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MINOR CONSTITUENTS IN PORTLAND CEMENT CLINKER

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ABSTRACT

The optical and structural properties of some minor phases in portland cement clinker as observed in thin sections, polished sections, and a new type of polished thin section are recorded. The similarity of such phases to those found in laboratory preparations is pointed out. Methods of determination of free CaO, free MgO, "light" interstitial material, and "dark" interstitial material are given. The "light" interstitial material is shown to be $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$. There are three kinds of "dark" interstitial material which have the properties of: (1) glass; (2) $3\text{CaO}\cdot\text{Al}_2\text{O}_3$; and (3) a prismatic crystalline material. The prismatic crystalline material apparently is a compound of the alkalis with some of the other oxides in the clinker. Glass is found in the majority of portland cement clinkers. At present, it is impossible to calculate precisely the compound composition from chemical analyses because of lack of knowledge of cooling conditions, the effect of minor constituents on phase relations, and other variables.

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I. INTRODUCTION

In a previous paper [1]¹ the structural characteristics of some constituents of portland cement clinker were described and the deviations of these constituents from the pure compounds were pointed out. Studies investigating the nature and extent of these deviations were suggested. This paper presents the results of a similar study restricted to the minor constituents.²

As in the previous study, the petrographic and metallographic microscopes and the X-rays were used. In addition, a combination

¹ Figures in brackets refer to references at the end of the paper.

² The authors have arbitrarily defined "minor constituents" as those phases which never occur in amounts greater than 25 percent in commercial portland cement clinker.

of the petrographic and metallographic methods was employed, which is described later in the paper.

As material for the investigation of structures there were available not only the laboratory-prepared clinkers which were made from mixtures of the separate oxides (or carbonates) and heat treated in a small platinum resistance furnace, but also about 60 samples of commercial portland cement clinker, of which a large majority were obtained through the generous cooperation of Mr. Dalton G. Miller.³

Following common usage in technical reports on cement constitution, a system of abbreviations is used in referring to the compounds, thus: $3\text{CaO} \cdot \text{SiO}_2 = \text{C}_3\text{S}$; $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3 = \text{C}_4\text{AF}$; $8\text{CaO} \cdot \text{Na}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 = \text{C}_8\text{NA}_3$, etc.

II. PREPARATION OF POLISHED THIN SECTIONS

A method of preparing mounts which could be observed both by transmitted and by reflected light was developed for the microscopic study of clinker. The clinker piece to be sectioned was heated in a resin having a high index of refraction⁴ until the resin became tough but not brittle. After grinding one face to a plane with fine emery the piece was cemented to an object slide with the same resin used for impregnation and the other surface then ground down until the section was of the required thickness (15 to 20 microns). After fine grinding with fine emery and alcohol the exposed surface of the clinker was polished with a mixture of jeweler's rouge and alcohol on a canvas-covered rotating lap. The polished surface was then etched. With a vertical illuminator and objective corrected for use without cover glass, attached to the tube of a petrographic microscope, the specimen could be examined either in reflected or transmitted light without changing its position on the stage of the microscope.

III. IDENTIFICATION OF FREE CaO AND FREE MgO

1. FREE CaO

Although free CaO is not a constituent of properly proportioned, well-mixed and well-burned portland cement clinker, it is so commonly present in small amounts in commercial clinker that its easy determination, both qualitatively and quantitatively, is of great importance.

Of the many methods which have been devised for the determination of free CaO, three very commonly used are White's reaction, the ammonium acetate method, and the determination by optical properties. White's reaction, [2] which results in the formation of calcium phenolate crystals by interreaction of the free lime with phenol in nitrobenzene and water, gives qualitative results.

The ammonium acetate method [3] is quantitative. The fact that both White's reaction and the ammonium acetate method give positive results for calcium hydroxide as well as for free lime may sometimes be a disadvantage.

The microscopic identification by optical properties makes use of the isotropy and high index of refraction (1.83) of free CaO. In quantitative estimation in thin sections of cement clinker the amount of free CaO is very likely to be underestimated because of overlap of birefringent constituents.

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⁴ Liquid Hyrax or Aroclor No. 4465 was found satisfactory.

Polished specimens prepared by the method described in the previous paper [1]⁶ are satisfactory for the observation of free CaO. A mixture of rouge and ethyl alcohol is substituted for the rouge-water mixture in polishing to avoid hydration of the free CaO. The specimen is then etched in a 1:1 water-alcohol mixture for 1 to 3 minutes, the shorter times being required at higher room temperatures. This method has been found to give more uniform results than Tavasci's method [4] of etching during polishing with a mixture of rouge, alcohol, and water. The etching treatment causes a decided darkening of the exposed surfaces of free CaO grains, probably because of formation of thin films of $\text{Ca}(\text{OH})_2$.

Free CaO usually occurs as rounded grains, either singly or in aggregates (fig. 1). Aggregates appear to be the result of imperfect batch mixing. Single grains, which are often located at the centers of C_3S , are evidently the result of imperfect diffusion during reaction to form dicalcium and tricalcium silicates.

The qualitative determination of free CaO in polished section has some advantages over other methods. It is more rapid than any of the other methods except White's and it permits observation of the structural relations to other clinker constituents. By use of one of the integrating stages [5] the free CaO may be determined quantitatively. It is possible that a rapid quantitative method could be devised in which the polished sample to be determined could be compared with a set of standard polished specimens composed of individuals varying by some convenient step, say 5 percent. The standards would, of course, have to be kept in a dry atmosphere to prevent the hydration of the free lime.

2. FREE MgO

In completely crystallized portland cement clinker all or nearly all of the MgO occurs as crystalline MgO (periclase), commonly known as free magnesia [6]. In clinker which have been solidified so rapidly that some glass is present, varying amounts of MgO will be dissolved in the glass [7, 8] depending upon the cooling rate, the amount of MgO, etc.

Because evidence is accumulating that excessive expansions in concrete have been caused by the hydration of crystalline MgO, the identification of free MgO is of great importance. So far only two methods of identification have been described which can be regarded as at all satisfactory. By one method the free MgO is left as undissolved residue after solution of the cement in a mixture of HNO_3 and HF [8], but because it is slowly soluble in this reagent this method gives results which are low.

The second method of identification, by means of the petrographic microscope, is of qualitative value. Even qualitative distinction, however, is difficult because crystalline MgO is isotropic and has an index of refraction very close to that of other constituents. In thin sections free MgO may easily be overlooked because it usually occurs in very small grains and may be masked by overlapping, birefringent constituents.

⁶ Besides the impregnating resins mentioned in the paper referred to, Bakelite resinoid 0014 has been used successfully. The specimens are immersed in the resinoid in small vials, subjected to vacuum produced by a faucet aspirator for 2 to 3 hours, heated overnight at 75 to 80° C and finally at 105 to 110° C for 24 hours. The vials are broken away from the hardened preparations before grinding and polishing.

A new method which, it is believed, gives better results than either of the preceding is the determination in polished specimens by reflected light. Free MgO observed by this method is found to occur in small, angular grains (fig. 2) with a reflectivity greater than that of other constituents except C_4AF . It can easily be seen in unetched sections or in sections etched with the milder reagents such as water and alcohol-water mixtures. Characteristics of free MgO in polished specimens were first observed in laboratory preparations in which MgO, the only crystalline phase determined by petrographic examination, was present in a glassy matrix. Failure, heretofore, to identify free MgO in polished sections was found to be caused by difficulty in proper polishing. Unless polished with extreme care, the edges of the MgO grains are fragmented and secondary scratches beginning from these fragmented areas cover the surface of the specimen. Crystalline MgO is known to have an unusually high thermal expansion. It seems probable that during cooling of the clinker the MgO crystals contract faster than the other constituents until they finally break away from the surrounding materials. During grinding and polishing the abrasive media collect in these peripheral cracks and widen them.

