

RESEARCH PAPER RP1512

*Part of Journal of Research of the National Bureau of Standards, Volume 29,**December 1942*FURTHER PHASE-EQUILIBRIUM STUDIES INVOLVING
THE POTASH COMPOUNDS OF PORTLAND CEMENT

By William C. Taylor*

ABSTRACT

The present research on the system $K_2O.23CaO.12SiO_2-CaO-5CaO.3Al_2O_3$ is a part of the program designed to determine the manner in which K_2O affects the compound composition of portland cement clinker. Thermal and optical data are presented and a phase-equilibrium diagram of this system has been constructed. The only compounds that were observed in the system under equilibrium conditions are the components of the system and $3CaO.Al_2O_3$. The effect of K_2O on the compound composition of clinker containing K_2O , CaO , MgO , Al_2O_3 , Fe_2O_3 , SiO_2 , and SO_3 has been studied also. The only compounds of K_2O found to be stable are K_2SO_4 and $K_2O.23CaO.12SiO_2$, the K_2O combining preferentially with the SO_3 present.

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I. INTRODUCTION

The compositions and the amounts of the various compounds in portland cement clinker are determined by the relations of the several oxides to one another during the thermal treatment given the raw mixture. Because of the complications attending studies of systems containing more than three components, the most convenient approach to relations of the oxides to each other consists in a series of investigations of binary and of ternary systems. The most advantageous

*Research Associate at the National Bureau of Standards, representing the Portland Cement Association.

course of study to be followed in this step-by-step process may be indicated by examining the products of reactions between an established clinker compound and an additional oxide or a newly established compound.

This procedure is being followed in determining the relation of the component K_2O to the other oxide components of clinker. Brown-miller [1]¹ found that $K_2O \cdot Al_2O_3$ is the only compound of K_2O that will crystallize from the melt in all portions of the K_2O - CaO - Al_2O_3 system studied. The present author [2] found that $K_2O \cdot Al_2O_3$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ form a binary system with one eutectic, no additional compounds being formed. In the same study, it was shown that for a given ratio of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ to $2CaO \cdot Fe_2O_3$, the solid solution of these two compounds and $K_2O \cdot Al_2O_3$ form a pseudobinary system with a definite lowest-melting composition. In the study that followed, it was found that $K_2O \cdot Al_2O_3$ reacts with $2CaO \cdot SiO_2$ and with $3CaO \cdot SiO_2$ to form a potash-lime-silica compound [3]. This compound was later shown in the study of the system $K_2O \cdot CaO \cdot SiO_2$ - $2CaO \cdot SiO_2$ to have the composition $K_2O \cdot 23CaO \cdot 12SiO_2$ [3]. Examination of the products of reactions involving $3CaO \cdot Al_2O_3$, $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, and $K_2O \cdot 23CaO \cdot 12SiO_2$ revealed that $K_2O \cdot 23CaO \cdot 12SiO_2$ exists in a region of the K_2O - CaO - Al_2O_3 - Fe_2O_3 - SiO_2 system in which portland cement compositions fall.

The present investigation of the system $K_2O \cdot 23CaO \cdot 12SiO_2$ - $CaO \cdot 5CaO \cdot 3Al_2O_3$ was undertaken for the purpose of establishing the existence or nonexistence of other compounds of potash in the system and of determining the fields of stability of the various compounds formed when mixtures of K_2O , CaO , Al_2O_3 , and SiO_2 comparable to portland cement clinker compositions are heated.

Since SO_3 and MgO are components of almost every commercial clinker, the effects of these oxides on the manner in which K_2O is combined in clinker were studied, and the results are included in this report.

II. EXPERIMENTAL METHOD

The compounds forming the components of the system $K_2O \cdot 23CaO \cdot 12SiO_2$ - $CaO \cdot 5CaO \cdot 3Al_2O_3$ were prepared first and the exact compositions determined by chemical analyses and microscopical examinations. This preparation of $5CaO \cdot 3Al_2O_3$ was found to melt sharply at a temperature between $1,454^\circ$ and $1,458^\circ$ C as measured by means of a calibrated thermocouple. Rankin and Wright give $1,455^\circ \pm 5^\circ$ C as the melting point of this compound [4].

Each of the compounds was heated to about $1,250^\circ$ C for one-half hour immediately before the proportioning of the various mixtures. The mixtures then were intimately ground in an agate mortar. Small charges for thermal study were taken from these base samples, the general procedure previously outlined [1, 2, 3] being followed. Similar methods were employed in the study of other high-temperature reactions reported in this paper.

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

III. THE SYSTEM $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2$ - CaO - $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$

1. BINARY SYSTEMS OF THE COMPONENTS

(a) THE SYSTEM $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2$ - CaO

Previous studies [3] have shown that there is no reaction between $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2$ and CaO , in the sense that no additional crystalline compound is formed. The liquidus temperatures in this system are beyond the limits of the equipment in use (about $1,600^\circ\text{C}$), and therefore the boundary curve is undetermined. Extrapolation of the boundary curve between the fields of $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2$ and CaO in the ternary system indicates that a simple eutectic may consist of about 85 percent of $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2$ and 15 percent of CaO (see fig. 1 showing the diagram of the system).²

