THE SYSTEM $CaO-SiO_2-H_2O$ AND THE HYDRATION OF THE CALCIUM SILICATES

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CONTENTS

I. INTRODUCTION

Many investigations of the system $CaO-SiO_2-H_2O$ have been made at ordinary temperature (15–30°C.), particularly during the last twenty years. However, the nature and disconcerting variety of the results make interpretation uncertain.

The difficulties arise mainly because the hydrous lime–silica products are gelatinous colloids. With change in the concentration of CaO in solution, the ratio CaO/SiO_2 for the solid phase continually alters instead of maintaining fixed values, as is usual for crystals of pure compounds of microscopic size. Accordingly, pronounced adsorption or some form of solid solution has generally been assumed. Water content, though not studied so extensively, is indicated to vary continuously with change in vapor pressure.

An abrupt change in the ratio of CaO to SiO_2 for the solid, with little change in the CaO in solution, is found at fairly low CaO concentration (0.04–0.15 g. per liter). Since the molar CaO/SiO_2 ratio for the solid increases in this region until it is 0.85–1.1, formation of $CaO \cdot SiO_2 \cdot aq$ is commonly assumed. The further, more gradual increase, that suggests adsorption or solid solution, raises the value to 1.4–2 at the CaO concentration corresponding to saturation with

$Ca(OH)_2$ (1.26–1.13 g. CaO per liter at 15–30°C.). The nature of this increase and the variation in the final value have both contributed to a conflict of opinion on the final state of actual chemical combination. Even the initial, more rapid rise in CaO/SiO_2 is variously interpreted. Several investigators believe that at low CaO concentrations $CaO \cdot 2SiO_2 \cdot aq$ is formed. Other compounds besides $CaO \cdot SiO_2 \cdot aq$ and $CaO \cdot 2SiO_2 \cdot aq$ have also been suggested. Though a number of investigators have drawn rather definite conclusions, the conflict in evidence and in opinion extends even to the most recent papers.

Many of the experimental studies have been made with the object of explaining the action of water on the tricalcium silicate, $3CaO \cdot SiO_2$, and β-dicalcium silicate, β-$2CaO \cdot SiO_2$, of portland cement. However, very dilute suspensions have generally been used, with frequent or continuous agitation, whereas cement itself is used in commercial practice as a plastic paste, without agitation, except initially. Such studies as have been made on pastes of the pure calcium silicates indicate, in general, a somewhat higher-limed hydrolysis product (CaO/SiO_2 about 2, or more) than has been obtained at the corresponding $Ca(OH)_2$ concentration (saturation) in most of the work with dilute suspensions. Thus, explanation of such differences constitutes an additional problem.

Owing to the confusing variety of results and opinions shown by the literature on the system $CaO–SiO_2–H_2O$, a critical, detailed review has been prepared. The aim has been to present an integrated account without, however, omitting details and discussions that show the actual differences in the data and opinions of the investigators. Though some of the details will be of interest mainly to the investigator contemplating further work in this field, the attempt was made to cover such matters rather thoroughly. There is much need for further, penetrating investigations made with full knowledge of what has already been found, a knowledge which, because of the state of the subject, is not attainable simply by study of the latest experimental papers. This review deals primarily with equilibria at ordinary temperatures. Of previous reviews, the more comprehensive and critical are those of Kühl and Mann in 1934 (97) and Bessey in 1938 (11).

II. A LITTLE EARLY HISTORY

For historical background it suffices to start with Le Chatelier's (117) classic dissertation on hydraulic mortars, published in 1887. Le Chatelier observed, as had others, that limewater and silica sol give a voluminous gelatinous precipitate. The molar CaO/SiO_2 ratio for the solid as first precipitated was 1.3, but the value was found to increase to 1.7 after six months of contact between precipitate and saturated limewater. Washing with water gradually removed CaO, until the ratio was about 1. Upon further washing, the successive portions of wash water came to about the same final concentration. Continued washing finally left only a residue of hydrous silica. Analysis of a precipitate that had been washed until the contacting solution remained only a little higher in CaO than the concentration (0.052 g./l.) at the apparent invariant point gave $1.06CaO:1SiO_2:2.47H_2O$. The method of drying was not stated.

Le Chatelier concluded that a compound, $CaO \cdot SiO_2 \cdot 2.5H_2O$, was formed which held additional lime by adsorption but remained up to lime saturation of the solution as the monocalcium compound. This opinion he reiterated in 1919 (119). In concluding that only the monocalcium compound was formed, he appears to have reasoned not only from the experiments described but also by analogy from the chemistry of the barium compounds. He showed that barium hydroxide and silica sol give a precipitate which appears amorphous at first but transforms to visible crystals of $BaO \cdot SiO_2 \cdot aq$ within a day. He tried in vain to precipitate a dibarium silicate.

Le Chatelier (117) also observed the formation of fine needle crystals in a hydrating cement. They were destroyed by ammoniacal salts, leaving gelatinous flocs which he believed to be hydrous silica. Hence, he concluded that the needles were composed of $CaO \cdot SiO_2 \cdot 2.5H_2O$, though he had obtained only gelatinous, amorphous-appearing solids in his precipitation experiments. From this occurrence of needles he drew support for his theory that cements harden by intergrowth and adhesion of elongated crystalline hydration products.

Michaelis, author of the opposing gel theory of cement hardening, published comprehensive addresses in 1906, 1907, and 1909 (133), in addition to numerous earlier papers. He precipitated silica sol with limewater and found that up to 1.5 moles of CaO could be brought into apparent combination with 1 mole of SiO_2. His work up to 1906 led him to a belief in hydrous compounds, similar to known hydrated magnesium silicates, with molar $CaO:SiO_2$ values of 3:2, 5:4, 4:3, and 1:1. By 1909 he had revised his ideas and recognized a continuous variation of the ratio of CaO to SiO_2 in the solid with change in the CaO concentration of the solution. He appears, however, to have retained a belief in the 1:1 compound; according to his computations, cements that hydrolyzed in large volumes of water appeared to give this compound. However, he had previously demonstrated to his satisfaction that continuous *leaching* eventually removed all the lime, leaving only hydrous silica.

Jordis and Kanter (77) in 1903 precipitated hydrated alkaline earth silicates at about 100°C., using silica sol or gel in saturated solutions of the respective hydroxides. In this way, crystalline $BaO \cdot SiO_2 \cdot H_2O$ and $SrO \cdot SiO_2 \cdot H_2O$ were obtained. The calcium compound was not distinctly crystalline and was more difficult to obtain in a pure state. However, analyses are reported that agree well with $CaO \cdot SiO_2 \cdot H_2O$. The authors concluded that a silicate containing more than 1 mole of alkaline earth to 1 mole of SiO_2 could not be formed in contact with water. Later (1906), Jordis (76) reported that the calcium silicate hydrate was prepared more satisfactorily by aid of calcium acetate. The product, $CaO \cdot SiO_2 \cdot 2H_2O$, was said to be amorphous but to be accurately the metasilicate. In an advance statement (1905) (75) the product was reported as $CaO \cdot SiO_2 \cdot H_2O$, and was called crystalline. Also of interest in this connection is a statement by Lafuma (105) that Becquerel obtained a crystalline calcium silicate, in an early experiment, by reaction of potassium silicate and calcium acetate "through the medium of parchment paper." Apparently, however, no analysis was reported.

Staining tests applied by Keisermann (1909–10) (81) and Blumenthal (1914) (16) to portland cement and calcium silicate "melts," hydrating on microscope slides, indicated that some fine needles and the gel that formed were composed of calcium silicate. The composition $CaO \cdot SiO_2 \cdot aq$ was inferred on the evidence of the earlier investigators, primarily Jordis and Kanter (77).

There were also other early studies, some of which will receive attention later. However, no data appear to have been reported prior to 1928 that give in detail the relations between solid composition and CaO in solution. Microscopical studies and attempts to identify the products of cement hydration constitute much of the early work. For the most part these attempts are now of little direct interest, since the methods of estimating free $Ca(OH)_2$ were generally very imperfect. Rebuffat (149) and others (118) concluded in favor of $2CaO \cdot SiO_2 \cdot aq$, but later the monocalcium silicate hydrate, $CaO \cdot SiO_2 \cdot aq$, appears to have received the widest acceptance as the most important siliceous product of cement hydration.[1] The experimental foundation for this belief was provided mainly by the works that have been discussed. Le Chatelier's formula, with the $2.5H_2O$, appears frequently in the early literature.

In a 1928 review on the setting and hardening of portland cement, Bogue (17) concluded that exact information on the major reactions of hydrating cement had not been advanced materially since the publication of Le Chatelier's dissertation.

III. THE LATER WORK: POSSIBLE CAUSES OF DIFFERENCES IN RESULTS

Since 1927, papers dealing systematically with the problems presented by the $CaO–SiO_2–H_2O$ system have appeared at frequent intervals. A few represent hydrothermal studies made at temperatures above 100°C. These are treated only incidentally in this review. For the most part they have no direct or certain significance with respect to the phenomena observed at ordinary temperatures (99, 175). Of the other studies, those that give apparent equilibria over a range in CaO concentration are represented in figure 1,[2] which shows the molar CaO/SiO_2 values[3] for the hydrous solids plotted against concentrations of CaO (mainly $Ca(OH)_2$) in solution. As previously mentioned, there are broad general similarities, but also pronounced individual differences.

Some of the differences in results are attributable, no doubt, to the differences in temperature, though the 40°C. and 20°C. curves (Nos. 11 and 12, figure 1) of Kühl and Mann (97) are more nearly the same than are some of the others.

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[1] See p. 13 of reference 93. At a symposium on the setting and hardening of cements and plasters, reported in the Journal of the Faraday Society (January, 1919), H. Le Chatelier, C. H. Desch, and A. A. Klein assumed $CaO \cdot SiO_2 \cdot aq$; G. A. Rankin tentatively assumed hydrous silica and adsorbed lime.

[2] Data obtained by Kryagova (90) have not been used in figure 1 because the units are thought to be incorrectly given by the author. For CaO/SiO_2 of about 1 in the solids the CaO in solution is reported as the exceptionally small quantity 0.005 g. per liter in tests with agitation, and as the exceptionally large quantity 0.6 g. per liter in tests made without agitation.

[3] In many cases these ratios were not obtained from direct analyses. Assumptions involved are considered in Section VI.

Experimental methods differed, of course, and evidently influenced the results, since there was commonly no complete check on the attainment of equilibrium. Some of the analytical procedures are also open to criticism.

Possibly of considerable importance, however, is the fact that, by reason of the colloidal states of the solid phases, complete thermodynamic equilibrium was actually not attained in any case. The solids may have remained significantly different in colloidal particle size in different investigations and even in different experiments within a single investigation. The resultant differences in adsorptive capacity may have contributed materially to the differences in curve slopes and to the range in the values of CaO/SiO_2 reached at lime saturation of the solution.

Also, differences in solubility caused by differences in particle size within the colloidal range could have affected the locations of the abrupt rises that are shown by the curves. Solubility differences could have contributed also to the fact that, in general, these rises are not truly vertical. If the common interpretation of them is correct, they represent what would normally be invariant points in the phase diagram, where two solid phases coexist with a solution of fixed composition, a composition determined by the solubilities of the two solids. Hence, if these solubilities change, the CaO concentration of the solution changes. Finally, it is at least conceivable that metastable compounds may have formed in some cases.

These possibilities—namely, that differences in colloidal state of subdivision may have contributed to differences in results—have received little mention in the literature on this system. However, Roller and Ervin (152) gave consideration to the possible effect of particle size on solubility and concluded from the general lack of evidence of aging that fairly definite solubilities might be maintained. Krasil'nikov and Kiselev (88) mention the degree of dispersion of the initial precipitate as having perhaps contributed to the different "invariant" concentrations found by different experimenters.

It is to be recognized that opinions differ as to the probable extent of the influence of fine particle size on solubility (66, 186) but solubility increases of at least 100 per cent appear to be distinct possibilities (66).

IV. RESULTS CONSIDERED IN RELATION TO INITIAL MATERIALS

The curves of figure 1 are arranged on the basis of a classification according to initial materials, which is shown in table 1. In the various cases, the silica was supplied as silica sol or gel; in solution as sodium silicate or as tetraethyl silicate; in calcium silicate "melts"; or in the practically pure anhydrous silicates, $3CaO \cdot SiO_2$, and β-$2CaO \cdot SiO_2$. That it is possible, starting with such a diversity of initial materials, to reach final states that are apparently not widely different is evident from the curves numbered 2, 8, 12, and 14.

The abrupt rise shown at the highest lime concentrations in a number of the curves of figure 1 was evidently caused, in general, simply by separation of $Ca(OH)_2$ as the solutions became saturated with this compound. (The CaO concentrations corresponding to saturation with $Ca(OH)_2$ at various temperatures have been indicated in figure 1 by use of I.C.T. data.) In certain cases the solutions became supersaturated with $Ca(OH)_2$; except for its lower terminus, Hedin's (67) curve, No. 10, is entirely for supersaturated solutions. Bessey (11) obtained the final rise in his curve, No. 8, at a CaO concentration so much lower than the 1.24 g. CaO per liter for a pure saturated solution of $Ca(OH)_2$ at

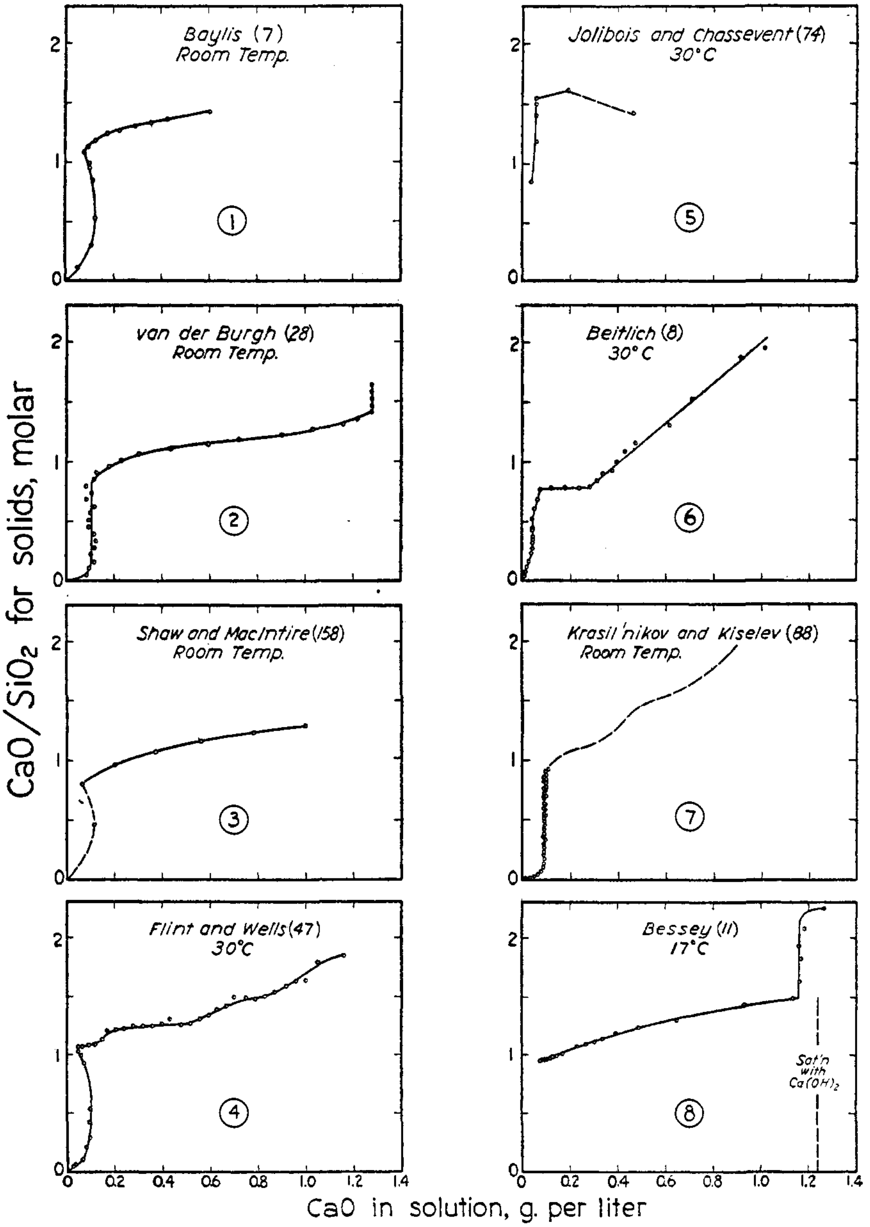

FIG. 1. The system $CaO-SiO_2-H_2O$; molar CaO/SiO_2 for solids *versus* CaO in solution

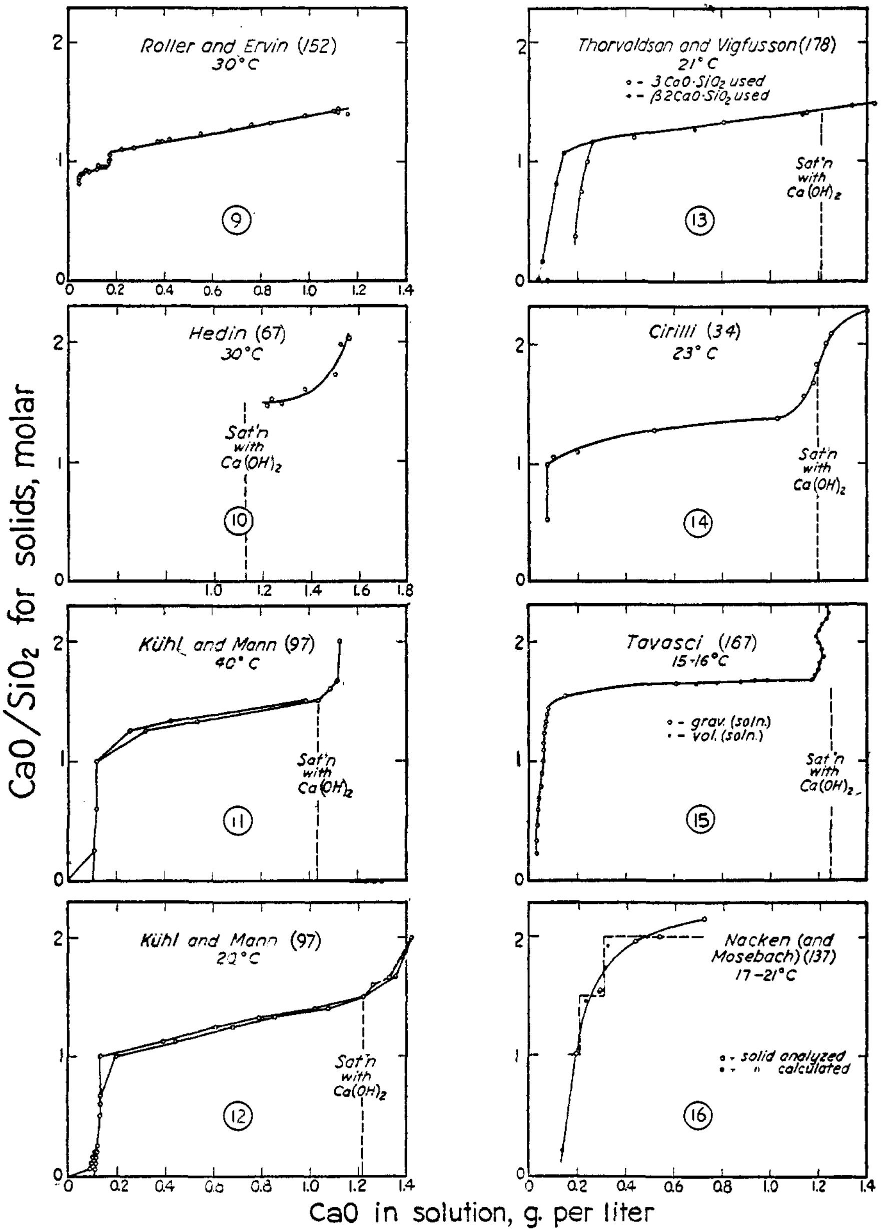

FIG. 1.—Continued

17°C. that he assumed separation of $2CaO \cdot SiO_2 \cdot aq$. Cirilli (35), however, has questioned the validity of this assumption. His own curve, No. 14, also begins to rise sharply before the CaO concentration is as high as for a pure saturated $Ca(OH)_2$ solution, but an x-ray spectrum showed $Ca(OH)_2$ in the solids (for $CaO/SiO_2 = 1.67$). Bessey obtained his data by adding water to a precipitate

TABLE 1

Initial materials used in the investigations represented in figure 1

IMMEDIATE SOURCE OF SILICA	INITIAL MATERIALS	CURVE NO.	TOTAL SiO_2	INVESTIGATORS
			grams per liter	
Silica sol or gel (including dried preparations)	Hydrous silica gel placed in water, and solid CaO added	1		Baylis (7)
		2	10	van der Burgh (28)
	Silica sol and limewater (for curve 3 a "solution-suspension" of $Ca(OH)_2$ was used)	3	1	Shaw and MacIntire (158)
		4	0.45 or less	Flint and Wells (47)
		5	0.28	Jolibois and Chassevent (74)
	"Silicic acid" (a C.P. reagent containing 20% H_2O) and limewater. Solid CaO was added in some cases.	6	0.6	Beitlich (8)
	Silica gel heated at 260°C., and later at 170°C.; retained 4.2% H_2O; used with limewater	7		Krasil'nikov and Kiselev (88)
Silicate solution	Sodium silicate and $Ca(NO_3)_2$; initial precipitate was $2.33CaO:1SiO_2:3.3H_2O$ and contained free $Ca(OH)_2$; dilute lime solution was added, and repeatedly diluted	8		Bessey (11)
	Sodium metasilicate and limewater; precipitate was placed in $Ca(OH)_2$ solutions of varied concentrations	9	About 0.06	Roller and Ervin (152)
	Tetraethyl silicate in alcohol solution was added to limewater	10		Hedin (67)
Lime-silica "melts"	Quickly cooled melts of lime and silica were placed in water or limewater	11	10 or less	Kühl and Mann (97)
		12		
Anhydrous calcium silicates	$2CaO \cdot SiO_2$ and water	13	0.02–2.8	Thorvaldson and Vigfusson (178)
	$3CaO \cdot SiO_2$ and water	13	0.01–1.0	
	For curves 13 and 16, varied initial proportions of solid and water were used to obtain each point. For curve 15, the solution was replaced by pure water at intervals. No details were given for curve 14.	14		Cirilli (34)
		15	3	Tavasci (167)
		16	0.05–0.9	Nacken (137)

analyzing $2.33CaO:1SiO_2:3.3H_2O$ in which a part of the CaO was present as free $Ca(OH)_2$. However, if free $Ca(OH)_2$ still remained in the solid that is represented along the vertical part of Bessey's curve, his microscope failed to reveal it.

It is of some interest that Beitlich (8) and Krasil'nikov and Kiselev (88), who used the least hydrous silica gels, obtained the curves (Nos. 6 and 7) that rise the highest in figure 1 (except for the pronounced increases in CaO/SiO_2 at apparent saturation of the solutions with $Ca(OH)_2$). However, in both investigations, the solids were in contact with the solutions for months, as shown by table 2. Possibly this long contact may have as much significance as the state of the initial material, since the gels may be capable of very slow adjustments. Flint and Wells (47), whose tests lasted for a month, also obtained high values of CaO/SiO_2 (curve 4). As reported in Section II, Le Chatelier obtained a value of 1.7 in a six-month test. Also, Klasse and Kühl (84), who kept precipitates in saturated $Ca(OH)_2$ for three weeks, obtained CaO/SiO_2 values of about 1.8.