Free MgO occurs in commercial clinker almost without exception as inclusions in the interstitial constituents and is, therefore, one of the later phases to crystallize.

Like free CaO, it may be determined quantitatively in polished sections by the use of the integrating stage, and rapid quantitative methods perhaps could be developed which depend upon comparison of the unknown with standard specimens in which free MgO had already been determined with the integrating stage.

Quantitative microscopic determinations of free MgO have been made on a number of commercial clinker specimens, the results of which will be published in a forthcoming paper [10]. It was found in most of the samples that free MgO as determined microscopically was less than total MgO determined chemically. This is a confirmation of other evidence [6, 8] that when glass is present MgO is partially or wholly dissolved in the glass.

IV. IDENTIFICATION OF OTHER INTERSTITIAL CONSTITUENTS

Cement clinker of normal composition is never completely liquid at maximum kiln temperatures (1,400 to 1,475° C), but always contains crystalline C_2S , C_3S , or both [11]. The liquid, containing most, if not all, of the Al_2O_3 , Fe_2O_3 , MgO, and alkalies, as well as some CaO and SiO_2 , solidifies during cooling and forms the interstitial material surrounding the C_2S and C_3S . Some C_2S , which occurs as granular fringes on the borders of C_3S crystals and as overgrowths on previously formed C_2S crystals, should strictly be considered as interstitial material, but since it retains the optical properties and etching characteristics of the coarse-grained C_2S , it will not be discussed here.

Polished sections of clinker which have been etched with a 1-percent alcoholic solution of HNO_3 ⁶ show two readily distinguishable forms of interstitial material [1, 4] which, for purposes of identification, are here called "light interstitial" and "dark interstitial."

⁶ This reagent is made by adding 1 ml of HNO_3 (sp gr 1.42) to 100 ml of ethyl alcohol.

1. THE "LIGHT" INTERSTITIAL PHASE

The light interstitial phase may readily be distinguished from other constituents in polished sections by its higher reflectivity and greater resistance to most etchants. This constituent was identified by Tavasci [4] as C_4AF and all the observations made by us confirm his identification. Examination with reflected polarized light shows definitely that the constituent is anisotropic, and comparisons of this phase (in clinker sections where it is well developed) with pure C_4AF show that the degree of anisotropy and reflectivity is about the same. The compound C_2F ($2CaO \cdot Fe_2O_3$), which might presumably exist in clinker under some conditions of cooling, has a higher reflectivity and a greater degree of anisotropy than the light interstitial phase so far observed in commercial clinker. Examination of clinker petrographically shows the presence of a birefracting, highly refractive constituent with the optical properties of C_4AF wherever the polished specimens of the same clinker contain the light interstitial constituent.

The crystalline habit of the light interstitial phase depends in part on the Al_2O_3/Fe_2O_3 ratio of the clinker and the cooling treatment to which it has been subjected. It is almost universally present as prisms. Where the Al_2O_3/Fe_2O_3 ratio is low and the cooling slow, the prisms tend to be large and broad. Where the Al_2O_3/Fe_2O_3 ratio is high the crystals are frequently very small, slender needles or are dendritic growths.

Optical properties determined either in transmitted or reflected light are not sufficiently precise to decide whether C_4AF exists in the pure form or whether it contains other material in solid solution. Indeed, quantitative microscopic determinations [10] on some clinker with low Al_2O_3/Fe_2O_3 ratios show more light interstitial material than can be accounted for by calculating all Fe_2O_3 as C_4AF . McMurdie [12] has shown that in the system $CaO-Al_2O_3-Fe_2O_3$, C_4AF may take into solid solution between 2.5 and 5 percent of C_3A and about 5 percent of C_5A_3 .

The influence of other oxides such as MgO upon the optical properties, particularly color and pleochroism, of C_4AF has been noted by other observers [13]. Schwiete and zur Strassen [14] also noted the change in color and pleochroism produced by the presence of MgO , and attempted to determine the amount of solid solution of MgO in C_4AF by the presence and intensity of X-ray diffraction lines of MgO in mixtures with C_4AF heated to high temperatures, as compared with X-ray lines of mechanical mixtures of the two compounds. They found that in the system $C_4AF-MgO$ the limit of solid solution of MgO in C_4AF was about 2 percent. As will be seen in the following brief study of the system $C_4AF-MgO$ by the present authors, the limits of solid solution as defined by Schwiete and zur Strassen were not confirmed.

(a) RELATIONS WITH MgO

Equilibrium relations of C_4AF and MgO were outlined by a combination of heating curve and quenching determinations. Mixtures containing C_4AF crystallize rapidly during quenching. It was found possible to prevent this by pointing the lower end of the envelop containing the charge, thus permitting the charge to penetrate the surface of the mercury quenching bath when dropped from the furnace.

The system was found to be a simple eutectic one. The eutectic composition and temperature (6.5 percent of MgO:93.5 percent of C_4AF , $1,347 \pm 3^\circ C$) were indicated by extrapolation of the two liquidus curves to the intersection. The temperature was confirmed by the temperature of the lowest break on the heating curve of a previously crystallized mixture of 90 percent of C_4AF :10 percent of MgO, and both temperature and composition by quenching tests on a mixture of 6.5 percent of MgO:93.5 percent of C_4AF . These results differ somewhat from those of Schwiete and zur Strassen, who located the eutectic at about 8 percent of MgO:92 percent of C_4AF and about $1,370^\circ C$. The equilibrium diagram as determined by the present authors is shown in figure 3 and the results of the quenches are given in table 1.

TABLE 1.—*Results of the quenches in the system $MgO-4CaO.Al_2O_3.Fe_2O_3$*

| Composition | | Temperature | Phases present |
|-------------|---------|-------------|--|
| MgO | C_4AF | | |
| Percent | Percent | $^\circ C$ | |
| 2.0 | 98.0 | 1355 | C_4AF +glass C_4AF +glass C_4AF +MgO |
| | | 1350 | |
| | | 1310 | |
| 4.0 | 96.0 | 1395 | Glass only C_4AF +glass |
| | | 1385 | |
| 5.0 | 95.0 | 1370 | Glass only C_4AF +glass C_4AF +glass C_4AF +MgO |
| | | 1360 | |
| | | 1350 | |
| | | 1340 | |
| 6.5 | 93.5 | 1352 | Glass only C_4AF +MgO |
| | | 1345 | |
| 7.5 | 92.5 | 1410 | Glass only MgO+glass |
| | | 1405 | |
| 10.0 | 90.0 | 1550 | MgO+glass |

In spite of the fact that the qualitative observations of previous workers were confirmed, namely, that the presence of MgO deepened the color and markedly increased the pleochroism of C_4AF , no other evidence of solid solution could be found in compositions containing 1 percent or more of MgO. Mixtures of 1 percent of MgO:99 percent of C_4AF were heated to temperatures near the liquidus, cooled at rates less than $0.5^\circ/\text{min}$ to $1340^\circ C$, a temperature just below that of the solidus, maintained at that temperature for $\frac{1}{2}$ hour or longer, and quenched. Microscopic examination of these charges always showed a small amount of material with the optical properties of crystalline MgO (isotropic, n_D about 1.735) and X-ray patterns of such charges failed to show any perceptible shift in the lines of C_4AF as compared with those of the pure compound. Mixtures of 50 percent of MgO and 50 percent of C_4AF , held for periods up to 16 hours at about $1340^\circ C$, after very slow cooling from higher temperatures showed no shift in the X-ray lines of either C_4AF or MgO as compared with the pure compounds. Evidence from the studies reported here indicates, therefore, that in the system $MgO-C_4AF$, solid solution of MgO in C_4AF must be less than 1 percent.

