

Effect of SO₃ on the Alkali Compounds of Portland Cement Clinker¹

Terry F. Newkirk²

This investigation shows that the compound Na₂O.8CaO.3Al₂O₃, which is known to be one of the forms in which Na₂O may occur in portland cement clinker, is unstable at clinking temperatures in the presence of SO₃. This compound reacts with SO₃ to form Na₂SO₄ and 3CaO.Al₂O₃. Any excess of Na₂O will remain as Na₂O.8CaO.3Al₂O₃, become a constituent of the clinker glass, or enter into solid solution with one of the other clinker components.

In clinker compositions containing both soda and potash together with SO₃, an alkali-sulfate phase is produced that contains both of the alkalis. For molecular ratios R₂O/SO₃ greater than unity, a preferential reaction of the SO₃ with K₂O is indicated. Empirical relationships between the alkalis and the SO₃ of the cement mixture indicate that the alkalis first combine with the SO₃ in the approximate molecular ratio K₂O/Na₂O=3 to the extent that the composition limits of the mixture permit. The composition of the alkali-sulfate phase for mixtures of varying soda-potash contents with R₂O/SO₃ molecular ratios equal to 1, 2, and 3 have been determined. Equations are developed for calculating the approximate composition of the alkali sulfate and the potential phase composition of clinker-type mixtures having other R₂O/SO₃ ratios.

1. Introduction

Portland cement clinker contains, in addition to the major constituent oxides of calcium, aluminum, and silicon, small quantities of other oxides that occur in the raw materials. The alkalis Na₂O and K₂O have a particular interest because of their unfavorable reaction with certain types of aggregate used in concrete, and during the burning process these minor oxides affect the temperature at which the first liquid forms and the nature and quantity of the phases that ultimately constitute the clinker. The nature and quantity of these phases determine, for the most part, the physical and chemical properties of the cement. Small amounts of the alkalis may have an effect on the phase relations in the cement clinker of a magnitude not commensurate with their low concentration in the mixture.

The nature of the alkali-bearing phases has been studied by various investigators [1, 2, 3]³ with mixtures containing CaO, Al₂O₃, SiO₂, and either Na₂O or K₂O. They recognized, however, that acidic oxides such as SO₃ and TiO₂, when present, may react with the alkalis during the burning process to produce new phases.

Taylor [3] found that, for mixtures approximating portland cement compositions and composed of K₂O, CaO, Al₂O₃, SiO₂, Fe₂O₃, and MgO, the stable compound of potash is K₂O.23CaO.12SiO₂. He reported, however, [4] that this compound is unstable when heated in the presence of SO₃, the reaction being represented by the equation,



¹ In portland cement terminology, the sulfur in clinker is usually referred to as SO₃ and is ordinarily reported as such in clinker analyses. For convenience, this terminology is utilized throughout this paper, and SO₃ is treated as one of the primary components in a multi-component system.

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

³ Figures in brackets indicate the literature references at the end of this paper.

He found molten potassium sulfate to be immiscible with the clinker liquid, to show no tendency to react with the components of mixtures containing 3CaO.SiO₂, 2CaO.SiO₂, 3CaO.Al₂O₃, 4CaO.Al₂O₃.Fe₂O₃, and MgO and to crystallize readily upon cooling. In 11 out of 19 commercial clinkers subjected to microscopic examination, he found the phase identified as potassium sulfate.

In a few subsequent experiments, Taylor [5] observed that a solid solution of sodium and potassium sulfates appeared upon heating certain mixtures of Na₂SO₄, K₂O.CaO.SiO₂ and 2CaO.SiO₂. As in the case of the potassium compound, he found sodium sulfate to be essentially immiscible with the clinker melt. A phase identified as K₂SO₄ occurred in several Na₂O-K₂O-CaO-SiO₂-SO₃ mixtures of high K₂O/Na₂O and K₂O/CaO ratios. The manner in which the soda was combined in these mixtures was not determined.

Eubank [6] made a preliminary investigation of the clinker phases produced upon heating mixes containing Na₂O and combinations of Na₂O and K₂O together with SO₃. As a result of microscopic studies of quenched and slowly cooled charges, he found that the compound Na₂O.8CaO.3Al₂O₃ is decomposed by heating with calcium sulfate in the range 1,300° to 1,470°.⁴ Charges containing equimolar quantities of these two compounds were found to consist only of 3CaO.Al₂O₃ and Na₂SO₄ after heat treatment, indicating complete reaction. The alkali sulfate produced in the reaction was found to be stable in the presence of 3CaO.SiO₂, 2CaO.SiO₂, 3CaO.Al₂O₃, and 4CaO.Al₂O₃.Fe₂O₃. Indications were obtained that if a solid solution of Na₂O and Fe₂O₃ in 2CaO.SiO₂ was prepared, the Na₂O was not removed from this solution by heating it with CaSO₄. Some of Eubank's mixes also contained K₂O either as K₂O.23CaO.12SiO₂ or as K₂SO₄ in addition to the soda compounds. Studies of these mixtures were inconclusive, due to

⁴ All temperatures are in deg. C.

the difficulty in distinguishing between certain of the compounds having practically identical optical properties. This made it evident that any further work on this subject would require the application of a different experimental method.

