

Thermal Length Changes of Some Refractory Castables

S. J. Schneider and L. E. Mong

The changes in length exhibited by a variety of refractory castables during complete heating and cooling cycles were determined. The tests consisted of determinations on castable specimens that had been heat treated at either 110°, 1,050°, or 1,300° C. A detailed description of the apparatus is given, especially that of the dilatometer assemblies. These assemblies incorporated differential transformers to give a record of length changes as they occurred. The data suggested that the same general length-change characteristics were exhibited by castables that had received the same curing and heat treatment. Length-change curves of all three groups illustrated silica inversions. Curves of the 110° C group indicated contractions associated with cement reactions, namely, the loss of water of hydration and the conversion of amorphous alumina to γ alumina.

1. Introduction

Invaluable aid can be gained by using thermal-expansion and contraction curves as guides in defining what allotropic changes occur, in determining at what temperatures reversible and irreversible volume changes take place; and by indicating the tendency of materials to spall [1].¹ This is especially true of refractories, the life and serviceability of which are directly affected by these thermal characteristics. This report endeavors to supply some of the needed information on one particular family of refractories, "the refractory castable." To provide a comprehensive study of this type of refractory, the investigation included length change determinations on commercial brands, as well as laboratory-prepared castables.

2. Specimens

2.1. Composition

Fourteen commercial brands and six laboratory-prepared groups of castables were used for tests conducted in this investigation. The commercial brands, selected to provide materials having a wide range of refractoriness, were obtained from a number of different manufacturers. Laboratory-prepared castables contained either 10, 20, or 30 percent of domestic high-alumina cement as the bonding material. These percentages of cement, in addition to appropriate amounts of aggregate, either calcined Kentucky flint clay or crushed high-heat-duty firebrick, constituted the experimental laboratory mixes. The more important properties of the aggregates, the cement, and the commercial castables used in this investigation were given by Heindl and Post in previous reports [2, 3].

2.2. Preparation

Prismatic 2- by 2- by 10-in. bars were prepared from the laboratory mixes and the commercial brands as outlined in Heindl's first report [2]. Four test specimens, approximately 1- by 1- by 7/4-in.,

were cut from each 2- by 2- by 10-in. bar. In order to insure proper dilatation values, the ends of each specimen were ground plane and perpendicular to the long axis. Irregular or rough ends could cause displacement or misalignment of the specimen, which in turn would result in erroneous expansion values. To facilitate grinding, a moderate coat of shellac was applied to the ends of all friable specimens.

3. Apparatus

3.1. Assembly

The apparatus used in this investigation is essentially automatic, needing little supervision once started. For the purpose of description, it can be divided into three separate units, each having its own distinct operation. They are (1) dilatometer, (2) furnace, and (3) instruments for temperature measurement and control. Figure 1 illustrates the assembled apparatus used for the determination of thermal length changes.

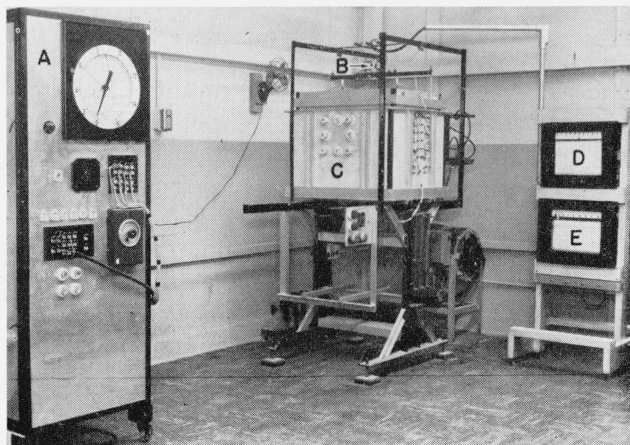


FIGURE 1. Assembled apparatus used for determining thermal length changes.

(A) Program controller; (B) dilatometer assemblies; (C) furnace; (D) differential length change recorder; (E) temperature recorder.

¹ Figures in brackets indicate the literature references at the end of this paper.

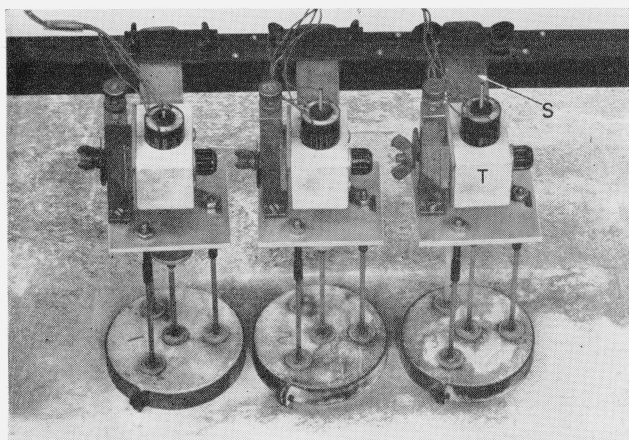


FIGURE 2. Upper portion of dilatometer assemblies.

(S) Spring that restrains upper portion of dilatometer assembly from horizontal but not from vertical movement; (T) differential transformer and mounting. The three outer sapphire rods support the mounting. The center rod connects armature to top of specimen.

