Improved calcium fluoride shapes

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IMPROVED CALCIUM FLUORIDE SHAPES

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ABSTRACT

The properties of calcium fluoride are discussed with relation to utilization in refractory crucibles or liners. Conventional methods of slip casting and dry pressing are found to be practical. Expansion, shrinkage, density, and porosity characteristics of the fired material are considered.

I. INTRODUCTION

Calcium fluoride, with a melting point of approximately 1350°C, has long been employed as a flux and mineralizer in cement and other products. Its use as a refractory is limited by its melting point and also to conditions permitting the presence of fluorides and for which the common oxide materials are unsuitable. These requirements occur in certain bomb reductions and in the melting of some metals.

This brief, exploratory study was made to ascertain the feasibility of application of conventional forming procedures to calcium fluoride. The techniques employed are possible in many laboratories and are suited to occasional production of small pieces.

Some of the properties which govern the usefulness of the resulting specimens were also determined.

II. PREVIOUS INVESTIGATIONS

The literature contains much information pertaining to the fluxing and mineralizing action of CaF$_2$($1,2,3$), but little mention is made of the refractory properties. Dony-Hensault and Polydoroff (4) discuss the use of linings capable of withstanding 1248°C. Eichner and Caillat (5) used calcium fluoride as a crucible for uranium metal and fluorine compounds at temperatures as high as 1200°C. Gray (6) reported attack of calcium fluoride by molten cerium.
Allison and Murray (7) studied many of the fundamental properties of CaF$_2$ in a sintering investigation. They found the coefficient of thermal expansion varied from approximately $21 \times 10^{-6}$ to $26 \times 10^{-6}$ depending on the density of the specimen considered.

Murray and Taylor (8) found free lime formation to be responsible for failure in crucibles formed from technical grade CaF$_2$ containing small amounts of silica. Tricalcium silicate was formed during firing and decomposed to form free lime when cooled. Subsequent hydration of the free lime caused disintegration.

III. INVESTIGATION

All of the material employed was chemically pure reagent grade calcium fluoride.* The powder was placed in fired calcium fluoride crucibles and calcined for one hour at 1000°C. The calcine was then dry milled in a porcelain ball mill for 23 and 48 hours at 60 rpm. It was washed from the mill and dried. The particle size distributions were determined by the hydrometer method (9) and are shown in Figure 1.

Pellets were formed from the dried powder in a hardened steel die. The pressures employed were approximately 10,000; 20,000; and 30,000 psi. A 10% water addition was made to facilitate pressing. The dry pressed bars used for thermal expansion were formed at approximately 6,600 psi with a similar water addition.

Bar shaped specimens were also slip cast in plaster molds from both particle distributions using hydrochloric acid and ammonium hydroxide to adjust the pH. In preparing these slips, the variation in viscosity with pH was studied with a MacMicheal viscosimeter.

IV. RESULTS

The pH-viscosity relation occurring in aqueous suspensions of calcium fluoride is noted in Figure 2 for one specific gravity. The same general curve was also found to occur at lower specific gravities. The influence of particle size is especially noticeable in these curves. The most satisfactory pH for slip casting was found to be approximately 5 for this specific gravity. This gave casts which were fairly rapid, freed from the mold in a reasonable length of time, and gave less mold attack than more acidic slips. The specific gravity of 2.1 was found to be satisfactory for the casting of small crucibles and solid shapes.

The linear shrinkage occurring on firing dry pressed and slip cast calcium fluoride in air is shown in Figure 3. All specimens were held at temperature one hour. The highest shrinkage occurs in the pellets compacted at the lowest pressure, 10,000 psi. This

*Supplied by Baker and Adamson.
Figure 1 - Particle Size Distributions. Ball Milled Calcium Fluoride.
Figure 2 - pH-Viscosity Relations of Aqueous Suspensions of Calcium Fluoride.
Figure 3 - Linear Shrinkage of Dry Pressed Calcium Fluoride.
is as expected since the dry pressing compaction is additive to
the compaction or sintering produced by elevation in temperature.
When the compacts are measured after pressing, the additional
dimensional change produced by heat treatment will be less in
the compacts of original greatest density. As will be seen later,
the highest shrinkage does not indicate greatest density nor
lowest porosity in a pressure sensitive material such as calcium
fluoride.

The shrinkage occurring in slip cast bars is average as compared
to the dry pressed specimens. Crucibles cast from this same batch
were found to be water tight and relatively impervious.

The relative density was determined on a basis of 3.18 gm/cc
as the theoretical crystal density. The results of this determina-
tion are shown graphically in Figure 4. The highest values are all
very close, the maximum density developed is with the finest
material compacted under the greatest pressure. This maximum is
achieved at about 1000°C and has a shrinkage, as noted in Figure 3,
of a little over 8%. The slight indication of a bloating condition,
not apparent in the pieces, but obvious from the decrease in the
relative densities above 1000°C makes it desirable to fire at this
temperature. Higher firing does not improve the properties.

The total porosities; i.e., all open and closed pores in the
fired volume, are plotted in Figure 5. Again a minimum is found
at approximately 1000°C. Many of the points are below 10%, indicat-
ing a very dense body. Many of these specimens would be water
tight under moderate pressures.

Thermal expansion data for the bars formed are shown in
Figure 6. The variation is slight between the different forming
and firing conditions. The average coefficient of thermal expan-
sion, between 500°C and 900°C is approximately 27.9 x 10^-6. This
indicates low thermal shock resistance as compared to values of
8 x 10^-6 for alumina and 14 x 10^-6 for magnesia (10).

V. CONCLUSIONS

1. Calcium fluoride may be slip cast in aqueous suspensions. For
the particle distributions studied, a pH of 5 and specific
gravity of 2.1 were found satisfactory. Particle size has a
noticeable effect on the viscosity at any pH.

2. Dry pressing was found to be a satisfactory method of forming.
Increased compacting pressures increased the density and
decreased the total porosity. Specimens fired to 1000°C were
quite dense and had low porosity.

3. Firing to temperatures above 1000°C is not required nor desirable.
A decrease in relative density and an increase in total porosity
were found to occur above this temperature.
Figure 4 - Relative Densities Calcium Fluoride Specimens.
Figure 5 - Total Porosities Calcium Fluoride Specimens.
Figure 6 - Thermal Expansion of Calcium Fluoride Bars.
4. Thermal expansion was found to be quite similar in all of the specimens measured. Thus changes in forming procedure or firing temperature are not successful in reducing the susceptibility of calcium fluoride to thermal shock.

VI. LITERATURE CITED


