RP414

# SYSTEM $CaO-Na_2O-Al_2O_3$

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## ABSTRACT

A part of the system $CaO-Na_2O-Al_2O_3$, in the region low in $Na_2O$, has been investigated by the methods of phase equilibria. The stability fields, boundary curves, and invariant points have been defined. Optical and X-ray data are presented and ternary diagrams introduced to indicate the composition and temperature relations and the course of crystallization in the system.

## CONTENTS

## I. INTRODUCTION

The studies reported in this paper are in continuation of a series begun several years ago to determine the constitution of Portland cement clinker and the part played by each of the compounds in the manufacture and utilization of that product. To-day those studies are fairly complete for the principal constituents of Portland cement, namely, for $CaO$, $SiO_2$, $Al_2O_3$, $Fe_2O_3$ and $MgO$; and from them the modern ideas on the constitution of cement have been evolved (1).[1]

Besides these components, there are many others occurring in small amounts in cements. Of the minor components, soda is one of the

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[1] The figures given in parentheses here and throughout the text relate to the reference numbers in the bibliography at the end of this paper.

more important, since it is common to practically all cements. Therefore a continuation of those studies has been made to determine the combinations which soda is capable of forming with the other constituents of the cement.

The system $CaO\text{-}Na_2O\text{-}Al_2O_3$ has now been examined and constitutes the subject of this report. This system, however, was not explored completely. Not only would special methods have to be adopted to solve it entirely, but, in cements, the concentration of soda is small; hence, the studies in the system could be confined to compositions low in $Na_2O$. Apparently only one compound of CaO and $Al_2O_3$, $3CaO.Al_2O_3$, occurs in normal Portland cements; accordingly, that region of the diagram $CaO\text{-}Na_2O\text{-}Al_2O_3$ in which $3CaO.Al_2O_3$ occurs is the field of greatest importance. Nevertheless, because of the complexity of the system, other portions of the diagram had to be investigated to understand fully the relations in that region.

## II. EXPERIMENTAL METHOD

Because of the volatility of $Na_2O$ at temperatures above 900°,[2] somewhat special methods had to be used in preparing the samples. Base compositions of CaO and $Al_2O_3$ were weighed in various proportions, thoroughly mixed by stirring in a small amount of water and then burned in a platinum resistance furnace. A portion of about 5 g of this base composition was weighed and to it the third component, $Na_2O$, was added in the form of $Na_2CO_3$. The compositions of the raw materials are indicated in Table 1.

TABLE 1

| Partial analysis by Carlson | | | | Partial analysis by J. T. Baker Chemical Co. | |
|---|---|---|---|---|---|
| | Calcium carbonate | | Alumina | | Sodium carbonate |
| | *Per cent* | | *Per cent* | | *Per cent* |
| CaO | 56.04 | $Al_2O_3$ | 94.48 | Insoluble | 0.02 |
| MgO | .07 | $SiO_2$ | .01 | Cl | .005 |
| $R_2O$ | .06 | $Fe_2O_3$ | .002 | $SO_4$ | .004 |
| $R_2O_3$ | .05 | CaO | Nil. | $R_2O_3$ | .005 |
| $SiO_2$ | .01 | Cl | Trace. | $SiO_2$ | .005 |
| Loss | 43.71 | $SO_3$ | Trace. | | |
| | | Loss | 1.42 | | |

An excess of the sodium carbonate over that desired in the final sample was required since some $Na_2O$ is volatilized on heating. After dry mixing of the components of the ternary composition, it was burned at a temperature of about 1,400°, pulverized and reburned at a higher temperature. Burning was done in an open platinum boat in a platinum-resistance furnace. After cooling in a desiccator, the sample was weighed and from the difference in weight the amount of $Na_2O$ remaining in the mixture was calculated.

Relatively low temperatures were used for the first burning because this procedure resulted in less loss of $Na_2O$ by volatilization than obtained with high initial burning temperatures.

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[2] Temperatures are given in °C.

The amount of $Na_2O$ lost on subsequent heatings at 1,400° to 1,500° was found to vary from less than 1 per cent of the total weight in samples low in soda to somewhat larger percentages in samples high in soda. In making up the compositions for these studies, an excess of about 25 per cent of sodium carbonate above the theoretical amount required was weighed into the base compositions; but this percentage excess could be reduced somewhat if the first burning were made at temperatures as low as about 1,100°. On twice burning such a mixture at 1,400° to 1,500° the composition was found usually to be within 1 per cent of that desired. Further adjustments could then be made to give the precise compositions required.

The second heating of the samples was necessary before final weighing because frequently not all of the carbon dioxide was evolved during the first burning, as evidenced by effervescence on treating with hydrochloric acid. Before final weighing, all samples were heated at least once to temperatures of about 1,500°.

Table 2 gives a few data on the amount of $Na_2O$ volatilized from these samples heated in an open platinum container. The loss usually was less than 1 per cent after the $Na_2O$ was once combined, but the amount of the loss was found to depend somewhat on the composition, the temperature, and the time of heating.

TABLE 2.—*Data showing the per cent loss in $Na_2O$ following several heat treatments*

| | Sample HU | | | Sample HT | | | Sample HS | | |
|---|---|---|---|---|---|---|---|---|---|
| | Temperature | $Na_2O$ | Loss | Temperature | $Na_2O$ | Loss | Temperature | $Na_2O$ | Loss |
| $Na_2O$ added (per cent) | --------- | 9.0 | ------ | --------- | 20.0 | ------ | --------- | 17.0 | ------ |
| $Na_2O$ after first heating | 1,450 | 6.3 | 2.7 | 1,450 | 13.8 | 6.2 | 1,450 | 12.5 | 4.5 |
| $Na_2O$ after second heating | 1,425 | 5.9 | .4 | 1,400 | 13.3 | .5 | 1,425 | 11.8 | .7 |
| $Na_2O$ after third heating | 1,525 | 5.0 | .9 | 1,475 | 12.6 | .7 | 1,425 | 11.5 | .3 |

These samples were then finely ground and portions taken for determining the temperature relations in the system. Heating curves were not obtained because the thermoelements are attacked by the $Na_2O$. Hence, the quenching method was used exclusively. In this method a small charge is inclosed in pure platinum foil and suspended in a quenching furnace (2) capable of reaching 1,630°. The samples were usually held in the furnace at desired temperature for 20 minutes, which was sufficient time for the attainment of equilibrium in most cases. Samples were then quenched in mercury or water and examined under a petrographic microscope. Samples dropped in mercury float on the surface and in some regions of the diagram cooling is not rapid enough to prevent quench growths; hence, water was frequently used. Crystallizations during quenching were troublesome in the regions in which the ternary compound $8CaO.Na_2O.3Al_2O_3$ crystallized. They can usually be recognized by wavy extinction under crossed nicols and by a brown color in ordinary light; also the refractive indices of such growths are slightly higher than those of the glass, but never as high as those of the true crystals. Often these growths form concentric bands around the primary phase.

The samples finally obtained as described above were too small for analysis, but the examination of other samples treated at corresponding temperatures indicated that the amount of soda lost due to volatilization from these especially prepared specimens was considerably less than that shown in Table 2. The samples listed in Table 2 were burned in open platinum boats whereas the samples for quenching were always carefully inclosed in platinum foil. Furthermore, in working with samples just above (by one-half per cent of $Na_2O$) the boundary between the fields of $3CaO.2Na_2O.5Al_2O_3$ and $5CaO.3Al_2O_3$, the primary phase always was $3CaO.2Na_2O.5Al_2O_3$, whereas, if the amount of $Na_2O$ lost were appreciable, the composition, after heating different samples of the same original composition for varying periods, would have been shifted to throw it into the field of $5CaO.3Al_2O_3$. It is felt that if such were the case different quenches of the same composition should have shown different primary phases. Such irregularities did not occur.

Because of the reaction of soda with the thermoelements, frequent calibration was necessary. It is believed that the reaction is principally with the rhodium and not with the platinum. Fused samples containing $Na_2O$ were frequently colored pink or brown and in such cases the samples showed reaction with the metal. No such discoloration was noticed in samples wrapped in the pure platinum foil and the foil could usually be pulled from melted samples leaving a charge with a smooth surface and no indication of reaction.

