NATURE OF THE PRISMATIC DARK INTERSTITIAL MATERIAL IN PORTLAND CEMENT CLINKER

By William C. Taylor*

ABSTRACT

As a result of a series of previous investigations by the phase equilibrium method, it has been concluded that K_2SO_4 and $K_2O.23CaO.12SiO_2$ are the only compounds containing K_2O that may exist when a mixture of K_2O, CaO, MgO, Al_2O_3, Fe_2O_3, SiO_2, and SO_3, in the proportions occurring in portland cement clinker, is heated and cooled under equilibrium conditions. Frequent observations of a prismatic dark interstitial phase in etched, polished sections of commercial clinker and in rapidly cooled laboratory clinkers led to the present study of the relation of this phase to the system $K_2O.23CaO.12SiO_2$-CaO-5CaO.3Al_2O_3 and to other systems involving K_2O. The prismatic phase has not been found to exist under equilibrium conditions, but has been produced only under conditions of rapid cooling. Both thermal and compositional conditions that have been found to be required for its formation suggest that it may be a metastable form of 3CaO.Al_2O_3 and monotropic with respect to the stable, isotropic, rectangular 3CaO.Al_2O_3. That portion of K_2O combined as K_2SO_4 has been found to have no effect in inducing the formation of the prismatic phase. The conditions necessary for the formation of this phase have been outlined. Although the exact composition has not been established definitely, because of the experimental difficulties that have been outlined, the close relationship between the prismatic phase and 3CaO.Al_2O_3 leads to the recommendation that this phase be referred to as "prismatic 3CaO.Al_2O_3" instead of the term "prismatic dark interstitial material."

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*Research Associate at the National Bureau of Standards, representing the Portland Cement Association.

I. INTRODUCTION

The relatively recent application of the metallographic method of microscopical examination, employing polished and etched specimens, to studies of portland cement clinker has been of great value in obtaining a more exact conception of the types and amounts of the various constituents present.

Certain phases appearing in the matrix between crystals of $3CaO.SiO_2$ and $2CaO.SiO_2$ are distinguished by the relatively rapid rate with which they are etched by water, and have come to be known collectively as "dark interstitial material." Some of these dark interstitial phases are crystalline and can be subdivided into rectangular and prismatic types, both of which are etched readily by water. An amorphous or glassy phase also is included in the dark interstitial group. The readiness with which it is etched by water is determined by its composition. Generally, it is not acted upon to as great a degree as are the crystalline phases of this classification, but in some instances very little difference exists.

In a paper published in 1938, Insley and McMurdie [1][1] report that the rectangular isotropic material is $3CaO.Al_2O_3$ and that the amorphous material is glass. The prismatic crystals were found to have a low double refraction with parallel extinction, and a mean refractive index approximating 1.72. These workers observed that when laboratory mixtures comparable to portland cement in composition were cooled from 1,450° to 1,250° C at a rate of 10° C per minute, only the Na_2O-bearing and the K_2O-bearing samples contained prismatic interstitial crystals similar to those observed in commercial clinker.

A bladed form of $3CaO.Al_2O_3$ was observed by Brown [2] in 1937 in thin sections of certain laboratory clinkers prepared from commercial mixes. This form was explained by Brown as due to a directional crystallization of the $3CaO.Al_2O_3$ conferred by the crystallizing $3CaO.SiO_2$. A bladed form of $3CaO.Al_2O_3$ has been observed by the present author in preparations free of alkali and is distinguished from the prismatic dark interstitial material by an undulatory extinction and the absence of sharp parallel extinction.

No K_2O compound having optical properties similar to those of the prismatic phase has been identified in any of the phase-equilibrium studies of K_2O-containing systems which are related to clinker compositions [3, 4, 5, 6]. The compound $8CaO.Na_2O.3Al_2O_3$, discovered by Brownmiller in the system Na_2O-CaO-Al_2O_3 [7], has the refractive indices: $\alpha=1.702$ and $\lambda=1.710$. It is possible that the presence of Fe_2O_3 raises these indices, because of solid solution, to values similar to those that have been observed for the prismatic phase. The system Na_2O-CaO-Al_2O_3-SiO_2 is now being investigated by Greene of this laboratory. On the basis of present data, it appears that $8CaO.Na_2O.-3Al_2O_3$ may be a final product of crystallization along with either or both $2CaO.SiO_2$ and $3CaO.SiO_2$. However, some Na_2O appears to be associated with CaO and SiO_2 in the formation of a ternary compound or in solid solution in $2CaO.SiO_2$ and, in view of the low soda content of most portland cement clinkers, rarely exceeding 1 percent, it is doubtful whether appreciable amounts of $8CaO.-Na_2O.3Al_2O_3$ would be found in commerical clinkers.

The purpose of this report is to present data relative to the probable composition of the prismatic dark interstitial material.

Included in these data are the results obtained by other investigators on the microscopic structure of commercial clinkers. The relation of the prismatic phase to the system $K_2O.23CaO.12SiO_2$–CaO–$5CaO.3Al_2O_3$ in particular, and to other systems, is discussed.

II. EXPERIMENTAL METHOD

The samples of mixtures used in this study were, in most cases, taken from the base samples employed in connection with phase-equilibrium studies of various systems conducted by the author. The thermal treatment to which the charges were subjected varied and is given in the text.

The microscopical study of the charges included the examination of powders and etched polished sections of all samples. In some cases, etched polished thin sections also were examined.

III. FORMATION OF THE PRISMATIC DARK INTERSTITIAL MATERIAL

1. DATA FROM OTHER SOURCES INDICATING THE NATURE OF THE PRISMATIC PHASE

An analysis was made of data obtained by other investigators in microscopical studies of clinker by the polished-surface method. These data are included in this paper because: (1) Definite suggestions on the nature of the prismatic phase are to be found in the results of the analysis, and (2) those results determined, to some degree, the direction of further study of the problem.

(a) STUDIES BY INSLEY AND OTHERS

In a study of 26 different commercial clinkers, Insley, Flint, Newman, and Swenson [8] report that the rectangular crystalline form of dark interstitial material, which has the optical properties of $3CaO.Al_2O_3$, was found in only 2 samples, and there in only very small amounts. The anisotropic (prismatic) form was a much more abundant constituent, and occurred in all samples examined. In samples with low $Al_2O_3:Fe_2O_3$ ratio, it was present in very small amounts and in localized clusters, but in samples with higher $Al_2O_3:Fe_2O_3$ ratio, the prismatic crystals were more abundant and distributed more uniformly.
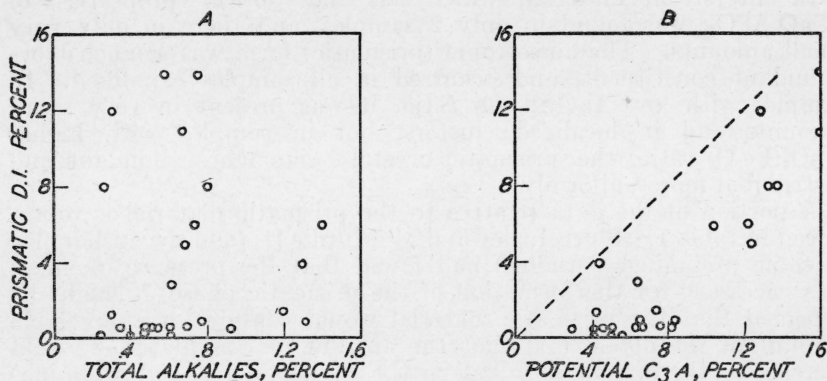
A portion of the data relative to the prismatic material is reproduced in table 1. Since Insley and McMurdie [1] (and the author also in some preliminary studies) had found that the presence of alkali was necessary for the formation of the prismatic phase, it might be expected that the prismatic material would contain an appreciable amount of the alkali, and that the amount of this material would increase as the amount of alkali in the clinker increases. Examination of their data, however, does not support this conclusion. In fact, the average alkali content of the six clinkers containing the greatest amounts of the prismatic phase, 8 to 14 percent, is only 0.56 percent, whereas the average alkali content for the nine clinkers containing 1 to 6 percent of the prismatic material is 0.92 percent. The lack of relationship between the alkali content and the amount of the prismatic phase is shown graphically in diagram A of figure 1.

of the prismatic phase. If all of this alkali were present in the 12 percent of prismatic material, the alkali content of this phase would be only 1.4 percent. Furthermore, in this calculation any alkali that might be in the 3 percent of glass present or in combination with other components is not considered.

