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PHASE EQUILIBRIUM RELATIONS IN A PORTION OF THE SYSTEM $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$

By Kenneth T. Greene and R. H. Bogue

ABSTRACT

A study of a portion of the system $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ has been made as a step in the solution of the problem of the state of combination of Na_2O in portland cement clinker. Quenching data are given for compositions in the tetrahedron formed by $2\text{CaO}\cdot\text{SiO}_2$, CaO , $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3$, and Al_2O_3 , and phase diagrams are shown for three composition planes through the space model. Five invariant points were located approximately, at one of which $2\text{CaO}\cdot\text{SiO}_2$, $3\text{CaO}\cdot\text{SiO}_2$, $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, and $\text{Na}_2\text{O}\cdot 0.8\text{CaO}\cdot 0.3\text{Al}_2\text{O}_3$ are in equilibrium with liquid. This point, which is not a eutectic, occurs at $1,440^\circ \pm 10^\circ\text{C}$ and has a composition of 3.5 percent Na_2O , 55.2 percent CaO , 31.0 percent Al_2O_3 , and 10.3 percent SiO_2 . Evidence was obtained of the formation, under favorable conditions, of a solid solution between $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}\cdot 0.8\text{CaO}\cdot 0.3\text{Al}_2\text{O}_3$ at temperatures below that of liquid formation. Present information indicates that Na_2O may be present in clinker in several possible forms: (1) in glass, (2) as $\text{Na}_2\text{O}\cdot 0.8\text{CaO}\cdot 0.3\text{Al}_2\text{O}_3$ or a solid solution of this compound and $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, (3) in solid solution in $2\text{CaO}\cdot\text{SiO}_2$, (4) as inclusions of a soda-bearing phase in $\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$ produced by ex-solution on inversion from $\alpha\text{-}2\text{CaO}\cdot\text{SiO}_2$.

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I. INTRODUCTION

In order to understand the state of chemical combination of the various component oxides of portland cement, it is necessary first to study the interrelations of these oxides as systems of few components, gradually extending the scope of the investigations to include other oxides and, consequently, more complicated systems, as more and more data become available. The phase equilibrium relations of the major oxides of portland cement, CaO , SiO_2 , Al_2O_3 , Fe_2O_3 , and MgO have been rather thoroughly determined and the results are well known. However, it is only within the last few years that a systematic

attempt has been made to study the effect of such minor components as SO_3 , K_2O , Na_2O , TiO_2 , etc., upon the constitution of portland cement clinker. This paper represents part of an investigation undertaken to determine the manner in which one of these minor components, Na_2O , combines with the other oxides of clinker.

The quaternary system $\text{Na}_2\text{O-CaO-Al}_2\text{O}_3\text{-SiO}_2$ is one of several which have a direct bearing on the effect of Na_2O on the phase composition of portland cement clinker. It is probably the most important of these systems, since it contains the three oxides which are usually in greatest abundance, CaO , SiO_2 , and Al_2O_3 . Ferric oxide is the only major component of clinker that is likely to have any radical effect on the phase relations as determined in the $\text{Na}_2\text{O-CaO-Al}_2\text{O}_3\text{-SiO}_2$ system, since MgO has been shown to exist in clinker essentially uncombined [1, 2, 3].

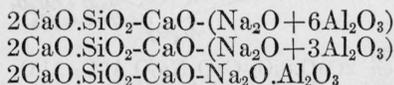
One of the four ternary systems bounding the four-component system, which has been determined, is the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ originally studied by Rankin and Wright [4]. Portions of the other three ternary systems, each of which contains Na_2O as a component, have also been studied. However, the only earlier work which has a direct application to portland cement compositions is that of Brown-miller and Bogue on the system $\text{Na}_2\text{O-CaO-Al}_2\text{O}_3$ [5]. They investigated the region of the smaller ternary system $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-CaO-Al}_2\text{O}_3$. The most important result of this work was the discovery of a compound having the formula, $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 0.3\text{Al}_2\text{O}_3$, and being capable of existing in equilibrium with $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. As $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ is a constituent of portland cement clinker, it appeared that this compound had a possibility of existence in clinkers containing Na_2O . However, the behavior of $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 0.3\text{Al}_2\text{O}_3$ in the presence of the calcium silicates, $3\text{CaO} \cdot \text{SiO}_2$, and $2\text{CaO} \cdot \text{SiO}_2$, had not yet been determined.

Certain limited portions of the quaternary system have also been investigated, but the ranges of composition of these are mostly far removed from the region of interest from the standpoint of portland cement. Consequently, such data will not be considered here. A previous paper from this laboratory by one of the present authors [6] dealt with solid solutions which the compound $2\text{CaO} \cdot \text{SiO}_2$ may form under suitable conditions in the system $\text{Na}_2\text{O-CaO-Al}_2\text{O}_3\text{-SiO}_2$, as well as in the system $\text{Na}_2\text{O-CaO-Fe}_2\text{O}_3\text{-SiO}_2$. It was shown that these solid solution phases have a hexagonal crystal structure and that this structure very likely is fundamentally that of the α form of $2\text{CaO} \cdot \text{SiO}_2$. The relation of these phases to the $2\text{CaO} \cdot \text{SiO}_2$ of commercial portland cement clinker was discussed at some length in this paper.

To determine whether $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 0.3\text{Al}_2\text{O}_3$ is the compound of Na_2O which is stable in mixtures of Na_2O , CaO , Al_2O_3 , and SiO_2 in which these oxides are present in the same proportions as in portland cement, it was necessary to study in some detail the phase equilibria in that part of the quaternary system which contains the compounds $3\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, and $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 0.3\text{Al}_2\text{O}_3$. For this purpose the portion of the system consisting of compositions which may be made up of the four compounds $2\text{CaO} \cdot \text{SiO}_2$, CaO , $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3$, and Al_2O_3 was chosen. When a regular tetrahedron is used to represent the larger oxide system $\text{Na}_2\text{O-CaO-Al}_2\text{O}_3\text{-SiO}_2$, the four compounds $2\text{CaO} \cdot \text{SiO}_2$, CaO , $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3$, and Al_2O_3 are at the apexes of a tetrahedron of unequal dimensions which occupies a space within the larger tetrahedron.

Various methods are possible for representing the space relations in the model of a four-component system. The ultimate purpose is to define the limits of the regions of primary crystallization of the various phases, called primary phase volumes, and to determine the temperature relations within the primary phase volumes and particularly on the surfaces, along the lines, and at the points where two, three, or four primary phase volumes adjoin one another. It is customary to select various lines or planes through the space model and to determine the manner in which these intersect the primary phase volumes. The lines or planes may represent binary or ternary systems within the quaternary system, they may represent joins which are not true binary or ternary systems, or they may depict planes having arbitrary compositional relationships. An example of the latter type is a series of planes parallel to one face of the tetrahedron, each plane containing a certain constant percentage of the fourth component. Lea and Parker [7] and Schairer [8] discuss in detail methods of studying quaternary systems, and give diagrams to illustrate the manner in which the data may be presented.

In the present investigation, the phase equilibrium relations of three composition planes through the tetrahedral space model have been studied, as well as a number of extra compositions situated between the planes. Each plane, which is triangular in shape, has the compounds $2\text{CaO}.\text{SiO}_2$ and CaO at two of its apexes. The third apex represents a mixture of Na_2O and Al_2O_3 in a certain definite proportion. All compositions in the same plane therefore contain Na_2O and Al_2O_3 in a constant molar ratio. One of the planes corresponds to one side of the smaller tetrahedron $2\text{CaO}.\text{SiO}_2-\text{CaO}-\text{Na}_2\text{O}.\text{Al}_2\text{O}_3-\text{Al}_2\text{O}_3$, whereas the other two occupy positions within it. They may be represented as follows:



The planes are arranged in order of increasing proportion of Na_2O .

Each of the first two planes is a section through the quaternary system, in which one of the three components is an arbitrary mixture of Na_2O and Al_2O_3 . In the third plane, however, the corresponding component is the definite chemical compound, sodium aluminate. Figure 1 shows the relation of these planes and of the smaller tetrahedron $2\text{CaO}.\text{SiO}_2-\text{CaO}-\text{Na}_2\text{O}.\text{Al}_2\text{O}_3-\text{Al}_2\text{O}_3$ to the tetrahedron representing the complete $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system.

II. EXPERIMENTAL METHOD

The quenching method of thermal study was used throughout this investigation. The procedure followed was in general similar to that described in previous publications of this laboratory pertaining to alkali systems [5, 9, 10]. In certain cases minor changes were made, as dictated by the conditions encountered.

As in the earlier work with alkalis, volatilization was a problem, particularly in compositions having a relatively high percentage of Na_2O . For this reason most of the mixtures were given no preliminary heat treatment prior to making the quenching determinations, and the time held at constant temperature was kept as short as possible

consistent with the attainment of equilibrium. By this means the volatilization of Na_2O was kept at a minimum, and in the great majority of cases it was not found necessary to add an excess of soda to compensate for this loss.

To test the extent of loss of Na_2O by volatilization, and also the accuracy of proportioning of the raw materials, several representative mixes were analyzed chemically for Na_2O after heating for one-half hour at temperatures near those of the quenching experiments. The samples analyzed cover a rather large range of Na_2O percentages, and the results indicate that, with the exception of those relatively

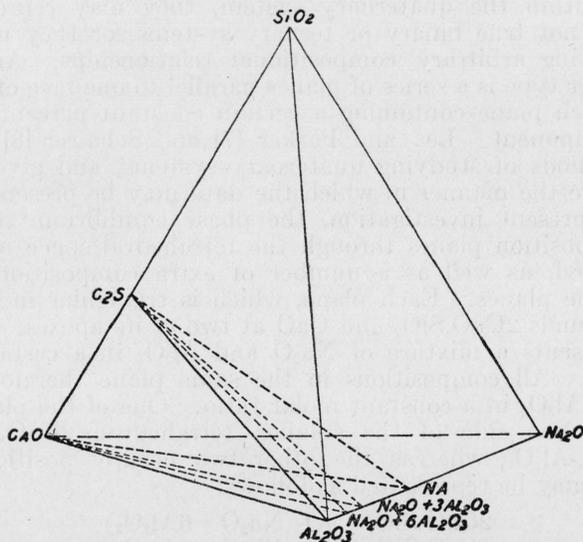


FIGURE 1.—Tetrahedron $2\text{CaO} \cdot \text{SiO}_2$ - CaO - Na_2O - Al_2O_3 - Al_2O_3 in relation to system Na_2O - CaO - Al_2O_3 - SiO_2 .

high in Na_2O , the volatilization is negligible and the amounts of Na_2O are close to those desired. The data are tabulated below.

Mix number	Na_2O desired %	Na_2O found %
19	11.34	10.99
24	3.78	3.79
60	1.69	1.63
101	5.90	5.89
204	3.88	3.97

The omission of preliminary heatings and grindings of the samples used in the quenching furnace made it essential that the raw materials be very thoroughly mixed the first time. This was accomplished by prolonged grinding together of the ingredients in an agate mortar. The distribution of solid phases in the quenched charges, as observed microscopically, indicated that satisfactory mixing had been obtained.

The presence of vapors of Na_2O in the quenching furnace made it necessary to recalibrate the thermocouple frequently. This was done at times against a standard couple, but more often checks were made against the known melting points of the pure compounds $\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$ ($1,391.5^\circ \text{C}$) and $\text{BaO} \cdot 2\text{SiO}_2$ ($1,418^\circ \text{C}$).

