

The Silicate Structure Analysis of Hydrated Portland Cement Paste

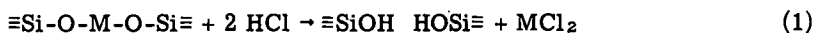
CHARLES W. LENTZ, Research Department, Dow Corning Corporation, Midland, Michigan

A new technique for recovering silicate structures as trimethylsilyl derivatives has been used to study the hydration of portland cement. By this method only the changes in the silicate portion of the structure can be determined as a function of hydration time. Cement pastes ranging in age from one day to 14.7 years were analyzed for the study. The hydration reaction is shown to be similar to a condensation type polymerization. The orthosilicate content of cement paste (which probably represents the original calcium silicates in the portland cement) gradually decreases as the paste ages. Concurrently a disilicate structure is formed which reaches a maximum quantity in about four weeks and then it too diminishes as the paste ages. Minor quantities of a trisilicate and a cyclic tetrasilicate are shown to be present in hydrated cement paste. An unidentified polysilicate structure is produced by the hydration reaction which not only increases in quantity throughout the age period studied, but also increases in molecular weight as the paste ages.

•THE SILICON atoms in silicate minerals are always in fourfold coordination with oxygen. These silicon-oxygen tetrahedra can be completely separated from each other, as in the orthosilicates, they can be paired, as in the pyrosilicates, or they can be in other combinations with each other to give a variety of silicate structures. If the mineral is composed only of Si and O, then there is a three-dimensional network of silicate tetrahedra. Quartz is an example of this type of structure.

If the minerals contain metallic elements in their structure such as Zn, Ca, Mg, etc., these atoms can serve the purpose of separating the various silicate structures from each other. For example, in a mineral containing the pyrosilicate structure the pairs of silicate tetrahedra are separated from other pairs of silicate tetrahedra by the metal atoms. Because the metallic elements are divalent, they also serve the purpose of linking the silicate structures together through metalloxy bridges. The polymer chemist would refer to these as cross-link sites. The silicate portion of a mineral, even though it may have a finite structure, is a part of a highly cross-linked inorganic polymer.

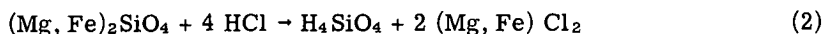
These metalloxy bridges are not acid stable, and, if the mineral structure is such that they can be contacted with an acid, the metal can be leached from the total structure. The metal atom is replaced by a hydrogen atom, and, since hydrogen is monovalent, it is a terminating group. Therefore, the silicate structures that were linked with a metalloxy bridge are now separated. The following equation illustrates this reaction:



Ideally the silicate portion of the mineral after dissolving in acid would be converted to the corresponding silicic acid. If the silicic acids were stable, they could be recovered and identified to give useful information about the structure of the mineral from which they were derived. Unfortunately, silicic acids are not stable. They condense, yielding high silicate polymers in which the original building blocks have completely

lost their original structural identity. If the H atom in the silicic acid is replaced with a stable terminating group, then it is possible to recover the silicic acid as a stable derivative.

A technique has been developed whereby it is possible to simultaneously acid leach and trimethylsilyl end-block a silicate mineral in such a way that the silicate portion of the mineral is recovered as a stable trimethylsilyl derivative (1). The following equations illustrate the two reactions using the orthosilicate mineral olivine as the silicate source:



This technique was developed using minerals having known structures. For example, the orthosilicate structure in olivine was recovered in 70 percent yield as the trimethylsilyl derivative. The pyrosilicate structure in hemimorphite was recovered in 77.6 percent yield, and 67.5 percent of the trisilicate structure in natrolite was recovered as the corresponding trimethylsilyl derivative. The conversion of the parent structure to the trimethylsilyl derivative is not quantitative. There are two side reactions which can occur; one of these is condensation of the silicic acids released by the acid leaching before trimethylsilylation is completed. An illustration of this side reaction can be found in the work cited above using minerals having an orthosilicate structure. An average of 9.9 percent of the silicate was recovered as the disilicate derivative.

The other side reaction that occurs is the acid cleavage of the siloxane linkage in the silicate structures. Again, referring to the mineral work cited above, the products resulting from this side reaction accounted for an average of 22.5 percent of the silicate when minerals containing the pyrosilicate and trisilicate structure were analyzed by this method. On the other hand, practically no acid cleavage of the cyclic tetrasilicate structure occurred. The extent of acid cleavage of the siloxane linkage is dependent on the structure of the silicate.

