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STUDIES ON A PORTION OF THE SYSTEM: $CaO-Al_2O_3-Fe_2O_3$

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ABSTRACT

A study has been made of the solidus and liquidus relations in the area $CaO-4CaO.Al_2O_3.Fe_2O_3-CaO.Al_2O_3$. Special attention has been given to the study of solid solutions. It was found that $3CaO.Al_2O_3$, $5CaO.3Al_2O_3$, and $CaO.Al_2O_3$ all take into solid solution Fe_2O_3 up to 2.5 percent. The $4CaO.Al_2O_3.Fe_2O_3$ also takes between 3 and 5 percent of the calcium aluminates into solution. In some cases the solid solution relations are such as to shift the conjugation lines away from the joins.

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I. INTRODUCTION

Phase-equilibrium studies[1] on many of the systems involving oxides occurring in significant amounts in portland cement clinker have shown which compounds are formed when mixtures of these oxides are crystallized under equilibrium conditions. Recently several investigators[2] have pointed out the possibility, and outlined the results, of disequilibrium conditions during cooling of the clinker. Others[3] have found by X-ray and optical methods that some of the principal constituents of clinker contain detectable and important amounts of other constituents in solid solutions. Insley found by a quantitative microscopic analysis of commercial clinker that the relative amounts of the compounds actually present often differ widely from the amounts calculated[4] from a chemical analysis.

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[1] R. A. Rankin and F. E. Wright, Am. J. Sci. [IV] **39,** 1 (1915); W. C. Hansen, L. T. Brownmiller, and R. H. Bogue, J. Am. Chem. Soc. **50,** 396 (1928).

[2] F. M. Lea and T. W. Parker, Build. Research Tech. Pap. 16 (1935); L. A. Dahl, Rock Products **26** (December 10, 1932).

[3] Herbert Insley, J. Research NBS **17,** 353 (1936) RP917; H. E. Schweite and W. Bussem, Tonind. Ztg. **56,** 801 (1932).

[4] R. H. Bogue, Ind. Eng. Chem. Anal. Ed. **1,** 192 (1929).

Because of these evidences of solid solutions in cement, the National Bureau of Standards has begun a study to determine which solid solutions may occur among the compounds present. In the original paper by Hansen, Brownmiller, and Bogue[5] on the system $CaO-Al_2O_3-Fe_2O_3$, in which discovery of the important compound $4CaO.Al_2O_3.Fe_2O_3$ was announced, it was stated that, in the presence of Fe_2O_3, the indices of refraction of $CaO.Al_2O_3$, $5CaO.3Al_2O_3$, and $3CaO.Al_2O_3$ were raised and that further work was necessary to outline the solid solutions involved. The principal purpose of this investigation is to determine the kind and amount of solid miscibility in the area $CaO-4CaO.Al_2O_3.Fe_2O_3-CaO.Al_2O_3$, and, as a first step, that portion of interest in cement technology was reexamined. The relation of the area studied to the ternary system $CaO-Al_2O_3-Fe_2O_3$ is shown in figure 1.

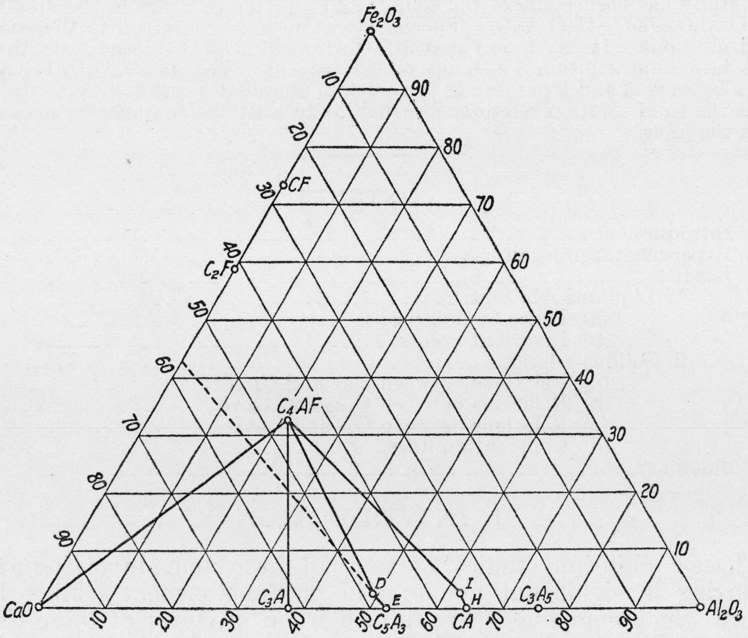

FIGURE 1.—*Relation of the area* $CaO-4CaO.Al_2O_3.Fe_2O_3-CaO.Al_2O_3$ *to the ternary system* $CaO-Fe_2O_3-Al_2O_3$.

