The agreement is close (Table IV). Isomeric *cis* and *trans* acids are shown to have nearly identical intrinsic constants.

Formulas 19 to 24 are given for calculating the dissociation constants of *higher* polyvalent acids, and of bases and ampholytes, where the intrinsic constants of the individual groups are known, and when the distances between the charges in the groups may be estimated. Formulas 26 to 29 summarize the relations between the "dissociation" (K), the "intrinsic" (K_0), the "titration" (G) and the "characteristic" (K_c) constants of a substance, and also give the activity correction.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE BUREAU OF STANDARDS, UNITED STATES DEPARTMENT OF COMMERCE]

STUDIES ON THE SYSTEM CALCIUM OXIDE-FERRIC OXIDE-SILICA[1,2]

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Many of the oxide systems in which ferric oxide is one of the components are of especial interest to the Portland cement industry because all Portland cements contain iron oxide in some type of combination. The combinations in which this oxide occurs in cement, its precise role in the manufacturing, in the setting and in the hardening processes are not known.

Of the ferric oxide systems pertaining to Portland cement, the $CaO.Fe_2O_3$ system is the only one that has been studied extensively. This system was investigated by Sosman and Merwin.[4] Two compounds of calcium oxide and ferric oxide were found by these investigators having the compositions, respectively, $CaO.Fe_2O_3$ and $2CaO.Fe_2O_3$. It was found also that both compounds appear to melt incongruently, the first at 1216° and the latter at 1436°. Andersen[5] studied this system later and confirmed the work of Sosman and Merwin. More recently Martin[6] prepared these two compounds and studied their behavior with various reagents. In a later paper Martin[7] reports several other compounds of calcium oxide with ferric oxide. His criteria for the existence of these compounds, however, appear to be inadequate.

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[1] Published by permission of the Director of the National Bureau of Standards of the U. S. Department of Commerce.

[2] Paper No. 1 of the Portland Cement Association Fellowship at the Bureau of Standards.

[3] Microscopic examinations by F. W. Ashton.

[4] Sosman and Merwin, *J. Wash. Acad. Sci.*, **6**, 532 (1916).

[5] Andersen, *Bull. Norwegian Geological Soc.*, Christiana, No. 1, **1922**. *Feuerfest*, **1**, 25, 48, 67 (1925).

[6] Martin, 3me Congrès Chimie Industriel, **1924**, **406**.

[7] Martin, *Mon. sci.*, **15**, 97 (1925).

Phase equilibria studies on the Fe_2O_3-SiO_2 system and the CaO-Fe_2O_3-SiO_2 system have not been reported. One finds, however, an occasional reference to these systems in the literature. Percy[8] mentions that silica added to mixtures of calcium oxide and ferric oxide reduces the latter at high temperatures, forming FeO-SiO_2 compounds. These are oxidized at lower temperatures forming CaO-Fe_2O_3 compounds. Martin[7] claims to have found some ternary compounds of CaO-Fe_2O_3-SiO_2 upon which he expects to give a report later.

The present investigation was undertaken with the object of determining the nature and identity of the compounds occurring in those portions of the system which are concerned with Portland cement. The investigation is not concerned with the determination of the temperature relations or stability fields except in so far as these may be found necessary to the correct interpretation of the constitution of Portland cement.

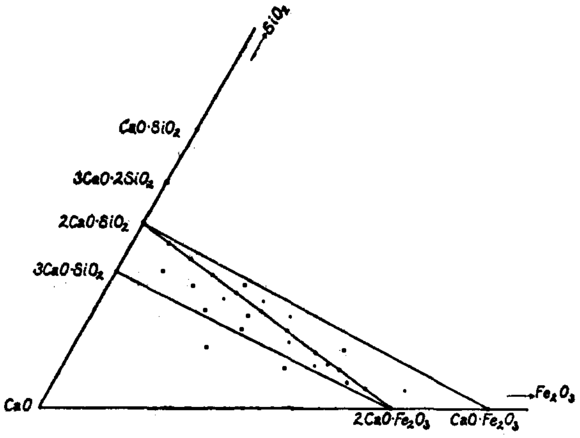

Fig. 1.—The fields investigated in the system CaO-Fe_2O_3-SiO_2.