Shaw and MacIntire (158), in preliminary work, experimented with dried gels. By shaking with an attrition agent, they apparently attained nearly complete reaction within a few days. From these tests, at low lime concentration, they concluded that within wide limits the degree of hydration of the gel does not influence its capacity for absorption of $Ca(OH)_2$. Jordis and Kanter (77) found difficulty in obtaining definite alkaline earth silicates, whether of calcium, barium, or strontium, when their hydrous silica had been dried below 23 per cent water.

Curve 5, which Jolibois and Chassevent (74) obtained by mixing silica sols and limewater, stands out from its neighbors by reason of the high values of CaO/SiO_2 that were obtained, in this case at low lime concentration. For CaO/SiO_2 values up to 1.5, the CaO concentration is practically invariant at a value which in Le Chatelier's experiments seemed to indicate coexistence of $CaO \cdot SiO_2 \cdot aq$ and a lower-limed solid, perhaps $SiO_2 \cdot aq$. It appears that a particularly high degree of adsorption may be responsible for the unusual shape of curve 5. The tests were of six months' duration. As initially precipitated, all the solids, except the one for the first point, had CaO/SiO_2 values close to unity.

Curve 4, obtained by Flint and Wells (47), who also used silica sol and limewater, has a ragged-appearing upper section. However, since each point was obtained in a separate test conducted without agitation, this variability may well have no fundamental significance. Flint and Wells made other tests in which they shook anhydrous calcium silicates with water, filtered off the resultant supersaturated solutions, and then allowed the filtrates to stand, so that they precipitated. The precipitated solids had considerably higher values of CaO/SiO_2 than the solids of curve 4 at the higher CaO concentrations.

One peculiarity evident only in the curves for the silica sol and gel groups of table 1 is the bow-shaped initial rise whereby the curve turns back on itself. This odd effect will be discussed later.

Curve 9 was obtained by Roller and Ervin (152) by using hydrous lime-silica

TABLE 2

Experimental conditions in investigations represented in figure 1

CURVE NO.	INVESTIGATORS	PERIOD OF CONTACT IN OBTAINING INDIVIDUAL CURVE POINTS	AGITATION	EACH POINT A SEPARATE PREPARATION (?)	SPECIAL INDICATIONS OF EQUILIBRIUM; SPECIAL MEASURES TAKEN TO ESTABLISH EQUILIBRIUM
1....	Baylis (7)	2–3 days	Intermittent (one ⅝-in. steel ball used)	No	Auxiliary tests indicated reversibility. Author states equilibrium was nearly reached in 4 hr.
2....	van der Burgh (28)	24 hr.	Continuous	No	None, except duplicate tests which checked well
3....	Shaw and MacIntire (158)	5 days	Continuous	Yes	Change between 2 and 5 days was slight; there was some subsequent change, but it could be attributed to attack on glass vessels on basis of preliminary work
4....	Flint and Wells (47)	1 month	None	Yes	None
5....	Jolibois and Chassevent (74)	6 months	50 days continuous, then stood, except continuous agitation last 4 days	Yes	None
6....	Beitlich (8)	Up to several months	Continuous	Yes	Tests were continued until the electrical conductivity of the solution became constant
7....	Krasil'nikov and Kiselev (88)	Up to 17 months	Agitated, but no details given	Yes	Tests of varied duration showed attainment of constant concentration in the region of vertical rise in CaO/SiO$_2$ (figure 1); also, after additions of water or saturated limewater this concentration again established itself; the curve portion above the vertical rise was not well established, since in that region 17-month tests gave higher CaO/SiO$_2$ values than 10-month tests

TABLE 2—*Continued*

CURVE NO.	INVESTIGATORS	PERIOD OF CONTACT IN OBTAINING INDIVIDUAL CURVE POINTS	AGITATION	EACH POINT A SEPARATE PREPARATION (?)	SPECIAL INDICATIONS OF EQUILIBRIUM; SPECIAL MEASURES TAKEN TO ESTABLISH EQUILIBRIUM
8....	Bessey (11)	Not stated	Not stated	No	Author states "allowed to come to equilibrium"; no details
9....	Roller and Ervin (152)	0.5–8 days	Continuous	Yes (except one point)	Tests of varied length showed attainment of constant concentrations; points obtained in tests involving, respectively, absorption and release of CaO fall on the same curve; both kinds of test are represented in each curve section except the vertical rise at the lowest CaO concentration
10....	Hedin (67)	16 hr. (?)	Apparently none, except such as was caused by vacuum distillation	Yes	Vacuum distillation at 30°C. during addition of SiO_2 solution maintained practically constant $Ca(OH)_2$ concentration during reaction; in preliminary tests 16 hr. standing preceded analysis; whether final preparations stood is not stated
11....	Kühl and Mann (97)	13 days	Continuous	Yes	Curves were obtained from both the high- and the low-lime directions; see main text of this review
12....	Kühl and Mann	17 days	Continuous	Yes	As for curve 11
13....	Thorvaldson and Vigfusson (178)	About 10 days to 3 weeks	Continuous (metal shot used)	Yes	Separate tests of progressively increased length were run until the $Ca(OH)_2$ concentration remained constant
14....	Cirilli (34)	Not stated	Not stated	Apparently yes	No details

TABLE 2—*Concluded*

CURVE NO.	INVESTIGATORS	PERIOD OF CONTACT IN OBTAINING INDIVIDUAL CURVE POINTS	AGITATION	EACH POINT A SEPARATE PREPARATION (?)	SPECIAL INDICATIONS OF EQUILIBRIUM; SPECIAL MEASURES TAKEN TO ESTABLISH EQUILIBRIUM
15....	Tavasci (167)	Apparently several hours to several days	Continuous (glass shot used)	No	Test intervals were spaced according to the apparent needs as indicated by the continuity of results
16....	Nacken (137)	18–34 days	Continuous	Yes	For some compositions tests of varied duration were made

products precipitated from sodium metasilicate (and thoroughly washed before being suspended in $Ca(OH)_2$ solutions). It is unique in that it shows an additional, short, vertical rise at 0.17 g. CaO per liter. Such a "step" not only does not appear so clearly in any of the other curves, but it seems definitely not to be a possibility in some, because of close spacing of the experimental points. However, the rise is so small that the formation of a new compound, which it apparently indicates, might conceivably have occurred in other cases but have been obscured either by adsorption or by failure to establish equilibrium with sufficient accuracy. It is of interest that curve 9 was obtained at 30°C., midway between the two temperatures employed by Kühl and Mann (97). The latter investigators point out that their 40°C. curve, No. 11, rises rapidly after $CaO/SiO_2 = 1$ up to an apparent break at 1.25, though, as they say, the experimental points are too few for a close interpretation.

Two of the curves, Nos. 15 and 16, from the group of four that were obtained in investigations in which $3CaO \cdot SiO_2$ was used, show unusually high CaO/SiO_2 values at relatively low CaO concentrations. The nature of the initial material is such that results of this kind suggest incomplete equilibrium. This possibility, as it applies to curve 16, appears to be borne out in a subsequent report by Nacken (138), who (with Mosebach (137))[4] established curve 16.

Roller and Ervin have suggested that Beitlich may have obtained the high CaO/SiO_2 value that he did because of his use of solid lime, which may have become entangled in the gel. However, Baylis (7) and van der Burgh (28) also used solid lime, apparently with no ill effects.

Curves 13 were obtained by Thorvaldson and Vigfusson (178), by starting with anhydrous $3CaO \cdot SiO_2$ and $2CaO \cdot SiO_2$. Keevil and Thorvaldson (80) state that they obtained similar results by using crystalline hydrates of these same compounds, prepared hydrothermally. Bessey (11) employed crystalline hydrates in somewhat similar tests but found them too inactive for his purpose.

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[4] The writer has not had access to the paper by Nacken and Mosebach, but according to Building Science Abstracts 8, No. 1612 (1935) it covers the same investigation as Nacken's paper and in rather more detail.

In contrast, Keevil and Thorvaldson reported that the crystalline hydrates were more reactive than the corresponding anhydrous compounds. Bessey used, for his tests, water that already contained 0.4 g. CaO per liter, a point of difference cited by Thorvaldson in later discussion of Bessey's paper (173).

V. PROBLEM OF ATTAINMENT OF COLLOIDAL EQUILIBRIUM

With respect to most of the investigations represented in figure 1, some uncertainty exists as to whether equilibrium was actually reached, even on the colloidal level. Only in the investigations of Kühl and Mann (curves 11 and 12) and of Roller and Ervin (curve 9) was the curve obtained from both the high- and the low-lime directions over most of its course. However, Krasil'nikov and Kiselev established the vertical part of their curve (No. 7) in this way, making, in all, forty-two tests in this region.[5] Some of the other investigators took special pains to continue their tests until the concentration of the solution had been indicated to remain constant. The measures taken by the various investigators are summarized in table 2.

Duration of test varied widely, as shown. Roller and Ervin appear to have established that a few hours to a few days were sufficient for the adjustment of their lime–silica precipitates, whereas Krasil'nikov and Kiselev found ten months to be too short a time at the higher lime concentrations in their experiments with activated silica gel containing only 4.2 per cent of water.

Roller and Ervin report that equilibrium appeared to be attained more rapidly when the solids had to lose CaO than when they had to gain it. Tavasci (168) held the same view. Kühl and Mann found, at 20°C., a very pronounced difference of this kind at the point where CaO/SiO_2 for the solid was unity. Roller and Ervin found the time requirement to be relatively great at an apparent invariant point where two solid phases should be present.

Those investigators who sought to obtain equilibrium without or with only occasional agitation of their preparations were evidently influenced by the large volume occupied by the hydrous solid. Le Chatelier found that 1 g. of the precipitate occupied 2 liters. Baylis (curve 1) reported that his precipitates occupied half the total sample volume and that he therefore considered intermittent agitation to be adequate. Shaw and MacIntire (curve 3) observed that the settled volume increased regularly with increase in the CaO used; about 0.9 g. of SiO_2 added as sol to limewater (900 ml. total volume) gave sediments of 50 to 300 ml. after 16 hr. of settling.

The fact that Thorvaldson and Vigfusson (curves 13) obtained, over most of the range in CaO concentrations, the same curve for β-$2CaO \cdot SiO_2$ as for $3CaO \cdot SiO_2$ was to be expected if colloidal equilibrium was actually attained in each case, and if the hydration products were of equivalent texture. The difference between the curves at low lime concentrations was not considered significant by the authors, who state that the analytical precision was poor in that region. They state also that the tests on β-$2CaO \cdot SiO_2$ were made in a steel tube with

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[5] Curve 7 of figure 1 was reproduced from microfilm; the many points in the region of the vertical rise could be reproduced only in a general way.

steel shot whereas, in the region concerned, a gold-lined tube and gold shot were used with $3CaO \cdot SiO_2$, to prevent extraneous reaction. However, the results obtained with the steel tube and shot agree best with ones obtained by other investigators. The significance of the portions of Thorvaldson and Vigfusson's curves that correspond to low CaO concentrations is considered further in Section XVI.

The drop in CaO concentration with increase in CaO/SiO_2 in solids above 0.5, that gives the bow shape, mentioned earlier, to the initial rise in some of the curves, strongly suggests either lack of complete colloidal equilibrium, non-maintenance of a fixed particle size, or analytical inaccuracy. Otherwise, it appears that such a reversal in curve direction should not occur. Whatever compounds are formed evidently constitute a series of hydrolysis products for which the CaO concentration would normally be expected not to decrease as CaO/SiO_2 increases.

Earlier it was noted that, since curves 15 and 16 were obtained by use of $3CaO \cdot SiO_2$, their unusual heights at moderately low CaO concentrations suggest the possible non-attainment of complete hydrolytic equilibrium. Nacken, who reported the data of curve 16, subsequently found (138) that in tests continued for nine months (instead of about 20–30 days as for curve 16) the CaO/SiO_2 values were markedly lowered. This was in spite of the fact that, as observed microscopically, most of the particles had appeared to hydrate clear to their centers within 3 days. Nacken considered that attack of the basic solution on the glass vessels had some influence on the long-time results but he came nevertheless to the conclusion that the short-time results probably represent only temporary equilibria. In spite of this, the relationships that Nacken supposed on the basis of the earlier results have subsequently been given considerable attention by others (39, 155), perhaps justifiably with respect to cement technology, since products formed during the first 20–30 days with consumption of a large part of the available water may tend to persist, whether they are equilibrium products or not. Nacken believed in the formation of rather definite stoichiometric compounds indicated by the dashed line in the figure. Schläpfer (155) notes that Nacken was unable to obtain similar results when using $2CaO \cdot SiO_2$. He reports that he, himself, has found that $2CaO \cdot SiO_2$ shaken with limewater containing 0.6 g. CaO per liter actually removes lime from solution, evidently by adsorption, since the $2CaO \cdot SiO_2$ gives the appearance of hydrolyzing.

Bessey (11) questioned whether curve 15 obtained by Tavasci represents equilibrium, since the methods used did not suffice to demonstrate equilibrium. Tavasci (168) defended his methods.

The work of Kühl and Mann (curves 11 and 12) is of special interest because of a unique method of investigation whereby, in spite of the fact that the solid particles hydrated only at their surfaces, the equilibrium relations appear to have been determined rather well. The investigators prepared melts of varied $CaO:SiO_2$ ratio and then sought to establish in each case the $Ca(OH)_2$ solution that would remain unchanged in CaO concentration as equilibrium was established at the surface of the solid. It was reasoned that if the amount of lime in solution remained unchanged, the equilibrium hydrate must have the same CaO/SiO_2

value as the melt itself. In practice the investigators were satisfied if the lime concentration changed only slightly. Indeed, at an invariant point, rather larger changes appear to have been considered satisfactory provided the invariant concentration was reached. Complete curves up to lime saturation[6] were established, both by starting with solutions more concentrated than the final ones, and *vice versa.* The near coincidence of these curves was believed to define with sufficient accuracy the course of the true equilibrium curve.

The principle of the procedure appears to be sound as long as the silica going into solution can be considered negligible. At the higher CaO concentrations, down almost to the concentration at the invariant point where the nearly vertical curve section is obtained, this assumption of negligible SiO_2 solubility is apparently justified. At the invariant point, however, there is reason to believe that the SiO_2 concentration is not insignificant. The SiO_2 removed from the solid must, then, affect somewhat the accuracy of determination of the terminal values of CaO/SiO_2 at this concentration. The degree of change in concentration permitted in attaining the invariant concentration would also affect the terminal CaO/SiO_2 values. However, in neither case should there be any effect on the accuracy with which the CaO concentration is determined at the invariant point.

The fact that the solid particles, though evidently very fine, hydrated only in a thin surface layer in spite of about 2 weeks of shaking with solution (2.1 g. solid in 70 ml. of solution) is largely due to the fact that the CaO/SiO_2 ratio was 2 or less. The $3CaO \cdot SiO_2$ hydrates and hydrolyzes much more rapidly. Thorvaldson and Vigfusson (178) show rate-of-hydrolysis curves (see later) that illustrate this difference for the β-$2CaO \cdot SiO_2$ and $3CaO \cdot SiO_2$ preparations with which they worked. They also report that, when they did not use their metal shot, *apparent* equilibrium, as determined by pH measurement and by titration, was attained while many of the solid particles still had unhydrated cores.

Hedin's experimental procedure (table 2), involving very slow precipitation with maintenance of constant $Ca(OH)_2$ concentration, appears to be well conceived.

VI. ANALYTICAL DETERMINATIONS

Just how dependent the differences in the various results shown in figure 1 may be upon inadequacies in the analytical work cannot now be fully established. However, a brief account will be given showing what determinations were made and giving a few additional details, mainly such as seem to have special significance. Unfortunately, most of the authors give little information regarding their analytical work.

The CaO in solution was determined volumetrically (by use of permanganate) for curve 9 and gravimetrically for curves 4 and 16, and for much of curve 15. Titration with acid was used for curves 11 and 12, but was checked to some extent by gravimetric tests. For curves 1, 2, 3, 7, and 13, the CaO concentrations

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[6] Both the solid and the dashed line shown in plot 12 of figure 1 for solutions supersaturated with $Ca(OH)_2$ were obtained from the low-lime side. The dashed line resulted when "dusted" melts containing some γ-$2CaO \cdot SiO_2$ were used.

were determined solely by acid titration. The methods of determining CaO concentrations for curves 8 and 14 were not stated, and the exact method used for curve 10 is uncertain, though the lime was apparently first precipitated as oxalate. For curves 5 and 6 the determinations were based on the electrical conductivity of the solution. When this determination is made simply by comparison with the conductivities of pure $Ca(OH)_2$ solutions, as was true relative at least to curve 6, it is subject to error at low CaO concentrations where the SiO_2 in solution becomes significant (152). In such tests, as well as in acid titrations, error can result also if alkalies are dissolved from glass vessels.

Tavasci (curve 15) found by checking against gravimetric determinations that acid titration based on phenolphthalein indicator gave CaO values that were too low when the CaO was 0.14 g. per liter or less. Titrations based on methyl orange were shown to be satisfactory. Results obtained with sodium silicate are similar (21, 183). Baylis (curve 1) also noted the difference between phenolphthalein and methyl orange end points, and used the latter in calculations. Shaw and MacIntire (curve 3) apparently used only the phenolphthalein indicator. Krasil'nikov and Kiselev (curve 7) used bromothymol blue after checking its suitability by potentiometric titration. The indicators used for curves 2 and 13 were not stated.

The CaO/SiO_2 values for the solids were commonly not determined directly, except sometimes for the final composition after a series of interrelated tests. Instead, they were generally computed from final solution concentrations and the amounts and compositions of initial solids and solutions. Curves for which the CaO/SiO_2 values of the solid products were not in general obtained by direct analysis are 1–6 inclusive, 11–13 inclusive, 15, and apparently 7 also. For the points on curves 9 and 10, and some of those (as marked) on 16, direct analyses of the solids were made. Whether each solid was analyzed for curves 8 and 14 was not reported.

For many of the curves, as represented in figure 1, the CaO/SiO_2 values were computed by assuming all the SiO_2 to be present in the solid. This is true of curves 2, 3, 6, 11, 12, 13, and part of 16 (all the calculated points), while the situation regarding curves 1, 7, 8, and 14 is not clear. In general, the practice of the investigators has been conformed to, but not all of them drew curves of this type. Thorvaldson and Vigfusson plotted the initial concentrations of $3CaO \cdot SiO_2$ and β-$2CaO \cdot SiO_2$ against "mols CaO retained." Their curves show abrupt breaks, or inflections, where the retained CaO is about 1 mole per mole of the silicate. Hence, points of inflection were said to occur "where the composition of the residue corresponds to monocalcium silicate." Neglect of the SiO_2 in solution is justifiable at the higher lime concentrations, and in general when the proportion of total SiO_2 to volume of solution is sufficiently large, but may have important consequences if the total SiO_2 is relatively small and the CaO concentrations are low. As the CaO concentrations drop below 0.1 g. per liter, the SiO_2 concentration increases rapidly (152). Thorvaldson and Vigfusson (curves 13) had to use relatively small quantities of solids to obtain the lower lime concentrations, since their procedure was simply that of adding water to the anhydrous calcium silicates. The possible consequences of this are considered in Section XVI.

The silica concentrations were determined for the solutions represented in curves 1, 4, 5, 7, and 15. Baylis (curve 1) and Krasil'nikov and Kiselev (curve 7) questioned whether the silica which they found was necessarily all in true solution. Roller and Ervin did not determine SiO_2 for the solutions used in establishing curve 9, but they did make SiO_2 determinations on similar solutions, separately prepared. Shaw and MacIntire (curve 3) also made supplementary SiO_2 determinations. Values obtained by the various investigators will be considered in Section IX. The determinations made by Roller and Ervin and by Krasil'nikov and Kiselev were colorimetric. Kryagova (90) has also made colorimetric determinations and gives considerable detail on his method.

Various investigators report precautions taken against the action of atmospheric carbon dioxide, but few appear to have determined the extent of carbon dioxide contamination. Tavasci (curve 15) found at the end of his tests, which involved many withdrawals of solution and replacements by water, that the carbon dioxide in the solids actually amounted to 45 per cent of the remaining SiO_2; he applied graduated corrections to the data obtained earlier. Roller and Ervin analyzed and found that only a small correction for carbon dioxide was needed in establishing curve 9. Hedin (curve 10) examined his products under the microscope and could observe no crystalline calcium carbonate. Bessey (curve 8) reported that he corrected for carbon dioxide.

Owing to the change in composition of the solid with change in the amount of CaO in solution, it is apparent that the washing of a precipitate preparatory to analysis could introduce error. Among early investigators, Jordis and Kanter (77) took precautions against such error by washing first with alcohol diluted 1:2, then with absolute alcohol, and finally with ether. Baylis (curve 1) restricted his volume of wash water to an amount about 50 per cent in excess of the volume of the precipitate. Roller and Ervin (curve 9) washed precipitates obtained at the higher lime concentrations with aqueous acetone "of such concentration (50% or stronger) that a precipitate of calcium hydroxide just was avoided." In a second wash the concentration of acetone was raised. Pure acetone was eventually used, followed by pure ether. Nacken, and Hedin, who also analyzed a number of hydrous products, do not give explicit details.

Shaw and MacIntire obtained evidence that when they used steel shot in a glass vessel results obtained after 2 days were apparently affected by attack upon the glass. (No shot were used in obtaining their curve 3.) Tavasci (curve 15), who used glass shot, concluded from the good agreement between his gravimetric and acidimetric determinations of CaO that contamination by alkali from the glass was negligible. Krasil'nikov and Kiselev (curve 7) made blank tests using only $Ca(OH)_2$ solution in their reaction vessels, which were glass ampoules. After seven months the more concentrated solutions had diminished in CaO by 7 per cent, but no SiO_2 was found in solution. In the weaker solutions the loss of CaO was inappreciable. Kühl and Mann (curves 11 and 12) considered that by using only glass flasks that had long been used for similar work, or new ones that had been well steamed, they largely avoided further leaching of the glass. Checks which they obtained between the results of acid titrations and gravimetric determinations for CaO appeared to confirm this. Thorvaldson and Vigfusson (curves 13) and also Bessey (curve 8) used metal vessels. Roller and Ervin (curve 9) made their supplementary solubility determinations by use of a paraffined reaction flask. Thorvaldson (173) and Bessey (12) have both expressed the opinion that the use of any kind of glass vessels is undesirable.

VII. CHEMICAL COMBINATION OF HYDROUS SILICA AND LIME

In the past it has occasionally been assumed that hydrous silica does not, or at least may not, undergo at room temperature any actual chemical combination with lime (23, 38, 145, 180). In view of the uncertainties that persist regarding the $CaO-SiO_2-H_2O$ system, and the resemblances between the properties of the hydrous lime–silica products and what might be expected of a gelatinous adsorptive system, such views are understandable. However, though serious question yet remains as to the state of combination of some of the lime in the higher-limed products, the evidence for chemical combination of the silica with at least a part of the lime now seems practically conclusive. Considerable evidence exists, as is shown by the following account.