It is apparent that the trimethylsilylation technique, at its present stage of development, does not quantitatively recover the silicate structures per se, but in all of the known cases studied the major derivative obtained from a mineral did represent the silicate structure of that mineral.

This technique has now been used to study the hydration of portland cement. The major constituents of portland cement (and the ones of concern in this study) are the orthosilicate minerals tricalcium silicate (C_3S) (2) and beta-dicalcium silicate ($\beta\text{-C}_2\text{S}$) (3). When these silicates are mixed with water, a reaction of variable rate begins which does not reach its conclusion for many years (4). The product of this reaction is a silicate hydrate. This latter silicate, which is called tobermorite gel, has been referred to as the most important constituent of hardened portland cement paste (5). Since the reactants and product of the hydration reaction are acid-soluble silicates, the trimethylsilylation method of analysis should be applicable to the study of the hydration reaction. Quite logically one may ask two pertinent questions: (a) Why is the trimethylsilylation reaction applicable to this study when the mineral work has already shown that the technique has inherent side reactions? and (b) What can be learned from such a study?

The answer requires some explanation. When the calcium silicates in portland cement undergo hydration, the conversion to tobermorite gel is a relatively slow chemical reaction. One of the best methods currently used for following this hydration reaction is X-ray diffraction. Using this method the disappearance of the original calcium silicates can be followed quite satisfactorily, but the silicate product of the hydration reaction crystallizes so slowly and poorly that there is not a corresponding increase of this product in hydrated portland cement paste that is quantitatively detectable by X-ray diffraction. Much has been written about the hydration product, tobermorite gel, but its formation from C_3S and $\beta\text{-C}_2\text{S}$ has not been made clear. If the trimethylsilylation method is used to study a series of hydrated cement pastes of different ages, then the data

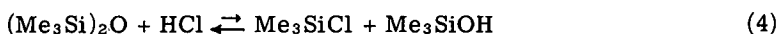
obtained, albeit not quantitative, should show the trends in structural changes occurring during hydration.

This paper is a study of the hydration reaction of portland cement, using the trimethylsilylation reaction to determine the silicate structure changes which occur from the time the original portland cement is first mixed with water until the paste has aged for nearly fifteen years.

EXPERIMENTAL

The reaction mixture employed in the trimethylsilylation method of analysis for silicate structures contains water, HCl, isopropyl alcohol (which constitutes the aqueous phase), and hexamethyldisiloxane (the water-immiscible siloxane phase).

The acid serves two purposes: (a) it reacts with the calcium silicate to remove the calcium as CaCl_2 and at the same time releases the silicate portion or anion as the corresponding silicic acid, and (b) it reacts with the $(\text{Me}_3\text{Si})_2\text{O}$ to produce the actual trimethylsilylating agent according to the following equation:



Whether trimethylchlorosilane or trimethylsilanol is the silylating agent is unknown. Either reagent is capable of reacting with the silicic acid in this particular reaction medium.

The $(\text{Me}_3\text{Si})_2\text{O}$ also serves two purposes: (a) it is the source of the trimethylsilylating reagent as described above, and (b) it is present in large excess to act as a solvent for the trimethylsilyl silicate derivatives as they are formed.

In this reaction medium and under the conditions of subsequent processing the three methyl groups covalently bonded to the silicon atom are stable. Only the siloxane linkage is subject to acid cleavage. The silicon introduced to the mixture as trimethylsilyl is monofunctional and serves only as an endblocker for the silicic acid. Therefore, it cannot become a silicate anion which is a silicon atom in tetrahedral arrangement with oxygen.

The role of the isopropyl alcohol is somewhat more complex. It probably increases the solubility of the $(\text{Me}_3\text{Si})_2\text{O}$ in the aqueous phase, allowing the equilibrium shown in Eq. 4 to be established much faster. The side reaction polymerization is probably retarded by this reagent because alcohols tend to stabilize silicic acids by forming hydrogen-bonded complexes at low pH (6). These micelles of alcohol may also contain the trimethylsilylating agent, which is then able to react with the silicic acid because of its proximity to it.

Test Specimens

The tricalcium silicate, β -dicalcium silicate, tricalcium silicate paste, and portland cement paste specimens used in this study were obtained from the Portland Cement Association.