III. PHASE EQUILIBRIA

1. GENERAL DISCUSSION

The data on the phase equilibrium relations, as determined by the quenching procedure, are presented in tables 1, 2, 3, and 4. These contain those critical determinations that furnish information necessary to the interpretation of the system. However, they represent only a fraction of the total number of quenching experiments performed. In order to reduce the length of the tables, many data that do not contribute essential information have been omitted. For example, in cases where it was desired to show only which crystalline phase is primary, the results of only one quench are given. Near invariant points or where the liquidus temperatures were determined, data on more than one quench are recorded. In the tables and diagrams the following abbreviations are used:

- $\text{C}_3\text{S} = 3\text{CaO} \cdot \text{SiO}_2$
- $\text{C}_2\text{S} = 2\text{CaO} \cdot \text{SiO}_2$
- $\text{C}_2\text{A} = 3\text{CaO} \cdot \text{Al}_2\text{O}_3$
- $\text{NC}_3\text{A}_3 = \text{Na}_2\text{O} \cdot 8\text{CaO} \cdot 3\text{Al}_2\text{O}_3$
- $\text{C}_5\text{A}_3 = 5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ ¹
- $\text{C}_2\text{AS} = 2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$
- $\text{CA} = \text{CaO} \cdot \text{Al}_2\text{O}_3$
- $\text{C}_3\text{A}_5 = 3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$
- $\text{N}_2\text{C}_3\text{A}_5 = 2\text{Na}_2\text{O} \cdot 3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$
- $\text{N}_2\text{C}_3\text{A}_{5\text{SS}} = 2\text{Na}_2\text{O} \cdot 3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$ solid solution with $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3$
- $\text{NA} = \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3$
- $\text{Tr.} = \text{Trace}$
- $\text{Amt.} = \text{Amount.}$

TABLE 1.—Quenching data for compositions in the $2\text{CaO} \cdot \text{SiO}_2-\text{CaO}-(\text{Na}_2\text{O} + 6\text{Al}_2\text{O}_3)$ plane

No.	Composition							Time	Temperature	Phases present
	Oxides				Components					
	Na_2O	CaO	Al_2O_3	SiO_2	C_3S	CaO	$(\text{Na}_2\text{O} + 6\text{Al}_2\text{O}_3)$			
CaO PRIMARY										
	%	%	%	%	%	%	%	hr	°C	
191	4.1	55.0	40.9	-----	-----	55.0	45.0	$\left\{ \begin{array}{l} 1/2 \\ 1/2 \\ 1/2 \end{array} \right.$	1, 530	CaO, glass.
									1, 520	C_2A , tr. CaO , glass.
192	3.7	56.0	36.8	3.5	10.0	49.5	40.5	$\left\{ \begin{array}{l} 1/2 \\ 1/2 \\ 1/2 \end{array} \right.$	1, 520	CaO, glass.
									1, 515	C_2A , CaO , glass.
193	3.3	57.0	32.7	7.0	20.0	44.0	36.0	$\left\{ \begin{array}{l} 1/2 \\ 1/2 \\ 1/2 \end{array} \right.$	1, 485	CaO, glass.
									1, 475	CaO , C_2A , tr. NC_3A_3 , glass.
194	2.9	58.0	28.6	10.5	30.0	38.5	31.5	$\left\{ \begin{array}{l} 1/2 \\ 1/2 \\ 1/2 \end{array} \right.$	1, 510	Tr. CaO , tr. C_3S , glass.
									1, 480	CaO , C_3S , glass.

¹ That the results of this investigation might be compared more readily with the literature on the $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system, the formula $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ is used throughout the paper, although it is recognized that strong evidence has been presented by various authors indicating that the correct formula is $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ [18, 19, 20, 21].

TABLE 1.—*Quenching data for compositions in the 2CaO.SiO₂-CaO-(Na₂O+6Al₂O₃) plane—Continued*

No.	Composition							Time	Temperature	Phases present			
	Oxides				Components								
	Na ₂ O	CaO	Al ₂ O ₃	SiO ₂	C ₂ S	CaO	(Na ₂ O+6Al ₂ O ₃)						
C₃S PRIMARY													
196	2.7	58.5	26.6	12.2	40.0	33.0	27.0	$\left\{ \begin{array}{l} \frac{1}{8} \\ \frac{1}{2} \\ \frac{1}{2} \end{array} \right.$	$\left\{ \begin{array}{l} 1,525 \\ 1,485 \\ 1,475 \end{array} \right.$	C ₃ S, tr. CaO, glass. C ₃ S, CaO, glass. Small amt. C ₂ S, tr. CaO, glass.			
197	3.0	56.3	30.2	10.5	30.0	36.8	33.2				$\left\{ \begin{array}{l} \frac{1}{8} \\ \frac{1}{2} \\ \frac{1}{2} \end{array} \right.$	$\left\{ \begin{array}{l} 1,460 \\ 1,450 \\ 1,475 \end{array} \right.$	C ₃ S, tr. CaO, tr. C ₂ S, glass. C ₃ S, C ₂ S, C ₃ A, glass. C ₂ S, tr. C ₂ S, glass.
199	3.0	56.6	29.1	11.3	32.5	35.4	32.1						
C₂S PRIMARY													
120	2.8	45.6	27.2	24.4	70.0	-----	30.0	$\left\{ \begin{array}{l} \frac{1}{8} \\ \frac{1}{2} \\ \frac{1}{2} \end{array} \right.$	$\left\{ \begin{array}{l} 1,510 \\ 1,500 \\ 1,360 \end{array} \right.$	Tr. C ₂ S, glass. C ₂ S, C ₂ AS, glass. C ₂ S, glass.			
132	1.8	59.0	18.2	21.0	60.4	19.6	20.0				$\left\{ \begin{array}{l} \frac{1}{8} \\ \frac{1}{2} \\ \frac{1}{2} \end{array} \right.$	$\left\{ \begin{array}{l} 1,355 \\ 1,450 \\ 1,450 \end{array} \right.$	C ₂ S, C ₂ A ₃ , glass. C ₂ S, glass. All glass.
133	2.8	51.6	27.2	18.4	52.8	17.2	30.0						
134	3.7	44.2	36.3	15.8	45.3	14.7	40.0	$\left\{ \begin{array}{l} \frac{1}{8} \\ \frac{1}{2} \\ \frac{1}{2} \end{array} \right.$	$\left\{ \begin{array}{l} 1,435 \\ 1,440 \\ 1,435 \end{array} \right.$	C ₂ S, C ₃ A, glass. C ₂ S, glass. C ₂ S, small amt. C ₃ A, glass.			
143	3.2	54.5	31.8	10.5	30.0	35.0	35.0				$\left\{ \begin{array}{l} \frac{1}{8} \\ \frac{1}{2} \\ \frac{1}{2} \end{array} \right.$	$\left\{ \begin{array}{l} 1,375 \\ 1,370 \\ 1,370 \end{array} \right.$	C ₂ S, N C ₂ A ₃ , glass. C ₂ S, C ₂ A ₃ , N C ₂ A ₃ , glass. Almost completely crystalline.
146	3.0	55.3	29.5	12.2	35.0	32.5	32.5						
153	3.5	51.0	35.0	10.5	30.0	31.5	38.5	$\left\{ \begin{array}{l} \frac{1}{8} \\ \frac{1}{2} \\ \frac{1}{2} \end{array} \right.$	$\left\{ \begin{array}{l} 1,370 \\ 1,370 \\ 1,370 \end{array} \right.$	C ₂ S, glass. C ₂ S, C ₂ A ₃ , glass. C ₂ S, glass.			
158	3.9	47.5	38.1	10.5	30.0	28.0	42.0				$\left\{ \begin{array}{l} \frac{1}{8} \\ \frac{1}{2} \\ \frac{1}{2} \end{array} \right.$	$\left\{ \begin{array}{l} 1,365 \\ 1,375 \\ 1,375 \end{array} \right.$	C ₂ S, C ₂ A ₃ , glass. C ₂ S, glass. Do.
165	3.7	50.5	36.2	9.6	27.5	32.6	39.9						
170	3.9	45.5	38.4	12.2	35.0	22.7	42.3	$\left\{ \begin{array}{l} \frac{1}{8} \\ \frac{1}{2} \\ \frac{1}{2} \end{array} \right.$	$\left\{ \begin{array}{l} 1,375 \\ 1,375 \\ 1,375 \end{array} \right.$	Do. Tr. C ₂ S, glass. C ₂ S, C ₂ A ₃ , glass.			
184	4.1	43.5	40.9	11.5	33.0	22.0	45.0				$\left\{ \begin{array}{l} \frac{1}{8} \\ \frac{1}{2} \\ \frac{1}{2} \end{array} \right.$	$\left\{ \begin{array}{l} 1,350 \\ 1,345 \\ 1,525 \end{array} \right.$	C ₂ S, C ₂ S, glass.
195	2.5	59.1	24.5	13.9	40.0	33.0	27.0						
198	2.8	57.0	28.0	12.2	35.0	34.1	30.9	$\left\{ \begin{array}{l} \frac{1}{4} \\ \frac{1}{2} \\ \frac{1}{2} \end{array} \right.$	$\left\{ \begin{array}{l} 1,475 \\ 1,460 \\ 1,450 \end{array} \right.$	C ₂ S, tr. C ₃ S, glass. C ₂ S, C ₂ S, glass. C ₂ S, C ₂ S, C ₃ A, glass. C ₂ S, C ₂ A, glass.			
C₃A PRIMARY													
140	4.6	50.0	45.4	-----	-----	50.0	50.0				$\left\{ \begin{array}{l} \frac{1}{2} \\ \frac{1}{2} \\ \frac{1}{2} \end{array} \right.$	$\left\{ \begin{array}{l} 1,450 \\ 1,505 \\ 1,465 \end{array} \right.$	C ₃ A, glass. Small amt. C ₃ A, glass. All glass.
141	4.1	51.5	40.9	3.5	10.0	45.0	45.0	$\left\{ \begin{array}{l} \frac{1}{2} \\ \frac{1}{2} \\ \frac{1}{2} \end{array} \right.$	$\left\{ \begin{array}{l} 1,460 \\ 1,450 \\ 1,450 \end{array} \right.$	Tr. C ₃ A, glass. All glass.			
142	3.7	53.0	36.3	7.0	20.0	40.0	40.0						
145	3.4	53.8	34.1	8.7	25.0	37.5	37.5				$\left\{ \begin{array}{l} \frac{1}{4} \\ \frac{1}{2} \\ \frac{1}{2} \end{array} \right.$	$\left\{ \begin{array}{l} 1,445 \\ 1,445 \\ 1,445 \end{array} \right.$	All glass. C ₃ A, glass. C ₃ A, tr. C ₂ S, glass.
147	3.3	54.2	32.9	9.6	27.5	36.3	36.2	$\left\{ \begin{array}{l} \frac{1}{2} \\ \frac{1}{2} \\ \frac{1}{2} \end{array} \right.$	$\left\{ \begin{array}{l} 1,445 \\ 1,440 \\ 1,450 \end{array} \right.$	All glass. C ₃ A, tr. C ₂ S, glass. All glass.			
160	4.3	49.3	42.9	3.5	10.0	42.7	47.3						
161	3.9	51.0	38.1	7.0	20.0	38.0	42.0				$\left\{ \begin{array}{l} \frac{1}{8} \\ \frac{1}{2} \\ \frac{1}{2} \end{array} \right.$	$\left\{ \begin{array}{l} 1,420 \\ 1,410 \\ 1,415 \end{array} \right.$	All glass. C ₃ A, glass. C ₃ A, tr. C ₂ S, glass.
162	3.6	51.9	35.8	8.7	25.0	35.6	39.4	$\left\{ \begin{array}{l} \frac{1}{8} \\ \frac{1}{2} \\ \frac{1}{2} \end{array} \right.$	$\left\{ \begin{array}{l} 1,420 \\ 1,415 \end{array} \right.$	All glass. C ₃ A, tr. C ₂ S, glass.			