3.2. The Dilatometer

Figures 2 and 3 show the assembly of parts for the dilatometer. Except for the use of a differential transformer in place of a dial indicator, the entire assembly is similar to that described by Geller and Yavorsky [4]. The transformer is preferable for this application because of its automatic recording features. Also, its internal frictional forces and its force exerted on the specimen are only a fraction of those produced by the dial indicator. Kelly and Harris [5] have reported expansion equipment that also utilizes differential transformers in a similar manner.

The theory and operation of the differential transformer are described in detail in various bulletins and manuals [6, 7]. In essence, the transformer consists of a primary coil, a secondary coil, and a permeable armature. The armature is attached directly to a sapphire rod, which in turn rests on top of the specimen. As the specimen expands or contracts, the armature correspondingly moves axially in the coils, thus generating a signal proportionate to the differential length change between the specimen and the sapphire rods. This signal, when amplified and balanced, is recorded on the strip chart of the differential length-change recorder (fig. 1 (D)). The percentage of thermal expansion or contraction was calculated from these data and corresponding temperature measurements. The sensitivity of the differential length-change measurements was considered to be 0.0005 in., and the accuracy was estimated to be ± 0.0005 in.

3.3. The Furnace

The furnace, a box-like structure composed of insulating firebrick suitable for use at 3,000° F, encased in a Transite and steel framework, (fig. 1 (C)) contained a chamber of 6½ in. wide, 13 in. long

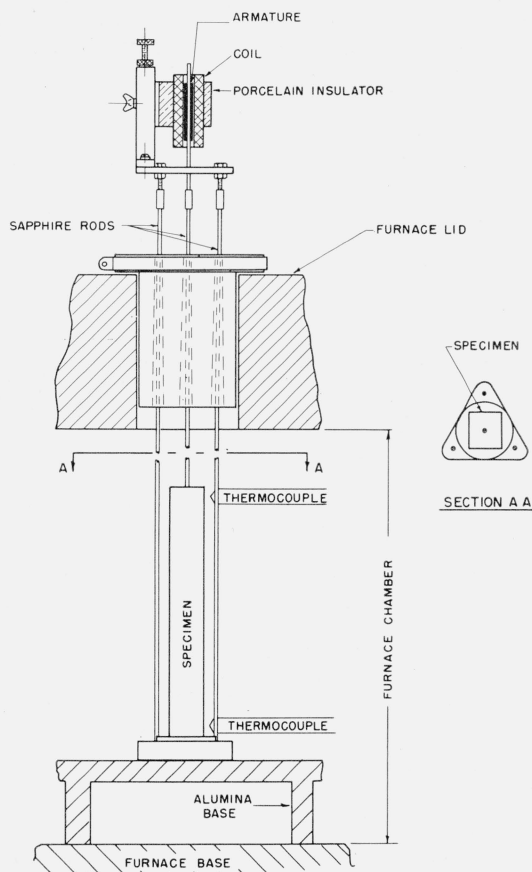


FIGURE 3. Schematic diagram of a dilatometer assembly and related parts.

One of the three sapphire rod supports is not shown in the vertical section.

and 13½ in. deep. In order to obtain uniform temperatures, the furnace utilized 16 silicon-carbide heating rods, 14 horizontal and 2 vertical, systematically spaced in the chamber. A variable transformer capable of supplying 50 amp at 270 v to the heating rods enabled the furnace to attain temperatures up to 1,500° C. A total of three dilatometer assemblies, each holding one specimen, can be heated simultaneously in this furnace. Figure 3 indicates the relative position of one specimen and dilatometer assembly in this furnace.

3.4. Temperature Measurement and Control

A circle-chart-recording potentiometer with a cam-type program attachment, (fig. 1 (A)) regulated furnace temperatures. Temperatures near the specimens were recorded on a six-point strip-chart recorder by means of six noble-metal thermocouples. The sensitivity and accuracy of the temperature measurement were estimated at 3 deg and ± 5 deg C, respectively. The relative positions of the thermocouples and specimen are indicated in figure 3. A few additional temperature readings obtained by means of thermocouples placed near the midpoint

of the specimens indicated that the vertical temperature gradient was approximately linear. The vertical gradient ranged between 5 deg and 15 deg C over a 7-in. span.

4. Experimental Procedure

All specimens were first cured for 24 hr at 21° C and 95-percent relative humidity, then air-dried for at least 3 months and finally heat treated at either 110°, 1,050°, or 1,300° C.² Specimens initially subjected to the latter two heat treatments were fired in a gas furnace at a rate of 37.5 deg C/hr with a 5-hr soaking period at the top temperatures. The furnace and specimens were cooled naturally to room temperature. For the 1,050° and 1,300° C heat treatments, the specimens were set in muffles.

Prior to the actual expansion determination, each specimen was dried overnight at 110° C, cooled, and then measured for length. Immediately following the length measurements, the specimens, specimen holders, differential transformers, and related parts were positioned in the furnace as shown in figure 3 and figure 1(B). The furnace temperature was raised by using a control cam that called for a 100-deg C rise per hour, with a 15-min holding period at each 100-deg C interval and at 250° and 550° C. After a 15-min holding period, the temperature existing in the specimen approached but did not attain the temperature indicated by the thermocouples. This error affected the results to approximately the same extent as the error in measuring length changes. When the strip chart of the recorder (fig. 1(D)) indicated a differential length change of at least 0.0005-in./min the furnace was shut off and allowed to cool to room temperature. The temperature at which this rate of differential length change occurred was called the "deformation temperature." Temperatures and differential changes in length were recorded, (figs. 1(D) and (E)) during both heating and cooling. One specimen, or more, from each heat treatment was tested in this manner.

