Stoichiometry of Tricalcium Silicate Hydration

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●ACCORDING TO Powers (1), during the hardening of portland cement the content of nonevaporable water increases linearly with the degree of hydration. It may be expected that this relationship results from the reaction of tricalcium silicate, the principal constituent of portland cement, with water according to the following equation:

$$3 \, CaO \cdot SiO_2 + c \, H_2O = n \, CaO \cdot SiO_2 \cdot p \, H_2O + (3 - n) \, Ca(OH)_2 \qquad (1)$$

As the amount of water consumed for hydration, c, is bound in the calcium silicate hydrate and in the calcium hydroxide, the following relationship exists between c, n, and p:

$$c = p + (3 - n)$$

or

$$p = n + c - 3$$

The reaction equation for the hydration of the tricalcium silicate receives then the following form:

$$3 \, CaO \cdot SiO_2 + c \, H_2O = n \, CaO \cdot SiO_2 \cdot (n + c - 3) \, H_2O + (3 - n) \, Ca(OH)_2 \quad (1a)$$
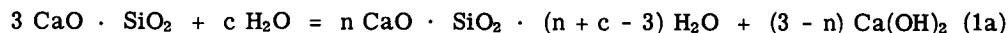
If c is constant, the difference between the lime content, n, and the water content, n + c - 3, of the calcium silicate hydrate has the value 3 - c and is therefore also constant.

Investigations by Kantro, Brunauer and Weise. (2, 3) have shown that the composition of the calcium silicate hydrates formed in the hydration of tricalcium silicate and β-dicalcium silicate changes with the duration of reaction. In the first hours rich-in-lime calcium silicate hydrates occur with molar CaO/SiO_2 ratios of about 3 or 2, depending upon whether tricalcium silicate or dicalcium silicate was used as the starting material. It is only after at least a week that CaO/SiO_2 ratios of about 1.5 occur.

In our own tests (4) it was established that even after a reaction time of 180 days the hydration products of the tricalcium silicate were proportionately richer in lime when less mixing water had been added. With a mixing water amount w_0 of 0.25 g H_2O/g C_3S, molar CaO/SiO_2, ratios of 2.0 are considerably exceeded in the calcium silicate hydrate, while, with high water additions w_0 of 1.0 g H_2O/g C_3S, much lower molar CaO/SiO_2 ratios are obtained in the calcium silicate hydrates.

This reveals that the lime content of the calcium silicate hydrate, i.e., the factor n in Eq. 1a, has a wide range of variation. Eq. 1a predicts that the water content of the calcium silicate hydrate must show an equimolar change with lime content, n, if the amount of water bound in the hydration process, c, is constant. This means that the only formal difference between rich-in-lime calcium silicate hydrates and others is their higher calcium hydroxide content. This corresponds with the opinion of Keil (5) that the third CaO existing opposite the C_2S in the C_3S has only the function of speeding up the hydraulic reaction by increasing the temperature.

It was thus the primary aim to establish whether, with a change in the mixing water addition, the amount of water bound by the tricalcium silicate remains constant although the composition of the calcium silicate hydrate changes. For this reason tricalcium silicate was mixed with various amounts of water, and after various times the degree

of hydration, the content of nonevaporable water and the calcium hydroxide content were determined. From these results it was possible to calculate the amount of water bound by the tricalcium silicate and the composition of the calcium silicate hydrate.

EXPERIMENTAL

Preparation of Samples

For the preparation of tricalcium silicate a mixture of calcium carbonate reagent grade and aerosil (very fine grain silica gel), after addition of a little distilled water, was shaped by hand into granules and heated for one hour at 1500 C in a gas-fired muffle furnace. After crushing in a porcelain ball mill the mixture was chemically analyzed and its composition corrected by an addition of calcium carbonate or aerosil. After further heating at 1500 deg the product still contained only a very small amount of free CaO and it was therefore ground for the tests to a specific surface of approximately 3500 cm^2/g (according to Blaine). Table 1 shows the composition of the tricalcium silicate sample.