Portland cement clinker ordinarily contains both soda and potash as well as SO_3 . It was necessary, therefore, to study further the effect of SO_3 on the alkali compounds of clinker containing both soda and potash. This study has provided a basis for the development of equations for approximating the potential phase composition of portland cement clinker containing known quantities of K_2O , Na_2O , and SO_3 . This information represents one more advance in our understanding of the formation of clinker, by means of which we may better define and control its constitution and behavior.

2. Experimental Method

2.1. Phase Analysis of Mixtures

A few $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-SO}_3$ mixtures to which had been added one or both of the alkali oxides were studied by the familiar quenching technique [7]. The quenched (or in a few cases slow-cooled) charges were crushed and examined in index oils under the petrographic microscope. After equilibrium was established in these mixtures at clinkering temperatures, the entire quantity of SO_3 (never more than equivalent to the alkalis) was found to be combined with soda or potash. In mixtures containing both alkalis, this sulfate consisted either of a single solid solution of Na_2SO_4 and K_2SO_4 or of an intimate mixture of two sulfate phases, depending upon the conditions of cooling. Excess Na_2O and K_2O remained as $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 0.3\text{Al}_2\text{O}_3$ and $\text{K}_2\text{O} \cdot 0.23\text{CaO} \cdot 0.12\text{SiO}_2$, respectively. Consequently, it appeared that the determination of the relative amounts of sodium and potassium sulfates formed by heating each mixture would provide data for including the sulfates in calculations of the potential phase composition of portland cement clinker from its oxide composition.

Several methods for determining the composition of the alkali sulfate were investigated. These included chemical analysis of water extracts, chemical analysis of concentrates obtained by sedimentation or centrifugation, correlation of the refractive index of the sulfate with its composition, and correlation of the characteristic temperatures of phase changes in the alkali sulfate with its composition. The last method was selected as the most reliable for the purpose at hand, the temperatures being determined by thermal analysis.

Preliminary thermal analyses of several mixtures of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $2\text{CaO} \cdot \text{SiO}_2$, and either K_2SO_4 or Na_2SO_4 , after these mixtures had been preheated at $1,400^\circ$ for 30 minutes, confirmed the findings of Taylor and Eubank that the alkali sulfate was essentially immiscible with the other components. It was therefore possible to determine the liquidus temperature or the temperature of characteristic inversions of the alkali-sulfate phase in each mixture without fear of

errors due to miscibility. The temperatures of these phase changes were correlated with corresponding temperatures on a phase diagram for the binary system $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4$. The approximate composition of the sulfate phase was then determined directly from the diagram.

Nacken [8] prior to 1907 studied the binary system $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4$ by means of cooling curves. A portion of this work was repeated by the author employing both direct and differential heating curves. The phase diagram that resulted was used in determining the composition of the sulfate in the $\text{K}_2\text{O-Na}_2\text{O-CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-SO}_3$ mixtures. This procedure served as a calibration of the method, since the same equipment and technique were employed with all mixtures.

2.2. Equipment and Raw Materials

A Leeds and Northrup "Speedomax" two-point recording potentiometer was used to record on a single chart both the differential and direct heating curves produced by the test charge undergoing thermal analysis. Since the alkali sulfate in many instances comprised only about 3 percent of the weight of the test charge, the differential emf was preamplified by a Leeds and Northrup low-level direct-current amplifier. With this arrangement, differential peaks of from $1\frac{1}{2}$ to 2 in. were produced by the melting of as little as 3 percent of the immiscible sulfate phase. Background "noise" was negligible even at the highest amplification. The temperature of the vertical tube furnace was raised automatically by a motor-driven variable transformer at a rate of approximately 10 deg per minute.

Platinum-10 percent rhodium thermocouples were used with an external ice-bath cold junction. These couples were calibrated periodically against an NBS-certified thermocouple and also with chemically pure salts as auxiliary standards.

The alumina and dehydrated silica gel used in preparing the mixtures were of greater than 99.9-percent purity. The other raw materials met the ACS specifications for chemical reagents.

2.3. Preparation of Mixtures

Thirteen mixtures having different $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4$ ratios were prepared for use in a limited study of the system $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4$. After weighing, the two sulfates were ground together in an agate mortar to pass a No. 200 sieve and thoroughly mixed. The mixtures were placed in covered platinum crucibles and heated in an electric muffle furnace for 10 minutes at a temperature near $1,200^\circ$, at which temperature the charge was completely melted. Each melt was stirred with a platinum-covered ceramic rod, after which the charge was cooled, crushed, screened and mixed. After a second similar treatment, the charges were ready for the thermal analyses, which served to define the pure binary system.