The cement pastes were made by mixing water and cement in the ratio of 0.7 to 1 using a Waring Blendor. The mixture was then poured into test tubes. After setting a short time the pastes were covered with a layer of water, and the tubes were sealed with a rubber stopper.

The aged cement pastes were prepared for analysis by the trimethylsilylation technique in the following manner. The cylinders of paste were removed from the tubes and about one-half inch of each end was cut off. The cylinders were cut into quarters, placed in a desiccator containing anhydrous calcium sulfate, and evacuated to a pressure of 0.025 mm Hg for a period of 48 to 72 hours. A dry ice trap was placed between the desiccator and vacuum pump. According to Dr. David Kantro of the Portland Cement Association the hydration reaction ceases within a few minutes after a vacuum is applied to the desiccator. Therefore, it is possible to study a one-day-old cement paste as such even though 48 hours are required to dry the specimen.

After the test specimens had been dried in the above manner, they were ground in a Waring Blendor to pass a 100 mesh sieve. The total exposure time to the air during grinding never exceeded 30 minutes.

The Acid Leaching-Trimethylsilylation Reaction

A weighed amount of the powdered specimen to be analyzed, usually 20 or 25 g, was slurried with water and added to the following mixture which had been stirring at room temperature for 1 hour: 125 g of ice, 150 ml of concentrated HCl (36 percent), 300 ml of isopropyl alcohol, and 200 ml of hexamethyl disiloxane [$(\text{Me}_3\text{Si})_2\text{O}$]. The addition time was 10 to 15 minutes and the temperature was maintained in the range of 20-23 deg. Stirring was continued for 2 hours at room temperature. The mixture was transferred to a separatory funnel and diluted with water to dissolve the salts formed by the reaction. The clear aqueous layer was separated and discarded. The siloxane layer was filtered to recover the acid-insoluble portion (when present) which was then washed with $(\text{Me}_3\text{Si})_2\text{O}$, dried, and analyzed for Ca, C, H, and Si.

The filtered siloxane phase, which contains the trimethylsilyl silicate derivatives, was washed once with water and then stirred for 2 hours at room temperature with 10 g of Amberlyst-15 (a high surface area sulfonic acid functional ion exchange resin). This step completes the trimethylsilyl substitution of those compounds containing hydroxyl groups without changing the silicate structure. For example, two species representing the disilicate structure are usually produced in the trimethylsilylation reaction, $(\text{Me}_3\text{SiO})_3\text{SiOSi}(\text{OH})(\text{OSiMe}_3)_2$ and $(\text{Me}_3\text{SiO})_3\text{SiOSi}(\text{OSiMe}_3)_3$. The Amberlyst-15 catalyzed reaction completes the trimethylsilyl substitution, converting the first compound to the second compound. The analysis of the crude reaction product is thus simplified by having fewer compounds in it to be resolved by g. l. c.

The siloxane phase was filtered into a weighed 500-ml distillation flask to separate it from the ion exchange resin. The ion exchange resin was thoroughly washed with $(\text{Me}_3\text{Si})_2\text{O}$ to insure complete transfer of silicate derivatives to the flask. Then the contents of the distillation flask were stripped to a pot temperature of 130-135 deg in order to concentrate the silicate derivatives by virtue of distilling most of the excess