The optical properties were determined with a petrographic microscope and the powder X-ray diffraction apparatus was employed to obtain the interplanar spacings of the compounds and for the identification of the phases in the samples. The radius of the cassettes is 8 inches and the effective wave length of the rays is 0.712 A.

The principal results of the study are shown diagrammatically in Figure 1.

## III. BINARY SYSTEMS OF THE COMPONENTS

### 1. SYSTEM $CaO-Na_2O$

No evidence was obtained of the existence of any binary compound in this system. When samples made of these components were heated, the $Na_2O$ was nearly completely volatilized and the optical properties of the CaO were apparently unchanged.

### 2. SYSTEM $CaO-Al_2O_3$

This system was studied by Rankin and Wright. The relations are given in their report, The Ternary System $CaO-Al_2O_3-SiO_2$. (3).

Four compounds were found: $3CaO.Al_2O_3$, which dissociates at 1,535° ± 5° into CaO and liquid; $5CaO.3Al_2O_3$, which melts at 1,455° ± 5°; $CaO.Al_2O_3$, which melts at 1,600° ± 5°; and $3CaO.5Al_2O_3$, which melts at 1,720° ± 10°. The $3CaO.Al_2O_3$ does not form a eutectic with CaO, but the composition CaO 57, $Al_2O_3$ 43, is the quadruple point at which the two compounds are stable in contact with liquid and vapor, the equilibrium temperature being 1,535° ± 2°. $3CaO.Al_2O_3$ forms a eutectic with $5CaO.3Al_2O_3$ having the composition CaO 50, $Al_2O_3$ 50 which melts at 1,395° ± 5°. $5CaO.3Al_2O_3$ forms a eutectic with $CaO.Al_2O_3$ having the composition CaO 47, $Al_2O_3$ 53 which melts at 1,400° ± 5°. $CaO.Al_2O_3$ forms a eutectic with $3CaO.5Al_2O_3$ of the composition CaO 33.5, $Al_2O_3$ 66.5 which melts at

1,590° ± 5°. $3CaO.5Al_2O_3$ forms a eutectic with $Al_2O_3$ of the composition CaO 24, $Al_2O_3$ 76 which melts at 1,700° ± 10°. It should be noted that the composition range within which $3CaO.Al_2O_3$ occurs as a primary phase on the liquidus curve is incorrectly stated on page 10 of the above paper, to be from CaO 50, $Al_2O_3$ 50, to CaO 59, $Al_2O_3$ 41. The range is given correctly in Tables B and C on pages 77 and 78 of the same paper to be from CaO 50, $Al_2O_3$ 50 to CaO 57, $Al_2O_3$ 43.

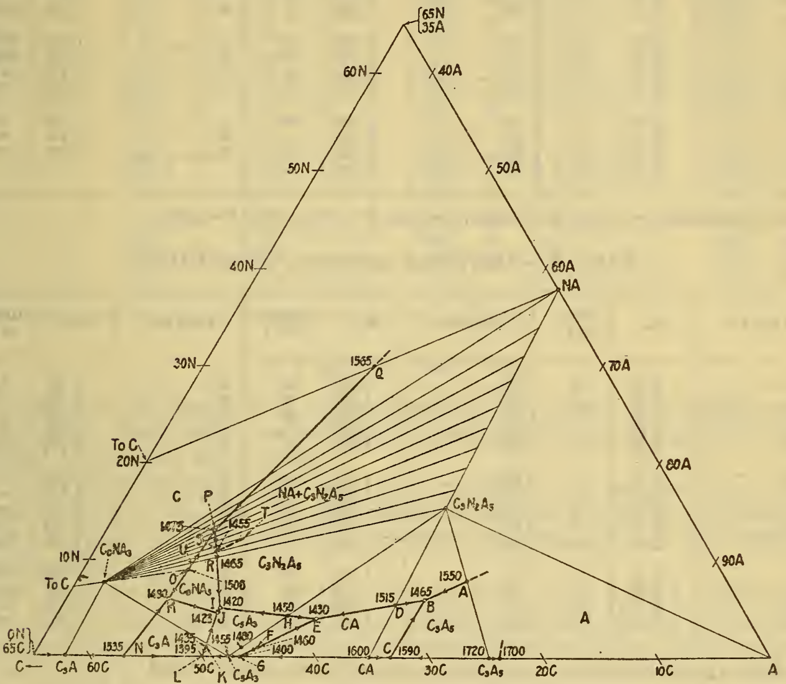

FIGURE 1.—*Diagram showing fields of primary crystallization and the binary systems within the ternary system $CaO$-$Na_2O$-$Al_2O_3$*

*C* = CaO; *A* = $Al_2O_3$; *N* = $Na_2O$.

The interplanar spacings of the X-ray diffraction pattern of $CaO.Al_2O_3$ and $3CaO.5Al_2O_3$ are given in Tables 3 and 4, respectively. Those of CaO, $3CaO.Al_2O_3$, and $5CaO.3Al_2O_3$ have been reported previously from this laboratory (4), but, as more satisfactory patterns of the latter two compounds have recently been obtained, these are given also in Tables 5 and 6.

TABLE 3.—*Interplanar spacings of* $CaO.Al_2O_3$

| Line No. | $d_{hkl}$ | Intensity [1] | Line No. | $d_{hkl}$ | Intensity [1] | Line No. | $d_{hkl}$ | Intensity [1] |
|---|---|---|---|---|---|---|---|---|
| 1 | 3.70 | m | 13 | 2.080 | w | 25 | 1.461 | m |
| 2 | 3.40 | w | 14 | 2.025 | m | 26 | 1.450 | m |
| 3 | 3.31 | w | 15 | 1.963 | w | 27 | 1.410 | m |
| 4 | 3.18 | m | 16 | 1.925 | s | 28 | 1.363 | wwb |
| 5 | 2.96 | ss | 17 | 1.835 | w | 29 | 1.341 | wwb |
| 6 | 2.85 | m | 18 | 1.750 | ww | 30 | 1.295 | wwb |
| 7 | 2.68 | w | 19 | 1.681 | w | 31 | 1.278 | ww |
| 8 | 2.52 | s | 20 | 1.656 | m | 32 | 1.255 | ww |
| 9 | 2.41 | s | 21 | 1.605 | ww | 33 | 1.181 | m |
| 10 | 2.335 | w | 22 | 1.578 | m | 34 | 1.153 | m |
| 11 | 2.195 | m | 23 | 1.523 | sb | 35 | 1.069 | ww |
| 12 | 2.140 | m | 24 | 1.481 | w | | | |

[1] ss=very strong; s=strong; m=medium; w=weak; ww=very weak; b=broad.

TABLE 4.—*Interplanar spacings of* $3CaO.5Al_2O_3$

| Line No. | $d_{hkl}$ | Intensity [1] | Line No. | $d_{hkl}$ | Intensity [1] | Line No. | $d_{hkl}$ | Intensity [1] |
|---|---|---|---|---|---|---|---|---|
| 1 | 3.62 | m | 15 | 2.055 | mb | 29 | 1.451 | wb |
| 2 | 3.50 | ss | 16 | 1.998 | w | 30 | 1.368 | m |
| 3 | 3.09 | s | 17 | 1.960 | m | 31 | 1.332 | w |
| 4 | 2.97 | s | 18 | 1.923 | ww | 32 | 1.306 | w |
| 5 | 2.87 | s | 19 | 1.900 | m | 33 | 1.284 | w |
| 6 | 2.75 | s | 20 | 1.866 | ww | 34 | 1.252 | w |
| 7 | 2.72 | s | 21 | 1.836 | ww | 35 | 1.178 | w |
| 8 | 2.59 | ss | 22 | 1.800 | m | 36 | 1.153 | ww |
| 9 | 2.52 | s | 23 | 1.759 | m | 37 | 1.134 | w |
| 10 | 2.43 | mb | 24 | 1.679 | w | 38 | 1.025 | ww |
| 11 | 2.32 | m | 25 | 1.624 | m | 39 | .962 | ww |
| 12 | 2.27 | m | 26 | 1.553 | m | 40 | .897 | ww |
| 13 | 2.185 | m | 27 | 1.533 | sb | 41 | .893 | ww |
| 14 | 2.125 | ww | 28 | 1.479 | ww | 42 | .875 | ww |

[1] ss=very strong; s=strong; m=medium; w=weak; ww=very weak; b=broad.