In Fig. 1 there are plotted on the triangular diagram the compositions of the two CaO-Fe_2O_3 compounds and of the four CaO-SiO_2 compounds known to exist from the studies previously reported on those systems.[9] Lines have been drawn, arbitrarily, connecting the compositions 2CaO.-SiO_2 and CaO.Fe_2O_3, 2CaO.SiO_2 and 2CaO.Fe_2O_3, and 3CaO.SiO_2 and 2CaO.Fe_2O_3. The assumption is made that the small triangles thus formed may represent the fields in which the three compounds forming the apices of each triangle exist together at equilibrium, provided that no ternary compounds exist in those areas. There is no *a priori* reason why this particular arrangement of the lines setting apart the fields should

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[8] Percy, *Phil. Mag.*, **45**, 455 (1873).

[9] Day, Shepherd and Wright, *Am. J. Sci.*, **22**, 265 (1906). Rankin and Wright, *ibid.*, **39**, 1 (1915).

be the correct one, but it is desirable to make some assumption and prove by experiment if this, or some other arrangement, correctly represents the observed facts.

Any compounds of CaO-Fe_2O_3-SiO_2 that might exist in Portland cement should be found in the region of this diagram below the line $2CaO.SiO_2$-$CaO.Fe_2O_3$. This investigation was limited, therefore, to a study of the compounds existing in this system, at equilibrium, below this line.

Experimental Part

Calcium carbonate, ferric oxide and silica were the raw materials used for preparing the samples to be studied. Chemicals of the highest quality obtainable were procured, and these subjected to repeated purifications. Microscopic examination showed the final products to be of very high purity.

TABLE I

ANALYSES OF PURIFIED RAW MATERIALS

	Calcium carbonate	Ferric oxide	Silica
SiO_2	nil	...	99.37
Al_2O_3	0.08	...	0.346
Fe_2O_3	.01	99.15	.018
FeO	...	nil	...
CaO	55.73	...	0.15
MgO	0.01	...	...
Alkalies	.04	...	...
CO_2	44.10	...	...
SO_3	trace	nil	...
Cl	trace	...	...
H_2O at 100°	...	...	0.02
Loss on ignition	...	0.93	.21

All grinding was done by hand in an agate mortar.

Temperatures were measured with platinum-platinumrhodium thermocouples in connection with a Leeds and Northrup precision potentiometer and galvanometer.

Microscopic examinations were made on powders with a research petrographic microscope. Refractive indices were determined by the immersion method, using liquid carefully checked on a refractometer.

All preliminary heatings were made in a platinum-wound, electric-tube furnace.[10] Platinum-lined Alundum boats were used as containers for the samples. The final heatings were made in a quenching furnace built in accordance with the design of the Geophysical Laboratory.[11] The

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[10] Compare Hansen and Bogue, "A continuously operating electric resistance furnace for service at high temperatures under closely controlled conditions." To be published.

[11] Shepherd, Rankin and Wright, *Am. J. Sci.*, **28**, 308 (1909).

temperature of this furnace was controlled by a regulator built as described by Adams.[12]

The compositions studied are represented by the dots in Fig. 1. For each composition, a sample of about 15 g. was prepared. The calcium carbonate, ferric oxide and silica were weighed with care and mixed by grinding until the sample appeared homogeneous. The entire sample was then given a preliminary heat treatment in the electric furnace for about two hours. The compositions on or below the line $2CaO.SiO_2$–$2CaO.Fe_2O_3$ were heated to about 1400°; those above this line were heated to about 1200° (see below). After this heating, the sample was re-ground and re-heated for another two-hour period. The sample was then examined optically, and by White's test[13] for free calcium oxide. Where appreciable amounts of free calcium oxide were found, the heatings were continued until the amounts of this constituent present were found to be negligible. The two samples below the line $3CaO.SiO_2$–$2CaO.Fe_2O_3$ were heated twice, but the above criterion for complete combination, that is, the disappearance of all free calcium oxide, was not applicable in these cases because these latter samples should contain free calcium oxide even when equilibrium is attained. The samples then were ground very thoroughly and used for the final heat treatments in the quenching furnace.