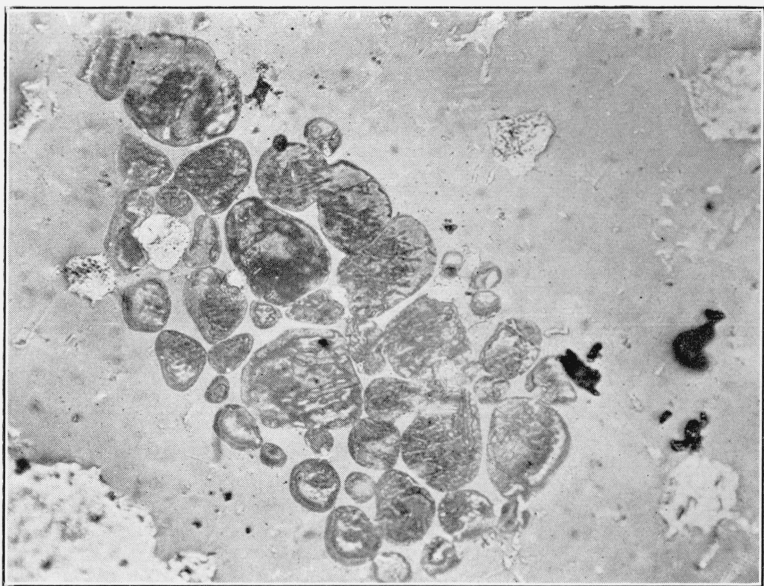


FIGURE 1.—Free CaO in commercial portland cement clinker.
Polished specimen, etched with 1:1 alcohol-water solution for 2 minutes. Reflected light.
Magnification 1,000X.

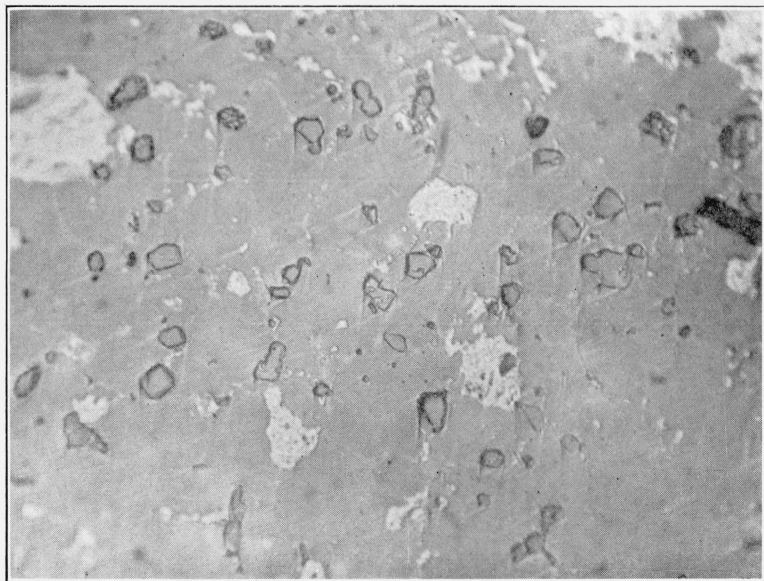


FIGURE 2.—Free MgO in commercial portland cement clinker.
Polished specimen, unetched. Reflected light. Magnification 500X.

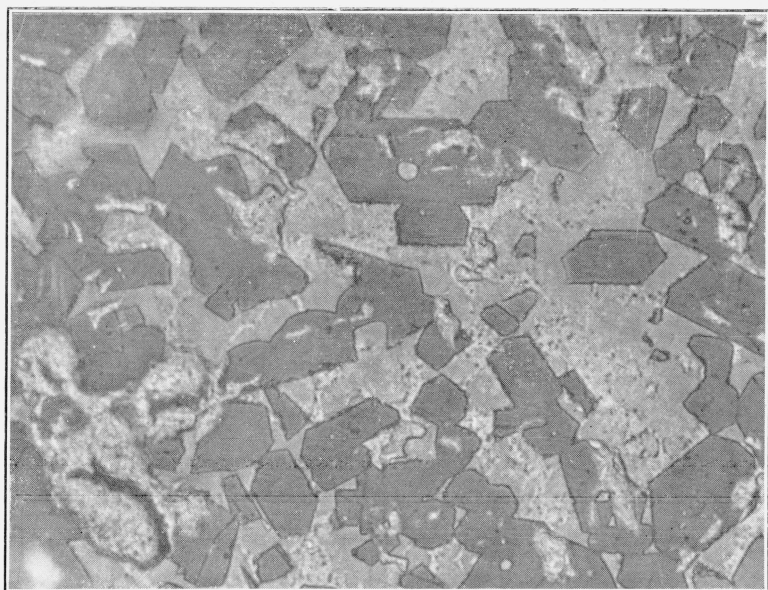


FIGURE 4.—*Amorphous type of dark interstitial material in commercial portland cement clinker.*

Polished specimen etched with water for 2 seconds followed by 1-percent HNO_3 in alcohol for 2 seconds. Reflected light. Magnification 500 \times .



FIGURE 5.—*Rectangular type of dark interstitial material in commercial cement clinker.*

Polished specimen etched with water for 2 seconds followed by 1-percent HNO_3 in alcohol for 2 seconds. The rectangular interstitial material encloses $3\text{CaO}\cdot\text{SiO}_2$ crystals, and in places contains regularly oriented minute inclusions. A, rectangular dark interstitial material; B, $3\text{CaO}\cdot\text{SiO}_2$; C, light interstitial material. Magnification 500 \times .

2. THE "DARK" INTERSTITIAL MATERIAL

The dark interstitial material is so called because it has a number of characteristics in polished sections which distinguish it from the other constituents of clinker. It has a decidedly lower reflectivity than the light interstitial material and etches more readily in a 1 percent alcoholic solution of HNO_3 . It lacks the internal structure of C_2S and the external hexagonal form of C_3S and it etches somewhat less readily than C_3S .