The same procedure was followed in obtaining necessary calculation and calibration data. The following equation was used throughout this investigation for the calculation of thermal length changes at any given temperature:

$$S = \frac{100R}{L} + A,$$

where

S = percentage length change,

R = differential length change in inches, as indicated by recorder (fig. 1(D)),

L = specimen length in inches at room temperature following 110° C heat treatment,

A = percentage expansion for sapphire taken from figure 4.

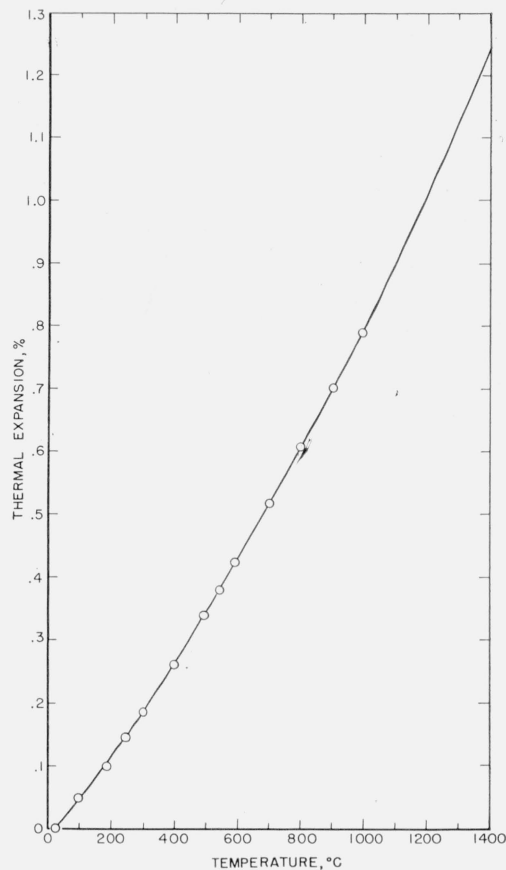


FIGURE 4. Thermal-expansion curve for one-eighth-inch-diameter sapphire rod measured along an axis $62^{\circ}30' \pm 1^{\circ}30'$ from C-axis.

Figure 4 was obtained from expansion tests conducted with the dilatometer, using a fused-silica specimen as a reference material. Expansion values above 1,000° C were extrapolated. The difference between these results and those obtained by others [4] did not exceed 0.0002 in./in. This discrepancy could be attributed to differences in rod orientation.

5. Results

Thermal length changes of neat high-alumina cement, commercial brands³ of castables, and laboratory-prepared castables are illustrated graphically in figures 5 through 12. All curves show the changes exhibited during complete heating and cooling cycles.

Repeated tests made on either fused-silica or polycrystalline alumina specimens proved the reproducibility of data. The difference in results obtained on these specimens from test to test was within experimental error. Figure 6 indicates the

² Percentage permanent linear-change values due to similar heat treatments determined on other specimens were reported previously by Heindl and Post [3].

³ The length-change curves of only 5 of the 14 commercial brands tested are reported in this paper. The five brands were considered typical of the entire lot.

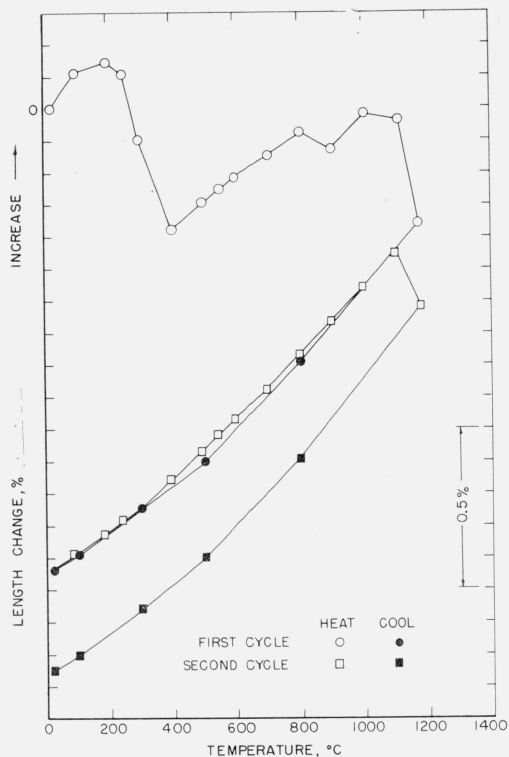


FIGURE 5. Thermal length changes of neat high-alumina cement after being cured for 28 days in a "fog room" and heat treated at 110° C.

Length-change values were determined by W. L. Pendergast and S. F. Holley, National Bureau of Standards.

reproducibility of results obtained on three specimens of ostensibly the same castable material. Small, but significant differences in the length change curves of these specimens are apparent.