TABLE 5.—*Interplanar spacings of* $3CaO.Al_2O_3$

| Line No. | $d_{hkl}$ | Intensity [1] | Line No. | $d_{hkl}$ | Intensity [1] | Line No. | $d_{hkl}$ | Intensity [1] |
|---|---|---|---|---|---|---|---|---|
| 1 | 4.07 | m | 19 | 1.821 | w | 37 | 1.204 | s |
| 2 | 3.32 | w | 20 | 1.785 | ww | 38 | 1.165 | w |
| 3 | 3.03 | w | 21 | 1.731 | m | 39 | 1.155 | ww |
| 4 | 2.83 | w | 22 | 1.693 | ww | 40 | 1.099 | w |
| 5 | 2.77 | w | 23 | 1.669 | ww | 41 | 1.053 | ww |
| 6 | 2.69 | ss | 24 | 1.640 | w | 42 | 1.034 | ww |
| 7 | 2.57 | ww | 25 | 1.611 | w | 43 | 1.017 | s |
| 8 | 2.46 | ww | 26 | 1.554 | ss | 44 | .998 | ww |
| 9 | 2.400 | w | 27 | 1.512 | ww | 45 | .966 | ww |
| 10 | 2.375 | w | 28 | 1.486 | w | 46 | .897 | m |
| 11 | 2.270 | w | 29 | 1.449 | w | 47 | .850 | ww |
| 12 | 2.200 | m | 30 | 1.426 | ww | 48 | .811 | ww |
| 13 | 2.135 | ww | 31 | 1.404 | w | 49 | .777 | ww |
| 14 | 2.085 | w | 32 | 1.360 | w | 50 | .746 | ww |
| 15 | 2.033 | w | 33 | 1.345 | s | 51 | .726 | ww |
| 16 | 1.981 | w | 34 | 1.315 | ww | 52 | .694 | ww |
| 17 | 1.947 | w | 35 | 1.262 | ww | 53 | .652 | ww |
| 18 | 1.905 | s | 36 | 1.231 | w | 54 | .620 | ww |

[1] ss=very strong; s=strong; m=medium; w=weak, ww=very weak.

TABLE 6.—*Interplanar spacings of $5CaO.3Al_2O_3$*

| Line No. | $d_{hkl}$ | Intensity [1] | Line No. | $d_{hkl}$ | Intensity [1] | Line No. | $d_{hkl}$ | Intensity [1] |
|---|---|---|---|---|---|---|---|---|
| 1 | 3.77 | m | 18 | 1.269 | m | 35 | 1.140 | ww |
| 2 | 3.18 | m | 19 | 1.599 | s | 36 | 1.110 | m |
| 3 | 2.98 | s | 20 | 1.554 | w | 37 | 1.091 | w |
| 4 | 2.67 | ss | 21 | 1.520 | m | 38 | 1.084 | w |
| 5 | 2.55 | m | 22 | 1.493 | w | 39 | 1.066 | w |
| 6 | 2.44 | s | 23 | 1.472 | m | 40 | 1.057 | w |
| 7 | 2.34 | m | 24 | 1.390 | s | 41 | 1.048 | ww |
| 8 | 2.180 | s | 25 | 1.353 | ww | 42 | 1.031 | w |
| 9 | 2.055 | w | 26 | 1.336 | w | 43 | 1.017 | w |
| 10 | 1.943 | s | 27 | 1.305 | m | 44 | .989 | ww |
| 11 | 1.906 | w | 28 | 1.290 | ww | 45 | .968 | ww |
| 12 | 1.846 | w | 29 | 1.274 | w | 46 | .927 | w |
| 13 | 1.800 | ww | 30 | 1.260 | w | 47 | .916 | ww |
| 14 | 1.764 | w | 31 | 1.234 | w | 48 | .900 | ww |
| 15 | 1.728 | m | 32 | 1.207 | w | 49 | .890 | w |
| 16 | 1.694 | w | 33 | 1.187 | ww | 50 | .857 | ww |
| 17 | 1.660 | s | 34 | 1.171 | w | 51 | .848 | ww |

[1] ss=very strong; s=strong; m=medium; w=weak; ww=very weak.

### 3. SYSTEM $Na_2O$-$Al_2O_3$

Matignon (5) found that there exists in the system $Na_2O$-$Al_2O_3$ one compound, $Na_2O.Al_2O_3$, which has a melting point at 1,650°. No optical properties were given.

The system $Na_2O$-$Al_2O_3$ was only partially investigated by the present authors due to the difficulties of working with compositions high in $Na_2O$ and to the high melting temperatures in the region approaching $Al_2O_3$.

On heating a mixture of the composition $Na_2O+Al_2O_3$ (37.8 per cent $Na_2O$; 62.2 per cent $Al_2O_3$) to 1,630°, a homogeneous phase was obtained; there was no melting or dissociation at that temperature. The melting point could not be determined because of the temperature limitations of the furnace.

The compound $Na_2O.Al_2O_3$ was found to crystallize as colorless rounded grains. It is biaxial negative with indices of refraction: $\alpha=1.566\pm0.003$, $\beta=1.575\pm0.003$, $\gamma=1.580\pm0.003$. The optic axial angle is medium small, about 30°. Twinning commonly occurs. The interplanar spacings of the X-ray diffraction pattern are given in Table 7.

No other binary compounds were detected in the system but, on heating a sample containing 3.5 per cent $Na_2O$ and 96.5 per cent $Al_2O_3$ for short periods at 1,100°, corundum and $\beta Al_2O_3$ were identified. On heating such samples at 1,500°, $\beta Al_2O_3$ and $Na_2O.Al_2O_3$ crystallized while corundum was absent. $\beta Al_2O_3$ was found to be the stable modification in the system $Na_2O.Al_2O_3$-$Al_2O_3$ at high temperatures in samples containing as large an amount as 96.5 per cent of $Al_2O_3$.

$\beta Al_2O_3$ was found to be uniaxial negative and to crystallize as plates with the optic axis parallel to the *c*-crystallographic axis. It belongs to the hexagonal crystal system. Determination of the indices of refraction on a sample of the compound furnished by the Norton Co. gave values: $\omega=1.678\pm0.003$; $\epsilon=1.635\pm0.003$. This sample which was made by fusion of $Al_2O_3$ with $Na_2CO_3$ appeared under the microscope to be practically pure $\beta Al_2O_3$. The crystals were large and well developed, whereas in the sample referred to above containing 3.5 per cent $Na_2O$, the small size of the crystals of the $\beta Al_2O_3$ prevented satisfactory measurement of the indices of refraction. However, the X-ray diffraction pattern of this sample of $\beta Al_2O_3$ and that of the sample furnished by the Norton Co. (6) were identical.

## IV. TERNARY COMPOUNDS

Two ternary compounds were found in the system $CaO$-$Na_2O$-$Al_2O_3$—one of a molecular composition $3CaO.2Na_2O.5Al_2O_3$ and the other $8CaO.Na_2O.3Al_2O_3$.

TABLE 7.—*Interplanar spacings of* $Na_2O.Al_2O_3$

| Line No. | $d_{hkl}$ | Intensity[1] | Line No. | $d_{hkl}$ | Intensity[1] | Line No. | $d_{hkl}$ | Intensity[1] |
|---|---|---|---|---|---|---|---|---|
| 1 | 2.94 | s | 13 | 1.599 | s | 25 | 1.048 | m |
| 2 | 2.68 | s | 14 | 1.523 | w | 26 | 1.028 | ww |
| 3 | 2.60 | ss | 15 | 1.497 | s | 27 | 1.010 | w |
| 4 | 2.55 | ss | 16 | 1.471 | w | 28 | .980 | ww |
| 5 | 2.38 | w | 17 | 1.458 | s | 29 | .975 | ww |
| 6 | 2.22 | ww | 18 | 1.415 | m | 30 | .955 | w |
| 7 | 2.145 | w | 19 | 1.362 | s | 31 | .918 | ww |
| 8 | 1.983 | ww | 20 | 1.302 | w | 32 | .910 | ww |
| 9 | 1.950 | m | 21 | 1.283 | w | 33 | .880 | ww |
| 10 | 1.869 | m | 22 | 1.176 | ww | 34 | .805 | ww |
| 11 | 1.805 | w | 23 | 1.119 | m | 35 | .782 | ww |
| 12 | 1.762 | m | 24 | 1.065 | ww | 36 | .762 | ww |

[1] ss=very strong; s=strong; m=medium; w=weak; ww=very weak.