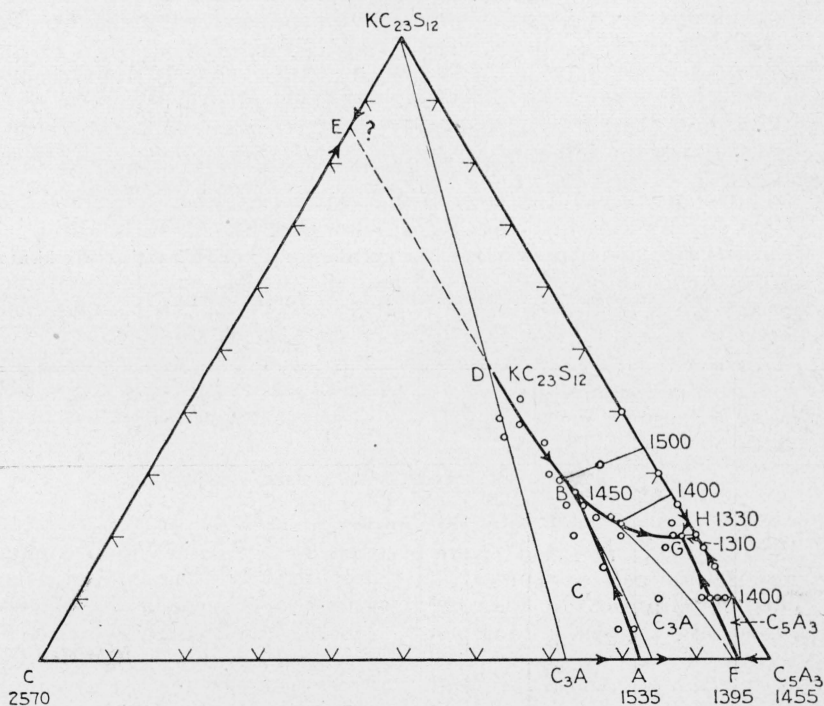


FIGURE 1.—Diagram showing fields of primary crystallization in the system $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2$ - CaO - $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$.

Figures shown are temperatures of invariant points or isotherms in degrees C. $\text{C} = \text{CaO}$, $\text{KC}_{23}\text{S}_{12} = \text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2$, $\text{C}_3\text{A} = 3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $\text{C}_5\text{A}_3 = 5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$.

(b) THE SYSTEM CaO - $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$

This system is a portion of the more inclusive system CaO - Al_2O_3 , reported in detail by Rankin and Wright in their paper "The Ternary System CaO - Al_2O_3 - SiO_2 " [4].

² Since liquidus temperatures could not be determined for all mixtures of the compounds $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2$, CaO , and $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, there is no assurance that these compounds constitute the components of a true ternary system. At temperatures below $1,600^\circ\text{C}$, the behavior of the mixtures is such as may be defined by a ternary system. Accordingly, the system is referred to as a ternary system throughout the paper.

(c) THE SYSTEM $K_2O \cdot 23CaO \cdot 12SiO_2 \cdot 5CaO \cdot 3Al_2O_3$

No intermediate compound is formed in this system. The eutectic, melting at $1,330^\circ \pm 5^\circ C$, (point *H*, fig. 1) consists of 21.5 percent of $K_2O \cdot 23CaO \cdot 12SiO_2$ and 78.5 percent of $5CaO \cdot 3Al_2O_3$ (oxide composition: K_2O , 0.96 percent; CaO , 50.68 percent; Al_2O_3 , 41.00 percent; and SiO_2 , 7.36 percent). The melting temperatures for the mixtures having compositions ranging from 0 percent of $K_2O \cdot 23CaO \cdot 12SiO_2$ and 100 percent of $5CaO \cdot 3Al_2O_3$ to 40 percent of $K_2O \cdot 23CaO \cdot 12SiO_2$ and 60 percent of $5CaO \cdot 3Al_2O_3$ are given in table 1.

Brownmiller [1] reported that $5CaO \cdot 3Al_2O_3$ does not crystallize as such in the ternary system K_2O - CaO - Al_2O_3 , but as a solid solution of K_2O in $5CaO \cdot 3Al_2O_3$. He observed that the index of refraction of this solid solution varied in accordance with the amount of K_2O dissolved. When the maximum amount of K_2O was present (about 2 percent), the index of refraction was 1.593; the refractive index of pure $5CaO \cdot 3Al_2O_3$ is 1.608. The existence of this solid solution was substantiated by regular shifts in the lines of the X-ray diffraction patterns. In the binary system $K_2O \cdot 23CaO \cdot 12SiO_2$ - $5CaO \cdot 3Al_2O_3$, and in the ternary system $K_2O \cdot 23CaO \cdot 12SiO_2$ - CaO - $5CaO \cdot 3Al_2O_3$ no evidence of solid solution of K_2O in $5CaO \cdot 3Al_2O_3$ was obtained, no deviation from the value 1.608 as the index of $5CaO \cdot 3Al_2O_3$ being obtained in any case.