For the hydration tests the tricalcium silicate was mixed with distilled water in amounts of w_0 = 0.25, 0.35, 0.45, 0.60, 0.80, 1.00, 1.50 and 2.00 g H_2O/g C_3S. For this purpose about 6 g tricalcium silicate was weighed into a porcelain dish, the corresponding amount of double-distilled water was added from a burette, the mixture mixed by hand and quickly placed in a plastic tube that was then sealed airtight. For every testing date two samples were prepared on different days. The samples were kept in a constant temperature room at 20 C. To prevent phase separation, all samples with water contents, w_0, of 0.45 or more were fastened to the rotating frame of a shaking machine so that the suspension moved slowly to and fro in the test tube.

The samples with w_0 = 0.25 and 0.35 remained crumbly; the water addition was not sufficient to form a cohesive plastic paste. With w_0 = 0.45, 0.60 and 0.80, pastes were formed which were hardened after seven days at the latest and showed high strengths after 28 days. With still higher water additions the pastes formed fluid suspensions which did not harden.

Analysis

After various hydration times the nonevaporable water, the free calcium hydroxide and the nonhydrated tricalcium silicate in the samples were determined. For this purpose, after smashing the plastic tube, the hardened sample was first rough-crushed and then, after addition of cyclohexane, ground in a mortar and finally in a ball mill. Subsequently the cyclohexane was filtered off through a glass filter and the residue dried by through suction of dry, CO_2-free air.

The higher water content samples which were not completely hardened could only be ground in cyclohexane after the excess water had been eliminated by a brief shaking of the moist reaction products with ethanol and subsequent filtering. In this process only very slight amounts of calcium hydroxide were dissolved in the ethanol and these were disregarded. Practically no calcium hydroxide was taken up by the cyclohexane used for grinding.

The calcium hydroxide in the ground and air-dried samples was determined by the method of Franke (6). For this purpose 0.1 g of the sample was boiled with a mixture of 12 ml acetoacetic ester and 80 ml isobutyl alcohol for one hour under a reflux condenser and the calcium hydroxide extracted in the filtrate was determined acidimetrically with 0.1 N hydrochloric acid and thymol blue as indicator.

TABLE 1

COMPOSITION OF TRICALCIUM SILICATE USED

Component	Theoretical Percent	Actual Percent
Free CaO		0.06
Loss on ignition		0.03
Insoluble residue		0.04
CaO	73.68	73.58
SiO_2	26.32	26.40
Al_2O_3 and MgO present only as impurities		

As the solvent mixture not only dissolves the calcium hydroxide but also attacks the calcium silicate hydrate, the procedure was altered by Pressler, Brunauer, Kantro and Weise (7) in such a manner that the CaO portion arising from the calcium silicate hydrates could be taken into account. Extraction is accordingly carried out in manifold ways and either the ratio of the amounts of extractant and sample (solvent variation method, SVM) or the time of extraction (time variation method, TVM) is changed. The extrapolation of the amount of solvent to 0 or of the extraction time to 0 yields the true calcium hydroxide content.

A number of preliminary tests with varying extraction times of 30, 60, 120 and 240 min showed that after 30 min the calcium hydroxide is not yet completely dissolved and that the amount of extracted calcium hydroxide between 60 and 240 min increases approximately linearly with the time of extraction. The calcium hydroxide content determined according to TVM by extrapolation of the time of extraction to 0 is 0.3 to 3 percent lower than the amount of calcium hydroxide extracted in 60 min. Correspondingly, the investigation of the hydration products of the tricalcium silicate by TVM yields molar ratios of CaO/SiO_2 higher by 0.005 to 0.05 than the single determination of the calcium hydroxide after an extraction time of 60 min. Since the primary purpose of the present work was to establish considerably greater variations in the CaO/SiO_2 ratio of the calcium silicate hydrates, the time-consuming investigation by TVM was not carried out and the calcium hydroxide was only determined after an extraction time of 60 min. The calcium hydroxide content was converted to g CaO/g C_3S by means of the loss on ignition.

Parallel with the chemical investigations, the calcium hydroxide was determined thermogravimetrically in the samples dried in vacuum at a water vapor pressure of ice at -79 C. At the same time the CO_2 content was established, which generally lay between 0.2 and 0.8 percent, but rose in certain cases, especially in the samples with maximum water additions, as high as 2 percent. Because the CO_2 stems from the calcium carbonate formed during the preparation of the sample by reaction with CO_2, an amount equivalent to the CO_2 was added to the determined calcium hydroxide content.