Hundred-gram quantities of the compounds $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 0.3\text{Al}_2\text{O}_3$ and $\text{K}_2\text{O} \cdot 0.23\text{CaO} \cdot 0.12\text{SiO}_2$ were pre-

pared and ground to pass a No. 200 sieve for use in making the mixtures of those compounds with calcium sulfate. The finely ground raw materials (CaCO_3 , K_2CO_3 , Na_2CO_3 , Al_2O_3 , SiO_2), which contained an excess of the alkalis to compensate for volatilization during heating, were ground in an agate mortar and subjected to repeated cycles of 1-hour burning, grinding, screening, and mixing. This was continued until microscopic observation and flame-photometer analysis indicated that the charges consisted of the desired compounds with only occasional traces of impurities. The $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 0.3\text{Al}_2\text{O}_3$ mix was burned at $1,350^\circ$ and the $\text{K}_2\text{O} \cdot 0.23\text{CaO} \cdot 0.12\text{SiO}_2$ at $1,450^\circ$. All burns and thermal analyses were carried out in platinum— $3\frac{1}{2}$ percent rhodium containers. An average of six burns was required for each compound, since both compounds are difficult to prepare, requiring repeated cycles of heating, grinding, screening, and mixing to secure complete reaction. A slight amount of the alkali may remain uncombined, even though the theoretical alkali content of the pure $\text{K}_2\text{O} \cdot 0.23\text{CaO} \cdot 0.12\text{SiO}_2$ or $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 0.3\text{Al}_2\text{O}_3$ is closely approximated and microscopic examination shows the material to consist essentially of the desired compound.

Ten-gram quantities were usually made of the final mixtures of $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 0.3\text{Al}_2\text{O}_3$, $\text{K}_2\text{O} \cdot 0.23\text{CaO} \cdot 0.12\text{SiO}_2$, and CaSO_4 . The desired quantities of these compounds were weighed on an analytical balance, thoroughly mixed, and ground in an agate mortar to pass a No. 200 sieve. The mixtures were then heated in a muffle at about $1,400^\circ$ for 30 minutes. They were removed, ground as before, mixed, and given a second similar heat treatment. Representative samples of each charge were observed under the petrographic microscope. Some of the charges required additional heatings before equilibrium was attained.

In all, 72 mixes representing 51 different compositions were prepared and studied. Thermal analyses were made of all of these mixes and of a number of single compounds.

3. Results

3.1. The System Na_2SO_4 - K_2SO_4

A diagram of the binary system Na_2SO_4 - K_2SO_4 as developed in the present investigation appears as figure 1. No attempt has been made to identify the low-temperature phases or to develop the details of the phase relationships in the portion below the continuous solid-solution region, as this was beyond the scope and purpose of this investigation. Points representing temperatures of phase changes as obtained by thermal analyses of the mixes have been plotted in this lower region as an aid to future investigations of this system. Further small breaks in the thermal analysis curves obtained while employing the highest amplification range of the direct-current amplifier suggest the possibility of even greater complexity in the low-temperature region. Additional phase changes might have been indicated in this region for the other compositions had the highest amplification been employed in each case.

It appears that the low-temperature phase rela-

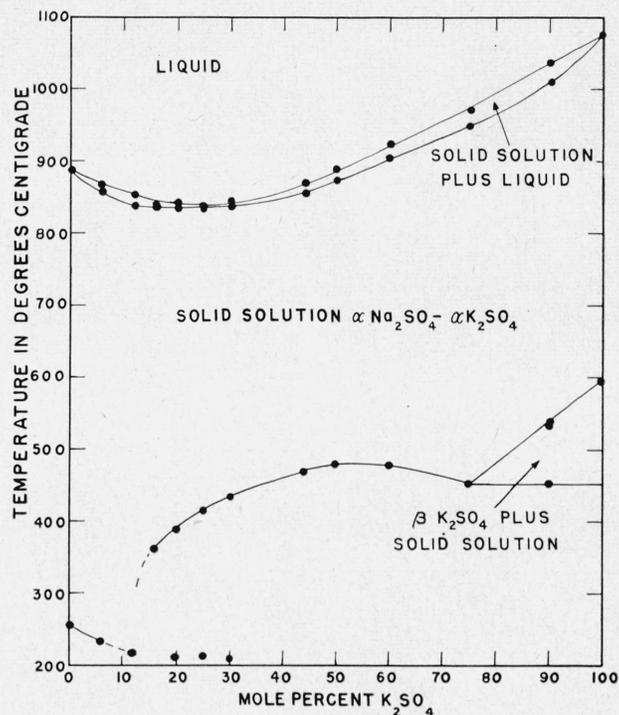


FIGURE 1. System Na_2SO_4 - K_2SO_4 .

tions in this system may be somewhat more complex than those reported by Nacken [8].

The continuous solid-solution region in this diagram was found to correspond to a single phase of uniaxial negative optical character, having refractive indices somewhat higher than those of the low-temperature forms.

The compositions of the mixtures investigated in this system, together with the temperatures of their phase changes, are given in table 1.

TABLE 1. Summary of thermal analysis data for the system K_2SO_4 - Na_2SO_4

Mix compositions	Temperature corresponding to differential peak		
	Solid transitions	Solidus	Liquidus
Mole percent K_2SO_4	$^\circ\text{C}$	$^\circ\text{C}$	$^\circ\text{C}$
0	258	888	888
6	232	857	869
12	227	849	852
16	363	838	840
20	211	835	841
	391	-----	-----
25	215	835	840
	244	-----	-----
	415	-----	-----
30	207	838	846
	432	-----	-----
44	235	856	870
	469	-----	-----
50	480	873	888
60	478	905	923
75	452	950	973
90	454	1,012	1,037
	532	-----	-----
100	595	-----	1,076