By following this procedure it is believed that the samples obtained were homogeneous, and that they correctly represented the compositions chosen. Melting of the samples was avoided because at the high temperature required for this the ferric oxide is to some extent reduced to ferroferric oxide, Fe_3O_4. The temperatures selected for the heat treatments were such that practically no reduction took place as determined by optical examination under the microscope.

To obtain equilibrium in the mixtures, a final heating was made on each at a very closely controlled temperature in the quenching furnace. Charges of about 0.5 g. of the above samples were wrapped in platinum foil and used for this heating. The compositions on or below the line $2CaO.SiO_2$-$2CaO.Fe_2O_3$ were heated to $1430 \pm 5°$ for one hour and then cooled slowly by a gradual decrease in the current supplied to the furnace. The compositions above this line were heated to $1210° \pm 5°$ for one hour and cooled slowly. If, upon examination, appreciable amounts of the compounds from the adjacent fields were found to be present, the samples were re-heated for longer periods and sometimes at higher temperatures.

General Discussion

It was found very difficult, in some cases, to reach complete equilibrium and obtain a mixture entirely free from the last traces of compounds from

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[12] Adams, *J. Optical Soc. Am.*, **9**, 599 (1924).

[13] White, *J. Ind. Eng. Chem.*, **1**, 5 (1910).

the adjacent fields. In most of the samples, however, there were found only the three compounds predicted on the basis of their position in the phase diagram, in accordance with the fields as tentatively drawn in Fig. 1. In the few samples where a trace of one of the other compounds was observed, the amount was so insignificant that there is no uncertainty regarding the results reported.

From our observations, the fields as shown in Fig. 1 are correct. The compounds $2CaO.SiO_2$, $CaO.Fe_2O_3$ and $2CaO.Fe_2O_3$ were found to be present, at equilibrium, in all samples which were within the triangle defined by these compounds at the apices. The compounds $2CaO.SiO_2$, $2CaO.Fe_2O_3$ and $3CaO.SiO_2$ were found to be present, at equilibrium, in all samples which were within the triangle defined by these three compounds. In the field defined by the compounds CaO, $3CaO.SiO_2$ and $2CaO.Fe_2O_3$, only two compositions were examined, but in these two the compounds present were those defining the field, namely CaO, $3CaO.SiO_2$ and $2CaO.Fe_2O_3$. Compositions on the line connecting $2CaO.SiO_2$ and $2CaO.Fe_2O_3$ were found to consist, at equilibrium, of only those two compounds. Except as mentioned above, there was no departure whatsoever from complete concordance with the diagram as given. The identification of all of these compounds was effected by the microscopic optical method previously mentioned.

No optical evidence was obtained to indicate the existence of any ternary compounds of CaO-Fe_2O_3-SiO_2 in the regions studied.

Occasionally the indices of the $2CaO.SiO_2$ appeared to be a little higher than those ordinarily obtained for this silicate. This happened so rarely, however, that it may represent only technical difficulties of measurement and probably has no significance in these studies.

In a few of the samples, the $2CaO.SiO_2$ and $3CaO.SiO_2$ crystals seemed to be coated with a yellowish or brownish film having the appearance of a glass. Whether this were actually the case could not be proved with certainty, however, because of the very rapid crystallization of the CaO-Fe_2O_3 compounds in these mixtures. A similar very rapid crystallization occurred in the two-component CaO-Fe_2O_3 system, as pointed out by Sosman and Merwin.[4]

An interesting observation was made on the behavior of the $2CaO.SiO_2$ in this system. In charges which were cooled quickly by quenching from high temperatures (1430° and 1600°), the $2CaO.SiO_2$ was found to occur in the alpha and beta forms, but in the slowly cooled samples this silicate was found to be present almost entirely in the gamma form and the charge was completely powdered.

In the CaO-Al_2O_3-SiO_2 system, the inversion of the dicalcium silicate is prevented by the presence of very small amounts of alumina, but in the CaO-Fe_2O_3-SiO_2 system only those samples which contained a high concentration of ferric oxide (above about 45%) failed to exhibit inversion.