The conjugation lines of the area are indicated.

II. EXPERIMENTAL PROCEDURE

The raw materials employed in this study were of reagent quality and consisted of precipitated $CaCO_3$ unusually free from alkalies, alumina with a total maximum impurity of less than 0.01 percent, and ferric oxide containing less than 0.004 percent of ferrous iron. Besides these oxides, some previously prepared $CaO.Al_2O_3$, $3CaO.Al_2O_3$, $5CaO.3Al_2O_3$, and $4CaO.Al_2O_3.Fe_2O_3$ were used. These compounds were made with similar raw materials and were found to be satisfac-

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[5] See footnote 1.

torily pure and homogeneous, by microscopic examination and melting-point determinations.

The compositions for study were carefully proportioned, corrections being made for the ignition losses of the starting materials determined at the time of proportioning. They were ground together dry in a mortar. The mixtures were then heated in an electrically heated furnace to about 1,000° C and then reground. In some cases new mixtures were prepared by mixing together previously prepared batches.

Each resistance furnace used was wound with 80-percent platinum–20-percent rhodium wire on a 1-inch refractory tube, and the temperature controls were of the type described by J. Roberts.[6] The thermocouples were standardized by frequent comparison with a standard thermocouple, which was used only in a furnace with a porcelain tube to prevent possible contamination from the windings.

The liquids with indices higher than 1.74 used to determine the indices of $4CaO.Al_2O_3.Fe_2O_3$ were solutions of sulphur and methylene iodide in phosphorus. These were made as described by C. D. West[7] and were standardized by the minimum deviation method.

For determining primary phase boundaries the quench method was used. Since this method has been discussed in many previous papers,[8] a description is unnecessary here.

Some difficulty was encountered with mixes high in $4CaO.Al_2O_3.Fe_2O_3$ because of crystallization during quenching. It was found that folding the platinum foil so that a point was formed on the bottom gave better results since the quench dropped deeper into the mercury. When quench growths occurred they usually could be distinguished from equilibrium crystals. However, the rapid crystallization of $4CaO.Al_2O_3.Fe_2O_3$ makes it difficult to determine with precision the limits of its primary phase field.

To study the solid solution present, a small amount (about 0.5 g) of the mixture under investigation was heated in a platinum foil envelope to a temperature such that all or at least a large part of the material was liquid. The furnace was then cooled slowly over a period of from 5 to 20 hours to a temperature below the solidus. This method gave nearly complete equilibrium at all times, and crystals in the final products were large enough to be studied and identified by means of the microscope. In some cases glasses of the desired composition were heated for several hours below the solidus to be certain that maximum solution had been obtained. This method produced such small crystals that the number of phases present could be determined but the crystals could not be studied properly.

Insignificant reduction of the ferric oxide was shown in two ways: first, the absence of compounds other than those known to be present in the system $CaO–Al_2O_3–Fe_2O_3$ and, second, similarity in the phase composition of specimens of the same mix heated for long and for short periods at high temperature.

The binary system $CaO–CaO.Al_2O_3$, which forms one side of this area, was worked out by Rankin and Wright.[9] This work was not repeated. The composition and temperature of the eutectic between

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[6] J. Optical Soc. Am. **11**, 171 (1925).

[7] Am. Mineral **21**, 245 (1936).

[8] G. W. Morey, J. Wash. Acad. Sci. **13**, 326 (1923); E. S. Shepard, R. A. Rankin, and F. E. Wright, Am. J. Sci. [IV] **28**, 293 (1909).

[9] Am. J. Sci. [IV] **39**, 1 (1915).

