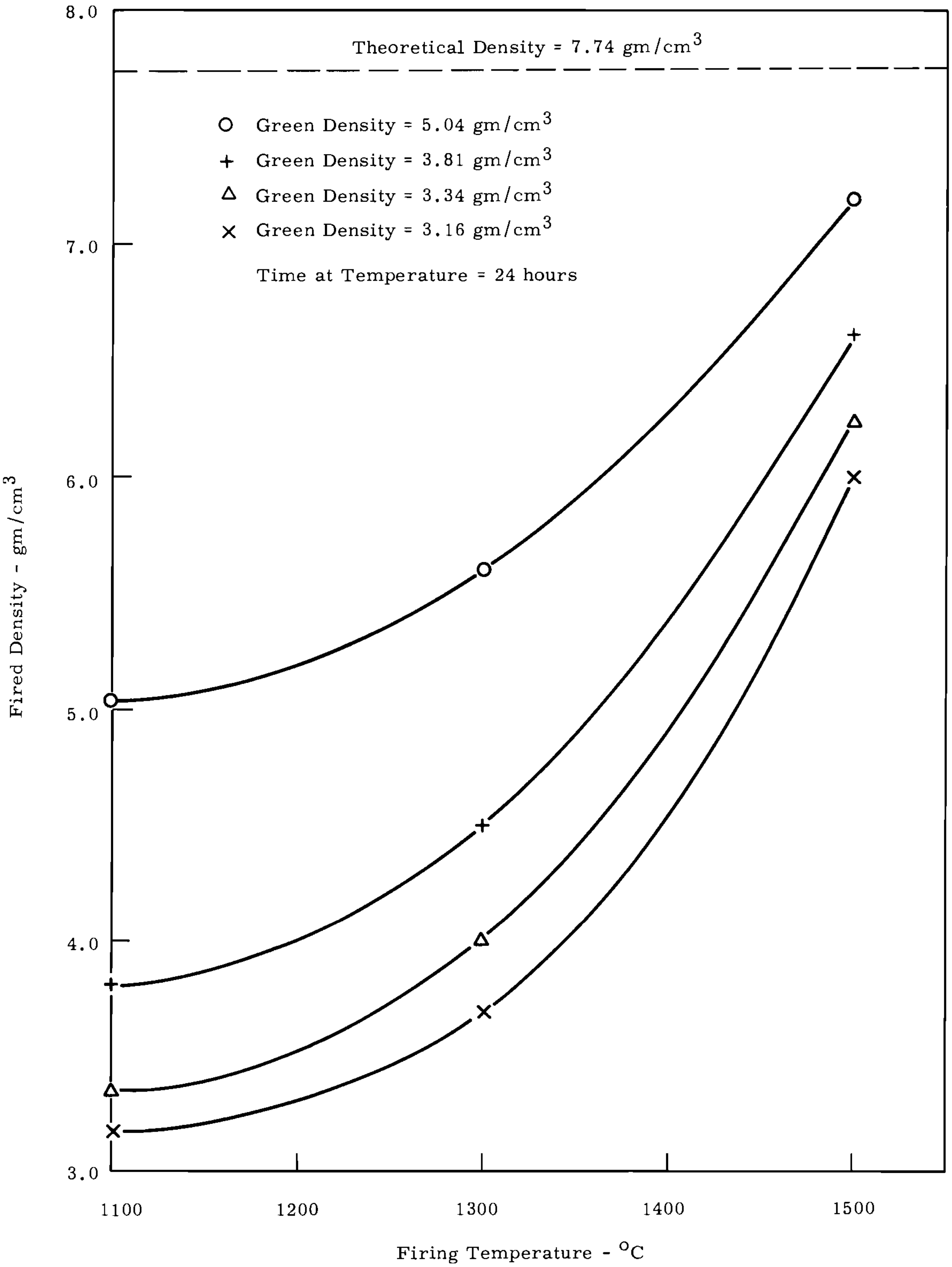

FIGURE 6 - Variation in Fired Density of Sm_2O_3 with Firing Temperature

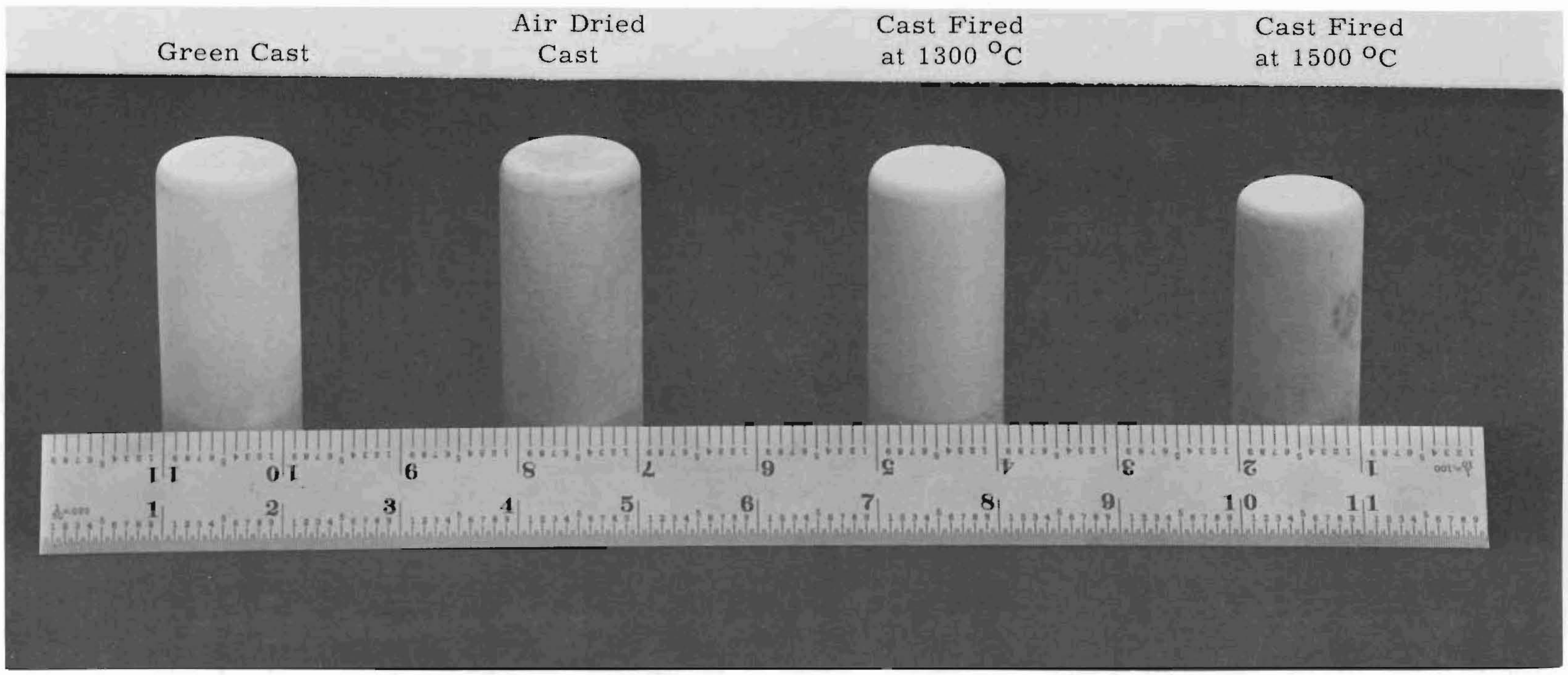

FIGURE 7 - Various Stages in the Firing of Sm_2O_3 Shapes

High density green shapes, on the other hand, could be dried and fired without cracking if the heating and cooling rates were carefully controlled in the range of 20-500°C. Even with high density green shapes some surface cracks developed if the drying and heating rates were too great. Normally, about a 6-8 hour drying period was required to prevent surface cracks from developing.

Typical flawed Sm_2O_3 shapes are shown in Figure 8. Shape 8-A shows surface cracks as a result of too rapid a drying rate; 8-B shows some spallation and a major crack due to too rapid a cooling rate; 8-C shows the effect of uneven heating; and 8-D shows a small amount of surface blistering and spallation. Figure 9 shows a shape that has been correctly fired. No cracking or spalling has occurred, and the only flaws are some small voids at the surface.