The unhydrated tricalcium silicate was determined by X-ray diffraction quantitatively, using an internal standard. For this purpose 0.1 g of calcium fluoride was added to an amount of 1 g of the dried sample. After suspension with 15 ml cyclohexane the mixture was ground for 20 min in a ball mill and after evaporation of the cyclohexane homogenized in a mortar.

For determination by the X-ray method two lines of the tricalcium silicate with d = 1.77 Å (triplet) and with d = 2.193 Å were studied along with the (220) line of the calcium fluoride with d = 1.931 Å. The tricalcium silicate content was taken as the mean of the two values yielded by the two lines. The intensity of each line was registered three times, with a new preparation each time, and integrated by planimeter. The standard curve was recorded with corresponding mixtures of tricalcium silicate and calcium silicate hydrate. As the (220) line of the calcium fluoride at 1.931 Å coincides with the (102) line of the calcium hydroxide at 1.927 Å the thermogravimetrically determined calcium hydroxide content had to be taken into account for the evaluation.

The unhydrated tricalcium silicate content and the loss on ignition revealed the degree of hydration; from this, in connection with the calcium hydroxide content, the molar CaO/SiO_2 ratio in the calcium silicate hydrate could then be calculated. The nonevaporable water is that water retained after the drying of the crushed sample in a vacuum with a water vapor pressure of ice at -79 C. It escapes when the sample is heated to 1000 deg, and was determined thermogravimetrically after the drying. It was necessary to correct for the amount of water equivalent to the CO_2 content, as water released in the carbonation of calcium hydroxide.

RESULTS

Progress of Hydration

Figure 1 shows the degree of hydration in percent after various reaction times as a function of the water addition. It emerges that in particularly low-in-water pastes with $w_0 = 0.25$ and 0.35, the degree of hydration increases with increasing addition of water.
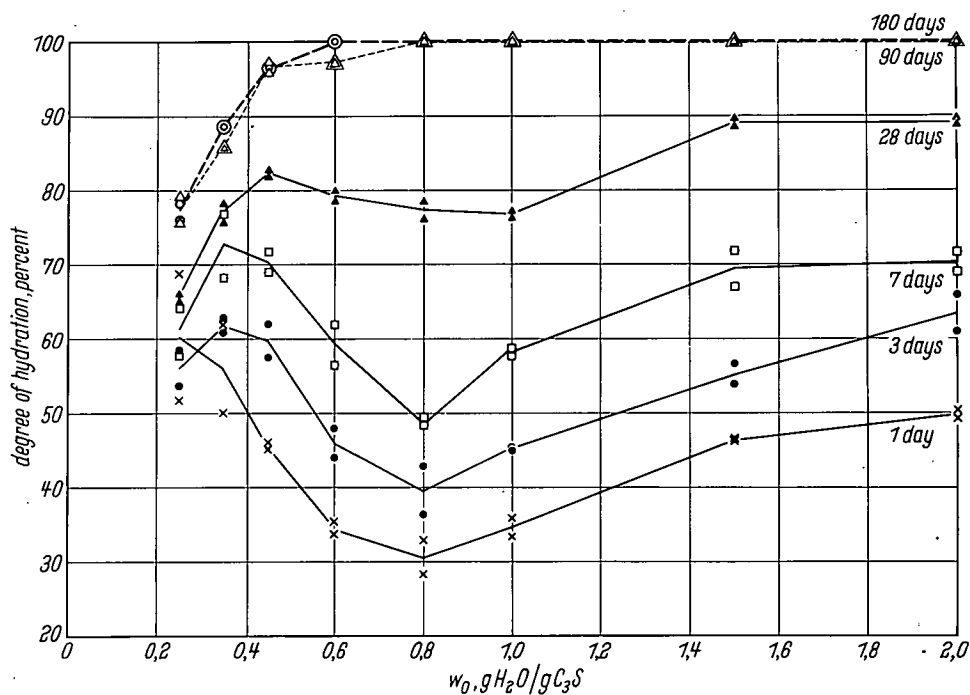
Figure 1. Degree of hydration as a function of mixing water w_0.

It would appear that in these mixtures the water supply is not sufficient for rapid progress of the reaction. With further increase in the amount of mixing water the degree of hydration declines until the 7-day date and with $w_0 = 0.80$ reaches a minimum, to rise again with still higher water additions. A similar behavior, i.e., a decline in the speed of reaction with increasing water content, was observed by Van Bemst (8, 9) with very high water additions only of about 45 to 180 ml per g tricalcium silicate, but not in the range of the w_0 values chosen here of 0.25 to 0.75. It is not possible to date to interpret these contradictory results.