3.2. Reaction of $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ with CaSO_4

Charges composed of equimolar quantities of $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ and CaSO_4 (mix 2, table 2) after quenching from above $1,400^\circ$ contained only $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and Na_2SO_4 . The sulfate appeared as a very finely divided phase of low birefringence surrounding the grains of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. A mixture of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and Na_2SO_4 in the proportions that would result from the complete reaction between equimolar quantities of $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ and CaSO_4 showed the same phases after quenching from above $1,400^\circ$. Differential thermal analyses of these mixtures after preliminary heating at $1,400^\circ$ showed definite peaks at a temperature corresponding closely to the melting point of Na_2SO_4 . The lower diagram in figure 2 is a reproduction of the curves obtained with chemically pure Na_2SO_4 . The upper diagram is a similar reproduction of the curves for mixture 2 after preheating. The correspondence in the temperature of the

two peaks is evident. Similar peaks were obtained in the thermal-analysis curves for mixes 37 and 38 (table 2), which consisted of $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ - CaSO_4 mixtures having $\text{Na}_2\text{O}/\text{SO}_3$ molar ratios of 2 and 3, respectively.

TABLE 2. Thermal analysis data

Mix number	Composition of alkali in total mixture	Significant solid inversion temperature	Liquidus temperature	R_2SO_4 composition
Series $\text{R}_2\text{O}/\text{SO}_3=1$				
	Mole fraction of K_2O in $\text{R}_2\text{O}(\text{K}_2)$	$^\circ\text{C}$	$^\circ\text{C}$	Mole fraction of $\text{K}_2\text{SO}_4(\text{K}_2)$
4	1.00	-----	1,061	0.965
35	.95	-----	1,036	.900
34	.85	-----	1,011	.842
32	.65	-----	924	.610
16	.50	-----	902	.544
51	.373	-----	860	.385
31	.35	-----	853	.375
30	.25	-----	842	.270
29	.10	208	864	.081
2	0	-----	885	.017
Series $\text{R}_2\text{O}/\text{SO}_3=2$				
36	1.00	-----	1,060	0.962
26	.95	-----	1,043	.917
24	.85	-----	994	.796
18	.75	-----	981	.765
27	.65	-----	973	.745
7	.50	-----	963	.720
17	.25	480	874	^a .460 to
28	.10	208	831	^a .195
37	0	388	882	.025
Series $\text{R}_2\text{O}/\text{SO}_3=3$				
47	1.00	-----	1,060	0.963
46	.95	-----	1,038	.904
45	.85	-----	994	.795
44	.75	-----	986	.780
43	.65	-----	983	.770
42	.50	-----	972	.745
41	.35	-----	968	.734
40	.25	-----	940	.653
39	.10	420	830	^a .202
38	0	-----	882	.025

^a Determined from solid inversion temperature.

3.3. Reaction of $\text{K}_2\text{O} \cdot 0.23\text{CaO} \cdot 12\text{SiO}_2$ with CaSO_4

In agreement with the work previously reported by Taylor [4], $\text{K}_2\text{O} \cdot 0.23\text{CaO} \cdot 12\text{SiO}_2$ was found to react with CaSO_4 in an equimolar ratio upon heating mixtures of those compounds in the region of clinkering temperatures. The observed reaction products after quenching the mixture from 900° were $\beta\text{-}2\text{CaO} \cdot \text{SiO}_2$, $\gamma\text{-}2\text{CaO} \cdot \text{SiO}_2$ and K_2SO_4 .

Preheated mixtures of $\text{K}_2\text{O} \cdot 0.23\text{CaO} \cdot 12\text{SiO}_2$ and CaSO_4 having molecular ratios $\text{K}_2\text{O}/\text{SO}_3$, of 1, 2, and 3 (4, 36, and 47, respectively, table 2) showed an endothermic transformation in the region of the K_2SO_4 melting point during thermal analysis. The temperature of this transformation was somewhat lower than that for pure potassium sulfate. This is believed to be due to the solution by the K_2SO_4 of a small amount of K_2O , which remained uncombined in the preparation of the $\text{K}_2\text{O} \cdot 0.23\text{CaO} \cdot 12\text{SiO}_2$.

