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Preliminary Study on Portions of the Systems Na_2O-CaO-Al_2O_3-Fe_2O_3 and Na_2O-CaO-Fe_2O_3-SiO_2

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Portions of the quaternary system Na_2O-CaO-Al_2O_3-Fe_2O_3 have been studied by the exploration of (1), the plane CaO-$4CaO.Al_2O_3.Fe_2O_3$-$(Na_2O+3Al_2O_3)$ and (2), planes above the base system CaO-$5CaO.3Al_2O_3$-$2CaO.Fe_2O_3$ containing successively increasing amounts of Na_2O up to 6 percent. A portion of the quaternary system Na_2O-CaO-Fe_2O_3-SiO_2 has been studied by the exploration of a plane containing 5 percent of Na_2O above the base system CaO-$2CaO.SiO_2$-$CaO.Fe_2O_3$.

In the pseudo system CaO-$4CaO.Al_2O_3.Fe_2O_3$-$(Na_2O+3Al_2O_3)$, the compound $Na_2O.8CaO.3Al_2O_3$ was found to exist as a primary phase, and the area in which the plane cuts the $Na_2O.8CaO.3Al_2O_3$ primary-phase volume was established. Three points on univariant curves were located. The iron phase ($4CaO.Al_2O_3.Fe_2O_3$ solid solution) was observed to exist in a solid-solution series.

In the system Na_2O-CaO-$5CaO.3Al_2O_3$-$2CaO.Fe_2O_3$, it was found that the compound $Na_2O.8CaO.3Al_2O_3$ appears at an Na_2O concentration of about 4.2 percent. However, because soda is taken into solid solution by other phases, it was not feasible at this time to determine the invariant point for $Na_2O.8CaO.3Al_2O_3$, $3CaO.Al_2O_3$, $5CaO.3Al_2O_3$, and $4CaO.Al_2O_3.Fe_2O_3$ solid solution.

In the system Na_2O-CaO-$2CaO.SiO_2$-$CaO.Fe_2O_3$, no ternary compounds were observed up to the 5-percent limit of Na_2O employed. A soda-containing phase was found to occur in solid solution with α $2CaO.SiO_2$, which may precipitate on cooling, forming inclusions in the β $2CaO.SiO_2$, or enter into reaction with the glassy phase.

I. Introduction

The role of the alkali elements in portland cement has become of increasing interest in recent years, due to the importance attached by some investigators to a reaction that may take place between the alkalies and certain siliceous aggregates [17, 14, 8].[1] The Portland Cement Association Fellowship, over a period of many years, has conducted an intensive study of the effect of the alkali elements on the phase composition of cement clinker. Both potash [19, 20, 21] and soda [2, 6] have been so studied. In continuation of this research, some of the preliminary investigations incident to the examination of the quinary system Na_2O-CaO-Al_2O_3-Fe_2O_3-SiO_2 have been completed and are herein reported.

Before direct attack can be made upon the quinary system, it is necessary to know the phase relations of its boundary quaternary systems. There are five such boundary systems.[2] N-C-A-F; N-C-A-S; N-C-F-S; N-A-F-S; and C-A-F-S. One of these, N-A-F-S, contains no lime and can be considered, from the point of interest in portland cement, as not significant in the investigation. Studies on the system C-A-F-S have been reported by Lea and Parker [12] and by Swayze [18]. A portion of the system N-C-A-S has been explored by Greene and Bogue [7]. The remaining two systems, N-C-A-F and N-C-F-S, require further examination, which is the purpose of this paper.

Studies of the system C-F-S [9, 3] have shown no ternary-compound formation. In an investigation of the system C-A-F [10], the ternary compound C_4AF was reported as the end member of a solid-solution series between C_2F and hypothetical C_2A. Swayze [18] has shown that this series extends to the composition C_6A_2F. As it

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

[2] The following customary abbreviated symbols are used interchangeably with the conventional formulas: $N=Na_2O$; $C=CaO$; $A=Al_2O_3$; $F=Fe_2O_3$; $S=SiO_2$; $M=MgO$; $B=BaO$. Thus $NC_8A_3=Na_2O.8CaO.3Al_2O_3$, etc.

has not yet been found possible to define the precise composition of the solid solution resulting from the crystallization of a given melt in this area, the formula C_4AF *ss* will be employed herein to indicate this iron-containing solid-solution phase. A study [2] of the system N-C-A has revealed that a ternary compound, NC_8A_3, is stable in the high-lime region of those components in equilibrium with C_3A. A subsequent investigation [7] indicated that this compound is also stable, in the system N-C-A-S, in the presence of C_2S and C_3S. It remained to study the reactions of NC_8A_3 in systems containing the iron phase, and further to observe the effects of additions of Na_2O upon compositions in the systems C-A-F and C-F-S. This has been accomplished, and preliminary results are herein presented on three studies: 1. Pseudo system C-C_4AF-(NA_3)[3]; 2. Portion of the system N-C-C_5A_3-C_2F; 3. Portion of the system N-C-C_2S-CF.