Between 7 and 90 days the samples with $w_0 = 0.6$ and more react extremely quickly. Consequently, the minimum in the degree of hydration with $w_0 = 0.8$ is almost compensated after 28 days and complete hydration reached after 90 days. The mixtures with $w_0 = 0.45$ and less practically cease hydration between 90 and 180 days. Their degree of hydration lies between 97 and 77 percent, and declines with decreasing water additions.

Lime Content of Hydration Products

Figure 2 shows the contents of free calcium hydroxide in g CaO/g C_3S as a function of the degree of hydration; on the left are the results of the chemical-analytical determination and on the right the values obtained by the thermogravimetric method. In this diagram all the samples having calcium silicate hydrates with the same CaO/SiO_2 ratio but with varying degree of hydration lie on a straight line through the origin. Thus, the slope of these straight lines indicates the CaO/SiO_2 ratio.

The figure shows that there is a wide variation in the composition of the calcium silicate hydrates. In the chemical-analytical determination of the calcium hydroxide the CaO/SiO_2 ratio lies between about 1.4 and 2.1, in the thermogravimetric determination of the calcium hydroxide between about 1.6 and 2.3. Given a high water addition with w_0 values of 0.6 and more, however, calcium silicate hydrates occur with approximately equal CaO/SiO_2 ratios of about 1.4 to 1.6 in the chemical and about 1.6
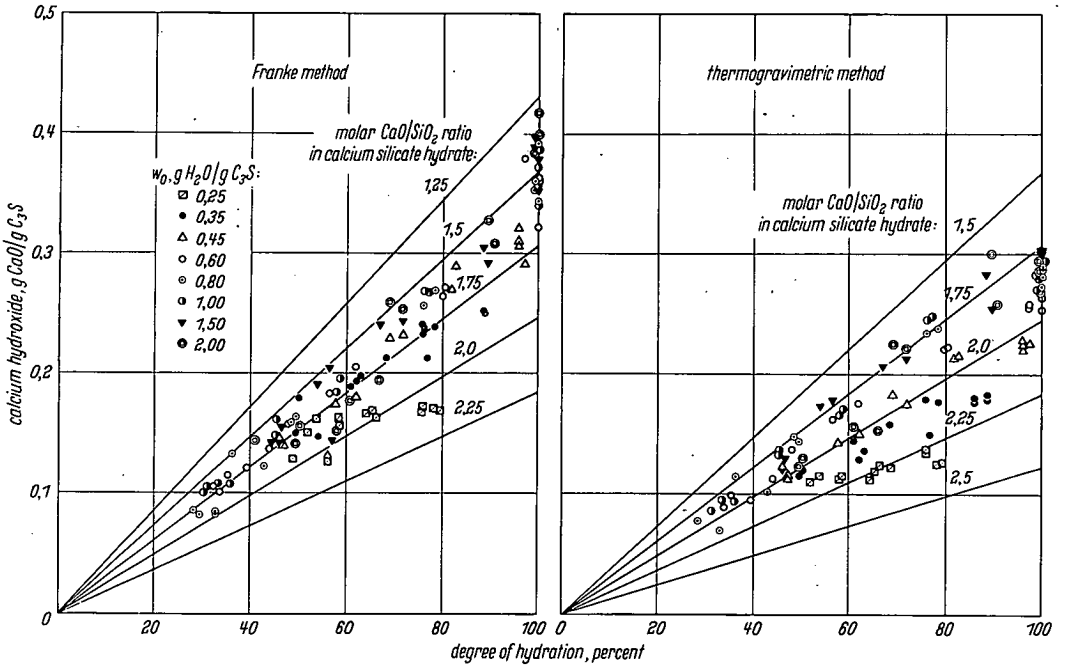
Figure 2. Content of calcium hydroxide formed during hydration of tricalcium silicate.
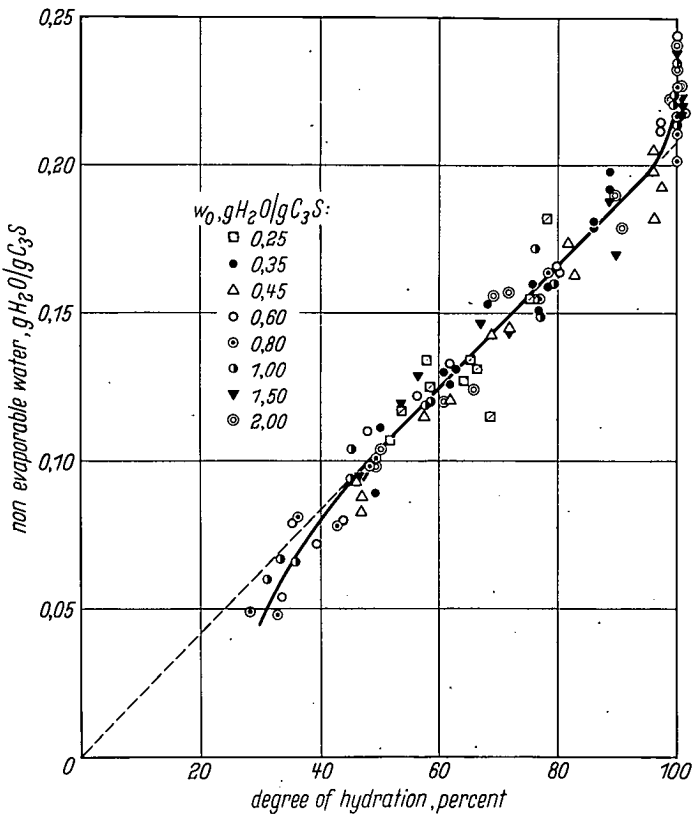