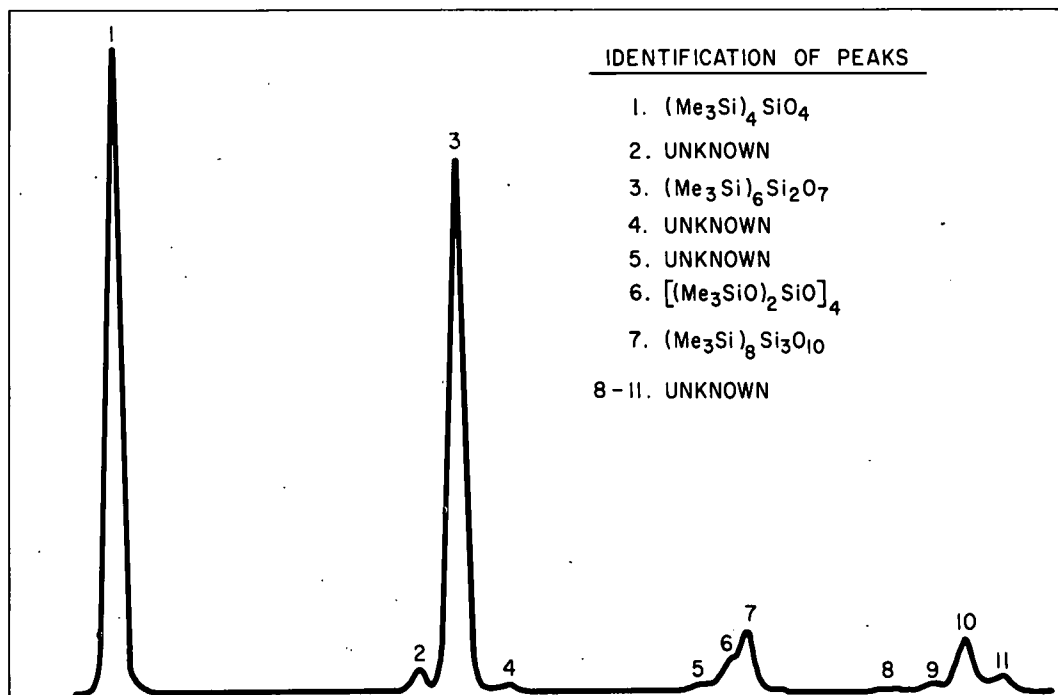


Figure 1. Chromatogram of the reaction product from a 28-day-old cement paste. [The solvent peak, $(\text{Me}_3\text{Si})_2\text{O}$, has been omitted from this reproduction.]

TABLE 1
ANALYSIS OF VARIOUS CALCIUM SILICATES AND HYDRATED CALCIUM SILICATES BY THE TRIMETHYLSILYLATION METHOD

Sample Description	Percent of Silicate Insoluble in Acid	g. l. c. Analysis					Peak No. 10	Carbon Assay of (SiO ₄) _x	Percent of Soluble Silicate				
		(Me ₃ Si) ₂ O	SiO ₄	Si ₂ O ₇	Si ₃ O ₁₀	(SiO ₃) ₄			SiO ₄	Si ₂ O ₇	Si ₃ O ₁₀	(SiO ₃) ₄	(SiO ₄) _x
β-Ca ₂ SiO ₄	7.9	39.7	51.7	6.9	1.1	0.3	Trace	27.4	73.6	14.6	4.7	0.5	3.8
Ca ₃ SiO ₅	7.6	35.0	57.9	5.8	0.8	0.2	Trace	26.85	76.4	11.3	3.0	0.3	4.8
Portland cement	1.4	40.8	52.6	5.5	0.8	None	None	30.1	81.9	12.6	3.6	—	1.4
1-day-old paste		35.6	50.1	10.2	1.4	0.8	0.8	29.0	65.1	19.8	5.3	1.6	3.0
7-day-old paste		41.7	35.0	15.7	2.0	1.1	2.0	29.5	39.8	26.7	6.0	1.9	6.4
28-day-old paste	0.3	39.5	27.1	22.9	2.4	1.4	3.2	29.9	28.7	34.3	6.4	2.4	13.8
3-month-old paste		42.1	22.8	25.4	2.0	1.3	3.4	29.5	21.6	32.9	4.9	2.0	20.4
4-year-old paste		50.5	21.2	20.1	1.6	1.5	2.2	29.3	17.6	24.3	3.5	2.0	39.3
14.7-year-old paste		47.0	23.5	19.6	2.1	1.4	3.0	28.86	17.0	20.6	3.8	1.7	48.4
2.7-year-old C ₃ S paste	7.6	50.9	14.2	24.4	2.4	1.8	2.8	28.8	9.5	22.4	3.9	1.9	50.8
Afwillite	2.9	42.5	50.0	6.5	0.6	0.2	0.2	28.7	65.8	12.6	2.2	0.4	16.8

(Me₃Si)₂O. The distillation flask was re-weighed to determine the weight of crude product.

G. l. c. Analysis

The crude product was analyzed by gas chromatography using a Model 720 F and M gas chromatograph. The columns were 2 ft long by 1/4 in. diameter and were packed with silica coated with a copolymer of dimethylsiloxane and phenylmethylsiloxane. The starting temperature for the analysis was 50 deg and the instrument was programmed at 25 deg per minute to a maximum temperature of 350 C. The recorder was equipped with a disc integrator which was used to determine the area of each peak on the chromatogram. Each peak represents a trimethylsilyl silicate species, which in turn represents a specific silicate structure. The chromatogram of the crude product obtained from the 28-day-old cement paste is shown in Figure 1. The peak areas were converted to weight percent values using calibration curves. The calibration curves were prepared in this laboratory using pure specimens of the various trimethylsilyl silicate derivatives to make known mixtures.