TABLE 1.—*Thermal data relative to the system*
 $K_2O \cdot 23CaO \cdot 12SiO_2$ - $5CaO \cdot 3Al_2O_3$

In this and in tables 1 to 6, inclusive, and also in the text where reference is made to the compositions of the various mixtures, the following abbreviations apply:

$KC_{23}S_{12}$ for $K_2O \cdot 23CaO \cdot 12SiO_2$ C_5S for $2CaO \cdot SiO_2$
 C_5A_3 for $5CaO \cdot 3Al_2O_3$ C_3A for $3CaO \cdot SiO_2$
 C for CaO C_4AF for $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$
 C_3A for $3CaO \cdot Al_2O_3$ KA for $K_2O \cdot Al_2O_3$

Sample	Composition		Temperature of quench	Examination
	$KC_{23}S_{12}$	C_5A_3		
	%	%	$^\circ C$	
0-----	0	100	1,454	All crystalline.
			1,458	All glass.
			1,325	$KC_{23}S_{12}$; C_5A_3 ; trace of glass.
1-----	10	90	1,385	C_5A_3 ; glass.
			1,395	Slight amount of C_5A_3 ; glass.
			1,405	Glass.
4-----	15	85	1,365	C_5A_3 ; glass.
			1,375	Glass.
5-----	18	82	1,350	C_5A_3 ; glass.
			1,360	Glass.
			1,325	$KC_{23}S_{12}$; C_5A_3 ; no glass.
2-----	20	80	1,333	Trace of $KC_{23}S_{12}$; C_5A_3 ; glass.
			1,340	C_5A_3 ; glass.
			1,345	Glass.
6-----	22	78	1,335	Trace of $KC_{23}S_{12}$; glass.
			1,340	Glass.
			1,325	$KC_{23}S_{12}$; C_5A_3 ; trace of glass.
3-----	25	75	1,375	Occasional grains of $KC_{23}S_{12}$; glass.
			1,385	Glass.
			1,415	$KC_{23}S_{12}$; glass.
7-----	30	70	1,435	Small amount of $KC_{23}S_{12}$; glass.
			1,445	Glass.
			1,325	$KC_{23}S_{12}$; C_5A_3 ; no glass.
8-----	40	60	1,335	$KC_{23}S_{12}$; glass.
			1,565	Small amount of $KC_{23}S_{12}$; glass.
			1,575	Glass.

In the report on the system $K_2O \cdot CaO \cdot SiO_2$ - $2CaO \cdot SiO_2$ [3], the crystals of $K_2O \cdot 23CaO \cdot 12SiO_2$ were described as irregularly shaped, somewhat rounded grains, exhibiting polysynthetic twinning. The

product observed in that study, for the most part, did not crystallize from a melt, and it was suggested that the crystals were pseudomorphs of α - $2\text{CaO} \cdot \text{SiO}_2$. In the binary system $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2$ - $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ and in the ternary system $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2$ - $\text{CaO} \cdot 5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ also, it was observed that the crystals of $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2$ known to have crystallized from a melt did not exhibit twinning. This material appeared as almost spherical grains having indices identical with the values obtained in the previous study for the grains least twinned; $\alpha=1.695$, $\gamma=1.703$.

2. THE TERNARY SYSTEM

No new compounds exist in equilibrium with the liquid in this system. The products of final crystallization are the components of the system and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$.

The fields of stability of these compounds are shown in figure 1. It will be seen that the field of CaO occupies by far the greatest portion of the diagram. The field of $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2$ is the next largest.

The melting temperatures in the CaO field are very high and, in moving away from the boundary curves, soon exceed the limits of the furnace employed. The melting temperatures in the $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2$ field, in general, likewise are very high.

Two quintuple points, that is, invariant compositions at which three solid phases may coexist with liquid and vapor, occur in the system. One quintuple point is a eutectic, whereas the other is not. The solid phases at the eutectic point, point *G*, are $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, and $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$. It occurs at the composition 20.0 percent of $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2$, 2.0 percent of CaO , and 78.0 percent of $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ (oxide composition: K_2O , 0.90 percent; CaO , 51.5 percent; Al_2O_3 , 40.7 percent; and SiO_2 , 6.9 percent). It melts at $1,330^\circ \pm 5^\circ \text{C}$.

At the other quintuple point, point *B*, $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2$, CaO , and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ exist with liquid and vapor. Since this point lies outside the triangle formed by lines joining the compositions of the solid phases, it is not a eutectic. It occurs at the composition 27.0 percent of $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2$, 13.0 percent of CaO , and 60 percent of $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ (oxide composition: K_2O , 1.2 percent; CaO , 58.3 percent; Al_2O_3 , 31.3 percent; and SiO_2 , 9.3 percent). The melting temperature is $1,450^\circ \pm 5^\circ \text{C}$.

3. THE BOUNDARY CURVES

There are two general classes of boundary curves in a ternary system:

1. Boundary curves along which two phases crystallize together. A tangent drawn to a point on this type of curve intersects a line joining the compositions of the two phases crystallizing out. All curves which terminate at a eutectic point belong to this class.

2. Boundary curves along which one phase crystallizes while the other partially or entirely disappears. A tangent drawn to any point on this type of curve intercepts a prolongation of a line joining the compositions of the two phases. When one phase disappears before a quintuple point is reached, the crystallization curve leaves the boundary and crosses a field to another boundary curve and proceeds along it until a quintuple point is reached.