6. Discussion of Results

6.1. Neat Cement

The thermal length-change characteristics of a neat high-alumina cement would influence the expansion or contraction properties of any castable, heat treated at 110° C, in which the cement is a constituent. Examination of the curve showing length changes of neat high-alumina cement during the first heating (fig. 5) reveals two features that appear as characteristics of both neat cement and castables. They are (1) rapid contraction occurring between 200° and 400° C, and (2) a lesser contraction between 800° and 900° C.

Due to the complex nature of high-alumina cement, there is no general agreement as to its exact constitution. Wells found that anhydrous high-alumina cement contained $\text{CaO}\cdot\text{Al}_2\text{O}_3$ and $3\text{CaO}\cdot 5\text{Al}_2\text{O}_3$ as its major constituents, and $2\text{CaO}\cdot\text{SiO}_2$ and iron compounds as its minor constituents [8]. Petrographic examination of the cement used in this investigation revealed that it was composed essentially of monocalcium aluminate, tetracalcium

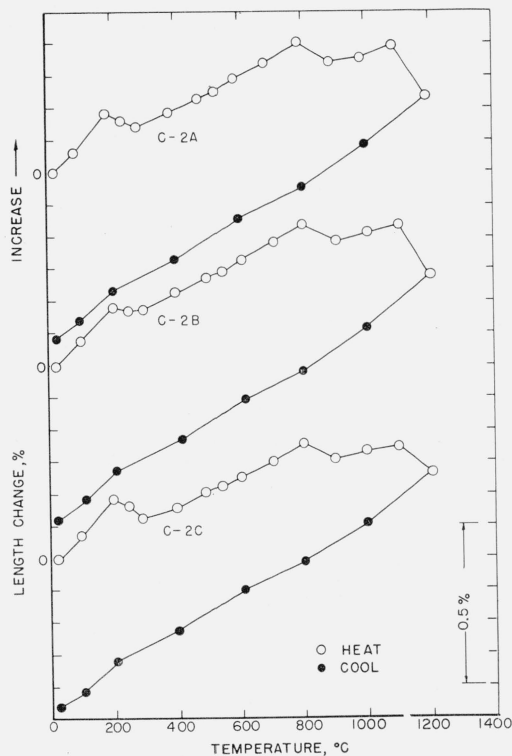


FIGURE 6. Thermal length changes of a commercial castable heat treated at 110° C.

Curves C-2A, C-2B, and C-2C represent three specimens cut from one bar, which was cast as a unit.

aluminoferrite, and glass (uncrystallized material) [2]. It is assumed that the cement, when hydrated, cured, and air-dried, contains varieties of hydrated alumina and hydrated calcium aluminates, possibly gibbsite ($\text{Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$) or hydrated amorphous alumina, together with one or more hexagonal calcium aluminate hydrates and perhaps tricalcium aluminate hexahydrate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$) [8]. These compounds have also been found by Wells et al., in their study of the $\text{CaO}\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$ system [9].

On the basis of these assumptions, explanation can be offered for the rapid contractions that occur between 200° and 400° C and between 800° and 900° C. It is logical to assume that the first contraction (200° to 400° C) is caused by the loss of water of hydration. This is substantiated by differential thermal analysis and by water-loss curves obtained in different investigations [3, 10]. Gibbsite, by losing its water of hydration, converts to the amorphous form of alumina, provided it is intimately mixed with the other hydrated cement constituents [11, 12]. It is noteworthy that studies by Pepler and Wells [13] indicated that boehmite ($\text{Al}_2\text{O}_3\cdot\text{H}_2\text{O}$) may be intermediately formed before the amorphous variety. Definite conclusions applicable to this particular investigation cannot be made because their work was performed above atmospheric pressure.

Gibbsite, when heated alone to temperatures as low as 600° C, apparently is converted to γ alumina. Inskip suggested that a greater "activation energy"

and a higher "threshold temperature" are required for this conversion when the amorphous alumina molecules are separated by rigid silica molecules, as they are in dehydrated kaolin [11]. The effect of the silica on the amorphous alumina conversion is evidently replaced by the effect of intimately mixed dehydrated calcium aluminates on the conversion of amorphous alumina in high-alumina cement. Differential thermal-analysis curves of dehydrated kaolin [11] and dehydrated high-alumina cement [3] show that the γ -alumina conversion is retarded until approximately 900° C. Comparison of these differential thermal-analysis curves with the length-change curve of high-alumina cement (figure 5) seem to offer evidence that the contraction occurring between 800° and 900° C is caused by the conversion of amorphous alumina to γ alumina. X-ray patterns taken on samples of neat high-alumina cement that had been heated to either 700° or 900° C, and then air-quenched, showed no perceptible γ alumina. However, petrographic examination⁴ of the 900° C sample did indicate material was present with an index of refraction similar to that of γ alumina. It could not be identified positively. The 700° C sample, when analyzed petrographically, contained no identifiable γ alumina.

6.2. Aggregate

The aggregate that is used in combination with cement to form refractory castables may vary in type and proportion, dependent on the desired end product. Calcined fire clays, blast-furnace slag, chrome ore, and varieties of crushed firebrick have all been used as the aggregate. Perhaps the aggregate most commonly employed in castables is crushed firebrick. Expansion curves of various firebricks and fire clays are reproduced in numerous articles and books [1, 14, 15]. The outstanding feature of the curves given in these references for the aggregates used in this investigation is the indication that silica is present as a major constituent. Thus, it can be expected that the changes in slope associated with silica inversions might also be present in the length-change curves of the castables.