The only silicate species that could be converted to weight percent values (because they were available in this laboratory for the preparation of known mixtures) were (Me₃Si)₄SiO₄, (Me₃Si)₃Si₂O₇, (Me₃Si)₂Si₃O₁₀, and [(Me₃Si)₂SiO₃]₄ representing the monomer, dimer, trimer, and cyclic tetramer silicates respectively. These species are abbreviated in the tables and figures as SiO₄, Si₂O₇, Si₃O₁₀, and (SiO₃)₄.

Some of the peaks on the chromatogram have not been identified, but in all cases they are minor constituents in the crude product. Two of these have been identified tentatively by recovering a small quantity from a gas chromatograph prep column and analyzing the material by infrared spectroscopy. A carbon analysis was also obtained to help make the tentative identification. The carbon content is used to determine the quantity of Me₃Si in the compound. It has not been possible to convert the g. l. c. data for the compounds tentatively identified to weight data because an insufficient quantity was available for the preparation of known mixtures. However, this does not seriously affect the data because these species represent a minor quantity.

The gas chromatograph analyzes only the volatile constituents in the crude product. The nonvolatile content was analyzed by the following method.

Nonvolatile or Polysilicate Determination

The crude reaction product contains a nonvolatile portion in addition to the volatile components which are analyzed by g. l. c. This nonvolatile portion is determined by weighing 5 g of crude product into a weighed 20-ml beaker and placing the beaker in a 175 deg oven. The portion remaining in the beaker after 40 hours is the nonvolatile fraction in the crude reaction product. It was determined that this treatment gives a residue which is free from volatile material that is detectable by g. l. c., except those reaction products which contain as high as 20 percent nonvolatile matter. In those cases only 1-2 g portions would yield a volatile-free residue. Apparently the thicker section of residue resulting from a 5-g sample could not release all of the volatile constituents in 40 hours at 175 deg.

The nonvolatile material in the crude reaction product is the trimethylsilyl derivative of a polysilicate. The quantity of silicate in this derivative is calculated by analyzing it for percent C, the source of which is the organic groups in the trimethylsilylating agent, and then using the following equations:

$$\frac{\text{Wt of nonvolatile, g} \times \% \text{ C} \times 81}{36} = \text{Wt of Me}_3\text{SiO}_{1/2} \text{ in polysilicate derivative}$$

$$\frac{(\text{Wt of nonvolatile}) - (\text{Wt of Me}_3\text{SiO}_{1/2})}{60} = \text{Mole Si as polysilicate}$$

The abbreviation used in the table and graphs for the polysilicate portion is $(\text{SiO}_{4/2})_x$. The experimental data are shown in Table 1.

DISCUSSION

The Silicates in Portland Cement

The major constituents in portland cement are tricalcium silicate (C_3S) and beta-dicalcium silicate ($\beta\text{-C}_2\text{S}$). Together they constitute about 75 percent of the cement. Both of them are orthosilicates. Specimens of each of these anhydrous calcium silicates were analyzed by the trimethylsilylation (TMS) technique. Theoretically they should convert to the orthosilicate derivative in 100 percent yield, but there are side reactions which reduce the yield of the derivative that represents the parent structure. In the case of the C_3S specimen, 7.6 percent of the silicate was recovered as an acid-insoluble material.

The trimethylsilyl silicate derivatives obtained from the C_3S specimen were the orthosilicate, accounting for 76.4 percent of the soluble silicon, the disilicate, 11.3 percent, a trisilicate, 3.0 percent, a cyclic tetramer silicate, 0.3 percent, and a polysilicate, 4.8 percent. The trimethylsilyl derivatives accounted for 95.8 percent of the soluble silicate. If all of the soluble silicate in this C_3S specimen is an orthosilicate, these data mean that only 76.4 percent of it can be recovered as the derivative representing the parent structure. They do not mean that only 76.4 percent of the silicate in the C_3S specimen is an orthosilicate.