CaO and $4CaO.Al_2O_3.Fe_2O_3$ were taken as reported by Hansen, Brownmiller, and Bogue.[10]

In this report, as in others of similar nature, a system of abbreviations is used in referring to the compounds as follows:

$$C=CaO;\ F=Fe_2O_3;\ A=Al_2O_3;\ \text{thus}\ C_4AF=4CaO.Al_2O_3.Fe_2O_3.$$

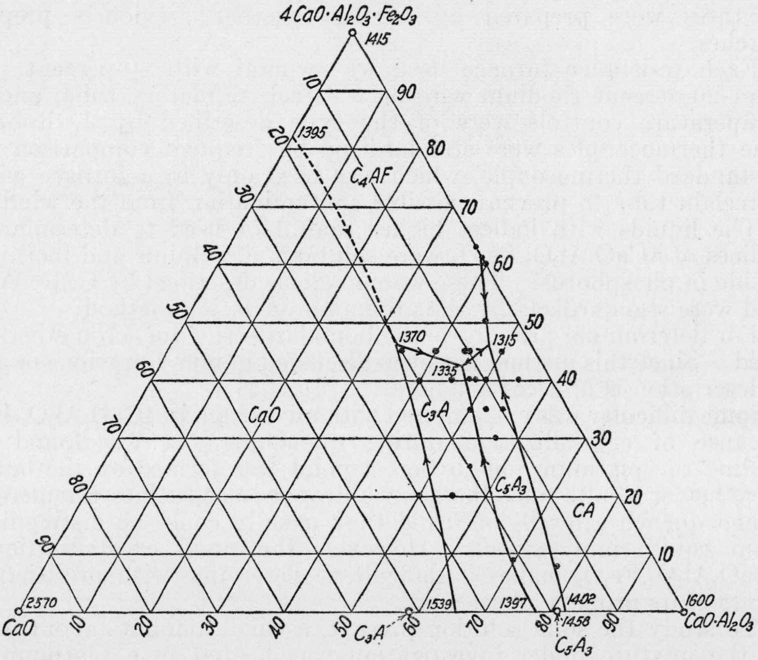

FIGURE 2.—*Liquidus relations in the area* $CaO–4CaO.Al_2O_3.Fe_2O_3–CaO.Al_2O_3$.

III. RESULTS

1. LIQUIDUS RELATIONS

(a) PHASE BOUNDARIES

Figure 2 represents the primary phase fields in the area and the location of the mixes studied. Table 1 gives the composition of the mixes and the results of the quenches. For ready reference to figure 2 the compositions are given in terms of the oxides and of the compounds at the apices of the triangle.

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[10] See footnote 1.