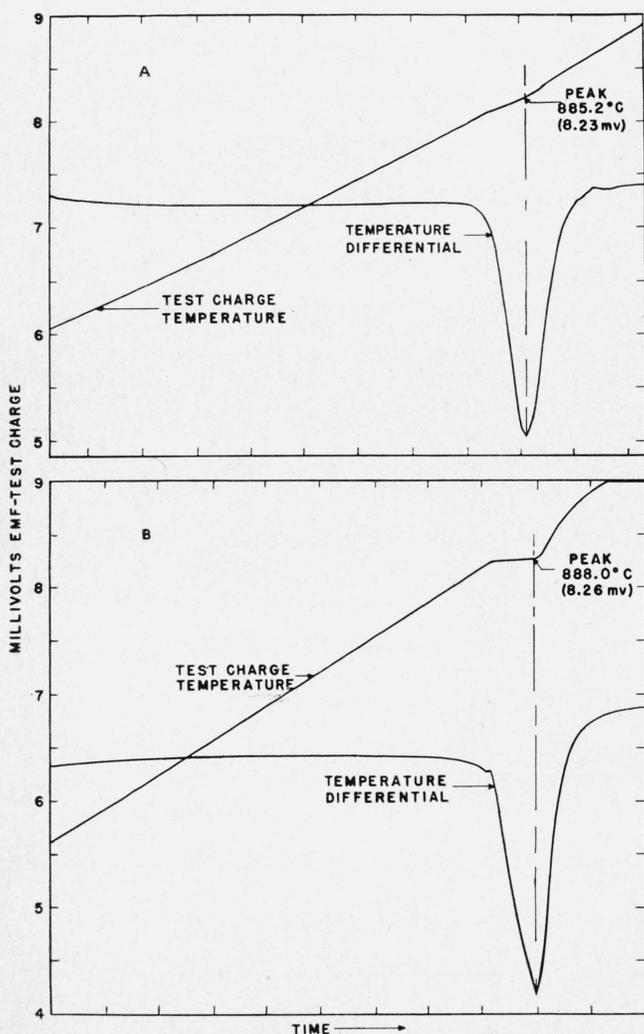


FIGURE 2. Thermal analysis curves: A, $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 3\text{Al}_2\text{O}_3 + \text{CaSO}_4$ (reaction products after preheating at $1,400^\circ\text{C}$); B, Na_2SO_4 .

The differential curves were obtained with different amplifier settings, and therefore their ordinates are not comparable.

3.4 Reaction of Combinations of $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ and $\text{K}_2\text{O} \cdot 0.23\text{CaO} \cdot 0.12\text{SiO}_2$ with CaSO_4

The reaction that takes place upon heating mixtures of $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, $\text{K}_2\text{O} \cdot 0.23\text{CaO} \cdot 0.12\text{SiO}_2$, and CaSO_4 was studied with 23 different compositions. These mixtures represented three series of compositions having $\text{R}_2\text{O}/\text{SO}_3$ molecular ratios of 1, 2, and 3. Each series of constant $\text{R}_2\text{O}/\text{SO}_3$ ratio consisted in turn of a number of preparations with different $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratios.

The charges, after a preheating treatment at $1,400^\circ$, were examined with a petrographic microscope and then subjected to thermal analysis. A quantitative phase analysis by microscopic means was not practicable, since the charges contained considerable fine-grained material, much of which consisted of different phases having similar optical properties. However, in general, these charges were found to consist of $\beta\text{-}2\text{CaO} \cdot \text{SiO}_2$, together with some $\gamma\text{-}2\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, and a very finely divided alkali-sulfate phase of low birefringence. Mixtures having $\text{R}_2\text{O}/\text{SO}_3$ ratios of 2 and 3 contained, in addition, one or both of the compounds $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ and $\text{K}_2\text{O} \cdot 0.23\text{CaO} \cdot 0.12\text{SiO}_2$. All of the mixtures exhibited an endothermic effect in the $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4$ melting range. The temperature at which this phenomenon occurred varied with the composition of the sulfate, and therefore with that of the mixture (table 2).

A charge composed of equimolar quantities of $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ and $\text{K}_2\text{O} \cdot 0.23\text{CaO} \cdot 0.12\text{SiO}_2$ and containing no CaSO_4 did not exhibit any thermal effect in the $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4$ melting range. No appreciable change in the phase composition was observed after heating this mixture at $1,400^\circ$ for 1 hour although a slight loss in the birefringence of the $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ was noted. This may have been due to the loss of part of the soda by volatilization.

The composition of the sulfate phase produced by the reaction of $\text{K}_2\text{O} \cdot 0.23\text{CaO} \cdot 0.12\text{SiO}_2$ and $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ with CaSO_4 was determined for each of the mixtures of these compounds, as described in section 2 by associating the temperature of phase changes of the alkali-sulfate in the mixtures with the phase-equilibrium diagram of figure 1, assuming complete insolubility of the clinker components in the sulfate phase.

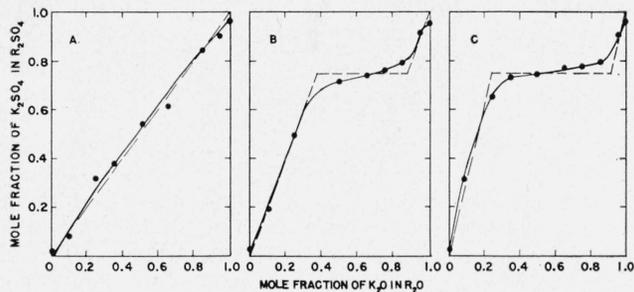


FIGURE 3. Relationship between the composition of the alkali and that of the alkali sulfate in cement clinker for mixtures with molecular ratios: A, $\text{R}_2\text{O}/\text{SO}_3=1$; B, $\text{R}_2\text{O}/\text{SO}_3=2$; C, $\text{R}_2\text{O}/\text{SO}_3=3$.

The relationship between the compositions of the mixtures of $\text{K}_2\text{O} \cdot 0.23\text{CaO} \cdot 0.12\text{SiO}_2$, $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, and CaSO_4 of three different $\text{R}_2\text{O}/\text{SO}_3$ and varying $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratios, and the compositions of the alkali-sulfate phases resulting from the reaction of these compounds upon heating at $1,400^\circ$, are shown in the three diagrams of figure 3 by solid lines in the experimental curves represented. The dashed lines on which calculations are based are discussed in section 4.