The observations of various authors have led them to ascribe to lime a peptizing, or dispersing, action on silica gel, which action is apparently similar to that produced by sodium hydroxide (30). Maffei and Battaglia (127) and Cirilli (32) observed that after the initial rate of removal of lime from solution by silica gel had fallen off, the rate again became greater, an effect which they attributed to dispersing action of the lime and alteration of the original gel structure. Van der Burgh (28) reported that in his (shaking) experiments, the solid phase which was at first in the form of fragments of gel changed into a very voluminous, flocky, snow-like mass. Mehrotra and Dhar (128) reported that hydrous silica gel was easily taken into colloidal solution by bases, including $Ca(OH)_2$. Flint and Wells (47) found that silica gel dissolves slowly in dilute $Ca(OH)_2$ solution at 30°C.; at 100°C. the action was much more rapid and it gave a clear solution, a result obtained also by Kryagova (90). Relative to chemical reaction, these various observations are suggestive only, but they show at least that the action of the lime is such as to destroy the original gel structure.

More direct evidence for chemical combination is provided by the following additional observations: Mehrotra and Dhar found in their tests at room temperature that gelatinous silica acts acidic, in that it "adsorbs" bases to a much greater extent than acids. Kolthoff and Stenger (86) found that $Ca(OH)_2$ was "adsorbed" much more strongly than alkali hydroxides, and hence appeared to form a relatively insoluble silicate. Maffei (126) analyzed data obtained after contact periods of systematically varied length, and showed that the constants of the Freundlich and Langmuir adsorption isotherms vary in a way that suggests that CaO is first adsorbed by silica gel and then reacts chemically. Indeed, Maffei's analysis indicates also that the products are subject to hydrolysis. Krasil'nikov and Kiselev (88) show graphically that curves obtained at early time intervals are like ordinary adsorption isotherms but that a progressive change occurs until the vertical section shown by curve 7 of figure 1 is obtained. This was found to be true whether the initial material was silica gel or naturally occurring tripoli or diatomite.

This vertical or roughly vertical curve section that appears at low CaO concentration in plots of CaO/SiO_2 in solids *versus* CaO in solution is considered by many to be rather good evidence of chemical reaction. A truly vertical rise does, under ordinary circumstances, indicate the coexistence of two solid phases in a three-component system; in the present case one of these phases would be a calcium silicate. The departures from a strictly vertical curve section can be accounted for by the difficulties of experimentation and the colloidal nature of the solids, as discussed earlier. Such aspects can account also for the fact that the SiO_2, as well as the CaO, is found to vary in concentration. It may also be that more than one phase transition is involved.

Klasse and Kühl (84) sought to produce calcium silicate hydrates by double decomposition of sodium silicates and calcium nitrate at 19°C. They believed that they were successful in their efforts to obtain $CaO \cdot SiO_2 \cdot aq$ by use of pure sodium metasilicate. The molar CaO/SiO_2 ratio for the product was always somewhat less than 1, but the difference appeared to be caused by hydrolysis, since it was reduced by using excess calcium nitrate. In this way a ratio of 0.96:1 was attained. Emley (44) precipitated what he believed to be hydrated monocalcium silicate, using calcium chloride and sodium metasilicate. The washed and dried product showed no free CaO or $Ca(OH)_2$ when tested by Emley's glycerol–alcohol solution method (see Section XIII).

Cirilli (32) allowed a freshly precipitated silica gel (about 80 per cent water) to interact with saturated limewater and obtained for the product a heat of solution of 362.6 cal. per gram of CaO, as compared with 557.9 cal. per gram of CaO for $Ca(OH)_2$. Thus, under the assumption that any unreacted silica would not be materially affected by the acid, the heat released in the formation of the lime–silica product was about 11 Cal. per mole of CaO. The value is large enough to suggest chemical reaction.

That silica gel in aqueous suspension can interact with CaO at room temperature until it becomes apparently completely acid soluble was observed at least as early as 1883, being reported in that year by Landrin (106). Lerch and Bogue (122) observed that a sample of hydrous silica that had stood in saturated $Ca(OH)_2$ solution for a year had changed till 97 per cent of the silica was acid soluble. The soluble part of the product had the composition $1.07CaO:1SiO_2$. Shaw and MacIntire (158) reported that "numerous qualitative tests with solid residues, in which the factors of CaO/SiO_2 ratio and time were sufficient to assure the formation of $CaSiO_3$ have shown that this product is quickly and completely dissolved by cold dilute (1+9) HCl." Such solutions no doubt soon become colloidal, but apparently silicic acid can form initially in a state of true solution (69).

That definite, negatively charged silicate ions exist in appreciable concentrations in weakly alkaline solutions at room temperature is indicated by the work of many investigators (153). Moreover, as the $Ca(OH)_2$ concentration of the solution is raised, precipitation occurs and the SiO_2 concentration falls to a very low value (47). Thus, precipitation of a calcium silicate is strongly indicated. It is significant in this connection that hydrated barium silicate precipitates at room temperature, as Le Chatelier (117) showed.

Keisermann (81) found that methylene blue stains only free silicic acid and not the silicates. It gave a negative test with the gel produced by action of water on the anhydrous calcium silicates, except when in acid solution, in which case the test was positive. Accordingly, a silicate was believed to have been demonstrated. Blumenthal (16) confirmed these observations. Later, Diehl made similar tests (for Nacken (137)) on hydrating tricalcium silicate and also obtained similar results. As previously noted, Keisermann and Blumenthal also observed needle formations which staining tests (especially those by Blumenthal) indicated were calcium silicate.

Richter and Radczewski (150) found that silica sol that had adsorbed lime showed initially no electron-diffraction pattern attributable to a crystalline product, but soon gave such a pattern under the continued action of the electron radiation. Eitel (40) concluded from this that the products of cement hydration pass only temporarily through the "colloid-amorphous" state and soon become crystalline though highly disperse, i.e., crystalline colloids.

Chassevent (31) examined by x-ray the products of the interaction of limewater and silica sol, at ordinary temperature, and obtained within about 2 hr. an x-ray spectrum which remained, within the limits of accuracy of the observations, unchanged for products of varied CaO/SiO_2 ratios (a characteristic confirmed by Cirilli (35)). Later, Mlle. Foret (49) prepared (hydrothermally, below 140°C.) crystalline $CaO \cdot SiO_2 \cdot aq$, the composition of which she verified by chemical analysis, and which gave an x-ray spectrum which she considered identical with that obtained by Chassevent. Strätling (165), Brandenberger (19), Forsén (53), and Cirilli (35) have obtained a similar x-ray spectrum for hydrous lime-silica products prepared at ordinary temperature. Except for Brandenberger, who did not express an opinion, these latter authors believed their compounds to be more highly limed than $CaO \cdot SiO_2 \cdot aq$. Whatever the actual compounds or solid solutions that may be formed, the x-ray tests alone appear to be strong evidence that the lime does combine chemically with the silica at ordinary temperature. However, to recapitulate, the evidence for compound formation may be summarized as follows:

Lime acts on silica gel with destruction of the gel's original structure. The lime taken up gives, at first, a characteristic adsorption curve, but this curve changes with time until it strongly suggests the existence of an invariant point denoting the presence of two solid phases. The attendant heat evolution is large enough to suggest chemical reaction. Also, the silica in solution decreases markedly with increase in lime concentration, consistent qualitatively with maintenance of a solubility product for calcium silicate. Moreover, the silica in the solid becomes completely soluble in a moderate volume of acid. Staining tests also indicate that the silica is combined, and one of the better tests for free CaO or $Ca(OH)_2$ has given a negative result when applied to a precipitate believed to contain as much lime as silica. Under electron radiation an electron-diffraction spectrum soon appears. Examination by x-ray gives a diffraction spectrum that is apparently the same as one produced by microscopically crystalline hydrated calcium silicate.

VIII. COMPOUNDS FORMED AT LOW LIME CONCENTRATIONS

The curves of figure 1 that begin at the origins of the plots show, in general, an initial short section where the increase in the CaO/SiO_2 value is less rapid than for the abrupt rise which follows. In this initial region the solid phase is commonly believed to be simply the hydrous silica, the lime being merely adsorbed (8, 47, 88, 171). However, the more nearly vertical curve section that follows suggests chemical reaction, as already noted.

Hydrous calcium silicates that have been assumed at low lime concentrations, tentatively or otherwise, by the authors whose data are shown, in part, by figure 1, are listed in table 3. In most cases, the constitutions of the compounds were suggested simply by the points at which breaks in the experimental curves were observed. However, a degree of judgment was usually exercised in arriving at simple combining proportions. In some cases the CaO/SiO_2 value for the assumed compound is less than for the experimental point, a difference which can be attributed to adsorption. In other cases the assumed ratio is greater than the experimental one. Unless the difference can be attributed to analytical inaccuracy, it would seem that failure to obtain complete equilibrium would be the most plausible explanation. Van der Burgh (28) suggested adsorption to account for the fact that his curve rounds off before CaO/SiO_2 reaches 1,[7] but he appears to have meant simply that adsorption proceeded as though the SiO_2 had completely reacted whereas some remained, evidently in poor contact with the solution.

TABLE 3

Compounds that may exist at low lime concentrations (investigations represented in figure 1)

CURVE NO.	INVESTIGATORS	COMPOUNDS ASSUMED OR SUGGESTED			
		$CaO\cdot 2SiO_2\cdot aq$ (1:2)	$3CaO\cdot 4SiO_2\cdot aq$ (3:4)	$4CaO\cdot 5SiO_2\cdot aq$ (4:5)	$CaO\cdot SiO_2\cdot aq$ (1:1)
1.........	Baylis (7)				x
2.........	van der Burgh (28)				x
3.........	Shaw and MacIntire (158)		x		x
4.........	Flint and Wells (47)	x			x
5.........	Jolibois and Chassevent (74)				x
6.........	Beitlich (8)	x		x	
7.........	Krasil'nikov and Kiselev (88)				x
8.........	Bessey (11)				x
9.........	Roller and Ervin (152)	x	x		x
11–12......	Kühl and Mann (97)				x
13.........	Thorvaldson and Vigfusson (178)				x
14.........	Cirilli (34)				x
15.........	Tavasci (167)	x			x
16.........	Nacken (137)				x

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[7] Of somewhat similar nature is the suggestion by Kühl and Mann (100) that adsorption may account for the fact that they did not obtain a curve section strictly perpendicular to the CaO axis.

Flint and Wells (47), Roller and Ervin (152), and Cirilli (32) had other reasons for assuming the compound $CaO \cdot SiO_2 \cdot aq$. Flint and Wells determined both SiO_2 and CaO in solution and plotted one against the other, with the CaO/SiO_2 value for the solids also shown. A change in curve direction in a region where this CaO/SiO_2 value increased rapidly from 0.537 to 0.930 was assumed to denote formation of $CaO \cdot SiO_2 \cdot aq$.

Roller and Ervin tested their sloping curve sections for agreement with the Freundlich adsorption isotherm, by assuming adsorption on hydrated calcium silicates of various molar ratios. For the curve section at the higher CaO concentrations the agreement was best, and indeed very satisfactory, when they assumed adsorption on $CaO \cdot SiO_2 \cdot aq$. As a further test they estimated ion activities and showed that $CaO \cdot SiO_2 \cdot aq$ apparently maintains a constant activity solubility product within the same region.

Cirilli determined heats of solution after exposing hydrous silica for successively increased times to saturated $Ca(OH)_2$ solution. The values per gram of CaO remained constant until CaO/SiO_2 reached 1; then they increased.

Curves 3, 5, 15, and 16 of figure 1 that are due to Shaw and MacIntire (158), Jolibois and Chassevent (74), Tavasci (167), and Nacken (137) do not, themselves, show clearly why the authors believed in $CaO \cdot SiO_2 \cdot aq$. Shaw and MacIntire suggested that their curve might not have represented complete equilibrium. Jolibois and Chassevent were influenced by the fact that their precipitates had, initially, $CaO:SiO_2$ values close to 1:1; also, by the fact that the apparent invariant concentration, 0.053 g. CaO per liter, checked that given by Le Chatelier (117), whose work suggested the 1:1 compound. Tavasci was guided also by Le Chatelier's value of 0.052 g. CaO per liter; he found 0.053 g. CaO per liter when CaO/SiO_2 in solids was about 1. He also found that the CaO concentration was the same for the two CaO/SiO_2 values 1.0 and 1.1. Nacken was influenced by the belief that he was obtaining a succession of definite compounds (see dashed line in curve 16, figure 1).

As mentioned in Section II, Jordis and Kanter appear to have produced a hydrated monocalcium silicate, but it was obtained at about 100°C. Le Chatelier's evidence, previously presented, is obviously more suggestive than conclusive with respect to exact compound composition. Schott (157) experimented with portland cement, using a special technique, and also obtained a colloidal product whose analysis was closely that of $CaO \cdot SiO_2 \cdot aq$. Hedin (67), working with Forsén (52), found that $3CaO \cdot SiO_2$ shaken with a large volume of water gives a voluminous precipitate analyzing initially 1.05–1.13 CaO to 1 SiO_2.

It will be recognized that some of the evidence on which the compound $CaO \cdot SiO_2 \cdot aq$ has been assumed is very weak and much of the rest merely suggests a compound having a $CaO:SiO_2$ ratio of *about* 1:1. The method of Roller and Ervin (based on the solubility product) appears somewhat more decisive, but it is dependent on acid-dissociation constants that are not well established (see Section X). Cirilli's heat data seem significant, but their simplicity may be deceptive. That is, since the solution was kept saturated with $Ca(OH)_2$, the equilibrium product toward which the reaction tended was always one having a

$CaO:SiO_2$ ratio considerably greater than 1:1. It would seem that either adsorption or formation of a compound higher limed than 1:1 tended to occur. Why the curve should break precisely at the 1:1 point is thus left somewhat obscure. On the other hand, Cirilli later (34) reported heat data for hydrolysis products of $3CaO \cdot SiO_2$ which show a break at the same 1:1 composition.

The x-ray studies mentioned in Section VII appear to be as good evidence as any for the formation of $CaO \cdot SiO_2 \cdot aq$ at ordinary temperature. Mlle. Foret's crystals, analyzed as $CaO \cdot SiO_2 \cdot aq$, gave the same spectrum as Chassevent's room-temperature preparations. Moreover, Mlle. Foret later (50) tried a CaO to SiO_2 ratio of 2 and found that the hydrothermal products obtained at 130°C. or less were still $CaO \cdot SiO_2 \cdot aq$, plus free CaO, and gave the same spectrum for the hydrated calcium silicate as before. However, as mentioned earlier, certain other investigators who obtained practically the same spectrum believed that it represented a compound higher limed than $CaO \cdot SiO_2 \cdot aq$.

Kühl and Mann (97), after reviewing the literature up to 1934, concluded that the formation of $CaO \cdot SiO_2 \cdot aq$ (presumably at room temperature) could be considered as established. In 1938 Thorvaldson (173) did not regard the matter as fully settled but Bessey (12) believed that there was little room for doubt.

Several experimenters have concluded that their data show that compounds lower in lime than $CaO \cdot SiO_2 \cdot aq$ are not formed at room temperature. Authors who make a definite statement to this effect are Kühl and Mann (102), Cirilli (32), and Krasil'nikov and Kiselev (88). Cirilli based his opinion on his evidence, already mentioned, that when silica gel is exposed to a solution kept saturated with $Ca(OH)_2$ the heat released per gram of CaO taken up remains constant until the ratio CaO/SiO_2 reaches 1. However, the fact that the solution was kept saturated with $Ca(OH)_2$ would seem to destroy the value of the evidence with respect to equilibrium at low lime concentration. Cirilli's (34) later heats of solution for hydrolysis products of $3CaO \cdot SiO_2$ cover only one composition that has a CaO/SiO_2 value below 1. The other authors relied on the fact that their data indicated that solutions in equilibrium with solids for which the CaO/SiO_2 value varied from about 0 to nearly 1 were almost invariant in CaO concentration. Van der Burgh (28), who obtained similar results, is not as explicit but appears to have been confident that $CaO \cdot SiO_2 \cdot aq$ is the first compound formed. Bessey (11) pointed out that the experiments of Lerch and Bogue (122), in which leaching of $3CaO \cdot SiO_2$ left a residue of hydrous silica, indicate that $CaO \cdot SiO_2 \cdot aq$ must dissolve incongruently, whereas Flint and Wells' (47) interpretation of their curve requires congruent solution. This discrepancy had been reported previously by Lea and Desch (114; see also 137). Bessey concluded from it that all of Flint and Wells' solubility curve up to a point at which CaO/SiO_2 for the solution exceeds 1 represents metastable conditions. Hence, he concluded that under equilibrium conditions $CaO \cdot SiO_2 \cdot aq$ is the lowest-limed silicate hydrate; this, however, is not a necessary conclusion from the Lerch and Bogue experiments.

The experimenters who expressed a belief in compounds lower limed than $CaO \cdot SiO_2 \cdot aq$ generally relied mainly on breaks in their curves. Roller and

Ervin (152) had no direct experimental data of their own for $CaO \cdot 2SiO_2 \cdot aq$, but considered that the solid next below their assumed compound $3CaO \cdot 4SiO_2 \cdot aq$ could not be silica. They believed that the solubility of gelatinous silica is greater than the concentration which they found at the invariant point in question. These authors found that their Freundlich isotherm test was indecisive with respect to $3CaO \cdot 4SiO_2 \cdot aq$. The decision in favor of this compound was made on the basis of the solubility product test. Assumptions were involved which will be indicated in Section X. Flint and Wells' solubility data (47) indicated an abrupt decrease in SiO_2 concentration beginning at the point where CaO/SiO_2 for the solid first reached 0.1. Though the solid did not attain a CaO/SiO_2 value of 0.5 until the SiO_2 concentration had dropped very materially, it was thought that equilibrium was probably not fully attained and that the break in the curve represented formation of $CaO \cdot 2SiO_2 \cdot aq$. The authors were apparently influenced also by consideration of the ions with one charge per silicon atom which their mathematical analysis suggested were present in solution (see later). There is of course other evidence also that such ions exist in solutions of moderate alkalinity (73, 181, 182).

To summarize, apparently one or more hydrated calcium silicates are formed at low lime concentrations, at ordinary temperature. One of these compounds is probably $CaO \cdot SiO_2 \cdot aq$. Whether there are others, and what their compositions may be, are matters that seem to be less well established.

IX. INVARIANT CONCENTRATIONS

Owing to the difficulties inherent in the investigation of a colloidal system, it is not surprising that a number of investigators have been content to treat as essentially invariant, and indicative of a phase transition, solutions that show changes of a few hundredths of a gram of CaO per liter during the rapid rise in the CaO/SiO_2 value for the solids. Changes in the SiO_2 concentration have also been disregarded. Sometimes the SiO_2 concentrations were not known, but investigators who determined them found marked variations at the assumed invariant point. Generally the SiO_2 concentration reached a maximum at about the start of the abrupt increase in CaO/SiO_2 in solids and then declined markedly during the completion of the rise. Disregard of such differences is traceable in some cases (7,88) to a belief that a part of the silica may have been in sol form. Not all authors disregarded the variations in either CaO or SiO_2; Shaw and MacIntire (158) and Flint and Wells (47) attached considerable importance to them.

In table 4 are assembled data obtained by the various investigators for the regions of abrupt change in the CaO/SiO_2 ratio in solids. The concentration ranges are given as maximum and minimum rather than initial and final values, since the maximum, especially for CaO, often occurs between the latter values. In such cases the final value is the one taken as minimum, since the initial value for the rise is commonly less definite. Maximum values are given first if they exceed the final values but not if they *are* the final values. The SiO_2 values corresponding to given CaO values are not in general brought out by this arrangement, but the minimum values are mates in all cases where reported, except for

TABLE 4

Concentrations of CaO *and* SiO_2 *in solution in regions where the* CaO/SiO_2 *value for the solid changes abruptly*

Some of the values reported were taken from curves; included are some concentration data for apparent invariant points but for which the corresponding CaO/SiO_2 values for the solids are not available

CURVE NO.	INVESTIGATORS	SOLID	SOLUTION		REMARKS
		CaO/SiO_2	CaO	SiO_2	
		molar	*grams per liter*	*grams per liter*	
1.....	Baylis (7)	0.2–1.08	0.12–0.08	0.22–0.05	
2.....	van der Burgh (28)	0.1–0.85	0.118–0.084		
3.....	Shaw and MacIntire (158)	0.46–0.80	0.12–0.07	0.23–0.03	
4.....	Flint and Wells (47)	0.1–1.07	0.102–0.049	0.33–0.05	
5.....	Jolibois and Chassevent (74)	0.83–1.53 1.17–1.53	0.033–0.053 0.055–0.053	0.22–0.06	
6.....	Beitlich (8)....	0.28–0.77 0.28–0.53	0.041–0.073 0.041–0.042		
7.....	Krasil'nikov and Kiselev (88)	0.1–0.9	0.090 0.086 0.087	0.20–0.03	The CaO values of 0.086 and 0.087 were obtained in experiments on tripoli and diatomaceous earth
8.....	Bessey (11)	–0.97	0.050–0.055	0.035–0.050	Concentration ranges reported by author without comment
9.....	Roller and Ervin (152)	0.82–0.87 0.97–1.08	0.050 0.173	0.041+ 0.006	The SiO_2 concentration of 0.041 g./l. was obtained at 0.056 g. CaO per liter, the lowest CaO concentration tested
12.....	Kühl and Mann (97)	0.1–1.0	0.11–0.13		
13.....	Thorvaldson and Vigfusson (178)	0.16–1.07	0.06–0.15		This line is for $2CaO \cdot SiO_2$
		0.37–1.10	0.19–0.24		This line is for $3CaO \cdot SiO_2$ (see Section XVI)
14.....	Cirilli (34, 35)	0.53–1.00	0.065–0.075		
15.....	Tavasci (167)	0.2–1.44	0.03–0.077	0.02–0.038	
	Le Chatelier (117)		0.052		
	Michaelis (134)	(0.5)	0.051	0.042	Results of a single test when CaO/SiO_2 in solids was about 0.5

TABLE 4—*Concluded*

CURVE NO.	INVESTIGATORS	SOLID	SOLUTION		REMARKS
		CaO/SiO_2	CaO	SiO_2	
		molar	*grams per liter*	*grams per liter*	
	Lafuma (104)		0.052		This invariant concentration was reported in work on portland cement
	Kolthoff and Stenger (86)		Less than 0.028		See discussion at end of reference 86
	Maffei (126)		0.09		The data suggest that the value is between 0.09 and 0.13; K. and K. (88) give it as 0.09
	Cummins and Miller (36)		0.11	0.18	pH given as 9.6; solid phases indicated were silica and $5CaO \cdot 6SiO_2 \cdot aq$
	Weisberg		0.046		Reported by Bessey (11); no reference given to previous publication
	Kind and Aleksandrovskiĭ (83)		0.118		Cited by Krasil'nikov and Kiselev (88)

Jolibois and Chassevent's tests and perhaps in Bessey's tests. Bessey reported his ranges without comment, and the statements made here do not necessarily apply in his case.

Where a concentration range is not reported this does not necessarily mean that the absence of one was demonstrated. In some of these cases only single determinations were available. However, the separate CaO concentrations reported for Krasil'nikov and Kiselev (88) and Roller and Ervin (152) can be considered to apply over the range of solids indicated. The range in CaO shown for van der Burgh (28) is perhaps best regarded as representing the precision rather than as denoting a definite trend.