There does appear, however, to be a relation between the calculated percentage of $3CaO.Al_2O_3$ present at complete crystalline equilibrium [9] and the amount of prismatic material observed. There is a trend toward increasing amounts of the prismatic phase as the percentage of calculated $3CaO.Al_2O_3$ increases. This relation is shown in diagram *B* of figure 1. The dotted line indicates the limiting amounts of the prismatic material that could be formed if the composition of this phase is essentially that of $3CaO.Al_2O_3$. As is to be expected, the amounts of the prismatic material generally are lower than the potential amount of $3CaO.Al_2O_3$, since varying amounts of glass from which more prismatic material might possibly crystallize were present.

<div align="center">(b) STUDIES BY WARD</div>

In a study of the effect of heat treatment and cooling rate on the microscopic structure of clinker, Ward [10] compared the structure of commercial clinkers as received with that of portions of the same clinker that had been reheated to clinkering temperatures and then cooled; one portion at a rapid rate, and another at a slow rate. These data are given in table 2. The amounts of glass reported are the values determined by a 2-second water-etch followed by etching for 3 seconds in a 1-percent alcoholic HNO_3 solution, and do not include the portion of the glassy phase etched by a KOH solution. The readiness with which a glass is etched by a particular reagent depends upon its composition. A glass low in Fe_2O_3 is readily etched by the treatment just mentioned, but a glass having a high Fe_2O_3 content is unaffected [11]. This type of glass is revealed by etching with a 10-percent KOH solution [12].

As shown in table 2, there is no relation between the percentage of the total alkalies, nor of the Al_2O_3 content, and the percentage of prismatic material. On the other hand, the total amount of the three forms of dark interstitial material (glass, rectangular $3CaO.Al_2O_3$, and prismatic material) bears a relation to the calculated $3CaO.Al_2O_3$ at crystalline equilibrium. The relation of the various types of dark interstitial material to the potential $3CaO.Al_2O_3$ content is plotted in figure 2. Dotted lines to indicate the maximum amounts that could be formed of a phase, sensibly $3CaO.Al_2O_3$ in composition, have been inserted in the diagrams as means for comparison.

Of the 10 slowly cooled clinkers, plotted in diagram *A* of figure 2, 3 show the dark interstitial material to be all prismatic and not rectangular, 1 shows 4 percent of prismatic to 7 percent of the rectangular, and in the remaining 6 the rectangular is rather high and the prismatic is substantially zero. It is interesting to note that each of the first three has an Al_2O_3:Fe_2O_3 ration of less than 1.38, whereas that for each of the last six is well above 1.38. The Al_2O_3:Fe_2O_3 ratio for the one showing both forms is 1.88. The value 1.38 is mentioned because in the quaternary system $CaO–Al_2O_3–Fe_2O_3–SiO_2$ [13] the course of crystallization has been shown to differ for cements having Al_2O_3:Fe_2O_3 ratios above and below 1.38.

TABLE 2.—*Data pertaining to the dark interstitial material (water-acid etch) in heat-treated and untreated commercial clinkers (Ward)*

[Order of increasing Al_2O_3:Fe_2O_3 ratio. $C_3A = 3CaO.Al_2O_3$]

Clinker [a]	Al_2O_3 corrected for TiO_2	Fe_2O_3 corrected for FeO	Al_2O_3:Fe_2O_3 ratio	Na_2O	K_2O	Total alkalies	Calculated C_3A at cryst. equil.	Rectangular C_3A micro.	Pris. D.I. micro.	Glass micro.	Total D.I.
	%	%		%	%	%	%	%	%	%	%
4S	4.61	7.11	0.65	0.41	0.10	0.57	0.2	0	2	0	2
4P	4.73	5.33	.89	.53	.20	.73	4	0	2	0	2
4Q	4.91	6.04	.81	.37	.12	.49	3	0	0.2	0	0.2
11S	4.24	4.89	.87	.52	.05	.57	3	0	3	1	4
11P	4.54	5.07	.90	.66	.16	.82	3	0	0	3	3
11Q	4.08	4.32	.95	.51	.08	.59	4	0	0	3	3
2S	4.97	5.12	.97	.27	.37	.64	5	0	3	0	3
2P	5.54	5.49	1.01	.33	.71	1.04	5	0	3	0	3
2Q	5.45	4.88	1.12	.24	.30	0.54	6	0	0	3	3
8S	4.86	2.98	1.63	.15	.25	.40	8	7	0.2	0	7.2
8P	4.95	3.02	1.64	.17	.49	.66	8	0	1	6	7
8Q	4.86	2.95	1.65	.10	.08	.18	8	0	0	7	7
10S	4.83	2.88	1.68	.26	.33	.59	8	4	Trace	2	6
10P	4.79	2.86	1.68	.34	.81	1.15	8	0	3	2	5
10Q	4.84	2.89	1.68	.26	.37	0.63	8	0	0.2	6	6.2
6S	5.81	3.08	1.88	.07	Trace	.07	10	6	0	2	8
6P	5.93	3.13	1.89	.10	0.11	.21	11	7	0.6	3	10.6
6Q	5.85	3.11	1.88	.08	.08	.16	10	0	0	9	9
3S	5.09	2.71	1.88	.35	Trace	.35	9	7	4	2	13
3P	5.37	2.24	2.40	.63	0.20	.83	10	0	10	7	17
3Q	5.16	1.98	2.60	.47	.10	.57	10	0	5	10	15
9S	5.59	2.23	2.51	.32	.22	.54	11	10	0	0	10
9P	5.56	2.22	2.51	.38	.54	.92	11	0	2	7	9
9Q	5.59	1.97	2.84	.33	.29	.62	12	0	0	8	8
1S	5.97	2.21	2.70	.10	0.97	1.07	12	12	0	0	12
1P	6.03	2.22	2.71	.10	1.58	1.68	12	0	13	1	14
1Q	5.71	1.90	3.00	.10	1.11	1.21	12	0	2	14	16
7S	6.64	2.35	2.82	.34	0.28	0.62	14	12	0.3	2	14.3
7P	6.85	2.35	2.91	.42	.58	1.00	15	2	7.0	6	15
7Q	6.80	1.96	3.47	.32	.38	0.70	15	0	0.2	14	14.2

[a] S clinkers were reheated and cooled slowly. P clinkers were the commercial products as received. Q clinkers were reheated and cooled quickly.

Of the 10 quickly cooled clinkers the interstitial material is composed principally of the amorphous type. No rectangular $3CaO.Al_2O_3$ is in any clinker and, with the exception of two clinkers, the amount of prismatic material is zero or not more than 0.2 percent. As shown in diagram *B* of figure 2, the amount of the amorphous type (glass) closely approaches the respective values calculated for potential $3CaO.Al_2O_3$.

The effect of variations in cooling conditions on the proportions of the three types of dark interstitial material is evident in the commercial clinkers examined by Ward. In clinkers in which the amount of prismatic material is less than the calculated amount of potential $3CaO.Al_2O_3$, the difference may be accounted for by the presence of the other types. The relation of the amount of the prismatic phase to the other forms of dark interstitial material to the calculated $3CaO.Al_2O_3$ is shown in diagram *C* of figure 2.

In diagram *D* (fig. 2) the total dark interstitial percentages are plotted against the potential $3CaO.Al_2O_3$ contents for all types of clinker. It is seen that the combined amounts of all the phases that are distinguished by the water-acid etch approach the values calculated for

potential 3CaO.Al$_2$O$_3$, indicating that these three types of material do not differ greatly in composition.