4. Derivation of Equations for Calculating the Alkali-Sulfate Composition in Clinker Mixtures

4.1. Mixtures with Molecular Ratio $\text{R}_2\text{O}/\text{SO}_3 \leq 1$.

Figure 3,A, illustrates the relationship between the mole fraction of K_2O in the total alkali (R_2O) of clinker-type mixtures having a molecular ratio $\text{R}_2\text{O}/\text{SO}_3=1$ and the mole fraction of potassium sulfate in the alkali sulfate (R_2SO_4). Mixtures with $\text{R}_2\text{O}/\text{SO}_3=1$ contained sufficient SO_3 to react with the entire quantity of both soda and potash. Inasmuch as the empirical relationship is nearly a linear one, it appears that the reaction approached completion. Thus for mixtures having a molecular ratio $\text{R}_2\text{O}/\text{SO}_3=1$, the ratio $\text{K}_2\text{O}/\text{Na}_2\text{O}$ in the sulfate is the same as that in the entire clinker mixture. Since the reason for this condition is the complete conversion of the alkalis to sulfates, the same rule may be expected to apply for mixtures having $\text{R}_2\text{O}/\text{SO}_3$ ratios less than unity.

If we let K_s = mole fraction of K_2SO_4 in the alkali sulfate, and K_c = mole fraction of K_2O in the total alkali (R_2O) of the clinker, then $K_s = K_c$.

4.2. Mixtures with Molecular Ratios $\text{R}_2\text{O}/\text{SO}_3 > 1$.

The composition relationship for mixtures that do not contain sufficient SO_3 to combine with the entire quantity of both alkalis, that is, those in which $\text{R}_2\text{O}/\text{SO}_3 > 1$, was found to be more complex than that in the previous example.

In figure 3,B, mixtures having a molecular ratio $\text{R}_2\text{O}/\text{SO}_3=2$ are represented. This curve is considerably different in form from the previous one. In mixtures in which the mole fraction, $\text{K}_2\text{O}/\text{R}_2\text{O}$ is 0.35 or less, the fraction of K_2SO_4 in the sulfate is about twice that of K_2O in the total alkali of the mixture. Above this value, the composition of the sulfate remains practically constant until the mole fraction, $\text{K}_2\text{O}/\text{R}_2\text{O}$ reaches 0.85, after which the K_2SO_4 content of the sulfate increases rapidly until it consists of pure K_2SO_4 .

Figure 3,C, shows a similar curve for mixtures having a molecular ratio $\text{R}_2\text{O}/\text{SO}_3=3$. This curve is of the same general shape as the previous one, the primary difference being in the slope of the first portion of the curve. Mixtures with the molecular ratio of 3 have a mole fraction of K_2SO_4 in the sulfate approximately three times that of the K_2O in the total alkali up to K_2O contents approaching

0.30 mole fraction of the total alkali. The composition of this sulfate again remains practically constant near 0.75 mole fraction K_2SO_4 until the alkali of the mixture becomes nearly pure K_2O , whereupon the K_2SO_4 content of the sulfate increases rapidly until only K_2SO_4 is present.

In deriving equations from these data for convenient calculation of the composition of the alkali sulfate formed in cement mixtures, it was found convenient to assume that the $CaSO_4$ always reacts with excess $Na_2O \cdot 0.8CaO \cdot 3Al_2O_3$ and $K_2O \cdot 2.3CaO \cdot 12SiO_2$ in such a manner as to form continuously a sulfate of constant composition as long as all three reactants are available. The composition of this sulfate may be expressed by a particular mole fraction of potassium sulfate, K_{s1} .

Let r = number of moles of R_2O in the clinker per mole of SO_3 . Since K_s = mole fraction of K_2SO_4 in the alkali sulfate (i. e., the number of moles of K_2SO_4 per mole of alkali sulfate), and K_c = mole fraction of K_2O in the alkalies of the clinker, then $1 - K_s$ = the mole fraction of Na_2SO_4 in the alkali sulfate, and $1 - K_c$ = the mole fraction of Na_2O in the alkalies of the clinker.

As SO_3 reacts with alkalies to form the alkali-sulfate phase with $K_s = K_{s1}$, it removes K_{s1} mole of K_2O and $(1 - K_{s1})$ mole of Na_2O for every mole of SO_3 . There are present, however, rK_c moles of K_2O and $r(1 - K_c)$ moles of Na_2O for every mole of SO_3 . Therefore, if K_2O is the first of the three oxides to reach depletion,

$$rK_c < K_{s1}, \text{ or } K_c < \frac{K_{s1}}{r} \quad (1)$$

If SO_3 is the first to reach depletion,

$$rK_c > K_{s1}, \text{ and } r(1 - K_c) > (1 - K_{s1}),$$

or,

$$\frac{K_{s1}}{r} < K_c < \frac{K_{s1} + (r - 1)}{r} \quad (2)$$

If Na_2O is the first to reach depletion,

$$r(1 - K_c) < (1 - K_{s1}), \text{ or } K_c > \frac{K_{s1} + (r - 1)}{r} \quad (3)$$

Within the range of composition represented by eq. 1, there will be in the sulfate phase rK_c moles of K_2O for every mole of SO_3 , and therefore

$$K_s = rK_c \quad (4)$$

Within the range specified by (2) it will be true, as mentioned above, that

$$K_s = K_{s1} \quad (5)$$

Within the range specified by (3), there will be in the sulfate phase $r(1 - K_c)$ moles of Na_2O , and therefore $1 - r(1 - K_c)$ moles of K_2O per mole of alkali sulfate. Thus

$$K_s = 1 - r(1 - K_c) \quad (6)$$

These equations appear in table 3, together with convenient weight formulas for r and K_c .