TABLE 1.—*Composition and results of quenched mixes*

Mix	Composition						Quenching temperature ±5° C	Phases present
	Fe_2O_3	Al_2O_3	CaO	C_4AF[1]	CA[1]	CaO[1]		
	%	%	%	%	%	%		
1	13.2	40.7	46.1	40	50	10	1,330 1,320 1,312	Glass+C_5A_3. Glass+C_5A_3+C_4AF. C_5A_3+C_4AF+CA.
2	11.6	42.9	45.5	35	55	10	1,340 1,325	Glass+C_5A_3. Glass+C_5A_3+C_4AF.
3	13.2	43.9	42.9	40	55	5	1,335 1,320	Glass+CA. Glass+CA+C_4AF.
4	14.8	41.8	43.4	45	50	5	1,340 1,330	Glass+CA. Glass+CA+C_4AF.
5	11.5	39.7	48.8	35	50	15	1,345 1,340	Glass+C_3A. Glass+C_3A+C_5A_3.
6	8.3	40.7	51.0	25	55	20	1,370 1,365 1,350 1,345	Glass only. Glass+C_3A. Glass+C_3A. Glass +C_3A+C_5A_3.
7	16.5	39.6	43.9	50	45	5	1,340 1,330	Glass only. Glass+CA+C_4AF.
8	13.2	37.5	49.3	40	45	15	1,360 1,350	Glass+C_3A. Glass+C_3A+C_4AF.
9	14.8	38.6	46.6	45	45	10	1,345 1,335 1,330	Glass only. Glass+C_4AF. Glass+C_4AF+C_5A_3.
10	14.8	35.4	49.8	45	40	15	1,375 1,370 1,365	Glass only. Glass+C_4AF. Glass+C_4AF+C_3A.
11	13.2	34.3	52.5	40	40	20	1,390 1,375 1,365	Glass+C_3A. Glass+C_3A. Glass+C_3A+C_4AF.
12	14.8	32.1	53.1	45	35	20	1,380 1,360	Glass+C_3A. Glass+C_3A+C_4AF.
13	6.6	36.5	56.9	20	50	30	1,500	Glass+CaO.
14	6.6	39.7	43.7	20	55	25	1,480	Glass+C_3A.
23	13.1	39.1	47.7	40.0	47.5	12.5	1,340 1,335 1,330	Glass only. Glass+C_5A_3. Glass+C_5A_3+C_4AF.
24	13.2	39.7	47.1	40.0	48.5	11.5	1,345 1,340 1,335 1,320 1,310	Glass only. Glass+C_5A_3. Glass+C_5A_3+C_4AF. Glass+C_5A_3+C_4AF. C_5A_3+C_4AF+CA.
25	14.8	38.2	47.0	45.0	44.5	10.5	1,360 1,350 1,325	Glass only. Glass+C_4AF. Glass+C_4AF+C_5A_3.
19	3.0	47.0	50.0	9.1	69.6	21.3	1,390	Glass+C_5A_3.
26	2.5	51.0	46.5	7.6	76.4	16.0	1,423 1,408	Glass only. Glass+CA.
44	20.7	37.2	42.1	63.0	37.0	--------	1,355 1,350	Glass+C_4AF. Glass+C_4AF+CA.
45	17.7	38.4	41.9	60	40.0	--------	1,355 1,350	Glass+CA. Glass+CA+C_4AF.
29	10.0	42.8	47.2	30	56.5	13.5	1,350 1,340 1,330	Glass only. Glass+C_5A_3. Glass+C_5A_3+C_4AF.
59	11.5	41.2	47.3	35	52.5	12.5	1,340	Glass+C_5A_3.

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[1] Composition is given in terms of C_4AF, CA, and CaO to permit ready identification of the points in figure 2.

As compared with the original report[11] on this system, the present investigation shifts the boundaries between the field of C_4AF and the fields of C_3A, C_5A_3, and CA much farther toward the C_4AF apex. For instance, in the present work the invariant point for C_4AF, C_3A, C_5A_3 and liquid is placed at CaO 38, Al_2O_3 48, and Fe_2O_3 14 percent, whereas in the original paper it is located at CaO 47, Al_2O_3 43, and Fe_2O_3 10 percent. F. M. Lea[12] also reports quenches which confirm in general the location of the boundaries as shown in figure 2.

Since solid solutions occur in this area, not all crystallization paths are straight lines from the starting point to the boundary curves. During cooling the solid phase in equilibrium with the liquid is not of constant composition; therefore, the course of liquid composition must deviate from a straight line so that it will at all times lie on the line determined by the point of origin and the composition of the solid phase in equilibrium with it.

(b) INVARIANT POINTS

Three ternary invariant points were determined in the course of the work. Their composition and temperatures are given in table 2.

TABLE 2.—*Ternary invariant points*

Liquid and vapor in equilibrium with—	Composition						Temperature (±5° C)
	Fe_2O_3	Al_2O_3	CaO	C_4AF	CA	CaO	
	%	%	%	%	%	%	°C
$CaO-C_4AF-C_3A$	15	32	53	46	34	20	1,370
$C_4AF-C_3A-C_5A_3$[1]	14	38	48	42	46	12	1,335
$C_4AF-C_5A_3-CA$[1]	15	40	45	46	48	6	1,315

[1] Eutectic.

2. SOLIDUS RELATIONS

Table 3 gives the composition and the results of slow crystallization of samples used to study the solid solutions. In the discussion of these results the terms "join" and "conjugation line" are used. A join is the straight line drawn between two compounds, and it may be of no more significance. A conjugation line is the line which separates areas in which the final phases resulting from equilibrium crystallization are different. As a general rule, conjugation lines are identical with possible joins, but in parts of this system it is found that they are not, as will be discussed later.

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[11] W. C. Hansen, L. T. Brownmiller, and R. H. Bogue, J. Am. Chem. Soc. **50**, 396 (1928).
[12] F. M. Lea. Private communication (November 20, 1936).