The following generalizations may be made in regard to these results.

1. The prismatic material is much more abundant in the plant cooled than in quickly or slowly cooled clinkers.

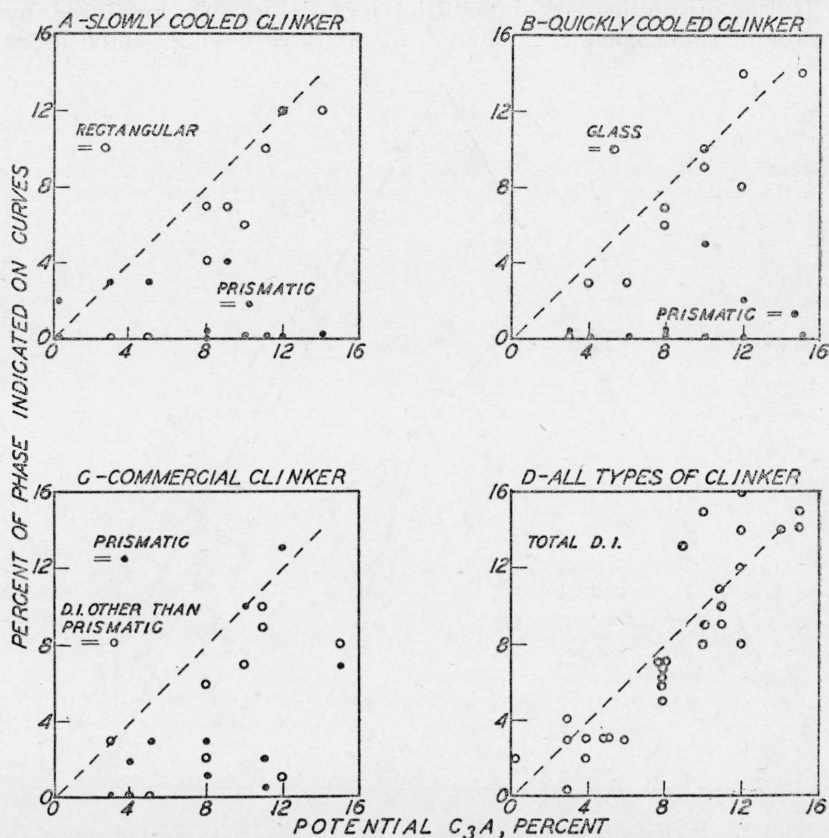2. The high glass content of the quickly cooled clinkers suggests

FIGURE 2.—*Relationship between the potential* 3CaO.Al$_2$O$_3$ *and the three types of dark interstitial material in clinkers subjected to different rates of cooling.*

[From data by Ward]

that very rapid cooling may prevent crystallization of the prismatic phase.

3. In the slowly cooled clinkers, rectangular 3CaO.Al$_2$O$_3$ apparently formed at the expense of the prismatic phase. The presence of as much as 1 percent of alkali did not interfere with this action.

These data suggest that the prismatic material is not a stable phase and that an intermediate rate of cooling may be a requisite for its formation. If the cooling rate is slow, that is, of a rate approaching that required for equilibrium conditions, the stable rectangular 3CaO.Al$_2$O$_3$ is formed regardless of the alkali content of the clinker.

curves separating the fields of stability is reproduced in figure 3. The compositions of the various charges being considered, and the crystallization curves followed under equilibrium conditions, are indicated on the diagram [6]. It is recognized that quickly cooled charges often do not follow the course of crystallization indicated by the equilibrium diagram, but in the cases about to be discussed, there was no evidence of serious departure from the curves.

(a) MIXTURES IN THE FIELD OF $K_2O.23CaO.12SiO_2$

Mixtures A and B in the field of $K_2O.23CaO.12SiO_2$ (see fig. 3) were prepared, having the following composition: Mix A, 40.0% of $K_2O.$-$23CaO.12SiO_2$; 60.0% of $5CaO.3Al_2O_3$; and 0% of CaO. Mix B, 39.6% of $K_2O.23CaO.12SiO_2$; 59.4% of $5CaO .3Al_2O_3$; and 1.0% of CaO.

Charges of mixture A in the binary system $K_2O.23CaO.12SiO_2$-$5CaO.3Al_2O_3$ were heated to 1,490° C and then cooled to a quenching temperature of 1,260° C at rates varying from 30° C per minute to 4° C per minute. According to the diagram, no crystalline phases other than $K_2O.23CaO.12SiO_2$ and $5CaO.3Al_2O_3$ should exist, and these compounds are known to be unaffected by the usual water-etching treatment. Polished sections of these charges were prepared. In no case were any distinguishing features brought out by an attempted etching of the polished section in water for 2 seconds; that is, no phase of the charge was noticeably affected by this treatment. Examination of the powdered samples revealed that the charges cooled at rates more rapid than 10° C per minute were composed of crystals of the above compounds and glass but, when cooled at slower rates, only $K_2O.23CaO.12SiO_2$ and $5CaO.3Al_2O_3$ were present.

Mixture B falls within the compositional triangle formed by connecting the points representing the compositions $K_2O.23CaO.12SiO_2$, $3CaO.Al_2O_3$, and $5CaO.3Al_2O_3$. The completely crystallized product of a melt of any mixture falling within this triangle is composed of these three compounds only. When the melt of mixture B is cooled, crystals of $K_2O.23CaO.12SiO_2$ alone are formed until the temperature at the boundary between the fields of $K_2O.23CaO.12SiO_2$ and $5CaO.$-$3Al_2O_3$ is reached (point O). On further cooling, these two compounds separate out together until the temperature falls to that of the eutectic, Y. At this point, $K_2O.23CaO.12SiO_2$, $5CaO.3Al_2O_3$ and $3CaO.$-Al_2O_3 crystallize simultaneously.

Charges of this mixture were given the same thermal treatments as those given mixture A. Polished sections for the most part consisted of material that was not etched by a 2-second immersion in water. In this respect the sections appeared similar to those of mixture A, but they differed in that they contained readily etched material in localized clusters. Fields in which concentrations of the readily etched material occurred were photographed. Figure 4 (A) is a photomicrograph of a polished section of a charge of mixture B that was cooled slowly at a rate of 4° C per minute. The darkly etched crystals are typical of rectangular $3CaO.Al_2O_3$. No prismatic dark material was observed in any portion of the charge. When a charge of the same mixture was cooled more rapidly, at a rate of 15° C per minute, no rectangular $3CaO.Al_2O_3$ was evident but dark prismatic material was formed. A localized cluster of the prismatic crystals is shown in figure 4 (B). In this charge and in other charges containing no Fe_2O_3, the mean

index of the prismatic phase was about 1.70, with a birefringence of 0.008 to 0.010.

(b) MIXTURES IN THE FIELD OF 5CaO.3Al₂O₃

Similar results were obtained in studies on mixtures C and D falling in the field of $5CaO.3Al_2O_3$ (fig. 3) having the following compositions: Mix C, 10.0% of $K_2O.23CaO.12SiO_2$; 90.0% of $5CaO.-3Al_2O_3$; and 0% of CaO. Mix D, 10.0% of $K_2O.23CaO.12SiO_2$; 89.0% of $5CaO.3Al_2O_3$; and 1.0% of CaO. No material that was appreciably etched by water after 2 seconds was observed in any of the charges prepared from mixture C. On the other hand, small amounts of rectangular $3CaO.Al_2O_3$ were observed in the slowly cooled samples of mixture D, and small amounts of the prismatic dark material in the rapidly cooled charges of that composition.

These results indicate that a requisite for the formation of material which may be etched by water in accordance with the procedure herein used is the existence of potential $3CaO.Al_2O_3$ in the mixture. The addition of 1 percent of CaO to mixtures A and C increased the potential $3CaO.Al_2O_3$ from 0.0 to 3.6 percent, and resulted in the formation of dark prismatic crystals or rectangular $3CaO.Al_2O_3$, depending on the heat treatment.