In order that the approximate composition of the alkali sulfate may be readily calculated for any clinker mixture from its oxide composition, the value of K_{s1} must be stated. Since this value corresponds to the horizontal portion of the curves in figure 3, B and C, it is readily found to be 0.75 ± 0.04 . Composition curves based on this value of K_{s1} and calculated by means of equations derived in the foregoing discussion have been constructed for three series of $K_2O-Na_2O-CaO-Al_2O_3-SiO_2-SO_3$ mixtures having R_2O/SO_3 molecular ratios (r values) of 1, 2, and 3. These appear as dashed lines in figure 3 for comparison with the experimental curves, which appear as solid lines. The two sets of curves are in reasonable agreement for each of the three molecular ratios. Consequently the composition of the sulfate phase in clinkers having other r values of the same order as those studied may be approximated by using the equations in table 3.

TABLE 3.—Procedure for calculating the approximate composition of the alkali sulfate in portland cement clinker

1. Calculate r (the R_2O/SO_3 molecular ratio in the cement mixture)

$$r = \frac{0.8500 K_2O + 1.2915 Na_2O}{1SO_3}$$

2. Calculate K_c (the mole fraction of K_2O in the total alkali of the cement mixture)

$$K_c = \frac{0.8500 K_2O}{r(SO_3)}$$

The formulas for the oxides in these two equations represent the weight percentages of these oxides in the clinker.

3. Calculate K_s (the mole fraction of K_2SO_4 in the sulfate) using the appropriate equation below as determined by the values for r and K_c :

If r is greater than 1.0—			
If r is equal to or less than 1.0, use the equation $K_s = K_c$	and K_c lies between 0 and 0.75/ r , use the equation $K_s = rK_c$	and K_c is equal to or lies between 0.75/ r and $(r - 0.25)/r$ use the equation $K_s = 0.75$	and K_c lies between $(r - 0.25)/r$ and 1.0, use the equation $K_s = 1 - r(1 - K_c)$

For clinkers in which the R_2O/SO_3 ratio is high, the amount of sulfate must be low, since the total alkali in the clinker rarely exceeds $1\frac{1}{2}$ percent. The amount of the sulfate phase then approaches a negligible quantity; thus a high degree of accuracy is not required in determining the composition of this sulfate phase.

5. Discussion

It appears from the results of this and earlier studies that when mixtures approximating portland cement compositions contain SO_3 , the alkalies in these mixtures will react with the SO_3 during the burning process to produce an alkali-sulfate phase. The present investigation confirms that this alkali-sulfate is immiscible with the primary clinker melt and stable in the presence of the major clinker components.

Cement mixtures containing only K_2O as the alkali, together with SO_3 , will, after burning, have the available SO_3 combined with the K_2O as the compound K_2SO_4 , which will appear in the form of crystals in the clinker. In the event that more K_2O is present than the quantity required to combine with the available SO_3 , this K_2O will become a constituent of the clinker glass or, if cooling is sufficiently slow, may appear as the compound $K_2O \cdot 2.3CaO \cdot 12SiO_2$.

If a cement mixture contains only Na_2O as the alkali, this oxide will combine with the available SO_3 to form Na_2SO_4 , which will appear as finely divided crystals in the clinker unless cooling has been extremely rapid. Soda in excess of that required to combine with the SO_3 will become a constituent of the glass or may enter into solid solution with $2CaO \cdot SiO_2$ or one of the other clinker components. If cooling were sufficiently slow, some of the excess soda might appear in the form of the compound $Na_2O \cdot 8CaO \cdot 3Al_2O_3$.

When both the alkalis, K_2O and Na_2O are present in cement mixtures together with SO_3 , they react at clinking temperatures to form a separate liquid phase, which changes to a single solid solution on cooling. This solid solution is stable above a temperature that varies from 400° to 600° , depending on the sulfate composition.

The sulfate phase has a constant composition if both $Na_2O \cdot 8CaO \cdot 3Al_2O_3$ and $K_2O \cdot 2.3CaO \cdot 12SiO_2$ are present at crystalline equilibrium. Under these conditions the mole fraction of K_2SO_4 in the sulfate is 0.75 ± 0.04 .

It is evident that the reaction of a portion of each of the alkalis with SO_3 during the burning of portland cement clinker will affect the final phase composition of the clinker. The formation of K_2SO_4 and Na_2SO_4 will greatly reduce the potential quantity of $K_2O \cdot 2.3CaO \cdot 12SiO_2$ and $Na_2O \cdot 8CaO \cdot 3Al_2O_3$, which would otherwise be formed in the event of complete equilibrium crystallization. This in turn regulates the quantity of $3CaO \cdot SiO_2$, $2CaO \cdot SiO_2$, and $3CaO \cdot Al_2O_3$ appearing in the clinker.