When both the CaO and SiO_2 concentrations are considered, it does not appear that any of the investigators demonstrated strict invariance.

For comparison with the values given in table 4 it may be remarked that various authors (7, 47, 152, 158) have found that the SiO_2 concentration is already reduced to less than 0.01 g. per liter when the CaO concentration has reached 0.15 g. per liter. The SiO_2 concentration continues to diminish, of course, as the CaO concentration is further increased.

As has been mentioned, Flint and Wells (47) treated their variations in CaO and SiO_2 concentrations as significant throughout. As shown in the previous section, they regarded each apparent cusp in the solubility curve as an invariant point representing a solid-phase transition. The evidence for this interpretation would have been much stronger had solids of varied CaO/SiO_2 ratios been found in apparent equilibrium with the solution represented at such a cusp. However, the preparations that were tried did not provide evidence of this nature. Krasil'nikov and Kiselev (88) pointed out that, as plotted in figure 1, Flint and Wells' data appear much like their own. The Russian authors obtained a CaO concentration so invariant that they attached no importance to the variation in SiO_2, which could be attributed to SiO_2 in sol form. Kryagova (90) has obtained results which he considers to be in essential agreement with those of Flint and Wells. However, Kryagova's comparison was made entirely on the basis of CaO/SiO_2 values, for both solutions and solids. When the individual concentrations are considered, and also when the comparison is carried to higher CaO/SiO_2 values for the solids, marked differences appear.

Relative to the retrogression in CaO concentrations obtained in several investigations as the CaO/SiO_2 ratio in solids approached 1, it is of interest that in two of these cases (Baylis (7), and Shaw and MacIntire (158)) the authors determined the pH as well as CaO and found that the former increased without significant retrogression as CaO/SiO_2 for the solids was increased. Baylis found pH values of 10.1 to 10.8 over the range in CaO/SiO_2 values of 0.1 to 1.1 for the solid. Shaw and MacIntire reported pH values a few tenths higher.

X. IONS IN SOLUTION: WORK OF FLINT AND WELLS AND OF ROLLER AND ERVIN

Owing to the difficulties presented by the $CaO-SiO_2-H_2O$ system, a knowledge of the silicate ions in solution has been sought by some of the investigators. Flint and Wells (47) sought this information for whatever clue it might give relative to compounds present in the solids. Roller and Ervin (152) estimated ion activities in order to apply the activity solubility product principle in their tests for particular solid compounds. In both cases the investigators worked directly with calcium silicate solutions. Previous studies of the silicate ions in solution have generally been made with alkali silicates. These other studies still leave much uncertainty but are commonly considered to indicate at least two stages of ionization, of either meta- or ortho-silicic acid (152) though a disilicate ion has also been assumed (72, 182). In recent articles (30, 147) the orthosilicate formulation is preferred over the metasilicate, because silicon is invariably found at the center of an oxygen tetrahedron in crystalline silicates (43) as well as in vitreous silica and soda-silica glasses (58). At the higher alkalinities (pH 10.7 and greater) apparently little or none of the silica in solution is in a colloidal state (153).

Flint and Wells concluded that the silicate ions were those of orthosilicic acid, H_4SiO_4, and that each of the four steps of acid ionization was dominant over a part of the range in $Ca(OH)_2$ concentration. They calculated each hydrolysis constant independently, treating as negligible the concentrations of silicate ions not directly involved. The final choice of concentration range for the calculation of each constant rested in part on the ratios of silicate CaO[8] to total SiO_2, and

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[8] The CaO in solution in excess of that equivalent to OH^- was called combined CaO by the authors and is here called silicate CaO. Concentrations of CaO, SiO_2, and OH^- were obtained experimentally.

in part on the degree of invariance shown by the resultant "constants" within the trial range. Ions of orthosilicic acid, rather than metasilicic acid, were assumed by necessity, since the experimental ratio of silicate CaO to SiO_2 was greater than 1 at the higher CaO concentrations.

The second hydrolysis constant came out a little larger than the first, but this anomaly was attributed simply to experimental inaccuracy. Acid ionization constants calculated from the third and fourth hydrolysis constants agreed satisfactorily with ones reported by other investigators, on the basis of electrometric titrations of sodium silicate solutions. The other ionization constants could not be similarly compared, since only two steps of acid ionization were assumed in these other investigations. On the whole it appeared that the calculations gave reasonable results, and, since the various constants had been found not to change much when calculated for different solutions, the authors apparently felt justified in their assumption that the silicate ions were those of H_4SiO_4.

The results of the study can be used, however, to show that in some cases neglected ions may have been present in considerable concentrations. For example, the third hydrolysis constant, K_{h_3}, can be used to check the appropriateness of the neglect of $H_3SiO_4^-$ in the determination of the second constant, K_{h_2}. When this check is applied to the data of test 1 of Flint and Wells' table 5, $[H_3SiO_4^-] \div [H_2SiO_4^{--}]$ is indicated to be 0.57. The neglected ion is thus indicated to have a concentration of more than half that of one of the ions directly involved. Owing to indications of this kind, the present writer has calculated the four hydrolysis constants simultaneously without neglecting any of the silicate-ion concentrations. Data from the four pH ranges utilized by Flint and Wells were employed, and the constants were calculated both without and with the use of activity coefficients. In the first case the practice corresponds to that of Flint and Wells. For the second calculation the activity coefficients were estimated by treating all anions as singly charged when computing ionic strength. Comparison with more precise methods indicated that this approximation, which was also used by Roller and Ervin, is reasonably satisfactory. Irrespective of the use of activity coefficients the third and fourth hydrolysis constants came out much the same as those derived by Flint and Wells, but the first and second hydrolysis constants were negative, indicating an unreal situation.[9] To eliminate the influence of this

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[9] The four equations for the four steps of hydrolysis of Ca_2SiO_4, the equation expressing the distribution of SiO_2, and the equation for balance of electric charges were solved simultaneously to express the concentrations of silicate ions and undissociated H_4SiO_4 in terms of the hydrolysis constants. The equation obtained was

$$\frac{A}{f_0} + \frac{(OH^-)}{f_1}(A - \underline{SiO_2})I + \frac{(OH^-)^2}{f_2}(A - 2\underline{SiO_2})II + \frac{(OH^-)^3}{f_3}(A - 3\underline{SiO_2})III + \frac{(OH^-)^4}{f_4}(A - 4\underline{SiO_2})IIII = 0 \quad (1)$$

where $\underline{SiO_2}$ is the total concentration of SiO_2 in moles per liter, (OH^-) is the activity of OH^- on the molar basis, f_0 is the activity coefficient (taken as unity) for the undissociated H_4SiO_4, and the other f's are the activity coefficients for silicate ions having the number anomalous result, similar simultaneous solutions were made using only the two lowest pH ranges and assuming only two steps of hydrolysis. This also gave values comparable with those found by Flint and Wells for the third and fourth hydrolysis steps.

Thus, there may well be two stages of hydrolysis corresponding to two stages of acid ionization, but the only support that remains for the assumption that other stages of ionization are involved is the experimental indication that in some solutions the ratio of silicate CaO to SiO_2 exceeds 1. This experimental evidence must be considered in the light of the fact that the solutions concerned were very highly supersaturated with calcium silicate, and actually precipitated before the potential readings that gave the $Ca(OH)_2$ concentration were obtained. Though the authors were able to show that readings obtained at lower lime concentrations were unaffected by such precipitation, the evidence is obviously not as strong as it would have been had the solutions been stable. It should be remarked, however, that supersaturated solutions were also obtained by the action of water on anhydrous β-$2CaO \cdot SiO_2$ and $3CaO \cdot SiO_2$. It was possible to test these solu-

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of charges given by the subscripts. The A is

$$2\underline{CaO} + \frac{K_w}{f_{1+}\,(OH^-)} - \frac{(OH^-)}{f_{1-}}$$

where $\underline{CaO}$ is the total concentration of CaO in moles per liter, K_w is the ionization constan for water, and the f_{1-} and f_{1+} are the activity coefficients for OH^- and H^+, respectively The $\frac{K_w}{f_{1+}\,(OH^-)}$ is the concentration of H^+ and was shown to be negligible in all instances The I, II, III, and IIII are reciprocals of K_{h_4}, $K_{h_3}K_{h_4}$, $K_{h_2}K_{h_3}K_{h_4}$, and $K_{h_1}K_{h_2}K_{h_3}K_{h_4}$ respectively, where the K's with their subscripts denote the four successive hydrolysis constants, with K_{h_1} representing the first step of hydrolysis, namely,

$$K_{h_1} = \frac{(HSiO_4^{---})\,(OH^-)}{(SiO_4^{----})}$$

The hydrolysis constants themselves are evaluated as follows:

$$K_{h_4} = \frac{1}{I},\ K_{h_3} = \frac{I}{II},\ K_{h_2} = \frac{II}{III},\ K_{h_1} = \frac{III}{IIII}$$

Equation 1 was set up for four different solutions, one for each of Flint and Wells' pH ranges within which $\underline{SiO_2}$, $\underline{CaO}$, and $\frac{(OH^-)}{f_{1-}}$ had been determined experimentally. From the four resultant equations the K_h values were determined by simultaneous solution. Using data for which the Flint and Wells table and test numbers are 3:8, 4:8, 5:7, and 6:1, the writer obtained the following results:

	ALL ACTIVITY COEFFICIENTS TAKEN AS UNITY	ACTIVITY COEFFICIENTS ESTIMATED FROM $-\log_{10} f = \frac{0.505z^2\sqrt{\mu}}{1 + z\sqrt{\mu}}$ (82)
K_{h_4}	7.0×10^{-5}	7.2×10^{-5}
K_{h_3}	4.7×10^{-3}	8.6×10^{-3}
K_{h_2}	-1.5×10^{-2}	-6.2×10^{-2}
K_{h_1}	-1.2×10^{-2}	-1.0×10^{-2}

tions before precipitation (190), and they also showed ratios of silicate CaO to SiO_2 that were greater than 1. Such evidence is obviously better, though the instability of the solutions is still a disturbing factor. One can imagine that the very strongly supersaturated solutions may have contained molecular aggregations too small for detection by the available means. It appears that precise determinations made on solutions that are not supersaturated are needed to settle these questions. Should a CaO/SiO_2 value greater than 1 be established, it might mean either that more than two stages of ionization of orthosilicic acid are involved or that a complex ion is formed.

Roller and Ervin's (152) study, based on the solubility product principle, proceeds from the following reasoning: If adsorption alone is responsible for the continuous increase in CaO/SiO_2 in the solids with increase in the CaO in solution, then the adsorbing compounds, being of constant composition, should maintain constant activity solubility products over their respective regions of stability.

In their first calculations Roller and Ervin simply assumed two stages of hydrolysis corresponding to two stages of acid ionization and used ionization constants that are approximate averages of published values. For various reasons they believed that the silicate ions were derived from orthosilicic acid. Hence they assumed the ions $H_2SiO_4^{--}$ and $H_3SiO_4^-$ although, as they point out, the analysis would still be the same if SiO_3^{--} and $HSiO_3^-$ were assumed instead. They did not have direct evidence of their own for the conclusion that the $H_2SiO_4^{--}$ does not dissociate significantly, for they did not determine experimentally the ratios of silicate CaO to SiO_2. The total CaO and SiO_2 concentrations were determined directly, but OH^- was estimated. This was feasible because the SiO_2 concentration was generally very small in relation to the total CaO concentration. Estimates were compared with acid titrations carried to the phenolphthalein end point.

Proceeding on the stated basis, the authors were able to show that the compound $CaH_2SiO_4 \cdot aq$ (or $CaO \cdot SiO_2 \cdot aq$) appears to maintain a constant activity solubility product over the range in CaO concentrations that extends to the right of the final, short vertical rise in their curve (No. 9) of figure 1. However, over the range in CaO to the left of this point, constancy could only be obtained by assuming an addition compound containing about eight of the doubly charged silicate ions to each of the singly charged ones. Believing such a compound to be unreasonable, the authors preferred to assume association of the silicate ions in solution, particularly in the region of the lower CaO concentrations, with production of dimers corresponding to the acid $H_4Si_2O_6$. Proceeding on this basis, they completely redetermined all anion activities, though again they simply assumed values for certain of the ionization constants on the basis of other published data (electrometric titrations). On this new basis, the compound $CaH_2SiO_4 \cdot aq$ still proved satisfactory in the higher CaO range where the dimer ions represented only a minor part of the SiO_2. Over the lower CaO range the compound $Ca_3(HSi_2O_6)_2 \cdot aq$ (or $3CaO \cdot 4SiO_2 \cdot aq$) maintained a constant ion product, and hence appeared to be the stable compound in that region.

By these studies Roller and Ervin appear to have added materially to the grounds for the adsorption hypothesis. They make the existence of certain compounds and ions appear plausible, but the ionization constants of silicic acid and the various activity coefficients can scarcely be said to be known well enough for any more definite conclusions. The present writer has found, by trial, that a somewhat different but apparently equally appropriate way of estimating the activity coefficients $\left(\text{namely, by use of the equation} -\log_{10} f = \frac{0.505z^2\sqrt{\mu}}{1+z\sqrt{\mu}}\ (82)\right)$ is sufficient to introduce a considerable progressive change in the ion product for $CaH_2SiO_4 \cdot aq$. Yet, complete constancy can be restored by making only such changes in the assumed acid ionization constants as are permitted by the range in the published values for the constants.

It does not appear that the silicate ions in solution have as yet been well established.

XI. ADSORPTION *versus* SOLID SOLUTION

The continuous increase in CaO/SiO_2 for the solids with increase in CaO in solution that occurs after the apparent formation of compounds at low CaO concentrations has been explained generally as denoting either adsorption or solid solution. If colloidal equilibrium is assumed to have been established, these are the only very obvious possibilities. According to the phase rule, the solution phase in a three-component system at constant temperature can change only when just one solid phase is present.[10] As brought out in Section III, some change is possible when two solid phases are present if the solid particles are submicroscopic in size, owing to the fact that the solubility of small particles varies with their sizes. However, it seems unlikely that such wide ranges in CaO concentration as are here concerned could be explained on this basis, or that, if the solid phases *are* of fixed composition and non-adsorptive, horizontal curve sections representing single solid phases should not appear in addition to the sloping sections (figure 1).

Several investigators followed Le Chatelier in assuming adsorption. Baylis (7), Shaw and MacIntire (158), Beitlich (8), and Roller and Ervin (152) reported that the data for their sloping curve sections conformed to Freundlich adsorption isotherms. However, only Roller and Ervin appear to have taken due account of the chemically bound CaO, by deducting the CaO in the assumed compound. In any case, agreement with a Freundlich isotherm is simply an indication rather than a proof of adsorption; also, disagreement does not disprove adsorption (59, 187). The use made of the solubility product principle by Roller and Ervin provides further evidence in support of adsorption but, as previously discussed, is also not decisive. The fact that Chassevent (31) obtained the same x-ray spectrum for gels of varied lime content is interesting, but the author himself remarked that the bands were broad and not sharply enough defined to eliminate the possibility of some solid solution. Baylis (7) made an observation that seems to warrant further investigation; he made silica gels with varied

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[10] Adsorbed material is not to be treated as an additional phase in applications of the phase rule (4).

amounts of water and found an apparent influence on the amount of CaO taken up, the denser gels taking up the least CaO.

Little relative to ion-exchange properties has been reported. However, in the presence of sodium hydroxide in the lime solution, the calcium silicate gel loses some of its CaO, which is replaced by a lesser amount of Na_2O (see Section XVII). Sloane, McCaughey, Foster, and Shreve (160) found that when β-$2CaO \cdot SiO_2$ that had been placed in a solution of calcium chloride was washed first with water and then with magnesium nitrate solution the first portion of magnesium nitrate solution increased markedly the rate at which lime was brought into solution. A similar test was later made by Steinour and Ledyard (163) on β-$2CaO \cdot SiO_2$ hydrating in plain water. Use of magnesium chloride solution increased the rate at which lime was brought into solution, though in this case no calcium chloride had been employed. To be considered, of course, in both cases, is the extent to which the results may have been influenced by double decomposition. However, Steinour (162) found, by electroösmosis, that β-$2CaO \cdot SiO_2$ particles in plain water, and in $Ca(OH)_2$ solution, carry a positive charge which can be varied by solutions of salts in accordance with the Schulze–Hardy rule, and can be reversed by sufficiently high concentrations of salts having negative ions of higher valence than 1. Calcium and barium salts having monovalent anions were found to increase the positive charge. In this connection it is of interest that Shaw and MacIntire (158) found that calcium chloride increased the CaO/SiO_2 value of the lime–silica gel.

Of the various investigators who assumed solid solution, Cirilli (32, 34) appears to have been the only one to advance experimental evidence for this preference. He found, as has already been reported, that the heat of solution of the gel, per gram of CaO, remained constant for gels for which the CaO/SiO_2 value was less than 1; but when CaO/SiO_2 was greater than 1, the increase in heat of solution was more than it should have been for $CaO \cdot SiO_2 \cdot aq$ plus $Ca(OH)_2$. However, though the difference reached a magnitude of about 20 cal. per gram of CaO at $CaO/SiO_2 = 1.5$, the present writer is more impressed by the degree of correspondence than by the differences, especially since there is no definite indication of a break in the curve as it is continued into the region beyond $CaO/SiO_2 = 1.5$, where Cirilli (35) found free $Ca(OH)_2$. Possibly the thermal discrepancy found by Cirilli can be accounted for on the basis of the fine subdivision of the adsorbed lime.

Bessey (11) and Cirilli (34) thought it probable that solid solutions are formed between $CaO \cdot SiO_2 \cdot aq$ and $3CaO \cdot 2SiO_2 \cdot aq$, because at the end of the gradual rise in CaO/SiO_2 this ratio was about 1.5. However, as Keevil and Thorvaldson (80) remarked, there is no very substantial evidence for assuming that the gel for which CaO/SiO_2 is 1.5 is the definite compound $3CaO \cdot 2SiO_2 \cdot aq$. The solid solution might be between $CaO \cdot SiO_2 \cdot aq$ and $2CaO \cdot SiO_2 \cdot aq$; the value of CaO/SiO_2 that happens to be reached when the solution becomes saturated with $Ca(OH)_2$ is not very informative (101). Bessey, of course, was influenced by the belief that not $Ca(OH)_2$, but $2CaO \cdot SiO_2 \cdot aq$, was formed next after the gradual rise in the curve.

Experimental evidence bearing upon the kind of solid solution that might be formed is meager. Kühl and Mann (102) regarded the gel as initially amorphous, evidently on the basis of negative results of early x-ray diffraction tests (92). Bessey (11) also wrote of the gel as amorphous. However, the latest x-ray evidence indicates a finely crystalline structure (Section VII). Büssem (25) presents a brief discussion in which he seems to imply mixed crystals, or solid solution based on supposed isomorphism of $CaO \cdot SiO_2 \cdot aq$ and $3CaO \cdot 2SiO_2 \cdot aq$. He mentions in this connection the fact that Chassevent, and Strätling, obtained practically the same x-ray spectrum, though they believed their gels to be $CaO \cdot SiO_2 \cdot aq$ and $3CaO \cdot 2SiO_2 \cdot aq$, respectively.

Lafuma (105), Tavasci (167), and Keevil and Thorvaldson (80) have suggested that the gel is zeolitic with respect to its variability in lime content. Though the term zeolitic is sometimes used very broadly (42), Lafuma makes it clear that he has in mind an open crystalline structure like that of the true zeolites. The expansible layer structure of colloidal clays, called zeolitic by some authors (42), can also be regarded as a possibility. In either case, the structures can evidently be regarded as solid solutions, since they constitute single phases.

A fact that needs to be borne in mind when considering these possibilities is that the solid can apparently vary continuously in equilibrium water content much as it does in CaO content but independently of the latter variation (see Section XV). It appears, also, that for some preparations the time required for complete readjustment in CaO or H_2O is no more than a few hours or a few days. Either an open or expansible structure or an exceedingly fine state of subdivision seems to be indicated. Indeed, if the gel is $CaO \cdot SiO_2 \cdot aq$ plus adsorbed lime, it would seem that the degree of subdivision of the solid must approach the molecular in one or more dimensions, because 0.5 to 1 mole of $Ca(OH)_2$ must be adsorbed per mole of $CaO \cdot SiO_2 \cdot aq$. In this connection, Roller and Ervin (152) have pointed out that Weiser, Milligan, and Bates (188) have apparently demonstrated similar degrees of adsorption by other compounds. An adsorptive or a zeolitic type of structure is suggested by x-ray studies made by Strätling (165). This investigator found that heating the colloidal hydrous calcium silicate to 250°C. did not change the x-ray spectrum. Also, Mlle. Foret (49) reported that variation in the water contents of her hydrothermally prepared crystalline monocalcium silicate hydrates did not change their x-ray spectra.

It seems worth mentioning that zeolitic or any other type of solid solution does not explain, as readily as does adsorption, the different CaO/SiO_2 values obtained in various supposed equilibrium studies at the same CaO concentrations. If the internal structures are the same, the CaO/SiO_2 values at equilibrium should apparently be the same also, except as they are influenced by different amounts of external adsorption. It seems possible, however, that an expansible layer structure might expand irregularly (68), with dependence upon the manner in which it had been prepared or upon traces of impurities. In any case, the fact should not be overlooked that a zeolitic solid solution can evidently be considered a special kind of internal adsorptive system. Indeed, synthetic ion-exchange resins, of zeolitic nature, are commonly called exchange-adsorbents, and provide data that conform to the Freundlich adsorption isotherm (136). When a zeolitic structure adsorbs physically simply by reason of its fine porosity, the process resembles physical adsorption (5); on the other hand, base exchange in a zeolite is evidently closely related to chemical adsorption.

XII. PRODUCTS FORMED IN SATURATED AND SUPERSATURATED LIMEWATER

Table 5 shows the CaO/SiO_2 values for the solids that were found by various authors to be in apparent equilibrium with solutions saturated or nearly saturated with $Ca(OH)_2$. Some values have also been added, with a plus sign, which were obtained in investigations in which the highest concentration of $Ca(OH)_2$ in solution was still considerably below the saturation value. Only studies in which the volume of solution was very large in proportion to the weight of solid are reported; studies made on pastes are reported in the next section. The states of chemical combination that were assumed by the various investigators are given in the final column of the table. Where the theoretical ratio is less than the experimental one, adsorption was ordinarily assumed. Klasse and Kühl (84) and Flint and Wells (47) obtained values distinctly below 2, but they were inclined to assume that, had equilibrium been fully attained, $2CaO \cdot SiO_2 \cdot aq$ might have resulted.