6.3. Castables, Heat Treated at 110° C

Because a refractory castable is a heterogeneous mixture of a hydraulic high-alumina cement and a heat-resistant aggregate, its thermal-expansion and contraction properties are, except where reactions between the two occur, a composite of the properties of the two separate ingredients. The curves of the laboratory-prepared castables that had been heat treated at 110° C (fig. 8) show the effects of varying percentages of cement.

Although no castable duplicated another in its length-change properties, a definite trend or pattern for each heat treatment is evident at temperatures

⁴The X-ray pattern of the 900° C sample was furnished by A. Posner, Research Associate, American Dental Association at National Bureau of Standards. The other X-ray pattern and all petrographic analyses were furnished by A. Van Valkenburg and G. Ugrinic, Mineral Products Division, National Bureau of Standards.

below 1,100° C. Common characteristics illustrating this general trend, for the 110° C heat-treatment group, are shown by figures 6, 7, and 8. By correlation of data, it is evident which length-change phenomena of castables can be attributed to the cement and which to the aggregate. The 200° to 300° C and the 800° to 900° C contractions, prevalent throughout these typical curves, are caused by cement reactions, namely, the loss of water of hydration and the conversion of amorphous alumina to the γ variety, respectively. Similarly, below 1,100° C, the aggregate is responsible for other noticeable features of the length-change curves, such as the changes in slope occurring in the room temperature to 200° C range. These changes appear to be due to inversions of tridymite and/or cristobalite. Published articles [1, 16] on the expansion properties of silica corroborate this conclusion.

Above 1,100° C, deviation from the general trend is apparent. When rapid contraction occurs, as shown in figures 7 (C-11) and 8 (C, D), normal sintering is taking place. Examination of photomicrographs showed that those castables heated by Heindl [3] at 1,350° C contained very porous material between the aggregate particles. This would indicate that a denser phase, such as a variety of glass, had been formed. The reasons for rapid contraction and subsequent expansion, as illustrated by figures 7 (C-13) and 8 (E), are debatable. A possible explanation is presented by petrographic analysis, which showed that a recrystallization process had occurred at the higher temperatures. These crystals were too small for positive identification [3]. Entrapped gas could possibly cause sudden expansion, or "bloating", at the higher temperatures. However, the common characteristics associated with "bloating" were not apparent.

Reaction between the cement and the aggregate definitely occurred above 1,100° C. This was clearly shown by photomicrographs and petrographic analyses [3]. Although there was no noticeable reaction in the castables heated at 1,050° C, there was considerable evidence of it in those heated at 1,350° C. Amorphous and glassy material, as well as the aforementioned crystals, were present in abundance.

The refractoriness of the castables depended upon the percentages of cement, as indicated by figure 8. Apparently the greater the cement percentage, the less refractory the castable. Table 1 better illustrates this point.

TABLE 1. Comparison of "deformation temperatures" with the composition of the laboratory-prepared castables of figure 8

Castable	Heat treatment	Aggregate	Cement	Deformation temperature ^a
	° C			° C
A	110	Firebrick	30	-1,265
B	110	do	20	+1,280
C	110	do	10	-1,320
D	110	Flint clay	30	-1,260
E	110	do	20	+1,310
F	110	do	10	-1,345

^a"Deformation temperature" is here defined as the temperature at which the specimen expanded or contracted at the rate of 0.0005 in./min. (-) indicates contraction, (+) indicates expansion.

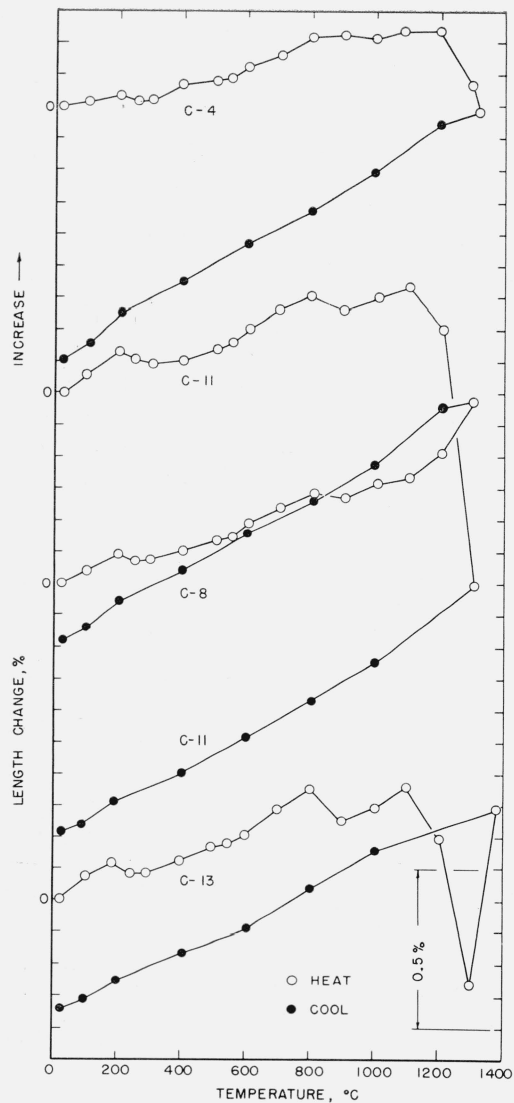


FIGURE 7. Thermal length changes of four commercial castables heat treated at 110°C .