(c) MIXTURE IN THE FIELD OF CaO

Mixture E (fig. 3), having the composition: 38.0% of $K_2O.23CaO.-12SiO_2$; 47.0% of $5CaO.3Al_2O_3$; and 15.0% of CaO, is located in the CaO field, close to the boundary curve between the fields of CaO and $K_2O.23CaO.12SiO_2$. One charge of this mixture was melted at 1,615° C, cooled to the temperature of the quintuple point 1,450° at a rate of 2° C per minute, and then quenched. The phase diagram indicates that on cooling, CaO first separates from the melt, then when point P is reached, CaO and $K_2O.23CaO.12SiO_2$ crystallize together. No $3CaO.Al_2O_3$ crystallizes until the temperature falls below the quintuple point X, at 1,450° C. Examination of a polished section revealed the presence of rounded grains of CaO and of $K_2O.-23CaO.12SiO_2$ embedded in a glass that was fairly readily etched by water. Neither the prismatic phase nor rectangular $3CaO.Al_2O_3$ was present. A second charge was cooled through the same range at the rapid rate of 30° C per minute. This specimen contained CaO, poorly crystallized grains of $K_2O.23CaO.12SiO_2$, and glass; but no prismatic material nor rectangular $3CaO.Al_2O_3$. Figure 5 (A) shows the appearance of the polished surface of the second charge after the water etch. The dark CaO grains, the light clusters of $K_2O.23CaO.-12SiO_2$, and the glass may be noted.

A third charge of mixture E was cooled to a lower temperature, namely from 1,650° to 1,330° C, at an intermediate rate of 7° C per minute. Crystallization in this charge would tend to occur as follows: first CaO; then CaO and $K_2O.23CaO.12SiO_2$ to point X, at 1,450° C, where $3CaO.Al_2O_3$ first appears; below 1,450° C, CaO disappears entirely and $3CaO.Al_2O_3$ and $K_2O.23CaO.12SiO_2$ crystallize together along the boundary XY. No $5CaO.3Al_2O_3$ should appear because the eutectic temperature, 1,310° C, is not reached. Microscopical examination of a polished section showed it to contain rectangular $3CaO.-Al_2O_3$, $K_2O.23CaO.12SiO_2$, and glass. No prismatic material was present. As shown in figure 5B, the $3CaO.Al_2O_3$ crystals were very

FIGURE 4.—*Polished sections of charges prepared from mixture B and quenched from a temperature below* $3CaO.Al_2O_3$ *liquidus; water-etched 2 sec.; reflected light,* ×*500.*

A, Slowly cooled charge, shows rectangular $3CaO.Al_2O_3$; B, rapidly cooled charge, shows prismatic crystals.

FIGURE 5.—*Polished sections of charges prepared from mixture E; water-etched 2 sec; reflected light,* ×500.

A, Rapidly cooled charge quenched from temperature above 3CaO.Al$_2$O$_3$ liquidus. Shows CaO (C), K$_2$O.23CaO.12SiO$_2$ (K), and glass (G); B, slowly cooled charge quenched from temperature below 3CaO. Al$_2$O$_3$ liquidus. Shows large rectangular crystals of 3CaO.Al$_2$O$_3$ (R), inclusion crystals of K$_2$O.23CaO. 12SiO$_2$ (K), and glass (G).
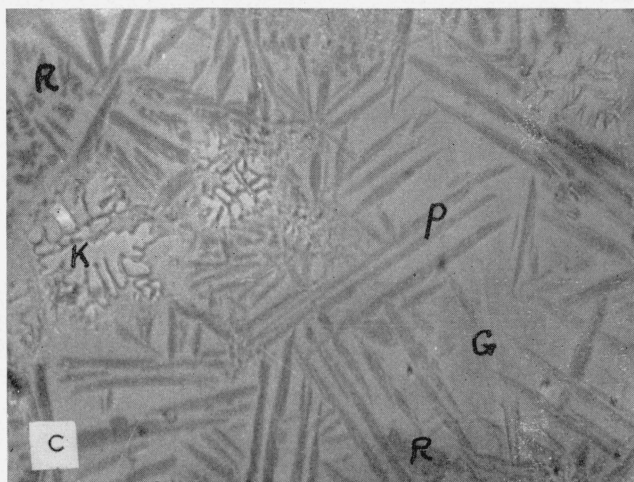
FIGURE 5.—(*Continued*)

C, Rapidly cooled charge quenched from same temperature as *B*. Shows prismatic crystals (*P*), $K_2O.$
$23CaO.12SiO_2$ (*K*), glass (*G*), and evidence of the formation of rectangular $3CaO.Al_2O_3$ (*R*).

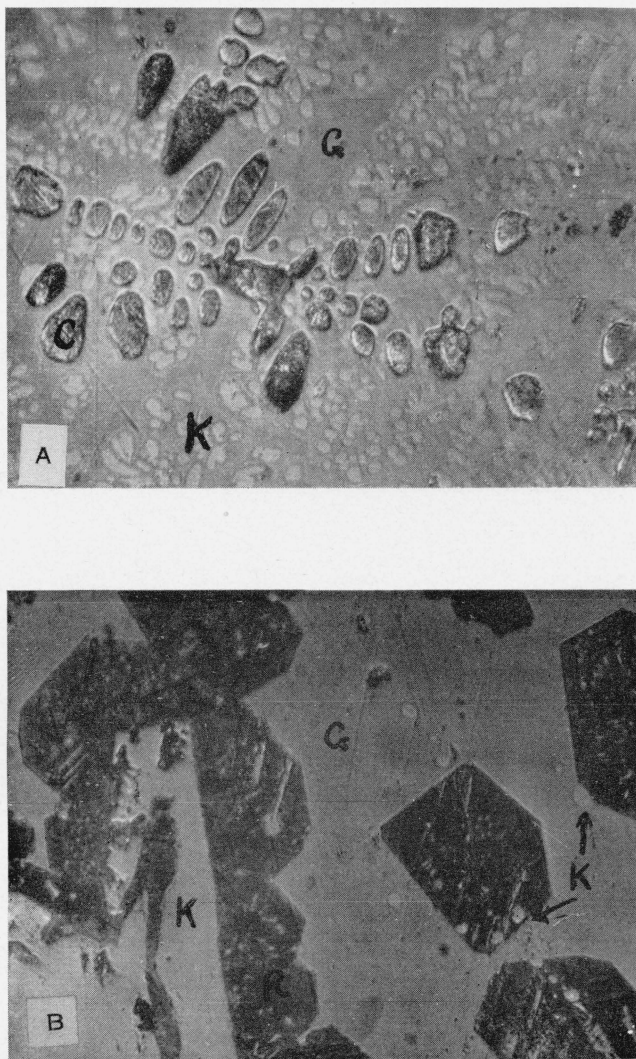FIGURE 6.—*Polished sections prepared from mixture F; water-etched 2 sec; reflected light,* ×500.

A, Rapidly cooled charge quenched from temperature below $3CaO.Al_2O_3$ liquidus. Shows alignment of small rectangular $3CaO.Al_2O_3$ grains and long irregular prismatic crystals; B, slowly cooled charge quenched from same temperature as A. Shows large crystals of rectangular $3CaO.Al_2O_3$ in glass.

large, and the $K_2O.23CaO.12SiO_2$ crystals were present as inclusions in the $3CaO.Al_2O_3$ or had their shape determined to a large extent by the $3CaO.Al_2O_3$ grains.

A fourth sample was cooled through the same range as the previous sample but at the rapid rate of 30° C per minute. As shown in figure 5 (C), most of the darkly etched material was of the prismatic form. There was evidence that the formation of rectangular $3CaO.Al_2O_3$ was under way.

A fifth charge was cooled from 1,650° C at the rapid rate of 30° C per minute to a temperature of 1,440° C, which is just below the temperature at which $3CaO.Al_2O_3$ first appears (1,450° C). In the polished section of this charge, a relatively small amount of prismatic material, some residual CaO, poorly crystallized $K_2O.23CaO.12SiO_2$, and glass were observed. No rectangular $3CaO.Al_2O_3$ appeared to be present.

