U. S. Department of Commerce
National Bureau of Standards

Research Paper RP2069
Volume 44, February 1950

Part of the Journal of Research of the National Bureau of Standards

Phase-Equilibrium Studies of the High-Lime Portion of the Quinary System Na_2O-CaO-Al_2O_3-Fe_2O_3-SiO_2[1]

By William R. Eubank [2]

Two means, one graphic and the other analytic, for studying the phase-equilibrium relations in a portion of the five-component system Na_2O-CaO-Al_2O_3-Fe_2O_3-SiO_2 are described. Using the graphic procedure, compositions in two series of planes in the quinary system were investigated by the quenching method. In each of the two series one component was held constant and another given different values in successive planes. In each plane two components remained constant while three were varied. In this way the minimum temperature for complete melting in each plane was determined. Data for a number of these planes were then employed to locate the quinary invariant point, which was found to have the composition, 1.0 Na_2O, 48.0 CaO, 31.0 Al_2O_3, 13.5 Fe_2O_3 and 6.5 percent of SiO_2. At this point the five crystalline phases, $Na_2O.8CaO.3Al_2O_3$, $3CaO.Al_2O_3$, Fe_2O_3-containing solid solution, $2CaO.SiO_2$, and $3CaO.SiO_2$ exist in equilibrium with liquid.

The temperature of the invariant point was found to be 1,310° ± 3° C. Compositions including the five constituents and approximating that of portland cement clinker will crystallize completely, upon slow cooling, at or near 1,310° C. The stable existence of the soda compound $Na_2O.8CaO.3Al_2O_3$ in the presence of the principal components of clinker was established. The data obtained permit a closer approximation of the amount of glass in rapidly cooled clinker. Dicalcium silicate and the iron-containing phase were observed to exist in various forms of solid solution.

Application of an analytic method for locating and following compositions within the quinary system has likewise been made. Equations have been developed and examples are given for depicting specific planes and points within these planes in the quinary system without the necessity of using geometric relations. The graphic and analytic methods, however, complement each other and together serve as a convenient procedure for studying any system of five components.

I. Introduction

Phase-equilibrium studies on the components of portland cement clinker have proved invaluable in predicting compound composition, explaining chemical activity, and in improving manufacturing practices. The four major components (lime, alumina, ferric oxide, and silica) have been considered, but many of the systems including the minor components (the alkalies, titania, manganese, and others) still await investigation. It is essential, therefore, to extend phase-equilibrium studies of this important material to include additional components and crystallization products.

The presence of soda in portland cement has long been recognized, but the part it plays in the complex cement systems has not yet been fully defined. In the present study the role of Na_2O is examined in a portion of the system N-C-A-F-S,[3] including the composition range of portland

---

[1] Part of a dissertation submitted to the Board of University Studies of the Johns Hopkins University in conformity with the requirement for the degree of Doctor of Philosophy, granted in June 1947.

[2] Research Associate at the National Bureau of Standards, representing the Portland Cement Association Fellowship.

[3] For convenience, the otherwise cumbersome formulas of the compounds encountered in this investigation are given in the following abbreviated forms:
$N=Na_2O$,
$C=CaO$,
$A=Al_2O_3$,
$F=Fe_2O_3$,
$S=SiO_2$.
Thus $NC_8A_3=Na_2O.8CaO.3Al_2O_3$.

cement. This investigation marks the first attempt, so far as is known, to study systematically and simultaneously the relations of these five components to each other.

Methods for defining the phase-equilibrium relations in binary, ternary, and quaternary systems are well known and have been extensively applied, but with systems of more than four components the difficulty of geometrical representation has severely restricted investigation. It has been customary in the treatment of quaternary systems to select regions that may be reduced to two or three components. In the present study a method is presented for the treatment of a five-component system by graphic methods and also by an analytic treatment developed in this laboratory.

The means of studying quinary systems is of particular interest for an understanding of the constitution not only of portland cement clinker but also of natural rocks and ceramic products, including glasses. The methods herein described for a study of the particular quinary system NC_8A_3-C-C_5A_3-C_2F-C_2S are of a general nature and may be applied to the study of other systems.

A brief review will first be given of the boundary systems previously investigated, followed by the description of the methods employed in this investigation and the results obtained. It should be pointed out that this study has been mainly exploratory, and that a more complete study of the system is a matter for future investigation.

II. Previous Work on Boundary Systems

Of the five quaternary systems bounding the quinary system N-C-A-F-S, one (N-A-F-S) contains no CaO and is not considered significant in this study. A portion of the system C-A-F-S covering the region C-C_5A_3-C_4AF-C_2S was reported in 1934 by Lea and Parker [1] [4] and, more recently, the region C-C_5A_3-C_2F-C_2S was examined by Swayze [2]. A portion of the system N-C-A-S covering the region NA-C-A-C_2S was investigated by Greene and Bogue [3]. Some preliminary studies on the system N-C-A-F in the regions (NA_3)-C-C_4AF and N-C-C_5A_3-C_2F and on the system N-C-F-S in the region N-C-CF-C_2S were reported recently by Eubank and Bogue [4].

Temperatures [5] and compositions of certain invariant points determined in these boundary systems are given in table 1.

Throughout this investigation the phase containing iron is designated by the short notation F*ss* indicating an Fe_2O_3-containing solid solution, and for brevity is called the "iron phase." A more quantitative but longer formula for this solid-solution phase is $C_6A_xF_{3-x}$, with x varying from 0 to 2. This represents any composition in a series of solid solutions extending from C_2F to C_6A_2F. These solid solutions have been reported by Swayze [2].

III. Experimental Procedure

The experimental procedure followed the quenching method as described by Bogue [5] with certain modifications. Identification of phases in the quenched charges was made with the petrographic microscope.

Because of the difficulty in obtaining sufficiently rapid cooling to form identifiable crystals, very small charges weighing only a few milligrams were used. Quenching in water, mercury, and liquid air was tried. Mercury did not prove satisfactory, because the charge floated on it with only its underside cooling rapidly. Good quenching resulted in liquid air, even though this has a lower heat capacity than water. Satisfactory results were obtained by quenching very small charges in water. Hydration of the quenched charge was not enough to interfere with petrographic observations.

Platinum envelopes (closed containers), and platinum pans (open containers) as used by Swayze [2], were compared. Loss of soda by volatilization at high temperatures was found to be greater in the case of the open pans. Therefore platinum envelopes were generally used but were reduced to the very small size of 2 to 3 mm square.

An arrangement was employed by means of which two charges of different composition could be quenched simultaneously at a particular temperature. Two pairs of heavy L-shaped platinum leads at the bottom of the quenching assembly were used to suspend, by means of fine platinum wire, two platinum envelopes on opposite

---

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

[5] All temperatures are given in degrees Centigrade. Temperature values determined in this study are considered reliable to within ±3 deg; however, temperatures could be controlled to within ±0.1 deg.

sides of the thermocouple junction. The voltage necessary to melt both fine suspension wires was applied at the top of the assembly. Two battery clips, each connecting one lead of each pair, made double quenching possible. This allowed the investigation to proceed more rapidly than is possible in a single-quench operation.

It was found convenient to have a thermocouple mounted in the furnace slightly below the level of the quenching assembly. The temperature of the furnace could then be read and adjusted to the desired value before the charges were introduced. A second thermocouple within the quenching assembly was used for precise temperature measurement. This thermocouple was recalibrated frequently against an NBS standard thermocouple or the melting point of pure $BaO.2SiO_2$ (m. p. 1,418°) [6]. A method of precise temperature control making use of a thyratron quenching-furnace thermostat [7] was developed for this investigation.

The cement compounds and base mixes used in this study were prepared from oxides or carbonates of unusually high purity. Two of these specially prepared starting materials, ferric oxide and silica gel, were of better than 99.99-percent purity by spectrographic analysis. Chemical analysis showed that the sodium and calcium carbonates contained a maximum of 0.04 percent of impurity and that the alumina contained no more than 0.10 percent of impurity. All compounds were ground in a mullite mortar to pass a No. 200 U. S. Standard Sieve. Compositions were dry-ground to insure thorough mixing. Homogeneity was checked by microscopic examination.

The practice of making powder-slides of important charges using Hyrax resin, refractive index 1.715, was continued [4], because this index is very close to that of several cement compounds. Restudy of these permanent specimen-preparations could then conveniently be made.

