[CONTRIBUTION FROM THE PORTLAND CEMENT ASSOCIATION FELLOWSHIP, BUREAU OF STANDARDS]

PHASE EQUILIBRIA IN THE SYSTEM $2CaO \cdot SiO_2$–MgO–$5CaO \cdot 3Al_2O_3$[1]

BY W. C. HANSEN

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Introduction

This investigation of the system $2CaO \cdot SiO_2$–MgO–$5CaO \cdot 3Al_2O_3$ was undertaken, in connection with researches on the constitution of Portland cement, to determine whether MgO and $2CaO \cdot SiO_2$ existed as individual compounds in this system or reacted to form other crystalline phases.

The system CaO–MgO–SiO_2 was investigated by Ferguson and Merwin[2], but a thorough study was not made of the region below the line $2CaO \cdot SiO_2$–$2MgO \cdot SiO_2$, Fig. 1.[3]

Klein and Phillips[4] studied two series of preparations in an effort to determine the manner in which MgO occurs in Portland cement. Their first series was prepared so as to have molecular replacements of CaO by MgO in the composition $2CaO \cdot SiO_2$. The compositions of the mixtures studied by them fall on the line $2CaO \cdot SiO_2$–$CaO \cdot MgO \cdot SiO_2$, Fig. 1. In the second series of preparations they made percentage replacements of CaO by MgO in the composition $2CaO \cdot SiO_2$. The compositions of this series of mixtures fall in the triangle $2CaO \cdot SiO_2$–$CaO \cdot MgO \cdot SiO_2$–MgO, Fig. 1. From a microscopic study of their preparations, Klein and Phillips concluded that β-$2CaO \cdot SiO_2$ and $CaO \cdot MgO \cdot SiO_2$ formed a limited series of solid solutions, and that a few per cent. of MgO could be combined with $2CaO \cdot SiO_2$ in this way in Portland cement.

The preparations studied by Klein and Phillips contained some SiO_2 in excess of that required to form $2CaO \cdot SiO_2$ with all of the CaO. In Portland cement there is more than sufficient CaO to convert all of the SiO_2 to $2CaO \cdot SiO_2$, and the compositions of Portland cements in terms of CaO, MgO and SiO_2 fall in the triangle $2CaO \cdot SiO_2$–MgO–$3CaO \cdot SiO_2$, Fig. 1. Therefore, if a solid solution of $CaO \cdot MgO \cdot SiO_2$ with $2CaO \cdot SiO_2$ exists in Portland cement, it is necessary that MgO be capable of combining with CaO and SiO_2 to form $CaO \cdot MgO \cdot SiO_2$ in products in which sufficient CaO is present to convert all of the SiO_2 to $2CaO \cdot SiO_2$. Whether MgO

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[1] Publication approved by the Director of the National Bureau of Standards of the U. S. Department of Commerce. Paper No. 18 of the Portland Cement Association Fellowship at the Bureau of Standards.

[2] Ferguson and Merwin, *Am. J. Sci.*, **48**, 81 (1919).

[3] The region below the line $2CaO \cdot SiO_2$–$2MgO \cdot SiO_2$ has been divided arbitrarily into a number of small triangles to simplify the discussion which is to follow.

[4] Klein and Phillips, *8th Int. Cong. Appl. Chem.*, **5**, 73 (1912).

has that ability or not should be shown by the behavior of $2CaO \cdot SiO_2$ and MgO in the system $2CaO \cdot SiO_2$–MgO–$5CaO \cdot 3Al_2O_3$. This system was chosen because the melting temperatures in a part of it are below 1600°, and because the results obtained in the presence of Al_2O_3 should be more nearly applicable to Portland cement than those obtained on mixtures of CaO, MgO and SiO_2 without Al_2O_3.

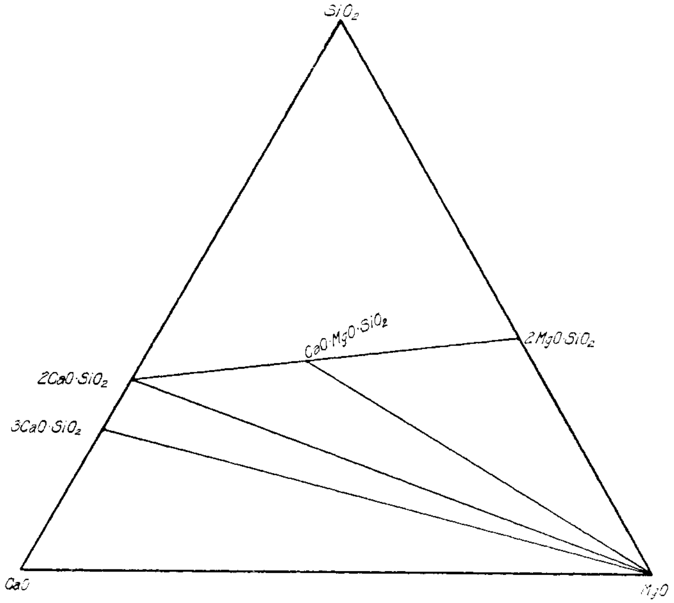

Fig. 1.—Triangular diagram representing a part of the system CaO–MgO–SiO_2.