The compositions limiting the field of primary crystallization of CaO are represented in the ternary diagram (fig. 1) by the curve *ABDE*. The section *AB* is the boundary curve between the fields of CaO and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, and the melting temperatures of the compositions fall from $1,535^\circ \pm 5^\circ\text{C}$ at *A* to $1,450^\circ \pm 5^\circ\text{C}$ at *B*. This boundary belongs to class 2, described above. For melts having compositions within the triangle $\text{CaO}-B-3\text{CaO} \cdot \text{Al}_2\text{O}_3$ the crystallization curve follows the boundary *AB*, with $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ crystallizing and the amount of solid CaO decreasing until the quintuple point is reached. If the original composition is within the triangle $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2-\text{CaO}-3\text{CaO} \cdot \text{Al}_2\text{O}_3$, CaO is one of the final products of crystallization. If this composition falls within the triangle $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2-3\text{CaO} \cdot \text{Al}_2\text{O}_3-5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, to the left of a line connecting *B* and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, the CaO entirely disappears when the temperature falls below that of the quintuple point *B*. For compositions falling within the area $3\text{CaO} \cdot \text{Al}_2\text{O}_3-B-A$, solid CaO wholly disappears before quintuple point *B* is reached and the crystallization curve leaves the boundary and crosses the $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ field, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ crystallizing alone until another boundary is reached; the curve then follows the boundary to the eutectic. The melting relations along the boundary *AB* are shown in table 2. Charges were quenched also at lower temperatures than those recorded in the table, but in several cases it was found that CaO grains persisted. This indicated that a slower rate of cooling would be required to establish equilibrium. It was considered inadvisable to maintain the charges at the relatively high temperatures for periods greater than 20 minutes, because of the likelihood of loss of potash through volatilization.

TABLE 2.—*Thermal data relative to the boundary curve separating the fields of CaO and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$*

Sample	Composition			Temperature of quench	Examination
	$\text{KC}_{23}\text{Si}_{12}$	C	C_3A		
	%	%	%	$^\circ\text{C}$	
17.....	5	18	77	1,500	C; C_3A ; glass.
				1,510	C; glass.
31.....	5	16	79	1,490	C_3A ; glass.
				1,500	Very small amount of C_3A ; glass.
25.....	15	15	70	1,500	Traces of C and C_3A ; glass.
				1,510	Glass.
26.....	20	16.6	63.4	1,500	C; glass.
				1,550	Glass.
19.....	25	15	60	1,450	C; slight amount of C_3A and $\text{KC}_{23}\text{Si}_{12}$; glass.
				1,500	C; glass.
				1,550	Glass.
22.....	25	13	62	1,455	Traces of C and C_3A ; glass.
				1,460	Glass.
30.....	27	13	60	1,450	C; C_3A ; $\text{KC}_{23}\text{Si}_{12}$; glass.
				1,455	Glass.

The boundary curve *BDE* separates the fields of CaO and $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2$. The section *DE* is an approximation, since the melting temperatures in this region extend beyond the limits of the equipment employed. It is admitted that there is no direct evidence that $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2$ is a congruently melting compound and that the invariant point between CaO and $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2$ is a eutectic. The data relative to the section *BD* are given in table 3.

The boundary curve *BG* separates the fields of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2$ and extends from the invariant point not a eutectic,

at which the solid phases $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2$, CaO , and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ coexist, to the eutectic where $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, and $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ exist in contact with liquid and vapor. The melting temperatures of compositions defined by this line decrease from $1,450^\circ \pm 5^\circ\text{C}$ to $1,310^\circ \pm 5^\circ\text{C}$. The melting relations are shown in table 4.

The boundary curve *HG*, separating the fields of $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2$ and $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, is short in comparison with the other boundary lines. Melting temperatures of compositions along this curve lie between that of the binary eutectic of $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2$ and $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, $1,330^\circ \pm 5^\circ\text{C}$, and that of the ternary eutectic of $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, and $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, $1,310^\circ \pm 5^\circ\text{C}$. Thermal data pertaining to this boundary are given in table 5.

The boundary curve *FG*, separating the fields of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, extends from the binary eutectic of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ to the ternary eutectic of the system. The temperatures along this line fall from $1,395^\circ \pm 5^\circ\text{C}$ to $1,310^\circ \pm 5^\circ\text{C}$. Data relative to this boundary are given in table 6.

TABLE 3.—*Thermal data relative to the boundary curve separating the fields of CaO and $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2$*

Sample	Composition			Temperature of quench	Examination
	$\text{KC}_{23}\text{Si}_{12}$	C	C_3A_3		
	%	%	%	$^\circ\text{C}$	
36.-----	29	14	57	1,425 1,500 1,520	C; $\text{KC}_{23}\text{Si}_{12}$; C_3A ; glass. C; $\text{KC}_{23}\text{Si}_{12}$; glass. Glass.
23.-----	30	15	55	1,500 1,525	C; $\text{KC}_{23}\text{Si}_{12}$; glass. C; glass.
29.-----	35	13	52	1,510 1,520	C; $\text{KC}_{23}\text{Si}_{12}$; glass. $\text{KC}_{23}\text{Si}_{12}$; glass.
32.-----	36	18	46	1,575 1,580	C; trace of $\text{KC}_{23}\text{Si}_{12}$; glass. C; glass.
34.-----	38	15	47	1,575 1,600	C; trace of $\text{KC}_{23}\text{Si}_{12}$; glass. Small amount of C; glass.
33.-----	39	17	44	1,575	C; glass.
35.-----	42	13	45	1,600	$\text{KC}_{23}\text{Si}_{12}$; glass.