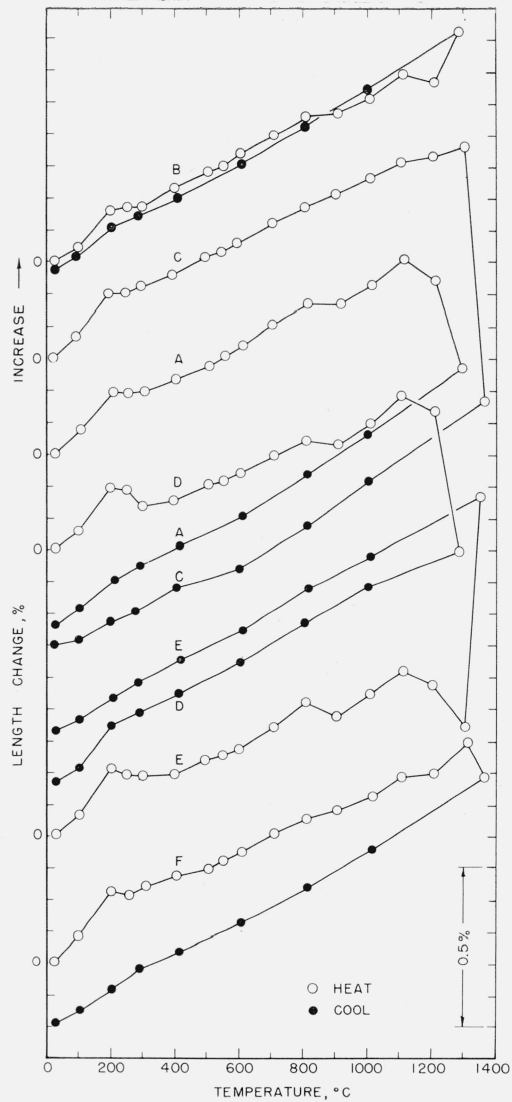


FIGURE 8. Thermal length changes of laboratory-prepared castables heat treated at 110°C .

Castables A, B, and C contained crushed firebrick aggregate and 30, 20, and 10 percent of high-alumina cement, respectively. D, E, and F contained calcined flint-clay aggregate and 30, 20, and 10 percent of high-alumina cement respectively.

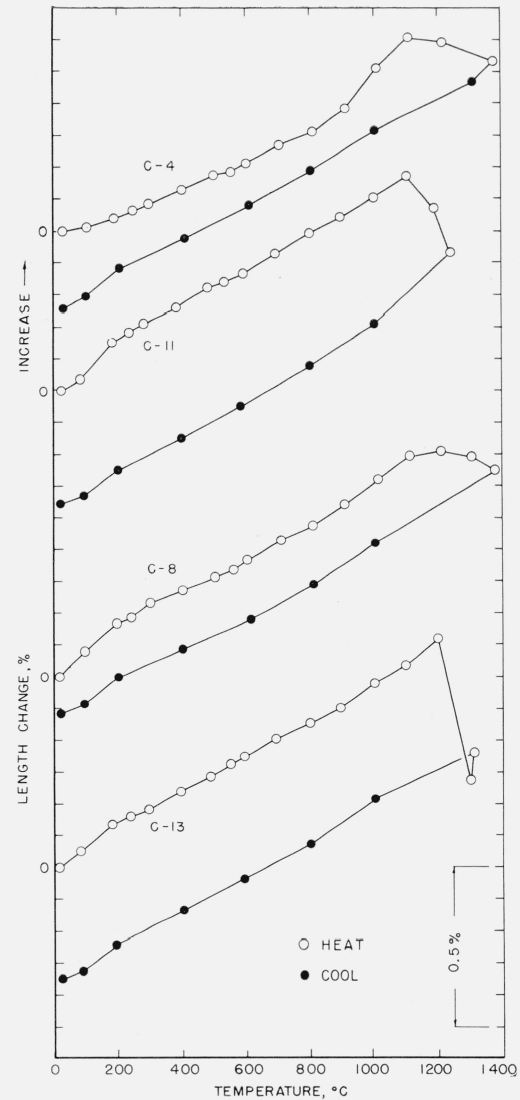


FIGURE 9. Thermal length changes of four commercial castables heat treated at $1,050^{\circ}\text{C}$.