By weight percentages the compound $3CaO.2Na_2O.5Al_2O_3$ contains 20.9 per cent $CaO$; 15.5 per cent $Na_2O$; 63.6 per cent $Al_2O_3$. This compound does not dissociate or melt at any temperature up to 1,630°. Optically it is biaxial positive; the mean refractive index is $1.592 \pm 0.005$; the birefraction is very weak, about 0.005; and it crystallizes as rounded grains. The interplanar spacings of the X-ray diffraction pattern of this compound are given in Table 8.

The compound $8CaO.Na_2O.3Al_2O_3$, having a composition of 54.9 per cent $CaO$, 7.6 per cent $Na_2O$, and 37.5 per cent $Al_2O_3$, dissociates into lime and liquid at 1,508°. Its composition lies outside the field in which it occurs as a primary phase. It is biaxial negative with a medium optic angle; indices of refraction are $\alpha = 1.702 \pm 0.003$, $\gamma = 1.710 \pm 0.003$. When the compound crystallizes as a primary phase, well-formed crystals are readily obtained. They often appear as polyhedrons with hexagonal or octagonal outline. When crystallization of the melt is rapid the compound separates as extremely fine crystalline material. In slowly cooled samples twinning is characteristic.

TABLE 8.—*Interplanar spacings of $3CaO.2Na_2O_5Al_2O_3$*

| Line No. | $d_{hkl}$ | Intensity[1] | Line No. | $d_{hkl}$ | Intensity[1] | Line No. | $d_{hkl}$ | Intensity[1] |
|---|---|---|---|---|---|---|---|---|
| 1 | 4.20 | s | 22 | 1.660 | w | 43 | 1.058 | w |
| 2 | 3.91 | s | 23 | 1.600 | w | 44 | 1.051 | m |
| 3 | 3.41 | m | 24 | 1.575 | w | 45 | 1.025 | ww |
| 4 | 2.97 | w | 25 | 1.544 | m | 46 | 1.014 | ww |
| 5 | 2.84 | s | 26 | 1.499 | s | 47 | 1.000 | ww |
| 6 | 2.67 | w | 27 | 1.485 | s | 48 | .975 | w |
| 7 | 2.58 | ss | 28 | 1.425 | m | 49 | .951 | ww |
| 8 | 2.49 | ww | 29 | 1.391 | m | 50 | .926 | ww |
| 9 | 2.43 | w | 30 | 1.363 | m | 51 | .906 | ww |
| 10 | 2.34 | w | 31 | 1.333 | ww | 52 | .854 | w |
| 11 | 2.25 | m | 32 | 1.302 | w | 53 | .841 | ww |
| 12 | 2.20 | m | 33 | 1.288 | m | 54 | .837 | ww |
| 13 | 2.14 | m | 34 | 1.263 | ww | 55 | .815 | ww |
| 14 | 2.06 | m | 35 | 1.240 | ww | 56 | .812 | ww |
| 15 | 1.990 | m | 36 | 1.214 | ww | 57 | .787 | ww |
| 16 | 1.934 | m | 37 | 1.188 | ww | 58 | .782 | ww |
| 17 | 1.863 | m | 38 | 1.161 | m | 59 | .744 | ww |
| 18 | 1.842 | m | 39 | 1.144 | m | 60 | .739 | ww |
| 19 | 1.805 | s | 40 | 1.162 | w | 61 | .734 | ww |
| 20 | 1.738 | m | 41 | 1.102 | w | 62 | .728 | ww |
| 21 | 1.697 | w | 42 | 1.080 | wwb |  |  |  |

[1] ss=very strong; s=strong; m=medium; w=weak; ww=very weak; b=broad.

The compound $8CaO.Na_2O.3Al_2O_3$ was never obtained as a perfectly homogeneous phase. Fairly well-crystallized samples were obtained by heating preparations for about two hours just below the dissociation temperature. Longer heating periods were avoided because of possible loss of soda due to volatilization. Neither could the compound be obtained by annealing a glass of its own composition for such a glass could not be prepared since all of the CaO did not go into solution at the temperatures obtainable.

The interplanar spacings of the X-ray diffraction pattern of this compound are given in Table 9.

A consideration of the composition and structure of $8CaO.Na_2O.3Al_2O_3$ is of some interest.

Before the structure of the $8CaO.Na_2O.3Al_2O_3$ had been determined, it was noted that the X-ray diffraction pattern of the new compound was closely similar to that of $3CaO.Al_2O_3$. This suggested that the composition of the compound might lie on the line joining $3CaO.Al_2O_3$ and $Na_2O$ and hence be represented by $3CaO.Al_2O_3$ plus some multiple of $Na_2O$, just as the ternary compound $3CaO.2Na_2O.5Al_2O_3$ may be represented by a composition $3CaO.5Al._2O_3$ plus $2Na_2O$. Accordingly, a mixture of $3CaO.Al_2O_3$ and $Na_2O$ was prepared and heated at 1,400°; a temperature well below the dissociation temperature of the ternary compound. Following this heat treatment the sample was examined and found to contain considerable free CaO. If the compound were merely an addition product of $Na_2O$ and $3CaO.Al_2O_3$ or a solution of $Na_2O$ in $3CaO.Al._2O_3$, no lime should have been displaced at that temperature. The displacement of CaO in the mixture indicated that the new compound was not such an addition product.

TABLE 9.—*Interplanar spacings of* $8CaO.Na_2O.3Al_2O_3$

| Line No. | $d_{hkl}$ | Intensity [1] | Line No. | $d_{hkl}$ | Intensity [1] | Line No. | $d_{hkl}$ | Intensity [1] |
|---|---|---|---|---|---|---|---|---|
| 1 | 3.37 | w | 10 | 2.03 | w | 19 | 1.492 | w |
| 2 | 3.03 | w | 11 | 1.915 | s | 20 | 1.347 | m |
| 3 | 2.68 | ss | 12 | 1.888 | s | 21 | 1.235 | w |
| 4 | 2.60 | w | 13 | 1.840 | ww | 22 | 1.210 | m |
| 5 | 2.53 | w | 14 | 1.797 | ww | 23 | 1.103 | w |
| 6 | 2.41 | w | 15 | 1.746 | w | 24 | 1.101 | w |
| 7 | 2.37 | w | 16 | 1.692 | wb | 25 | 1.055 | w |
| 8 | 2.20 | s | 17 | 1.628 | w | 26 | 1.019 | m [2] |
| 9 | 2.10 | w | 18 | 1.558 | ss | 27 | .899 | w |

[1] ss=very strong; s=strong; m=medium; w=weak; ww=very weak; b=broad.
[2] Very broad.

If we consider the composition $8CaO.Na_2O.3Al_2O_3$, we observe that it may be represented as $3(3CaO.Al_2O_3)$ in which one CaO has been replaced by $Na_2O$. Bragg (7) has shown that in the silicates and associated compounds, the X-ray configuration is dependent upon the framework of the oxygen atoms; that is, when packed as closely as possible, the oxygen atoms form the basis of the structure of the compound whereas the other atoms lie between them. One criterion for such close packing is that the index of refraction of a compound with that structure lies above 1.70; $3CaO.Al_2O_3$ and $8CaO.Na_2O.3Al_2O_3$ both have indices above 1.70. The other atoms merely expand this oxygen lattice.

From the similarity of the X-ray diffraction patterns it would seem that the above conditions fit the case here. It might further be remarked that the crystal structure is a function of the unit cell and not of the chemical molecule; that is, the unit cell is some integral multiple of the chemical molecule and hence there is no difficulty encountered in the consideration of the replacement of one $Na_2O$ for one CaO from three molecules of $3CaO.Al_2O_3$. Thus the unit cell of $3CaO.Al_2O_3$ may contain three times as many molecules as the unit cell of $8CaO.Na_2O.3Al_2O_3$. A solution of the structure of both of these compounds to the end of allocating the exact positions of all of the atoms should be of interest.