Equations that take into account the effect of SO_3 on the potential phase composition of $K_2O-Na_2O-CaO-Al_2O_3-SiO_2-Fe_2O_3-SO_3$ mixtures approximating the composition of portland cement clinker have been derived in the manner of Dahl [9]. These equations, in the convenient weight percentage form, appear in table 4. The application of the equations in table 4(B) (for those mixtures having R_2O/SO_3 molecular ratios greater than 1.0) requires the preliminary calculation of the value of K_s , the mole fraction of K_2SO_4 in the sulfate, for the mixture as outlined in table 3. This numerical value of K_s , together with the weight percentage of each of the oxides in the clinker is then substituted in the equations in table 4(B).

This preliminary calculation is unnecessary if the given mixture has an R_2O/SO_3 molecular ratio equal to or less than 1.0, inasmuch as the equations in table 4 (A) apply directly to this case.

The use of the equations in tables 3 and 4 should

TABLE 4. Equations for the calculation of the potential phase composition of clinker-type mixtures, assuming complete equilibrium crystallization to yield only the compounds indicated

The formulas represent weight percentages of the corresponding compounds in the mixtures. In using the equations in part B (those for mixtures having R_2O/SO_3 molecular ratios greater than 1.0) the value of K_s should be calculated by the method outlined in table 3.

A. Mixtures having R_2O/SO_3 molecular ratios equal to or less than 1.0	
$3CaO \cdot SiO_2$ -----	=4.0710 CaO-7.6024 SiO_2 -6.7187 Al_2O_3 -1.4296 Fe_2O_3 +3.6826 Na_2O +2.4238 K_2O -2.8516 SO_3
$2CaO \cdot SiO_2$ -----	=8.6024 SiO_2 +5.0683 Al_2O_3 +1.0784 Fe_2O_3 -2.7780 Na_2O -1.8284 K_2O +2.1511 SO_3 -3.0710 CaO
$3CaO \cdot Al_2O_3$ -----	=2.6504 Al_2O_3 -1.6918 Fe_2O_3
$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	=3.0430 Fe_2O_3
$CaSO_4$ -----	=1.7005 SO_3 -2.1960 Na_2O -1.4453 K_2O
Na_2SO_4 -----	=2.2914 Na_2O
K_2SO_4 -----	=1.8500 K_2O
B. Mixtures having R_2O/SO_3 molecular ratios greater than 1.0	
$3CaO \cdot SiO_2$ -----	=4.0710 CaO-7.6024 SiO_2 -1.4296 Fe_2O_3 -6.7187 Al_2O_3 +2.4238 K_2O +3.6826 Na_2O -2.8516 SO_3
$2CaO \cdot SiO_2$ -----	=8.6024 SiO_2 +1.0784 Fe_2O_3 +5.0683 Al_2O_3 -23.769 K_2O -2.7780 Na_2O +2.1511 (12 K_s +1) SO_3 -3.0710 CaO
$3CaO \cdot Al_2O_3$ -----	=2.6504 Al_2O_3 -13.075 Na_2O +10.123 (1- K_s) SO_3 -1.6918 Fe_2O_3
$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	=3.0430 Fe_2O_3
$K_2O \cdot 2.3CaO \cdot 12SiO_2$	=22.345 K_2O -26.288 K_s (SO_3)
$Na_2O \cdot 8CaO \cdot 3Al_2O_3$	=13.170 Na_2O -10.197 (1- K_s) SO_3
K_2SO_4 -----	=2.1764 K_s (SO_3)
Na_2SO_4 -----	=1.7743 (1- K_s) SO_3

be of assistance in controlling the composition of the cement and in regulating burning processes to produce clinker of the desired phase composition.

The mixtures that have been the subject of investigation were designed to furnish data on the stability of the alkali compounds $K_2O \cdot 2.3CaO \cdot 12SiO_2$ and $Na_2O \cdot 8CaO \cdot 3Al_2O_3$ in the presence of SO_3 and on the equilibrium products resulting from heating mixtures of these components. These mixtures, while not in themselves of portland cement clinker composition, were composed of the primary components present in commercial clinker. Furthermore, the phases that appeared in the mixtures after equilibrium was attained were among those commonly found in commercial clinker. These factors provide the basis for applying the experimental data to portland cement technology.

It should be noted that other acidic oxides such as P_2O_5 or TiO_2 when present in the clinker may enter into reaction with the alkalis and otherwise alter the phase relations. The potential phase composition given in table 4 will then be affected. Likewise, the details of the phase relationships in the senary system $K_2O-Na_2O-CaO-Al_2O_3-SiO_2-Fe_2O_3$ are as yet unknown, although a study of this system is being implemented. It has been determined on the basis of microscopic examination of quenched charges containing $Na_2O \cdot 8CaO \cdot 3Al_2O_3$ and $K_2O \cdot 2.3CaO \cdot 12SiO_2$, that these two compounds are stable when heated together below $1,500^\circ$. These compounds have consequently been included in the list of compounds in table 4 (B). It is recognized, however, that a certain amount of solid solution may occur between them and the others that have been included in the potential phase composition. It is further recognized that changes in table 4 may be

necessitated as a result of the detailed study of pertinent portions of the indicated senary system.

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