The dark interstitial material may be separated into three types on the basis of microscopic observations in both transmitted and

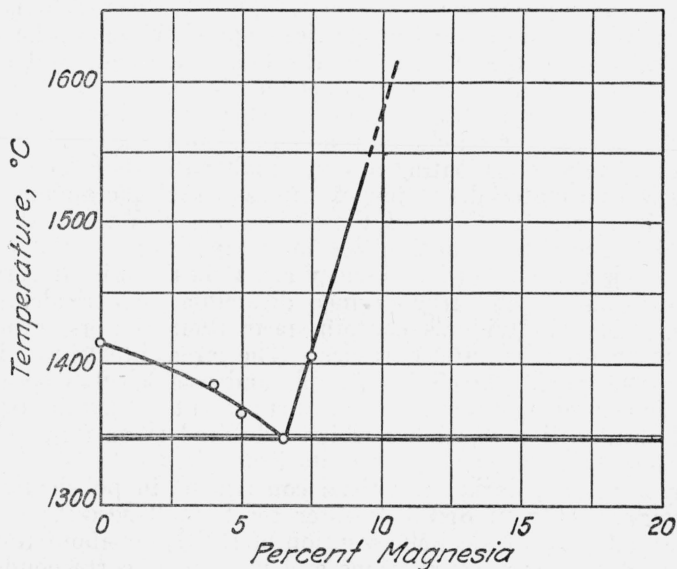


FIGURE 3.—Equilibrium diagram of the system $\text{MgO}-4\text{CaO}.\text{Al}_2\text{O}_3.\text{Fe}_2\text{O}_3$.

reflected light. These types are not always sharply delimited and distinction is sometimes difficult. They will here be called the amorphous, the rectangular and the prismatic types.

The amorphous type of dark interstitial material is the most abundant and most commonly occurring of the three types. Where observations can be made this phase is isotropic in microscopic preparations and its shape is imposed by surrounding constituents. In some other properties, notably index of refraction, it varies considerably. It etches readily in a 1 percent alcoholic solution of HNO_3 . In distilled water⁷ for 2 to 3 seconds this type etches somewhat less readily than the other two types of dark interstitial material but somewhat more readily than either C_2S or C_3S . Its color and index of refraction apparently depend upon the composition of the clinker and the cooling conditions. In most clinker having a low $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ ratio the amorphous dark interstitial material has no apparent color when viewed microscopically and has an index of refraction somewhat less than 1.70 [1], whereas in clinker with a high $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$

⁷ Dr. G. W. Ward, of the Portland Cement Association, suggested this etchant for distinguishing amorphous from other types of dark interstitial material. It is the most sensitive of any thus far tried.

ratio it has a green color in microscopic preparations viewed by transmitted light, and its index is generally greater than 1.74.

The clinker constituents associated with the amorphous type of dark interstitial material also vary somewhat. C_4AF is generally intimately associated with it (figure 4), but in a few clinkers large areas have been found in which interstitial material other than the dark amorphous is absent. Apparently rapid cooling is necessary to prevent the crystallization of C_4AF in small clinker pieces or in the outer layer of larger pieces. Amorphous material has been observed associated with the prismatic crystalline type and is sometimes present as outer irregular layers on the prisms.

All the properties of the amorphous type indicate that it is glass, with composition and optical properties dependent upon the chemical composition of the clinker and the heat treatment and cooling conditions to which the clinker has been subjected.

The rectangular type has been observed in only about four of the 70 samples of commercial clinker studied and in these four it occurred only sporadically, constituting a very small percentage of the total dark interstitial material. A few examples of such rectangular forms are seen in figure 5. Some of these show a series of parallel etch lines which suggest discontinuities in composition in the crystal. Although this constituent is evidently a matrix material it is seen to inclose crystals of the earlier-formed dicalcium and tricalcium silicates and some individuals contain, near their centers, groups of similarly oriented minute particles. The area illustrated is not typical of the particular clinker sample and was selected because of the unusual number of rectangular forms present. Examination of a polished thin section of clinker which exhibited these forms showed that the crystals were nearly or quite isotropic.

The rectangular, dark, interstitial constituent in polished section etches very readily in distilled water for 2 to 3 seconds and less readily in a 1 percent alcoholic solution of HNO_3 for about the same time (fig. 5). In etching relations and in form it corresponds very closely to well-crystallized preparations of C_3A . Although it is very difficult to detect with transmitted light in powdered clinker, material has been isolated which apparently corresponds to this constituent. It is isotropic or very nearly so with an index of refraction close to 1.72. All of the properties observed indicate that the rectangular type is very similar to C_3A , with index of refraction raised somewhat by the iron oxide [12, 15].

Brown [16] also identified an isotropic crystalline material as an interstitial (matrix) phase in portland cement clinker, but his observations differ from ours in that he found it to be a characteristic constituent occurring in grains 350 microns or more in diameter, whereas we can find it only as rare and localized crystals with a diameter never in excess of 70 microns.

A more abundant and characteristic constituent is the prismatic type of dark interstitial material. Of the 70 samples of commercial clinker examined, the type was found to some extent in at least 20 samples and of these 13 contained large amounts. It is noteworthy that in all 20 of these samples the Al_2O_3/Fe_2O_3 ratio was >1.8 .

This constituent occurs as prismatic crystals which are etched readily by water (fig. 6) and somewhat less readily by HNO_3 -alcohol solution (fig. 7). The crystals are usually associated with C_4AF in

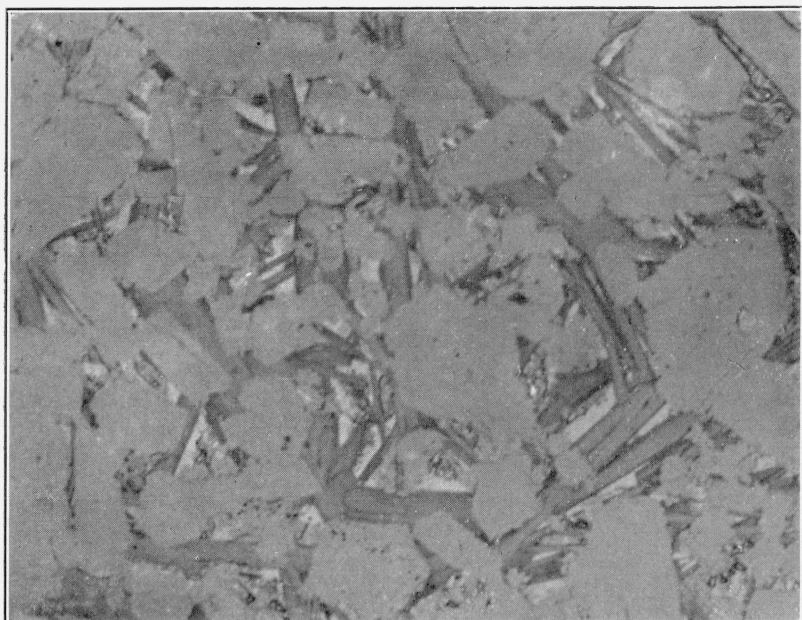


FIGURE 6.—*Prismatic dark interstitial material in commercial cement clinker.*
Polished specimen etched with water for 2 seconds. Magnification 500 \times .

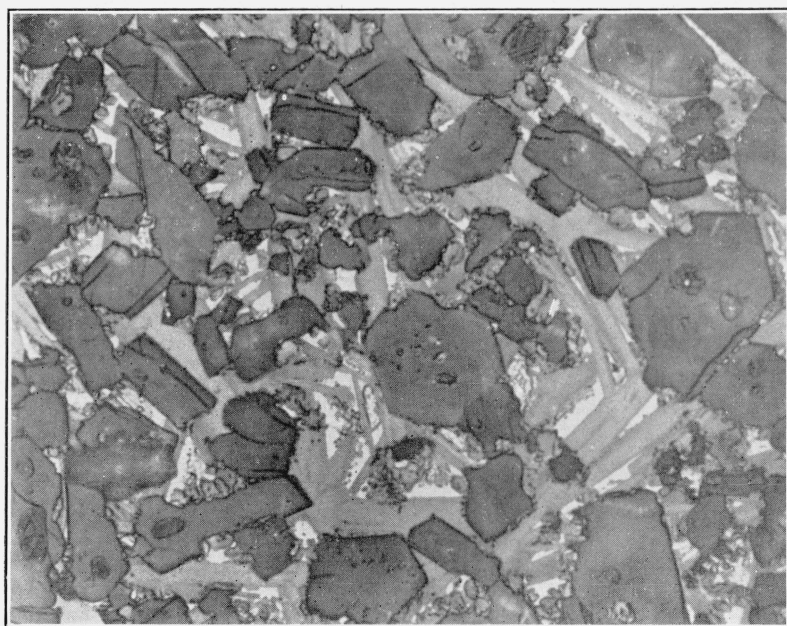


FIGURE 7.—*Same field as figure 6 etched with water for 2 seconds followed by 1-percent HNO₃ in alcohol for 2 seconds.*
Magnification 500 \times .