It is sometimes difficult or impossible to identify with certainty all of the material shown in a polished surface of a sample that has been etched only by water. In the specimens discussed above, all the phases mentioned, and only those, were observed in powdered samples of the respective charges. In this discussion, interest is centered chiefly on the water-etched material.

In the above study neither charge that was quenched at a temperature above that at which $3CaO.Al_2O_3$ first appears contained any of the prismatic phase nor any rectangular $3CaO.Al_2O_3$. When quenched below this temperature, the slowly cooled specimen contained rectangular $3CaO.Al_2O_3$, but no prismatic material, whereas the rapidly cooled samples contained the prismatic phase.

(d) MIXTURES IN THE FIELD OF $3CaO.Al_2O_3$

With melts of compositions from which, according to the phase diagram, $3CaO.Al_2O_3$ is the first solid phase to appear, it was found that there is a very narrow range in cooling conditions conducive to the formation of the prismatic material. Mixture F on the boundary separating the fields of CaO and of $3CaO.Al_2O_3$ and mixture G in the field of $3CaO.Al_2O_3$ were prepared (see fig. 3), having the following compositions: Mix F, 15.0% of $K_2O.23CaO.12SiO_2$; 70.0% of $5CaO.-3Al_2O_3$; and 15.0% of CaO. Mix G, 10.0% of $K_2O.23CaO.12SiO_2$; 80.0% of $5CaO.3Al_2O_3$; and 10.0% of CaO.

Upon cooling melts of these mixtures as rapidly as 30° C per minute, the prismatic phase usually was surrounded with a sheath of isotropic material having the optical properties of $3CaO.Al_2O_3$. Often in the same charge, trains of small crystals of rectangular $3CaO.Al_2O_3$ were alined as though they had resulted from an original prismatic crystal. An example of this condition is shown in figure 6(A), which is a photomicrograph of a water-etched polished section of a charge of mixture F. This charge was cooled from 1,475° to 1,375° C at the rapid rate of 30° C per minute. The alinement of the small, rectangular $3CaO.Al_2O_3$ grains and the long, irregular, prismatic crystals are evident in the field shown in this photomicrograph. At rates of cooling more rapid than 30° per minute, bundles of fibrous crystals formed. Apparently these were the prismatic crystals in question, since they were etched by water, but they were too fine to permit an accurate determination of their optical properties. When the same composition was cooled through the same range very slowly, 4° C per minute, no prismatic material was present, but large

crystals of rectangular $3CaO.Al_2O_3$ in glass were formed, as shown in figure 6(B).

These and comparable studies dealing with compositions within the system $K_2O.23CaO.12SiO_2-CaO-5CaO.3Al_2O_3$ furnish evidence that the prismatic phase may be a metastable form of $3CaO.Al_2O_3$ that crystallizes when charges containing potash are cooled at rapid rates. The prismatic phase did not appear in charges of any composition falling outside of the regions of the system where $3CaO.Al_2O_3$ appears at complete crystalline equilibrium, nor did it ever appear in charges quenched from temperatures above those of the liquidus for $3CaO.Al_2O_3$ as defined in the phase-equilibrium diagram (fig. 3). On the other hand, the prismatic phase did appear in charges quenched from temperatures below those of the liquidus for $3CaO.Al_2O_3$.

3. IN MIXTURES OF COMPOSITIONS BEYOND THE LIMITS OF THE SYSTEM $K_2O.23CaO.12SiO_2-CaO-5CaO.3Al_2O_3$

In a previous investigation by the author [5], it was reported that a mixture (H), represented by $3(3CaO.SiO_2)+9(2CaO.SiO_2)+K_2O.Al_2O_3+Fe_2O_3$, was heated to 1,400° C and cooled to 1,295° C at the slow rate of 2.5° C per minute, and that the product consisted of only two phases; $K_2O.23CaO.12SiO_2$ and $4CaO.Al_2O_3.Fe_2O_3$. In the present study, this mixture was heated to 1,450° C and then cooled to 1,295° C at various rates more rapid than the above. These charges all crystallized readily and consisted of $K_2O.23CaO.12SiO_2$, $4CaO.Al_2O_3.Fe_2O$ and small amounts of glass, varying somewhat with the rate of cooling. In no case was any prismatic dark interstitial material observed.

Another preparation (I) was made, using 75 percent of mix $H+25$ percent of $3CaO.Al_2O_3$. One sample was heated to 1,400° C and cooled to 1,295° C at the slow rate of 2° C per minute. This charge contained only $K_2O.23CaO.12SiO_2$, $4CaO.Al_2O_3.Fe_2O_3$, and rectangular $3CaO.Al_2O_3$. A second sample cooled through the same range at the more rapid rate of 10° C per minute contained $K_2O.23CaO.12SiO_2$, $4CaO.Al_2O_3.Fe_2O_3$, and the prismatic phase. No rectangular $3CaO.Al_2O_3$ and very little glass were observed. The prismatic dark interstitial material in this, and other charges containing Fe_2O_3, had indices of refraction that agreed with those reported by Insley and McMurdie [1] for this phase.

The above results indicate that the prismatic dark interstitial material cannot be formed unless some of the Al_2O_3 in a mixture is potentially available for $3CaO.Al_2O_3$ ($Al_2O_3:Fe_2O_3 > 0.64$). Again the results suggest that the components of $3CaO.Al_2O_3$ may crystallize in either of two forms—isotropic rectangular or anisotropic prismatic. The rate of cooling appears to be the determining factor.

It was desired to determine what effect an excess of K_2O over that required for the compound $K_2O.23CaO.12SiO_2$ might have on the formation of the prismatic and the rectangular phases. Assuming that this excess K_2O would form $K_2O.Al_2O_3$ [3], a mixture (J) was designed to contain the following phases after being heated and cooled under equilibrium conditions: 19.3% of $K_2O.23CaO.12SiO_2$; 19.6% of $K_2O.Al_2O_3$; 60.7% of $3CaO.Al_2O_3$; and 0.4% of CaO.

In a charge heated to 1,400° C and cooled to 1,320° C at the very slow rate of ½° C per minute, all of the above phases and a small
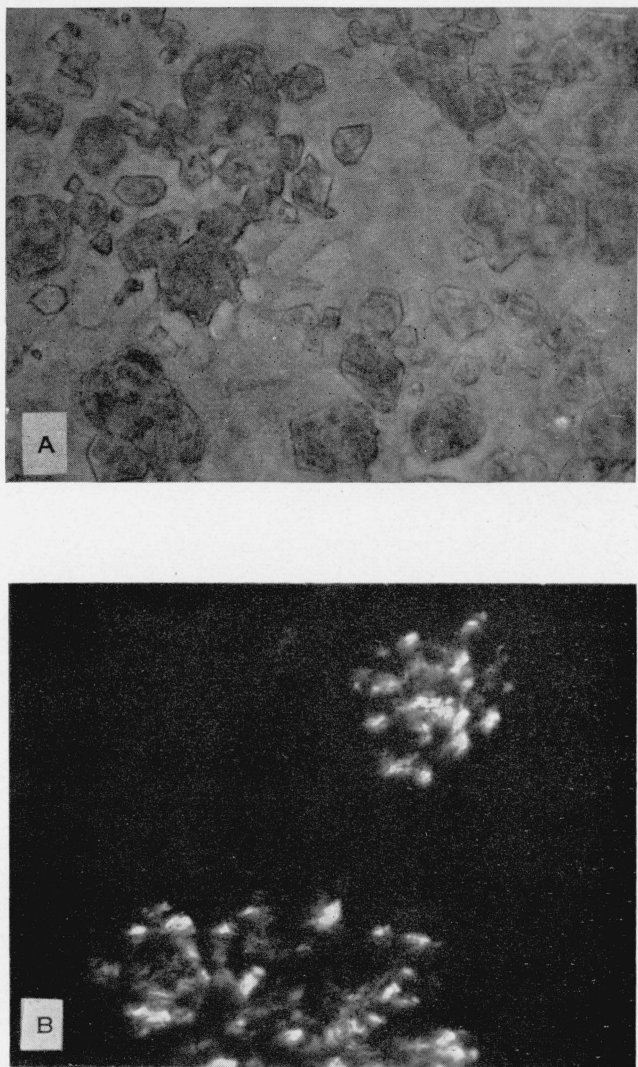
FIGURE 7.—*Polished thin sections prepared from mixture J.*