II. Experimental Procedure

The phase-equilibrium relations of a four-component system may be expressed in various ways [12, 16]. In the present study two of these methods are employed. In the study of the pseudo-ternary system C-C_4AF-(NA_3), a plane was passed through the tetrahedron N-C-A-F in such a way as to cut the space model at the compositions C, (AF) and (NA_3), (see fig. 1). In the study of the systems N-C-C_5A_3-C_2F and N-C-C_2S-CF, planes were passed through the space model parallel to the soda-free surface (see figs. 3 and 4). In all cases the triangular diagrams obtained by these planes represent arbitrary pseudo-ternary systems. The advantage of this procedure is that the planes may thus be represented in the form of a ternary diagram (see fig. 2). However, it is evident that the information that 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 usually this cannot be done for a plane through a quaternary system unless the plane represents a true ternary system.

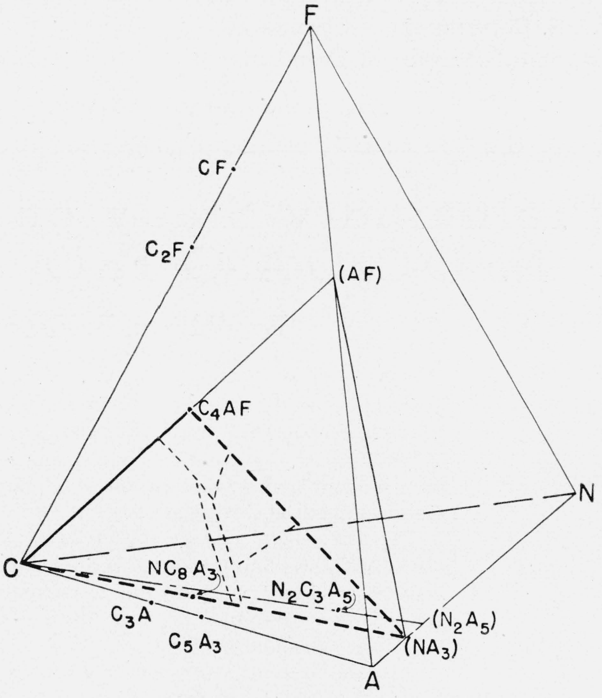

FIGURE 1.—*Tetrahedron,* N-C-A-F, *within which is shown the pseudoternary system,* C-C_4AF-(NA_3), *as a part of the plane cutting the tetrahedron at* C-(AF)-(NA_3).

This arises from the fact that crystalline phases in equilibrium with liquids at various temperatures usually have compositions outside the original plane. However, by judicious choice of planes, these difficulties may be largely reduced.

The quenching method of investigation [2, 1, 7] was employed, except that in some cases the charge was allowed to cool slowly in order that secondary phases might be examined. The phases were identified by optical petrographic methods.

Both envelopes of platinum foil, and open platinum pans as first used by Swayze and Brown [18], were employed in this study. It was found that the alkali loss was much more rapid from the open pans. Therefore, in most cases, platinum envelops were used to hold the charges for burning.

Volatilization of small amounts of soda from the charges during heating was found to occur when envelopes were employed, but could be controlled and provided for. The charges were held at the reaction temperature for the shortest period consistent with complete reaction. This period for equilibrium varied with composition and was usually short, only a few minutes, for the high-fluidity iron-containing mixes. How-

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[3] The parenthesized expressions (NA_3), (N_2A_5) and (AF) are used to indicate arbitrary compositions and are not intended to be understood either as compounds or phases.

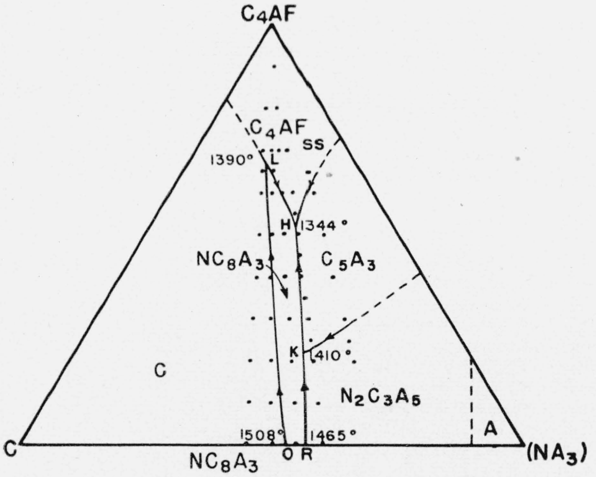

FIGURE 2.—*Field of intersection of the* C-C_4AF-(NA_3) *plane with the* NC_8A_3 *primary phase volume.*

The dots indicate compositions studied.

ever, in the absence of SiO_2 or in the presence of less than 4 percent of Na_2O, longer periods, sometimes more than an hour, were required. The loss of soda was found to be less when it was added in certain combined forms, as NA or NS_2. As the loss of soda was found to be proportional to the concentration, a definite excess of Na_2O was provided in the preparation of the charges. Analytical checks indicated that the losses were satisfactorily compensated.