Experimental Procedure

The results of the chemical analyses[5] of the raw materials used in this investigation are given below.

RESULTS OF ANALYSES

	Calcium carbonate	Magnesia	Silica	Alumina
CaO	55.55	0.50	0.02	0.02
MgO	.07	84.22	neg.	.08
SiO_2	.03	.08	99.37	neg.
Al_2O_3	.01	.02	.50	98.35
Fe_2O_3	neg.	.01	.03	.10
Cl	.04	.001	neg.	.01
SO_3	neg.	neg.	neg.	neg.
CO_2	43.63	...	...	...
Loss on ignition	43.97	15.31	.11	1.55

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[5] By H. C. Stecker.

The equipment used in these studies has been described in other papers[6,7] from this Laboratory.

The compositions studied are shown as dots in Fig. 2. Fifteen to twenty gram samples of each of the compositions were made up by melting, in platinum, a carefully prepared mixture of the components. The samples were crushed in a steel mortar and ground to fine powders in an agate mortar for use in the experiments described later.

Small charges of the above samples were wrapped in platinum and held at the temperatures and for the time periods given in Table I, and then quenched by dropping into water. The quenched charges were examined microscopically to determine the temperature and phase relations which are given in Table I and Fig. 2.

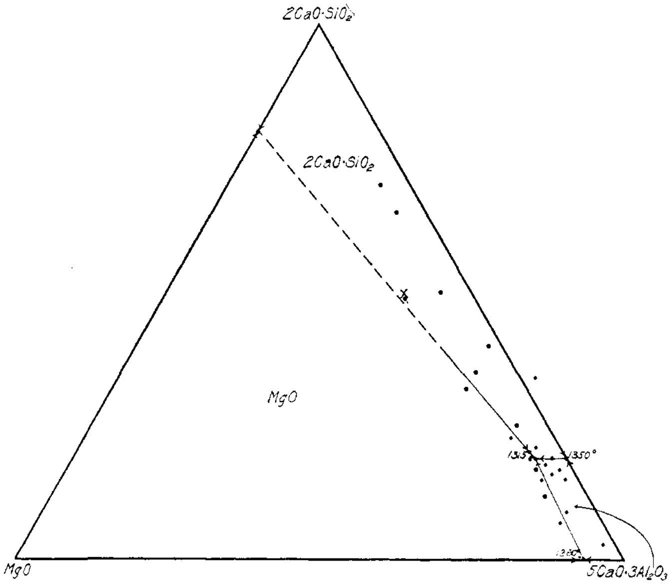

Fig. 2.—Diagram of the system $2CaO.SiO_2$–MgO–$5CaO.3Al_2O_3$, showing fields in which each component separates as a primary phase.

Similar charges were carefully annealed to allow complete crystallization, and these were studied microscopically to determine the optical properties of the crystalline phases. Indices of refraction were determined by the immersion method.

In all of the annealed samples the three compounds γ-$2CaO{\cdot}SiO_2$, $5CaO{\cdot}3Al_2O_3$ and MgO were the only phases present. The indices of refraction of these compounds agreed with those given for them by Wright.[8]

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[6] W. C. Hansen and R. H. Bogue, This Journal, **48**, 1261 (1926).

[7] W. C. Hansen and R. H. Bogue, *Ind. Eng. Chem.*, **19**, 1260 (1927).

[8] (a) Wright, *Am. J. Sci.*, **28**, 293 (1909); (b) **39**, 1 (1915).

No optical evidence was obtained to show the formation of any solid solution of MgO with $5CaO{\cdot}3Al_2O_3$ or with γ-$2CaO{\cdot}SiO_2$.