TABLE 1.—*Quenching data for compositions in the $2CaO.SiO_2-CaO-(Na_2O+6Al_2O_3)$ plane—Continued*

No.	Composition							Time	Temperature	Phases present
	Oxides				Components					
	Na ₂ O	CaO	Al ₂ O ₃	SiO ₂	C ₂ S	CaO	(Na ₂ O+6Al ₂ O ₃)			
NC₃A₃ PRIMARY										
152	%	%	%	%	%	%	%	hr	°C	
	4.0	49.0	40.0	7.0	20.0	36.0	44.0	1/2	1,400	All glass.
								1/3	1,390	Tr. NC ₃ A ₃ , tr. C ₃ A ₃ , glass.
								1/3	1,385	NC ₃ A ₃ , C ₃ A ₃ , glass.
								1/3	1,375	Tr. NC ₃ A ₃ , glass.
								1/3	1,370	NC ₃ A ₃ , C ₃ A ₃ , C ₂ S, glass.
154	3.8	50.0	37.5	8.7	25.0	33.7	41.3	1/3	1,365	C ₃ A ₃ , C ₂ S, prob. NC ₃ A ₃ and C ₃ A, small amt. glass.
								1/3	1,360	Almost completely crystalline.
C₅A₃ PRIMARY										
150	5.1	45.0	49.9	-----	-----	45.0	55.0	1/2	1,450	All glass.
								1/2	1,445	C ₅ A ₃ , glass.
151	4.5	47.0	45.0	3.5	10.0	40.5	49.5	1/3	1,425	All glass.
								1/3	1,420	C ₅ A ₃ , glass.
156	5.0	42.5	49.0	3.5	10.0	36.0	54.0	1/3	1,440	All glass.
								1/3	1,435	C ₅ A ₃ , glass.
157	4.4	45.0	43.6	7.0	20.0	32.0	48.0	1/3	1,410	All glass.
159	4.1	46.3	40.9	8.7	25.0	30.0	45.0	1/3	1,405	Tr. C ₅ A ₃ , glass.
163	4.2	47.0	41.8	7.0	20.0	34.0	46.0	1/3	1,390	Do.
								1/3	1,400	Perhaps tr. C ₅ A ₃ , glass.
164	4.0	48.1	39.2	8.7	25.0	31.9	43.1	1/3	1,395	C ₅ A ₃ , glass.
								1/3	1,370	Do.
								1/3	1,365	C ₅ A ₃ , C ₂ S, glass.
168	4.8	41.0	47.2	7.0	20.0	28.0	52.0	1/3	1,390	All glass.
								1/3	1,380	C ₅ A ₃ , glass.
169	4.2	44.0	41.3	10.5	30.0	24.5	45.5	1/3	1,375	All glass.
								1/3	1,360	C ₅ A ₃ , glass.
175	5.1	38.7	49.9	6.3	18.0	27.0	55.0	1/3	1,400	All glass.
								1/4	1,390	C ₅ A ₃ , perhaps tr. CA, glass.
181	4.6	41.3	45.4	8.7	25.0	25.0	50.0	1/3	1,370	All glass.
								1/3	1,365	C ₅ A ₃ , glass.
183	4.6	40.4	45.4	9.6	27.5	22.5	50.0	1/3	1,350	Tr. C ₅ A ₃ , glass.
								1/3	1,345	C ₅ A ₃ , tr. C ₂ AS, glass.
C₂AS PRIMARY										
122	4.6	32.6	45.4	17.4	50.0	-----	50.0	1/3	1,510	All glass.
								1/3	1,505	C ₂ AS, glass.
128	4.8	30.9	47.7	16.6	52.5	-----	47.5	1/4	1,500	Tr. C ₂ AS, glass.
135	4.6	36.9	45.4	13.1	37.7	12.3	50.0	1/3	1,475	All glass.
								1/3	1,460	C ₂ AS, glass.
137	5.1	33.2	49.9	11.8	34.0	11.0	55.0	1/3	1,450	Tr. C ₂ AS, glass.
180	5.1	34.0	49.9	11.0	31.5	13.5	55.0	1/4	1,425	C ₂ AS, glass.
182	4.6	39.5	45.4	10.5	30.0	20.0	50.0	1/3	1,375	Tr. C ₂ AS, glass.
185	4.1	41.6	40.9	13.4	38.5	16.5	45.0	1/3	1,395	C ₂ AS, glass.
186	4.1	42.5	40.9	12.5	35.8	19.2	45.0	1/3	1,375	All glass.
								1/3	1,350	C ₂ AS, glass.
187	4.4	41.5	43.1	11.0	31.5	21.0	47.5	1/2	1,350	C ₂ AS, glass.

TABLE 1.—*Quenching₂ data for compositions in the 2CaO.SiO₂-CaO-(Na₂O+6Al₂O₃) plane—Continued*

No.	Composition							Time	Temperature	Phases present	
	Oxides				Components						
	Na ₂ O	CaO	Al ₂ O ₃	SiO ₂	C ₂ S	CaO	(Na ₂ O+6Al ₂ O ₃)				
CA PRIMARY											
171	5.5	33.0	54.5	7.0	20.0	20.0	60.0	}	$\frac{1}{4}$	1,425	CA, tr. N ₂ C ₂ A ₅ , glass.
172	5.1	37.2	49.9	7.8	22.5	22.5	55.0		$\frac{1}{8}$	1,410	CA, N ₂ C ₂ A ₅ , glass.
173	5.5	34.4	54.5	5.6	16.0	24.0	60.0	}	$\frac{1}{4}$	1,400	CA, glass.
176	5.5	31.6	54.5	8.4	24.0	16.0	60.0		$\frac{1}{4}$	1,435	Tr. CA, glass.
179	5.1	35.6	49.9	9.4	27.0	18.0	55.0	}	$\frac{1}{4}$	1,430	CA, tr. N ₂ C ₂ A ₅ , glass.
189	6.0	30.1	59.0	4.9	14.0	21.0	65.0		$\frac{1}{4}$	1,450	Tr. CA, glass.
									$\frac{1}{8}$	1,400	CA, glass.
									$\frac{1}{8}$	1,465	All glass.
									$\frac{1}{6}$	1,455	Tr. CA, glass.
N₂C₂A₅ PRIMARY											
155	5.5	40.0	54.5	-----	-----	40.0	60.0	}	$\frac{1}{8}$	1,470	All glass.
166	6.0	35.0	59.0	-----	-----	35.0	65.0		$\frac{1}{8}$	1,465	N ₂ C ₂ A ₅ , C ₂ A ₃ , glass.
167	5.4	38.0	53.1	3.5	10.0	31.5	58.5	}	$\frac{1}{4}$	1,475	N ₂ C ₂ A ₅ , glass.
174	5.5	35.8	54.5	4.2	12.0	28.0	60.0		$\frac{1}{4}$	1,425	All glass.
188	6.0	31.3	59.0	3.7	10.5	24.5	65.0	}	$\frac{1}{4}$	1,420	Tr. N ₂ C ₂ A ₅ , glass.
									$\frac{1}{2}$	1,435	N ₂ C ₂ A ₅ , glass.
									$\frac{1}{4}$	1,475	All glass.
									$\frac{1}{4}$	1,465	N ₂ C ₂ A ₅ , glass.
C₂A₃ PRIMARY											
123	5.5	26.1	54.5	13.9	40.0	-----	60.0	}	$\frac{1}{4}$	1,550	C ₂ A ₃ , glass.
124	6.4	19.5	63.6	10.5	30.0	-----	70.0		$\frac{1}{6}$	1,600	Do.
126	5.1	29.3	49.9	15.7	45.0	-----	55.0	}	$\frac{1}{8}$	1,475	Do.
136	5.5	29.5	54.5	10.5	30.2	9.8	60.0		$\frac{1}{8}$	1,460	Do.
177	5.5	30.2	54.5	9.8	28.0	12.0	60.0	}	$\frac{1}{4}$	1,460	Do.
178	5.5	30.9	54.5	9.1	26.0	14.0	60.0		$\frac{1}{4}$	1,450	Do.
190	6.0	28.9	59.0	6.1	17.5	17.5	65.0	}	$\frac{1}{4}$	1,440	C ₂ A ₃ , tr. CA, glass.
									$\frac{1}{4}$	1,435	C ₂ A ₃ , CA, glass.
									$\frac{1}{6}$	1,460	C ₂ A ₃ , glass.
Al₂O₃ PRIMARY											
125	6.9	16.3	68.1	8.7	25.0	-----	75.0	}	$\frac{1}{6}$	1,600	α -Al ₂ O ₃ , C ₂ A ₃ , glass.
									$\frac{1}{4}$	1,550	α -Al ₂ O ₃ , more C ₂ A ₃ , glass. Probably in Al ₂ O ₃ field.

TABLE 2.—Quenching data for compositions in the $2CaO.SiO_2-CaO-(Na_2O+3Al_2O_3)$ plane—Continued

No.	Composition							Time	Temperature	Phases present
	Oxides				Components					
	Na ₂ O	CaO	Al ₂ O ₃	SiO ₂	C ₂ S	CaO	(Na ₂ O+3Al ₂ O ₃)			
CaO PRIMARY										
78	%	%	%	%	%	%	%	hr	°C	Small amt. CaO, glass. NC ₃ A ₃ , glass.
	8.4	50.0	41.6	-----	-----	50.0	50.0	1/2	1,510	
79	8.4	48.3	41.6	1.7	5.0	45.0	50.0	1/2	1,500	Tr. CaO, glass.
90	7.6	51.2	37.4	3.8	11.0	44.0	45.0	1/2	1,490	NC ₃ A ₃ , tr. CaO, glass.
100	6.7	53.0	33.3	7.0	20.0	40.0	40.0	1/2	1,500	CaO, glass.
101	5.9	54.5	29.1	10.5	30.0	35.0	35.0	1/2	1,490	NC ₃ A ₃ , CaO, glass.
102	5.1	56.1	24.9	13.9	40.0	30.0	30.0	1/2	1,485	CaO, glass.
105	5.5	55.3	27.0	12.2	35.0	32.5	32.5	1/2	1,465	NC ₃ A ₃ , CaO, glass.
107	5.7	53.7	28.4	12.2	35.0	30.9	34.1	1/2	1,450	CaO, glass.
								3/4	1,455	CaO, C ₂ S, glass. Near boundary.
								1	1,440	CaO, glass.
								1	1,445	CaO, tr. C ₂ S, tr. C ₂ S, glass.
								1	1,440	NC ₃ A ₃ , C ₂ S, CaO, glass.
								1	1,445	Tr. CaO, glass.
								1/2	1,440	CaO, tr. C ₂ S, glass.
								1/2	1,435	C ₂ S, NC ₃ A ₃ , glass.
C ₂ S PRIMARY										
109	4.8	56.5	23.9	14.8	42.5	28.8	28.7	3/4	1,525	C ₂ S, C ₂ S, glass. Near boundary.
C ₂ S PRIMARY										
50	1.7	58.6	8.3	31.4	90.0	-----	10.0	1/2	1,500	C ₂ S, glass.
51	3.4	52.1	16.6	27.9	80.0	-----	20.0	1/2	1,500	Do.
52	5.1	45.6	24.9	24.4	70.0	-----	30.0	1/2	1,375	C ₂ S, C ₂ AS, glass.
60	1.7	66.3	8.3	23.7	67.9	22.1	10.0	1	1,450	C ₂ S, glass.
61	3.4	59.0	16.6	21.0	60.4	19.6	20.0	1/2	1,400	C ₂ S, C ₂ AS, glass.
62	5.1	51.6	24.9	18.4	52.8	17.2	30.0	1/2	1,400	C ₂ S, C ₂ S, small amt. glass. Probably in C ₂ S field.
63	6.7	44.2	33.3	15.8	45.3	14.7	40.0	1/2	1,500	C ₂ S, glass.
66	7.6	40.5	37.4	14.5	41.5	13.50	45.0	1/2	1,340	Do.
70	6.7	41.2	33.3	18.8	54.0	6.0	40.0	1/2	1,325	C ₂ S, N ₂ C ₂ A ₃ ss, glass.
73	7.6	39.1	37.4	15.9	45.5	9.5	45.0	1/2	1,350	Tr. C ₂ S, glass.
88	6.0	52.1	29.7	12.2	35.0	29.2	35.8	1/2	1,390	C ₂ S, C ₂ AS, glass.
89	5.6	53.1	27.4	13.9	40.0	27.0	33.0	1/2	1,440	Tr. C ₂ S, glass.
92	7.6	43.5	37.4	11.5	33.0	22.0	45.0	1/2	1,435	C ₂ S, NC ₃ A ₃ , glass.
95	6.8	48.2	33.6	11.4	32.6	27.0	40.4	1/2	1,440	C ₂ S, glass.
103	4.2	57.6	20.8	17.4	50.0	25.0	25.0	1/2	1,425	C ₂ S, tr. C ₂ S, glass.
106	4.6	56.8	22.9	15.7	45.0	27.5	27.5	1/2	1,375	Tr. C ₂ S, glass.
								1/2	1,525	C ₂ S, tr. C ₂ S, glass.
NC ₃ A ₃ PRIMARY										
74	9.3	45.0	45.7	-----	-----	45.0	55.0	1/2	1,470	NC ₃ A ₃ , glass.
75	9.3	43.4	45.7	1.6	4.5	40.5	55.0	1/2	1,450	All glass.
80	8.4	46.5	41.6	3.5	10.0	40.0	50.0	1/2	1,445	NC ₃ A ₃ , small amt. N ₂ C ₂ A ₃ , glass.
81	8.4	44.8	41.6	5.2	15.0	35.0	50.0	1/2	1,460	Near boundary.
85	7.4	49.0	36.6	7.0	20.0	36.0	44.0	1/2	1,425	All glass.
87	6.5	51.0	32.0	10.5	30.0	31.5	38.5	1/2	1,455	NC ₃ A ₃ , glass.
								1/2	1,420	NC ₃ A ₃ , glass.
								1/2	1,460	Tr. NC ₃ A ₃ , glass.
								1/2	1,450	All glass.
								1/2	1,440	NC ₃ A ₃ , glass.