IV. Methods for Studying a Quinary System

Two means, one graphic and the other analytic, may be used in tracing the phase-equilibrium relations in a system of five components. The first of these, the graphic method, was used for the most part in this study. The analytic method was developed by Dahl [8, 9] subsequent to the use of the graphic method. Both methods will be presented and their applications discussed.

1. Graphic Method

Phase studies in a quaternary system are usually made with a series of triangular sections (diagrams) through a tetrahedron. These may be located in the tetrahedron by choosing various ratios of two of the components and holding these constant for each plane (triangular diagram) or, as is more often the case, planes parallel to the base with a constant amount of the fourth component in each plane may be studied, allowing the other three components to vary. Each plane will represent the intersection of that plane with one or more primary-phase volumes. Invariant points are likely to be located between planes, since the choice of a plane with the exact amount of the fourth component for an invariant point would be accidental. Such points would have to be extrapolated from the data obtained for the planes above or below it, or additional planes between the two might be studied.

The best means for beginning the investigation of the quinary system would seem to be that of first studying the corresponding invariant points in the boundary quaternary systems. Some of these invariant points [4] were determined preliminary to the study of this quinary system. A small tetrahedron, 20 percent on a side, was chosen containing the compositions of these invariant points for the boundary quaternary systems, for example, T_1 and T_2, figure 1 [1]. For

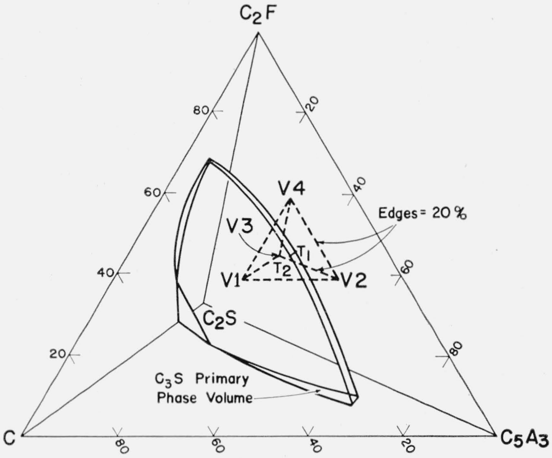

FIGURE 1. *Location of a small tetrahedron containing quaternary invariant points* [1].

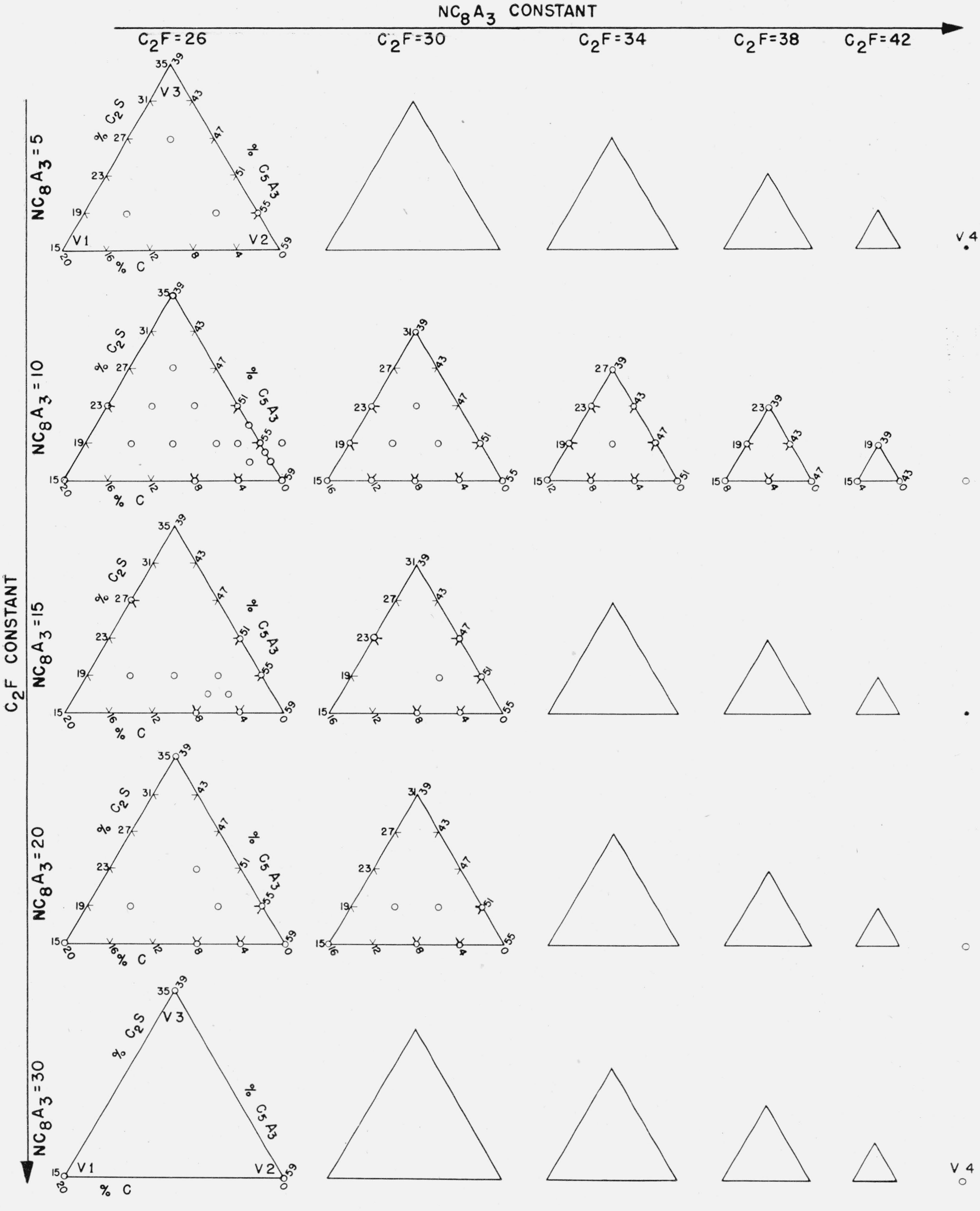

FIGURE 2. *Circled points represent compositions studied within the quinary system* NC_8A_3-C-C_5A_3-C_2F-C_2S.

Only NC_8A_3 is given as a quinary composition. The remaining four components are given as the quaternary components of figure 1. When X percent of NC_8A_3 was added, the percentage of each of the four quaternary components was multiplied by $(100-X)/100$ to bring all compositions within the quinary system. For example, a particular point in the 10 NC_8A_3-26 C_2F plane will contain 10 percent of NC_8A_3 0.90 × 26 percent of C_2F, and 0.90 × the percentages of the other three indicated in the triangular diagram.

points located in this tetrahedron, X percent of the fifth component would be added and $100-X$ percent taken of the remaining four. This would bring the compositions to be studied within the quinary system. Both oxide and compound compositions at the vertices of this small tetrahedron to which soda is to be added are given in the following tabulation.

Vertex	Oxide Composition,[a] Percent			
	CaO	Al_2O_3	SiO_2	Fe_2O_3
1	59. 15	20. 35	5. 23	15. 27
2	48. 72	30. 78	5. 23	15. 27
3	52. 17	20. 35	12. 21	15. 27
4	47. 40	20. 35	5. 23	27. 02
	Compound Composition, Percent			
	CaO	C_5A_3	C_2S	C_2F
1	20	39	15	26
2	0	59	15	26
3	0	39	35	26
4	0	39	15	46

[a] All compositions referred to in this work are given in weight percent.

Compositions in the quinary system may be followed by the two series of planes (triangular diagrams) shown in figure 2. In the first series the iron phase is allowed to vary, whereas in the second the soda phase is varied. In each particular plane both the iron phase and soda are maintained constant and the other three components allowed to vary. The composition melting at the lowest temperature in each plane locates a point on a bivariant surface in the quinary system. The locus of these points for each series of planes intersects a univariant curve. This intersection, usually a directional change point, may be located by plotting the various components or ratios of the components for a number of intersection points. It is not likely that this point of intersection will be on any plane chosen, but it will occur between planes and can thus be estimated by the extension of the curves. A number of these intersection points will define a univariant curve that may be followed to the invariant point.