There is not, however, the same reason to assume some definite silicate compound at the lime saturation point as there is at the top of the nearly vertical curve section (figure 1) that occurs at low CaO concentration. The change from a gradual slope to a nearly vertical one that occurs at lime saturation means simply that $Ca(OH)_2$ begins to precipitate. Kühl and Mann (97) found that when the solution supersaturates with respect to $Ca(OH)_2$, the curve (No. 12, figure 1) continues smoothly beyond the saturation point. The rise becomes more rapid as the saturation point is passed, but the authors were inclined to attribute this to deposition of some $Ca(OH)_2$. Hedin (67), however, obtained a similar shape of supersaturation curve (No. 10, figure 1) and was unable to detect free $Ca(OH)_2$ microscopically. As $Ca(OH)_2$ might be deposited in a very fine state, the inability to observe it probably does not demonstrate its absence. Of some interest in this connection is the fact that Thorvaldson and Vigfusson (178) found that their curves (No. 13, figure 1) passed through the lime saturation point without a significant change in slope. In the investigations of Kühl and Mann, and of Hedin, CaO/SiO_2 values of 2 were reached and the authors were of the opinion that much of the controversy in the literature as to the CaO/SiO_2 value obtainable in the gel is the result of varied degrees of supersaturation. The ability of $3CaO \cdot SiO_2$ and β-$2CaO \cdot SiO_2$ to form supersaturated $Ca(OH)_2$ solutions which can remain supersaturated for long periods is well known (87, 103, 122, 137, 167). Hedin advanced the idea that if $2CaO \cdot SiO_2 \cdot aq$ has begun to form as a result of supersaturation of the solution with $Ca(OH)_2$, it may perhaps still continue to form after the concentration of the solution has been lowered.

Forsén (52) reported experiments which led him to conclude that the hydrated calcium silicate in equilibrium with saturated limewater is $2CaO \cdot SiO_2 \cdot 4H_2O$.

TABLE 5

*Composition of lime-silica gel found in apparent equilibrium with saturated limewater**

CURVE NO.	INVESTIGATORS	MOLAR CaO/SiO_2 IN SOLIDS	INTERPRETATION GIVEN
1	Baylis (7)	1.2–1.5	$CaO \cdot SiO_2 \cdot aq$ plus adsorbed lime
2	van der Burgh (28)	1.4	$CaO \cdot SiO_2 \cdot aq$ plus adsorbed lime
3	Shaw and MacIntire (158)	1.3	$CaO \cdot SiO_2 \cdot aq$ plus adsorbed lime
4	Flint and Wells (47)	1.85	No definite conclusion, but $2CaO \cdot SiO_2 \cdot aq$ suggested
5	Jolibois and Chassevent (74)	1.6+	$CaO \cdot SiO_2 \cdot aq$ plus adsorbed lime (see also reference 31)
6	Beitlich (8)	2.0	$2CaO \cdot SiO_2 \cdot aq$
7	Krasil'nikov and Kiselev (88)	1.9+	No definite conclusion
8	Bessey (11)	2.1	$2CaO \cdot SiO_2 \cdot aq$
9	Roller and Ervin (152)	1.45	$CaO \cdot SiO_2 \cdot aq$ plus adsorbed lime
10	Hedin (67)	1.5	$3CaO \cdot 2SiO_2 \cdot aq$
11 12	Kühl and Mann (97)	1.5	No definite conclusion
13	Thorvaldson and Vigfusson (178)	1.45	No definite conclusion
14	Cirilli (34)	1.4	$3CaO \cdot 2SiO_2 \cdot aq$ (Cirilli called the saturation ratio 1.5)
15	Tavasci (167)	1.7	$5CaO \cdot 3SiO_2 \cdot aq$
16	Nacken (137)	2.15+	$2CaO \cdot SiO_2 \cdot aq$ (in reference 137; in reference 138 a marked decrease in ratio was reported)
	Keevil and Thorvaldson (80)	1.5	No definite conclusion
	Le Chatelier (117)	1.7	$CaO \cdot SiO_2 \cdot aq$ plus adsorbed lime
	Klasse and Kühl (84)	1.8	$2CaO \cdot SiO_2 \cdot aq$
	Kühl and Wang Tao (103)	1.5†	$3CaO \cdot 2SiO_2 \cdot aq$
	Koyanagi (87)	1.0†	$CaO \cdot SiO_2 \cdot aq$
	Michaelis (132, 133)	1.5	At first M. assumed $3CaO \cdot 2SiO_2 \cdot aq$; later he drew no definite conclusions
	Maffei and Battaglia (127)	1.25	No definite conclusion (value given is taken from M. and B.'s table 1, data for silica sol)
	Landrin (107)	1.33‡	L. appears to assume $4CaO \cdot 3SiO_2 \cdot aq$

* A plus sign indicates that the CaO/SiO_2 value shown was the highest obtained in an investigation in which the highest concentration of $Ca(OH)_2$ was still far short of saturation. Shaw and MacIntire's value was obtained when the solution was nearly saturated with $Ca(OH)_2$.

† Experiments on portland cement clinker (corrected).

‡ From reference 107 it is not wholly clear whether the final solution was completely saturated with $Ca(OH)_2$. However, the ratio 1.33 was considered to represent the maximum possible absorption of lime.

Solutions obtained by treating $3CaO \cdot SiO_2$ with water were poured into saturated $Ca(OH)_2$ solutions (proportions of 1:4 by volume). Precipitates were formed which after drying at 105°C. had in each case approximately the composition

$2CaO \cdot SiO_2 \cdot 4H_2O$. On the other hand, Hedin (67), whose initial studies were made in collaboration with Forsén, reports precipitations of similar character in which the values of CaO/SiO_2 attained in the products were not as high. The $3CaO \cdot SiO_2$ extracts and the saturated $Ca(OH)_2$ solutions were mixed in the proportions of 1:1 and 1:5. The precipitates, removed after 24 hr., showed on analysis the compositions $1.6CaO:1SiO_2:aq$ and $1.8CaO:1SiO_2:aq$, respectively.

The investigations of Kühl and Wang Tao (103), and of Koyanagi (87), cited in table 5, fall in a special category since they are not strictly $CaO–SiO_2–H_2O$ studies but were made by use of portland cement clinker, with correction for hydration products containing Al_2O_3 and Fe_2O_3. The results are of special interest, however, because they are distinctly different for the two investigations, and this appears to be attributable largely, though not entirely, to one circumstance. That is, Kühl and Wang relied on physical separation of $Ca(OH)_2$ crystals, whereas Koyanagi supplemented this procedure by testing and correcting for free $Ca(OH)_2$ retained by the gelatinous precipitate. The corrections for Fe_2O_3 were not the same in the two investigations, but the effect of the difference was small and unimportant. The experimental procedure consisted in shaking grains of the clinker with saturated limewater. Voluminous hydration products separated from the grains and were separately analyzed. When the experiments were continued for a long time, coarse $Ca(OH)_2$ crystals formed and settled out.

As shown by table 5, Koyanagi's corrected CaO/SiO_2 value was 1, in agreement with adsorption theories, whereas Kühl and Wang obtained 1.5, in agreement with the gross compositions reported by several other investigators. The test for free $Ca(OH)_2$ used by Koyanagi was the glycerol–alcohol solution method, with titration with ammonium acetate (123). As used for *hydrated* lime the test has given difficulty, apparently because of inadequate solution of the crystals of $Ca(OH)_2$, with resultant low values for $Ca(OH)_2$ (15, 18). However, such an effect is in the wrong direction to account for the difference in the results obtained by Kühl and Wang and by Koyanagi. As a matter of fact, Koyanagi's final values of molar CaO/SiO_2, even before correction for the free $Ca(OH)_2$, were distinctly less than those of Kühl and Wang, being only about 1.3. Probably a little alkali hydroxide was present in solution in both investigations, though the concentrations must have been small since Kühl and Wang, and Koyanagi, used 10 and 20 parts of limewater to 1 part of clinker, respectively. (For effects of alkalies see Section XVII.)

Bessey (11) has criticized Koyanagi's conclusions on the ground that "lime which may be present in excess of a 1:1 lime:silica ratio is apparently in a weak state of combination and is likely to react with glycerol or other reagents in a manner similar to free lime." In this connection it is of interest that Hedin (67) used ethylene glycol to extract free $Ca(OH)_2$ from a product obtained by reacting sodium silicate with a suspension of $Ca(OH)_2$. The extracted product had a CaO/SiO_2 value of 1.5. Like Bessey, Hedin was fearful that the reagent could extract chemically combined lime, so he abandoned the procedure. However, when he used tetraethyl silicate with saturated limewater in the absence of solid $Ca(OH)_2$ the product, though not extracted, also had a CaO/SiO_2 value of 1.5. This seems to indicate that the ethylene glycol was not too aggressive a solvent, and no reason is seen why glycerol would be more active. However, the fact remains that Koyanagi found CaO/SiO_2 equal to 1.0, whereas Hedin found 1.5. It may at least be noted that Hedin dried his product at 105°C. before extraction, whereas Koyanagi apparently dried his at room temperature (*in vacuo*), though it was heated later during the free lime test.

Koyanagi found that for test periods of only 7–10 days the corrected CaO/SiO_2 value was about 1.2–1.3, but that as the test periods were extended the value dropped to 1.0 and remained there. From the higher initial ratio Koyanagi assumed that a metastable silicate higher limed than $1CaO:1SiO_2$ is first formed. This silicate could have a considerably higher CaO/SiO_2 value than 1.3, since in Koyanagi's preparations some $CaO \cdot SiO_2 \cdot aq$ would probably have been present along with it.

From this survey it is obvious that the extent of actual chemical combination attained in calcium silicate gel in equilibrium with saturated or supersaturated limewater is still obscure.

XIII. CALCIUM SILICATE PASTES AND RELATED SUBJECTS

The two calcium silicates of portland cement, $3CaO \cdot SiO_2$ and β-$2CaO \cdot SiO_2$, can both develop saturated solutions of $Ca(OH)_2$ when placed in contact with limited amounts of water. That this is true under apparent equilibrium conditions, brought about by vigorous agitation with an attrition agent, is evident from curves 13 of figure 1. It is also true under quiescent conditions. Indeed, either compound can cause supersaturation with respect to $Ca(OH)_2$ (122), but this condition, though somewhat persistent, must nevertheless be temporary. Accordingly, when these anhydrous calcium silicates are made up with water to the consistency of portland cement pastes, the final solutions in the hardened pastes are evidently saturated solutions of $Ca(OH)_2$.

Experimental determination of the composition of the hydrous calcium silicate that is formed in pastes is beset with difficulty, because of the intimate mixture of this product with $Ca(OH)_2$ that has precipitated and with any anhydrous material that has not yet reacted. When finely ground $3CaO \cdot SiO_2$ is used, the latter difficulty is not serious because the hydration is practically complete in specimens that have been stored for several months. However, β-$2CaO \cdot SiO_2$ contains much unhydrated material even after two years (18), unless the hardened paste is repeatedly ground and remixed with water. As to the calcium hydroxide that precipitates, the attempt is generally made either to dissolve it out or to apply a quantitative analytical test for it. In early studies the methods used appear to have been generally unsatisfactory (121). Methods have been developed in recent years that are reasonably adequate for the determination of free CaO in unhydrated cement and in preparations of the clinker compounds, but neither these nor other current methods are generally accepted as being wholly satisfactory for the accurate determination of

$Ca(OH)_2$ in the hydrated products. As mentioned earlier, inaccuracy has apparently been caused in some cases by difficulty in dissolving the $Ca(OH)_2$ crystals (15, 18). Some investigators (18, 51) have heated their hydrous products to 530°C. or more in order to dehydrate the $Ca(OH)_2$ before dissolving the lime. However, in tests on six-month specimens, Work and Lasseter (191) found less free lime in preheated (850°C.) specimens than in others not heated, a result opposite to that to be expected if the test made without heating is inadequate simply because of difficultly soluble $Ca(OH)_2$. It may be that the heating sometimes causes significant recombination of lime with calcium silicate, though tests made by Work and Lasseter on specimens that had hydrated for relatively short periods did not indicate this.

Various methods of determining $Ca(OH)_2$ in hydrated cements were discussed and compared by Bessey (13, 15) at the symposium held by cement chemists and technologists at Stockholm in 1938 (141). In a calorimetric method developed by Bessey (10), the $Ca(OH)_2$ is estimated from the difference in heat of hydration of samples previously heated to 350° and 550°C., respectively, the $Ca(OH)_2$ having been found to dehydrate between these temperatures. The other methods in common use are all extraction, or lime-dissolution, methods; Bessey made comparative tests on hydrated portland cements using, besides the calorimetric method, a half-saturated lime-solution method due to Bakewell and Bessey (3), the glycerol–alcohol solution method of Emley (44) which was first used successfully with unhydrated cements by Lerch and Bogue (121, 123), and the ethylene glycol method of Schläpfer and Bukowski (26, 156). Still other methods and also modifications of some of these have been published, but it is not the purpose here to review the various procedures. It may be noted, however, that more recently a new solvent has been proposed by Franke (54), one composed of acetoacetic ester and isobutyl alcohol.

Application of such methods to the hydrated pastes of $3CaO \cdot SiO_2$ or of portland cement has given the CaO/SiO_2 values that are shown in table 6. In the case of the cements, these ratios have been corrected for CaO in aluminates and ferrites. The methods of determining the $Ca(OH)_2$ are indicated. Bessey made tests by the four different methods already mentioned but relied primarily on the results of the calorimetric method, which were indeed practically the same as those obtained with limewater. The other two methods gave rather different results, but the average CaO/SiO_2 values were still much the same.

From table 5 it might have been expected that the CaO/SiO_2 values of table 6 would have fallen principally within the range 1.4–2.0. However, if the results obtained with cements are excluded as being subject to more sources of error than the others, there remain five values between 2.0 and 2.4 and only one that is lower. Thus, it appears that tests on pastes generally give somewhat higher values than are obtained in equilibrium studies on dilute suspensions.

Several experimenters (18, 23, 173, 191) have made studies on β-$2CaO \cdot SiO_2$ pastes but evidently without complete hydration having been attained in any case. None of these investigators found much free $Ca(OH)_2$. Lerch and Bogue (18) found that after two years the β-$2CaO \cdot SiO_2$ had liberated only 0.9 per cent of its CaO, though it had "fixed" 12 per cent of water so that it was not removable by drying at 105°C. Brown and Carlson (23) found no appreciable $Ca(OH)_2$ in a β-$2CaO \cdot SiO_2$ paste that had, by repeated grinding and mixing, been hydrated to the extent of about 25 or 30 per cent of the $2CaO \cdot SiO_2$.

TABLE 6

Composition of hydrous calcium silicate as formed in pastes

INVESTIGATOR	METHOD OF DETERMINING FREE $Ca(OH)_2$	INITIAL SOLID	AMOUNT OF WATER USED	DURATION OR NATURE OF TREATMENT	CaO/SiO_2 IN HYDROUS CALCIUM SILICATE*
			per cent of initial solid		
Assarsson and Sundius (2)	Glycerol–alcohol	Portland cement			1.9
Work and Lasseter (191)	Glycerol–alcohol	$3CaO \cdot SiO_2$	45–100	3 and 6 months	1.6–1.7
Bogue and Lerch (18)	Glycerol–alcohol with preliminary dehydration of $Ca(OH)_2$	$3CaO \cdot SiO_2$	50	1 and 2 yr.	2.2
Brown and Carlson (23)	Glycerol–alcohol	$3CaO \cdot SiO_2$	75	10 days "kneaded"	2.4
Schläpfer (155) (and Berchem)	Ethylene glycol	$3CaO \cdot SiO_2$ Portland cement	45–49		2.1 1.5
Haegermann (63)	Glycerol–alcohol with preliminary dehydration of $Ca(OH)_2$	$3CaO \cdot SiO_2$		Repeated grinding and mixing with water	2.0
Bessey (13)	Calorimetric	Portland cements (six different ones)	"Thin paste"	Repeated grinding and mixing with water	1.5
Meyers (131)		$3CaO \cdot SiO_2$	"Plastic"	Several months	2.2

* After correction for free $Ca(OH)_2$.

Though Lerch and Bogue found little hydrolysis beyond $CaO/SiO_2 = 2$ in pastes, they believed from earlier study that the equilibrium composition for hydrous calcium silicate in contact with a large excess of saturated limewater corresponds to $CaO/SiO_2 = 1.5$. They therefore concluded that the pastes do not reach equilibrium. Bessey, who obtained CaO/SiO_2 values of 1.5 in his paste studies (13), believed on the basis of his other work (11) that in the system $CaO–SiO_2–H_2O$ the equilibrium CaO/SiO_2 value is 2.0 at lime saturation. He concluded, however, that 1.5 is probably an equilibrium value for cement and that it differs from 2 because of the other components in solution besides CaO and SiO_2 (14).

In pastes the gel, forming compactly and evidently to a considerable extent as coatings over the still hydrating cores of the particles, may not represent the final equilibrium product but may be conditioned by the composition of the initial solid. This may perhaps explain why the hydration products formed around the grains of $3CaO \cdot SiO_2$ and β-$2CaO \cdot SiO_2$ are found, in most studies, to have relatively high values of CaO/SiO_2. It might also be supposed on similar grounds that a coating forming over hydrous silica might have a relatively low CaO/SiO_2 value. It is of interest, therefore, that van der Burgh (28), who allowed saturated limewater to act on silica gel under quiescent conditions, found that thin membranes of reaction products were formed, which in different tests had CaO/SiO_2 values of only 0.85, 0.81, 0.81, and 0.90. Recall also the test by Lerch and Bogue (122), reported in Section VII, in which a sample of hydrous silica kept in saturated limewater until 97 per cent of the silica was acid-soluble showed CaO/SiO_2 of only 1.07 in the acid-soluble part.

Since β-$2CaO \cdot SiO_2$ apparently has the orthosilicate structure with separate SiO_4^{4-} anions (20, 43), it may be that a hydration product involving these atom groupings is relatively easily formed. At the boundary between anhydrous particle-core and gel coating the scarcity of free space may make it difficult for $Ca(OH)_2$ to crystallize, and may promote local supersaturation favoring formation of a high-limed product. This might account for the meager hydrolysis of β-$2CaO \cdot SiO_2$ in pastes, as compared with the hydrolysis obtained in such studies as that of Thorvaldson and Vigfusson (178) in which the conditions for readjustment of the initial gel composition were evidently much better.

With respect to $3CaO \cdot SiO_2$, the crystal structure of this compound may also promote the formation of a hydrated dicalcium silicate, even though that product may not be the final equilibrium one. Early theorizing from the standpoint of structural chemistry (129) led various investigators to the belief that $3CaO \cdot SiO_2$ is a basic salt in which one of the oxygen atoms is not directly attached to silicon. Though the original grounds for this deduction were inadequate (62), the conclusion itself now seems almost certainly correct. The detailed crystal structure of $3CaO \cdot SiO_2$ has not been worked out, but there is every reason to believe that the silicon–oxygen arrangement is determined by the same principles as in other silicates. That is, oxygen atoms are invariably found to form tetrahedra about the silicon atoms (43). Accordingly, $3CaO \cdot SiO_2$ is evidently composed of the ions $3Ca^{++}$, SiO_4^{4-}, and O^{--} (25, 62). The formation of $Ca(OH)_2$ from one mole of CaO per mole of $3CaO \cdot SiO_2$ is therefore not hydrolysis in the usual sense but rather a direct hydration of CaO that is released upon dissolution of the solid (102). It may be presumed that the strong tendency for this one CaO to form $Ca(OH)_2$ is at least one of the reasons why

$3CaO \cdot SiO_2$ is so much more reactive toward water than is β-$2CaO \cdot SiO_2$. As the O^{--} ion unites with water and, with Ca^{++}, forms $Ca(OH)_2$, the remainder of the $3CaO \cdot SiO_2$ is evidently enabled to hydrate also, perhaps without any immediate hydrolysis (80). Some authors (191)[11] have observed relative to the initial stages of the hydration that for each mole of water that goes to form $Ca(OH)_2$, approximately 1 mole of water is firmly bound by the silicate.

Some investigators (103) have believed that the calcium silicates can hydrate without complete solution of the whole original siliceous structure. While some experimental results do suggest this (103), there seems to be good evidence that both $3CaO \cdot SiO_2$ and $2CaO \cdot SiO_2$ dissolve in a normal manner when in the presence of ample water (52, 67). Possibly, however, under the crowded conditions at the interface between anhydrous particle and hydrous gel layer, the silicate ions do not necessarily all pass through a true solution phase during the hydration (96).

Diehl, in observations reported by Nacken (137), found that $3CaO \cdot SiO_2$ particles mounted on a gelatin base hydrated as pseudomorphs. A fringe of hydrate was observed to grow inward with the passage of time leaving, after a few days, a completely hydrated product patterned after the original particle and apparently of the same size. In some cases a second fringe was observed after a few days, which grew inward through the part already hydrated, thus appearing to indicate that the product first formed is not the final equilibrium one. The products gave a slight indication of double refraction, and an x-ray picture was obtained which seemed to indicate fine crystallinity. Baylis (7) observed that particles of precipitated calcium silicate lose lime to acid solutions and leave skeletons of hydrous silica that retain the shapes of the original particles. Thorvaldson and Shelton obtained siliceous skeletons upon treating crystalline calcium silicate hydrate with acid (174, 177).

That the bonding of hydrous reaction product onto the unreacted remainder of a calcium silicate particle may be very firm and highly effective in slowing up further hydration and hydrolysis is indicated by observations of Thorvaldson and Vigfusson (178). These investigators found, as previously mentioned, that when they did not use metal shot their solutions ceased to change in concentration while the solid particles still had unreacted cores. Also, Kühl and Wang Tao (103) found that when clinker grains are shaken with water the impacts between particles, with resultant disturbance of the hydration layers, are important in promoting further reaction. They found that the rate at which the clinker grains hydrated was distinctly less when 3 g. was shaken with 300 ml. of water or limewater than when 30 g. was used. In this connection it is worth noting that Nacken (137) used only a gram or two of $3CaO \cdot SiO_2$ per liter, without an attrition agent. The fact that less hydrolysis occurred than in some of the other studies may be traceable to this. In a few tests in which he did use an attrition agent, the hydrolysis was much increased.

Rate-of-hydration curves obtained by Thorvaldson and Vigfusson (178)

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[11] Krauss and Jörns (89) made a similar observation, but their nominal $3CaO \cdot SiO_2$ was prepared from a melt and was therefore evidently $2CaO \cdot SiO_2$ plus CaO (37).

for 200-mesh $3CaO \cdot SiO_2$ and β-$2CaO \cdot SiO_2$ shaken in water with metal shot are shown in figure 2. The peculiar shape of the curve for β-$2CaO \cdot SiO_2$ was said to be characteristic. Though no such irregularity was found by Lerch and Bogue (122), the fact that it was consistently obtained with one preparation of β-$2CaO \cdot SiO_2$ is still of interest. To Thorvaldson and Vigfusson it suggested that the hydrolysis takes place in two steps determined by the constitution of the molecule of β-$2CaO \cdot SiO_2$. To the present writer it suggests interference by a coating of hydrate which was difficult to dislodge. The lime liberation during the initial abrupt rise in the curve would produce a concentration of about 0.14 g. CaO per liter, evidently sufficient for formation of $CaO \cdot SiO_2 \cdot aq$. It can therefore be assumed that the β-$2CaO \cdot SiO_2$ became coated with monocalcium silicate hydrate which was in equilibrium with the solution and resisted removal. After the slowly continuing hydration had materially increased the bulk of the hydrate layer, it might have torn loose more easily.