TABLE 2.—*Quenching data for compositions in the 2CaO.SiO₂-CaO-(Na₂O+3Al₂O₃) plane—Continued*

No.	Composition							Time	Temperature	Phases present
	Oxides				Components					
	Na ₂ O	CaO	Al ₂ O ₃	SiO ₂	C ₂ S	CaO	(Na ₂ O+3Al ₂ O ₃)			
C₃A₃ PRIMARY										
	%	%	%	%	%	%	%	hr	°C	
91	7.6	45.4	37.4	9.6	27.5	27.5	45.0	$\left\{ \begin{array}{l} 1/8 \\ 1/2 \\ 1/2 \\ 1/2 \\ 1/2 \end{array} \right.$	1,375 1,360 1,355 1,360 1,345	All glass. Tr. C ₃ A ₃ glass. C ₃ A ₃ , N ₂ C ₃ A ₅ glass. C ₃ A ₃ , tr. C ₂ S, glass. C ₃ A ₃ , C ₂ S, N ₂ C ₃ A ₅ ss, glass.
93	7.6	44.4	37.4	10.6	30.3	24.7	45.0	$\left\{ \begin{array}{l} 1/8 \\ 1/2 \\ 1/2 \\ 1/2 \end{array} \right.$	1,335 1,335 1,370 1,360	All crystalline. All glass. All glass. C ₃ A ₃ , glass.
94	7.8	44.4	38.4	9.4	26.9	26.9	46.2	$\left\{ \begin{array}{l} 1/8 \\ 1/2 \\ 1/2 \end{array} \right.$	1,370 1,360 1,360	All glass. C ₃ A ₃ , glass. C ₃ A ₃ , glass.
C₂A₃ PRIMARY										
53	6.7	39.1	33.3	20.9	60.0	-----	40.0	$\left\{ \begin{array}{l} 1/2 \\ 1/2 \end{array} \right.$	1,430 1,420	All glass. C ₂ A ₃ , glass.
54	8.4	32.6	41.6	17.4	50.0	-----	50.0	$\left\{ \begin{array}{l} 1/2 \\ 1/2 \\ 1/2 \end{array} \right.$	1,420 1,415 1,435	All glass. C ₂ A ₃ , glass. All glass.
59	7.6	35.8	37.4	19.2	55.0	-----	45.0	$\left\{ \begin{array}{l} 1/2 \\ 1/2 \\ 1/2 \end{array} \right.$	1,425 1,425 1,395	C ₂ A ₃ , glass. C ₂ A ₃ , glass. All glass.
72	7.6	37.7	37.4	17.3	49.5	5.5	45.0	$\left\{ \begin{array}{l} 1/2 \\ 1/2 \end{array} \right.$	1,395 1,385	All glass. C ₂ A ₃ , glass.
N₂C₃A₅ SOLID SOLUTION PRIMARY										
55	10.1	26.1	49.9	13.9	40.0	-----	60.0	$\left\{ \begin{array}{l} 1/2 \\ 1/2 \end{array} \right.$	1,500 1,565	Tr. N ₂ C ₃ A ₅ ss, glass. Tr. N ₂ C ₃ A ₅ ss, glass.
56	11.8	19.5	58.2	10.5	30.0	-----	70.0	$\left\{ \begin{array}{l} 1/2 \\ 1/2 \\ 1/8 \end{array} \right.$	1,525 1,525 1,525	N ₂ C ₃ A ₅ ss, tr. "unstable" C ₃ A ₃ , glass.
58	9.3	29.3	45.7	15.7	45.0	-----	55.0	$\left\{ \begin{array}{l} 1/2 \\ 1/2 \\ 1/2 \end{array} \right.$	1,425 1,405 1,400	Tr. N ₂ C ₃ A ₅ ss, glass. All glass. All glass.
64	8.4	36.8	41.6	13.2	33.7	12.3	50.0	$\left\{ \begin{array}{l} 1/2 \\ 1/2 \\ 1/2 \end{array} \right.$	1,400 1,400 1,550	Tr. N ₂ C ₃ A ₅ ss, glass. All glass. All glass.
65	10.1	29.5	49.9	10.5	30.2	9.8	60.0	$\left\{ \begin{array}{l} 1/2 \\ 1/2 \\ 1/2 \end{array} \right.$	1,525 1,400 1,400	N ₂ C ₃ A ₅ ss, glass. All glass. All glass.
71	8.4	34.3	41.6	15.7	45.0	5.0	50.0	$\left\{ \begin{array}{l} 1/2 \\ 1/2 \\ 1/2 \end{array} \right.$	1,375 1,410 1,410	Tr. N ₂ C ₃ A ₅ ss, glass. N ₂ C ₃ A ₅ ss, glass. N ₂ C ₃ A ₅ ss, glass.
76	9.3	41.9	45.7	3.1	9.0	36.0	55.0	$\left\{ \begin{array}{l} 1/2 \\ 1/2 \\ 1/2 \end{array} \right.$	1,400 1,410 1,450	N ₂ C ₃ A ₅ ss, N ₂ C ₃ A ₅ , glass. N ₂ C ₃ A ₅ ss, glass. N ₂ C ₃ A ₅ ss, glass.
77	9.3	37.1	45.7	7.9	22.5	22.5	55.0	$\left\{ \begin{array}{l} 1/2 \\ 1/2 \\ 1/2 \end{array} \right.$	1,400 1,400 1,450	Tr. N ₂ C ₃ A ₅ ss, glass. Tr. N ₂ C ₃ A ₅ ss, glass. N ₂ C ₃ A ₅ ss, glass.
82	8.4	43.0	41.6	7.0	20.0	30.0	50.0	$\left\{ \begin{array}{l} 1/2 \\ 1/2 \\ 1/2 \end{array} \right.$	1,400 1,375 1,410	Tr. N ₂ C ₃ A ₅ ss, glass. N ₂ C ₃ A ₅ ss, C ₃ A ₃ , glass. Tr. N ₂ C ₃ A ₅ ss, glass.
83	8.4	41.3	41.6	8.7	25.0	25.0	50.0	$\left\{ \begin{array}{l} 1/2 \\ 1/2 \end{array} \right.$	1,375 1,410	N ₂ C ₃ A ₅ ss, C ₃ A ₃ , glass. Tr. N ₂ C ₃ A ₅ ss, glass.
Al₂O₃ PRIMARY										
57	13.5	13.0	66.5	7.0	20.0	-----	80.0	$\left\{ \begin{array}{l} 1/2 \\ 1/2 \\ 1/4 \end{array} \right.$	1,600 1,575 1,550	βAl ₂ O ₃ , glass. βAl ₂ O ₃ , N ₂ C ₃ A ₅ ss, glass. βAl ₂ O ₃ , N ₂ C ₃ A ₅ ss, "unstable" C ₃ A ₃ , glass.

TABLE 3.—Quenching data for compositions in the system $2CaO.SiO_2-CaO-Na_2O.Al_2O_3$

No.	Composition							Time	Temperature	Phases present
	Oxides				Components					
	Na ₂ O	CaO	Al ₂ O ₃	SiO ₂	C ₂ S	CaO	NA			
CaO PRIMARY										
37	%	%	%	%	%	%	%	hr	°C	CaO, C ₃ S, glass. Do. CaO, tr. C ₂ S, glass. CaO, tr. NA, glass. Small amt. CaO, quench growths. glass. CaO, NA, quench growths, glass.
	3.8	68.0	6.2	22.0	63.0	27.0	10.0	1/2	1,550	
								1	1,500	
39	7.6	60.5	12.4	19.5	56.0	24.0	20.0	1/2	1,550	
								1/2	1,500	
41	11.3	52.9	18.7	17.1	49.0	21.0	30.0	1/3	1,550	
								1/2	1,500	
C ₃ S PRIMARY										
18	7.6	59.0	12.4	21.0	60.4	19.6	20.0	1/2	1,600	C ₃ S, quench growths, glass. C ₃ S, small amt. C ₂ S, glass. C ₃ S, small amt. C ₂ S, tr. CaO, glass. C ₃ S, small amt. C ₂ S and CaO, glass.
								1/3	1,550	
20	5.7	62.6	9.3	22.4	64.1	20.9	15.0	1/3	1,550	
								1	1,500	
C ₂ S PRIMARY										
12	3.8	58.6	6.2	31.4	90.0	-----	10.0	1/2	1,500	C ₂ S, small amt. glass. C ₂ S, glass. Tr. C ₂ S, quench growths, glass.
13	7.6	52.1	12.4	27.9	80.0	-----	20.0	1/2	1,550	
14	11.3	45.6	18.7	24.4	70.0	-----	30.0	1/3	1,550	
24	3.8	61.8	6.2	28.2	81.0	9.0	10.0	1/4	1,600	C ₂ S, C ₃ S, tr. CaO, glass. C ₂ S, tr. CaO, glass. C ₂ S, glass.
								1/3	1,550	
25	7.6	54.9	12.4	25.1	72.0	8.0	20.0	1	1,500	
C ₂ S PRIMARY										
26	11.3	48.0	18.7	22.0	63.0	7.0	30.0	1	1,500	C ₂ S, glass. Tr. C ₂ S, glass. C ₂ S, quench growths, glass. All crystalline. Tr. C ₂ S, glass. C ₂ S, NA, quench growths. Evidence of melting. All crystalline.
28	13.2	42.3	21.8	22.7	65.0	-----	35.0	1/4	1,500	
								1/2	1,410	
29	14.2	40.7	23.3	21.8	62.5	-----	37.5	1/2	1,400	
								1/4	1,475	
								1/2	1,410	
32	7.6	57.7	12.4	22.3	64.0	16.0	20.0	1/2	1,400	C ₂ S, CaO, quench growths, glass. C ₂ S, CaO, glass. C ₂ S, glass.
34	5.7	61.3	9.3	23.7	68.0	17.0	15.0	1/4	1,600	
35	9.4	54.1	15.6	20.9	60.0	15.0	25.0	1/4	1,550	
36	4.7	63.1	7.8	24.4	70.0	17.5	12.5	1/2	1,550	
C ₂ S PRIMARY										
26	11.3	48.0	18.7	22.0	63.0	7.0	30.0	1	1,500	C ₂ S, glass. Tr. C ₂ S, glass. C ₂ S, quench growths, glass. All crystalline. Tr. C ₂ S, glass. C ₂ S, NA, quench growths. Evidence of melting. All crystalline.
28	13.2	42.3	21.8	22.7	65.0	-----	35.0	1/4	1,500	
								1/2	1,410	
29	14.2	40.7	23.3	21.8	62.5	-----	37.5	1/2	1,400	
								1/4	1,475	
								1/2	1,410	
32	7.6	57.7	12.4	22.3	64.0	16.0	20.0	1/2	1,400	C ₂ S, CaO, quench growths, glass. C ₂ S, CaO, glass. C ₂ S, glass.
34	5.7	61.3	9.3	23.7	68.0	17.0	15.0	1/4	1,600	
35	9.4	54.1	15.6	20.9	60.0	15.0	25.0	1/4	1,550	
36	4.7	63.1	7.8	24.4	70.0	17.5	12.5	1/2	1,550	
NA PRIMARY										
15	15.1	39.1	24.9	20.9	60.0	-----	40.0	1/2	1,460	All glass. NA, glass. Small amt. glass. All crystalline. NA, quench growths, glass. Glass, quench growths. NA, quench growths, glass. NA, CaO, quench growths, glass. All crystalline.
16	18.9	32.6	31.1	17.4	50.0	-----	50.0	1/2	1,450	
								1/2	1,415	
19	11.3	51.6	18.7	18.4	52.8	17.2	30.0	1/2	1,550	
								1/2	1,500	
								1/4	1,400	
27	15.1	41.2	24.9	18.8	54.0	6.0	40.0	1	1,350	
30	13.2	44.6	21.8	20.4	58.5	6.5	35.0	1/4	1,450	
								1/4	1,450	
								1/2	1,500	
33	11.3	50.5	18.7	19.5	56.0	14.0	30.0	1	1,360	NA, C ₂ S, glass. All crystalline.
								1	1,350	