TABLE 3.—*Final products of slow crystallization.*

Mix	Composition (by weight)						Phases present (ss=solid solution)
	Fe_2O_3	Al_2O_3	CaO	C_4AF	CA	CaO	
	%	%	%	%	%	%	
16	2.5	47.5	50.0	7.6	71.0	21.4	C_5A_3 (*ss*)+C_3A (*ss*).
17	2.5	49.5	48.0	7.6	74.2	18.2	C_5A_3 (*ss*)+CA (*ss*).
18	2.5	48.5	49.0	7.6	72.6	19.8	C_5A_3 (*ss*) only (index 1.620±0.002).
19	3.0	47.0	50.0	9.1	69.6	21.3	C_5A_3 (*ss*)+C_3A (*ss*)+C_4AF (*ss*).
20	2.5	43.7	53.8	7.6	65.2	27.2	C_5A_3 (*ss*)+C_3A (*ss*)+trace C_4AF.
21	3.0	34.0	63.0	9.1	49.6	41.3	C_3A (*ss*)+CaO+C_4AF.
22	2.8	53.2	44.0	8.5	79.5	12.0	C_5A_3 (*ss*)+CA (*ss*)+trace of C_4AF.
24	13.2	39.7	47.1	[1] 40.0	------	------	C_5A_3 (*ss*)+C_4AF (*ss*)+CA (*ss*).
26	2.5	51.0	46.5	7.6	76.4	16.0	C_5A_3 (*ss*)+CA (*ss*).
27	2.6	49.7	47.7	[1] 8.0	------	------	C_5A_3 (*ss*)+CA (*ss*)+trace of C_4AF.
28	3.3	49.1	47.6	10.0	------	------	C_5A_3 (*ss*)+CA (*ss*)+C_4AF.
29	10.0	42.8	47.2	[1] 30.0	------	------	C_5A_3 (*ss*)+CA (*ss*)+C_4AF.
30	31.3	22.6	46.1	[1] 95.0	------	------	C_4AF (*ss*).
32	1.6	50.7	47.7	[2] 5.0	------	------	C_3A (*ss*) (index 1.72±0.002).
34	2.5	36.5	61.0	[2] 7.5	------	------	C_3A (*ss*)+C_4AF.
37	30.9	22.9	46.2	[1] 94.0	------	------	C_4AF (*ss*)+small amount of C_5A_3.
38	31.6	21.7	46.7	[2] 96.0	------	------	C_4AF (*ss*)+trace of C_3A.
40	1.8	43.6	54.6	5.6	65.7	28.7	C_5A_3 (*ss*)+C_3A (*ss*).
41	1.5	35.9	62.6	4.6	54.2	41.2	C_3A (*ss*)+CaO.
42	29.7	25.4	44.9	90.0	10.0	------	C_4AF (*ss*)+CA.
46	31.3	23.2	45.5	95.0	5.0	------	C_4AF (*ss*) only.
47	30.4	24.3	45.3	92.5	7.5	------	C_4AF (*ss*)+small amount of CA.
48	1.6	62.5	35.9	5.0	95.0	------	CA (*ss*)+C_5A_3.
49	3.3	60.2	36.5	10.0	90.0	------	CA (*ss*)+C_5A_3+C_4AF.
50	2.5	61.3	36.2	7.5	92.5	------	CA (*ss*)+C_5A_3.
51	2.5	63.0	34.5	--------	[3] 97.5	------	CA (*ss*) only.
52	5.0	61.3	33.7	--------	[3] 95.0	------	CA (*ss*)+C_3A_5+C_4AF.
53	3.75	62.15	34.1	--------	[3] 96.25	------	CA (*ss*)+C_3A_5+C_4AF.
54	3.0	56.7	40.3	9.1	85.7	5.2	CA (*ss*)+C_5A_3 (*ss*)+small amount of C_4AF.
55	3.3	54.6	42.1	10.0	81.3	8.7	CA (*ss*)+C_5A_3 (*ss*)+small amount of C_4AF.
56	4.1	60.8	35.1	--------	[4] 95.9	------	CA (*ss*)+C_4AF.
57	2.1	62.7	35.2	--------	[4] 97.9	------	CA (*ss*) only.
58	3.1	61.7	35.2	--------	[4] 96.9	------	CA (*ss*)+C_4AF.