Some writers have suggested that it is the glass present in Portland cement clinker which functions to prevent the inversion of $2CaO.SiO_2$ to the gamma form and, therefore, to prevent the dusting of the clinker. It may be argued that the ready inversion of the $2CaO.SiO_2$ in the CaO-Fe_2O_3-SiO_2 system, considered in conjunction with the observed absence of glass in this system, tends to corroborate the above theory. There is some question, however, whether this hypothesis is adequate to explain the non-inversion of the silicate in some cases where such inversion does not take place.

A belief in the existence of a definite compound of the composition $3CaO.SiO_2$ seems increasingly to be accepted. The present study adds further evidence in support of this belief, for a definite crystalline phase, having the optical properties ascribed by Wright[9] to $3CaO.SiO_2$, has been found to be present in these preparations.

By a comparison of the appearance under the microscope of the iron-containing grains in Portland cement clinker with the calcium oxide–ferric oxide compounds in these preparations, it seems probable that only a small part of the ferric oxide in clinker may be present as crystalline $2CaO.Fe_2O_3$ or $CaO.Fe_2O_3$. Most of the ferric oxide in cement clinker appears to be present in some form other than that of these crystalline ferrites. Magnetite has been observed frequently in clinker, and some of the iron appears to be present as a dark-colored interstitial glass. Other compounds of iron may also be present. It is, therefore, necessary to study other systems before the exact manner of combination of the ferric oxide in clinker can be ascertained.

Charges of some of the samples were quenched from 1600° and from 1430° in mercury covered with water. In the greater number of these quenches crystallization was complete; in a few, traces of glass could be observed. This rapid crystallization makes it very difficult if not impossible to study, by quenching methods, the temperature relations and order of crystallization in this part of the system. These relations may be investigated later by the use of heating curves if it is found that these are necessary to a complete understanding of the constitution of Portland cement. The results obtained in this study, however, seem not to justify the complete study of this system until results in other ternary systems containing ferric oxide are available.

Summary

Three fields in the CaO-Fe_2O_3-SiO_2 system have been studied and the compounds existing in these fields at equilibrium have been determined. A diagram is given in which the fields studied and the compounds existing in each at equilibrium are shown.

No optical evidence has been obtained which would indicate the existence of any ternary compounds of $CaO\text{-}Fe_2O_3\text{-}SiO_2$ in the region studied.

Further evidence is cited tending to confirm the existence of $3CaO.SiO_2$. It has been found that the inversion of $2CaO.SiO_2$ to the gamma form takes place in cooled charges of $CaO\text{-}Fe_2O_3\text{-}SiO_2$ except where the concentration of $2CaO.SiO_2$ is low and the concentration of the $CaO\text{-}Fe_2O_3$ compounds is high.

Attention is called to the probability that only a part of the ferric oxide in Portland cement clinker is present as the crystalline $2CaO.Fe_2O_3$ or $CaO.Fe_2O_3$.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE ULTRAVIOLET ABSORPTION SPECTRUM OF FORMIC ACID

BY H. C. RAMSPERGER AND C. W. PORTER

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The absorption of ultraviolet light by formic acid was determined by the method developed by Porter and Iddings.[1] Formic acid vapor in a quartz cell and in a water thermostat was exposed to the radiation of a quartz mercury lamp. The light passing through the cell was photographed through a Hilger quartz prism spectrograph. On the same plate another photograph was taken of the same source of light through the same cell evacuated and through a copper gauze screen of known absorption. The blackening of the plate is the same in the two photographs at any wave length for which the particular screen and the formic acid vapor have the same absorption.

The points of equal intensities on the pairs of photographs taken for comparison could not be identified visually with greater accuracy than a range of 10 Ångström units. We resorted, therefore, to the following device. The photographic negative was placed in a lantern slide projector and an enlarged image of the spectrum was thrown on the slit of a thermopile which was connected with a galvanometer. The galvanometer deflections were read at short intervals as the plate was moved over the range selected by visual inspection. The photograph taken for comparison was then projected upon the slit of the thermopile and readings were made as before. Positions of equal intensities in the two negatives could be located within a range of 3 Å. The method is so successful that we have constructed a special holder for such negatives. The holder, which is readily attached to a Balopticon, is provided with racks and pinions that make possible very rapid and accurate adjustments.

An attempt to plot the absorption curve for formic acid vapor from meas-

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[1] Porter and Iddings, THIS JOURNAL, **48**, 40 (1926).