Raw materials were specially prepared and of unusually high purity. The Fe_2O_3 and SiO_2 were better than 99.99 percent pure on a dry basis, and other reagents were better than 99.90 percent.

These raw materials were ground to pass a No. 200 sieve and, after proportioning, further ground in an agate mortar. Microscopic examination showed satisfactory mixing. One-hundred gram quantities of C_5A_3, C_2S, (NA_3), C_2F, C_4AF, NA, and NS_2 were prepared. Each mix was given at least two burns with intermediate grinding and mixing in each case. These materials, together with $CaCO_3$, were then used as base mixes for preparing 1-g compositions to be studied by the quenching method. Because of the possible loss of soda, no preliminary burns were given these mixes.

Water was found to be the most satisfactory quenching medium. Charges were removed from the water immediately after quenching and dried on the top of the furnace. The hydration resulting from this procedure was insignificant, and the efficiency of cooling was superior to that obtained with the use of mercury. The size of the charge was kept small (2 to 10 mg) to improve further the rapidity of freezing.

Permanent mounts of all charges were made, using Hyrax resin of refractive index 1.715. This procedure, which was emphasized by Brown [18], provides a permanent record of the investigation and permits the reexamination of specimens as the need arises.

In many cases, several quenches of a given mix were necessary before the temperature range was reached where the information obtained became pertinent to the investigation. Only those data that are of critical significance are herein recorded. In most instances, glass was the predominant phase, with small amounts of the various crystalline phases appearing embedded in the undercooled matrix.

The thermocouples were recalibrated at frequent intervals because of attack by the soda vapors. For this purpose pure diopside, CMS_2 (1391.5° C), or barium disilicate, BS_2 (1,418° C), were employed, the melting points of these compounds having been confirmed with a couple standardized by the National Bureau of Standards.

Special high-index media were prepared for measuring the refractive indices of the iron compounds. These were made by heating together purified piperine and a mixture of arsenic and antimony tri-iodides according to the method of Larsen and Merwin [11]. These media gave indices ranging from 1.88 to 2.06.

III. Experimental Results

1. Pseudo system C-C_4AF-(NA_3)

The reactions of NC_8A_3 in the presence of iron and alumina compounds, and the character of solid-solution formation between these compounds, were studied by an examination of the pseudo system C-C_4AF-(NA_3). The composition (NA_3) was selected as one of the component vertices so that the plane chosen would include the compound NC_8A_3. This is indicated in figure 1, where the pseudo system is shown to be a portion of a plane cutting the space model at the points C, (AF), and (NA_3). The pseudo system C-C_4AF-(NA_3), indicated in the figure as a scalene triangle within the tetrahedron, is shown to better advantage in figure 2, where it is reproduced as an equilateral triangle. The compositions studied are indicated by dots, and are defined in table 1, together with