A, Polished surface of slowly cooled charge; water-etched 3 sec; reflected light; magnification, ×1000.   Rectangular $3CaO.Al_2O_3$, $K_2O.23CaO.12SiO_2$, and glass present; *B*, same field as *A* but viewed with transmitted light, crossed nicols.   Shows birefringent $K_2O.23CaO.12SiO_2$;
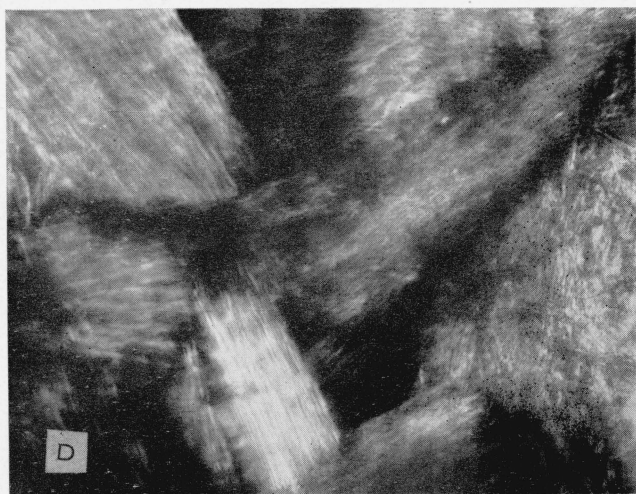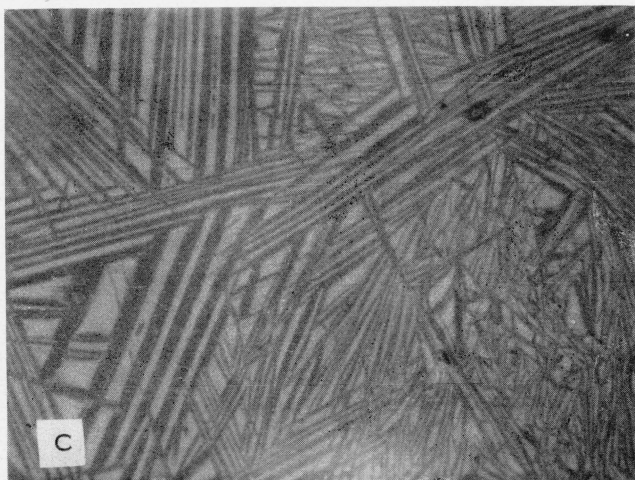
FIGURE 7.—(*Continued*).

C, Polished surface of rapidly cooled charge quenched from same temperature as *A*; water-etched 2 sec; reflected light; magnification ×1000. Shows abundant growth of dark prismatic crystals; *D*, same field as *C* but viewed with transmitted light, crossed nicols. Show birefringent prismatic crystals.

amount of glass were observed by examination of powdered samples in oil. The $3CaO.Al_2O_3$ was in the isotropic form.

Two charges of this mixture (*J*) were then differently heat treated and polished thin sections prepared. Both charges were heated to 1,500° C and then cooled to 1,370° C. The first charge was cooled slowly at a rate of $1\frac{1}{2}°$ C per minute. Figure 7 (A) shows the appearance of the water-etched polished surface in reflected light. The well-formed crystals of rectangular $3CaO.Al_2O_3$ and the absence of prismatic crystals may be noted. Figure 7 (B) shows the same field viewed by transmitted light through crossed nicols. The clusters of birefringent material are $K_2O.23CaO.12SiO_2$. The second charge was cooled more rapidly at a rate of 10° C per minute. Glass, a small amount of CaO, poorly crystallized grains of $K_2O.23CaO.12SiO_2$, and much prismatic dark material were observed. Figure 7 (C) is a photomicrograph of the surface after etching with water for 2 seconds. This figure may be compared with figure 7 (A), the only variable being the rate of cooling. Figure 7 (D) shows the same field (7, C) viewed by transmitted light through crossed nicols. The abundance of birefringent prismatic crystals may be noted.

It should be mentioned that efforts to obtain the prismatic modification in compositions containing no SiO_2 were unsuccessful. Although the study of the relation of the prismatic phase to the system $K_2O.23CaO.12SiO_2–CaO–5CaO.3Al_2O_3$ has indicated that the composition of this phase is very close to that of $3CaO.Al_2O_3$, the possibility remains that some SiO_2 (and possibly other components) is present in solid solution or is an integral part of the unit-cell structure. In either case the amount of SiO_2 involved must be small. No measurable reductions in the amount of the observed total calcium silicates, as compared with the theoretical amount calculated as being present, have been found by other workers to occur in clinkers containing appreciable amounts of the prismatic phase [8, 10]. Any crystalline $K_2O.23CaO.12SiO_2$ present likely was included with the amounts of the calcium silicates reported in the data to which reference has been made. The above potash compound was not known at the time of these studies. L. S. Brown has recently reported that he has observed $K_2O.23CaO.12SiO_2$ in sections of commercial clinker [14].

In the present study, the formation of the prismatic phase was induced by adding as little as 5 percent of $3CaO.SiO_2$ to a mixture containing 11.0 percent of K_2O, 48.0 percent of CaO, and 41.0 percent of Al_2O_3. The 1.32 percent of SiO_2 introduced by this amount of $3CaO.SiO_2$ would be sufficient to form 3.85 percent of $K_2O.23CaO.12SiO_2$. Small quantities of this latter compound were observed in the charges, but no exact measurements of the amounts were made because, in these particular cases, some of the components likely were contained in the glass that also was present.

4. EFFECT OF K_2O AS K_2SO_4 ON THE FORMATION OF THE PRISMATIC MATERIAL

It has been reported by the author, in connection with another investigation [6], that in mixtures of K_2O, CaO, MgO, Al_2O_3, Fe_2O_3, SiO_2 and SO_3 comparable to portland cement clinker, K_2O combines preferentially with SO_3 to form K_2SO_4, and that any K_2O in excess of that required for K_2SO_4 combines with CaO and

SiO_2 to form $K_2O.23CaO.12SiO_2$. It was shown also in the same study that the components of K_2SO_4 do not enter the clinker melt, molten K_2SO_4 being immiscible with the liquid composed of other clinker components. Since K_2O in the form of K_2SO_4 is not contained in the melt from which the prismatic phase crystallizes, K_2O in this form would not be expected to aid in the formation of the prismatic material.

Mixture K was prepared adding 10 percent of K_2SO_4 to 90 percent of the mixture that corresponds to the liquid composition for an $Al_2O_3:Fe_2O_3$ ratio of 2.62 on the $3CaO.SiO_2-2CaO.SiO_2$ surface at 1,400° C in the quaternary system $CaO-Al_2O_3-Fe_2O_3-SiO_2$ [13]. The composition of the resulting mixture K was 50.7% of CaO; 23.6% of Al_2O_3; 9.0% of Fe_2O_3; 6.7% of SiO_2; and 10.0% of K_2SO_4. Charges of this preparation were cooled through various temperature ranges and at various rapid rates. Although the $CaO-Al_2O_3-Fe_2O_3-SiO_2$ portion of the sample had a potential $3CaO.Al_2O_3$ content of 17 percent, no prismatic dark interstitial material was observed in any of the charges.

Potassium oxalate was incorporated with mixture K in an amount calculated to give a mixture having 1 percent of K_2O in excess of that combined as K_2SO_4. A charge was cooled from 1,440° to 1,220° C at the rapid rate of 12° C per minute. A large amount of prismatic crystals was formed in this specimen.