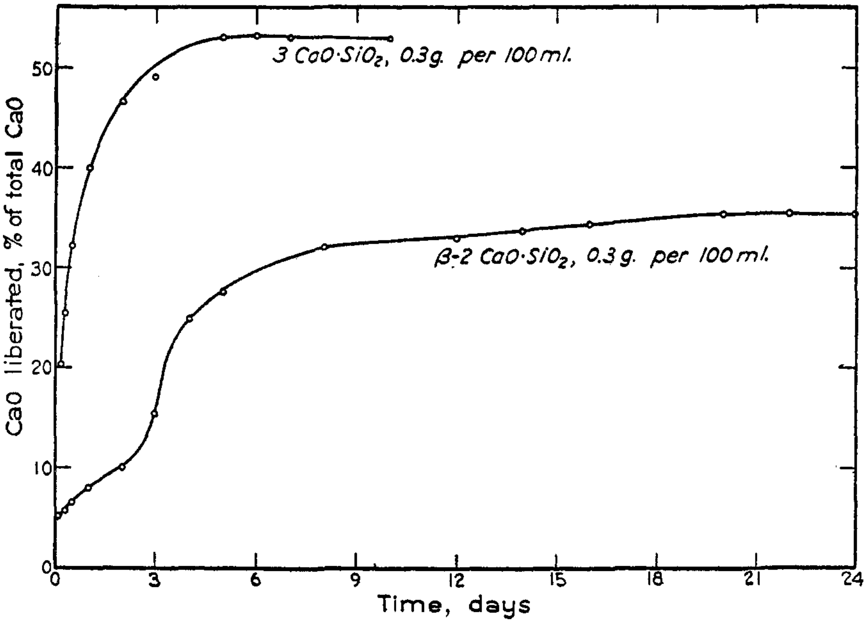

FIG. 2. Rates of hydrolysis of 200-mesh $3CaO \cdot SiO_2$ and β-$2CaO \cdot SiO_2$; metal shot was used as attrition agent (Thorvaldson and Vigfusson (178)).

Phenomena that can be attributed to an adherent coating have also been observed in studies in which the initial solid was hydrous silica. Cummins and Miller (36), who shook diatomaceous earth with limewater and followed the reaction by conductivity measurements, observed an initial, extremely rapid reaction followed by a period of inhibited reaction which appears to have begun within an hour and continued for several hours, after which the rate again became greater. The authors attributed the inhibition to a coating of hydrated calcium silicate gel but did not explain the subsequent rise. Maffei and Battaglia (127) and Cirilli (32) reported that the rate of interaction between silica gel and limewater falls off at an early period and subsequently increases; they attributed the increase to a dispersing, or peptizing, action of the lime, as noted earlier.

The various opinions on the diminutions and subsequent increases in rate of reaction are of course largely speculative. Still another idea, advanced by Lorenz and Haegermann (124) to explain an observed slowing up and subsequent increase in rate of hydrolysis of cement grains, is that during the period of apparent marked reduction in hydrolysis lime is being absorbed by the cement particles.

XIV. MICROSCOPICAL STUDIES

Between 1908 and 1915 numerous investigators (1, 16, 55, 56, 81, 85, 108, 135, 148, 154, 164) examined microscopically the hydration of samples of portland cement clinkers or cements and in some cases direct calcium silicate preparations ("melts"). Generally, a very little of the powdered sample was placed in a drop or two of water over which a cover glass was placed and sealed. Ambronn (1), observing clinker grains, reported that fine crystal needles and little hexagonal platelets grew out from the borders of the grains. After some days he also observed much larger hexagonal plates, and gel formation. Keisermann (81) verified these observations and determined to his satisfaction the constituent oxides of the various formations, by means of staining methods which he developed. As previously mentioned (Section VII), he concluded that the fine needles and gel consisted of calcium silicate. He identified the large hexagonal plates as $Ca(OH)_2$, and the platelets as a calcium aluminate. He also observed and identified all these products, except the platelets, in hydrating calcium silicate "melts". In this latter case the needle crystals developed only after some days, and they radiated from seemingly random points throughout the slide. Keisermann also obtained the needles through reaction of finely powdered, dried $Ca(OH)_2$ and hydrous silica. After 4 weeks, both large and small needles appeared, as well as a gel mass. Blumenthal's microscopical work (16), also mentioned earlier, was largely a repetition of Keisermann's, but in the identification of the fine needles it was apparently more thorough. Blumenthal confirmed Keisermann's identifications.

The fine needles, described as calcium silicate, were apparently first seen and identified by Le Chatelier (see Section II). Numerous other investigators (11, 27, 56, 61, 108, 135, 142, 154, 179) besides Ambronn, Keisermann, and Blumenthal have also observed them, generally in the hydration of cement or clinker. This is of considerable interest, since Klein and Phillips (85) and later Lerch and Bogue (122) reported their inability to find them though they devoted considerable effort to the attempt, using methods of observation recommended by Ambronn and Keisermann. Lay (108), who said that the needle crystals grew into platelets, may perhaps have mistaken platelets on edge for needle crystals; Blumenthal remarked that platelets on edge appeared at first like short thick needles. Perhaps some of the "silicate" needles reported in observations on cements were not silicate at all, but represented hydrated calcium aluminate or calcium sulfoaluminate. However, from the various descriptions there seems little reason to doubt that a considerable number of investigators did see crystal needles very similar to those which Keisermann and Blumenthal identified as calcium silicate and considered to be monocalcium silicate hydrate.

The extreme thinness of the calcium silicate needles has been stressed by various investigators. Ambronn (1) said that the needles could be seen in ordinary observations only by the use of a very narrow cone of light but that they stood out plainly under dark-field illumination obtained by use of a Zeiss paraboloid condenser. Keisermann (81) also said that they were hard to find. Scheidler (154) said that if the clinker was cooled too rapidly the needles would not form. That their number is dependent on the proportion of water used is indicated by Keisermann (81), Muth (135), and others. Muth (135) reported that the needles formed most voluminously when the proportion of water was large, were stable in solution that was well below saturation with $Ca(OH)_2$, and hence could not be simply $Ca(OH)_2$. However, Tippmann, who also observed needles, at first (179) called them calcium silicate but later (180) contended that they were $Ca(OH)_2$ and that hydrous silica does not react chemically with lime at ordinary temperatures. This last conclusion was strongly disputed by Kühl (95), who said in the course of the controversy that he considered that Keisermann and Blumenthal had demonstrated that their needle crystals contained silica. Ward (185) observed occasional long thin needles during the hydration of $K_2O \cdot 23CaO \cdot 12SiO_2$ (169); he also observed vermiform outgrowths from hydrating $3CaO \cdot SiO_2$ and β-$2CaO \cdot SiO_2$ grains. He considered both formations to be dicalcium silicate hydrate. Brown (22) has observed birefringent fibrous fringes on hydrating particles of $3CaO \cdot SiO_2$ in portland cement clinker of relatively low $3CaO \cdot Al_2O_3$ content. Also, in one instance he has obtained distinct needle crystals radiating from hydrating clinker grains. No gel formation was visible when the needles were first observed. Later, when gel had developed, the needles appeared less perfect than at first. The clinker grains used in preparing the slide were of rather uniform size, about 10 to 15 microns in diameter.

It has been reported that the silicate needles later change into gel. Scheidler (154) apparently said this, and Kühl and Mann (98) believed that Muth did also. Muth (135), however, wrote simply of the needle formation being depressed, with greater development of gel, in preparations made up with less water than others. Indeed, Muth said that he observed no change in the needles, but he attributed to Ambronn a belief that they finally decomposed. This seems also to be a misunderstanding, for Ambronn (1) said that he could still see the needles through gel that formed around them. Pulfrich and Linck (142) reported that the needles were destroyed when the gel formation began. They considered it erroneous, however, to say that the needles "change" to gel, because transformation of gel to crystals is not reversible. Pulfrich and Linck appear, nevertheless, to have believed that the needles are composed of calcium silicate. They thought that needles are formed only when a large proportion of water is used. This agreed with their observations, in connection with which they used glycerol solutions in order to reduce the amount of water while still employing enough liquid for convenient observations. Glycerol, however, is not an appropriate diluent (98, 179), since it can dissolve lime and may also have a specific effect on crystal formation. Like Keisermann, Pulfrich and Linck also obtained needle crystals through reaction of hydrous silica and $Ca(OH)_2$, but only after adding solid $Ca(OH)_2$ and shaking at 100°C. The needles developed after some weeks, growing eventually to lengths of 0.1 to 0.2 mm.

Le Chatelier (119) remarked years after his original investigation that crystalline hydrated calcium silicate had never been observed microscopically. This statement was challenged by von Glasenapp (57) on the basis of his own observations of needle formations. It is doubtful, however, that Le Chatelier really intended to retract his original identification (117) of crystal needles as $CaO \cdot SiO_2 \cdot 2.5H_2O$. His later discussion relates to the tendency of initially formed colloidal particles to develop into visible crystals, a change to be expected on thermodynamic grounds but for which there is indeed no direct microscopic evidence in the case of the hydrous calcium silicate. Kühl (94) has noted an increase in the birefringence of hydrated portland cement over a period of twenty years, but there is no assurance that this resulted from the growth of silicate crystals. After hydrating calcium silicates for two years, Bogue and Lerch (18) could obtain no indications of crystalline hydrates, other than $Ca(OH)_2$, either microscopically or by x-ray diffraction.

Owing to the fineness of the needles, their optical properties are hard to determine. Probably for this reason, and no doubt also because of actual differences between some of the needles observed, the accounts of the optical properties have been conflicting. A number of investigators (1, 16, 61, 135, 142) have reported that the needles are somewhat birefringent, whereas others (27, 57) found them to be wholly isotropic. Tippmann (179) said that the needles which he observed were originally isotropic but became birefringent, and this he attributed to surface carbonation. Blumenthal (16) reported that needles observed by him were birefringent with negative elongation. Pulfrich and Linck (142) distinguished thin and thick needles. The refractive indices of the thin needles were $\alpha = 1.498$, $\gamma = 1.500$ (error $= 0.0015$). Those of the thicker needles were a few units higher in the third decimal place. Grün, Tremmel, and Kunze (61) reported long thin needles with refractive indices of 1.47 to 1.53. The needles that Ward obtained with $K_2O \cdot 23CaO \cdot 12SiO_2$ had a mean refractive index close to 1.62, showed parallel extinction, and were biaxial, optically positive.

The gel itself has some interesting features, as observed under the microscope. Ambronn (1) noted that the gel forms at first as minute globules, and he describes how these droplets form along the needles like strings of pearls, and on the platelets and unchanged clinker grains. Finally the drops unite to form hyaline coatings. Lay (108) reported that the droplets also form on the slide and cover glass, often in regular geometric arrangements. The observations of both of these authors were made on slides of hydrating cement clinker. Ward (185), examining hydrating $3CaO \cdot SiO_2$ grains, observed that the vermiform growths, previously mentioned, changed in a few hours to round, gel-like particles. Eventually the individual grains were surrounded either by individual globules or by a more or less continuous gelatinous coating of the same refractive index as the globules (1.43 to 1.49). Finally, the $3CaO \cdot SiO_2$ grains were completely converted into individual lumps of gel which, as seen in a photomicrograph, appear to have retained essentially the original grain shapes. In this connection Brown (22) reports that hydration products of the silicates in portland cement quite commonly appear as pseudomorphs of the original mineral grains, in agreement with the observations reported by Nacken (137). Ward (185) reported that a thin groundmass gel formed like an etch over the cover glass, and on the slide carrying the $3CaO \cdot SiO_2$. This gel had a refractive index of 1.54, about the same as for the principal gel formation that he found in thin sections of hydrated cement.

Brown and Carlson (23) found that air-dried gels produced by the hydration of $3CaO \cdot SiO_2$ and β-$2CaO \cdot SiO_2$ had refractive indices of 1.515 and 1.53, respectively. Heating either gel for 1 hr. at 900°C. raised its index to 1.695. From observations on hydrating portland cement these authors noted that gel and calcium hydroxide crystals began to form almost immediately. The gel was found to form around every cement particle and in a few days the spaces between the particles were filled with either gel or calcium hydroxide, except for occasional air bubbles. The gel, in all stages of dryness, gave no evidence of fine crystallinity. In the moist form it was found to react instantly with carbon dioxide, forming minute calcium carbonate crystals. This carbonation was observed to occur more easily "in the gel than in areas of recognized crystalline hydroxide."

Most of the early microscopical studies of the hydration of calcium silicates were made with the object of learning something about the hydration of portland cement in construction work. However, since in order to observe the individual grains a much larger proportion of water was needed than is used in ordinary cement practice, the significance of the results for cement technology has been challenged, notably by Kühl (91). Kühl later (96) adopted the point of view that excess water could be used if it was saturated with $Ca(OH)_2$, like the solution in cement paste. He pointed out, however, that the latter solution generally contains an appreciable concentration of alkalies, as well as $Ca(OH)_2$. In early studies, Read (148) used limewater in making microscopic observations, but few investigators have followed this lead. So far as the present writer has been able to determine, the recorded occurrences of the silicate needles are all for studies in which plain water was used. Ward (185), who did not obtain silicate needles (except when hydrating $K_2O \cdot 23CaO \cdot 12SiO_2$), found that in saturated $Ca(OH)_2$ solution the reactions of $3CaO \cdot SiO_2$ and β-$2CaO \cdot SiO_2$ were similar to those in plain water but that there was a noticeable decrease in the rate of hydration. The addition of gypsum, potassium hydroxide, or sodium hydroxide had no visible effect on the nature of the reaction products of the silicates. Nacken (137) noted no decrease in the rate of hydration of his $3CaO \cdot SiO_2$ when he used saturated limewater, but did when he also added solid $Ca(OH)_2$. As previously mentioned, Muth (135), who treated cement with various proportions of water, found the least needle formation in his least dilute preparations. In cement pastes, in which the proportion of water is still less, Kühl (94) contends that the hydration products are almost entirely ultramicroscopic in structure, except for occasional $Ca(OH)_2$ crystals.

Bessey (11) has reported an accidental preparation of weakly birefringent parallel or fibrous material having a refractive index of about 1.51 and a composition corresponding approximately to $3CaO \cdot 2SiO_2 \cdot aq$. This apparently crystalline material formed on sand–lime brick stored in water, apparently at room temperature.

The electron microscope has been used by Radczewski, Müller, and Eitel (144) to study the hydration of $3CaO \cdot SiO_2$. Some very fine crystal needles were observed which were believed to be a calcium silicate hydrate. Sliepcevich, Gildart, and Katz (159) took electron microscope pictures of products obtained by evaporating solutions in which particles of $3CaO \cdot SiO_2$ and β-$2CaO \cdot SiO_2$ had been hydrating (separately). Besides $Ca(OH)_2$ particles, and some ill-defined material, rhombic formations were noted. These latter closely resembled calcium carbonate crystals obtained by carbonation of $Ca(OH)_2$, but the authors believed them to be of different composition, since carbon dioxide was thought to have been excluded. The $Ca(OH)_2$ produced by hydrolysis is shown by electron microscopy to form initially in large measure as rounded particles of nearly perfect circular (and half-circular) cross section, 1 micron and less in diameter (143, 144, 159).

In hydrothermal studies, at temperatures above 100°C., crystalline hydrated calcium silicates are readily formed, as established both by x-ray and by the microscope. Non-equilibrium forms are apparently easily obtained, with the result that the early studies in this field do not establish the equilibria. In a recent paper (71), however, a tentative phase diagram is advanced. It is not the purpose here to attempt a systematic account of hydrothermal studies, which were reviewed in 1938 by Thorvaldson (174) and by Büssem (25). It may be remarked, however, that hydrates having $CaO:SiO_2$ ratios of 1:1, 3:2, 2:1, and 3:1 have all been reported, the latter, however, having only been obtained out of contact with liquid water.

The only direct connection between these hydrothermal products and the products obtained at ordinary temperatures is that provided by Mlle. Foret's x-ray identifications (49) of her crystalline $CaO \cdot SiO_2 \cdot aq$ (obtained at about 130°C.) with Chassevent's (31) gelatinous calcium silicate.

Refractive indices of "artificially hydrated calcium silicates" are tabulated by Bessey (11). Values of 1.59 to 1.64 are reported for various preparations of $2CaO \cdot SiO_2 \cdot aq$. For $3CaO \cdot 2SiO_2 \cdot aq$ and $CaO \cdot SiO_2 \cdot aq$ the values range from 1.57 to 1.60. X-ray and optical data on natural and synthetic crystalline hydrated calcium silicates are given by McMurdie and Flint (125) and Flint, McMurdie, and Wells (45) (see also an earlier paper by Vigfusson (184)).

XV. BOUND WATER

Isotherms showing the water content of the gelatinous calcium silicate in relation to vapor pressure, at apparent equilibrium, have been obtained by a few investigators. The curves are shown in figure 3. Bessey's curve is for his 17°C. $1CaO:1SiO_2$ preparation (11). Lefol's preparations (120) had 1.2 to 1.3 moles of CaO per mole of SiO_2, but on the basis of Le Chatelier's work (117) the CaO in excess of $1CaO:1SiO_2$ was regarded as adsorbed. Berchem's tests (9) were made on $3CaO \cdot SiO_2$ that had hydrated for 71 days and must therefore have contained much free $Ca(OH)_2$. Powers (139) used specimens obtained by hydrating $3CaO \cdot SiO_2$ and β-$2CaO \cdot SiO_2$ for over three years, the original aqueous

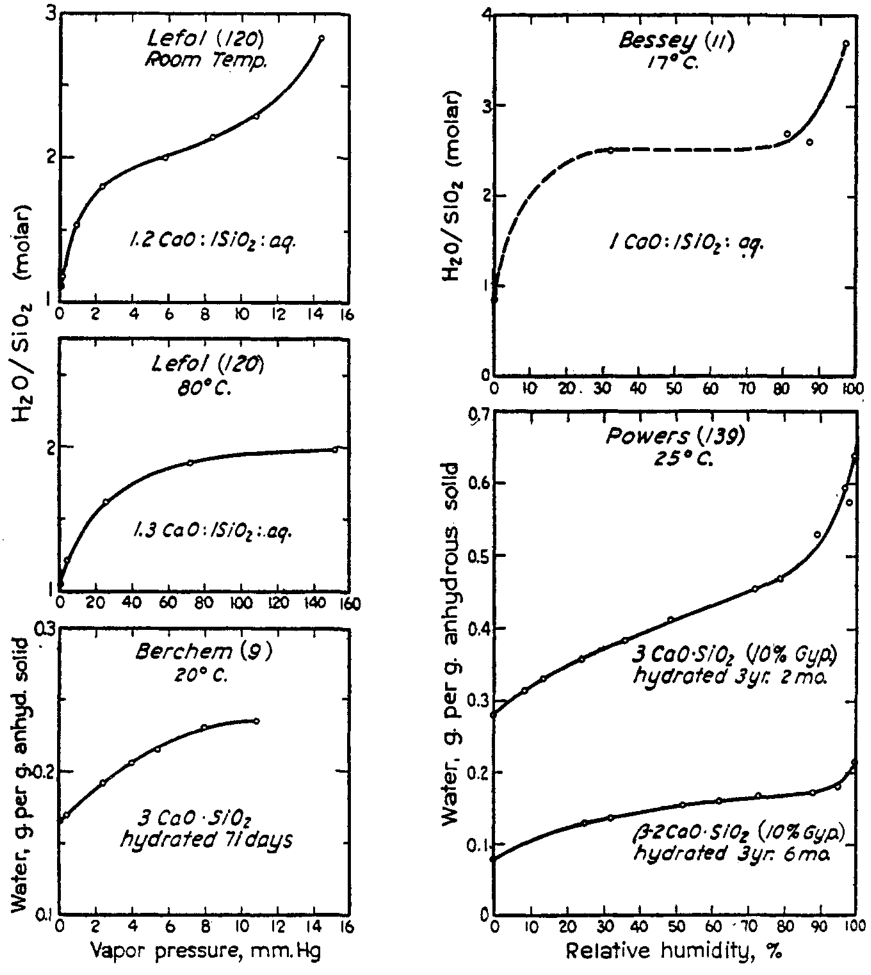

FIG. 3. Isothermal dehydration curves for hydrous calcium silicate preparations. For Lefol's room-temperature curve the three highest points were obtained by rehydration.

pastes having been made up with 10 per cent additions of gypsum which is believed to have remained primarily unreacted. Probably a large part of the β-$2CaO \cdot SiO_2$ (at the centers of the original particles) remained unhydrated. All curves of figure 3 were obtained by progressive *dehydration*, except that in Lefol's room-temperature curve H_2O/SiO_2 values above 2 were obtained by rehydration.

Lefol concluded from the flatness of the curves in the neighborhood of 2 moles of water, and their termination at about the 1 mole level, that definite hydrates having 1 and 2 moles of water are indicated. His initial preparations, containing about 2 moles of water, were obtained by drying *in vacuo* over calcium chloride. Lefol also made other tests in which the $1.2CaO:1SiO_2:2H_2O$ preparation was heated, with uniform increase in temperature, and was weighed at intervals without interrupting the treatment. The curve obtained showed that the loss of water began at about 80°C. and that the rate of loss decreased rather abruptly at about 160°C., when the water content was about 1.2 moles. Under continuous heating at 145°C. (in a separate test) the water was reduced to about 1 mole and then remained constant. Hence, 1 mole of water was assumed to be combined with 1 mole of $CaO \cdot SiO_2$. Since more than 1 mole of CaO was present per mole of SiO_2, it would appear that the extra lime, if adsorbed (as was assumed), would remain at 145°C. as $Ca(OH)_2$, and that correction should be made for the water thus combined in estimating the water in $CaO \cdot SiO_2 \cdot aq$. However, Lefol makes no mention of any such correction, and it is clear that the data in figure 3 are uncorrected.

Bessey, also, concluded from his curve that the gel probably contains a definite hydrate, evidently $CaO \cdot SiO_2 \cdot 2.5H_2O$, though this is not stated. Berchem, however, regarded his curve as determined by the pore structure of the gel, and believed it to be without significance as to the hydrates present. Powers drew similar conclusions, reporting that his curves represented water held not as definite hydrates, but in a manner typical of colloidal gels.

Isobars showing the retention or loss of water by hydration products of calcium silicates at a succession of temperatures are shown in figure 4. The $3CaO:1SiO_2$ preparation used by Krauss and Jörns (89) was evidently a mixture of $2CaO \cdot SiO_2$ and CaO, since it was quenched from a melt (37). Meyers (131) maintained a pressure of only about 0.1 micron of mercury; thus he obtained the "steps," L, in his curves at lower temperatures than did Krauss and Jörns, who maintained a pressure of 7 mm. of mercury. These steps can be attributed to dehydration of $Ca(OH)_2$, since they occur at about the temperatures to be expected, in view of the pressure maintained. Except for these steps and the irregularities up to about 100°C., the curves show the same colloidal, adsorptive, or zeolitic character as the isotherms. Forsén's (53) isobars resemble those obtained by Meyers, but they were not carried to temperatures high enough to dehydrate $Ca(OH)_2$ if any was present.

Isotherms and isobars have also been obtained for hydrated portland cement. In their indications regarding hydrous calcium silicates they are reasonably consistent with the curves obtained directly on such materials. Hence they will not be considered further here, except for the remark that the isotherms show hysteresis, the dehydration curve not being retraced throughout by the rehydration curve (140). As mentioned earlier, it is primarily the dehydration isotherms that have been determined for the hydrous calcium silicates.

Although, because of their rather flat central portions, isotherms such as Lefol's do appear to suggest definite hydrates, it should be realized that very similar curves are obtainable with a number of finely porous adsorptive substances, and in many such cases the curve is attributed wholly to adsorption and capillarity (24). Indeed, the isotherms show a sensitivity of water content to vapor pressure that is similar to the sensitivity of CaO/SiO_2 to CaO concentration. Thus, the bonding of the water remains uncertain in much the same way that the bonding of the CaO is uncertain. Even the fact that the gel still retains a considerable amount of water at seemingly negligible vapor pressure is not good assurance that this residual water is all held as some definite hydrate (109).