TABLE 1.—*Results of quenches in the system* $C\text{-}C_4AF\text{–}(NA_3)$

No.	Composition				Temperature	Time	Petrographic examination
	Na_2O	CaO	Al_2O_3	C_4AF			
				NC_8A_3 FIELD			
	%	%	%	%	°C	*min*	
1	9.35	45.0	45.65	0	1,478	50	NC_8A_3, $N_2C_3A_5$, glass.
					1,489	60	NC_8A_3, trace $N_2C_3A_5$, glass.
					1,501	35	Glass, trace NC_8A_3.
2	8.45	40.5	41.05	10	1,461	65	NC_8A_3, $N_2C_3A_5$, glass.
					1,473	60	All glass.
3	7.45	36.0	36.55	20	1,433	55	NC_8A_3, $N_2C_3A_5$, glass.
					1,444	40	NC_8A_3, glass.
					1,463	30	Trace NC_8A_3, glass.
					1,470	30	All glass.
4	6.55	31.5	31.95	30	1,428	30	NC_8A_3, glass.
					1,439	35	All glass.
5	5.6	27.0	27.4	40	1,416	30	NC_8A_3, glass.
					1,423	35	All glass.
6	4.68	22.5	22.82	50	1,390	30	NC_8A_3, iron phase, glass.
					1,401	30	NC_8A_3, glass.
					1,417	35	All glass.
7	3.74	18.0	18.26	60	1,380	30	NC_8A_3, iron phase, glass.
					1,391	35	All glass.
16	4.25	25.0	20.75	50	1,429	30	Trace NC_8A_3, mostly glass.
					1,439	30	All glass.
17	3.4	20.0	16.6	60	1,380	30	NC_8A_3, glass.
					1,391	30	All glass.
35	5.1	20.0	24.9	50	1,340	40	NC_8A_3, C_5A_3, glass.
					1,346	30	All glass.
				C_4AF *ss* FIELD			
8	2.8	13.5	13.7	70	1,392	30	Iron phase, glass.
					1,404	35	All glass.
9	1.87	9.0	9.13	80	1,401	30	Iron phase, glass.
					1,412	35	All glass.
10	0.93	4.5	4.57	90	1,429	30	Iron phase, quench growth glass.
					1,438	30	All glass.
18	2.55	15.0	12.45	70	1,370	30	Iron phase, glass.
					1,380	30	All glass.
28	2.3	16.5	11.2	70	1,400	35	Iron phase, trace CaO, glass.
					1,412	35	All glass.
29	1.53	11.0	7.47	80	1,394	30	Iron phase, glass.
					1,408	20	All glass.
36	4.1	16.0	19.9	60	1,320	30	Iron phase, C_5A_3, glass.
					1,382	30	Small amt. iron phase, glass.
					1,395	30	All glass.
37	3.1	12.0	14.9	70	1,397	30	Trace iron phase, glass.
					1,411	35	All glass.
40	4.6	18.0	22.4	55	1,383	20	Trace iron phase, glass.
					1,395	40	All glass.
46	3.0	17.5	14.5	65	1,370	30	Iron phase, quench growths, glass.
					1,380	45	All glass.
55	4.2	10.0	20.8	65	1,395	35	Iron phase, quench growths, glass.
					1,404	32	All glass.
				C_5A_3 FIELD			
33	7.1	28.0	34.9	30	1,384	30	$N_2C_3A_5$, NC_8A_3, C_5A_3, glass.
					1,387	30	Trace C_5A_3, glass.
					1,391	30	All glass.
34	6.1	24.0	29.9	40	1,342	35	NC_8A_3, C_5A_3, quench growths, glass.
					1,352	55	C_5A_3, trace NC_8A_3, glass.
					1,360	30	All glass.
35	5.1	20.0	24.9	50	1,340	30	C_5A_3, NC_8A_3, glass.
					1,346	30	All glass.
38	7.6	30.0	37.4	25	1,381	30	C_5A_3, NC_8A_3, $N_2C_3A_5$, glass.
					1,390	30	Small amount C_5A_3, glass.
					1,400	30	All glass.

TABLE 1.—*Results of quenches in the system* C-C^4AF-(NA^3)—Continued

No.	Composition				Temperature	Time	Petrographic examination
	Na_2O	CaO	Al_2O_3	C_4AF			
C_5A_3 FIELD—Continued							
39	6.6	26.0	32.4	35	1,376	35	C_5A_3, NC_8A_3, glass.
					1,380	30	Trace C_5A_3, glass.
					1,385	30	All glass.
44	5.96	15.0	29.04	50	1,410	25	Trace C_5A_3, glass.
45	4.7	12.0	23.3	60	1,384	30	C_5A_3, iron phase, quench growths, glass.
					1,398	30	Small amount C_5A_3, glass.
					1,404	30	Trace C_5A_3, glass.
47	8.4	21.0	40.6	30	1,516	35	C_5A_3, $N_2C_3A_5$, glass.
					1,551	30	C_5A_3, glass.
48	7.1	18.0	34.9	40	1,454	30	C_5A_3, $N_2C_3A_5$, glass.
					1,470	30	C_5A_3, trace $N_2C_3A_5$, glass.
					1,488	55	Trace C_5A_3, glass.
50	8.1	12.0	39.9	40	1,498	35	C_5A_3, $N_2C_3A_5$, glass.
					1,540	45	C_5A_3, glass.
54	5.6	22.0	27.4	45	1,340	30	C_5A_3, NC_8A_3, glass.
					1,347	35	All glass.
$N_2C_3A_5$ FIELD							
30	10.2	40.0	49.8	0	1,485	30	$N_2C_3A_5$, glass.
					1,495	30	Do.
31	9.2	36.0	44.8	10	1,450	30	Do.
32	8.2	32.0	39.8	20	1,420	30	Do.
					1,430	30	All glass.
42	9.5	24.0	46.5	20	1,460	30	$N_2C_3A_5$, glass.
					1,490	35	Do.
43	8.9	22.5	43.6	25	1,495	45	Do.
CaO FIELD							
11	8.5	50.0	41.5	0	1,501	35	NC_8A_3, glass.
					1,514	35	CaO, NC_8A_3, glass.
					1,526	30	CaO, rounded grains, glass.
12	7.6	45.0	37.4	10	1,485	30	CaO, NC_8A_3, quench growths, glass.
					1,495	35	CaO, glass.
13	6.8	40.0	33.2	20	1,483	35	CaO, NC_8A_3, glass.
					1,495	30	Do.
					1,504	30	CaO, large grains, glass.
14	5.9	35.0	29.1	30	1,475	35	CaO, NC_8A_3, glass.
					1,487	30	Small amount CaO, glass.
15	5.1	30.0	24.9	40	1,439	35	NC_8A_3, CaO, glass.
					1,450	30	CaO, glass.
					1,461	30	All glass.
21	7.7	55.0	37.3	0	1,514	35	Small grains CaO, glass.
					1,526	30	Do.
22	6.9	49.5	33.6	10	1,485	30	CaO, NC_8A_3, quench growths, glass.
					1,495	35	Large rounded grains CaO, glass.
23	6.1	44.0	29.9	20	1,483	35	CaO, NC_8A_3, quench growths, glass.
					1,495	30	CaO, NC_8A_3, glass.
					1,504	30	Large grains CaO, glass.
24	5.4	38.5	26.1	30	1,475	35	CaO, quench growths, glass.
					1,487	30	Small amount CaO, glass.
25	4.6	33.0	22.4	40	1,439	35	CaO, small amount NC_8A_3, glass.
					1,461	30	CaO, glass.
26	3.8	27.5	18.7	50	1,439	30	CaO, NC_8A_3, quench growths, iron phase, glass.
					1,448	30	CaO, quench growths, glass.
27	3.1	22.0	14.9	60	1,391	30	CaO, quench growths, NC_8A_3, iron phase, glass.
					1,404	30	CaO, glass.
53	2.7	19.0	13.3	65	1,400	35	Do.
					1,409	35	All glass.