Visualization of the relations between a large number of bivariant surfaces is limited by conventional three-dimensional representation. It is possible, however, to show diagrammatically the relations between such surfaces at a single invariant point, as is shown in figure 3. Five univariant curves meet at an invariant point. These are boundaries of the bivariant surfaces intersecting at that point. The number of curves and surfaces meeting at the invariant point and the number of solid phases represented for each meet the requirements of the phase rule for a condensed system. Five solid phases are in equilibrium with liquid at the invariant point. Five univariant curves along which four solid phases are in equilibrium with liquid intersect at this point. Five bivariant surfaces on which three solid phases are in equilibrium with liquid meet at the invariant point. The volumes bounded by these surfaces may be considered trivariant with two solid phases in equilibrium with liquid. The tetravariant primary-phase regions for the five solid phases cannot be shown in a conventional space model. Phase-equilibrium relations at a quinary invariant point are pictured arbitrarily in figure 3.

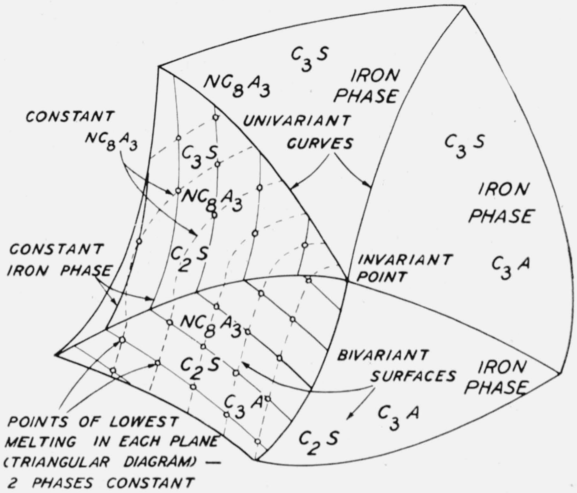

FIGURE 3. *Successive percentages of the iron phase are shown along the solid lines on the bivariant surface at the left.*

Successive percentages of the soda phase are represented by dashed lines. The intersections of these two sets of lines represent the composition point of the lowest temperature for complete melting determined for each plane when both the iron and soda phases were held constant. A univariant curve is the locus of points of directional change in the curves representing constant NC_8A_3 or constant iron phase. A univariant curve may then be followed to the quinary invariant point.

Each triangle in figure 2 is analogous to a straight line in the space model of a quaternary system A-B-C-D, parallel to one of the edges, thus fixing the percentages of two of the components of the system. Such a line may be represented by two equations, for example, $A=5$ and $C=45$. It is apparent that the line may not intersect any univarant curve and that it will intersect a bivariant surface at only one point. Similarly, a quaternary system within a quinary system may be represented by an equation, and a ternary system within a quinary system may be represented by two equations. Interpretation of the data obtained from the triangles in figure 2 requires a knowledge of the manner in which invariant points, univariant curves, etc., in a quinary system appear in triangular diagrams. The following tabulation shows how these relations in a quinary system appear in a triangular diagram and a space model (tetrahedron), according to Dahl [10].

Geometric relations in quinary system	Tetravariant hypervolume	Trivariant volume	Divariant surface	Univariant curve	Invariant point
Number of solid phases in equilibrium with liquid and vapor	1	2	3	4	5
Intersections with triangular diagram	Area	Curve	Point	(a)	(b)
Intersections with space model	Volume	Surface	Curve	Point	(c)

[a] May appear as a point in the triangular diagram, but only when *both* of the two equations of the triangular diagram are satisfied by some point on the univariant curve. The point in the diagram then represents that particular point.

[b] May appear as a point in the triangular diagram, but only when *both* of the two equations of the triangular diagram are satisfied by the invariant point.

[c] May appear as a point in a space model, but only when the equation of the space model is satisfied by the invariant point.

2. Analytic Method

In representing phase-equilibrium relations of a quinary system within a triangular diagram or space model, conditions are imposed that indicate the manner in which compositions in these figures are different from all other compositions in the quinary system. A set of intrinsic equations, that is, equations involving components of a system and lacking a constant term, may be used to express these conditions. For example, in dealing with the system NC_8A_3-C-C_5A_3-C_2S-C_2F, it may be decided to work for a time with compositions limited to 10 percent of C_2F. A space model (tetrahedron) may be used to represent the composition relations under this condition, since the sum of the percentages of the remaining components is constant. The equation of the space model is $C_2F=10$. When the percentages of two of the components are fixed, for example if $C_2F=10$ and $NC_8A_3=5$, the sum of the remaining components is 85 percent, and relations between the remaining components may be shown in a triangular diagram.

Dahl has recently published a paper on the analytic treatment of multi-component systems using intrinsic equations [9]. This has been followed by another paper [8] on the properties and application of parametric equations. Dahl's equations are derived directly in terms of composition without considering geometric relations and may be applied to multi-component systems without the necessity of thinking in terms of hyperspace.

The number of intrinsic equations required to define a secondary system of m components in a primary system of N components is equal to the difference $N-m$. For example, a binary system is represented by a single equation when it is in a ternary system but requires three equations if it is in a quinary system. The number of terms that may appear in the equations also increases with the complexity of the system. A binary system within a quinary system may, however, be expressed by parametric equations using only one parameter. A ternary system requires two parameters, and so on. Parametric equations may therefore be used to define binary and ternary systems within a quinary system and intrinsic equations may be used in defining the more complicated quaternary systems within a quinary system. Thus, both types of equations may be employed in defining relations in a quinary system. The intrinsic equations may be set up in the manner of Dahl by using algebraic and determinant methods in connection with oxide or compound formulas and their molecular weights.

A parameter is introduced in order to express the composition of each component in terms of that variable. To define a system of m components in an N-component system, N parametric equations and $m-1$ parameters are required. To illustrate the procedure as applied to systems requiring more than one parameter, the ternary system NC_8A_3-C_4AF-C_3S may be defined within the quinary system, N-C-A-F-S. The data needed are the compositions of the components of the ternary system as calculated from their molecular weights. Two parameters are required. This is illustrated in the following tabulation, in which the parameters are r and s. The weight fraction of NC_8A_3 is r, that of C_4AF is s, and that of C_3S is $1-r-s$. Thus, by varying r and s between 0 and 1, with $r+s$ not exceeding 1, compositions in any part of the ternary system NC_8A_3-C_4AF-C_3S within the quinary system N-C-A-F-S can be located and studied. The sum of the parametric expressions in the equations must be equal to 100 percent.

Primary component	NC_8A_3	C_4AF	C_3S	Parametric equation
	Percent	*Percent*	*Percent*	
N	7.6	----	-----	$N=7.6r.$
C	54.9	46.2	73.7	$C=18.8r-27.5s+73.7.$
A	37.5	20.9	-----	$A=37.5+r20.9s.$
S	----	----	26.3	$S=26.3r-26.3s+26.3.$
F	----	32.9	-----	$F=32.9s.$
Weight fraction	r	s	$(1-r-s)$	

Parametric equations may be used to trace compositions in planes within the quinary system. This serves the same purpose as the series of planes described in the graphic method, but without the necessity of considering geometric relations. For this study compositions in the quinary system are confined to a subordinate system in which the components are those at the vertices of the small tetrahedron in figure 1, with NC_8A_3 as the fifth component. The first step in the analytic method is to obtain parametric equations in which the percentage of each component of the quinary system is expressed in terms of weight fractions of components of the subordinate system. This is shown in the tabulation below.

Composition points of subordinate system	A	B	C	D	E	Weight fraction
	CaO	C_2S	C_5A_3	C_2F	NC_8A_3	
	%	%	%	%	%	
V1	20	15	39	26	0	v
V2	0	15	59	26	0	w
V3	0	35	39	26	0	x
V4	0	15	39	46	0	y
V5	0	0	0	0	100	$1-v-w-x-y$

Equations for the quinary system are:

$$A=20v, \tag{1}$$

$$B=15v+15w+35x+15y, \tag{2}$$

$$C=39v+59w+39x+39y, \tag{3}$$

$$D=26v+26w+26x+46y, \tag{4}$$

$$E=-100v-100w-100x-100y+100. \tag{5}$$

Parametric equations for a ternary system (triangular diagram) require only two parameters, and the second step is to eliminate two of the parameters in eq 1 to 5. These parameters may be selected arbitrarily, and in this case x and y are chosen. Since C_2F and NC_8A_3 are to be maintained constant in each triangle, as in figure 2, it will be assumed that D and E are equal to the constants D_1 and E_1, respectively. Transposing eq 4 and 5, and simplifying, the following equations are obtained:

$$26x+46y=D_1-26v-26w, \tag{4a}$$

$$x+y=-0.01E_1-v-w+1. \tag{5a}$$

Solving for x and y,

$$x=-0.05D_1-0.023E_1-v-w+2.3, \tag{6}$$

$$y=0.05D_1+0.013E_1-1.3. \tag{7}$$

Substituting in eq 1 to 3,

$$A=20v \tag{8}$$

$$B=-20v-20w+0.61(100-E_1)-D_1, \tag{9}$$

$$C=20w+0.39(100-E). \tag{10}$$

Upon substituting in eq 8 to 10, the values of D_1 and E_1 to be maintained constant in any given triangle, equations for A, B, and C will be obtained in terms of the parameters v and w. For example, if D_1 and E_1 (that is, C_2F and NC_8A_3) are to be given the values 23.4 and 10.0 percent, respectively, substitution of these values in eq 8 to 10 yields the following equations for compositions in the triangle.

$$A=20v, \tag{8a}$$

$$B=-20v-20w+31.5, \tag{9a}$$

$$C=20w+35.1. \tag{10a}$$

Substitution of 23.4 and 10.0 for D_1 and E_1, respectively, in eq 6 leads to the equation,

$$x=0.9-v-w.$$

Since the weight fractions of the subordinate components cannot be negative, $(v+w)$ in the triangle under consideration cannot exceed 0.9.