In its field of primary crystallization, $3CaO.Al_2O_3$ often crystallizes as well-formed polyhedrons with hexagonal or octagonal outline. In ordinary light these crystals appear similar to the well-formed crystals of $8CaO.Na_2O.3Al_2O_3$. Yet $3CaO.Al_2O_3$ is reported as belonging to the isometric system whereas $8CaO.Na_2O.3Al_2O_3$ does not belong to that system, since it is clearly birefracting.

Rankin and Wright (3) have reported that $3CaO.Al_2O_3$ is faintly birefracting, which birefraction they attribute to strain. In this study, the compound $3CaO.Al_2O_3$ showed a distinct but weak birefraction when large grains were available; this was noticeable both in the binary system $CaO-Al_2O_3$ and in the ternary system $CaO-Na_2O-Al_2O_3$.

Furthermore Harrington (4) found that his X-ray diffraction patterns of $3CaO.Al_2O_3$ did not altogether conform to the cubic structure and he assigned the compound to a pseudo-cubic system. His samples of $3CaO.Al_2O_3$ were carefully prepared and annealed for long periods in order to avoid strain in the crystals. Such treatment, however, did not alter the X-ray diffraction patterns. Hence, from these structural considerations, it is suggested that $3CaO.Al_2O_3$ does not belong to the isometric system and only because of its extremely low birefraction has it been so classified.

The nature of the compound $3CaO.2Na_2O.5Al_2O_3$ will be discussed more fully below.

## V. STABILITY FIELDS

The fields of stability of the various compounds in the ternary diagram are shown in Figure 1. Each of the components as well as all of the binary and ternary compounds which were found have stability fields in the system.

In the field of $3CaO.5Al_2O_3$ both the stable and unstable forms of that compound were formed. Usually the stable modification crystallized from the melt although occasionally the unstable modification appeared. No definite region of stability was found for either form.

The compound $5CaO.3Al_2O_3$ does not crystallize as such in the presence of $Na_2O$ but as a solid solution of soda, in some form, in $5CaO.3Al_2O_3$. Whenever reference is made in this paper to the compound $5CaO.3Al_2O_3$ in the ternary diagram, this solid solution is indicated. As the amount of solid solution increases to its maximum, containing about 1 per cent of $Na_2O$, the index of refraction of $5CaO.3Al_2O_3$ is lowered from 1.61 to 1.59. The X-ray diffraction pattern shows a regular shift of the position of its lines as the amount of soda taken up is increased.

Whenever $3CaO.Al_2O_3$ and $8CaO.Na_2O.3Al_2O_3$ crystallized from the melt, well-formed crystals of both of these compounds were found. The crystals showed considerable similarity in appearance, but there was no indication of any solid solution of the two at the liquidus and the boundary curve separating the two fields was easily located.

A boundary separating the fields in which $Na_2O.Al_2O_3$ and $3CaO.2Na_2O.5Al_2O_3$ appear as primary phases could not be located. The properties of the primary phase in the region bounded by the radial lines (fig. 1), but lying to the right of the boundary *RPQ*, varied from those of $3CaO.2Na_2O.5Al_2O_3$ through insensible gradations to those of $Na_2O.Al_2O_3$. Throughout this region, also, the product of final crystallization consisted of two phases: $8CaO.Na_2O.3Al_2O_3$ and a second phase which had properties intermediate between $3CaO.2Na_2O.5Al_2O_3$ and $Na_2O.Al_2O_3$. For these reasons it appears probable that a continuous series of solid solutions exists between those two compounds. The consideration may be simplified by regarding $Na_2O.Al_2O_3$ as taking up $CaO.Al_2O_3$ in solution to a limiting composition of $3(CaO.Al_2O_3)+2(Na_2O.Al_2O_3)$. Since this limit can not be exceeded, it functions as a compound and may properly be regarded as such. The tie line $8CaO.Na_2O.3Al_2O_3$-$3CaO.2Na_2O.5Al_2O_3$ may thus be considered as expanded to include all compositions up to the position $8CaO.Na_2O.3Al_2O_3$-$Na_2O.Al_2O_3$. From the phase-rule viewpoint, that whole area may be regarded as consisting of an infinite number of tie lines passing from the origin, $8CaO.Na_2O.3Al_2O_3$, to the solid solution line $3CaO.2Na_2O.5Al_2O_3$-$Na_2O.Al_2O_3$. It should be pointed out that these tie lines indicate the mean products of final crystallization, but can not be regarded as crystallization curves; that is, the precise composition of the crystals formed at any given temperature from any given composition of liquid, in this area, can be established only by experimentation (8) which has not been conducted in the present study.

No attempt was made to define a boundary separating the field in which the $Na_2O.Al_2O_3$ appears in solid solution with $3CaO.2Na_2O.5Al_2O_3$ and the field in which $Na_2O.Al_2O_3$ separates as primary phase.

## VI. QUINTUPLE POINTS

Three quintuple invariant points were found in the system which represent ternary eutectics; that is, invariant compositions at which three solid phases coexist with liquid and vapor, occurring inside the triangle formed by the three solid phases (9).

The eutectic for $3CaO.5Al_2O_3$, $CaO.Al_2O_3$, and $3CaO.2Na_2O.5Al_2O_3$ (point *B*, fig. 1) occurs at a composition 27.5 per cent CaO, 6.0 per cent $Na_2O$, 66.5 per cent $Al_2O_3$, and melts at 1,465°.

The eutectic for $5CaO.3Al_2O_3$, $CaO.Al_2O_3$, and $3CaO.2Na_2O.5Al_2O_3$ (point *E*) occurs at a composition 38.0 per cent CaO, 4.0 per cent $Na_2O$, 58.0 per cent $Al_2O_3$, and melts at 1,430°.

The eutectic for $5CaO.3Al_2O_3$, $8CaO.Na_2O.3Al_2O_3$, and $3CaO.2Na_2O.5Al_2O_3$ (point *I*), occurs at a composition 46.0 per cent CaO, 5.0 per cent $Na_2O$, and 49.0 per cent $Al_2O_3$, and melts at 1,420°.

Three quintuple invariant points were found in the system which are not eutectics, that is, they are invariant compositions at which three solid phases coexist with liquid and vapor occurring outside the triangle formed by the three solid phases.

The invariant point for $3CaO.Al_2O_3$, $5CaO.3Al_2O_3$, and $8CaO.Na_2O.3Al_2O_3$ (point *J*) occurs at a composition 46.5 per cent CaO, 4.5 per cent $Na_2O$, and 49.0 per cent $Al_2O_3$. The melting temperature is 1,423°.

The invariant point for CaO, $3CaO.Al_2O_3$, and $8CaO.Na_2O.3Al_2O_3$ (point *M*) occurs at a composition of 50.0 per cent CaO, 6.0 per cent $Na_2O$, and 44.0 per cent $Al_2O_3$. The melting temperature is 1,490°.

The invariant point for CaO, $8CaO.Na_2O.3Al_2O_3$, and solid solutions of $Na_2O.Al_2O_3+3CaO.2Na_2O.5Al_2O_3$ (point *P*) occurs at a composition of 42.5 per cent CaO, 13.0 per cent $Na_2O$, and 44.5 per cent $Al_2O_3$. The melting temperature is 1,475°.

In addition to the above, some evidence was obtained to indicate that an invariant point occurs along the boundary *PI*, which separates the fields of $8CaO.Na_2O.3Al_2O_3$, and solid solutions of $Na_2O.Al_2O_3$ with $3CaO.2Na_2O.5Al_2O_3$, in the neighborhood of point *S*. This would then represent the composition at which the $Na_2O.Al_2O_3$ had taken up its maximum of $CaO.Al_2O_3$ in solid solution and simultaneously was in equilibrium with $8CaO.Na_2O.3Al_2O_3$. It would thus be the origin of a boundary *ST* separating the field of $3CaO.2Na_2O.5Al_2O_3$ from that in which increasing percentages of $Na_2O.Al_2O_3$ are present in the primary phase.

## VII. BOUNDARY CURVES

Many of the boundary curves shown in Figure 1 are normal in all respects and need not be detailed. A few, however, are of especial interest.