the heat treatments and the phases observed in the quenched charges.

From a study of about 50 compositions in this system, the boundaries defining the area of intersection of this plane with the primary-phase volume of NC_8A_3 were located. This field was found to be rather narrow and to extend from a point near the C_4AF vertex to the base line, C-(NA_3). As NC_8A_3 melts incongruently [2], its composition falls outside of the field for that compound. The boundary curves defining the area of NC_8A_3 in this system are indicated in the figures. The boundary curves extending away from that field, and originating at points on univariant curves, were not studied at length, and are indicated by dashed lines. The intersection point *H*, for C_5A_3, C_4AF *ss*, and NC_8A_3, was determined. Two other intersection points, *K* for C_5A_3, NC_8A_3, $N_2C_3A_5$, and *L* for CaO, C_4AF *ss*, NC_8A_3, also were located. The compositions and melting temperatures of these points, as of the points on the base-line, C-(NA_3) [7], are given in table 2.

TABLE 2.—*Intersection points in the pseudo system* C-C_4AF-(NA_3)

Point	Phases	Composition				Temperature
		CaO	Al_2O_3	Fe_2O_3	Na_2O	
COMPOSITIONS, EXPRESSED AS OXIDES						
		%	%	%	%	° *C*
H	C_5A_3, C_4AF *ss*, NC_8A_3	44. 0	34. 2	17. 1	4. 7	1, 344±5
K	C_5A_3, NC_8A_3, $N_2C_3A_5$	42. 8	42. 8	7. 2	7. 8	1, 410±10
L	C, C_4AF *ss*, NC_8A_3	48. 4	26. 8	22. 3	2. 5	1, 390±10
O [2]	C, NC_8A_3	46. 8	44. 2	------	9	1, 508
R [2]	$N_2C_3A_5$, NC_8A_3	43. 2	46. 5	------	10. 3	1, 465

COMPOSITIONS, EXPRESSED AS COMPONENTS

Point	CaO	C_4AF	(NA_3)
	%	%	%
H	20	52	28
K	32	22	46
L	17	67	16

The curves in figure 2 are sections through bivariant surfaces in the quaternary system N-C-A-F. The intersections of these curves are points on univariant curves in the quaternary system. As the system C-C_4AF-(NA_3) is a pseudo system, none of these points can be considered to be invariant points. Such a point could be an invariant point, but only if the plane selected arbitrarily happened to pass through an invariant point. Intersection points *H* and *L* are on the univariant curves for C_4AF *ss*, C_5A_3 and NC_8A_3 and for CaO, C_4AF *ss* and NC_8A_3, respectively.

A primary-phase region for C_3A exists in the plane C-AF-A (fig. 1), but is absent in the plane C-AF-(NA_3). On the other hand, a narrow region for NC_8A_3 exists in the plane C-AF-(NA_3), but is absent in the plane C-AF-A. It is to be expected, then, that between the two planes there is an Na_2O concentration at which the C_3A region disappears, and an Na_2O concentration at which the NC_8A_3 region appears. It is probable that these are the concentrations of Na_2O at invariant points. The Na_2O concentration at which NC_8A_3 appears is considered in the investigation of the system N-C-C_5A_3-C_2F.

The formation of iron-containing solid solution was observed by measurements of the refractive indices of the quenched charges. The α index (yellow-brown pleochroism) was measured in each case. Red filters, transmitting the equivalent wavelengths of red lithium light, were at first employed, but the values obtained were found not to differ from those obtained with unfiltered white light. It seems that the high-index media used, because of their reddish-brown color, act as filters, making the use of additional filters unnecessary. The refractive index of the crystalline pleochroic iron phase in this system was found to decrease with decreasing iron content of the charge. Thus, as the calculated percentage of C_4AF was reduced from 90 to 30 percent, the α index of the iron phase was lowered from 2.03 to 1.91.