Further studies were made in this connection with two other mixtures (L and M), in which all the K_2O was calculated to be present as K_2SO_4. These had the compositions: Mix L, 25.0% of $3CaO.SiO_2$; 25.0% of $2CaO.SiO_2$; 25.0% of $3CaO.Al_2O_3$; 0% of $4CaO.Al_2O_3.Fe_2O_3$; and 25.0% of K_2SO_4. Mix M, 35.0% of $3CaO.SiO_2$; 35.0% of $2CaO.SiO_2$; 15.0% of $3CaO.Al_2O_3$; 10.0% of $4CaO.Al_2O_3.Fe_2O_3$; and 5.0% of K_2SO_4. Charges of these two samples were cooled from 1,475° C at rates varying from 10° C per minute to the very rapid rate which obtained when the charge was removed from the furnace and allowed to cool in air. No prismatic dark interstitial material was observed in any of the specimens, confirming again the view that K_2O as K_2SO_4 does not aid in the formation of the prismatic phase.

IV. DISCUSSION

In the study of the system $K_2O.23CaO.12SiO_2-CaO-5CaO.3Al_2O_3$ [6], no evidence was obtained of the formation under conditions of equilibrium of prismatic dark interstitial material. This phase has been obtained in this and other systems only under conditions of nonequilibrium induced by rapid cooling. No range of real stability appears to exist for this phase. It would appear from the conditions, both thermal and compositional, necessary for the formation of the prismatic phase that it is a metastable form of $3CaO.Al_2O_3$, and monotropic (i. e., having no definite transition point) with respect to the stable, isotropic, rectangular $3CaO.Al_2O_3$.

It is not possible, on the basis of present data at least, to state definitely that the prismatic material has the composition exactly that of $3CaO.Al_2O_3$. The difficulties encountered in trying to determine the composition of a metastable phase, that thus far has been observed only in systems containing at least four oxide components, are evident. This phase has never been obtained in a pure state on which a chemical analysis or a melting-point determination could be made.

The ratio of the amount of prismatic material to the amount of alkali in various specimens has been found to be extremely variable. The maximum possible value of this ratio has not been established. It has been shown with certain compositions in this study that the amount of prismatic material formed appears to be limited by the calculated potential amount of $3CaO.Al_2O_3$. In certain other specimens, however, having high potential $3CaO.Al_2O_3$ contents, there was evidence that the optimum condition for the formation of the maximum amount of the prismatic phase did not prevail. This optimum condition often is not easily attained; too rapid cooling inhibits the crystallization of the potential quantity of the prismatic phase, and too slow cooling permits the formation of the rectangular form of dark interstitial material at the expense of the prismatic. With some compositions the range of cooling rates favorable to the formation of the prismatic material is extremely limited. It has been observed, with many samples in this study, that the prismatic phase would be concentrated near the surface, next to the platinum capsule enclosing it, and the rectangular form in the interior where the cooling was slightly slower. It has been observed also that some charges contained the prismatic phase in the interior and only the amorphous form of dark interstitial material (glass) near the surface.

It appears that the rate of cooling for the optimum formation of the prismatic phase varies with the composition of the raw mixture. For example, it was found that extremely rapid cooling was required for the production of the prismatic phase in charges having compositions within the field of $3CaO.Al_2O_3$ in the system $K_2O.23CaO.12SiO_2$-$CaO-5CaO.3Al_2O_3$. On the other hand, it was shown in the data obtained by Ward on heat-treated commercial clinkers that relatively slow cooling was favorable to the formation of the prismatic material in mixtures having low-potential $3CaO.Al_2O_3$ contents (low Al_2O_3: Fe_2O_3 ratios).

Indefinite results are obtained in attempts to establish the composition of the prismatic dark interstitial material by the measurement of the amounts of the phases in specimens of known oxide compositions for the following reasons:

1. Unless the amount of the prismatic phase closely approaches that of the calculated potential $3CaO.Al_2O_3$ in a sample, it is uncertain that a close approach has been made to the optimum conditions required for the formation of the prismatic material.

2. No etchant has yet been found to distinguish definitely the potash compound $K_2O.23CaO.12SiO_2$ from the two calcium silicates in polished sections of clinker. For this reason, it is difficult to identify and measure $K_2O.23CaO.12SiO_2$ with exactness. The amount of potash combined in this compound in a given sample, therefore, is difficult to determine.

3. Glass of an undeterminable composition (undeterminable because of the existence of nonequilibrium conditions) is commonly associated with the prismatic phase. It is probable that some alkali is contained in the glass.

4. Calculations of composition based on the quantities of the phases present may be considerably in error, because the extent to which solid solution may occur among the various phases is not known.

Certain comparisons that have been made between the observed amount of prismatic material and the chemically determined amount of

alkali in a specimen show that the amount of alkali which possibly could be a component of the prismatic phase is a very small percentage of the composition. For example, an experiment was made by heating a mixture composed of 10% of $K_2O.23CaO.12SiO_2$; 15% of $3CaO.Al_2O_3$; 20% of $4CaO.Al_2O_3.Fe_2O_3$; 30% of $3CaO.SiO_2$; and 25% of $2CaO.SiO_2$ to 1,530° C and then cooling to 1,290° C at a rate of 8° C per minute. An examination of a water-etched polished section [2] showed 14 percent of prismatic dark interstitial material and 2 percent of glass. If the K_2O in the $K_2O.23CaO.12SiO_2$ that may be present and the K_2O in the 2 percent of glass are not considered (for the reasons outlined above), it might be argued that the 0.5 percent of K_2O in the sample [3] is contained in the 14 percent of the prismatic material and, therefore, the K_2O content of this phase is 3.6 percent. (It will be recalled, however, that the maximum possible alkali content of the prismatic phase in clinker 20 of the group examined by Insley was calculated, on the above basis, to be only 1.4 percent.)

Just how K_2O (or Na_2O)[4] functions in the formation of the prismatic phase is not wholly clear. It is known that small amounts of certain compounds sometimes modify the crystalline form of another compound. Rankin and Merwin, in a study of the system $CaO–MgO–Al_2O_3$ [15] observed that a new form of alumina, $\beta–Al_2O_3$, occurred occasionally in charges of alumina that had been melted and slowly cooled. The presence of a small amount of MgO (0.5 percent) materially assisted in the formation of the new form, whereas melted alumina containing small amounts of either CaO or SiO_2 was found to crystallize on cooling as the α-form (corundum). Stillwell [16], in analyzing samples of $\beta–Al_2O_3$, came to the conclusion that the presence of Na_2O was essential for the formation of this form; in some samples, for example, the Na_2O content reached about 5 percent. On the other hand, in connection with the work of Rankin and Merwin, H. S. Washington analyzed a sample of $\beta–Al_2O_3$ that had been separated from artificial alumina abrasive and found it to be pure Al_2O_3. Later, Bragg, Gottfried, and West, in their study of the structure of $\beta–Al_2O_3$ [17], proposed a structure that contains Na+23Al+35 O atoms in the unit cell. This corresponds to the composition $Na_2O.23Al_2O_3$. In a still later study, Brownmiller observed that $\beta–Al_2O_3$ crystallizes in the binary system $K_2O–Al_2O_3$ [3]. Microscopical examinations of heated mixtures in this system showed the presence of two phases, $K_2O.Al_2O_3$ and $\beta–Al_2O_3$.