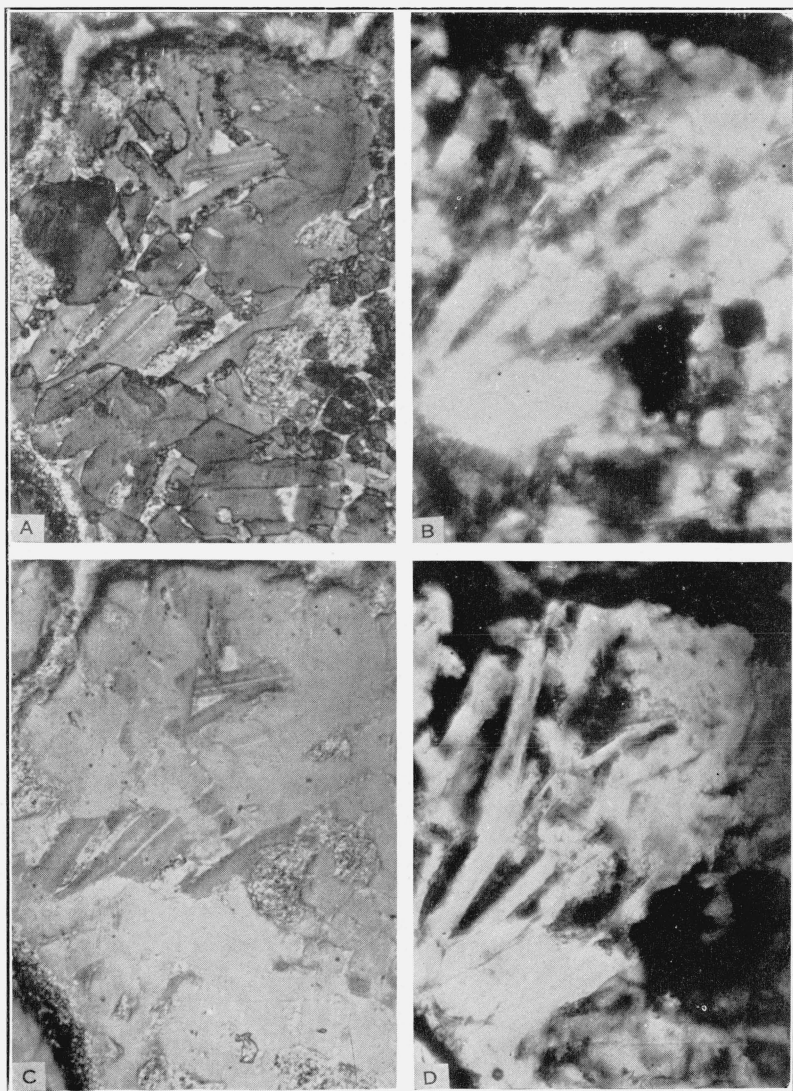


FIGURE 8.—Polished thin section of portland cement clinker.

A, With reflected light, after etching with water for 2 seconds, followed by 1-percent HNO_3 in alcohol for 2 seconds; *B*, same field as *A*, but viewed with transmitted light, crossed nicols; *C*, same field as *A* with reflected light after etching for 2 seconds to show prismatic dark interstitial material; *D*, same field as *A*, but viewed with ordinary transmitted light. Magnification $500\times$.

the matrix material, and sometimes prisms of the dark interstitial constituent alternate with prismatic crystals of C_4AF in parallel orientation. Examination of polished thin sections of clinker containing well-developed prismatic crystals shows that such crystals have a low but distinct double refraction with parallel extinction. Figure 8 shows photomicrographs of the same field of a polished thin section of commercial portland cement clinker; figure 8 (A) in reflected light after etching with distilled water followed with 1 percent HNO_3 in alcohol, figure 8 (B) in transmitted light with crossed nicols, figure 8 (C) in reflected light after etching with distilled water, figure 8 (D) in ordinary transmitted light. The etching characteristics and the double refraction of the prismatic dark interstitial crystals are clearly shown. Observation of a number of polished thin sections indicates that the double refraction is somewhat variable, but is of the same order as that of tricalcium silicate (0.005). Prismatic interstitial crystals identified microscopically in powdered clinker were found to have a mean index approximating 1.72. The similarity of many of the optical properties of this phase to those of C_3S affords an obvious explanation of failure to identify it by the usual petrographic methods. Etching characteristics of the two phases are so different, however, that distinction is easy in polished specimens (figs. 6 and 7).

In searching for the composition of the prismatic interstitial material attention was turned to the possible effect of alkalis, because cements are known to contain as much as 1.2 percent of Na_2O and 1.7 percent of K_2O . To determine experimentally the effects of these oxides, a laboratory preparation was made up containing CaO , Al_2O_3 , Fe_2O_3 , and SiO_2 in about the proportions in an average portland cement clinker. The mixture, on the ignited basis, contained 67.7 percent of CaO , 22.9 percent of SiO_2 , 6.3 percent of Al_2O_3 , and 3.1 percent of Fe_2O_3 and had a potential compound composition of 55 percent of C_3S , 24 percent of C_2S , 12 percent of C_3A , and 9 percent of C_4AF . Na_2CO_3 was added to one portion of this and K_2CO_3 to another portion, so that the resulting mixtures contained 1.5 percent of Na_2O , and 1.5 percent of K_2O , respectively. The alkali-free, the Na_2O -bearing and the K_2O -bearing, samples were then heated at $1,450^\circ C$ for 15 minutes, cooled from $1,450$ to $1,250^\circ C$ at 10° per minute, and air-quenched from the latter temperature. Polished sections and powder preparations were made from each sample. The alkali-free sample when examined in reflected light (figs. 9 and 10) was seen to contain the irregular and rectangular types of dark interstitial material with no trace of prismatic crystals. In transmitted light the interstitial phase associated with C_4AF was isotropic with an index of refraction about 1.72.

The Na_2O -bearing and K_2O -bearing samples contained definite prismatic interstitial crystals (figs. 11 to 14, inclusive) which had the same etching characteristics as the corresponding prismatic type of dark interstitial material in portland cement clinker. In powder preparation, the prismatic crystals were associated with C_4AF in the interstitial materials, were definitely doubly refracting with extinction parallel to the prism axis, and both had mean indices of refraction near 1.72. No differences could be seen between the prismatic crystals in the Na_2O -bearing and those in the K_2O -bearing samples. Prismatic crystals with the same forms and optical properties were also produced in experimental clinker containing 0.7 percent

of alkalis and in another clinker containing 0.7 percent each of both Na_2O and K_2O (figs. 15, 16).