Considerable difficulty was encountered in crystallizing the iron phase in the low-iron compositions of the NC_8A_3 field. Even when the charge was allowed to cool with the furnace, the cooling rate was still not slow enough to permit satisfactory crystallization of this phase. By a controlled slow cooling, effected by gradual reduction of electrical input into the furnace, the iron phase could be identified microscopically; but crystals large enough for index-of-refraction measurements could not be obtained in charges in which the calculated C_4AF concentration was below 25 percent.

The results of this study have located the boundaries of the NC_8A_3 primary phase region in a system in which C_4AF is a component. The iron phase has been identified as a solid solution, the composition of which varies with the iron concentration. Evidence has previously been reported [6] leading to the suggestion that C_3A and NC_8A_3 form, under suitable conditions, a solid-solution phase at temperatures below the liquidus. No indication of this was found in the present study. However, in the following investigation, C_3A and NC_8A_3 were sometimes observed as what appeared to be mix-crystals.

2. Portion of the System N-C-C_5A_3-C_2F

From the study above reported, we learn that the soda compound NC_8A_3 exists at equilibrium on the liquidus over a part of the plane represented by the pseudo-ternary system C-C_4AF-(NA_3), as well as in the pseudo-binary system C-(NA_3), as shown by the diagram of figure 1. It was necessary to ascertain further the point in the quaternary system N-C-A-F where the soda compound NC_8A_3 first appears. From figure 1 it is obvious that this will be found within the wedge bounded by C, A, (NA_3) and (AF), i. e., in a region more remote from N than the plane previously studied. The procedure employed was to set up a space model of the system N-C-A-F as before, in which the ternary system C-C_5A_3-C_2F [18] appears on one of the faces, as shown in figure 3. A series of planes parallel to the above face was then drawn at specified Na_2O concentrations, each plane containing a fixed Na_2O value. These planes were arbitrarily spaced at Na_2O concentrations of 2, 4, and 6 percent, the intention being to continue study of successive planes until NC_8A_3 appeared as a primary phase. About 10 composition points were investigated in each soda plane as well as in the soda-free base plane.

It was found that the planes containing 2 percent and 4 percent of Na_2O did not show NC_8A_3 as a primary phase; but when the plane containing 6 percent of Na_2O was explored, it was found to cut the primary-phase volume of NC_8A_3 in a narrow elliptical section extending from about 3 to 22 percent of C_2F. Additional planes containing 5 and 4.5 percent of Na_2O were found also to cut the primary-phase volume of NC_8A_3, which locates between 4.0 and 4.5 percent the Na_2O concentration at which NC_8A_3 first appears. Further planes to locate this concentration more precisely were not explored; but it was concluded that the Na_2O concentration could be placed at about 4.2 percent.

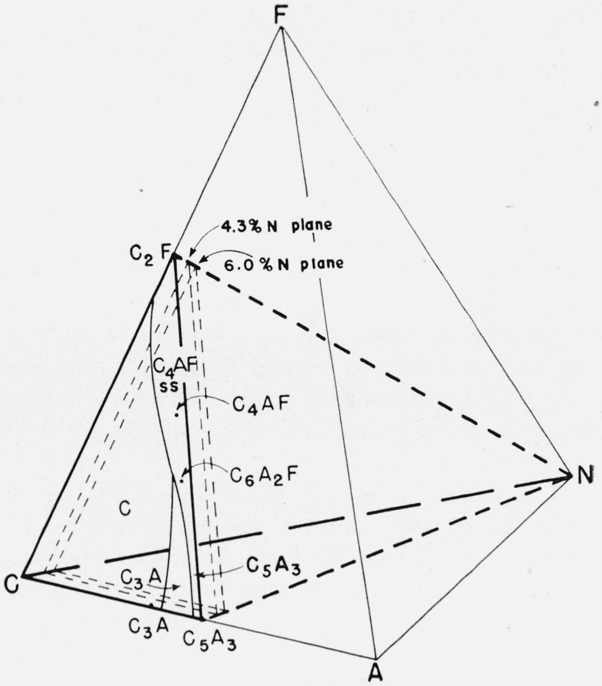

FIGURE 3.—*Tetrahedron,* N-C-A-F, *on one face of which is shown the ternary system* C-C_5A_3-C_2F [18], *and within which appears the quaternary system* N-C-C_5A_3-C_2F.

These exploratory studies indicate that the temperature of the quaternary invariant point may be higher, rather than lower, than the 1,335° C [10, 18], reported for the soda-free, ternary invariant point for C_5A_3, C_3A, iron phase and liquid. The explanation appears to be that certain phases, especially C_5A_3 and the iron phase, are not pure and the resulting solid solutions may melt at higher temperatures than the pure compounds. It is theoretically possible for solid solution freezing-point curves to pass through either maxima or minima. The latter phenomenon, however, is the more common. Examples of each of these cases are discussed by Findlay [4] and others.