In the sense that β-alumina is referred to as a form of alumina because the material is essentially alumina, if not entirely so, it is suggested that the prismatic dark interstitial material be considered as prismatic $3CaO.Al_2O_3$. All the data thus far obtained indicate that the composition of the prismatic phase is at least very close to that of $3CaO.Al_2O_3$. No measurable reductions in the amounts of the calcium silicates have been observed upon the formation of this phase. This and the close relation between the amounts of prismatic material and the calculated potential amount of $3CaO.Al_2O_3$. in clinker indicate that if any components other than those of $3CaO.Al_2O_3$ are contained in the prismatic material, or if any solid

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[2] By G. W. Ward.
[3] Analyzed by Leonard Bean. The 10 percent of $K_2O.23CaO.12SiO_2$ used in the original mixture contributes 0.46 percent of K_2O to the composition.
[4] Insley and McMurdie [1] have shown that the presence of Na_2O also promotes the formation of a prismatic phase having similar optical properties.

solution exists, the amount is so slight that consideration of the phase as $3CaO.Al_2O_3$ introduces no significant error in the computation of the compound composition of clinker. Furthermore, no evidence has been obtained, so far as is known, of the properties of cements being affected by the existence of one form to the exclusion of the other, and there appears to be no reason for modifying the clause in the specifications for certain cements which limits the calculated amount of $3CaO.Al_2O_3$ permitted.

The conditions apparently necessary for the formation of prismatic $3CaO.Al_2O_3$ are

(a) The composition of the raw mixture must be such as to permit potentially the formation of $3CaO.Al_2O_3$.

(b) The phase must crystallize from a melt that contains some K_2O, or Na_2O, or both, and SiO_2, although the amount of prismatic $3CaO.Al_2O_3$ formed appears to be independent of the amounts of these oxides.

(c) The rate of cooling must be such as to permit crystallization of the prismatic phase from the melt, but yet not subject these crystals to prolonged heat treatment. Slow cooling, which permits an approach to equilibrium conditions, favors the formation of isotropic, rectangular $3CaO.Al_2O_3$ at the expense of the anisotropic, prismatic $3CaO.Al_2O_3$.

V. SUMMARY

A study has been made of the nature of the prismatic dark interstitial material, so called because of its appearance in etched, polished sections of portland cement clinker.

Microscopical data obtained on commercial clinker by other investigators have been presented, and the relation of the amounts of the prismatic phase to the calculated potential amounts of $3CaO.Al_2O_3$ has been shown.

A study was made of the relation of the prismatic dark interstitial material to the system $K_2O.23CaO.12SiO_2$—CaO—$5CaO.3Al_2O_3$. It was found that in this system, the prismatic phase is not stable and does not appear in samples that have been cooled at rates approaching those of equilibrium conditions. It was obtained only under conditions of rapid cooling. Both thermal and compositional conditions found to be required for its formation suggest that it may be a metastable form of $3CaO.Al_2O_3$ and monotropic with respect to the stable, isotropic, rectangular $3CaO.Al_2O_3$.

The results of studies on samples having compositions beyond the limits of the system $K_2O.23CaO.12SiO_2$—CaO—$5CaO.3Al_2O_3$ likewise show the close relationship between $3CaO.Al_2O_3$ and the prismatic phase.

It was found that the K_2O which is combined as K_2SO_4 in clinker does not induce the formation of prismatic dark interstitial material.

While definite proof has not been presented that the composition of the prismatic phase is exactly that of $3CaO.Al_2O_3$, the data show the composition of the prismatic phase to be very close to that of $3CaO.Al_2O_3$. Since the amounts of the other clinker phases, and the properties of cements, do not appear to be affected measurably by the presence of one form of crystalline dark interstitial material to the exclusion of the other, it is suggested that the prismatic phase be considered as a metastable form of $3CaO.Al_2O_3$ and referred to as

"prismatic $3CaO.Al_2O_3$" instead of the indefinite term "prismatic dark interstitial material."

Conditions necessary for the formation of prismatic $3CaO.Al_2O_3$ have been outlined.

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The author is indebted to G. W. Ward for the photomicrographs presented in this paper.

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—2.5000 to 1.0000	0.0001	18
1.0000 to 2.5000	.0001	15
2.500 to 5.000	.001	15
5.00 to 10.00	.01	12

(1939) XV+535 pages; bound in buckram, $2.00.

MT3. TABLES OF CIRCULAR AND HYPERBOLIC SINES AND COSINES FOR RADIAN ARGUMENTS:

Contains 9 decimal place values of sin x, cos x, sinh x and cosh x for x (in radians) ranging from 0 to 2 at intervals of 0.0001.
(1939) XVII+405 pages; bound in buckram, $2.00.

MT4. TABLES OF SINES AND COSINES FOR RADIAN ARGUMENTS:

Contains 8 decimal place values of sines and cosines for radian arguments ranging from 0 to 25 at intervals of 0.001.
(1940) XXIX+275 pages; bound in buckram, $2.00.

MT5. TABLES OF SINE, COSINE, AND EXPONENTIAL INTEGRALS, VOLUME I:

Values of these functions to 9 places of decimals from 0 to 2 at intervals of 0.0001.
(1940) XXVI+444 pages; bound in buckram, $2.00.

MT6. TABLES OF SINE, COSINE, AND EXPONENTIAL INTEGRALS, VOLUME II:

Values of these functions to 9, 10, or 11 significant figures from 0 to 10 at intervals of 0.001 with auxiliary tables.
(1940) XXXVII+225 pages; bound in buckram, $2.00.

MT7. TABLE OF NATURAL LOGARITHMS, VOLUME I:

Logarithms of the integers from 1 to 50,000 to 16 places of decimals.
(1941) XVIII+501 pages; bound in buckram, $2.00.

MT8. TABLES OF PROBABILITY FUNCTIONS, VOLUME I:

Values of these functions to 15 places of decimals from 0 to 1 at intervals of 0.0001 and from 1 to 5.6 at intervals of 0.001.
(1941) XXVIII+302 pages; bound in buckram, $2.00.

[Continued from p. 3 of cover]

MT9. TABLE OF NATURAL LOGARITHMS, VOLUME II:

Logarithms of the integers from 50,000 to 100,000 to 16 places of decimals.
(1941) XVIII+501 pages; bound in buckram, $2.00.

MT10. TABLE OF NATURAL LOGARITHMS, VOLUME III:

Logarithms of the decimal numbers from 0.0001 to 5.0000, to 16 places of decimals.
(1941) XVIII+501 pages; bound in buckram, $2.00.

MT11. TABLES OF THE MOMENTS OF INERTIA AND SECTION MODULI OF ORDINARY ANGLES, CHAN-
NELS, AND BULB ANGLES WITH CERTAIN PLATE COMBINATIONS:

(1941) XIII+197 pages; bound in green cloth. $2.00.

MT12. TABLE OF NATURAL LOGARITHMS, VOLUME IV:

Logarithms of the decimal numbers from 5.0000 to 10.0000, to 16 places of decimals.
(1941) XXII+506 pages; bound in buckram, $2.00.

MT13. TABLE OF SINE AND COSINE INTEGRALS FOR ARGUMENTS FROM 10 TO 100:

(1942) XXXII+185 pages, bound in buckram, $2.00.

MT14. TABLES OF PROBABILITY FUNCTIONS, VOLUME II:

Values of these functions to 15 places of decimals from 0 to 1 at intervals of 0.0001 and from
1 to 7.8 at intervals of 0.001.
(1942) XXI+344 pages; bound in buckram, $2.00.

MT15. The hypergeometric and Legendre functions with applications to integral equations of
potential theory. By Chester Snow, National Bureau of Standards. Reproduced from original
handwritten manuscript.

(1942) VII+319 pages; bound in heavy paper cover. $2.00.

MT16. TABLE OF ARC TAN X:

Table of inverse tangents for positive values of the angle in radians. Second central differences
are included for all entries.

Range of x		Interval between successive arguments
0 to	7	0.001
7 to	50	.01
50 to	300	.1
300 to	2,000	1
2,000 to	10,000	10

(1942) XXV+169 pages; bound in buckram, $2.00.

Payment is required in advance. Make remittance payable to the "National Bureau of Standards," and send with order, using the blank form facing page 3 of the cover.

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Copies of these publications have been sent to various Government depositories throughout the country, such as public libraries in large cities, and colleges and universities, where they may be consulted.

A mailing list is maintained for those who desire to receive announcements regarding new tables as they become available.