In all samples annealed below the eutectic temperature, 1315 ± 5°, the $2CaO{\cdot}SiO_2$ was present as the γ-form. It was necessary, therefore, to quench samples from above this temperature to prevent the inversion of the β-$2CaO{\cdot}SiO_2$ to the γ-$2CaO{\cdot}SiO_2$. By doing this, the β-form was obtained embedded in a glass. The microscopic examination of such samples requires that one obtain edges of the grain free from glass for index of refraction determination. The results obtained on such edges are not so reliable as those obtained on crystals entirely free from glass; however, the study of these β-$2CaO{\cdot}SiO_2$ grains did not give any evidence to indicate any solid solution of MgO with β-$2CaO{\cdot}SiO_2$.

TABLE I

BINARY EUTECTICS

Composition	Melting temp., °C.	Reference
6.5% MgO + 93.5% $5CaO{\cdot}3Al_2O_3$	1380±5	Rankin and Merwin[9]
20% $2CaO{\cdot}SiO_2$ + 80% $5CaO{\cdot}3Al_2O_3$	1350±5	Rankin and Wright[8b]

TERNARY EUTECTIC

Composition	Melting temp., °C.
5% MgO + 19% $2CaO{\cdot}SiO_2$ + 76% $5CaO{\cdot}3Al_2O_3$	1315±5

QUENCHINGS WHICH DETERMINE THE ABOVE TERNARY EUTECTIC AND THE BOUNDARY CURVES, FIG. 2

Composition[a]			Temp., ±5°C.	Time of heating, minutes	Phases present
MgO	C_2S	C_5A_3			
2	3	95	1335	15	Glass + C_5A_3 + MgO
2	3	95	1370	30	Glass + C_5A_3
2	3	95	1290	240	$C_5A_3^+$, MgO + C_2S^+, trace glass
5	9	86	1290	240	$C_5A_3^+$, MgO, C_2S
5	9	86	1350	15	Glass + C_5A_3 + MgO
5	9	86	1360	15	Glass
10	32	58	1475	15	Glass + MgO
5	25	70	1380	15	Glass
7	23	70	1345	15	Glass + C_2S
7	23	70	1380	15	Glass
7	23	70	1330	15	Glass + C_2S + MgO
4	21	75	1325	15	Glass + C_2S + MgO
4	21	75	1350	15	Glass
4	21	75	1315	15	Glass + MgO + C_2S + C_5A_3
4	21	75	1345	15	Glass + C_2S
6	19	75	1335	15	Glass
6	19	75	1320	15	Glass + MgO
6	19	75	1315	15	Glass + C_2S + MgO + C_5A_3
5	70	75	1340	30	Glass + C_2S + MgO
11.2	48.1	40.7	1600	15	Glass + C_2S + MgO
11.2	48.1	40.7	1290	60	C_2S + C_5A_3 + MgO
2	15	83	1330	15	Glass + C_5A_3 + C_2S
2	15	83	1355	15	Glass

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[9] Rankin and Merwin, THIS JOURNAL, **38**, 568 (1916).

TABLE I (*Concluded*)

Composition[a]			Temp., ±5°C.	Time of heating, minutes	Phases present
MgO	C_2S	C_5A_3			
2	15	83	1345	15	Glass + C_5A_3
2	11	87	1340	15	Glass + C_5A_3
2	19	79	1340	15	Glass + C_2S + C_5A_3
4	18	78	1315	30	Glass + C_2S + C_5A_3 + MgO
4	18	78	1320	15	Glass + C_2S + C_5A_3
4	18	78	1330	15	Glass + C_5A_3
4	16	80	1325	15	Glass + C_5A_3 + C_2S
4	16	80	1340	15	Glass + C_5A_3
2	17	81	1330	15	Glass + C_5A_3 + C_2S
2	17	81	1340	15	Glass + C_5A_3
6	17	77	1330	15	Glass + C_5A_3 + MgO
6	17	77	1320	15	Glass + C_5A_3 + MgO
6	17	77	1310	15	Glass + C_5A_3 + MgO + C_2S
6	15	79	1340	15	Glass + MgO
6	15	79	1330	15	Glass + MgO + C_5A_3
7	12	81	1340	15	Glass + MgO
7	7	86	1350	15	Glass + MgO
5	19	76	1315	15	Glass + MgO + C_5A_3 + C_2S
5	19	76	1320	30	Glass + trace C_5A_3

[a] The formulas for $2CaO{\cdot}SiO_2$ and $5CaO{\cdot}3Al_2O_3$ have been written C_2S and C_5A_3, respectively.

If MgO were capable of replacing a part of the CaO in $2CaO{\cdot}SiO_2$, the CaO replaced would be expected to react with either $5CaO{\cdot}3Al_2O_3$ to form $3CaO{\cdot}Al_2O_3$ or with $2CaO{\cdot}SiO_2$ to form $3CaO{\cdot}SiO_2$. In none of the samples was it possible to identify either $3CaO{\cdot}Al_2O_3$, $3CaO{\cdot}SiO_2$ or free CaO.