Figure 3. Content of nonevaporable water in hydration products of tricalcium silicate.

to 1.9 in the thermogravimetrical determination of the calcium hydroxide, which show little change with progressive hydration. In samples with low water content, richer-in-lime calcium silicate hydrates are formed whose CaO/SiO_2 ratio rises with decreasing w_0 values and also rises as hydration progresses.

## Water Content of Hydration Products

Figure 3 shows the content of nonevaporable water in g H_2O/g C_3S as a function of the degree of hydration. This reveals that in the range between 50 and 95 percent hydration a linear relationship exists between water content and degree of hydration that is independent of the amount of mixing water w_0, and consequently independent also of the composition of the calcium silicate hydrate. The slope of the straight line indicates that in the aforementioned limits 1 g tricalcium silicate reacts with 0.21 g water. The behavior of tricalcium silicate is thus similar to that of portland cement, which, when completely hydrated, according to Powers (1) binds about 0.23 g water per g cement, depending upon cement composition.

Tricalcium silicate samples which are hydrated to less than 50 percent apparently contain less water per g C_3S. In this range, however, the number of results is inadequate to secure the curve statistically. The hydration products which are present in the completely hydrated samples reveal a definitely higher water content of 0.225 g H_2O/g C_3S which, as shown in Figure 2, corresponds to a somewhat lower CaO/SiO_2 ratio in their calcium silicate hydrates. This result was only found in the chemical-analytical determination of calcium hydroxide. With the thermogravimetrical determination of calcium hydroxide no difference is indicated in the CaO/SiO_2 ratio of the calcium silicate hydrate between the completely hydrated and the partially hydrated samples.

<div align="center">DISCUSSION</div>

Stoichiometry of Hydration Reaction

The take-up of a constant amount of water of 0.21 g H_2O/g C_3S or 2.66 mol H_2O/mol C_3S leads to the following reaction equation for the hydration of tricalcium silicate:

$$3 \, CaO \cdot SiO_2 + 2.66 \, H_2O = n \, CaO \cdot SiO_2 \cdot (n - 0.34) \, H_2O +$$
$$(3 - n) \, Ca(OH)_2 \qquad (2)$$
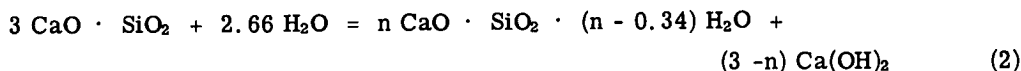
According to this, the difference between the CaO/SiO_2 ratio, n, and the H_2O/SiO_2 ratio of the calcium silicate hydrate that occurs as the hydration product is constant and amounts to 0.34, while the CaO/SiO_2 ratio may vary between about 1.5 and 3.0.