The effects of solid-solution formation have been noted by a number of investigators, and the readiness with which C_5A_3 enters into such solution has been reported. In the presence of Fe_2O_3, the refractive indices of the C_5A_3 phase have been found to be markedly raised [10]. As much as 8 percent of C_4AF may be taken up by C_5A_3, and up to 5 percent of C_5A_3 or C_3A may be taken up by C_4AF [13]. In the system N-C-A [2], the C_5A_3 phase crystallizes as a solid solution with Na_2O, and as little as 1 percent of Na_2O raises the melting point of C_5A_3 25 degrees. Likewise, in the system N-C-A-S [7], the invariant point for C_2S, C_3A, C_5A_3 and NC_8A_3 has been reported to occur at a temperature 30 degrees higher than that of the corresponding soda-free invariant point for C_2S, C_3A, and C_5A_3. From these results it appears that the formation of solid solutions involving C_5A_3 with Fe_2O_3 or Na_2O, as well as those concerned with the iron phase [18] may be responsible for the increased temperature in the compositions under discussion in the present investigation.

There seems to be some possibility of the existence of solid solution also in the case of C_3A and NC_8A_3. Occasionally, large isotropic grains of C_3A were seen to contain fine granules of grey birefringent material. The birefringence of this granular material corresponds to that for NC_8A_3. Such a large grain then has a mottled birefringence. This presents some evidence that fine grains of NC_8A_3 may be embedded in the C_3A matrix, resulting from a reaction of alkali with C_3A. Whether or not this is a solid solution is still not certain.

3. Portion of the System N-C-C_2S-CF

In former studies of the system C-F-S in the region of portland cement [9, 3], no ternary compounds were found. It was necessary, however, to extend that study by the introduction of Na_2O as a component. Accordingly, the quaternary system N-C-F-S was set up in a manner similar to that employed in the previous studies on the system N-C-A-F. Figure 4 shows the tetrahedron N-C-F-S on one face of which are given the boundary curves and joins of the system C-C_2S-CF [3]. A plane parallel to the plane of this system cutting the tetrahedron at 5-percent Na_2O concentration was explored, and is indicated on the diagram. Twenty compositions in this plane and five compositions in the soda-free plane were studied.

The burning and quenching techniques employed were the same as previously used, with the exception that additional burns of some mixes were made wherein the charge was allowed to cool slowly so that the secondary phases present might be examined.

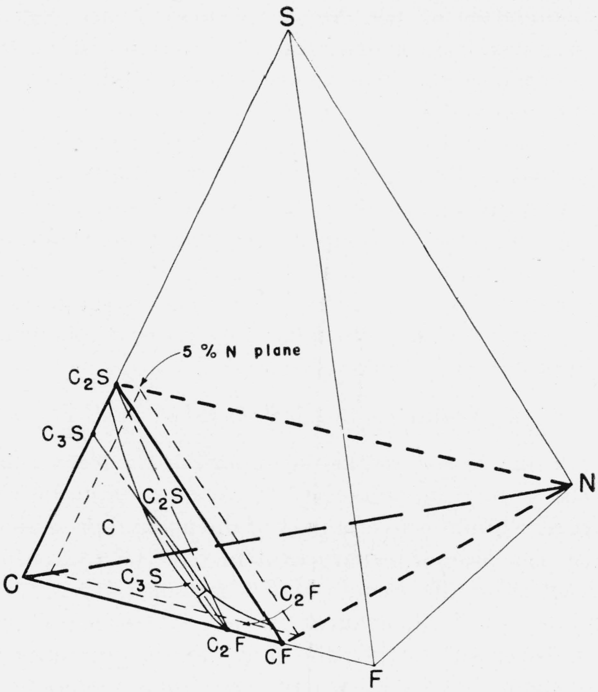

FIGURE 4.—*Tetrahedron,* N-C-F-S, *on one face of which is shown the ternary system,* C-C_2S-CF [3], *and within which appears the quaternary system* N-C-C_2S-CF.

It was observed that no ternary compounds were formed in this system with Na_2O additions of 5 percent. The temperature of liquid formation was lowered, however, due to the presence of Na_2O. Even in the presence of Na_2O, however, it was observed that charges near the C_2S-C_2F join and close to C_2S in composition were very refractory, showing little liquid at temperatures up to 1,550° C. As the composition moved away from the C_2S point and contained increasing concentrations of C_2F, the amount of liquid formed was found to increase. In a mix containing only 31.5 percent of CaO, the charge was completely liquid at 1,320°. In charges containing 15 percent or more of Fe_2O_3, it was noted that the C_2S grains were usually surrounded by a dark matrix, which appeared more opaque as the iron concentration increased. This phase occurred in both the crystalline and glassy states; when crystalline, its birefringence was deep red. In many cases a region of higher birefringence (yellow to bright red) existed at the interface of this phase and the C_2S crystals, which would seem to indicate some reaction between the C_2S and the surrounding phase. It is possible that soda-containing solid solutions within the C_2S react to some extent with the iron-containing matrix. Many fine inclusions thought to contain soda were frequently observed in the C_2S grains.