[1] On join $C_4AF-C_5A_3$.
[2] On join C_4AF-C_3A.
[3] On join $CA-Fe_2O_3$.
[4] On join CA−CF.

Figure 3 indicates the joins, conjugation lines, and limits of solid solution. Figure 1 shows the conjugation lines of the area on a diagram of the full ternary system $CaO–Al_2O_3–Fe_2O_3$. It is seen that there is solid solution of Fe_2O_3 in each of the three calcium aluminates. The ratio in which the various compounds take up Fe_2O_3 and lime varies and the relations between each compound and C_4AF are discussed separately.

(a) RELATIONS BETWEEN C_3A AND C_4AF

On the join $C_3A–C_4AF$ the solid solution is of a simple nature. C_3A takes up to 5 percent of C_4AF in solution; thus a mix of composition *A* (fig. 3) crystallizes to a single phase of its own composition. The index of refraction of C_3A, when pure, is 1.71, that of the composition *A* is 1.720+0.002.

C_4AF takes up between 2.5 and 5 percent of C_3A. This appears to lower the indices of C_4AF very little. Any composition on the join from *L* to *A* will crystallize to these two solid solutions. This join is not a binary system since C_3A melts to CaO and liquid, and CaO is the primary phase over a large part of the join.

(b) RELATIONS BETWEEN C_5A_3 AND C_4AF

Mixes on the join C_5A_3–C_4AF do not give these two compounds alone on crystallization. In such mixes C_5A_3 takes Fe_2O_3 and CaO into solid solution, the CaO and Fe_2O_3 being in the ratio indicated by the intersection of the line *ED* (fig. 1) extended, with the CaO–Fe_2O_3 side, leaving a liquid deficient in lime to form only C_4AF and C_5A_3 and from which (fig. 3) some CA crystallizes at equilibrium. Any mix between *E* and *D* (fig. 2) will give a single phase. The index of refraction of pure C_5A_3 is 1.608, that of the composition *D* is 1.620 ±0.002. Any mix on the join between *F* and *E* will crystallize to two phases, a solid solution of C_5A_3 of a composition between *D* and *E* and a solid solution of CA.

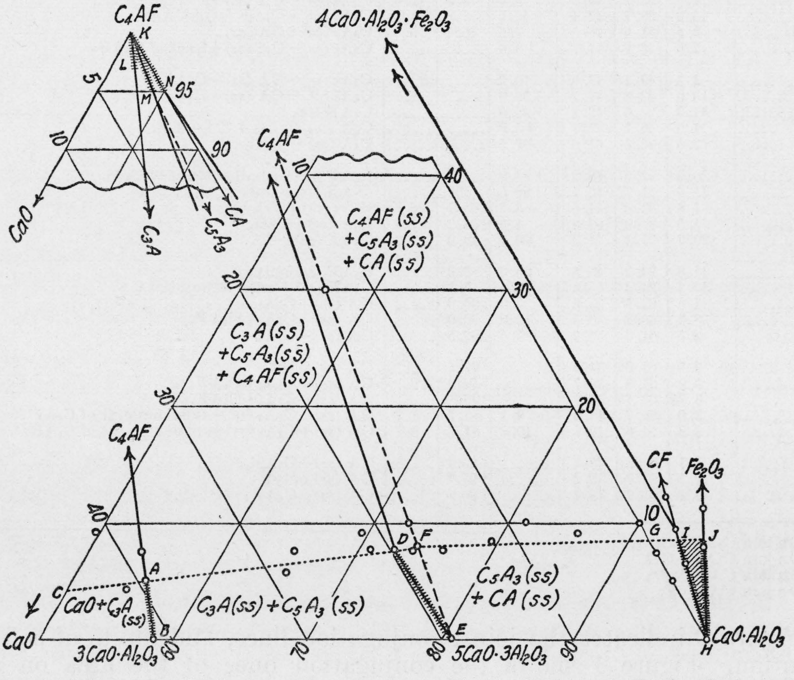

FIGURE 3.—*Solidus relations in the area* CaO–4CaO.Al_2O_3.Fe_2O_3–CaO.Al_2O_3, *showing the lines and areas of solid solution and the joins and conjugation lines.*

C_4AF may take up about 5 percent of C_5A_3 into solid solution, thus lowering the indices of refraction (N_D) of C_4AF to α 1.94±0.01, γ 1.99±0.01. The pure material has the indices α 1.98±0.01 and γ 2.07±0.01. Any composition on this join between *M* and *F* will give, on complete crystallization, C_5A_3 (*ss*)[13] of composition *D*, C_4AF (*ss*) of composition *M*, and CA (*ss*) of composition *I*.