Dimensional Control

Dimensional control of the slip cast shape is difficult to maintain during the firing operation. Uneven shrinkage can give badly distorted shapes, while even under the most closely controlled conditions dimensional variations of 2-3% are common. In addition, there is always some variation in shape dimensions due to one surface of the shape being in contact with the setter plate during the firing process. Figure 10 shows the dimensions of a typical rare earth oxide shape before and after firing (with optimum control of the firing process). The shape has a slight taper to facilitate its removal from the mold. In firing, the small end was placed in contact with the setter plate to give a more uniform diameter.

EVALUATION OF SLIP CASTING PROCESS

In evaluating slip casting as a process for fabricating promethium sesquioxide into useable shapes, the evaluation must be based on the requirements set forth in Section 3, above. Since the experimental work was limited and not all the variables could be studied in detail, the over-all evaluation of the process that follows is based on qualitative impressions gained during the course of the work and in some cases have not been verified by experimental work.

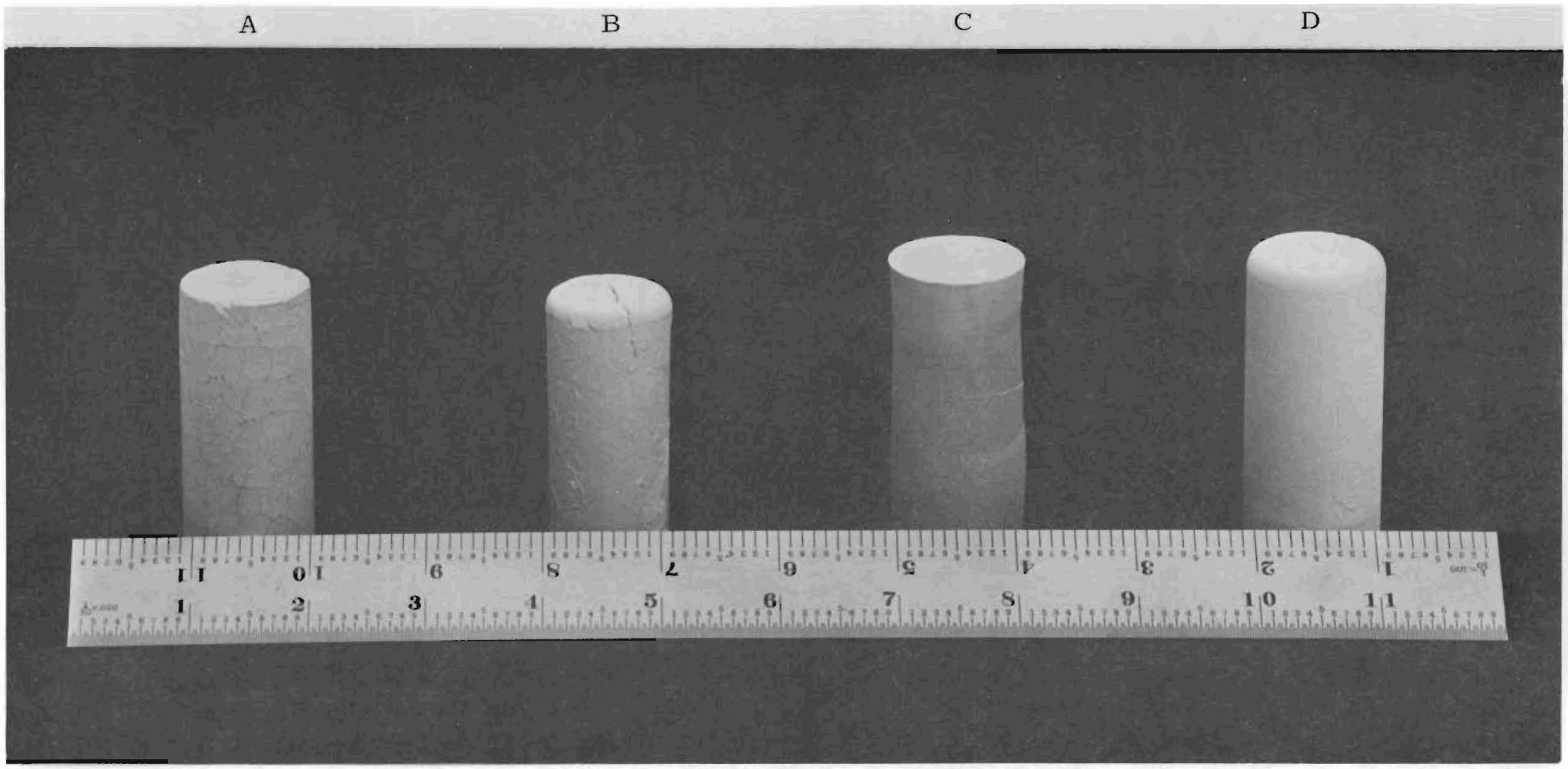

FIGURE 8 - Fired Shapes of Sm_2O_3 Showing Flaws due to Incorrect Firing

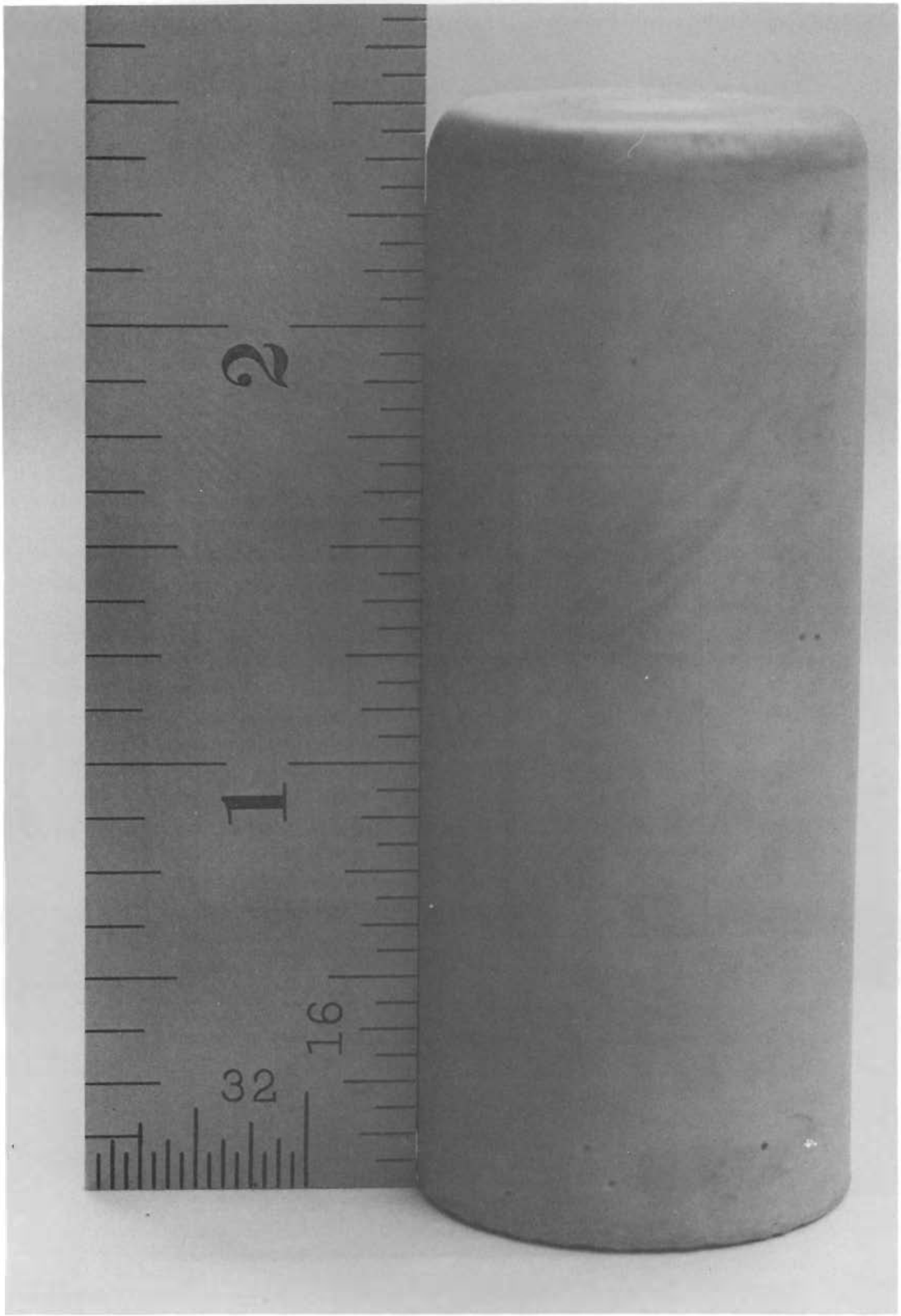

FIGURE 9 - Samarium Sesquioxide Shape Correctly Fired

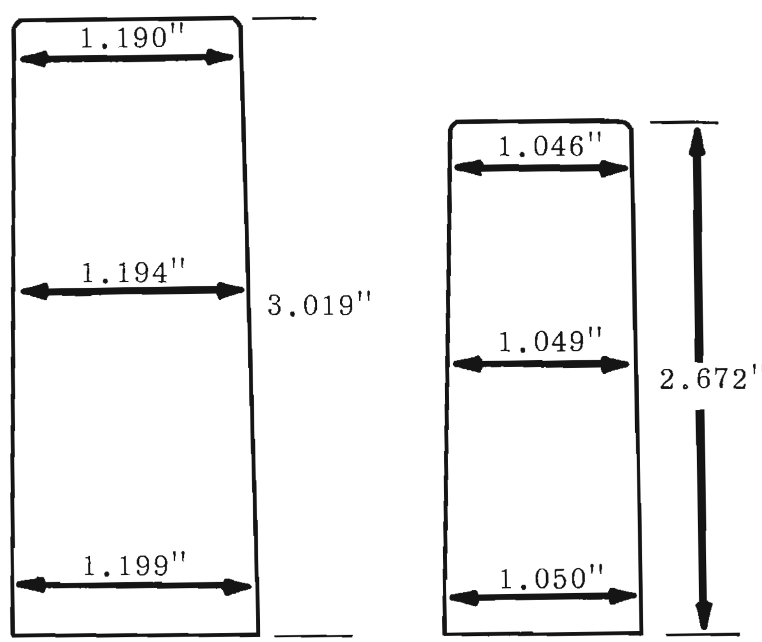

FIGURE 10 - Shape Dimensions Before and After Firing