TABLE 4.—*Thermal data relative to the boundary curve separating the fields of $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$*

Sample	Composition			Temperature of quench	Examination
	$\text{KC}_{23}\text{Si}_{12}$	C	C_3A_3		
	%	%	%	$^\circ\text{C}$	
30.-----	27	13	60	1,450 1,455	$\text{KC}_{23}\text{Si}_{12}$; C; C_3A ; glass. Glass.
20.-----	23	12	65	1,420 1,425 1,430	$\text{KC}_{23}\text{Si}_{12}$; C_3A ; glass. Slight amount of C_3A ; glass. Glass.
21.-----	23	10	67	1,410 1,420	Small amount of $\text{KC}_{23}\text{Si}_{12}$ and C_3A intercrystallized; glass. Glass.
18.-----	22	9	69	1,390 1,400	Traces of $\text{KC}_{23}\text{Si}_{12}$ and C_3A ; glass. Glass.
16.-----	20	10	70	1,300 1,370 1,400	$\text{KC}_{23}\text{Si}_{12}$; C_3A ; C_3A_3 . $\text{KC}_{23}\text{Si}_{12}$; C_3A ; glass. C_3A ; glass.
27.-----	18	5	77	1,410 1,330 1,350	Glass. C_3A ; glass. Glass.
15.-----	20	3	77	1,320 1,325	$\text{KC}_{23}\text{Si}_{12}$; C_3A ; glass. Slight amount of $\text{KC}_{23}\text{Si}_{12}$; glass.
13.-----	20	2	78	1,330 1,305 1,310 1,310	Glass. $\text{KC}_{23}\text{Si}_{12}$; C_3A ; C_3A_3 ; no glass. Glass. $\text{KC}_{23}\text{Si}_{12}$; C_3A ; C_3A_3 ; slight amount of glass.

* Maximum temperature attained during heat treatment.

TABLE 5.—*Thermal data relative to the boundary line separating the fields of $K_2O.23CaO.12SiO_2$ and $5CaO.3Al_2O_3$*

Sample	Composition			Temperature of quench	Examination
	$KC_{23}S_{12}$	C	C_5A_3		
	%	%	%	$^{\circ}C$	
6-----	22	0	78	1,335 1,340	Small amount of $KC_{23}S_{12}$ glass. Glass.
14-----	22	2	76	1,300 1,310 1,320 1,340	
2-----	20	0	80	1,340 1,345	C_5A_3 ; glass. Glass.
13-----	20	2	78	1,305 1,310	
15-----	20	3	77	1,310 1,320 1,325 1,330	$KC_{23}S_{12}$; C_3A ; C_5A_3 ; no glass. Glass. Slight amount of $KC_{23}S_{12}$; glass. Glass.

^a Maximum temperature attained during heat treatment.

TABLE 6.—*Thermal data relative to the boundary curve separating the fields of $3CaO.Al_2O_3$ and $5CaO.3Al_2O_3$*

Sample	Composition			Temperature of quench	Examination
	$KC_{23}S_{12}$	C	C_5A_3		
	%	%	%	$^{\circ}C$	
11-----	0	4.15	95.85	1,395 1,385	Eutectic according to Rankin and Wright. Occasional grain of C_5A_3 ; glass.
12-----	10	2	88	1,395 1,380 1,390	
9-----	10	3	87	1,380 1,390 1,305 1,320	Trace of C_5A_3 ; glass. Glass. C_3A ; C_5A_3 ; $KC_{23}S_{12}$; no glass. C_3A ; C_5A_3 ; glass.
13-----	20	2	78	1,365 1,385 1,305 1,310 1,310	

^a Maximum temperature attained during heat treatment.

IV. EFFECT OF SO_3 ON THE CONSTITUTION OF CLINKERS CONTAINING K_2O

In a previous paper [3], it was reported that some evidence had been obtained that $K_2O.23CaO.12SiO_2$ reacts with $CaSO_4$ to form $2CaO.SiO_2$ and K_2SO_4 . Further studies on the effect of SO_3 on the compounds of clinker containing K_2O are included in the present report.

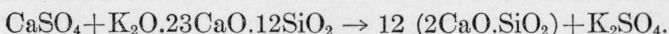
1. STABILITY OF K_2SO_4 WITH CLINKER COMPOUNDS

A mixture was prepared by intimately grinding equimolecular proportions of $CaSO_4$ and $K_2O.23CaO.12SiO_2$.

Mix 1	
$KC_{23}S_{12}$	$CaSO_4$
Mole % 50	Mole % 50

Five different charges were obtained by subjecting this mixture to various thermal treatments. The maximum temperatures varied from 1,500° to 1,300° C, and the quenching temperatures from 1,300° to 850° C; the rate of cooling in each case was about 5° C per minute. The charges immediately after quenching were of medium hardness but, on standing, tended to dust, because of the inversion of β -2CaO.SiO₂ to γ -2CaO.SiO₂. Microscopically, all of the charges appeared to be quite similar. Both forms of 2CaO.SiO₂ and a slightly birefringent interstitial phase having a mean index of refraction of about 1.495 were observed. No glass or anhydrite (CaSO₄) appeared to be present.

The relatively low indices of the interstitial material suggested that it might be arcanite (K₂SO₄), the indices of this mineral being: α =1.493, β =1.494, and γ =1.497. The reaction indicated may be expressed as:



Accordingly, another sample containing equal amounts of K₂SO₄ and 2CaO.SiO₂ by weight was prepared.

Mix 2	
C ₂ S	K ₂ SO ₄
% 50	% 50

All the charges resulting from the various thermal treatments, appeared to consist of only two phases in apparently equal amounts: β -2CaO.SiO₂ and K₂SO₄. On standing, there was some inversion of β -2CaO.SiO₂ to γ -2CaO.SiO₂ but the tendency to dust was not so great as in the products of the previous samples, in which the proportion of 2CaO.SiO₂ to K₂SO₄ was greater.