It is necessary, therefore, to conclude, in the system $2CaO{\cdot}SiO_2{\cdot}MgO$–$5CaO{\cdot}3Al_2O_3$, that MgO does not form appreciable solid solutions with γ- or β-$2CaO{\cdot}SiO_2$, and that MgO is not capable of replacing CaO in $2CaO{\cdot}SiO_2$.

Discussion

These experiments demonstrate the inability of MgO to form $CaO{\cdot}MgO{\cdot}SiO_2$ in certain products in which there is sufficient CaO to convert the SiO_2 to $2CaO{\cdot}SiO_2$. This is brought out more forcibly if the composition x, Fig. 2, is considered. The composition of x may be expressed as $3(3CaO{\cdot}Al_2O_3) + 4(CaO{\cdot}MgO{\cdot}SiO_2)$ or as $5CaO{\cdot}3Al_2O_3 + 4(2CaO{\cdot}SiO_2) + 4MgO$. A sample of this composition, after being fused, dusted completely, due to the formation of γ-$2CaO{\cdot}SiO_2$. A charge of it quenched from 1600° consisted of grains of β-$2CaO{\cdot}SiO_2$ and MgO embedded in a glass. A charge heated to 1600°, cooled slowly during several hours and then annealed for several hours at 1300°, dusted completely and consisted of γ-$2CaO{\cdot}SiO_2$, $5CaO{\cdot}3Al_2O_3$ and MgO.

Further evidence of the inability of $CaO{\cdot}MgO{\cdot}SiO_2$ to exist in products where there is sufficient CaO to convert the SiO_2 to $2CaO{\cdot}SiO_2$ was obtained by fusing a mixture having the composition[10] $4CaO{\cdot}2MgO{\cdot}Al_2O_3{\cdot}Fe_2O_3 + 2(CaO{\cdot}MgO{\cdot}SiO_2)$. This mixture dusted completely owing to the formation of γ-$2CaO{\cdot}SiO_2$. Also a sample having the composition $4CaO{\cdot}2MgO{\cdot}Al_2O_3{\cdot}Fe_2O_3 + 2MgO{\cdot}SiO_2$ dusted completely after being fused.

Summary

1. A study has been made of the system $2CaO{\cdot}SiO_2$–MgO–$5CaO{\cdot}3Al_2O_3$. A diagram is given showing the fields in which each of these compounds separates as primary phases.

2. No evidence was obtained to show that MgO formed solid solutions with either $2CaO{\cdot}SiO_2$ or $5CaO{\cdot}3Al_2O_3$ or that MgO was capable of replacing CaO in these compounds.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY AT IOWA STATE COLLEGE]

REACTIONS IN LIQUID HYDROGEN SULFIDE.
IV. THIOHYDROLYSIS OF ESTERS

BY A. W. RALSTON[1] AND JOHN A. WILKINSON

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Esters are well known to hydrolyze in water solutions, forming the free acids and alcohols. In a similar way the esters of the thio-organic acids should thiohydrolyze in liquid hydrogen sulfide to give the free acids and the mercaptans.

Of the several methods that are used to measure the degree of hydrolysis of esters in water solutions the one that is most applicable in the case of the thiohydrolysis in liquid hydrogen sulfide is that based on the determination of the conductance of the solutions.[2] The degree of hydrolysis is determined by measuring the conductance of the hydrogen sulfide solutions of the pure acid, the thiohydrolyzed ester and of the solution of the ester saturated with the base or mercaptan. It has been found that the solution of the mercaptan in liquid hydrogen sulfide does not conduct the current. Therefore, the conductance of the ester solution saturated with the mercaptan will be due to the unhydrolyzed ester alone.

The thiohydrolysis may be calculated from the expression

$$h = \frac{\lambda e - \lambda}{\lambda a - \lambda}$$

where h is the fraction of the ester thiohydrolyzed, λe is the equivalent

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[10] W. C. Hansen and L. T. Brownmiller, *Am. J. Sci.*, **15**, 225 (1928).

[1] This paper is from a portion of the work presented by A. W. Ralston to the Graduate Faculty at Iowa State College in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Walker, *Z. physik. Chem.*, **4**, 333 (1889); Bredig, *ibid.*, **13**, 214–321 (1894); Noyes, Kato and Sosman, THIS JOURNAL, **32**, 159 (1910).