(c) RELATIONS BETWEEN CA AND C_4AF

Mixes on the join CA and C_4AF do not give these two compounds alone on complete crystallization, but have a relation similar to that between C_5A_3 and C_4AF. In this case, CA takes Fe_2O_3 and CaO into

[13] Solid solution, abbreviated *ss*.

solid solution, seemingly in the ratio of CaO. Fe_2O_3, as indicated by the line *HI*. This results in a liquid deficient in Al_2O_3 to form only C_4AF and CA, therefore C_5A_3 is formed from mixes on this join. Any mix between *H* and *I* will crystallize to a single phase. Pure CA had indices of $\alpha=1.643$, $\gamma=1.663$. The CA (*ss*) of composition *I* has indices of $\alpha\,1.650\pm0.002$, $\gamma\,1.667\pm0.002$. Mixes on the join $CA-Fe_2O_3$ (the line *HJ*) with less than 2.5 percent of Fe_2O_3 also crystallize to a single phase and, therefore, any composition in the triangle *IHJ* on crystallization forms a single homogeneous phase consisting of solid solutions of CF and Fe_2O_3 in CA. Any mix on the join $CA-C_4AF$ between *H* and *G* will crystallize to two phases, a solid solution of a composition between *H* and *I* and a solid solution of a composition between *E* and *D*.

C_4AF takes about 5 percent of CA into solid solution. This lowers the indices of refraction about the same as does the solid solution of 5 percent of C_5A_3.

(d) CONJUGATION LINES

Since two[14] of the equilibrium crystalline products produced in this system are not pure compounds or of compositions lying on joins of the system, it is necessary to draw the conjugation lines in positions different than the joins. Thus the line dividing the area in which the final products are C_4AF (*ss*), C_3A (*ss*) and C_5A_3 (*ss*) from that in which they are C_4AF (*ss*), C_5A_3 (*ss*) and CA (*ss*) will pass through the point *D* rather than along the join $C_4AF-C_5A_3$. Similarly, the line dividing the area in which the final products are C_4AF (*ss*), C_5A_3 (*ss*) and CA (*ss*) from that in which they are C_4AF (*ss*), CA (*ss*), and C_3A_5 (*ss*) must pass through the point *I* rather than along the join C_4AF-CA.

Because of the small range of composition within the solid solution area near the C_4AF apex the compositions between the conjugation lines were not studied. It is reasonable to assume that the area *KNML* (fig. 3) is one in which one phase only results from crystallization.

The line *CADG* across figure 3 indicates the limit of compositions which form only two phases on complete crystallization. All mixes containing a greater amount of ferric oxide produce three phases, one of which is C_4AF (*ss*).

The join $CA-C_4AF$ is neither a conjugation line nor a binary system, therefore the point where the boundary between the primary phases of CA and C_4AF (fig. 2) crosses the join is of no significance. Also, since the area $CaO-C_4AF-CA$ is not bounded by three binary systems, this area is not a true ternary system.

X-ray diffraction patterns have been made of the solid solutions of C_3A, C_5A_3, and CA and all showed slight but distinct shifts in the crystal lattice.

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[14] The solid solution of the aluminates in C_4AF is assumed to be such that the composition of the resulting C_4AF(*ss*) lies on a join.

IV. SUMMARY

The solidus and liquidus relations in the area $CaO-4CaO.Al_2O_3.Fe_2O_3-CaO.Al_2O_3$ have been determined. Limited solid solutions between the iron compound and the three calcium aluminates were encountered. The solution was in some cases of a type that shifted the conjugation lines away from the joins. $4CaO.Al_2O_3.Fe_2O_3$ takes between 3 and 5 percent of the calcium aluminates in solid solution.

The author wishes to express his thanks to Dr. Herbert Insley for help and advice during the work and to R. H. Ewell, who prepared some of the mixes used.

WASHINGTON, February 2, 1937.