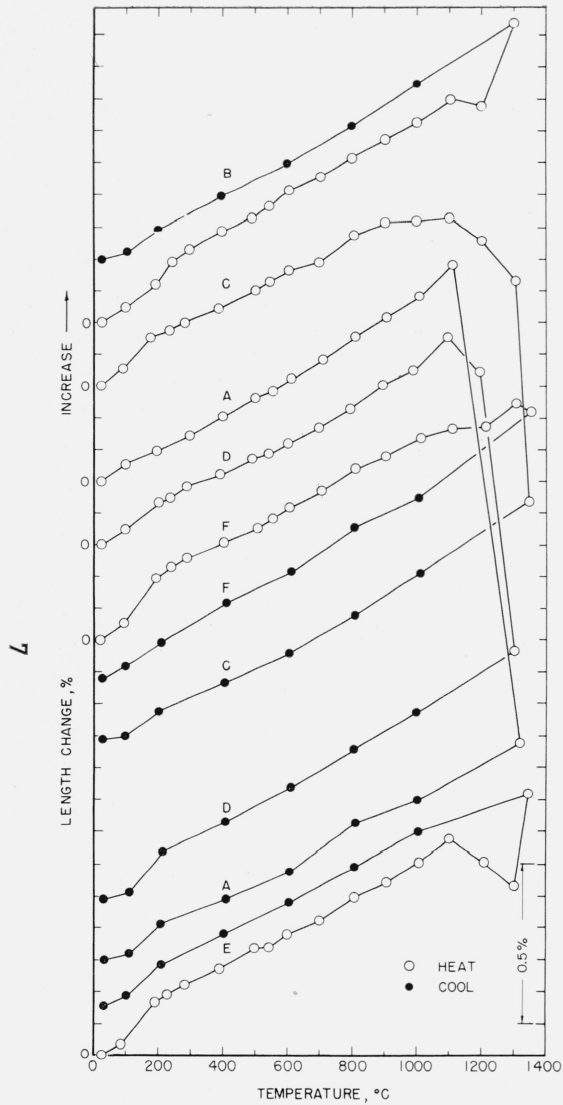


FIGURE 10. Thermal length changes of laboratory-prepared castables heat treated at 1,050° C.

Castables A, B, and C contained crushed firebrick aggregate and 30, 20, and 10 percent of high-alumina cement respectively. D, E, and F contained calcined flint-clay aggregate and 30, 20, and 10 percent of high-alumina cement respectively.

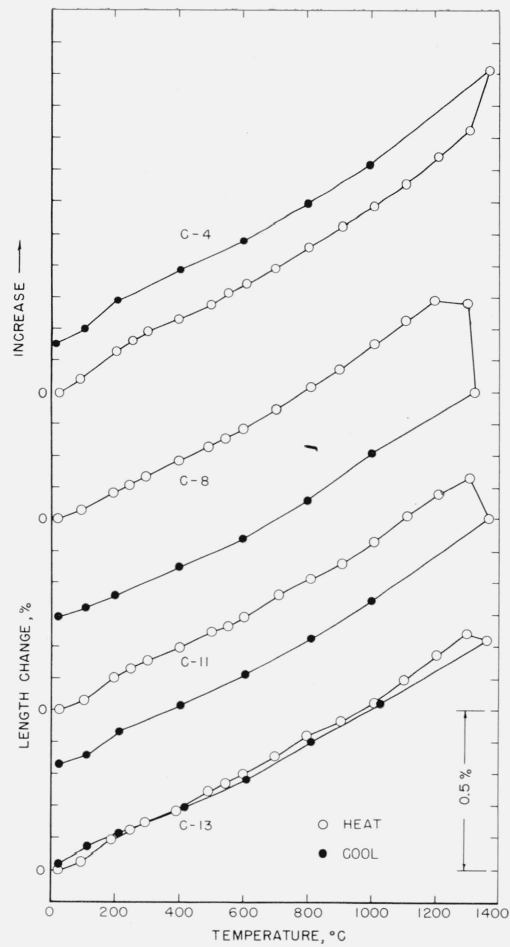


FIGURE 11. Thermal length changes of four commercial castables heat treated at 1,300° C.

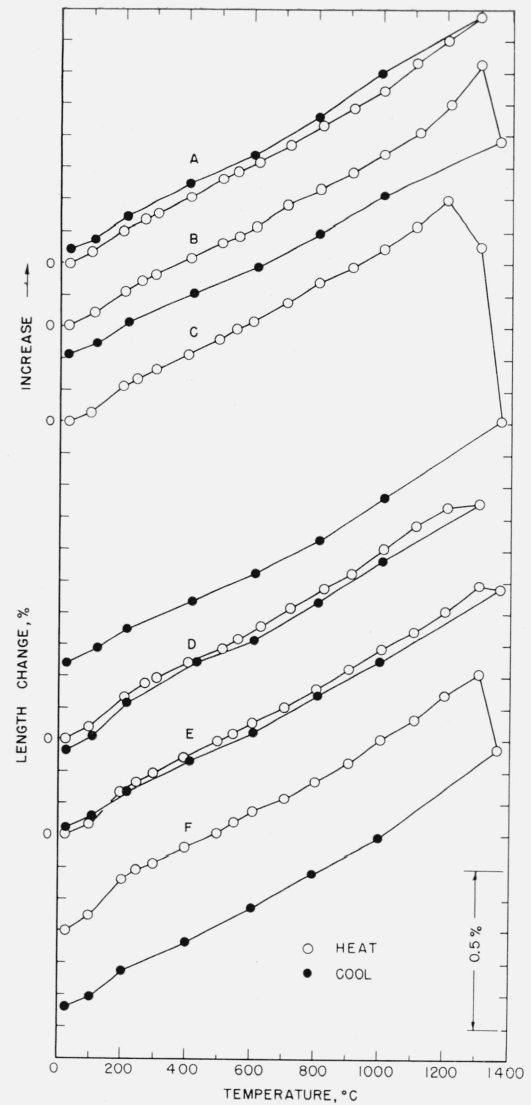


FIGURE 12. Thermal length changes of laboratory-prepared castables heat treated at 1,300° C.