Thus, by varying the weight fractions v and w, within the limits specified, any composition of the ternary system in which $D=23.4$ and $E=10$ within the quinary system may be obtained. For example, the test composition 10N26F5, discussed later and given in table 4, is located within this plane when $v=0$ and $w=0.72$ and can then be studied. Additional parametric equations for other planes and points within planes may be found in a similar manner. The lowest melting composition for each plane is then determined experimentally. As described earlier, the locus of these points crosses a univariant curve, which may then be traced to the invariant point.

V. Results

The compositions studied by use of the graphic method are indicated by the circled points in the two series of triangular diagrams given in figure 2. These compositions, along with the quenching data and the results of petrographic examination, are given in tables 2 through 4. Only the data necessary to locate the liquidus or to identify both primary and secondary phases are presented. For many compositions only one quench was required when it was obvious that the liquidus temperature was increasing, i. e., compositions were getting farther from the invariant point. In these cases the appearance of primary and secondary phases was more important than the location of the exact liquidus temperature.

TABLE 1. *Invariant points for systems bounding the quinary system* NC_8A_3-C-C_5A_3-C_2F-C_2S

System [a]	Investigator and reference	Temperature	Percent composition				
			Na_2O	CaO	Al_2O_2	SiO_2	Fe_2O_3
C-C_5A_3-C_4AF-C_2S:		°C					
C_3S, C_3A, F *ss*, C_2S and liquid	Lea and Parker [1]	1,338	0	54.8	22.7	6.0	16.5
C, C_3A, F *ss*, C_3S and liquid		1,341	0	55.0	22.7	5.8	16.5
C-C_5A_3-C_2F-C_2S:							
C_3A, C_2F, C_2S, C_3S, liquid	Swayze [2]	1,338	0	53.5	22.3	6.0	18.2
C, C_3A, C_2F, C_3S, liquid		1,342	0	53.9	21.2	5.8	19.1
NA-C-A-C_2S:							
NC_8A_3, C_3A, C_2S, C_3S liquid	Greene and Bogue [3]	1,440	3.5	55.2	31.0	10.3	0
NC_8A_3, C, C_3A, C_3S, liquid		1,442	3.5	56.0	31.0	9.5	0
NC_8A_3, C, C_3S, C_2S, liquid		1,445	5.0	54.1	28.6	12.3	0
(NA_3)-C-C_4AF:							
NC_8A_3, C_5A_3, F *ss*, liquid	Eubank and Bogue [4]	1,344	4.7	44.0	34.2	0	17.1
NC_8A_3, C, F *ss*, liquid		1,390	2.5	48.4	26.8	0	22.3
N-C-C_2F-C_2S	Eubank and Bogue [4]	No ternary compounds found in compositions up to 5% Na_2O.					

[a] For convenience the otherwise cumbersome formulas of the compounds encountered in this investigation are given the following abbreviated forms: $N=Na_2O$, $C=CaO$, $A=Al_2O_3$, $F=Fe_2O_3$, and $S=SiO_2$. Thus $NC_8A_3=Na_2O.8CaO.3Al_2O_3$, etc.

TABLE 2. *Quenching data on quaternary invariant-point compositions with and without addition of soda*

Test No.	Temperature	Methof of quenching	Quench liquid	Phases observed
Point T_1 of Lea and Parker [1]. CaO 55.0, Al_2O_3 22.7, SiO_2 5.8, Fe_2O_3, 16.5				
	°C			
T5	1, 342	Open pan	Water	CaO, F *ss* in glass.
T8	1, 345	do	Liquid air	CaO, C_3S, F *ss* in glass.
T11	1, 347	Small envelope	Water	CaO, C_3S in glass.
T6	1, 347	Open pan	do	CaO, F *ss* in glass.
T9	1, 348	do	Liquid air	CaO in glass.
T7	1, 352	do	Water	All glass.
T12	1, 352	Small envelope	do	Do.
T10	1, 353	Open pan	Liquid air	Do.
Point 1 of Swayze [2]. CaO 53.9, Al_2O_3 21.2, SiO_2 5.8, Fe_2O_3 19.1				
S5	1, 345	Open pan	Water	C_3S, F *ss*, trace CaO in glass.
S7	1, 348	Small envelope	Liquid air	F *ss*, C_3S in glass.
S9	1, 348	do	Water	Do.
S8	1, 354	do	Liquid air	All glass.
S10	1, 354	do	Water	Do.
S6	1, 355	Open pan	do	Do.
Point 1 of Swayze plus 2% Na_2O [a]				
S11	1, 377	Small envelope	Water	Small amount CaO in glass.
S12	1, 397	do	do	Do.
S13	1, 409	do	do	All glass.
Point 1 of Swayze plus 4% Na_2O [a]				
S14	1, 377	Small envelope	Water	Small amount CaO in glass.
S15	1, 387	do	do	Do.
S16	1, 405	do	do	All glass.

Point 2 of Swayze plus NC_8A_3 [a]

No.	CaO	C_5A_3	C_2S	C_2F	NC_8A_3	Temperature	Phases observed
						°C	
10NS2–1	8. 1	38. 4	15. 5	27. 9	10. 0	1, 325	Small crystals F *ss* in glass.
20NS2–1	7. 2	34. 2	13. 8	24. 8	20. 0	1, 325	Do.
Additions of NC_8A_3; NC_8A_3 subtracted from C_5A_3							
10NS2–2	9. 1	32. 7	17. 2	31. 0	10. 0	1, 330	Little glass, small crystals unreacted compounds.
20NS2–2	9. 1	22. 7	17. 2	31. 0	20. 0	1, 330	Small amounts F *ss*, C_3A, CaO in glass.
30NS2–1	9. 1	12. 7	17. 2	31. 0	30. 0	1, 330	Much CaO, traces F *ss* in glass.
40NS2–1	9. 1	2. 7	17. 2	31. 0	40. 0	1, 330	More CaO, F *ss* in glass.

[a] When x% of soda phase was added, $(100-x)$% of each constituent of the quaternary composition point was taken. Unless otherwise stated, all quenches were made in small platinum envelopes into water.