Further study was made by subjecting mixtures of K₂SO₄ and other clinker compounds to various heat treatments. Mixture 3 contained equal amounts by weight of the four compounds:

Mix 3			
C ₃ S	C ₂ S	C ₃ A	K ₂ SO ₄
% 25	% 25	% 25	% 25

All the original compounds were identified in powder samples of slowly cooled charges and apparently were present in unchanged amounts. In the polished surface sections, the crystal forms and etching properties of 3CaO.SiO₂, β -2CaO.SiO₂, and 3CaO.Al₂O₃ were normal. The K₂SO₄, for the most part, appeared as interstitial material; and although K₂SO₄ is soluble in water, its appearance in reflected light was not changed appreciably by either the water or the acid treatment to which the specimen was subjected. It is possible that the polishing treatment given the specimens was not suitable for imparting a satisfactory polish on the surfaces of the softer K₂SO₄ grains.

Results similar to the above were obtained with mixture No. 4, composed as follows:

Mix 4				
C ₃ S	C ₂ S	C ₃ A	C ₄ AF	K ₂ SO ₄
% 35	% 35	% 15	% 10	% 5

2. RELATION BETWEEN K₂SO₄ AND THE GLASSY PHASE

Most commercial clinkers contain, in addition to the crystalline compounds, varying amounts of glassy material. This constituent is the result of a condition whereby the rates of cooling from the maximum temperatures existing in the kiln are so rapid that complete crystallization of the components is not attained. Since K₂SO₄ melts at a relatively low temperature, 1,076° C, it was considered probable that the components of this compound would often be contained in the glass of clinker.

Accordingly, two mixtures were prepared, one, mix 5, corresponding to the liquid composition for an Al₂O₃:Fe₂O₃ ratio of 2.62 on the 3CaO.SiO₂-2CaO.SiO₂ surface at 1,400° C in the quaternary system CaO-Al₂O₃-Fe₂O₃-SiO₂ [5],

Mix 5				
C ₂ S	C ₃ A	C ₅ A ₃	C ₄ AF	K ₂ SO ₄
% 21.2	% 17.0	% 31.4	% 30.4	% 0
Mix 6				
90				10

and the second, mix 6, consisting of 90 percent of mix 5 and 10 percent of K₂SO₄. These mixtures were heated at 1,400°C for 15 minutes and then quenched from this temperature. Examination of the charge revealed that the completely molten sample of mix 6 had separated into two distinct portions. The top portion was shown by the microscope to consist of K₂SO₄ crystals. The bottom portion was entirely glass and agreed optically with the glass that was obtained by quenching the mixture containing no K₂SO₄, mix 5. These results show that molten K₂SO₄ is immiscible with the clinker melt (with reference to the principal oxides, at least) and, furthermore, because of the readiness with which it crystallizes, K₂SO₄ is not likely to be contained in the glass of clinker.

3. CONSIDERATION OF THE CONSTITUTION OF CLINKER CONTAINING K_2O AS INFLUENCED BY SO_3

It is significant that the introduction of as much as 5.4 percent of K_2O in the form of K_2SO_4 to the glass composition just considered released no free CaO . When only 1 percent of K_2O in the form of the easily decomposed potassium oxalate, instead of K_2SO_4 , was added to 99 percent of the same mixture (mix 5)

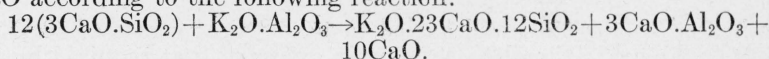
Mix 5				
C_3S	C_3A	C_5A_3	C_4AF	K_2O (as oxalate)
%	%	%	%	%
21.2	17.0	31.4	30.4	0
Mix 7				
99				1

and the resulting mixture subjected to the same heat treatment, the charge was found to consist of 4 percent of crystalline CaO in glass.

These results show, then, that when SO_3 is present, K_2O combines with SO_3 to form K_2SO_4 and as such does not become a part of the normal clinker melt. On the other hand, when SO_3 is not present, K_2O becomes a component of the liquid and some CaO is displaced by this change in composition.

The manner in which SO_3 influences the nature of the potash compound formed in clinker is demonstrated further by the following series of experiments:

1. It has been reported previously [3] that $3CaO.SiO_2$ and $K_2O.Al_2O_3$ react to produce $K_2O.23CaO.12SiO_2$, $3CaO.Al_2O_3$, and uncombined CaO according to the following reaction:



A mixture of the composition

Mix 8	
C_3S	KA
%	%
90	10

was heated to $1,400^\circ C$ and cooled to $1,300^\circ C$ at a rate of $1^\circ C$ per minute. It was estimated that about 20 percent of uncombined CaO and about 70 percent of $K_2O.23CaO.12SiO_2$ were in the charge. Some $3CaO.Al_2O_3$ and $K_2O.Al_2O_3$ also were observed.

2. A second mixture was prepared by adding to the mixture just cited SO_3 in the form of CaSO_4 in an amount calculated to be sufficient to combine with the K_2O , present as $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3$, to form K_2SO_4 . The resulting composition before heat treatment was as follows:

Mix 9		
C_3S	KA	CaSO_4
% 84.2	% 9.4	% 6.5

Examination of powder specimens and a polished section of a charge of this mixture that had been cooled from $1,450^\circ$ to 950° C at a rate of 5° C per minute showed no free CaO ; the only phases being $3\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, and K_2SO_4 .