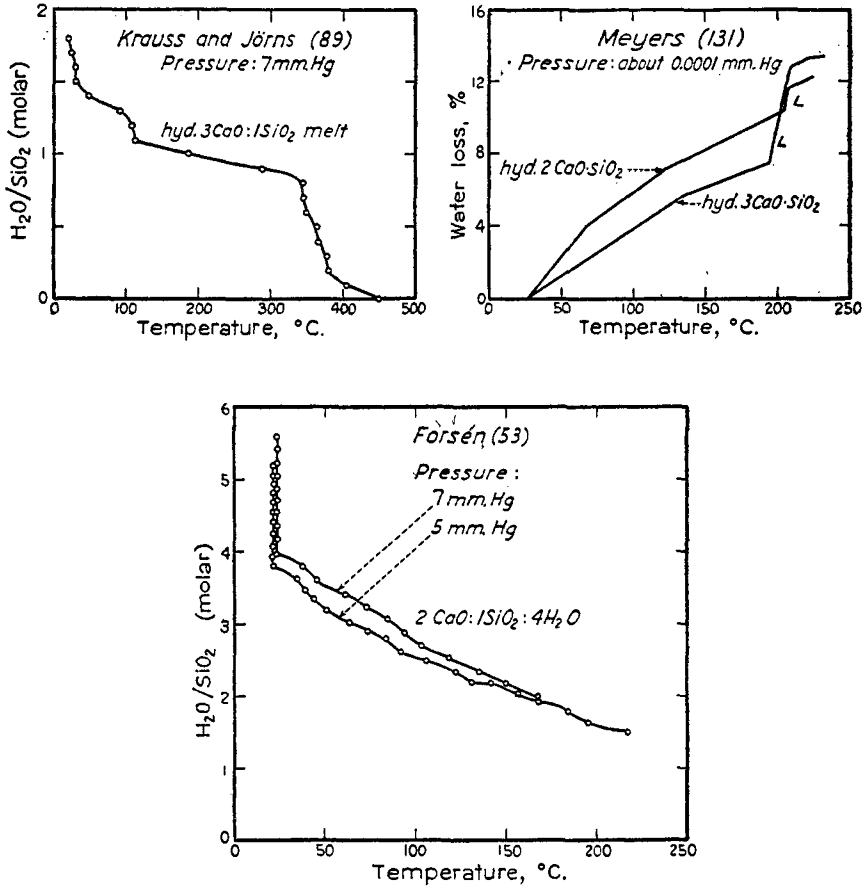

FIG. 4. Isobaric dehydration curves for hydrous calcium silicate preparations

Nevertheless, it is evident that a considerable amount of water is firmly held. The amounts that remain at very low vapor pressure, and at rather high temperatures, attest to this. Cirilli (33), like Lefol, found that on heating an approximate $1CaO:1SiO_2:aq$ preparation at a fairly high temperature (130°C.) 1 mole of water was retained even on prolonged heating. Roller and Ervin (152) cite these findings of Cirilli and Lefol as indications that 1 mole of water is constitutional.

Cirilli (33) also found that upon heating directly to a higher temperature (160°C.) actually more water was retained than at 130°C. and that the product had an unusually high heat of solution. He concluded, therefore, that something other than simple dehydration was involved. In his early studies (33) Cirilli obtained the same heat of solution, in acid, for $1CaO:1SiO_2:aq$ both before and after drying from 70 to 13.4 per cent (or 1 mole) of water. Removal of this last mole of water at 650°C. apparently gave SiO_2 and $2CaO \cdot SiO_2$, since the latter was indicated by the x-ray spectrum. Cirilli later (34) reported heats of solution for samples of $1CaO:1SiO_2:aq$ having water contents ranging from 1 to 26 moles. In contrast with the earlier results, the data show a gradual rise in the heat of solution with reduction in water from 26 to 2 moles and a much more pronounced rise thereafter.

Other investigators have determined the "fixed water" by some arbitrary standardized procedure. Work and Lasseter (191) compared methods of four different types, using hydrated cement as test material. These methods were: oven drying for 1–4 hr. at 90°, 105°, and 130°C.; grinding with absolute alcohol at room temperature; extraction at the boiling point with benzene (80–82°C.), toluene (111°C.), and xylene (139°C.); and evacuation at 4–10 mm. of mercury at room temperature for 2 hr. The cement had been mixed originally with 30 per cent of its weight of water, but the exact amount retained at the time of the tests is not stated. Results are reported as the losses of water during the various treatments, expressed in percentages of the weight of the sample after ignition at 850°C. Except for the evacuation at 4–10 mm., which gave a distinctly low result (9.2 per cent water), and the 90°C. oven drying, which gave about 13 per cent water, the various tests gave remarkably similar results: 14.6 to 18.0 per cent water loss. On the basis of these tests, oven drying for 3 hr. at 105°C. was adopted, and the water retained at 105°C. but lost at 850°C. was called the combined water. During drying, a stream of dry carbon dioxide-free air was slowly passed over the crucible. Tricalcium silicate, made up as a very wet mix and hydrated for six months, showed, per mole of SiO_2, 1.8 moles of water of hydration plus 1.4 moles in $Ca(OH)_2$ as determined by the glycerol–alcohol method (123).

Boque and Lerch (18) determined "fixed water" by drying for 24 hr. at 105°C. and igniting at 1000°C. Their $3CaO \cdot SiO_2$, ground till 90 per cent passed the 200-mesh sieve and made up with 50 per cent of its weight of water, showed at six months 1.1 moles of water of hydration besides 0.8 mole in $Ca(OH)_2$ (glycerol–alcohol method, after heating at about 530°C.). At two years the water in $Ca(OH)_2$ had not increased, but the water of hydration was 1.6 moles.

Hedin (67) took precipitated calcium silicates and dried them over calcium chloride in an atmosphere free from carbon dioxide, then over phosphorus pentoxide, and finally in a drying oven at 105°C., drying to constant weight each time. Results are given below:

$CaO:SiO_2$	MOLES WATER RETAINED ON DRYING		
	Over $CaCl_2$	Over P_2O_5	At 105°C.
1.07:1	2.48	1.72	1.33
1.50:1	3.48	2.73	2.01
2.07:1	4.01	3.56	2.64

Hedin's product that was extracted with ethylene glycol (see Section XII) was dried in a desiccator at 105°C. It then had the composition $1.5CaO:1SiO_2:1.57H_2O$.

Forsén (52) gives the following compositions for products "dried at 105°C.":

$1.06CaO:1SiO_2:1.17H_2O$
$1.13CaO:1SiO_2:1.07H_2O$
$2.06CaO:1SiO_2:4.27H_2O$
$1.99CaO:1SiO_2:3.79H_2O$
$2.05CaO:1SiO_2:3.84H_2O$

Cirilli (34) states that his products that had CaO/SiO_2 ratios equal to 1:1 and 3:2 retained water corresponding to $CaO \cdot SiO_2 \cdot H_2O$ and $3CaO \cdot 2SiO_2 \cdot 3H_2O$ when they were dried to constant weight *in vacuo* over phosphorus pentoxide and potassium hydroxide.

Nacken (137) does not describe his drying procedure but reports water values that vary erratically, as, for example: $1.96CaO:1SiO_2:2.1H_2O$ and $2.10CaO:1SiO_2:0.97H_2O$. In his various preparations of varied CaO/SiO_2 ratio the range in moles of water per mole of silica was 0.97–3.9. Keevil and Thorvaldson (80) state that the apparent monocalcium silicate obtained by hydrolysis of $3CaO \cdot SiO_2$ retains 1 mole of water after drying to constant weight over quicklime. Koyanagi's supposed monocalcium silicate retained approximately 2 moles of water after drying to constant weight in a vacuum desiccator.

XVI. THE PHASE DIAGRAM FOR THE SYSTEM $CaO–SiO_2–H_2O$

It will be evident from the foregoing sections that there is not as yet any possibility of drawing a precise ternary diagram for the system $CaO–SiO_2–H_2O$ that would be generally accepted. Indeed, if particle size and adsorptive capacity are as important as has been suggested, it does not appear that a single precise diagram that does not take these properties into account could represent adequately all the valid relationships when the solids remain as colloids. However, the results of individual experimenters can of course be represented in this way, if the data are sufficiently complete.

Flint and Wells (47), and also Nacken (137), made use of ordinary rectangular plots of SiO_2 concentration *versus* CaO concentration, with the compositions of equilibrium solids suitably indicated, and with the anhydrous solids of the system represented by lines drawn from the origins with slopes equal to the CaO/SiO_2 values. As Nacken had not actually determined SiO_2 concentrations, he drew his solubility curve along the CaO axis.

Bessey (11) employed the equilateral triangular plot to represent a combination of his own and other data. He treated Flint and Wells' relationships at the lower lime concentrations as metastable. Equilibrium solids were assumed to be $Ca(OH)_2$, $2CaO \cdot SiO_2 \cdot aq$, solid solutions between $3CaO \cdot 2SiO_2 \cdot aq$ and $CaO \cdot SiO_2 \cdot aq$, and $SiO_2 \cdot aq$.

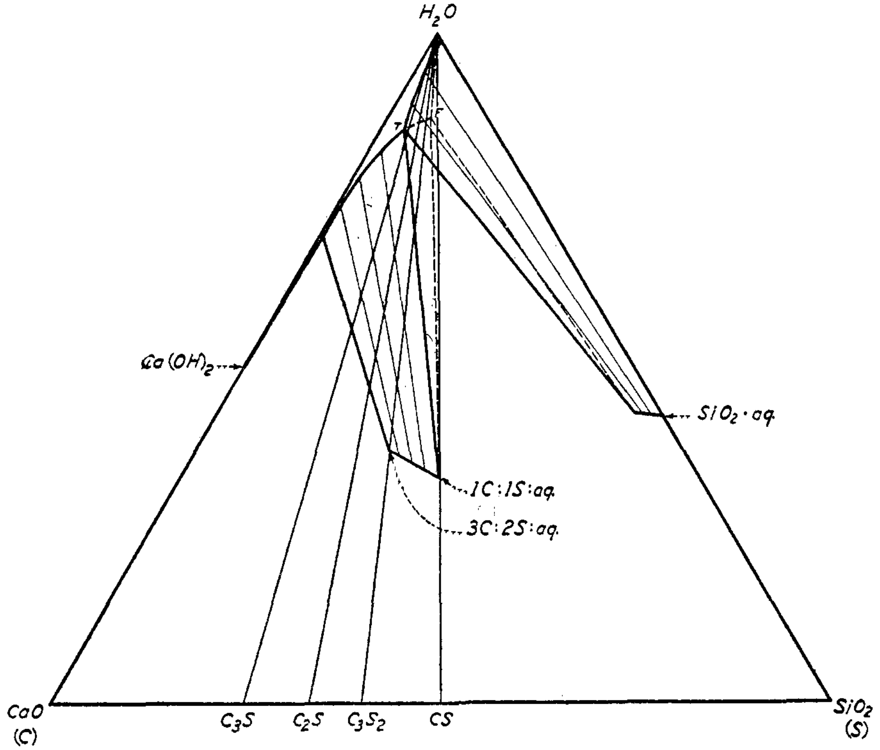

FIG. 5. Hypothetical phase diagram for the system $CaO–SiO_2–H_2O$ at ordinary temperature with exaggerated solubilities (presented only as an aid to discussion).

Owing to low solubilities of the solids involved, the equilateral triangle is not a very satisfactory means for presenting data for the $CaO–SiO_2–H_2O$ system if the components are expressed in uniform units. However, because it is so well known, it is used in figure 5 to illustrate a few points, though with solubilities exaggerated and the water contents of the solids arbitrarily assumed. The hydrous solids are taken as: $Ca(OH)_2$, a product varying in composition from $1CaO:1SiO_2:aq$ to $1.5CaO:1SiO_2:aq$, and $SiO_2 \cdot aq$ with some adsorbed $Ca(OH)_2$. These assumptions regarding solids are in substantial agreement with the apparent indications of Thorvaldson and Vigfusson's data (curve 13, figure 1).

Tie lies connect points on the solubility curves with the equilibrium solids. The appearance of the plot in this respect does not disclose whether the solids are solid solutions or single compounds with adsorbed lime; either assumption can be made if no further evidence is available. Lines drawn to the water apex from the points representing the anhydrous calcium silicates cut through the other tie lines wherever the indicated liquid–solid equilibria can be produced simply by adding water to the anhydrous compounds. For example, curves 13, figure 1, seem to indicate that addition of enough water to $3CaO \cdot SiO_2$ will give as the resultant solid phase a compound lower limed than $CaO \cdot SiO_2 \cdot aq$, perhaps $SiO_2 \cdot aq$ as assumed in figure 5; accordingly, the invariant point T is placed so that the lines from it to the two solids $CaO \cdot SiO_2 \cdot aq$ and $SiO_2 \cdot aq$ are both cut by the line from $3CaO \cdot SiO_2$ to H_2O. This is simply a graphical representation of the fact that if the equilibrium solids are to have CaO/SiO_2 lower than in $3CaO \cdot SiO_2$, the solution phase must have $CaO/SiO_2 > 3$. (The dashed lines of figure 5 are considered later.)

TABLE 7

Concentrations of solutions in equilibrium with calcium silicate gels as determined by Roller and Ervin (152)

CaO	SiO_2	CaO	SiO_2
millimoles/liter	*millimoles/liter*	*millimoles/liter*	*millimoles/liter*
0.99	0.690	2.81	0.107
1.01	0.660	2.84	0.112
1.18	0.442	2.92	0.108
1.52	0.293	3.16	0.0924
1.64	0.267	3.41	0.0821
1.83	0.215	3.52	0.0777
2.55	0.140	4.54	0.0510
2.69	0.119	6.24	0.0337
2.70	0.114	8.76	0.0238

If the deduction just stated could be accepted as valid, it would mean that Thorvaldson and Vigfusson had established an important fact regarding the CaO/SiO_2 value of the solution at the invariant point without having made a single determination of SiO_2 in solution. However, the deduction is in poor agreement with experimental data obtained by certain of the other investigators. It is, for example, at variance with many of the data of table 4. Though presence of silica sol accounts, no doubt, for a number of the high silica values that have been reported, it is believed that considerable reliance can be placed in the data of Flint and Wells (47) and Roller and Ervin (152) that were obtained at the high-lime side of the invariant point in question. The data of these authors seem to be in reasonable agreement in this region; the values tabulated by Roller and Ervin are given in table 7.[12]

[12] In figure 4 of Roller and Ervin's paper the Ca^{++} scale is displaced one division to the right, as compared with the tabulated values.

According to table 7, the CaO/SiO_2 ratio exceeds 3 only at CaO concentrations above about 1.2 millimoles per liter, or 0.07 g. CaO per liter. This concentration is above that at the invariant points indicated by some of the investigations, though below the CaO concentrations at the invariant points suggested by the curves (No. 13, figure 1) based on the data of Thorvaldson and Vigfusson. As a further step in analysis, it is advisable to consider the possible consequences of the fact that curves 13 of figure 1 are based on the assumption that the SiO_2 in solution can be neglected in computing CaO/SiO_2 for the solid. A trial has shown that even if the Thorvaldson and Vigfusson data are corrected for dissolved SiO_2, by use of table 7, the points at which the curves break are but

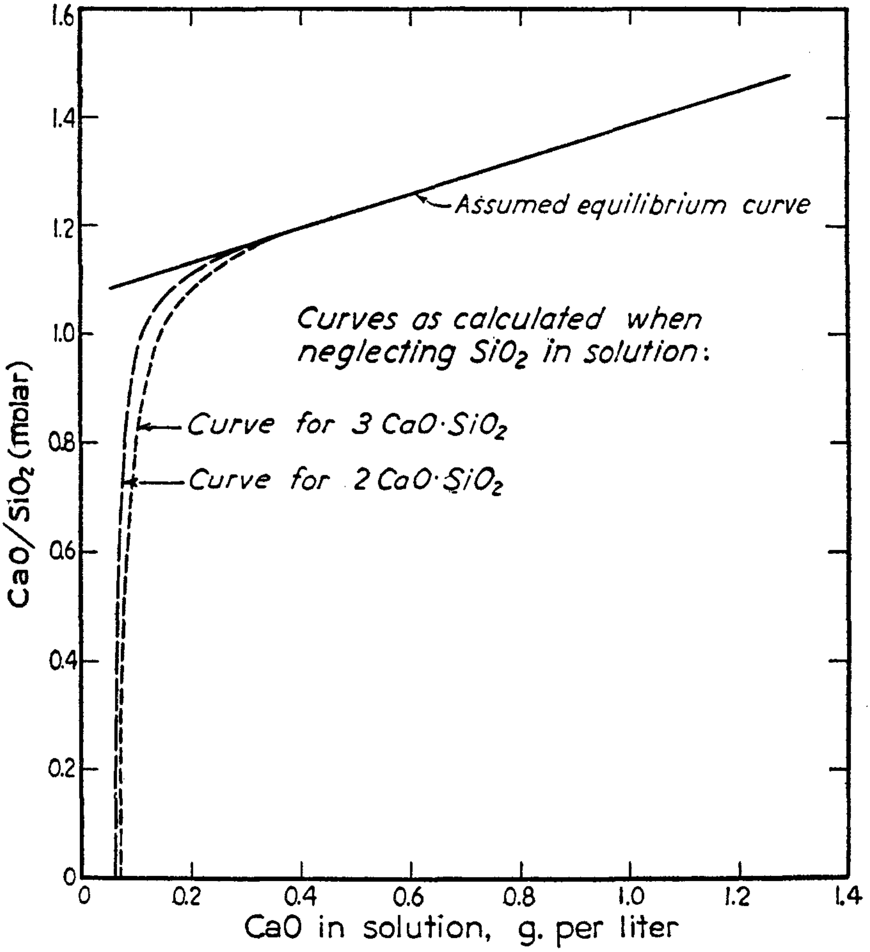

FIG. 6. Hypothetical curves for CaO/SiO_2 for solids *versus* CaO in solution. Used to illustrate the possible effects of neglecting SiO_2 in solution when each preparation is made simply by adding water to anhydrous calcium silicate.

little affected. However, this comparison is not very significant because the authors conceded poor analytical accuracy at the lower CaO concentrations. The accuracy would indeed have to be poor in order to account for the large discrepancy between the two curves in this region. Consequently, it is of interest to consider what effect the neglect of SiO_2 could have in an analogous hypothetical case.

In figure 6 the upper straight line represents a hypothetical relationship between CaO/SiO_2 in solids and CaO in solution, one that resembles the upper portion of Thorvaldson and Vigfusson's curve but is extended to lower CaO concentrations. The lower curves, one for $3CaO \cdot SiO_2$ and one for $2CaO \cdot SiO_2$, were developed from the straight curve by assuming SiO_2 in solution in accordance with the solubility data of Roller and Ervin, letting CaO/SiO_2 be the ratio of CaO in solids to *total* SiO_2 as in curves 13 of figure 1. It is evident that this method, applied at sufficiently low concentrations of CaO, produces inflections rather similar to those obtained by Thorvaldson and Vigfusson, though no invariant point has been assumed. Furthermore, though the curves for $3CaO \cdot SiO_2$ and $2CaO \cdot SiO_2$ are much closer together than curves 13 of figure 1, they are in the same order. This outcome does not prove that Thorvaldson and Vigfusson did not establish an invariant point, but it does suggest uncertainty in the matter. In this connection it is to be recalled (from Section II) that Michaelis reported that cements treated with large volumes of water seemed to hydrolyze only so far as to produce the monocalcium silicate. Leaching of course is a different matter and apparently leads eventually to $SiO_2 \cdot aq$ (122). Nacken (137) who, like Thorvaldson and Vigfusson, simply added water to $3CaO \cdot SiO_2$ also obtained one point for which CaO/SiO_2 is much less than 1 (see curve 16, figure 1), but he also did not actually analyze the solid, and did not correct for SiO_2 in solution.

Point *F*, with its dashed connecting lines, has been entered in figure 5 to show how the invariant point, represented by *T*, must be shifted in order to locate it in accordance with Bessey's ratio of CaO/SiO_2 for the invariant solution (11). The point must, in any case, fall at the high-lime side of the $CaO \cdot SiO_2$ —— H_2O line, since the monocalcium silicate hydrate evidently dissolves incongruently, giving a solution with higher CaO/SiO_2 values than the compound itself (11).

Figure 5 shows the chemical compositions of all the anhydrous calcium silicates that have regions of stability in the $CaO–SiO_2$ system at atmospheric pressure (37, 146). Not shown by the plot is the fact that $CaO \cdot SiO_2$ and $2CaO \cdot SiO_2$ can exist in two and three enantiotropic forms, respectively. The $3CaO \cdot SiO_2$ does not have a thermodynamically stable form at room temperature (29, 116, 130), but it is stable in a practical sense and shows no dissociation when maintained at room temperature (111). Tricalcium silicate reacts with water much more rapidly than the $2CaO \cdot SiO_2$ and the still lower-limed calcium silicates (1a, 6, 18, 47, 85, 113, 191). Also, the high-temperature (α- and β-) forms of $2CaO \cdot SiO_2$ are distinctly more reactive than the low-temperature γ-form. In some preparations, the γ-form and the lower-limed calcium silicates appear almost inert toward water. The β-$2CaO \cdot SiO_2$ has been cited earlier in this review as the form that is present in portland cement. There has, however, been some controversy on this point (112, 166), since the α- and β-forms have been reported as having similar properties (64, 146). Complex twinning has been thought to characterize the α-form, but Insley (70) has suggested that crystals that show this intricate twinning may simply be β-$2CaO \cdot SiO_2$ that was originally of the α-form, the complex twinning having been caused by the inversion. Greene (60) has recently presented evidence that supports this view.

None of the anhydrous calcium silicates are stable in contact with their aqueous solutions at room temperature (47, 113). Nor do any of the hydrated calcium silicates that may be formed dissolve congruently in water, since leaching of even the highest-limed calcium silicate, $3CaO \cdot SiO_2$, leaves finally a solid phase consisting only of hydrous silica (122). However, Flint and Wells (47) found that $CaO \cdot SiO_2$ (pseudowollastonite?) forms a supersaturated solution of great stability. They report a time study of the compositions of the solutions that form when the various calcium silicates are shaken with water.

Hydrous silica has been represented in figure 5 simply by $SiO_2 \cdot aq$. The existence of definite hydrates of silica has been reported from time to time, only to be denied by other investigators. For example, Thiessen and Koerner (172) and Spychalski (161) reported vapor-pressure isotherms which suggested the presence of definite hydrates in specially prepared silica gels, but their results could not be confirmed by Weiser, Milligan, and Coppoc (189). As discussed by Hurd (69), several investigators have concluded that within the elemental solid units of a silica gel the silica is probably anhydrous. However, whether the water is held entirely superficially or not, a considerable amount, namely, 0.3 to 1.0 mole per mole of SiO_2, is firmly held, apparently as hydroxyl groups (30, 41). It has been pointed out that this is a rather large amount to be held entirely superficially (41).