TABLE 3. *Quenching data on boundaries of the small tetrahedron figure 1, with and without additions of soda*

Test No.[a]	Compound composition					Temperature	Petrographic examination
	CaO	C_5A_3	C_2S	C_2F	NC_8A_3		
	Percent	*Percent*	*Percent*	*Percent*	*Percent*	°*C*	
V1-1	20	39	15	26	----------	1,399	Large amounts free CaO in glass.
-2						1,435	Do.
-3						1,501	Considerable free CaO in glass.
-4						1,521	Small amounts free CaO in glass.
V2-1	0	59	15	26	----------	1,312	C_3A,F *ss*—composition gradients in glass.
-2						1,325	Small amount C_3A,F *ss* in glass.
-3						1,345	Traces F *ss* in glass.
-4						1,365	All glass.
V3-1	0	39	35	26	----------	1,350	Small crystals C_2S, F *ss* in glass.
-2						1,362	Do.
-3						1,380	Traces crystals C_2S,F *ss* in glass.
-4						1,392	All glass.
V4-1	0	39	15	46	----------	1,353	Large amounts F *ss* in glass.
-2						1,366	Considerable F *ss* in glass.
-3						1,375	All glass.
	Vertex composition						
	V1	V2	V3	V4			
	Percent	*Percent*	*Percent*	*Percent*	*Percent*		
123V -1	33.3	33.3	33.3	----------	----------	1,378	Small crystals C_2S in glass.
-2						1,401	Do.
-3						1,412	Traces C_2S in glass.
124V -1	33.3	33.3	----------	33.3	----------	1,347	Many F *ss* crystals in glass.
-2						1,358	Traces F *ss* crystals in glass.
-3						1,368	All glass.
134V -1	33.3	----------	33.3	33.3	----------	1,375	F *ss*, protected phases, C_2S in glass.
-2						1,406	Traces C_2S in glass.
234V -1	----------	33.3	33.3	33.3	----------	1,378	Do.
10V2-1	----------	90	----------	----------	10	1,334	Traces C_3A and F *ss* in glass.
-2						1,345	All glass.
20V2-1	----------	80	----------	----------	20	1,345	Small amount C_3A in glass.
-2						1,358	Traces C_3A in glass.
30V2-1	----------	70	----------	----------	30	1,359	NC_8A_3,C_2S in glass.
-2						1,382	NC_8A_3,C_3A in glass.
50V2-1	----------	50	----------	----------	50	1,359	NC_8A_3,C_3A in glass.
-2						1,382	Large crystals NC_8A_3 in glass.
10V3	----------	----------	90	----------	10	1,411	Many rounded grains NC_8A_3, C_2S in glass.
20V3	----------	----------	80	----------	20	1,409	C_2S in glass.
30V3	----------	----------	70	----------	30	1,407	Traces NC_8A_3 in glass.
10V4-1	----------	----------	----------	90	10	1,360	Small crystals F *ss*, C_3A in glass.
-2						1,375	All glass.
20V4	----------	----------	----------	80	20	1,360	Traces F *ss* in glass.
30V4-1	----------	----------	----------	70	30	1,355	Large crystals F *ss*, C_3A in glass.
-2						1,375	All glass.

[a] V refers to the vertices of the small tetrahedron of figure 1.

TABLE 4. *Quenching data on planes (fig. 2) within the quinary system*

Test No.	Percent composition					Temperature	Petrographic examination
	CaO	C_5A_3	C_2S	C_2F	NC_8A_3		
10%, NC_8A_3[a] 26% C_2F plane							
						°*C*	
10N26F1	10.8	38.7	17.1	23.4	10.0	1,390	Many free CaO grains in glass.
10N26F2-1	3.6	45.9	17.1	23.4	10.0	1,332	C_3A, NC_8A_3, F *ss* in glass.
-2						1,342	All glass.
10N26F3	3.6	38.7	24.3	23.4	10.0	1,360	Many small rounded grains C_2S, NC_8A_3 in glass.
10N26F4	3.6	49.5	13.5	23.4	10.0	1,342	Small amounts C_3A, traces NC_8A_3 in glass.
10N26F5-1	0	49.5	17.1	23.4	10.0	1,310	F *ss*, C_2S, NC_8A_3 in glass.
-2						1,316	Small amounts F *ss*, C_2S, NC_8A_3 in glass.
-3						1,320	All glass.
10N26F6	7.2	45.9	13.5	23.4	10.0	1,342	NC_8A_3 in glass.
10N26F7-1	0	45.9	20.7	23.4	10.0	1,336	Do.
-2						1,342	Small amount NC_8A_3 in glass.
10N26F8	1.8	47.7	17.1	23.4	10.0	1,320	C_2S, NC_8A_3, F *ss* in glass.
10N26F9	0	51.3	15.3	23.4	10.0	1,320	Small amount F *ss* in glass.
10N26F10	1.8	49.5	15.3	23.4	10.0	1,320	F *ss*, C_3A, NC_8A_3 in glass.
10N26F11	.9	50.4	15.3	23.4	10.0	1,320	F *ss* in glass.
10N26F12	7.2	38.7	20.7	23.4	10.0	1,353	Many small crystals C_2S, NC_8A_3, C_3S in glass.
10N26F13	3.6	42.3	20.7	23.4	10.0	1,353	Many small crystals C_2S, NC_8A_3, more glass.
10N26F14	7.2	42.3	17.1	23.4	10.0	1,353	Small amount C_3A in glass.
10N26F15	10.8	35.1	20.7	23.4	10.0	1,331	Large amount C_3A, fine crystals F ss in glass.
10N26F16	0	50.4	16.2	23.4	10.0	1,330	Small amounts C_3A, F *ss*, NC_8A_3 in glass.
10% NC_8A_3, 30% C_2F plane							
10N30F1	3.6	45.9	13.5	27.0	10.0	1,320	Many crystals F *ss*, C_3A, traces NC_8A_3 in glass.
10N30F2	0	49.5	13.5	27.0	10.0	1,320	Many crystals F *ss*, traces C_2S, NC_8A_3 in glass.
10N30F3	3.6	42.3	17.1	27.0	10.0	1,322	F *ss*, C_3A, small amounts C_2S, NC_8A_3 in glass.
10N30F4	0	45.9	17.1	27.0	10.0	1,322	Small amounts F *ss*, C_2S, NC_8A_3 in glass.
10N30F5	7.2	38.7	17.1	27.0	10.0	1,336	Traces C_3A in glass
10N30F6	3.6	38.7	20.7	27.0	10.0	1,336	Large grains C_2S in glass.
10N30F7	14.4	35.1	13.5	27.0	10.0	1,320	Some glass, quench growths, unreacted materials.
10N30F8	0	35.1	27.9	27.0	10.0	1,320	Many F *ss*, C_2S, NC_8A_3 crystals in glass.
10N30F9	7.2	35.1	20.7	27.0	10.0	1,330	C_3A, fine quench growths in glass.
10N30F10	10.8	35.1	17.1	27.0	10.0	1,331	Many crystals C_3A, F *ss* in glass.
10N30F11	10.8	38.7	13.5	27.0	10.0	1,331	Many crystals C_3A, F *ss* in glass.
10N30F12	7.2	42.3	13.5	27.0	10.0	1,331	Many crystals C_3A, F *ss* in glass.
10% NC_8A_3, 34% C_2F plane							
10N34F1	10.8	35.1	13.5	30.6	10.0	1,320	Small crystals F *ss*, C_2S, NC_8A_3, little glass.
10N34F2	0	45.9	13.5	30.6	10.0	1,320	Many F *ss* crystals in glass.
10N34F3	0	35.1	24.3	30.6	10.0	1,320	C_2S, C_3S, F *ss* in glass.
10N34F4	3.6	38.7	17.1	30.6	10.0	1,320	F *ss*, C_2S, C_3A in glass.
10N34F5	3.6	35.1	20.7	30.6	10.0	1,323	F *ss*, C_2S in glass.
10N34F6	7.2	35.1	17.1	30.6	10.0	1,323	Many crystals F *ss*, small amounts C_2S, C_3A, NC_8A_3 in glass.
10N34F7	7.2	38.7	13.5	30.6	10.0	1,331	Small crystals F *ss*, C_3A in glass.
10N34F8	3.6	42.3	13.5	30.6	10.0	1,331	Traces F *ss*, C_3A, mostly glass.
10N34F9	0	42.3	17.1	30.6	10.0	1,332	Small amount F *ss*, traces C_3A mostly glass.
10N34F10	0	38.7	20.7	30.6	10.0	1,332	Several crystals F *ss*, C_2S, traces NC_8A_3 in glass.

---

[a] When X% of soda phase was added, (100−X)% of each constituent of the quaternary composition point was taken.