At *E* a curve separating the fields of $5CaO.3Al_2O_3$ and $CaO.Al_2O_3$ leaves with temperatures increasing to point *F*, 1,460°, which is a maximum. From *F* the temperature again drops to *G*, 1,400°, the eutectic of $5CaO.3Al_2O_3$ and $CaO.Al_2O_3$. Thus the ternary eutectic *E* melts at a higher temperature (1,430°) than the binary eutectic of $5CaO.3Al_2O_3$ and $CaO.Al_2O_3$ (1,400°). It may be remarked that point *F* may be considered the point at which the boundary curve separating the fields of $5CaO.3Al_2O_3$ and $CaO.Al_2O_3$ enters the ternary diagram because $5CaO.3Al_2O_3$ does not exist as such in this ternary system, but only as a solid solution of $5CaO.3Al_2O_3$ with the third component soda. Hence the binary eutectic to be considered in this case is not one of $CaO.Al_2O_3$ with pure $5CaO.3Al_2O_3$ but one of $CaO.Al_2O_3$ with the solid solution of $5CaO.3Al_2O_3+Na_2O$ with a melting point of 1,460° and falling at point *F* rather than point *G*.

From *I* the curve separating the fields of $8CaO.Na_2O.3Al_2O_3$ and $5CaO.3Al_2O_3$ leaves with temperatures increasing to point *J*, 1,423°, the quintuple point at which $3CaO.Al_2O_3$, $8CaO.Na_2O.3Al_2O_3$, and $5CaO.3Al_2O_3$ are in equilibrium. The temperatures of melting of points *I* and *J* are so close as to be practically indistinguishable with the control available. Yet a little consideration will show that point *I* is the eutectic rather than *J*, for the eutectic composition must be within the triangle joining the compounds taking part in the eutectic melting. The three solid phases in equilibrium with liquid and vapor at *J* are $3CaO.Al_2O_3$, $8CaO.Na_2O.3Al_2O_3$, and $5CaO.3Al_2O_3$; but *J* lies in the triangle $5CaO.3Al_2O_3$–$8CaO.Na_2O.3Al_2O_3$–$3CaO.2Na_2O.5Al_2O_3$; hence it can not be the eutectic. At point *I*, $5CaO.3Al_2O_3$, $8CaO.Na_2O.3Al_2O_3$, and $3CaO.2Na_2O.5Al_2O_3$ are in equilibrium with liquid and vapor, and since *I* lies in the triangle joining those compounds it must be the eutectic.

From *J* the boundary curve separating the field of $5CaO.3Al_2O_3$ from $3CaO.Al_2O_3$ leaves with temperatures increasing to a maximum at point *K*, 1,435°, and then falling to *L*, the binary eutectic of $5CaO.3Al_2O_3$ and $3CaO.Al_2O_3$ at 1,395°. This behavior is similar to that discussed above along the boundary curve *E–F–G* and is due to the existence of a solid solution of $Na_2O$ in this system. Hence point *K* is the quadruple point at which $3CaO.Al_2O_3$ and solid solution $5CaO.3Al_2O_3+Na_2O$ are at equilibrium with liquid and vapor, and from which the boundary curve separating the fields of crystallization enters the ternary diagram.

From *M* the boundary *M–O* leaves with temperatures increasing to *O*, 1,508°, which is the maximum on the curve *M–O–P* separating the field of CaO and $8CaO.Na_2O.3Al_2O_3$.

Since *O* is the maximum on this curve, the compound which is dissociating must lie on a line joining *O* with the primary phase which separates when the compound dissociates. Inasmuch as *O* lies on the boundary separating the field of CaO from the field of $8CaO.Na_2O.3Al_2O_3$, the composition of the compound must lie on the line joining *O* with CaO. While the compound $8CaO.Na_2O.3Al_2O_3$ was never obtained as a perfectly homogeneous phase, yet it was in the neighborhood of this composition that the best samples of the compound were obtained. Final decision as to the composition was then made when the point *O* was located and *O*-CaO drawn.

From *O* the temperatures drop to point *P*, 1,475°, the quintuple point at which CaO, $8CaO.Na_2O.3Al_2O_3$, and solid solutions of $Na_2O.Al_2O_3+3CaO.2Na_2O.5Al_2O_3$ are in equilibrium. The temperatures of melting then rise along the boundary separating the fields of CaO and $Na_2O.Al_2O_3$ to point *Q*, 1,565° ± 10°, the binary eutectic of CaO and $Na_2O.Al_2O_3$.

From *P* the temperatures drop along the boundary separating the field of $8CaO.Na_2O.3Al_2O_3$ from the field of solid solutions of $Na_2O.Al_2O_3 + 3CaO.2Na_2O.5Al_2O_3$ toward *S*.

Point *R* represents the binary eutectic of $8CaO.Na_2O.3Al_2O_3$ with $3CaO.2Na_2O.5Al_2O_3$ which falls at 1,465°. However, at *S* melting occurs at a temperature of 1,455°. At 1,465° there are still two crystalline phases with liquid and vapor.

If $3CaO.2Na_2O.5Al_2O_3$ and $Na_2O.Al_2O_3$ form a continuous series of solid solutions, as seems probable, then melting might be characterized by a minimum, such as found at 1,455° in the region of point *S*. Until the system $3CaO.2Na_2O.5Al_2O_3$-$Na_2O.Al_2O_3$ is fully established, the boundary curve *P–S–R* must remain only partially explained.

## VIII. BINARY SYSTEMS WITHIN THE TERNARY DIAGRAM

### 1. SYSTEM $3CaO.5Al_2O_3$-$3CaO.2Na_2O.5Al_2O_3$

These two compounds form a true binary system with a eutectic (point *A*) at a composition: 22.8 per cent CaO; 8.0 per cent $Na_2O$; 69.2 per cent $Al_2O_3$. This eutectic melts at 1,550°. The unstable modification of $3CaO.5Al_2O_3$ appeared in some of the samples in this system, but no definite region of stabilty of this modification was found.

### 2. SYSTEM $CaO.Al_2O_3$-$3CaO.2Na_2O.5Al_2O_3$

The eutectic of these two compounds (point *D*) lies at a composition 30.3 per cent CaO, 5.4 per cent $Na_2O$, and 64.3 per cent $Al_2O_3$. It melts at 1,515°.

### 3. SYSTEM $5CaO.3Al_2O_3$-$3CaO.2Na_2O.5Al_2O_3$

There is a eutectic formed in this system (point *H*) at a composition 40.4 per cent CaO, 4.3 per cent $Na_2O$, and 55.3 per cent $Al_2O_3$. It melts at 1,450°. The melting temperatures do not decrease regularly from the melting point of $5CaO.3Al_2O_3$ but increase from 1,455°, the melting point of $5CaO.3Al_2O_3$, to 1,480° when about 1 per cent of $Na_2O$ is present. This increase is due to solid solution formation of soda, as previously described, in $5CaO.3Al_2O_3$.

### 4. SYSTEM $3CaO.2Na_2O.5Al_2O_3$-$Na_2O.Al_2O_3$

No melting was observed in this system up to temperatures of 1,630°. On examination of three samples in the system, a homogeneous phase was found with refractive indices which varied between those of $Na_2O.Al_2O_3$ and $3CaO.2Na_2O.5Al_2O_3$. These samples were plainly striated with an appearance somewhat as exsolid solutions; that is, crystalline material which existed as a solid solution at high temperatures, but, due to reduced solubility at lower temperatures, separated into two phases on cooling. The X-ray patterns of these samples showed a structure similar but not identical to that of $3CaO.2Na_2O.5Al_2O_3$. The system can not be defined with precision from the data at hand as equipment permitting the employment of higher temperatures is required. The correlation of all of the data indicates, however, that the system consists of a series of solid solutions of $CaO.Al_2O_3$ in $Na_2O.Al_2O_3$ with the end member at the composition $3CaO.2Na_2O.5Al_2O_3$.

### 5. SYSTEM $CaO$-$Na_2O.Al_2O_3$

These two compounds form a true binary system with a eutectic (point *Q*) at 20 per cent CaO, 30 per cent $Na_2O$, and 50 per cent $Al_2O_3$. It melts at 1,565° ± 10°. Samples of $Na_2O.Al_2O_3$ in this system are highly twinned; polysynthetic twinning is common.