XVII. EFFECTS OF ALKALIES AS ADDITIONS TO THE $CaO-SiO_2-H_2O$ SYSTEM

The possible effects of the addition of alkali oxides to the system $CaO-SiO_2-H_2O$ are of considerable interest to cement technologists. Portland cements contain amounts of chemically combined $Na_2O + K_2O$ that range from 0.2 per cent or less to well in excess of 1 per cent. A large part dissolves quickly; indeed, as much as half of the potash and 10 to 20 per cent of the soda have been extracted from certain cements of normal fineness in only 7 min. simply by making a paste with water (79). It is reasonable to expect that the alkalies in the liquid phase in concrete may sometimes amount to 10 g. Na_2O, or K_2O, per liter (78). To a considerable extent these alkalies form the corresponding hydroxides in solution (115), thus raising the pH above that for saturated $Ca(OH)_2$. The initial basicity is limited, however, by reaction between alkali hydroxides and the gypsum in cement (151). Also, if the clinker contains sulfur trioxide, much of the potassium oxide may enter the solution as potassium sulfate (170). Within about a day, however, the sulfate is largely removed from solution through calcium sulfoaluminate formation (115), and then practically all dissolved alkali is present as hydroxide.

Shaw and MacIntire (158) reported a few experiments on the effects of sodium chloride and sodium hydroxide as additions to the $CaO-SiO_2-H_2O$ system. They found that both of these alkali compounds decreased the CaO/SiO_2 value of the gel and that the sodium hydroxide was particularly effective. A few additional observations were reported at the symposium held by cement chemists and technologists in Stockholm in 1938 (141). Lea (110) remarked that the incongruent solubility of hydrated calcium monosilicate is higher in 3 per cent sodium chloride solution than in water. Thorvaldson (176) stated that at a given alkalinity the CaO/SiO_2 value of the gel is lower when sodium sulfate is present. Bessey (14) speculated that alkali hydroxide in solution might lower the CaO/SiO_2 value of the equilibrium solid. To test this, Forsén (53) introduced 0.5 g. of his supposed $2CaO \cdot SiO_2 \cdot aq$ into the filtrate from a suspension of $3CaO \cdot SiO_2$ in 2 per cent potassium hydroxide solution. After 72 hr. he found the $2CaO \cdot SiO_2 \cdot aq$ to be unchanged. Forsén (52) also reported that hydrolysis of $3CaO \cdot SiO_2$ proceeds rapidly even in potassium hydroxide "of considerable concentration." Later, Hedin (67) reported that the rate of this reaction is almost independent of the pH of the solution. His strongest potassium hydroxide solution was 10 per cent, or about 1.8 normal. In contrast, Lerch and Bogue (122) considered that they effectively stopped the hydrolysis of $3CaO \cdot SiO_2$ and of lower-limed silicates by using sodium hydroxide solution of pH 13.72 (evidently about 1.1 normal) at 30°C.

Kalousek (78) has now reported an extensive systematic study of selected portions of the system $Na_2O-CaO-SiO_2-H_2O$ at 25°C. He determined the compositions of solutions and gels that coexist with solid $Ca(OH)_2$. Also, at selected sodium oxide concentrations, he investigated preparations that precipitate a gel, but not any $Ca(OH)_2$. The sodium oxide concentrations ranged from 0.2 to 152 g. per liter. The initial materials were solutions of sodium silicate and sodium hydroxide, crystalline calcium hydroxide, and additional water, as needed. Preparations were contained in ceresin-lined flasks which were shaken a number of times during the first day and once daily thereafter. Analyses were made after 2 to 18 weeks. These periods were selected arbitrarily, but "neither the solid phase nor solution underwent any determinable changes in time periods of from several weeks to several months." Precipitates were washed with aqueous alcohol solutions of progressively increased alcohol content, up to 95 per cent alcohol, and finally with ether, after which the residue was left in the laboratory air for 1 day. The alcohol contents of the wash solutions were chosen by testing the original filtrate and selecting the maximum alcohol content which just failed to produce a suspension. The solutions and most of the precipitates were analyzed for Na_2O, CaO, and SiO_2. Combined water was determined by difference. The gross CaO/SiO_2 values, as determined for the solids, were checked against values computed from the mix proportions and the analyses of the filtrates.

These gross CaO/SiO_2 values as established in single tests did not disclose the CaO/SiO_2 values for the gels when solid $Ca(OH)_2$ was present. Accordingly, the CaO/SiO_2 values for the gels in equilibrium with solid $Ca(OH)_2$ were determined by making in each instance a series of preparations in which CaO was varied while maintaining a fixed concentration of Na_2O. The plots of CaO/SiO_2 for solids *versus* CaO (or SiO_2) in solution showed, by the breaks in the curves, the values of CaO/SiO_2 that were sought.

When the Na_2O in solution was 0.2 g. per liter, the gel in equilibrium with solid $Ca(OH)_2$ had the composition $0.003Na_2O:1.94CaO:1.0SiO_2:3.2H_2O$. As the Na_2O concentration of the solution was raised while still maintaining solid $Ca(OH)_2$, the gel composition altered, with Na_2O increasing and CaO decreasing, until at 20 g. Na_2O per liter the gel composition was approximately $0.25Na_2O:1.0CaO:1.0SiO_2:2.8H_2O$. Except for minor and rather random deviations, this composition remained practically constant as the concentration of Na_2O was increased to 101 g. per liter. (At higher Na_2O concentrations CaO/SiO_2 for the gel was not determined.) With increase in the Na_2O in solution, the SiO_2 concentration increased to over 1.1 g. per liter. In other tests in which the solutions were not saturated with $Ca(OH)_2$ the SiO_2 in solution was increased much more. The gels in equilibrium with these solutions had CaO/SiO_2 values well below 1, but their Na_2O/SiO_2 values held close to 0.2 over wide ranges in Na_2O and SiO_2 in solution.

The author discusses the significance which his results may have with respect to concretes. He considers that the alkali content of the cement keeps the CaO/SiO_2 value for the gel considerably lower than it would otherwise be. He finds, however, no agreement between his results and the compositions that have been reported for the gelatinous accumulations found in concretes made with destructive "reactive" aggregates. Analyses of these latter gels show mainly silica, alkali oxides, and water. Kalousek attributes their compositions to the semi-permeable nature of hardened cement paste and the resultant osmotic effects, as assumed by Hansen (65).

Kalousek does not comment upon the possible modes of retention of the Na_2O and CaO in the gels. It may be noted, however, that the results obtained in the presence of solid $Ca(OH)_2$ show considerable agreement with the theory of adsorption on $CaO \cdot SiO_2 \cdot aq$, extra CaO in the gel being replaceable with Na_2O, though not on an equimolal basis. The CaO/SiO_2 value of 1.94:1 that was obtained when Na_2O was only 0.2 g. per liter is of interest for comparison with results of other studies, as given in table 5. For zero Na_2O concentration the value should evidently be about the same, though a little higher.

XVIII. CALCIUM SILICATE GEL IN HYDRATED PORTLAND CEMENT

The siliceous product of portland cement hydration is generally believed to be a hydrous lime–silica gel such as is formed in the CaO–SiO_2–H_2O system at high $Ca(OH)_2$ concentration (113). As previously mentioned, this viewpoint has inspired much of the work that has been done on the CaO–SiO_2–H_2O system. In the present review, it has led to the inclusion of some experiments and observations made directly on hydrating cements. Therefore, a brief discussion of some of the evidence for calcium silicate gel in hydrated cement is thought advisable.

It is significant, first of all, that the calcium silicates, $3CaO \cdot SiO_2$ and β-$2CaO \cdot SiO_2$, modified a little by some solid solution, generally constitute 75 per cent, or more, of normal portland cement clinker. Moreover, various investigations (for example, (18)) have shown that these compounds are themselves hydraulic cements reacting with water to form products comparable in eventual strength development to the hydrated portland cement. To be considered also are the staining tests which have indicated in microscopic studies (16, 81, 137) that the cement gel contains CaO and combined SiO_2, but no Al_2O_3, and further that the Al_2O_3 forms a calcium aluminate hydrate. There is also other good evidence that the Al_2O_3 forms non-siliceous products in cement: calcium sulfoaluminate and calcium aluminate hydrate (113). Oxides other than CaO, SiO_2, and Al_2O_3 amount to less than 10 per cent of the clinker and often none of them exceeds 3 per cent; it seems reasonable therefore to assume in hydrated portland cement a hydrous calcium silicate gel, one that is modified, however, by some content of alkalies, as indicated by the work of Kalousek (78), and by intimate intermixture with other products of cement hydration (23). Indeed, rather decisive evidence as to the constitution of the gel in cement has now been provided by Strätling (165), who found that the gelatinous hydration product of cement, when separated from unreacted material, shows the same x-ray spectrum as hydrous calcium silicate gel. Büssem (25) reports that Brandenberger (19) obtained similar evidence regarding portland cement, but Brandenberger's account shows that hydrated $3CaO \cdot SiO_2$, rather than cement, was examined.

It may be noted, next, that some investigators have presented evidence that has led them to suppose that hydrous calcium aluminosilicates may be formed during the hydration of cement. In that case, the amount of calcium silicate gel would be somewhat reduced.

Strätling (165), working with zur Strassen, found that, after some months, products that were formed by shaking $3CaO \cdot SiO_2$ and $3CaO \cdot Al_2O_3$ (two constituents of cement) together in water showed not only the x-ray spectrum that he obtained with hydrous calcium silicate but also another. This latter spectrum was one that he had also obtained under other circumstances, circumstances which led him to believe that it was a quaternary phase, $2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot aq$, though he did not obtain it in a pure state. However, though he obtained the x-ray spectrum of the hydrous calcium silicate in a test on hydrated portland cement, he did not then obtain the spectrum for the assumed quaternary phase. He believed, nevertheless, that at equilibrium the alumina should be represented in $2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot aq$.

Flint, McMurdie, and Wells (46) discovered the garnet–hydrogarnet series of solid solutions. These are compositions of the general formula $3CaO \cdot (Al_2O_3, Fe_2O_3) \cdot 3(2H_2O, SiO_2)$ that are formed, under suitable conditions, at elevated temperature (about 100°C. and higher). The authors speculated as to whether similar compounds might be formed in hydrated portland cement at ordinary temperature but stated, explicitly, that they had no proof of such occurrence.

Later, Flint and Wells (48) discovered hydrous calcium silicoaluminates analogous to the calcium sulfoaluminates which occur in one or more forms in hydrated portland cement. One of these silicoaluminates was produced from certain binary mixtures of cement compounds that had been placed in water and stored for three years at room temperature. However, no success was had with mixtures of $3CaO \cdot SiO_2$ and $3CaO \cdot Al_2O_3$. The authors suggest that the silicoaluminates may possibly play a rôle in cement hydration, perhaps through the formation of solid solution with the sulfoaluminates. In this connection they mention a calcium sulfosilicoaluminate reported by Lafuma (104). Inspection of Lafuma's paper shows however, that the author did not establish that he had only a single solid phase. The composition he reported was $9CaO \cdot 4SiO_2 \cdot Al_2O_3 \cdot 7CaSO_4 \cdot 80H_2O$.

It must be concluded that there is still no direct evidence that a hydrous calcium aluminosilicate is formed during the normal hydration of portland cement.

XIX. SUMMARY OF RESULTS AND CONCLUSIONS FROM PAST INVESTIGATIONS

Results of the various investigations of the system $CaO-SiO_2-H_2O$ at ordinary temperature, and the conclusions drawn from them, are summarized below:

1. A common method of studying phase relations in the system $CaO-SiO_2-H_2O$ is to plot the molar CaO/SiO_2 value for the solid phase against the CaO concentration of the solution. The curves of this kind for data obtained at ordinary temperatures in different investigations have varied widely, as shown by figure 1. In general, however, the curve rises rapidly before the CaO concentration reaches 0.15 g. per liter, and it attains a CaO/SiO_2 value of about 0.85–1.1. The rise then becomes much more gradual but continues, throughout, while the CaO concentration is further increased. The values of molar CaO/SiO_2 attained in the solids, in various investigations, when the solutions were saturated with $Ca(OH)_2$ (about 1.2 g. CaO per liter) have ranged from 1.4 to 2.
2. The solid products are ordinarily colloidal and give no evidence of crystallinity when observed through the light microscope. An x-ray spectrum of a few lines has been obtained, however, by several different investigators, and the spectrum is reported to be the same, within the limits of error, for products of varied molar CaO/SiO_2 (above 1).
3. Though some of the individual differences in the curves may be attributable to differences in the initial materials, essentially the same general shape of curve as described above has been obtained in instances where the hydrous lime-silica products were formed by reaction between silica sol or gel and limewater, sodium silicate and limewater, and anhydrous calcium silicate and water.
4. Divergent results can no doubt be accounted for partially, and perhaps largely, on the basis of incomplete attainment of colloidal equilibrium, and other insufficiencies in experimental work. The possible effects of moderate differences in temperature are also to be considered. However, since the solid products are colloidal, it is to be recognized that only colloidal equilibrium is attained in any case. Differences in adsorptivity and in solubility, as a result of differences in particle size, may therefore be important.
5. Apparently, the initial abrupt rise of the curve denotes chemical combina-

tion of the silica with lime. This inference is supported by various lines of evidence, including the fact that the silica in the $1CaO:1SiO_2$ product is completely acid-soluble. Whether more than one hydrous calcium silicate is formed during this initial rise is in dispute, since the rise is found to be practically vertical in some investigations but not in others. Moreover, values reported for the SiO_2 concentrations of the solutions in this region have shown pronounced variation both within the individual investigations and with respect to different investigations. The variation has been considered important by some investigators, while by others it has been attributed simply to the presence of colloidal silica.

6. Many investigators believe that the initial abrupt rise in the CaO/SiO_2 value for the solid represents formation of $CaO \cdot SiO_2 \cdot aq$. This judgment now has the support of x-ray evidence, since crystalline $CaO \cdot SiO_2 \cdot aq$ prepared hydrothermally at 100–140°C. has been reported (49) to give the same spectrum as the gel obtained at room temperature. Formation of still lower-limed calcium silicate hydrates has also been assumed.

7. Whether CaO held in excess of 1 mole per mole of SiO_2 is chemically combined with the silica or is simply adsorbed is a disputed matter. Thermal data have been advanced in support of chemical combination, but applications of the solubility product principle and the Freundlich adsorption isotherm have favored adsorption. In any case, the fact that the additional lime is acquired over a wide range in CaO concentrations in solution appears to point to either adsorption or some kind of solid solution.

8. The SiO_2 in solution increases, at first, as the CaO concentration is increased from zero, and is indicated to attain its maximum value in the region of abrupt rise in the CaO/SiO_2 ratio of the solids. Thereafter, it falls rapidly and is indicated to be less than 0.01 g. SiO_2 per liter at 30°C., when the CaO concentration is 0.15 g. CaO per liter. Maximum values as high as 0.3 g. SiO_2 per liter have been reported, but whether they are equilibrium values has been questioned. Metastability and silica sol formation have been suggested. Some investigators believe that the maximum SiO_2 concentration is only about 0.05 g. SiO_2 per liter or less. Owing to the strong decrease in SiO_2 concentration on the high CaO side of the point of maximum concentration, nearly all the CaO is present as $Ca(OH)_2$ in solutions in which CaO is more than about 0.2 g. per liter.

9. None of the anhydrous calcium silicates are stable in contact with their aqueous solutions at room temperature. Also, none of the hydrated calcium silicates that may be formed in such solutions appear to be capable of dissolving congruently in water, for leaching of even the highest-limed calcium silicate, $3CaO \cdot SiO_2$, leaves finally a solid phase consisting only of hydrous silica.

10. By reason of hydrolysis, a large part of the curve for CaO/SiO_2 in solids *versus* CaO in solution can be established simply by adding water (in varied proportions) to either of the high-limed calcium silicates, $3CaO \cdot SiO_2$ or $2CaO \cdot SiO_2$, none of the soluble products being removed from the system. Indeed, it has been indicated that either compound, employed in this way, can advance the hydrolysis until the solid phase is lower limed than $CaO \cdot SiO_2 \cdot aq$

and is, perhaps, $SiO_2 \cdot aq$. If this is possible, it means that the molar CaO/SiO_2 in solution must exceed 3:1 at the invariant point where $CaO \cdot SiO_2 \cdot aq$ and the lower-limed compound are in equilibrium. Such a ratio at this point is, however, larger than is indicated by some of the other evidence, and it appears that the matter needs further investigation.

11. The gelatinous solid having a CaO/SiO_2 value of less than 2, that has been obtained in apparent equilibrium with saturated $Ca(OH)_2$ solution in many investigations, indicates that both $3CaO \cdot SiO_2$ and β-$2CaO \cdot SiO_2$ should react with water with precipitation of $Ca(OH)_2$, a fact that has also been established by direct experiment. In spite of this, β-$2CaO \cdot SiO_2$ made up with water as a paste appears to hydrate with very little further hydrolysis after saturating the solution with $Ca(OH)_2$. Also, much of the data for hydration of $3CaO \cdot SiO_2$ in a paste indicates that only a third, or less, of the CaO is liberated as $Ca(OH)_2$. It thus appears that during hydration in pastes the hydrolysis is often less than for equilibrium. Here again, however, the data are not wholly consistent. Also, the methods of determining $Ca(OH)_2$ are apparently somewhat faulty.

12. At least at concentrations of CaO above that at which CaO/SiO_2 for the solid reaches 1, all the SiO_2 in the liquid phase is apparently in true solution. Probably at the higher CaO concentrations the silicate ions are primarily those of orthosilicic acid, H_4SiO_4, though this is not fully established. At lower CaO concentrations some investigators believe that the silicate ions associate to form dimers. At the higher CaO concentrations the molar ratio of "silicate CaO" to SiO_2 has been reported to exceed 1 in solutions supersaturated with the calcium silicate.

13. The amount of water held by the hydrous calcium silicates under varied circumstances has been less investigated than the relative amounts of CaO and SiO_2. However, the water content is found to decrease with each decrease in external vapor pressure, after the manner of many other colloidal materials. In compositions approaching $CaO \cdot SiO_2 \cdot aq$ the first molecule of water appears to be rather firmly held and may be constitutional.

14. Under some circumstances, mainly during the hydration of the anhydrous silicates in the presence of considerable water, fine needle crystals have formed, which, mainly on the basis of staining tests, have been called calcium silicate, or silicate hydrate, and have frequently been represented as $CaO \cdot SiO_2 \cdot aq$. The conditions under which these needles form have not been well established and various investigators have been unable to obtain them.

15. The addition of sodium hydroxide to the $CaO{-}SiO_2{-}H_2O$ system when the solution is maintained saturated with $Ca(OH)_2$ has been found to reduce the CaO-to-SiO_2 ratio of the gelatinous product that is in equilibrium with the solid $Ca(OH)_2$. The CaO in the gel in excess of 1 mole per mole of SiO_2 is found to be replaceable by about 0.25 mole of Na_2O.

16. Portland cement, which contains about 75 per cent of $3CaO \cdot SiO_2$ and β-$2CaO \cdot SiO_2$, produces on hydration a gelatinous product which is evidently largely a lime–silica gel such as is formed in the system $CaO{-}SiO_2{-}H_2O$, except that it presumably contains some alkali also. However, all the products of

cement hydration are closely intermingled. The solution phase is saturated with $Ca(OH)_2$ and is commonly supersaturated during the early stage of the hydration.

XX. NEED FOR FURTHER RESEARCH

It is evident from the foregoing that in spite of the large amount of work done, some of it apparently skillful and painstaking, few precise numerical data on compositional relationships in the system $CaO–SiO_2–H_2O$ at ordinary temperature can yet be advanced as necessarily having general validity. This does not mean, however, that the various researches have been of little value. Indeed, the broad outlines of the picture appear to have been rather well established. Also, as previously discussed, it is probably inherent in the colloidal nature of the solids formed in this system that the gross compositions must vary somewhat with circumstances other than the final temperatures, vapor pressures, and solution concentrations. Nevertheless, it should eventually be possible to advance the knowledge of the $CaO–SiO_2–H_2O$ system at ordinary temperature far beyond its present state.

Some of the past work could advantageously be repeated with modifications suggested by the uncertainties that now exist. Baylis' observations (7) led him to conclude that the concentration of the initial silica gel affects the amount of CaO that can be taken up. If further systematic study confirms this, it would seem to limit the possibilities with respect to the nature of the final product. Hedin (67) believes that colorimetric determination of SiO_2 gives only the silica in true solution, but Krasil'nikov and Kiselev (88) appear to be less confident. Some method of distinguishing adequately between colloidal and dissolved silica could aid materially in establishing more thoroughly the invariant points of the system. Thorvaldson and Vigfusson (178) believe that their anhydrous silicates, $3CaO \cdot SiO_2$ and β-$2CaO \cdot SiO_2$, hydrolyzed in large volumes of water until the molar CaO/SiO_2 of the solid phase was less than 1, but the composition of the final solid was obtained indirectly, and without allowance for SiO_2 in solution. As the result is of much interest, repetition of some of the experiments with direct analysis of final solids and solutions for both CaO and SiO_2 seems advisable. Flint and Wells (47) concluded that the relatively high-limed solutions of the $CaO–SiO_2–H_2O$ system have molar ratios of "silicate CaO" to SiO_2 greater than 1, but they worked with strongly supersaturated solutions. Perhaps development of analytical methods of sufficiently high precision may eventually enable this conclusion to be checked with solutions that are not supersaturated. Various investigators believe that they have observed needle crystals of calcium silicate hydrate which have formed at room temperature. Apparently, there is a reasonable possibility that by special techniques crystals of microscopic size could be formed at room temperature in quantities sufficient to enable their compositions and properties to be determined. Indeed, some of the crystalline calcium silicate hydrates obtained hydrothermally might well be further investigated with respect to equilibria at room temperature.

The past work has indicated that attainment of colloidal equilibrium is sometimes slow and uncertain. In future studies, the more promising of the methods already used can be selected and applied, with approach to equilibrium from both the high- and low-lime sides. More attention can be focused, also, upon the nature of the bond between the CaO and SiO_2 in the hydrous solids. Greatly needed, in this connection, is a reliable quantitative test for $Ca(OH)_2$ in the presence of the hydrous calcium silicate gel but the reliability of such a test is not easy to prove. Possibly one of the current methods is sufficiently accurate, but if so this needs to be better established. These methods have considerable utility, however, especially for relative purposes. It is, therefore, somewhat surprising that they have been little used (for $Ca(OH)_2$, as distinct from CaO) except in studies on hydrated pastes, and on commercial cements. Free $Ca(OH)_2$ tests applied in studies like those represented in figure 1 might provide information of distinct value. In view of the possibilities of adsorption it would be of interest to apply such tests to solids obtained at all $Ca(OH)_2$ concentrations.

The cause of the increase in the CaO/SiO_2 value of the solid with increase in the CaO concentration of the solution should also become more evident if electrokinetic tests were made and if more work were done with other metallic ions besides Ca^{++}. Ion-exchange studies would bear directly on the questions of solid structure and the state of combination of the CaO.

The calorimetric approach, employed by Cirilli, appears to warrant further use. Also, electron microscopy and both x-ray and electron diffraction can undoubtedly be used to further advantage. Radioactive calcium might also prove serviceable in studying adsorption.

In many of the investigations of the past the experimenters have contented themselves with determinations of the gross compositions of the colloidal products, in relation to solution compositions. In the future it should be possible to bring improved methods to bear upon the problem of the structure of the colloidal products and to distinguish more clearly between the chemical and physical forces that are involved.

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