TABLE 4. *Quenching data on planes (fig. 2) within the quinary system*—Continued

Test No.	Percent composition					Temperature	Petrographic examination
	CaO	C_5A_3	C_2S	C_2F	NC_8A_3		
10% NC_8A_3, 38% C_2F plane							
10N38F1	7.2	35.1	13.5	34.2	10.0	1,328	Many small crystals F *ss*, few large crystals C_3A in glass.
10N38F2	0.0	42.3	13.5	34.2	10.0	1,328	Many crystals F *ss*, traces free CaO in glass.
10N38F3	.0	35.1	20.7	34.2	10.0	1,330	Several crystals F *ss*, C_2S, NC_8A_3 in glass.
10N38F4	3.6	35.1	17.1	34.2	10.0	1,330	Several crystals F *ss*, C_2S, NC_8A_3 in glass.
10N38F5	0.0	38.7	17.1	34.2	10.0	1,330	Many crystals F *ss*, some C_2S, small amounts NC_8A_3 in glass.
10N38F6	3.6	38.7	13.5	34.2	10.0	1,330	Many crystals F *ss*, some large crystals C_3A, C_2S (twinned) in glass.
10% NC_8A_3, 42% C_2F plane							
10N42F1	3.6	35.1	13.5	37.8	10.0	1,331	Small crystals F *ss*, small amounts C_2S, NC_8A_3 in glass.
10N42F2	0.0	38.7	13.5	37.8	10.0	1,331	Small crystals F *ss*, small amounts C_2S, NC_8A_3 in glass.
10N42F3	.0	35.1	17.1	37.8	10.0	1,330	Small crystals F *ss*, small amounts C_2S, NC_8A_3 in glass.
5% NC_8A_3, 26% C_2F plane							
5N26F1	11.6	40.8	18.0	24.7	5.0	1,342	Free CaO, NC_8A_3 in glass.
5N26F2–1	3.8	48.4	18.0	24.7	5.0	1,342	NC_8A_3 in glass.
–2						1,355	All glass.
5N26F3	3.8	40.8	25.6	24.7	5.0	1,363	Many crystals NC_8A_3, C_2S in glass.
5N26F5–1	0.0	52.2	18.1	24.7	5.0	1,321	Many crystals F *ss*, C_2S, NC_8A_3 in glass.
						1,332	All glass.
10% NC_8A_3, 22% C_2F plane							
10N22F1	3.6	49.5	17.1	19.8	10.0	1,320	Many crystals C_3A, C_2S in glass, small amounts NC_8A_3 and F *ss*.
10N22F2	0.0	53.1	17.1	19.8	10.0	1,320	Traces C_2S in glass.
10N22F3	.0	49.5	20.7	19.8	10.0	1,320	Several crystals C_2S, some NC_8A_3 in glass.
10N22F4	3.6	53.1	13.5	19.8	10.0	1,320	Many crystals C_3A, some F *ss*, traces NC_8A_3, C_5A_3 in glass.
15% NC_8A_3, 26% C_2F plane							
15N26F1	0.0	43.4	19.5	22.1	15.0	1,320	C_2S, NC_8A_3 in glass.
15N26F2	6.8	43.4	12.7	22.1	15.0	1,320	NC_8A_3,C_3A in glass.
15N26F3	3.4	43.4	16.1	22.1	15.0	1,318	Small amounts NC_8A_3,C_3A,C_2S,F *ss* in glass.
15N26F4	6.8	40.0	16.1	22.1	15.0	1,318	Small amounts NC_8A_3,C_2S,F *ss* in glass.
15N26F5	0.0	46.8	16.1	22.1	15.0	1,321	NC_8A_3,C_3A,C_2S in glass.
15N26F6	3.4	45.1	14.5	22.1	15.0	1,321	Do.
15N26F7	5.1	43.4	14.5	22.1	15.0	1,323	Do.
15N26F8	3.4	46.8	12.7	22.1	15.0	1,323	Do.
15N26F9	6.8	33.2	22.9	22.1	15.0	1,330	C_2S,C_3S,NC_8A_3 in glass.
15N26F10	10.2	36.6	16.1	22.1	15.0	1,330	Free CaO,NC_8A_3, in glass.

TABLE 4. *Quenching data on planes (fig. 2) within the quinary system*—Continued

Test No.	Percent composition					Temperature	Petrographic examination
	CaO	C_5A_3	C_2S	C_2F	NC_8A_8		
				15% NC_8A_3, 30% C_2F plane			
15N30F1	0.0	43.4	16.1	25.5	15.0	1,330	Small amounts F *ss*, NC_8A_3 in glass.
15N30F2	3.4	43.4	12.7	25.5	15.0	1,330	Do.
15N30F3	3.4	40.0	16.1	25.5	15.0	1,330	Do
15N30F4	6.8	33.2	19.5	25.5	15.0	1,330	F *ss*, C_2S in glass.
15N30F5	0.0	40.0	19.5	25.5	15.0	1,330	Do.
15N30F6	6.8	40.0	12.7	25.5	15.0	1,330	F *ss*, NC_8A_3 in glass.
				20% NC_8A_3, 26% C_2F plane			
20N26F1	9.6	34.4	15.2	20.8	20.0	1,330	NC_8A_3,free CaO,C_3A in glass.
20N26F2	3.2	40.8	15.2	20.8	20.0	1,330	NC_8A_3,C_3A in glass.
20N26F3	3.2	34.4	21.6	20.8	20.0	1,330	C_2S,C_3S,NC_8A_3 in glass.
20N26F4	3.2	44.0	12.0	20.8	20.0	1,330	NC_8A_3,C_3A in glass.
20N26F5	0.0	44.0	15.2	20.8	20.0	1,330	Do.
20N26F6	6.4	40.8	12.0	20.8	20.0	1,330	Do.
				20% NC_8A_3, 30% C_2F plane			
20N30F1	6.4	34.4	15.2	24.0	20.0	1,330	Large crystals F *ss*, C_3A, traces C_2S, NC_8A_3 in glass.
20N30F2	6.4	37.6	12.0	24.0	20.0	1,330	Large amounts C_3A,small amounts F *ss*, traces NC_8A_3 in glass.
20N30F3	3.2	37.6	15.2	24.0	20.0	1,330	Do.
20N30F4	0.0	40.8	15.2	24.0	20.0	1,330	Do.
20N30F5	9.6	31.2	15.2	24.0	20.0	1,330	Considerable C_3A,F *ss* in glass.
20N30F6	12.8	28.0	15.2	24.0	20.0	1,330	Do.

The procedure for locating invariant points within the quinary system may be followed systematically by reference to the above mentioned figure and tables. Selection of a small tetrahedron to which the fifth component, the soda phase, was to be added, was made by studying the relations in the boundary systems as discussed in conjunction with figure 1.

Invariant points for the soda-free quaternary system have been reported by other investigators [1, 2]. Lea and Parker's point T_1 and Swayze's point 1 were reported as invariant points at which CaO, C_3S, C_3A, and iron phase are in equilibrium with liquid. Compositions for point T_1 and point 1 were investigated by the quenching methods described earlier, table 2. The observed liquidus temperature was 1,350° C for each of these compositions. This is higher than the 1,341° reported by Lea and Parker for composition T_1 and the 1,342° reported by Swayze for point 1. It is likely that these departures from the published data result from differences in the impurities of the reagents used by the several investigators. Since such variations produce slight changes in composition, the liquidus temperature obtained by the present author in the quaternary system cannot be assumed to be the liquidus temperature of the true invariant-point composition.

The effect of soda in the forms of the oxide and the compound NC_8A_3 on this liquidus temperature is worthy of note, table 2. Additions of 2 and 4 percent of Na_2O raised the liquidus temperature above 1,400°, an increase of more than 50 deg. On the other hand, when soda was added in the form of NC_8A_3 (10 to 20%), the stable soda phase in clinker, the liquidus was lowered about 20 deg. to 1,330°. The addition of Na_2O in the form of the oxide causes extensive changes in the potential compound composition of the mixture, through formation of NC_8A_3. The effect of the addition of Na_2O in the form of the oxide cannot therefore be readily interpreted. It is preferable to add

Na_2O in the form of NC_8A_3, and this practice was followed in the remainder of the investigation.

The vertices of the small tetrahedron with additions of the soda phase were studied first, see table 3 and figure 2. It was found that those compositions obtained by adding NC_8A_3 to vertices *V2* and *V4*, representing higher concentrations of C_5A_3 and C_2F, respectively, melted at lower temperatures than the other two. Actually, compositions obtained by adding NC_8A_3 to vertex *V1*, higher CaO content, contained free CaO even when heated above 1,550°.

The centers of the faces of the tetrahedron were next studied. These compositions were prepared by mixing equal weight proportions of three vertex compositions. The center of the *V1–V2–V4* face had the lowest melting temperature.

When 10 to 30 percent of NC_8A_3 was added to each of the *V2*, *V3*, and *V4* vertex compositions the liquidus temperature was increased except in the case of the 10-percent addition to vertex *V2*, which reduced the liquidus temperature to 1,339°.