TABLE 4.—*Quenching data for additional compositions located between the 2CaO.SiO₂-CaO-(Na₂O+6Al₂O₃) and 2CaO.SiO₂-CaO-(Na₂O+3Al₂O₃) planes*

No.	Composition								Time	Temper- ature	Phases present
	Oxides				Components						
	Na ₂ O	CaO	Al ₂ O ₃	SiO ₂	C ₂ S	CaO	(Na ₂ O+ 6Al ₂ O ₃)	(Na ₂ O+ 3Al ₂ O ₃)			
%	%	%	%	%	%	%	%	hr	°C		
200	4.4	53.7	29.7	12.2	35.0	30.9	17.1	17.0	$\left\{ \begin{array}{l} \frac{1}{2} \\ \frac{1}{3} \end{array} \right.$	1,435	C ₂ S, glass.
										1,430	C ₂ S, small amt. NC ₃ A ₃ , glass.
										1,425	C ₂ S, glass.
201	3.8	53.7	30.3	12.2	35.0	30.9	25.6	8.5	$\left\{ \begin{array}{l} \frac{1}{2} \\ \frac{1}{3} \\ \frac{1}{4} \\ \frac{1}{4} \end{array} \right.$	1,425	C ₂ S, glass.
										1,420	C ₂ S, tr. NC ₃ A ₃ , glass.
										1,415	C ₂ S, NC ₃ A ₃ , glass.
										1,450	C ₂ S, CaO, tr. C ₃ S, glass.
202	4.2	55.3	28.3	12.2	35.0	32.5	16.3	16.2	$\left\{ \begin{array}{l} \frac{1}{4} \\ \frac{1}{4} \end{array} \right.$	1,440	C ₂ S, small amt. NC ₃ A ₃ , tr. C ₃ S, glass. C ₁ A not observed.
										1,435	C ₂ S, NC ₃ A ₃ , glass. C ₁ A not observed.
										1,445	C ₂ S, glass.
203	3.6	55.3	28.9	12.2	35.0	32.5	24.4	8.1	$\left\{ \begin{array}{l} \frac{1}{4} \\ \frac{1}{4} \\ \frac{1}{4} \\ \frac{1}{4} \end{array} \right.$	1,440	C ₂ S, C ₃ A, NC ₃ A ₃ , glass.
										1,435	C ₂ S, C ₁ A, NC ₃ A ₃ , glass.
										1,445	All glass.
										1,440	NC ₃ A ₃ , possibly C ₃ A, glass.
204	3.9	54.4	31.1	10.5	30.0	35.0	26.3	8.7	$\left\{ \begin{array}{l} \frac{1}{4} \\ \frac{1}{4} \\ \frac{1}{4} \end{array} \right.$	1,435	NC ₃ A ₃ , C ₂ S, possibly C ₂ A, glass.
										1,450	Tr. C ₃ S, tr. CaO, glass.
										1,445	C ₂ S, tr. CaO, glass.
205	3.8	55.3	30.6	10.3	29.5	36.0	25.9	8.6	$\left\{ \begin{array}{l} \frac{1}{4} \\ \frac{1}{4} \\ \frac{1}{4} \end{array} \right.$	1,435	C ₂ S, NC ₃ A ₃ , probably C ₂ A, glass.
										1,450	Small amt. C ₃ A, tr. C ₃ S, tr. CaO, glass.
										1,440	C ₂ S, C ₂ A, C ₃ S, NC ₃ A ₃ , glass.
206	3.5	55.2	31.0	10.3	29.5	36.0	30.2	4.3	$\left\{ \begin{array}{l} \frac{1}{2} \\ \frac{1}{2} \end{array} \right.$	1,440	C ₂ S, C ₃ A, NC ₃ A ₃ , glass.
										1,430	C ₂ S, C ₃ A, NC ₃ A ₃ , glass.

The phase equilibria in the various composition planes studied can be represented by diagrams that resemble those used for ternary systems. However, it must be borne in mind that the information which can be obtained from the diagram of an arbitrary plane through a quaternary system is in general much more limited than that which can be derived from the diagram of a true ternary system. The course of crystallization upon cooling a given melt can be followed on the diagram of a ternary system, but in general this is not possible for a plane through a quaternary system. This is due to the fact that the liquids and crystalline phases in equilibrium at various temperatures usually have compositions outside of the original plane.

When a plane is passed through the tetrahedron representing a quaternary system, it intersects the boundary surfaces defining the various primary phase volumes within the tetrahedron. This gives a diagram showing a field or region for each primary phase as a result of the intersection of the corresponding phase volume. Diagrams of this type are shown in figures 3, 4, and 5, for the planes studied in this investigation. In order that the relation to the ternary system CaO-Al₂O₃-SiO₂ may be more evident, the corresponding portion of this system is reproduced from Rankin and Wright in figure 2. The diagrams of figures 2, 3, 4, and 5 thus form a series that illustrates the effect of substituting successively increasing amounts of Na₂O for Al₂O₃ in the system CaO-Al₂O₃-SiO₂. As mentioned previously, the ratio of Na₂O to Al₂O₃ remains constant in any particular plane.

As the calcium silicates 2CaO.SiO₂ and 3CaO.SiO₂ are major crystalline phases of portland cement clinker, the interpretation of

the system $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ in relation to cement is simplified by keeping $2\text{CaO}\cdot\text{SiO}_2$ and CaO at two of the apexes of each composition plane.

2. THE PLANE $2\text{CaO}\cdot\text{SiO}_2-\text{CaO}-(\text{Na}_2\text{O}+6\text{Al}_2\text{O}_3)$

The diagram of this plane is shown in figure 3, and is based on the data of table 1. There is considerable resemblance to the corresponding part of the $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system (fig. 2), with the differ-

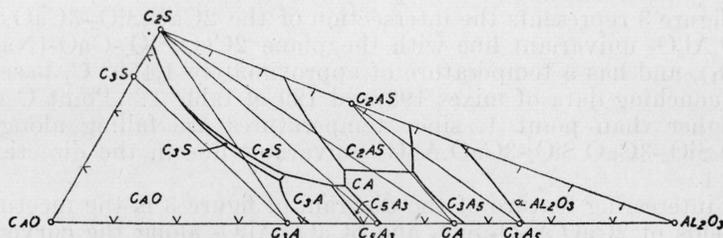


FIGURE 2.—Part of system $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$.

ence that two additional crystalline phases have made their appearance. These are the Na_2O -bearing compounds, $\text{Na}_2\text{O}\cdot 0.8\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ and $2\text{Na}_2\text{O}\cdot 3\text{CaO}\cdot 5\text{Al}_2\text{O}_3$. A total of 11 primary phase regions are indicated. The others are those of CaO , $3\text{CaO}\cdot\text{SiO}_2$, $2\text{CaO}\cdot\text{SiO}_2$, $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$, $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$, $\text{CaO}\cdot\text{Al}_2\text{O}_3$, $3\text{CaO}\cdot 5\text{Al}_2\text{O}_3$, and $\alpha\text{-Al}_2\text{O}_3$.

The area in which $\text{Na}_2\text{O}\cdot 0.8\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ is the primary phase is seen to be very narrow. In the neighborhood of points A and B (fig. 3)

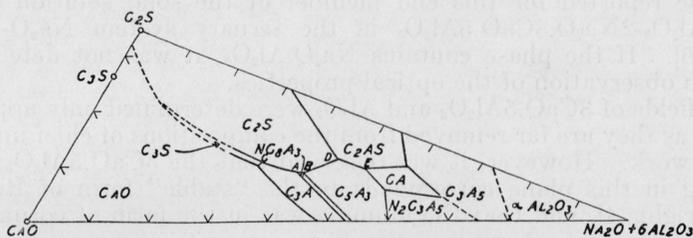


FIGURE 3.—Composition plane $2\text{CaO}\cdot\text{SiO}_2-\text{CaO}-(\text{Na}_2\text{O}+6\text{Al}_2\text{O}_3)$.

the fields of four crystalline phases meet nearly in a single point. The composition where this actually occurs is the invariant point for $2\text{CaO}\cdot\text{SiO}_2$, $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}\cdot 0.8\text{CaO}\cdot 3\text{Al}_2\text{O}_3$, and liquid. It is located slightly outside the plane of the diagram in the direction of lower $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratios. The composition of this point, designated invariant point 4, is estimated to be 3.5 percent Na_2O , 50.2 percent CaO , 37.6 percent Al_2O_3 , and 8.7 percent SiO_2 . The temperature is $1,365 \pm 10^\circ \text{C}$. It is not a eutectic. Mix 154 of table 1 is near its composition. The temperature of $1,365^\circ \text{C}$ for point 4 is worthy of note, as it is higher, rather than lower, than the corresponding ternary invariant point in the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$. The $2\text{CaO}\cdot\text{SiO}_2-3\text{CaO}\cdot\text{Al}_2\text{O}_3-5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ eutectic in the $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system is at $1,335^\circ \text{C}$ [4]. The explanation for this appears to be the fact that the $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ in the quaternary system is not

pure, but contains Na_2O in solid solution. An analogous situation was found by Brownmiller and Bogue in the ternary system $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3$ [5].

The important invariant point, not a eutectic, where $2\text{CaO}\cdot\text{SiO}_2$, $3\text{CaO}\cdot\text{SiO}_2$, $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, and $\text{Na}_2\text{O}\cdot 0.8\text{CaO}\cdot 0.3\text{Al}_2\text{O}_3$ are in equilibrium with liquid, designated invariant point 1, also lies outside of this plane, but in the direction of higher $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratios. Its composition and temperature were established by determinations on supplementary mixtures and will be presented later in this report. Point C of figure 3 represents the intersection of the $2\text{CaO}\cdot\text{SiO}_2-3\text{CaO}\cdot\text{SiO}_2-3\text{CaO}\cdot\text{Al}_2\text{O}_3$ univariant line with the plane $2\text{CaO}\cdot\text{SiO}_2-\text{CaO}-(\text{Na}_2\text{O}+6\text{Al}_2\text{O}_3)$, and has a temperature of approximately $1,450^\circ\text{C}$, based on the quenching data of mixes 198 and 199 of table 1. Point C must be higher than point 1, since temperatures are falling along the $2\text{CaO}\cdot\text{SiO}_2-3\text{CaO}\cdot\text{SiO}_2-3\text{CaO}\cdot\text{Al}_2\text{O}_3$ univariant line in the direction of point 1.