Castables A, B, and C contained crushed firebrick aggregate and 30, 20, and 10 percent of high-alumina cement, respectively. D, E, and F contained calcined flint-clay aggregate and 30, 20, and 10 percent of high-alumina cement, respectively.

6.4. Castables, Heat Treated at 1,050° or 1,300° C

The length-change curves of those castables heat treated at 1,050° C (figs. 9, 10) or 1,300° C (figs. 11, 12) indicate that a general trend or pattern is again apparent at temperatures below 1,100° C. Length-change characteristics common to most of the curves, best illustrated by figures 9(C-11) and 12(F), are the changes in slope that occur between room temperature and 200° C. These changes again indicate the presence of a combination of tridymite and cristobolite. Examination of typical 1,050° or 1,300° C length-change curves show that the contractions between 200° and 300° C and between 800° and 900° C (figs. 7 and 8), have been eliminated by heating at elevated temperatures. Because these contractions were permanent and nonreversible, they obviously would not appear after the specimens had experienced either a 1,050° or a 1,300° C heat treatment. Above 1,100° C, castables previously heat treated at 1,300° C reacted somewhat differently from those heat treated at 110° or 1,050° C. Castables heat treated at the latter temperatures (figs. 7, 8, 9, 10) exhibited the same general characteristics above 1,100° C. Those heat treated at 1,300° C (figs. 11, 12) either expanded or contracted, but never did both.

7. Summary

The thermal length-change properties of commercial brands of refractory castables and laboratory-prepared castables were determined by using dilatometer assemblies that incorporated differential transformers as their sensing or indicating device. The effect of heat treatment was shown by length-change determinations on castables initially heat treated at 110°, 1,050°, or 1,300° C. The data are presented graphically. For comparative purposes, the curve for neat high-alumina cement is included.

Examination of the data indicates that the same general length-change characteristics were exhibited by castables that had received the same curing and heat treatment.

Below 1,100° C, the thermal length-change properties of those castables heat treated at 110° C were influenced by the original properties of their constituents, high-alumina cement and heat-resistant aggregate. Length-change curves of this castable group distinctly indicate length changes associated

with reactions of the cement, especially the loss of water of hydration and the conversion of amorphous alumina to γ alumina, and silica inversions of the aggregate.

Typical curves of both the 1,050° and 1,300° C groups indicated possible silica inversions. However, the length changes related to cement reactions were absent from these curves. As evidenced by curves of all three groups, sintering of the castables began only at temperatures above 1,100° C.

8. References

- [1] F. H. Norton, *Refractories*, p. 482 (McGraw-Hill Book Co., Inc., New York, N. Y., 1949).
- [2] R. A. Heindl and Z. A. Post, Refractory castables: Preparation and some properties, *J. Amer. Cer. Soc.* [7] **33**, 230 (1950).
- [3] R. A. Heindl and Z. A. Post, Refractory castables: II, some properties and effects of heat-treatments, *J. Amer. Cer. Soc.* [5] **37**, 206 (1954).
- [4] R. F. Geller and P. J. Yavorsky, Effects of some oxide additions on the thermal length changes of zirconia, *J. Research NBS* **35**, 87 (1945) RP1662.
- [5] H. J. Kelly and H. M. Harris, An automatically recording thermal-expansion apparatus, *J. Amer. Cer. Soc.* [10] **39**, 344 (1956).
- [6] Automatic Temperature Control Co., Inc., Phila., Pa., Bul. R-30.
- [7] Automatic Temperature Control Co., Inc., Phila., Pa., Instruction manuals.
- [8] L. S. Wells, Reaction of water on calcium aluminates, *BS J. Research* **1**, 951 (1928) RP34.
- [9] L. S. Wells, W. F. Clarke and H. F. McMurdie, Study of the system $\text{CaO-Al}_2\text{O}_3\text{-H}_2\text{O}$ at temperatures of 21° and 90° C, *J. Research NBS* **30**, 367 (1943) RP1539.
- [10] M. L. Longchambon, *Les Pétons Refractaires*, Mémoires, Société des Ingénieurs Civils de France, Cent-Huitième Année, Fascicule II, Mars-Avril (1955).
- [11] H. Insley and R. H. Ewell, Thermal behavior of the kaolin minerals, *J. Research NBS* **14**, 615 (1935) RP792.
- [12] R. Roy, D. M. Roy and E. E. Francis, New data on thermal decomposition of kaolinite and halloysite, *J. Am. Ceram. Soc.* [6] **38**, 198 (1955).
- [13] R. B. Peppler and L. S. Wells, The system of lime, alumina, and water from 50° to 250° C, *J. Research NBS* **52**, 75 (1954) RP2476.
- [14] R. A. Heindl, The thermal expansion of refractories to 1,800° C, *BS J. Research* **10**, 715 (1933), RP562.
- [15] R. A. Heindl and W. L. Pendergast, Fire clays; Some fundamental properties at several temperatures, *BS J. Research* **5**, 213 (1930) RP194.
- [16] R. P. Hall and H. Insley, Phase diagrams for ceramists, *J. Am. Ceram. Soc.*, pt. II, fig. 25 (1947).

WASHINGTON, April 5, 1956.