A similar relationship may also be deduced from the results obtained by Brunauer and Kantro (10). It is shown by their results that the water content of calcium silicate hydrates formed in the hydration of tricalcium silicate and β-dicalcium silicate changes parallel with the lime content. Consequently, the difference between CaO/SiO_2 and H_2O/SiO_2 remains almost constant with a mean value in the tests of 0.41. This corresponds to a water content of 2.59 mol H_2O/mol C_3S or 0.204 g H_2O/g C_3S.

A similar finding also results from the analytic values indicated (10) for the hydration of tricalcium silicate at 25 C. In contrast to the results of the present investigation, however, the constant difference between CaO/SiO_2 and H_2O/SiO_2, and correspondingly a linear relationship between degree of hydration and water content, only occurs at degrees of hydration above 60 percent when there is no longer any considerable change in the CaO/SiO_2 ratio of the calcium silicate hydrates. The amount of bonded water calculated from this of 2.50 mol H_2O/mol C_3S or 0.197 g H_2O/g C_3S is only slightly smaller than the water content of 0.21 g H_2O/g C_3S established in the present investigation.
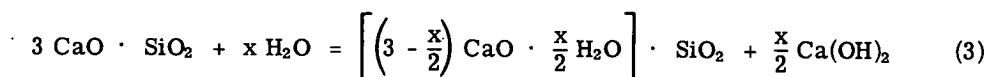
According to Taylor (11), no connection exists between lime and water contents in calcium silicate hydrates with CaO/SiO_2 ratios below 1.5. In contrast to this, however, results of Brunauer and Greenberg (12) reveal that in low lime calcium silicate hydrates, prepared by the shaking of calcium hydroxide and silica gel at 23 and 50 C, the difference

between CaO/SiO_2 and H_2O/SiO_2 remains almost constant. It changes only from 0.33 to a maximum 0.38 while the CaO/SiO_2 ratio rises from 0.98 to 1.44.

Summarizing, it may be stated that tricalcium silicate binds a constant amount of water in its hydration although the lime content of the calcium silicate hydrate may vary within wide limits. This reveals that the water content of the calcium silicate hydrate must also change in the same way as the lime content, i.e., that the various calcium silicate hydrates differ formally from each other only by a different calcium hydroxide content. A similar relationship probably exists, too, in the case of low-lime calcium silicate hydrates that have been prepared from calcium hydroxide and silica gel.

Properties of Hydration Products

A crystal structure similar to tobermorite is generally attributed to the calcium silicate hydrates. Its principal characteristic, according to Megaw and Kelsey (13), is a central double layer of the composition $[CaO_2]^{2-}$ which is occupied on both sides by chains of SiO_4 tetrahedrons. As the CaO/SiO_2 ratio in this combined layer only amounts to 0.67 it is assumed in explanation of the higher and variable lime content that Ca^{2+} and $(OH)^{-}$ ions can be taken up into interstitial spaces of the tobermorite structure (14) and that the SiO_4 chains are more or less incomplete (15) or are completely absent on one side of the $[CaO_2]^{2-}$ layer (16). In this way CaO/SiO_2 ratios up to about 2, but not higher, can be explained. Nor can the great changes in lime content of the calcium silicate hydrates be explained by a varying portion of the "intermediary phase," the high-lime hydration products of tricalcium silicate observed by Trojer (17) in microscopic examination of concrete. Trojer presumes that at the beginning of hydration calcium ions leave the lattice of the tricalcium silicate and are replaced by two protons each. The formation of the intermediary phase could thus be described by the following reaction equation:

$$3\ CaO \cdot SiO_2 + x\ H_2O = \left[\left(3 - \frac{x}{2}\right) CaO \cdot \frac{x}{2} H_2O\right] \cdot SiO_2 + \frac{x}{2} Ca(OH)_2 \qquad (3)$$

According to the results of the present investigation x is constant and equal to 2.66. The composition of the intermediary phase, therefore, would have to correspond to the formula:

$$(1.67\ CaO,\ 1.33\ H_2O) \cdot SiO_2$$
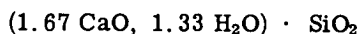
i.e., it would have to show a constant and not extremely high lime content. But this is contradicted by the findings of the investigation. This shows that the intermediary phases only play an insignificant role in the hydration of the tricalcium silicate. It is possible, however, that they are formed in major quantities at the beginning of hydration and that the lower contents of combined water at degrees of hydration below 50 percent (Fig. 3) may be attributed to this.