Brownmiller [17] in a study of the system $\text{CaO-Na}_2\text{O-Al}_2\text{O}_3$ discovered a compound which he described as having the composition $8\text{CaO.Na}_2\text{O.3Al}_2\text{O}_3$ with the following optical properties: $\alpha=1.702$, $\gamma=1.710$, biaxial (-), medium 2V. These properties, with the exception of somewhat lower indices of refraction, agree well with those of the prismatic material found in the Na_2O -bearing laboratory preparation and in the prismatic interstitial material in cement clinker. Experiments made by the present authors show that the laboratory-prepared compound in the presence of Fe_2O_3 also has increased indices which are practically identical with those of the prismatic crystals in commercial clinker. Preliminary work by the present authors has cast some doubt on the validity of the formula $8\text{CaO.Na}_2\text{O.3Al}_2\text{O}_3$. Further studies are being made to answer this question as well as to discover the composition of the prismatic crystals in preparations containing K_2O .

V. DISCUSSION

As Lerch [8] has pointed out, the behavior of portland cement in use depends to some extent upon the amount of glass present. Inevitably, also, the composition of the glass, as well as of the other interstitial phases, must play some part in the behavior of the cement. Characteristics of interstitial phases are dependent principally upon chemical composition of the clinker and the heat treatment, including cooling conditions, during and after clinkering. Lea and Parker [11] have shown that, in clinker composed only of CaO , Al_2O_3 , Fe_2O_3 and SiO_2 , the order of crystallization of C_3A and C_4AF is determined by the ratio $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ when cooled under conditions of complete equilibrium. When the ratio is greater than 1.38, C_3A crystallizes before C_4AF ; when the ratio is less than 1.38, C_4AF precedes C_3A . In commercial clinker, which frequently contains small amounts of MgO , Na_2O , K_2O , TiO_2 , Mn_2O_3 , FeO , SO_3 and P_2O_5 , quantitative microscopic determinations [10] as well as the structure of the interstitial phases indicate that the ratio at which C_4AF crystallizes last is somewhat higher than for the 4-component system.

Cooling conditions are at least as important as composition in determining the constitution of the interstitial phases. The almost universal presence of glass indicated by our own examinations, as well as by the indirect method of Lerch [8] shows that some glass is present in the great majority of clinker samples whatever the ratio of Al_2O_3 to Fe_2O_3 , and that therefore sufficiently rapid cooling to arrest crystallization must have occurred some time during the progress of the clinker from the clinkering zone in the kiln to the storage pile.

In clinker with low $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ ratio, such as the "low-heat" cement clinker, C_4AF crystallizes as well developed prisms leaving the glassy interstitial phase low in iron and consequently with a fairly low index of refraction [1]. In clinker with a high $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ ratio, a partial crystallization of "dark interstitial" phases may produce a residual glass with a higher Fe_2O_3 content and consequently a deeper color and higher index of refraction. This appears to be true in spite of the fact that C_4AF has a high crystallization potential

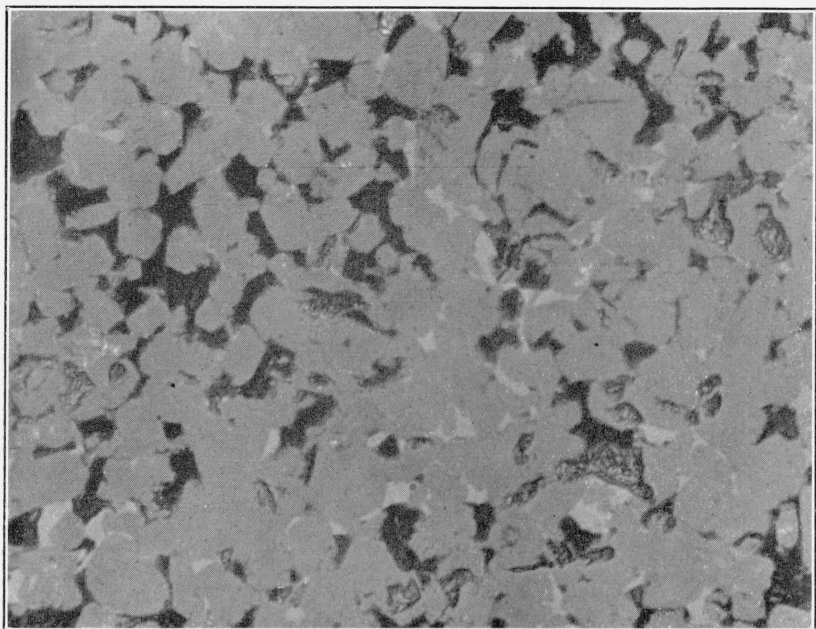


FIGURE 9.—*Laboratory-prepared cement clinker containing no alkalis.*
Polished sample etched with water for 2 seconds. Reflected light. Magnification 500 \times .

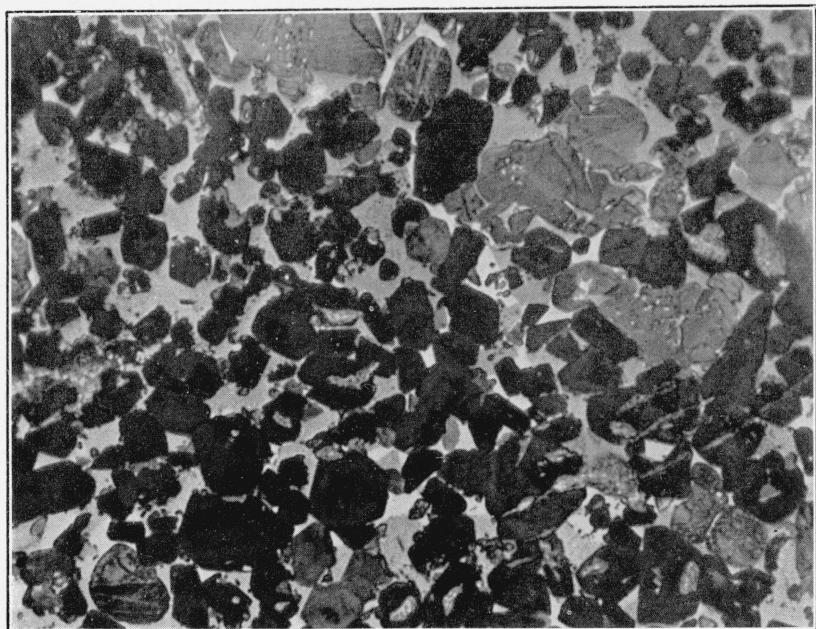


FIGURE 10.—*Same field as figure 12, but etched with water for 2 seconds followed by 1-percent HNO₃ in alcohol for 2 seconds.*
Reflected light. Magnification 500 \times .