3. A third mixture composed of 99 percent of the second plus 1 percent of K_2O , introduced as potassium oxalate,

Mix 10	
Mix 9	K_2O (as oxalate)
% 99	% 1

was heated to $1,450^\circ$ C and cooled to $1,000^\circ$ C at a rate of 5° C per minute. This additional K_2O , being in excess of that required by the SO_3 to form K_2SO_4 , caused the reappearance of free CaO and $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2$. The other phases observed were $3\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, and K_2SO_4 .

That K_2O combines preferentially with SO_3 to form K_2SO_4 is a point to be considered in the design of raw mixtures in the industry. The introduction of potash into the raw mixture may produce an effect such as to make much more difficult the production of clinker free of uncombined CaO ; or the introduction of potash may be of little consequence in this respect, depending upon whether or not sufficient SO_3 is present to combine with the K_2O . The marked effect on the combination of CaO due to that portion of the K_2O which is available to form $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2$ has been demonstrated by results obtained in a previous study [3].

4. POTASSIUM SULFATE IN COMMERCIAL CLINKER

In addition to the data obtained in this investigation, other workers have obtained results which indicate that K_2SO_4 is likely to be found

in commercial clinker. In 1936, L. S. Brown, then of the Lone Star Cement Corporation, observed in dust taken between a kiln coating and the underlying brick, and subsequently in clinker, a low-index phase that was tentatively identified as an alkali sulfate [6]. Kalousek, Jumper, and Tregoning report that a correlation exists between the amounts of water-extractable K_2O and the amounts of the available SO_3 in the clinker, which indicates that K_2O is present in many clinkers partly as K_2SO_4 [7]. Woods, in a study of the volatilization of alkalis from two clinker raw mixtures during calcination, observed that the addition of $CaSO_4$ to the mixtures inhibits the volatilization of potash [8].

The correlationship was examined between the K_2O and SO_3 contents of 26 commercial clinkers together with portions of them which had been slowly and quickly cooled after reheating to clinkering temperatures. These clinkers, totaling 78 in number, were available from a study being conducted in this laboratory on the effect of heat treatment on the structure and other properties of clinker. The percentages of K_2O and SO_3 in these clinkers³ are plotted in figure 2. In general, there is an increase in the K_2O content as the amount of SO_3 increases. In most cases the percentage of K_2O lies in the diagram to the right of the K_2SO_4 composition line, which indicates that generally the amount of potash in a clinker is in excess of that required for the formation of K_2SO_4 from the SO_3 available.

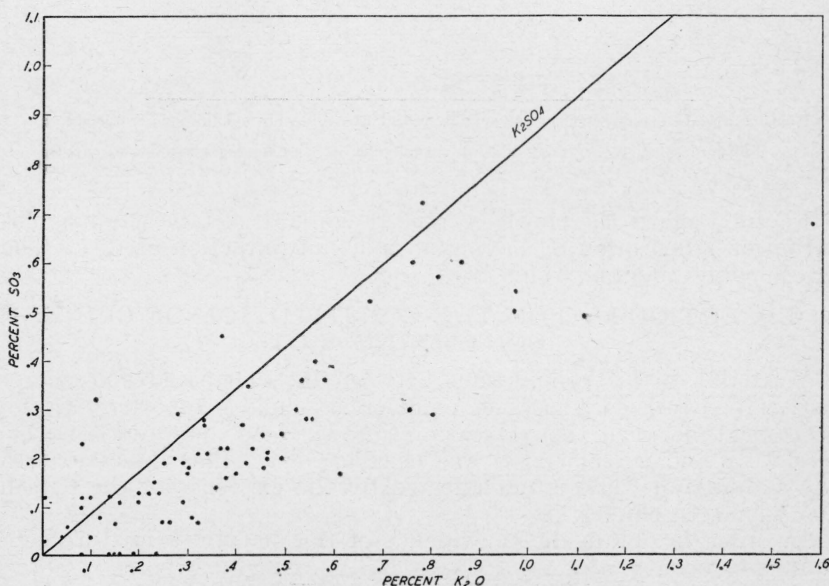


FIGURE 2.—Relationship between the K_2O and the SO_3 content of a number of commercial clinkers (including quickly and slowly cooled portions of the same).

The solid line indicates the loci of compositions containing equimolar amounts of these oxides.

³ Analyses by C. L. Ford, Portland Cement Association, Chicago, Illinois.

Nineteen clinkers of the above lot were examined by means of the petrographic microscope for K_2SO_4 crystals. Potassium sulfate was identified in 11 of the 19 clinkers. This compound was observed in all but two instances in which the calculated potential K_2SO_4 was over 0.24 percent and in no case where the calculated K_2SO_4 fell below that value. The results of the microscopical examinations, together with the percentages of SO_3 and K_2O determined by analyses, and the calculated K_2SO_4 percentages are given in table 7.