- Density. By selecting the proper casting and firing conditions, rare earth oxide casts of moderately high densities (90-95% of theoretical) can be prepared quite readily. To produce shapes of higher densities will require firing temperature above 1500°C. The rare earth oxide casts show a good uniformity of density, at least for the right circular cylinders that were prepared in this work.

- Physical Strength. The unfired casts of Nd_2O_3 and Sm_2O_3 show good green strength and can be handled quite readily as long as reasonable care is taken. The air dried casts have strengths equivalent to the green casts, but the oxide at the surface has a powdery texture. The air dried shapes, therefore, should be handled as little as possible to prevent the loose powder from sloughing off. The fired casts have excellent strength and texture. They can be handled readily and will stand a great deal of mechanical shock without damage. The above comments apply only to those casts which have been processed correctly, however, to prevent cracking and spalling. Fired casts which do have cracks show poor physical strength and little resistance to mechanical shock.

- Dimensional Control. As in any slip casting process, dimensional control is very poor. Uneven shrinkage and warpage can be eliminated by careful firing, but even under the most carefully controlled conditions the reproducibility of the process is no better than ± 2-3% based on the physical dimensions of the fired shapes.

- Physical Operation. The physical requirements of the slip casting process are such that they can be performed in either a remotely operated facility or a gloved box. However, operation in a remote facility would require manipulators with a good lifting capacity to handle items such as the ball mills.

- Operator Exposure. If the process were to be carried out in a glove box, a fair amount of handling would be required. Since it would be difficult to shield the various pieces of equipment, the operators would receive substantial quantities of radiation to their hands.

- Physical Containment. Most of the work would be carried out with Pm_2O_3 in slurry form or as a compacted shape. There would be little handling of loose dry powder; therefore, the physical containment of the oxide would be relatively simple. However, in handling the slurries a number of items of equipment would build up quantities of promethium which would result in a high background radiation level in a gloved box.

Based on the above factors, the following conclusions have been reached with regard to the use of slip casting for fabricating promethium sesquioxide shapes.

1. If close dimensional control is required, slip casting is not a suitable process for compacting promethium sesquioxide. Where dimensional control is not critical, slip casting can be used to prepare Pm_2O_3 shapes of moderately high density very readily.
2. Because of (a) the physical handling required and (b) the buildup of promethium in the process equipment, any production slip casting operation would have to be performed in a remotely operated facility. For making a limited number of shapes, however, the work could probably be done in a gloved box without excessive operator exposure.

ACKNOWLEDGEMENTS

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