In this investigation soda was added as the glassy compound NS_2. As this compound crystallizes only under carefully controlled conditions of very slow cooling, no NS_2 crystals were observed in any of the burns. However, only one liquid phase was observed and, because a liquid phase was always present, it is probable that the soda was concentrated there.

No C_3S was observed in the 5-percent Na_2O plane studied. Apparently this compound is not stable in the presence of Na_2O of that concentration. It has been observed that soda reacts with C_3S, converting it to free CaO and C_2S, and then enters into solid solution with the C_2S. Hence soda causes free CaO to form, which would not otherwise appear, thus enlarging its primary-phase region. Conversely, the size of the C_3S primary-phase region is decreased, or disappears entirely as in the concentrations herein reported. The location of the C_2S and iron-phase fields appear essentially unchanged in the 5-percent Na_2O plane.

IV. Discussion

In the investigations herein reported, SiO_2 and Al_2O_3 were not present together in any of the compositions studied. The purpose, as already explained, was to provide the necessary information preliminary to the extension of the studies to the quinary system N-C-A-F-S.

The work has revealed that the extension of the field of CaO due to the introduction of Na_2O, as previously reported for the system N-C-A-S [7], applies also in the systems and regions covered in the present study. Also, the presence of soda was observed to lower the temperature of formation of first liquid. However, the influence of soda on the burnability of portland cement clinker cannot be stated with assurance until the simultaneous phase-equilibrium relations of all five components have been completed.

Likewise, the nature of the soda phase in portland cement clinker cannot be stated with assurance until the completion of the quinary system. At the present state of information, it appears that the phase NC_8A_3 is stable over a wide range and probably constitutes the principal soda phase in clinker, although soda has been observed to enter into several different solid solutions. It is possible that this phase may interact with calcium sulfate, as was found to be the case with the potash compound $KC_{23}S_{12}$ [21]. In that case we might expect Na_2SO_4 and C_3A to be produced, a reaction for which we have some evidence.

It had previously been shown [6] that soda enters into solid solution with α C_2S following interaction with C_3S by which CaO is liberated. When the α C_2S solid solution inverts to the β form on cooling, the soda appears to be precipitated, perhaps as NC_8A_3, and to remain as inclusions in the crystallized silicate grains. Further evidence of this reaction was obtained in the present study, where the C_2S phase was observed in all three of its polymorphic forms. Soda-containing charges that were rapidly quenched from 1,300° C or above were sometimes observed to contain α C_2S, characterized by its glassy appearance and α index close to 1.713 [6]. The crystals in many cases were found to contain very fine dark inclusions. The α to β inversion temperature was found to be lowered from 1,456° C, as reported by Newman and Wells [15]) by as much as 156 degrees. The β form of C_2S, readily identified by its twinned structure, was found in slowly cooled burns. These crystals contained inclusions of fairly large rounded grains that are believed to be due to the exsolution of a soda-containing phase. The slowly cooled charges contained considerable amounts of γ C_2S, and often dusted due to the inversion of the β C_2S to the gamma form.

Occasionally in charges of high-iron concentration, small areas of brighter color and higher birefringence were observed in the dark-brown glass surrounding the grains of dicalcium silicate. It appears probable that these areas are caused by an interaction of the soda (coming out of solution in the C_2S) with the surrounding glass.

The petrologic significance of certain ternary subsystems in the high-silica portion of the system N-C-A-S has recently been reported by Goldsmith [5]. Although these investigations consider concentrations of silica much higher than those encountered in this study, certain relations such as those of solid solution appear to be similar. The predominance of solid solutions in these systems is worthy of note. It was stated that the only substantially pure phase existing either in natural magmas or synthetic melts in this range of compositions is the mineral quartz. All other phases exist in some form of solid solution. A similar situation seems to exist in the systems under consideration here. In this case it is likely that the only pure phase encountered is free CaO, the remaining phases reacting with each other to a more or less extent to form solid solutions.

Certain of these solid solutions may be defined only in terms of the oxide components of the large quaternary system N-C-A-S. In other words, ternary subsystems having various compounds such as C_4AF or C_5A_3 as components may be nonternary. That is, phases encountered are not capable of being expressed in terms of the end members of the ternary system considered, and liquids formed upon crystallization of solid solutions fall outside that ternary system in composition. One reason for this appears to arise from the nature of these solid solutions, in which solution takes place in the form of the smaller oxide units, rather than the larger ones involving compounds.

At the liquidus, such systems may behave as ordinary ternary systems. However, as stated earlier, below the liquidus the composition of both solid solutions and liquids is usually outside the given plane. Courses of crystallization cannot be traced readily, and the phase-equilibrium relations in general increase in complexity in these systems containing solid solutions.

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