TABLE 7.— SO_3 and K_2O contents of clinkers and a comparison of the K_2SO_4 contents as calculated and as observed microscopically

[Order of increasing calculated K_2SO_4]				
Clinker	SO_3	K_2O	K_2SO_4 calculated	K_2SO_4 microscopically observed
	%	%	%	
24P ^a -----	0.00	0.23	0.00	Not observed.
17P-----	(b)	.19	.00	Do.
26Q-----	0.04	.04	.07	Do.
6P-----	.32	.11	.20	Do.
11P-----	.11	.16	.24	Do.
3P-----	.11	.20	.24	Do. ^c
22Q-----	.17	.61	.37	Observed.
22P-----	.24	.93	.52	Not observed.
8P-----	.25	.49	.55	Observed.
9P-----	.28	.54	.61	Do.
13P-----	.40	.56	.87	Do.
1Q-----	.49	1.11	1.07	Do.
25Q-----	.52	0.67	1.13	Do.
14P-----	.54	.97	1.18	Do.
2P-----	.61	.71	1.31	Not observed.
20P-----	.60	.76	1.31	Observed.
15P-----	.60	.86	1.31	Do.
1P-----	.68	1.58	1.48	Do.
25P-----	1.09	1.10	2.04	Do.

^a P=Commercial clinkers; Q=the same, quickly cooled after reheating to clinkering temperatures.

^b Trace.

^c This clinker contained a very small amount of a birefracting phase having a mean index of refraction lower than that of K_2SO_4 ; the phase may be Na_2SO_4 ($\alpha=1.471$, $\epsilon=1.477$, $\gamma=1.484$). Sample contained 0.63 percent of Na_2O .

Figure 3 shows the powdered clinker No. 25P of table 7 a magnification of $\times 500$ in an oil having an index of refraction of 1.52. The arrow points to a grain of K_2SO_4 .

V. EFFECT OF MgO ON THE CONSTITUTION OF CLINKER CONTAINING K_2O

Ward [9], in his comparisons between the calculated and microscopically observed phases of commercial clinker, reports that the agreement between the values for free MgO as determined microscopically and as calculated was usually good. This indicates that the stability of MgO is not affected by the existence of the potash compounds in clinker.

In order to obtain direct evidence of this nature, a mixture containing

Mix 11	
$KC_{23}S_{12}$	MgO
% 99	% 1

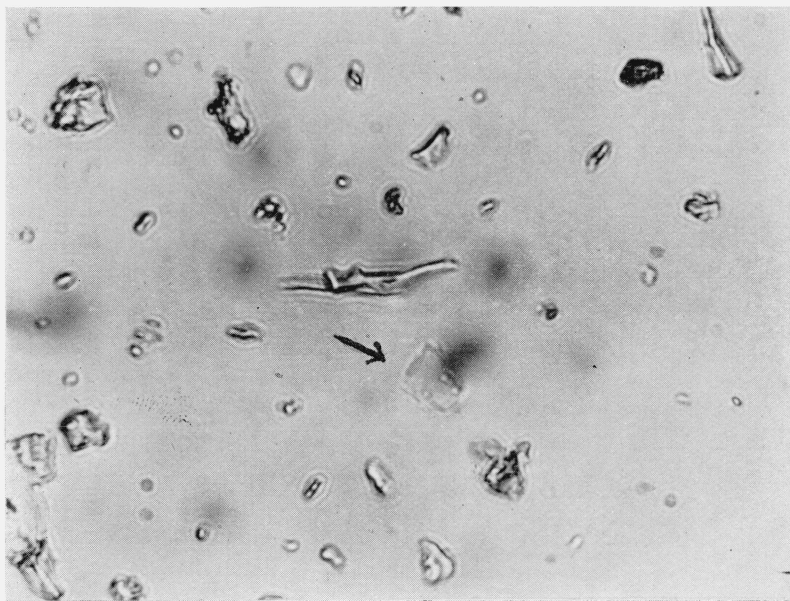


FIGURE 3.—Powdered portland cement clinker immersed in oil of refractive index 1.52, showing grain of K_2SO_4 .

Magnification, $\times 500$.

was prepared and a sample heated at 1,525° C for 1 hour. The resulting charge showed no evidence of melting and, upon examination, was found to consist of only two phases: $\text{K}_2\text{O} \cdot 0.23\text{CaO} \cdot 12\text{SiO}_2$ and periclase (MgO).

A second mixture containing

Mix 12	
K_2SO_4	MgO
% 99	% 1

was prepared also. A charge was heated at 1,400° C for 1 hour. A microscopical examination revealed no evidence of interaction of the K_2SO_4 and MgO .

VI. SUMMARY

The system $\text{K}_2\text{O} \cdot 0.23\text{CaO} \cdot 12\text{SiO}_2$ - CaO - $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ has been investigated by the phase-equilibrium method, and the results are presented. A phase diagram has been constructed.

The only crystalline phase other than the components observed in the system under equilibrium conditions was the compound $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, normal in crystalline form and optical properties. No evidence of any high-temperature modifications of any of the compounds of the system was obtained.

When both SO_3 and K_2O are components of clinker, it was found that K_2O combines preferentially with SO_3 to form K_2SO_4 . In mixtures of K_2O , CaO , Al_2O_3 , Fe_2O_3 , SiO_2 , and SO_3 in proportions comparable to those in portland cement clinker, any K_2O in excess of that required for the formation of K_2SO_4 combines with CaO and SiO_2 to form $\text{K}_2\text{O} \cdot 0.23\text{CaO} \cdot 12\text{SiO}_2$, provided crystallization occurs under equilibrium conditions. Potassium sulfate has been identified in several commercial clinkers.

No reaction of either K_2SO_4 or $\text{K}_2\text{O} \cdot 0.23\text{CaO} \cdot 12\text{SiO}_2$ with MgO has been observed, which indicates that the presence of MgO does not affect the manner in which K_2O is combined in clinker.

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WASHINGTON, July 28, 1942.