An interesting feature of the diagram of figure 3 is the meeting of the fields of $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ and $5\text{CaO}\cdot 0.3\text{Al}_2\text{O}_3$ along the curve DE. This is unexpected as these two compounds are incompatible in the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$, as is evident in figure 2. One possible explanation for this behavior is the taking up in solid solution of about 1 percent of Na_2O by the $5\text{CaO}\cdot 0.3\text{Al}_2\text{O}_3$, as reported by Brownmiller and Bogue [5]. However, such an explanation is not necessarily the true one, as the mere presence of Na_2O as a fourth component may be sufficient to cause both $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ and $5\text{CaO}\cdot 0.3\text{Al}_2\text{O}_3$ to be mutually stable in the presence of liquid.

The primary phase crystallizing in the region labeled $2\text{Na}_2\text{O}\cdot 0.3\text{CaO}\cdot 0.5\text{Al}_2\text{O}_3$ in figure 3 has optical properties corresponding to those reported for this end member of the solid solution series $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3-2\text{Na}_2\text{O}\cdot 0.3\text{CaO}\cdot 0.5\text{Al}_2\text{O}_3$ in the ternary system $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3$ [5]. If the phase contains $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3$, it was not detectable through observation of the optical properties.

The fields of $3\text{CaO}\cdot 0.5\text{Al}_2\text{O}_3$ and Al_2O_3 were determined only approximately as they are far removed from the compositions of chief interest in this work. However, it was observed that the $3\text{CaO}\cdot 0.5\text{Al}_2\text{O}_3$ crystallizing in this plane corresponds to the "stable" form of Rankin and Wright [4], and that the alumina was in the form of corundum, or $\alpha\text{Al}_2\text{O}_3$.

3. THE PLANE $2\text{CaO}\cdot\text{SiO}_2-\text{CaO}-(\text{Na}_2\text{O}+3\text{Al}_2\text{O}_3)$

Figure 4 shows the equilibrium diagram for this plane. It is constructed from the data of table 2. A number of marked changes in the primary phase regions have occurred in comparison to the preceding plane. Eight crystalline phases are indicated on the diagram, as follows: CaO , $3\text{CaO}\cdot\text{SiO}_2$, $2\text{CaO}\cdot\text{SiO}_2$, $\text{Na}_2\text{O}\cdot 0.8\text{CaO}\cdot 0.3\text{Al}_2\text{O}_3$, $5\text{CaO}\cdot 0.3\text{Al}_2\text{O}_3$, $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$, $2\text{Na}_2\text{O}\cdot 0.3\text{CaO}\cdot 0.5\text{Al}_2\text{O}_3$ solid solution, and $\beta\text{-Al}_2\text{O}_3$.

The composition of the compound $\text{Na}_2\text{O}\cdot 0.8\text{CaO}\cdot 0.3\text{Al}_2\text{O}_3$ is located on the $\text{CaO}-(\text{Na}_2\text{O}+3\text{Al}_2\text{O}_3)$ side, but as this phase melts incongruently to CaO and liquid, it is in the CaO primary phase area. The field of $\text{Na}_2\text{O}\cdot 0.8\text{CaO}\cdot 0.3\text{Al}_2\text{O}_3$ is displaced away from the CaO apex, and extends from the $\text{CaO}-(\text{Na}_2\text{O}+3\text{Al}_2\text{O}_3)$ side toward the $2\text{CaO}\cdot\text{SiO}_2$ apex. It may be observed that $\text{Na}_2\text{O}\cdot 0.8\text{CaO}\cdot 0.3\text{Al}_2\text{O}_3$ exists in equilibrium with $2\text{CaO}\cdot\text{SiO}_2$ and liquids whose compositions lie on the curve FG. The

experimental results indicate that the $3\text{CaO}\cdot\text{SiO}_2$ field narrows to a point not indicated in figure 4, slightly to the left of point F, since $3\text{CaO}\cdot\text{SiO}_2$ and $\text{Na}_2\text{O}\cdot 0.8\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ were not observed to exist together in equilibrium with liquid in any of the quenched charges. It is probable, therefore, that $3\text{CaO}\cdot\text{SiO}_2$ crystallizing from compositions in this plane decomposes upon cooling into $2\text{CaO}\cdot\text{SiO}_2$ and CaO just before the crystallization of $\text{Na}_2\text{O}\cdot 0.8\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ begins.

It follows from the near meeting of the fields for the four compounds CaO , $3\text{CaO}\cdot\text{SiO}_2$, $2\text{CaO}\cdot\text{SiO}_2$, and $\text{Na}_2\text{O}\cdot 0.8\text{CaO}\cdot 3\text{Al}_2\text{O}_3$, that an invariant point for these phases and liquid must be located near point F, but at a slightly smaller $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio. Point F has a composition very close to that of mix 107, table 2, and the invariant point, which will be referred to as point 3, is estimated to have the following composition: 5.0 percent Na_2O , 54.1 percent CaO , 28.6 percent Al_2O_3 , and 12.3 percent SiO_2 . It has a temperature estimated to be $1,445^\circ \pm 10^\circ \text{C}$, based on data for mixes 105 and 107. Point 3 is not a eutectic.

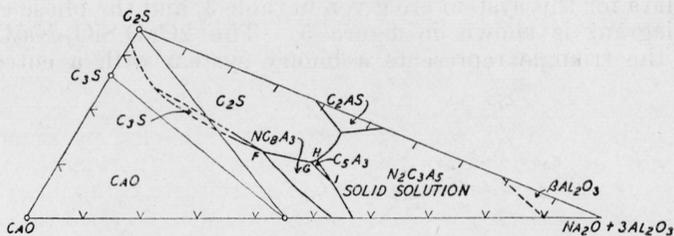


FIGURE 4.—Composition plane $2\text{CaO}\cdot\text{SiO}_2-\text{CaO}-(\text{Na}_2\text{O} + 3\text{Al}_2\text{O}_3)$.

It will be noted that the primary phase area of $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ is very small, and that if the plane of the diagram were imagined to swing gradually toward higher $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratios, the points G, H, and I would converge on a single point which represents the invariant point for the phases $2\text{CaO}\cdot\text{SiO}_2$, $\text{Na}_2\text{O}\cdot 0.8\text{CaO}\cdot 3\text{Al}_2\text{O}_3$, $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$, $2\text{Na}_2\text{O}\cdot 0.3\text{CaO}\cdot 0.5\text{Al}_2\text{O}_3$ solid solution, and liquid. It is designated as point 5, and has the following estimated composition: 8.0 percent Na_2O , 46.1 percent CaO , 35.5 percent Al_2O_3 , and 10.4 percent SiO_2 . Point 5 must be a eutectic as it lies within the composition tetrahedron formed by $2\text{CaO}\cdot\text{SiO}_2$, $\text{Na}_2\text{O}\cdot 0.8\text{CaO}\cdot 3\text{Al}_2\text{O}_3$, $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$, and $2\text{Na}_2\text{O}\cdot 0.3\text{CaO}\cdot 0.5\text{Al}_2\text{O}_3$. It is a eutectic, regardless of the amount of $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3$ in solid solution in $2\text{Na}_2\text{O}\cdot 0.3\text{CaO}\cdot 0.5\text{Al}_2\text{O}_3$. The temperature of point 5, based on data for mix 93, is estimated to be $1,340^\circ \pm 10^\circ \text{C}$.

The composition of point 5 lies close to the $2\text{CaO}\cdot\text{SiO}_2-\text{Na}_2\text{O}\cdot 0.8\text{CaO}\cdot 3\text{Al}_2\text{O}_3-2\text{Na}_2\text{O}\cdot 0.3\text{CaO}\cdot 0.5\text{Al}_2\text{O}_3$ join, which means that the percentage of $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ at complete crystallization will be very small, provided that the compounds are pure. On this basis the phase composition was calculated to be 29.8 percent $2\text{CaO}\cdot\text{SiO}_2$, 34.8 percent $\text{Na}_2\text{O}\cdot 0.8\text{CaO}\cdot 3\text{Al}_2\text{O}_3$, 34.8 percent $2\text{Na}_2\text{O}\cdot 0.3\text{CaO}\cdot 0.5\text{Al}_2\text{O}_3$ and 0.6 percent $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$. However, it is known that the $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ contains about 1 percent Na_2O in solid solution, which would increase the $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ to 1.0 percent. Moreover, if the $2\text{Na}_2\text{O}\cdot 0.3\text{CaO}\cdot 0.5\text{Al}_2\text{O}_3$ in equilibrium at the eutectic temperature contains $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3$ in solid solution, as is indicated by a lowering of the mean index of refraction from 1.592 to about 1.587, the proportion of $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ will be

further increased. Since the actual amount of this latter solid solution is not known, it is not possible to calculate the exact phase composition resulting from complete crystallization of a melt of the composition of point 5.

The compound $3\text{CaO}\cdot 5\text{Al}_2\text{O}_3$ was not observed as a primary phase in the plane $2\text{CaO}\cdot\text{SiO}_2\text{-CaO-(Na}_2\text{O} + 3\text{Al}_2\text{O}_3)$. However, the form of $3\text{CaO}\cdot 5\text{Al}_2\text{O}_3$ termed "unstable" by Rankin and Wright [4] occurs as a secondary phase in mix 56, and as a tertiary phase in mix 57. It appears to be in a state of stable equilibrium in these charges. The crystals have an index of refraction of about 1.67 and a low double refraction.

The form of Al_2O_3 which crystallizes from mixtures in this plane is $\beta\text{Al}_2\text{O}_3$, which appears to be in stable equilibrium. The optical properties agree with those reported by Brownmiller and Bogue [5].

4. THE SYSTEM $2\text{CaO}\cdot\text{SiO}_2\text{-CaO-Na}_2\text{O}\cdot\text{Al}_2\text{O}_3$

The data for this system are given in table 3, and the phase equilibrium diagram is shown in figure 5. The $2\text{CaO}\cdot\text{SiO}_2\text{-Na}_2\text{O}\cdot\text{Al}_2\text{O}_3$ side of the triangle represents a binary system with a eutectic at

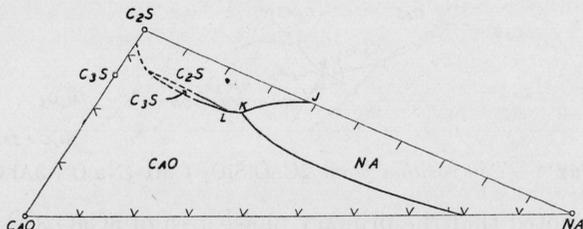


FIGURE 5.—System $2\text{CaO}\cdot\text{SiO}_2\text{-CaO-Na}_2\text{O}\cdot\text{Al}_2\text{O}_3$.

61 percent $2\text{CaO}\cdot\text{SiO}_2$ and 39 percent $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3$, or on an oxide basis, 14.7 percent Na_2O , 39.7 percent CaO , 24.3 percent Al_2O_3 , and 21.3 percent SiO_2 . This eutectic has a temperature of $1,405^\circ \pm 10^\circ\text{C}$ and is indicated by the letter J in figure 5.

Except for the existence of a small amount of solid solution in the $2\text{CaO}\cdot\text{SiO}_2$, and probably also in the $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3$, the system $2\text{CaO}\cdot\text{SiO}_2\text{-CaO-Na}_2\text{O}\cdot\text{Al}_2\text{O}_3$ is ternary. Due to experimental difficulties the phase relations as determined are not considered to be as accurate as those obtained with mixture of lower $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratios. Not only is the rate of volatilization of Na_2O higher, but the time required for the attainment of equilibrium, particularly in charges containing crystalline $3\text{CaO}\cdot\text{SiO}_2$, is much increased. This compound was found to form extremely slowly by reaction of $2\text{CaO}\cdot\text{SiO}_2$ and CaO . Increasing the temperature does not appreciably accelerate the combination as the CaO tends to form large, unreactive crystals. Consequently, for charges where $3\text{CaO}\cdot\text{SiO}_2$ was expected as a stable phase, the original mixes were prepared with $3\text{CaO}\cdot\text{SiO}_2$ instead of $2\text{CaO}\cdot\text{SiO}_2$ and CaO . In this way it is believed that a nearer approach to equilibrium was attained.