The variable composition of the calcium silicate hydrates may be explained, however, if one departs from the finding that high-lime and low-lime calcium silicate hydrates differ only in their calcium hydroxide content. Electron microscope photos have shown that the low-lime calcium silicate hydrates develop in sheets or in foils while the high-lime hydrates form fibers (18, 19, 20) which, as the electron diffraction investigations revealed, consist of rolled-up foils (21). The platelike form corresponds to a structure of symmetrical tobermorite layers which are occupied on both sides by SiO_4 chains. The tube form of the rich-in-lime calcium silicate hydrates, however, is inconsistent with this.

It is assumed, therefore, by Gard, Howison and Taylor (16) that in the presence of a large amount of lime the tobermorite layers possess SiO_4 chains on one side only and the other side is occupied by $(OH)^{-}$ ions. A similar crystal structure is shown in the hexagonal-plate kaolinite and the tube-shaped halloysite.

The exchange of SiO_4 chains for $(OH)^{-}$ ions results in an increase of the CaO/SiO_2 ratio of the whole combined layer to 1.33 and the corresponding surface receives the

composition $Ca_4(OH)_8$. It is possible that such an arrangement of equivalent amounts of Ca^{2+} and $(OH)^-$ ions on one side of the $[CaO_2]^{2-}$ double layer attracts additional Ca^{2+} and $(OH)^-$ ions and endeavors to assume the more stable hexagonal atom arrangement of calcium hydroxide. The stresses arising from this might be responsible for the rolling up of the foils into tubes. An attachment of $Ca(OH)_2$ layers to the combined layer, occupied on only one side by SiO_4 chains, with a CaO/SiO_2 ratio of 1.33 offers an explanation of the variable lime content of the calcium silicate hydrates. With an attachment of one $Ca(OH)_2$ layer the CaO/SiO_2 ratio increases to 2.0; with an attachment of two $Ca(OH)_2$ layers, to 2.67. Moreover, this would also explain the variations in the content of free calcium hydroxide which occur in the different methods of determining the calcium hydroxide. It may be assumed that the distorted $Ca(OH)_2$ layers do not yield X-ray lines nor do they show, within a very narrow temperature range, the dehydration behavior that is characteristic for calcium hydroxide, but that they are partially dissolved during the extraction of the free calcium hydroxide.

SUMMARY

Tricalcium silicate was hydrated with various water additions between 0.25 and 2.0 g H_2O/g C_3S. The crushed samples were analyzed after hydration times of up to 180 days. The unhydrated tricalcium silicate was determined by X-ray diffraction method, the calcium hydroxide was determined chemical-analytically and thermogravimetrically, and the nonevaporable water by drying in vacuum with a water vapor partial pressure of ice at -79 C.

The chemical analysis of the calcium hydroxide yielded values that were about 35 percent higher than those obtained by the thermogravimetric method. From the calcium hydroxide content and the degree of hydration it was possible to establish the lime content of the calcium silicate hydrates formed during hydration. According to these findings, in pastes with a high water addition of 0.6 g H_2O/g C_3S and more, calcium silicate hydrates were formed with about the same molar CaO/SiO_2 ratios of 1.4 to 1.6 if the calcium hydroxide is determined chemically and of 1.6 to 1.9 if it is determined thermogravimetrically. There is only slight change in the composition as hydration progresses. In the samples containing less water, rich-in-lime calcium silicate hydrates occur whose CaO/SiO_2 ratio rises with decreasing initial water contents to about 2.3 and which also become richer in lime with progressive hydration. The content of nonevaporable water increases linearly with the degree of hydration in the range between 50 percent and 95 percent hydration, independently of the initial water content, even though calcium silicate hydrates occur with widely varying composition. This reveals that 1 g tricalcium silicate binds 0.21 g water in its hydration. At the beginning of hydration poorer-in-water hydration products occur while richer-in-water hydration products are present in completely hydrated samples. The linear relationship between combined water and degrees of hydration would appear to indicate that the only difference between low-lime and high-lime calcium silicate hydrates lies in the different calcium hydroxide content. It is presumed that the high-lime calcium silicate hydrates consist of tobermorite-like layers with attached calcium hydroxide layers.

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