Having studied the boundaries of the small tetrahedron with and without additions of soda, planes within the tetrahedron were selected (fig. 2). To points within the tetrahedron representing quaternary compositions, x percent of the soda phase was added, and $100-x$ percent of the amount of each of the four quaternary constituents making up this point was taken. In the plane studied, 10 percent of NC_8A_3 was added, and the C_2F was held constant at 26 percent (quaternary composition). The remaining three components were then allowed to vary. The lowest melting composition in this plane, 10N26F5 [6] listed in table 4, was found to be all liquid at 1,318°. The iron phase appeared to be the primary phase. At only 2 deg. below this liquidus temperature, however, three solid phases were in equilibrium with liquid. This point, then, is on a bivariant surface in the quinary system and is probably near a univariant curve that extends to the invariant point. It is unusual that the first plane studied should be so close to the invariant point.

The next plane considered, 10 percent of NC_8A_3 and 30 percent of C_2F, contained no composition melting as low as the composition indicated by 10N26F5 in the previous plane. The iron phase appeared in larger quantities. A few points in the $10NC_8A_3$-$34C_2F$, $10NC_8A_3$-$38C_2F$, and $10NC_8A_3$-$42C_2F$ planes were studied to complete the series, but none of them melted as low as 1,318°. The plane $10NC_8A_3$-$22C_2F$ was also studied. Quenched charges in this plane contained the iron phase in small quantities but only as a secondary phase. This indicated that the invariant-point composition was at a higher value of C_2F, that is, between 22 and 26 percent of C_2F (quaternary composition).

In the next series of planes the iron phase was held constant, and the soda phase varied from 5 to 30 percent (quinary composition). In the $5NC_8A_3$-$26C_2F$ plane, NC_8A_3 did not appear as the primary phase, and the minimum liquidus temperature was again higher than that for the $10NC_8A_3$-$26C_2F$ plane.

The $20NC_8A_3$-$26C_2F$ plane was likewise at a higher liquidus temperature but contained NC_8A_3 as the primary phase. Compositions in the $20NC_8A_3$-$30C_2F$ plane were studied. At this C_2F concentration (24% in the quinary system) *F ss* and C_3A appeared as the predominant phases. Compositions of minimum liquidus temperature in this plane were still further removed from the invariant point. Therefore, the invariant point would appear to contain less than 20 percent of NC_8A_3 and near 26 percent (23.4% in the quinary system) of C_2F.

The 15 percent NC_8A_3—26 percent C_2F plane was then studied. The temperature found for the point of lowest melting, 1,320°, was somewhat lower than that found in other planes, with the exception of the $10NC_8A_3$-$26C_2F$ plane. *F ss* did not appear as a primary phase (22.1% of C_2F in the quinary system). The primary phase in the compositions melting at lower temperatures was NC_8A_3.

A few points were studied in the $15NC_8A_3$-$30C_2F$ plane. At this C_2F concentration (25.5% in the quinary system) *F ss* was the primary phase indicating an excess of C_2F.

From the information gained in the study of these planes, additional compositions were chosen for study. These points are not shown in figure 2 but are given, together with petrographic observations of the quenched charges, in table 5.

These data indicated that the invariant point should contain less C_2F, more NC_8A_3, and more SiO_2 than point 10N26F5 in the $10NC_8A_3$-$26C_2F$

---

[6] For convenience and economy of space, the test number designation is used in place of the more complete form, for example, 10N=10 percent of NC_8A_3, and 26F=26 percent of C_2F, and 5=the fifth composition studied in this plane.

TABLE 5. *Quenching data on intermediate planes within the quinary system*

Test No.	Percent Composition					Temperature	Petrographic examination
	CaO	C_5A_3	SiO_2	C_2F	NC_8A_3		
			NC_8A_3 and C_5A_3 varied				
						°C	
10N1	7.0	53.5	6.5	23.0	10.0	1,318	Small amounts C_3A, C_2S, F *ss* in glass.
12N1-1	7.0	51.5	6.5	23.0	12.0	1,314	Small amounts C_2S, C_3A, F *ss* in glass.
-2						1,318	All glass.
14N1-1	7.0	49.5	6.5	23.0	14.0	1,314	Traces NC_8A_3, C_2S, C_3S, C_3A in glass.
-2						1,318	All glass.
16N1	7.0	47.5	6.5	23.0	16.0	1,319	Small amounts NC_8A_3, C_2S, F *ss* in glass.
18N1	7.0	45.5	6.5	23.0	18.0	1,318	Do.
20N1	7.0	43.5	6.5	23.0	20.0	1,320	Do.
			NC_8A_3 and CaO varied				
10N2	10.5	50.0	6.5	23.0	10.0	1,318	C_3A, F *ss*, C_2S in glass.
12N2	8.5	50.0	6.5	23.0	12.0	1,318	Do.
14N2-1	6.5	50.0	6.5	23.0	14.0	1,314	NC_8A_3, C_2S, C_3A, F *ss* in glass.
-2						1,318	All glass.
16N2	4.5	50.0	6.5	23.0	16.0	1,318	NC_8A_3, F *ss*, C_3A in glass.
18N2	2.5	50.0	6.5	23.0	18.0	1,320	C_3A, NC_8A_3, F *ss* in glass.
			CaO and C_5A_3 varied				
13N1	14.0	43.0	6.5	23.0	13.5	1,330	C_2S, C_3S in glass.
13N2	12.0	45.0	6.5	23.0	13.5	1,330	Do.
13N3-1	10.0	47.0	6.5	23.0	13.5	1,320	Traces F *ss*, C_2S in glass.
-2						1,329	All glass.
13N4-1	8.0	49.0	6.5	23.0	13.5	1,315	Small amounts F *ss*, NC_8A_3, C_2S, C_3S in glass.
-2						1,320	All glass.
13N5-1	6.0	51.0	6.5	23.0	13.5	1,315	Small amounts C_2S, C_3A, NC_8A_3, F *ss* in glass.
-2						1,320	All glass.
13N6-1	4.0	53.0	6.5	23.0	13.5	1,315	C_3A, NC_8A_3, F *ss* in glass.
-2						1,320	Traces C_3A in glass.
13N7-1	2.0	55.0	6.5	23.0	13.5	1,320	F *ss*, C_3A, traces C_5A_3 in glass.
13N8-1	0	57.0	6.5	23.0	13.5	1,320	C_5A_3, C_3A in glass.
			C_2F and SiO_2 varied				
13N9	7.0	50.0	5.5	24.0	13.5	1,315	Traces F *ss*, C_3A in glass.
13N10-1	7.0	50.0	6.5	23.0	13.5	1,310	Traces NC_8A_3, C_3A, C_2S, C_3S, F *ss* in glass.
-2						1,312	All glass.
13N11	7.0	50.0	7.5	22.0	13.5	1,317	Small amounts C_2S, C_3S, C_3A in glass.
13N12	7.0	50.0	8.5	21.0	13.5	1,317	Many fine crystals C_2S, C_3S, NC_8A_3 in glass.
13N13	7.0	50.0	9.5	20.0	13.5	1,317	Do.

plane. Consequently, NC_8A_3 was varied from 10 to 20 percent in two series of compositions. In both series SiO_2 and C_2F were held constant at 6.5 and 23.0 percent, respectively (quinary composition). In the first series CaO was also held constant at 7.0 percent and C_5A_3 and NC_8A_3 varied, the sum of the latter two being constant. In the second series C_5A_3 was held constant at 50.0 percent, and CaO and NC_8A_3 varied with their sum constant.

Similar results were obtained for each series. The minimum temperature for complete melting (1,316°) appeared at slightly less NC_8A_3 content than that for two 14-percent NC_8A_3 compositions included in the preceding paragraph. This temperature is lower than that of any composition previously studied.

From these data it was deduced that the NC_8A_3 value for the invariant point was near 13.5 percent. Because of this, another series of compositions (table 5) was prepared containing 13.5 NC_8A_3, 6.5 SiO_2, and 23.0 percent of C_2F, and varying amounts of C_5A_3 and CaO. The lowest temperature for complete melting appeared between points containing 8.0 CaO and 49.0 percent C_5A_3 and 6.0 CaO and 51.0 percent C_5A_3. Slightly below the liquidus temperature four solid phases were in equilibrium with liquid indicating that the compositions were on univariant curves near the invariant point.

The final series was prepared to contain the composition midway between these points. C_2F and SiO_2 were varied, and the other three components held constant. This intermediate composition, 13N10, melted at 1,312°. At 1,310° four and possibly five solid phases were observed in equilibrium with liquid. These crystalline phases in a glassy matrix are shown in figure 4 at a magnification of 470 diameters. The same field is shown both with and without crossed nicols.