The results indicate that the phase equilibrium relations are in general as shown in figure 5. Point K is a ternary eutectic for $2\text{CaO}\cdot\text{SiO}_2$, CaO , $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3$, and liquid. It occurs at a compound composition of approximately 56 percent $2\text{CaO}\cdot\text{SiO}_2$, 16 percent CaO ,

and 28 percent $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3$, or in terms of oxides, 11 percent Na_2O , 52 percent CaO , 17 percent Al_2O_3 , and 20 percent SiO_2 . The temperature, based on data for mix 33, table 3, is $1,355 \pm 10^\circ\text{C}$.

It will be noticed that the primary field of $3\text{CaO}\cdot\text{SiO}_2$ in figure 5 is drawn as narrowing to a point at L. The basis for this is the fact that $3\text{CaO}\cdot\text{SiO}_2$ was never observed in charges containing crystalline $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3$. The solid phases in equilibrium with $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3$ were always $2\text{CaO}\cdot\text{SiO}_2$ and CaO . Accordingly, point L represents an invariant point for $3\text{CaO}\cdot\text{SiO}_2$, $2\text{CaO}\cdot\text{SiO}_2$, CaO , and liquid, and indicates a lower temperature limit of stability for $3\text{CaO}\cdot\text{SiO}_2$ in this system. Thus $3\text{CaO}\cdot\text{SiO}_2$ should decompose into $2\text{CaO}\cdot\text{SiO}_2$ and CaO when the temperature is lowered below that of point L. A partial decomposition of $3\text{CaO}\cdot\text{SiO}_2$ was observed for several charges in the system, but attempts to locate the temperature of point L were not successful because of the slowness of the reaction. When once formed, $3\text{CaO}\cdot\text{SiO}_2$ tends to persist in the melt, although held at constant temperature for many hours. According to the phase diagram, point L should have a temperature above $1,355^\circ\text{C}$.

This behavior of $3\text{CaO}\cdot\text{SiO}_2$ is interesting in the light of the work of Carlson [11], who found that $3\text{CaO}\cdot\text{SiO}_2$ tends to dissociate into $2\text{CaO}\cdot\text{SiO}_2$ and CaO when heated at temperatures between $1,000^\circ$ and $1,300^\circ\text{C}$. The possibility was pointed out by Jänecke [12] that with a suitable third component, a ternary system with CaO and $2\text{CaO}\cdot\text{SiO}_2$ might be obtained in which the field of $3\text{CaO}\cdot\text{SiO}_2$ narrows to a point at both ends, meeting the boundary curve between CaO and $2\text{CaO}\cdot\text{SiO}_2$ at an invariant point. It is interesting to note that Eitel has since reported that such a situation exists in the system $2\text{CaO}\cdot\text{SiO}_2-\text{CaO}-\text{CaF}_2$ [13]. It appears from the present work that $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3$ also is such a component. The theoretical considerations involved in a limited temperature range of stability for $3\text{CaO}\cdot\text{SiO}_2$ are discussed by Lea and Parker [7].

The $2\text{CaO}\cdot\text{SiO}_2$ phase which was observed in the binary system $2\text{CaO}\cdot\text{SiO}_2-\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3$ has the optical properties of the β form. This was confirmed by X-ray diffraction patterns.² If there is any solid solution in the β - $2\text{CaO}\cdot\text{SiO}_2$ it must be very small. However, in several compositions in the interior of the system the $2\text{CaO}\cdot\text{SiO}_2$ phase corresponded in properties to one of the α - $2\text{CaO}\cdot\text{SiO}_2$ solid solutions described in a previous paper [6]. The extent of this solid solution was not determined and the relation which it may bear to the stability of the $3\text{CaO}\cdot\text{SiO}_2$ has not been investigated. A somewhat similar situation with regard to solid solution appears to exist for the $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3$. Along the join $2\text{CaO}\cdot\text{SiO}_2-\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3$ the properties agree with those of the pure compound, but in compositions containing added CaO a slight increase in the indices of refraction indicate that the phase may be one in the solid solution series $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3-2\text{Na}_2\text{O}\cdot 3\text{CaO}\cdot 5\text{Al}_2\text{O}_3$.

5. ADDITIONAL COMPOSITIONS LOCATED BETWEEN THE $2\text{CaO}\cdot\text{SiO}_2-\text{CaO}-(\text{Na}_2\text{O}+6\text{Al}_2\text{O}_3)$ AND $2\text{CaO}\cdot\text{SiO}_2-\text{CaO}-(\text{Na}_2\text{O}+3\text{Al}_2\text{O}_3)$ PLANES

To locate invariant point 1 at which $2\text{CaO}\cdot\text{SiO}_2$, $3\text{CaO}\cdot\text{SiO}_2$, $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, and $\text{Na}_2\text{O}\cdot 8\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ are in equilibrium with liquid, it became necessary to investigate a number of mixtures not included in

² All X-ray patterns were made by H. F. McMurdie.

the original composition planes. The additional data are given in table 4. They show that mix 206 is approximately the composition of point 1. The phases, $2\text{CaO}\cdot\text{SiO}_2$, $3\text{CaO}\cdot\text{SiO}_2$, $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}\cdot 0.8\text{CaO}\cdot 0.3\text{Al}_2\text{O}_3$, and glass, were identified in a charge of mix 206 quenched at $1,440^\circ\text{C}$. The composition is therefore placed at 3.5 percent Na_2O , 55.2 percent CaO , 31.0 percent Al_2O_3 , and 10.3 percent SiO_2 , and the temperature at $1,440^\circ \pm 10^\circ\text{C}$. Point 1 is not a eutectic, and therefore a mixture of this composition does not become completely crystalline on cooling when $1,440^\circ$ is reached, but continues to contain liquid down to $1,340^\circ$, the temperature of point 5, the only quaternary eutectic in this part of the system.

One other quaternary invariant point, not a eutectic, is located near point 1. This is the point for CaO , $3\text{CaO}\cdot\text{SiO}_2$, $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}\cdot 0.8\text{CaO}\cdot 0.3\text{Al}_2\text{O}_3$, and liquid. Using figures 3 and 4, it is estimated by interpolation that this point, referred to as point 2, has a composition only slightly higher in CaO and lower in SiO_2 than point 1, or approximately 3.5 percent Na_2O , 56.0 percent CaO , 31.0 percent Al_2O_3 , and 9.5 percent SiO_2 . According to theory, point 2 must have a higher temperature than point 1, but it can be only slightly higher, since both points must have temperatures below that of point 3, which has been determined as $1,445^\circ \pm 10^\circ\text{C}$. To indicate this relationship point 2 is accordingly given the temperature $1,442^\circ \pm 10^\circ\text{C}$.

IV. DISCUSSION

1. CRYSTALLIZATION IN THE SYSTEM

For purposes of discussion and comparison, the data obtained for the five quaternary invariant points determined in this investigation are grouped together in table 5. Of these only point 5 is a eutectic. The others are reaction points, and melts of these compositions upon complete equilibrium crystallization consist of sets of solid phases differing from those in equilibrium with liquid at the respective invariant points. A melt of the composition of point 2 when cooled under equilibrium conditions becomes completely crystalline at $1,365^\circ\text{C}$, the temperature of point 4, and consists of $2\text{CaO}\cdot\text{SiO}_2$, $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, $5\text{CaO}\cdot 0.3\text{Al}_2\text{O}_3$, and $\text{Na}_2\text{O}\cdot 0.8\text{CaO}\cdot 0.3\text{Al}_2\text{O}_3$. Melts having compositions of points 1, 3, and 4 become completely crystalline at $1,340^\circ\text{C}$, the temperature of point 5, and consist of $2\text{CaO}\cdot\text{SiO}_2$, $5\text{CaO}\cdot 0.3\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}\cdot 0.8\text{CaO}\cdot 0.3\text{Al}_2\text{O}_3$, and $2\text{Na}_2\text{O}\cdot 0.3\text{CaO}\cdot 0.5\text{Al}_2\text{O}_3$ solid solution.

The existence of invariant point 1 shows that the compounds $2\text{CaO}\cdot\text{SiO}_2$, $3\text{CaO}\cdot\text{SiO}_2$, $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, and $\text{Na}_2\text{O}\cdot 0.8\text{CaO}\cdot 0.3\text{Al}_2\text{O}_3$ may be final products of crystallization in mixtures of Na_2O , CaO , Al_2O_3 , and SiO_2 approaching in composition that of portland cement clinker. Such mixtures are located in the tetrahedron formed by the compositions of the four solid phases in equilibrium at point 1. When these mixtures are heated, the first stable liquid is produced at $1,440^\circ\text{C}$, and this liquid has the composition of point 1. Conversely, when melts in this tetrahedron are cooled under equilibrium conditions, the last liquid (of the composition of point 1) disappears at $1,440^\circ\text{C}$.

TABLE 5.—Quaternary invariant points in the system $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$

Point	Temperature	Solid phases	Composition			
			Na_2O	CaO	Al_2O_3	SiO_2
	$^{\circ}\text{C} \pm 10^{\circ}$		%	%	%	%
1	1,440	$\text{C}_2\text{S}, \text{C}_3\text{S}, \text{C}_3\text{A}, \text{NC}_3\text{A}_3$	3.5	55.2	31.0	10.3
2	1,442	$\text{CaO}, \text{C}_3\text{S}, \text{C}_3\text{A}, \text{NC}_3\text{A}_3$	3.5	56.0	31.0	9.5
3	1,445	$\text{CaO}, \text{C}_3\text{S}, \text{C}_2\text{S}, \text{NC}_3\text{A}_3$	5.0	54.1	28.6	12.3
4	1,365	$\text{C}_2\text{S}, \text{C}_2\text{A}, \text{C}_3\text{A}_2, \text{NC}_3\text{A}_2$	3.5	50.2	37.6	8.7
5	1,340	$\text{C}_2\text{S}, \text{C}_3\text{A}_3, \text{NC}_3\text{A}_3, \text{N}_2\text{C}_3\text{A}_4$	8.0	46.1	35.5	10.4

The various possible courses of crystallization are many and complex for mixtures in the $2\text{CaO}.\text{SiO}_2-3\text{CaO}.\text{SiO}_2-3\text{CaO}.\text{Al}_2\text{O}_3-\text{Na}_2\text{O}-.8\text{CaO}.\text{Al}_2\text{O}_3$ tetrahedron. However, the liquids of all such compositions eventually arrive at point 1 as the melt is cooled. In some melts the liquid composition passes through point 2 before point 1 is reached. $3\text{CaO}.\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}.\text{O}.\text{O}.\text{O}.\text{Al}_2\text{O}_3$ do not crystallize out together until either point 2 or point 1 is reached. In melts whose course of crystallization passes through point 2, $3\text{CaO}.\text{Al}_2\text{O}_3$ appears before $\text{Na}_2\text{O}.\text{O}.\text{O}.\text{Al}_2\text{O}_3$ when the $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio of the original mixture is less than that of point 2. Likewise, in melts whose course of crystallization does not pass through point 2, but arrives at point 1 directly, $3\text{CaO}.\text{Al}_2\text{O}_3$ crystallizes before $\text{Na}_2\text{O}.\text{O}.\text{O}.\text{Al}_2\text{O}_3$ when the $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio of the original mixture is less than that of point 1. Since points 1 and 2 have the same $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio within experimental error, this ratio determines whether $3\text{CaO}.\text{Al}_2\text{O}_3$ or $\text{Na}_2\text{O}.\text{O}.\text{O}.\text{Al}_2\text{O}_3$ is first to crystallize on cooling the melts under discussion. On a weight basis, the $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio of points 1 and 2 is 0.11. Therefore in mixtures which have $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratios less than 0.11, $3\text{CaO}.\text{Al}_2\text{O}_3$ appears before $\text{Na}_2\text{O}.\text{O}.\text{O}.\text{Al}_2\text{O}_3$, whereas in those which have $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratios greater than 0.11, $\text{Na}_2\text{O}.\text{O}.\text{O}.\text{Al}_2\text{O}_3$ precedes $3\text{CaO}.\text{Al}_2\text{O}_3$.