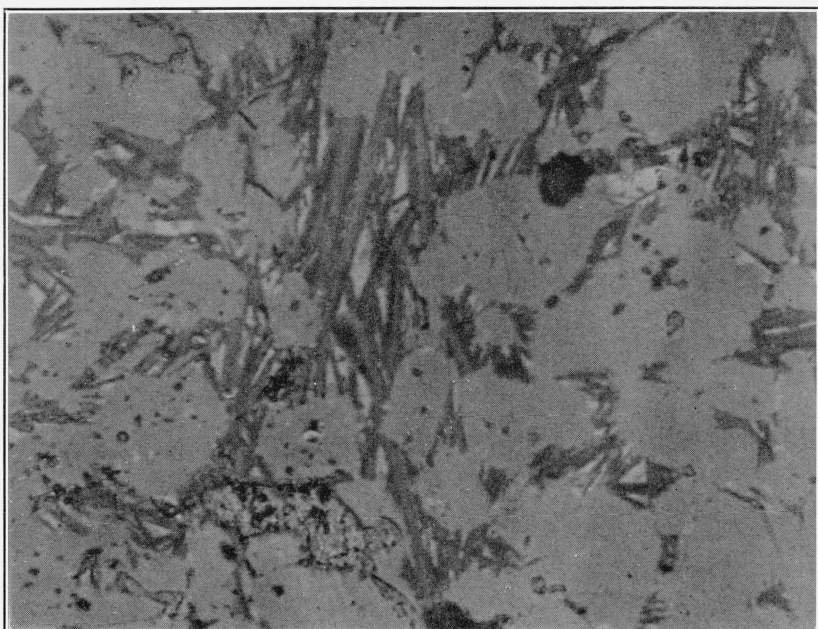


FIGURE 11.—Laboratory-prepared cement clinker containing 1.5 percent of Na_2O . Polished sample etched with water for 2 seconds. Reflected light. Magnification $500\times$.

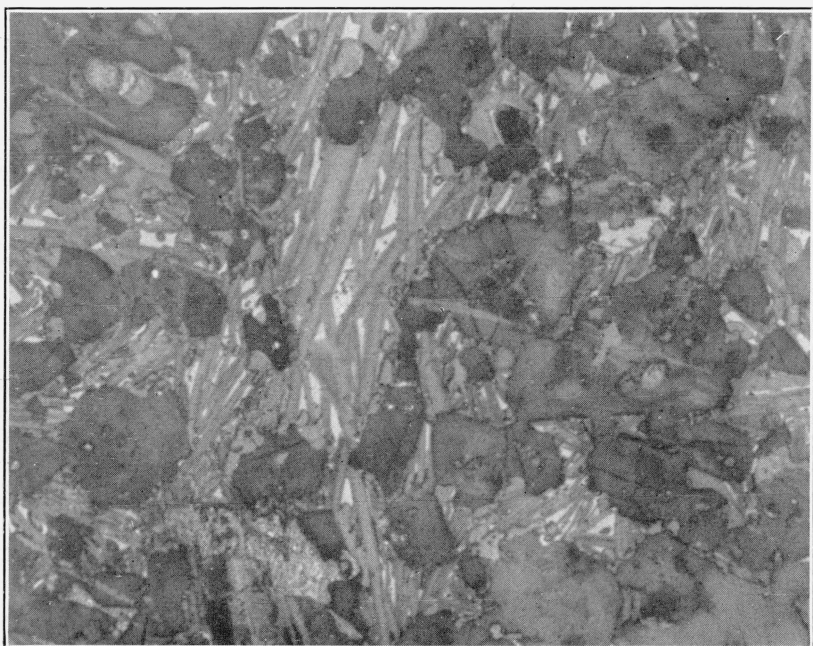


FIGURE 12.—Same field as figure 11, but etched with water for 2 seconds followed by 1-percent HNO_3 in alcohol for 2 seconds. Reflected light. Magnification $500\times$.

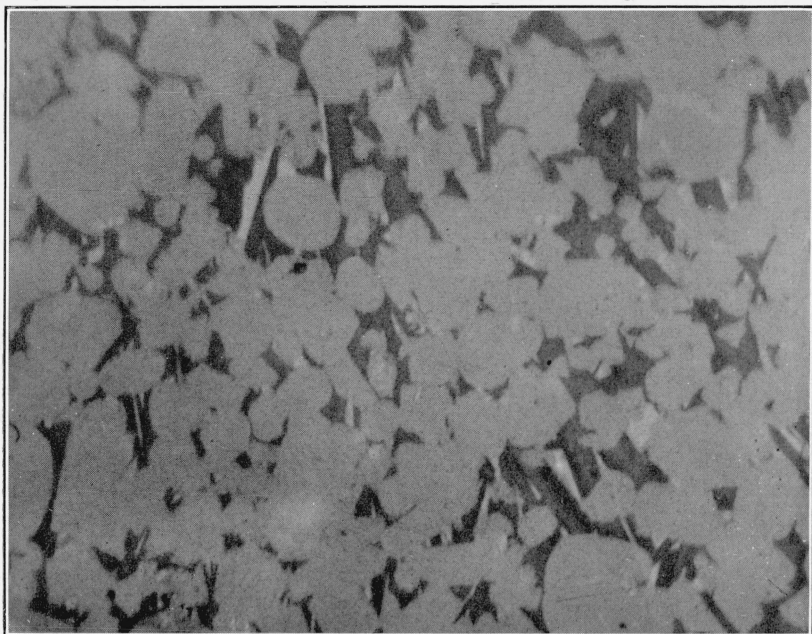


FIGURE 13.—*Laboratory-prepared cement clinker containing 1.5 percent of K_2O . Polished sample etched with water for 2 seconds. Reflected light. Magnification 500 \times .*

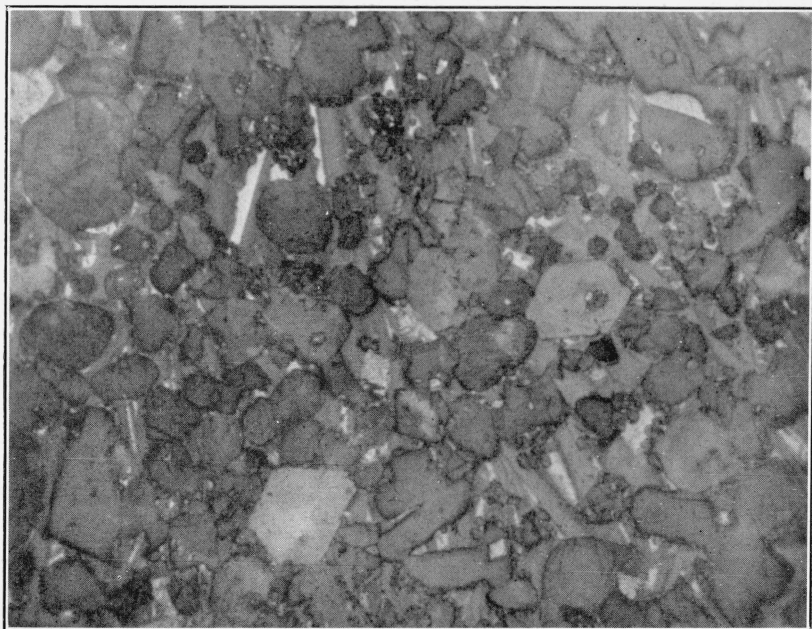


FIGURE 14.—*Same field as figure 13, but etched with water for 2 seconds followed by 1-percent HNO_3 in alcohol for 2 seconds.*