The lower part of the field consists of a large, isotropic crystal of C_3A (phase 1, fig. 4, A) having a refractive index slightly below that of the mounting medium (1.715). It contains a few dark inclusions and extinguishes under crossed nicols (fig. 4, B). Near the upper part of the field a few small crystals of C_3A also appear. The iron-containing solid solution, F*ss*, phase 2, has much higher refractive indices than either the glassy matrix or the mounting medium and is in high relief. It is colored brownish-red to tan showing pleochroism and under crossed nicols gives high-order interference colors with red being predominant. Phase 3 is C_2S, which appears near the left

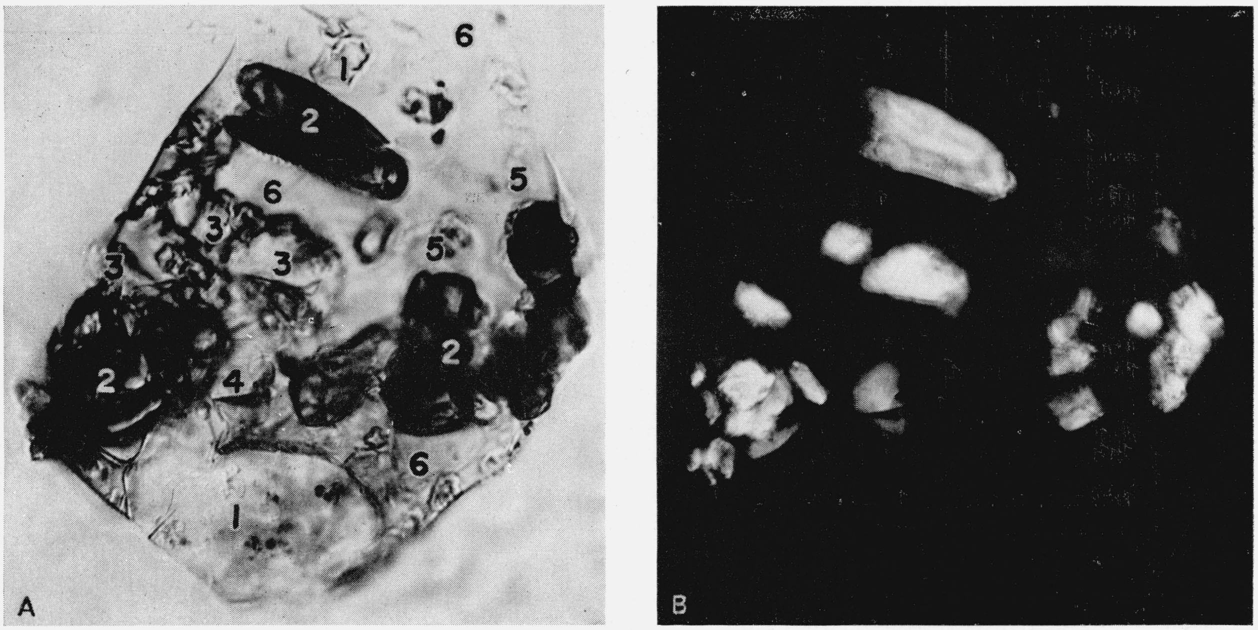

FIGURE 4. (*A*) *Invariant poin composition quenched from 1,310° C showing crystals of* C_3A (*1*), *F ss* (*2*), C_2S (*3*), NC_8A_3) (*4*), *and* C_3S (*5*) *embedded in a glassy matrix* (*6*), *total magnification 470 diameters.* (*B*) *Same field under crossed nicols. 470 diameters.*

center of the field as clear crystals showing white to yellow birefringence. Phase 4 consists of small, transparent, flat grains of NC_8A_3 having a comparatively lower degree of birefringence. A possible phase 5, interpreted as C_3S, occurs in very small grains having low birefringence (gray). Because of the similarity in optical properties of this phase and small particles of NC_8A_3, identification was difficult. Phase 6, the glassy matrix, is light tan in color (probably caused by the presence of iron) with a refractive index higher than that of the mounting medium.

Although color plays an important part in differentiating the above phases, other optical properties were also used for actual identification. It was not feasible to reproduce these micrographs in color. Also, in the relatively large specimen that was required for viewing the five crystalline phases it was difficult to focus all phases simultaneously.

From this and similar observations it appears that the invariant point for NC_8A_3, C_3A, F*ss*, C_3S, C_2S, and liquid is about 1,310° C and is near the composition point represented by 13N10. The oxide composition of this point is about 1.0 percent-Na_2O, 48.0 percent-CaO, 31.0-percent Al_2O_3, 13.5 percent-Fe_2O_3, and 6.5-percent SiO_2. Five-component mixes in this quinary system approximating the composition of portland-cement clinker will crystallize completely at about 1,310° C upon slow cooling.

VI. Discussion

In this investigation it was noted that additions of Na_2O considerably lowered the temperature of appearance of first liquid. Certain low-melting mixes, for example, 10N26F5, table 4, showed some liquid formation when heated as low as 1,290° C. Hansen [12] in studying a high-lime, low-alumina mix having the composition 2.2 Na_2O, 65.7 CaO, 6.4 Al_2O_3, 3.2 Fe_2O_3, 22.5 percent SiO_2 found that the first indications of melting occurred at 1,315°. Much higher temperatures are required for complete melting. In the present investigation, however, the invariant composition melts completely at about 1,310°.

The effect of MgO on the quinary invariant points is important to the chemistry of cement, as this component is present in the commercial product. Magnesia, together with the five components considered in this study, represents about 99 percent of the constitution of clinker. Since there has been no evidence of new phases formed when MgO is present [11], it is probable that only a lowering of the melting temperature results. Swayze [2] found that about 5 percent of MgO could be dissolved in the liquids studied in the system $CaO\text{-}C_5A_3\text{-}C_2F\text{-}C_2S$ as a result of which the temperatures at invariant points were lowered by about 35 deg. It may be permissible on the same basis to predict that MgO may lower the quinary invariant temperature from 1,310°, found in this investigation, to about 1,275°. Hansen [12] found that melting started at about this temperature (1,280°) when a mixture of these six components was burned.

The results also indicate that a closer computation of the actual percentage of liquid formed may be made when mixes containing Na_2O are burned. Thus, instead of adding the percentage of Na_2O present to the calculated percentage of liquid as has been suggested [13], one must also consider the effect of formation of NC_8A_3 on the relative proportions of CaO and Al_2O_3.

The observations made in this study have established the stable existence of the soda compound NC_8A_3 in the presence of the principal components of portland cement clinker.

Under certain conditions Na_2O may react with other components, producing new phases. The data also indicate that a closer approximation of the glass composition in rapidly cooled clinker can be made.

The data obtained for the quinary system represent equilibrium conditions, whereas in the commercial clinkering operation this is not the case and must be considered when applying these data. Application is further limited, since the effects of the small amounts of minor constituents such as Mn_2O_3, TiO_2, Li_2O, and others on the phase-equilibrium relations of the system are not known. More information on the quinary system itself will be necessary in order that wider application to the problems of cement manufacture may be made.

VII. References

[1] F. M. Lea and T. W. Parker, Phil. Trans. Royal Soc. [A], **234,** No. 731, 1 (1934).

[2] M. A. Swayze, Am. J. Sci. **244,** 1; 65 (1946).

[3] K. T. Greene and R. H. Bogue, J. Research NBS **36,** 187 (1946) RP1699; PCAF Paper 47.

[4] W. R. Eubank and R. H. Bogue, J. Research NBS **40,** 225 (1948) RP1867; PCAF Paper 50.

[5] R. H. Bogue, The chemistry of portland cement (Reinhold Pub. Co., New York, N. Y., 1947).

[6] K. T. Greene and W. R. Morgan, J. Am. Ceram. Soc. **24,** 111 (1941).

[7] W. R. Eubank, Precision thermostat for high temperatures (publication pending).

[8] L. A. Dahl, Parametric equations in the treatment of multi-component systems, J. Phys. Colloid Chem. (publication pending).

[9] L. A. Dahl, J. Phys. Colloid Chem. **52,** 698 (1948); PCAF Paper 51.

[10] L. A. Dahl, J. Chem. Education **26,** 411 (1949); PCAF Paper 52.

[11] H. F. McMurdie and H. Insley, J. Research NBS **16,** 467 (1936) RP884.

[12] W. C. Hansen, B. S. J. Research **2,** 55 (1930) RP132; PCAF Paper 22.

[13] F. M. Lea and T. W. Parker, Build. Res. Tech. Pap. No. 16 (1935).

WASHINGTON, November 8, 1948.