Since the lines connecting the following compositions do not lie wholly within the fields of primary crystallization they do not form true binary systems. The following three systems are of that type:

### 6. SYSTEM $8CaO.Na_2O.3Al_2O_3$-$3CaO.2Na_2O.5Al_2O_3+Na_2O.Al_2O_3$

At the point (*R*) where the tie line of the limiting composition of the solid solution series cuts the boundary separating the fields of primary crystallization, a eutectic appears to be formed having the composition 43.7 per cent CaO, 10.2 per cent $Na_2O$, and 46.1 per cent $Al_2O_3$. It melts at 1,465°. $8CaO.Na_2O.3Al_2O_3$ appears along the liquidus in this system from the composition of the eutectic (*R*) to a composition *U*, 46.0 per cent CaO, 9.7 per cent $Na_2O$, and 44.3 per cent $Al_2O_3$ where the tie line joining the compounds intersects the boundary *MP*. On the lime side of that region, the $8CaO.Na_2O.3Al_2O_3$ dissociates into CaO and liquid; between *R* and $3CaO.2Na_2O.5Al_2O_3$ the latter compound is the primary phase.

This binary system may be regarded as extending from $8CaO.Na_2O.3Al_2O_3$ to any point on the line $3CaO.2Na_2O.5Al_2O_3$-$Na_2O.Al_2O_3$, but compositions along the line $8CaO.Na_2O.3Al_2O_3$-$Na_2O.Al_2O_3$ were not examined.

### 7. SYSTEM $5CaO.3Al_2O_3.$-$8CaO.Na_2O.3Al_2O_3$

The compound $8CaO.Na_2O.3Al_2O_3$ does not appear on the liquidus in this system.

### 8. SYSTEM $3CaO.Al_2O_3$-$8CaO.Na_2O.3Al_2O_3$

In spite of the similarity in structure and habit of these compounds, no evidence of solid solution formation between them was found at the liquidus. The line joining these compositions merely represents one boundary of the limiting areas which determine the final products of crystallization in the adjacent triangles.

The systems CaO-$8CaO.Na_2O.3Al_2O_3$ and $Na_2O.Al_2O_3+3CaO.2Na_2O.5Al_2O_3$-$Al_2O_3$ were not investigated.

## IX. COURSE OF CRYSTALLIZATION

Three types of crystallization are found in this system. These will be discussed with the use of the diagram of Figure 2, which shows only a part of the field.

1. The crystallization proceeds to a boundary curve along which one solid phase partially disappears while the other crystallizes, the process becoming complete at the quintuple point for that boundary curve. This type of crystallization may be represented by a composition at point *a*. The primary phase to separate on cooling a melt

of that composition is $8CaO.Na_2O.3Al_2O_3$. As that compound separates, the composition of the liquid follows the line *a b*. When *b* is reached, $3CaO.2Na_2O.5Al_2O_3$ appears with the $8CaO.Na_2O.3Al_2O_3$. These two phases separate together, the mean composition of the solid following the line $8CaO.Na_2O.3Al_2O_3$-$3CaO.2Na_2O.5Al_2O_3$ and that of the liquid following the line *b I*. When *I* is reached the mean composition of the solid phase is represented by point *c*. $5CaO.3Al_2O_3$ then separates with the other crystalline phases and the mean composition of the solid phase follows the line *c a*, ending at *a*.

2. The crystallization curve proceeds to a quintuple point but at that point one solid phase entirely disappears and the crystallization curve proceeds along a boundary to another quintuple point. The primary phase at point *d* is CaO which separates until the liquid reaches the composition *e*. Tricalcium aluminate then crystallizes with CaO along the line CaO-$3CaO.Al_2O_3$ until the mean composition of the solid phases arrives at point *f* when the composition of the liquid will be at *M*. $8CaO.Na_2O.3Al_2O_3$ then appears and the composition of the solid phase follows the line *f g* while the liquid remains at *M*. When the mean composition of the solid phases is represented by point *g*, the CaO disappears, having been dissolved during the simultaneous crystallization of $3CaO.Al_2O_3$ and $8CaO.Na_2O.3Al_2O_3$. The mean composition of the solid then follows the line *g h* while the liquid changes from *M* to *J*. At *J*, $5CaO.3Al_2O_3$ appears and the composition of the solid follows the line *h d*, and ends at *d*.

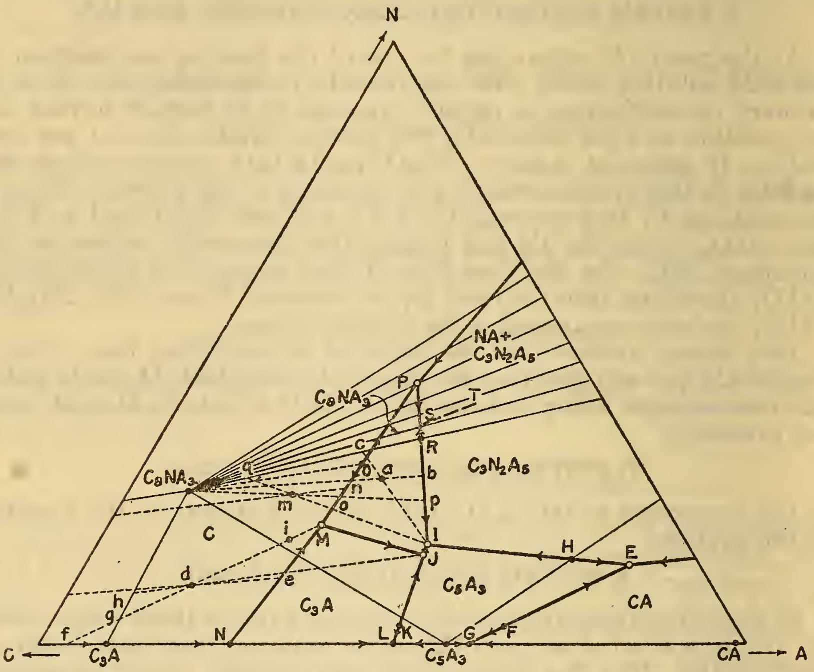

FIGURE 2.—*Diagram showing course of crystallization in a part of the system* $CaO$-$Na_2O$-$Al_2O_3$

If the original composition had been located within a restricted area above the line connecting $8CaO.Na_2O.3Al_2O_3$ and $5CaO.3Al_2O_3$, as at *i*, the crystallization curve would not have ended at *J*, but would have proceeded to the ternary eutectic at *I*.

3. The crystallization curve proceeds to a boundary along which one solid phase entirely disappears before a quintuple point is reached; it then leaves the boundary and crosses a field to another boundary curve along which it proceeds to a quintuple point. The primary phase at point *m* is $CaO$ which separates until the liquid has the composition of point *n*. $8CaO.Na_2O.3Al_2O_3$ then appears and the mean composition of the solid phase passes along the line connecting $CaO$ and $8CaO.Na_2O.3Al_2O_3$ until the composition of $8CaO.Na_2O.3Al_2O_3$ is reached. The liquid then has the composition of point *o*. On further cooling, $8CaO.Na_2O.3Al_2O_3$ separates alone while the composition of the liquid changes from *o* to *p*. At *p*, $3CaO.2Na_2O.5Al_2O_3$ appears and the mean composition of the solid changes from $8CaO.Na_2O.3Al_2O_3$ to point *q* while the liquid follows *p I* to *I*. At *I*, $5CaO.3Al_2O_3$ appears and the mean composition of the solid changes from *q* to *m*, where the crystallization ends.

## X. SIGNIFICANCE OF THE SYSTEM $CaO$-$Na_2O$-$Al_2O_3$ IN PORTLAND CEMENT

As stated in the introduction of this paper, that portion of the $CaO$-$Na_2O$-$Al_2O_3$ system in the neighborhood of $3CaO.Al_2O_3$ and low in soda is the region which is directly concerned with Portland cement. From this work alone, however, we can not predict the combinations of soda in cement; to do so a study must be made of systems involving the other components of cements with soda. However, we are able to say the following: Of the compounds of $CaO$, $Na_2O$, and $Al_2O_3$ which are important in solving the final status of the $Na_2O$ in cement, $8CaO.Na_2O.3Al_2O_3$ alone is of significance. This is due to the existence in Portland cement of $3CaO.Al_2O_3$ alone, of the compounds of lime and alumina, and the finding in this study that the field of $3CaO.Al_2O_3$ adjoins that of $8CaO.Na_2O.3Al_2O_3$, but not that of $3CaO.2Na_2O.5Al_2O_3$. The stability of $8CaO.Na_2O.3Al_2O_3$ with the other constituents of cement, $3CaO.SiO_2$, $2CaO.SiO_2$, $4CaO.Al_2O_3.Fe_2O_3$, and $MgO$, must, therefore, be determined before the composition of the compounds of soda in cements can be defined.