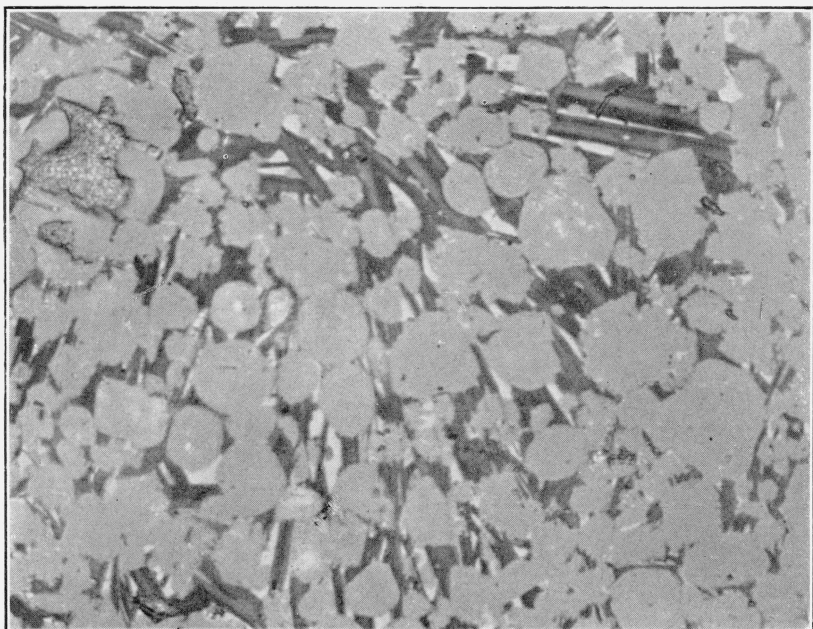


FIGURE 15.—*Laboratory-prepared cement clinker containing 0.7 percent each of Na_2O and K_2O .*

Polished sample etched with water for 2 seconds. Reflected light. Magnification 500 \times .



FIGURE 16.—*Same field as figure 15, but etched with water for 2 seconds, followed by 1-percent HNO_3 in alcohol for 2 seconds.*

Reflected light. Magnification 500 \times

and often crystallizes as extremely fine needles or dendritic forms, probably a product of devitrification of the glass.

The amount and composition of the glass also determine the amount of MgO crystallizing as the oxide. Quantitative microscopic analyses [10] show that the amount of free MgO is characteristically less than the total MgO in commercial clinker. As might be expected from phase relations [6], MgO is one of the last phases to crystallize in cement compositions, and therefore any glass formed will be saturated with MgO.

Crystalline interstitial materials other than C_4AF occur frequently in clinker with high Al_2O_3/Fe_2O_3 ratios, but are rarely if ever encountered in clinker with low ratios. Usually these crystalline interstitial compounds are prismatic in character and are apparently compounds of lime and alumina with alkalis. Their development depends upon cooling rates as well as composition, and wide variations may be observed in different pieces from the same clinker batch.

The precise computation of the actual compound composition of clinker from the chemical composition appears to be quite impossible without a more complete knowledge of the poly-component equilibrium system comprising the oxides in commercial clinker, and a determination of the temperatures in individual kiln installations at which crystallization is arrested and the formation of glass begins.

Quantitative microscopic methods using polished, etched specimens and reflected light are available, but at present lack precision, because: (1) the compositions of solid solution phases have not been accurately determined, and (2) no etching method permitting sharp distinction between crystalline and glassy dark interstitial material has been developed. Ward's⁸ method of etching with distilled water to distinguish between the rapidly etched crystalline material and the slowly etched glassy material is promising, but further studies of etching time and temperature are necessary for adequate control. The lack of uniformity in structure of commercial clinker also complicates the quantitative determination of compounds. Even where distribution of the major constituents is fairly uniform, rapid chilling of the outer portion of a clinker piece may produce a glass quite different from the glassy or crystalline interstitial materials in the interior of the piece.

VI. SUMMARY

The minor constituents in commercial portland cement clinker and in laboratory preparations of similar composition have been studied by microscopic and thermal methods. The microscopic methods included the examination of powdered preparations and thin sections with transmitted polarized light, polished etched sections with reflected light, and a combination of reflected and transmitted light using polished, etched thin sections.

Free MgO may be identified in polished unetched sections of commercial clinker and free CaO in sections etched with alcohol-water mixtures. Both free CaO and free MgO may be determined quantitatively in such sections.

The light interstitial material in cement clinker is shown to be $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$. New determinations of the relations in the binary system $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ -MgO have been made. $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ takes less than 1 percent of MgO into solid solution.

⁸ See footnote 4.

The dark interstitial material consists of three types: amorphous, rectangular, and prismatic. The amorphous material is glass. Characteristics and associations of the glassy material are given. Glassy material occurs in most commercial portland cement clinker. The rectangular material is $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, and is found only rarely in commercial clinker. The prismatic interstitial material frequently observed in commercial clinkers is probably a compound of lime, alumina and alkalis with a small amount of $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ in solid solution. Its close similarity to $3\text{CaO}\cdot\text{SiO}_2$ in optical properties has prevented its identification by petrographic methods. It is readily distinguished from $3\text{CaO}\cdot\text{SiO}_2$ in polished section by the use of suitable etchants. It is frequently found in commercial cement clinker with a moderately high $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ ratio. Laboratory-prepared clinker composed of CaO , Al_2O_3 , Fe_2O_3 and SiO_2 when cooled at moderate rates, contains rectangular dark interstitial material, whereas the same preparation with small amounts of Na_2O , K_2O , or both, contains prismatic dark interstitial material. The K_2O compound forming the prismatic crystals has not been identified. The Na_2O compound has properties very like those of the compound to which the formula $8\text{CaO}\cdot\text{Na}_2\text{O}\cdot 3\text{Al}_2\text{O}_3$ has been assigned by its discoverer.

Changes in composition of the minor constituents depending upon chemical composition and cooling condition of the clinker are discussed. Difficulties in quantitative determination of the compound composition of clinker are enumerated.

VII. REFERENCES

- [1] H. Insley, *J. Research NBS* **17**, 353 (1936) RP917.
- [2] A. H. White, *Ind. Eng. Chem.* **1**, 5 (1909).
- [3] Wm. Lerch and R. H. Bogue, *Ind. Eng. Chem. Anal. Ed.* **2**, 296 (1930).
- [4] B. Tavasci, *Giorn. Chim. Ind. Applicata* **16**, 538 (1934).
- [5] C. K. Wentworth, *J. Geol.* **31**, 228 (1923).
- [6] H. F. McMurdie and H. Insley, *J. Research NBS* **16**, 467 (1936) RP884.
- [7] Wm. Lerch and L. T. Brownmiller, *J. Research NBS* **18**, 609 (1937) RP997.
- [8] Wm. Lerch, *J. Research NBS* **20**, 77 (1938) RP1066.
- [9] Wm. Lerch and W. C. Taylor, *Concrete* **45**, 199, 217 (1937).
- [10] H. Insley, E. P. Flint, and J. A. Swenson (in preparation).
- [11] F. M. Lea and T. W. Parker, *Dept. Scientific and Ind. Research, Bldg. Research Tech. Pap.* 16 (1935).
- [12] H. F. McMurdie, *J. Research NBS* **18**, 475 (1937) RP987.
- [13] R. H. Bogue, *Ind. Eng. Chem. Anal. Ed.* **1**, 192, footnote (1929).
- [14] H. E. Schweite and H. zur Strassen, *Zement* **23**, 511 (1934).
- [15] W. C. Hansen, L. T. Brownmiller, and R. H. Bogue, *J. Am. Chem. Soc.* **50**, 396 (1928).
- [16] L. S. Brown, *Tricalcium aluminate and the microstructure of portland cement clinker*, American Society for Testing Materials, *Proc.* **37**, pt. 2, 277 (1937).
- [17] L. T. Brownmiller and R. H. Bogue, *Am. J. Sci.* **23**, 501 (1932).
- [18] L. T. Brownmiller, *Am. J. Sci.* **29**, 260 (1935).

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