2. SOLID SOLUTIONS

Although it has been demonstrated by the present work that $3\text{CaO}.\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}.\text{O}.\text{O}.\text{Al}_2\text{O}_3$ may exist together as distinct phases in stable equilibrium with liquid at the invariant point where $2\text{CaO}.\text{SiO}_2$ and $3\text{CaO}.\text{SiO}_2$ are also present, the data thus far reported do not give any information concerning the relation between these compounds below the temperature of liquid formation. Previous data of this laboratory have indicated that, with slow cooling or prolonged heating at lower temperatures, $3\text{CaO}.\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}.\text{O}.\text{O}.\text{Al}_2\text{O}_3$ form a complete solid solution series in the ternary system $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3$ [14]. In order to test the possibility of the formation of similar solid solutions in the quaternary system, a mix was made up which was calculated to have the following potential compound composition: 39.9 percent $3\text{CaO}.\text{Al}_2\text{O}_3$, 40.1 percent $\text{Na}_2\text{O}.\text{O}.\text{O}.\text{Al}_2\text{O}_3$, and 20.0 percent $2\text{CaO}.\text{SiO}_2$. A sample of this mixture was given two 30-minute heatings at $1,425^{\circ}\text{C}$, with intermediate grinding, and was examined microscopically and a portion taken for X-ray analysis.

Under the microscope the charge appeared to consist of a large amount of material having a mottled gray interference color, along with a small amount of $2\text{CaO}.\text{SiO}_2$. No glass was detected. The double refraction of the predominant material was appreciably less

than that of $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 3\text{Al}_2\text{O}_3$. No distinct grains of either $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ or $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ could be identified. Although the double refraction did not appear to be entirely uniform, there was definite evidence that a reaction had taken place to produce a phase or phases that were neither pure $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ nor pure $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 3\text{Al}_2\text{O}_3$.

Unfortunately, the powder diffraction patterns of both $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ are very similar. By comparing the data of McMurdie [15] for $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ with that of Brownmiller and Bogue [5] for $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, only minor differences are seen. The pattern for the mixture of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ and $2\text{CaO} \cdot \text{SiO}_2$ mentioned in a previous paragraph, is also very similar, but resembles that of $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ more than that of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. It contains a number of pairs of lines located close together. Such pairs occur also with $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, but to a lesser extent, while in the pattern of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ only single lines occur. In table 6 are shown the interplanar spacings calculated for the charge prepared from the mixture, in comparison to the more important lines of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 3\text{Al}_2\text{O}_3$.

TABLE 6.—*Powder diffraction patterns of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, and a mixture of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, and $2\text{CaO} \cdot \text{SiO}_2$ after heating to $1,425^\circ \text{C}$*

[VS=very strong, S=strong, M=medium, W=weak, VW=very weak]

$3\text{CaO} \cdot \text{Al}_2\text{O}_3$ (McMurdie)		$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot 2\text{CaO} \cdot \text{SiO}_2$ mixture ¹		$\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ (Brownmiller and Bogue)	
<i>dhkl</i>	Estimated intensity	<i>dhkl</i>	Estimated intensity	<i>dhkl</i>	Estimated intensity
3.34	VW	3.41	W	3.37	W
		3.33	VW		
2.70	VS	2.69	VS	2.68	VS
2.39	W	2.42	W	2.41	W
		2.37	W	2.37	W
2.258	VW	2.27	VW		
2.200	M	2.196	M	2.20	S
2.039	VW	2.036	W	2.03	W
1.984	VW				
1.951	VW	1.958	VW		
1.907	S	1.918	S	1.915	S
		1.888	M	1.888	S
1.826	VW	1.745	VW	1.746	W
1.556	S	1.564	S	1.558	VS
		1.547	M		
1.346	M	1.356	W	1.347	M
		1.346	M		
1.206	M	1.213	M	1.210	M
		1.197	W		
1.106	W	1.102	W	1.103	W
1.023	M	1.023	M	1.019	₂ M
		1.015	M		

¹ Lines corresponding to those of $2\text{CaO} \cdot \text{SiO}_2$ are omitted.

₂ Very broad.

These microscopical and X-ray data are limited, but it seems justifiable to conclude that at temperatures below that of liquid formation in the system $\text{Na}_2\text{O} \cdot \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, and $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ may combine under suitable conditions to form a solid solution phase having intermediate optical properties and a crystal structure similar to that of $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 3\text{Al}_2\text{O}_3$.

In the majority of the compositions studied in this investigation the $2\text{CaO} \cdot \text{SiO}_2$ possessed optical properties corresponding to those of the β form. In a few cases, however, as in the system $2\text{CaO} \cdot \text{SiO}_2$ -

$\text{CaO}-\text{Na}_2\text{O}.\text{Al}_2\text{O}_3$, the $2\text{CaO}.\text{SiO}_2$ appeared to be one of the α - $2\text{CaO}.\text{SiO}_2$ solid solutions described in a previous paper [6]. No definite region of occurrence for this phase in contrast to β - $2\text{CaO}.\text{SiO}_2$ was observed, and the amounts of Na_2O and Al_2O_3 in solid solutions were not determined. Consequently in the tables and diagrams the two forms of $2\text{CaO}.\text{SiO}_2$ are not differentiated.

Measurements of indices of refraction have indicated that solid solution of Na_2O and Al_2O_3 may occur to a limited extent in β - $2\text{CaO}.\text{SiO}_2$ [6]. There is evidence that such solid solution may also take place in the ternary system $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$. Preliminary experiments with compositions along the join $2\text{CaO}.\text{SiO}_2-\text{Na}_2\text{O}.\text{CaO}.\text{SiO}_2$ have given apparently a single phase up to a molar ratio of 1 $\text{Na}_2\text{O}.\text{CaO}.\text{SiO}_2$ to 14 $2\text{CaO}.\text{SiO}_2$. It was at first thought that this might represent a new ternary compound of the approximate formula $\text{Na}_2\text{O}.\text{29CaO}.\text{15SiO}_2$. It has a complexly twinned structure very similar to that of the $\text{K}_2\text{O}.\text{23CaO}.\text{12SiO}_2$ phase described by Taylor [16]. However, the powder diffraction patterns obtained for the Na_2O phase have always corresponded to that of β - $2\text{CaO}.\text{SiO}_2$, with a slight shift of some of the lines. Consequently, it must be concluded that it is not a distinct compound but rather a solid solution phase. As mentioned in the previous paper [6], it is probable that the twinning results from the inversion of the $2\text{CaO}.\text{SiO}_2$ from the α to the β form.

3. APPLICATIONS TO PORTLAND CEMENT CLINKER

The results of this investigation are limited in their application to commercial portland cement by the fact that one of the major components of clinker, Fe_2O_3 , has been excluded. Furthermore, the exact effect of a number of the minor components is not yet known. Nevertheless, on the basis of present information, it is possible to reach a much more definite conclusion than heretofore regarding the state of the Na_2O in clinker. A number of possibilities are indicated, depending not only on the composition of the clinker, but perhaps even more on the heat treatment which it receives.

If cooling has been rapid so that glass is present in the clinker, some of the Na_2O will always be found in this glass. The percentage of Na_2O occurring in this manner will depend upon individual conditions, but some indication may be obtained from the phase equilibrium data for the $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system. For example, a glass resulting from the quenching of a liquid near in composition to that of point 1 contains approximately 3.5 percent Na_2O . However, if this same melt is allowed to crystallize independently until the composition of the remaining liquid approaches that of point 5, and then is quenched, the resulting glass will contain upward of 8 percent Na_2O .

The results thus far obtained indicate that when the cooling takes place at a slower rate, some of the Na_2O in a clinker may crystallize as the compound $\text{Na}_2\text{O}.\text{8CaO}.\text{3Al}_2\text{O}_3$, or more likely as a solid solution phase of this compound and $3\text{CaO}.\text{Al}_2\text{O}_3$. It is probable that this phase is closely related to the "prismatic dark interstitial" material found in some commercial portland cement clinkers. The compound, $\text{Na}_2\text{O}.\text{8CaO}.\text{3Al}_2\text{O}_3$ has been observed in the present work to form prismatic crystals when the cooling rate was suitable, and Taylor [17] has shown that the dark prismatic phase of clinker is closely related to

$3\text{CaO}\cdot\text{Al}_2\text{O}_3$. Although he found no proportionality between the percentage of alkali in a clinker and the amount of the dark prismatic phase which may be produced, the presence of either Na_2O or K_2O appears to be necessary for its formation.

The fact that $2\text{CaO}\cdot\text{SiO}_2$ can form solid solutions containing Na_2O makes this another possible manner of occurrence in clinker. The opinion was expressed in a previous paper [6] that because of their instability, the α - $2\text{CaO}\cdot\text{SiO}_2$ solid solutions which may be formed at clinkering temperatures, probably are not present in normally cooled clinker. However, since the material held in solid solution at the higher temperature is precipitated as inclusions in the $2\text{CaO}\cdot\text{SiO}_2$ grains when they invert to the β form, some of the Na_2O will be contained in these inclusions. This fact may be of importance in the hydration of cement, since β - $2\text{CaO}\cdot\text{SiO}_2$ hydrates slowly and the alkali imbedded in the grains might be protected from the action of the water for considerable lengths of time.

Addition of Na_2O to the system $\text{CaO}\text{-}\text{Al}_2\text{O}_3\text{-}\text{SiO}_2$ was found to result in an enlargement of the primary phase region of CaO . This is evident from an examination of figures 2, 3, 4, and 5. This is important since it means that certain compositions in the alkali-free system would not contain free CaO at clinkering temperatures, but after addition of Na_2O would contain stable CaO . In this way Na_2O can affect adversely the combination of the CaO in the cement mix.

V. SUMMARY

The portion of the quaternary system $\text{Na}_2\text{O}\text{-}\text{CaO}\text{-}\text{Al}_2\text{O}_3\text{-}\text{SiO}_2$ of importance to portland cement technology has been studied by the quenching method. The phase equilibrium data are presented in the form of tables and phase diagrams, and features of interest are discussed.

Mixtures located in three definite composition planes passing through the four-component tetrahedron, as well as a number of additional compositions, were investigated. A total of 12 crystalline compounds were observed to have primary phase volumes within this portion of the system.

Five of the quaternary invariant points occurring in this part of the system have been located approximately. Of these only one is a eutectic; the other four are reaction points. It was found that $2\text{CaO}\cdot\text{SiO}_2$, $3\text{CaO}\cdot\text{SiO}_2$, $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, and $\text{Na}_2\text{O}\cdot 0.8\text{CaO}\cdot 0.3\text{Al}_2\text{O}_3$ are capable of coexisting with liquid at one of these reaction points. The temperature of this point is $1,440^\circ \pm 10^\circ\text{C}$ and the composition is 3.5 percent Na_2O , 55.2 percent CaO , 31.0 percent Al_2O_3 , and 10.3 percent SiO_2 .

Evidence was obtained indicating that at temperatures below that of liquid formation, $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}\cdot 0.8\text{CaO}\cdot 0.3\text{Al}_2\text{O}_3$ may combine under suitable conditions to form a solid solution phase of intermediate properties and crystal structure.

Based on present information, and necessarily ignoring the effect of Fe_2O_3 and minor components, it is concluded that the Na_2O in portland cement clinker may occur in several possible ways, depending on individual conditions:

1. As a component of glass.

2. As $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ or a solid solution of that compound with $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. Such a phase may be associated with the prismatic dark interstitial material frequently observed in clinker.
3. As a solid solution of a soda-bearing phase in $2\text{CaO} \cdot \text{SiO}_2$.
4. As inclusions of a soda-bearing phase in $\beta\text{-}2\text{CaO} \cdot \text{SiO}_2$ produced by ex-solution on inversion from $\alpha\text{-}2\text{CaO} \cdot \text{SiO}_2$.

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