Any direct attempt to identify $8CaO.Na_2O.3Al_2O_3$ in a commercial or laboratory cement probably would be unsuccessful. Identification by the microscope would be extremely difficult, since the compound must necessarily be present only in small amounts and the similarity of optical properties of $8CaO.Na_2O.3Al_2O_3$ and the other cement compounds makes difficult its differentiation from them by microscopic means. Likewise, the X-ray method can not be used to advantage because the principal lines of the diffraction pattern of $8CaO.Na_2O.3Al_2O_3$ coincide with those of $3CaO.Al_2O_3$, and only if $8CaO.Na_2O.3Al_2O_3$ were present in excessive amounts could we hope to establish its presence in cements. Hence thermal studies alone furnish the basis for establishing the nature of the soda compounds in cement. If thermal studies show that $8CaO.Na_2O.3Al_2O_3$ is stable in the presence of $3CaO.SiO_2$, $2CaO.SiO_2$, $4CaO.Al_2O_3.Fe_2O_3$, and $MgO$ we are assured that $Na_2O$ may exist in cement in the form of that ternary compound. In that case the $Na_2O$ may replace some of the $CaO$ from $3CaO.Al_2O_3$ and form the new combination $8CaO.Na_2O.3Al_2O_3$. Former studies in this laboratory have indicated that $Na_2O$ replaces CaO when the former is added to cement compositions, but this does not necessarily mean that the replacement must be in $3CaO.Al_2O_3$. It might be a replacement in $4CaO.Al_2O_3.Fe_2O_3$ or the silicates. All of these questions can be solved only by further study of the soda systems with the other components of cement.

## XI. SUMMARY

A part of the system $CaO-Na_2O-Al_2O_3$ has been investigated by the method of phase equilibria and the results presented.

Two ternary compounds were found in the system, having the compositions: $3CaO.2Na_2O.5Al_2O_3$ and $8CaO.Na_2O.3Al_2O_3$.

The stability fields of the phases in the system have been defined, the boundary curves indicated and the invariant points located. The compositions and melting points of the compounds and of the invariant points are summarized in Table 10. The optical properties of the ternary compounds and of $Na_2O.Al_2O_3$ and $\beta Al_2O_3$ are given in Table 11. The interplanar spacings of the X-ray diffraction patterns are listed for the ternary compounds and for the binary compounds which have not previously been reported. Diagrams are presented which indicate the stability fields, temperature relations, and course of crystallization in the system.

## XII. ACKNOWLEDGMENTS

The authors gratefully acknowledge their indebtedness to Dr. W. C. Hansen, formerly of this staff, for his contributions to this study. The investigation was begun by Doctor Hansen and brought by him to partial completion in the region of the compound $3CaO.2Na_2O.5Al_2O_3$. Both for this important contribution and continued interest and advice in the final solution of the system the authors take pleasure in giving full recognition and thanks.

Table 10.—*Compositions and melting points*

COMPOUNDS

| Composition | CaO | $Na_2O$ | $Al_2O_3$ | Melting point °C. | Authority |
|---|---|---|---|---|---|
| $C_3A$ | 62.2 | | 37.8 | [1] 1,535 | Rankin et al. |
| $C_5A_3$ | 47.8 | | 52.2 | 1,455 | Do. |
| CA | 35.4 | | 64.6 | 1,600 | Do. |
| $C_3A_5$ | 24.8 | | 75.2 | 1,720 | Do. |
| NA | | 37.8 | 62.2 | 1,650 | Matignon. |
| $C_3N_2A_5$ | 20.9 | 15.5 | 63.6 | >1,630 | Brownmiller. |
| $C_8NA_3$ | 54.9 | 7.6 | 37.5 | [1] 1,508 | Do. |

BINARY EUTECTICS

| Composition | CaO | $Na_2O$ | $Al_2O_3$ | Melting point °C. | Authority |
|---|---|---|---|---|---|
| $C_3A-C_5A_3$ | 50.0 | | 50.0 | 1,395 | Rankin et al. |
| $C_5A_3-CA$ | 47.0 | | 53.0 | 1,400 | Do. |
| $CA-C_3A_5$ | 33.5 | | 66.5 | 1,590 | Do. |
| $C_3A_5-A$ | 24.0 | | 76.0 | 1,700 | Do. |
| C-NA | 20.0 | 30.0 | 50.0 | 1,565 | Brownmiller. |
| $C_3N_2A_5-C_3A_5$ | 23.0 | 8.0 | 69.0 | 1,550 | Do. |
| $C_3N_2A_5-CA$ | 30.5 | 5.0 | 64.5 | 1,515 | Do. |
| $C_3N_2A_5-C_5A_3$ | 40.0 | 4.5 | 55.5 | 1,450 | Do. |
| $C_3N_2A_5-C_8NA_3$ | 43.2 | 10.3 | 46.5 | 1,465 | Do. |

[1] Dissociation temperatures.

TABLE 10.—*Compositions and melting points*—Continued

QUADRUPLE POINTS NOT EUTECTICS

| Compositions | CaO | $Na_2O$ | $Al_2O_3$ | Melting point | Authority |
|---|---|---|---|---|---|
| | | | | °C. | |
| $C$-$C_3A$ | 57.0 | -------- | 43.0 | 1,535 | Rankin et al. |
| $C$-$C_8NA_3$ | 46.8 | 9.0 | 44.2 | 1,508 | Brownmiller. |

TERNARY EUTECTICS

| Compositions | CaO | $Na_2O$ | $Al_2O_3$ | Melting point | Authority |
|---|---|---|---|---|---|
| $C_3A_5$-$CA$-$C_3N_2A_5$ | 27.5 | 6.0 | 66.5 | 1,465 | Brownmiller. |
| $CA$-$C_5A_3$-$C_3N_2A_5$ | 38.0 | 4.0 | 58.0 | 1,430 | Do. |
| $C_5A_3$-$C_8NA_3$-$C_3N_2A_5$ | 46.0 | 5.0 | 49.0 | 1,420 | Do. |

QUINTUPLE POINTS NOT EUTECTICS

| Compositions | CaO | $Na_2O$ | $Al_2O_3$ | Melting point | Authority |
|---|---|---|---|---|---|
| $C_5A_3$-$C_3A$-$C_8NA_3$ | 46.5 | 4.5 | 49.0 | 1,423 | Brownmiller. |
| $C_3A$-$C$-$C_8NA_3$ | 50.0 | 6.0 | 44.0 | 1,490 | Do. |
| $C$-$C_8NA_3$-$C_3N_2A_5$+$NA$ | 42.5 | 13.0 | 44.5 | 1,475 | Do. |

TABLE 11.—*Optical properties of some of the compounds examined*

| Refractive indices, ±0.003 | Optic axial angle | Character | Appearance |
|---|---|---|---|
| $NA$ $\alpha=1.566$; $\beta=1.575$; $\gamma=1.580$ | About 30° | Biaxial negative. | Colorless, rounded grains; twining common. |
| $\beta Al_2O_3$ $\omega=1.678$; $\epsilon=1.635$ | Optic axis parallel to c-crystallographic axis. | Uniaxial negative. | Plates; hexagonal system. |
| $C_3N_2A_5$ Mean index 1.592; weak birefraction. | ------------------------ | Biaxial positive. | Rounded grains. |
| $C_8NA_3$ $\alpha=1.702$; $\gamma=1.710$ | Medium angle | Biaxial negative. | Polyhedrons with hexagonal or octagonal outline. |

The authors are indebted also to Dr. Herbert Insley, of the Bureau of Standards, who gave assistance in the microscopical identification of the phases, and to Dr. Frank C. Kracek, of the Geophysical Laboratory, for his advice and suggestions in the interpretation of data.

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WASHINGTON, April 20, 1931.