A $\beta\text{-C}_2\text{S}$ specimen was also analyzed for silicate structure using the TMS method. The results were similar to those obtained with C_3S , i. e., 73.6 percent of the soluble silicate was recovered as the orthosilicate derivative, 14.6 percent as the disilicate, 4.7 percent as the trisilicate, 0.5 percent as the cyclic tetramer silicate, and 3.8 percent as a polysilicate. Again some acid-insoluble silica was obtained (7.9 percent of the silicon in the original specimen). The same conclusions apply to these results as for C_3S .

C_3S and $\beta\text{-C}_2\text{S}$ are not the only constituents of portland cement. The other materials are tricalcium aluminate, tetracalcium aluminoferrite, and calcium sulfate. They do not form hydrolytically stable organosilyl derivatives. In order to determine if these species interfere with the TMS method of analysis and also to establish a base line of

distribution of silicate derivatives obtained from the portland cement used in this study, a sample of the portland cement was analyzed. The results are similar to those obtained with the C_3S and $\beta-C_2S$ specimens. That is, 81.9 percent of the acid-soluble silicate was obtained as the orthosilicate derivative, 12.6 percent as a disilicate, 3.6 percent as a trisilicate, and 1.4 percent as a polysilicate. No cyclic tetramer silicate was observed. The total acid-soluble silicate accounted for as organosilyl derivatives was 99.5 percent. Only 1.4 percent of the silicon in the original portland cement was recovered as acid-insoluble silica.

If it can be assumed that the acid-insoluble silica is the result of incomplete conversion of the raw material silicates to C_3S and $\beta-C_2S$, then it would appear that the conditions employed in the preparation of this portland cement converted a greater percentage of the raw material to acid-soluble silicates than the conditions used in the preparation of the C_3S and $\beta-C_2S$ specimens. In general, the distribution of silicate species derived from C_3S , $\beta-C_2S$, and portland cement are in agreement with this assumption. That is, the highest recovery of orthosilicate derivative was obtained from portland cement which also contained the lowest quantity of insoluble silica.

The important point in this discussion so far is that 81.9 percent of the silicon in portland cement is recovered as the orthosilicate derivative, which is in general agreement with the data obtained from the C_3S and $\beta-C_2S$ specimens. This means that the

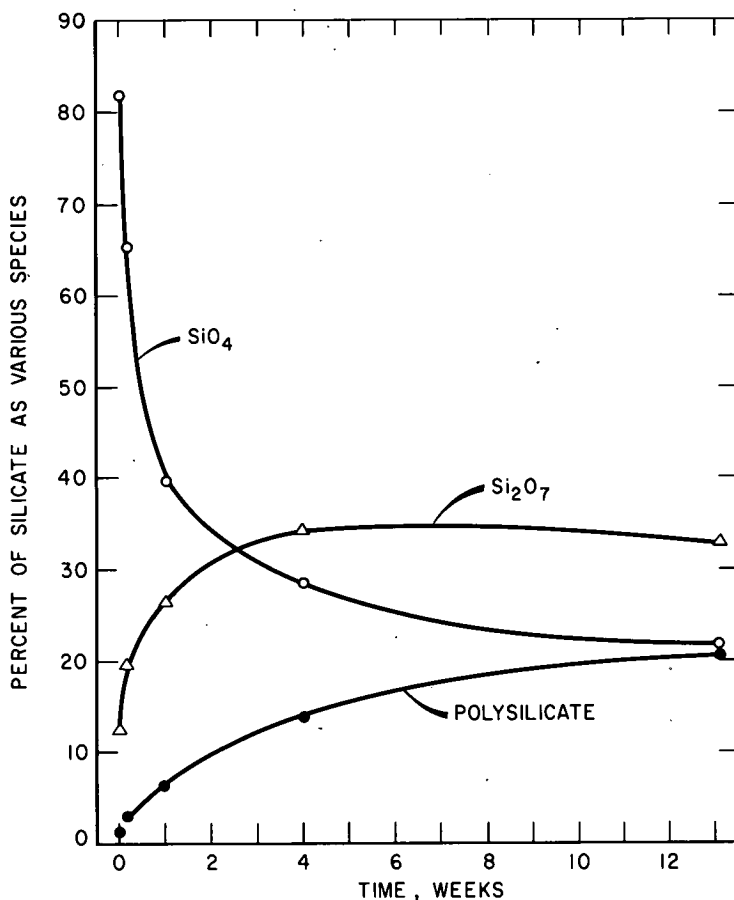


Figure 2. The major silicate structure changes in hydrated portland cement from the original cement to three months hydration time.

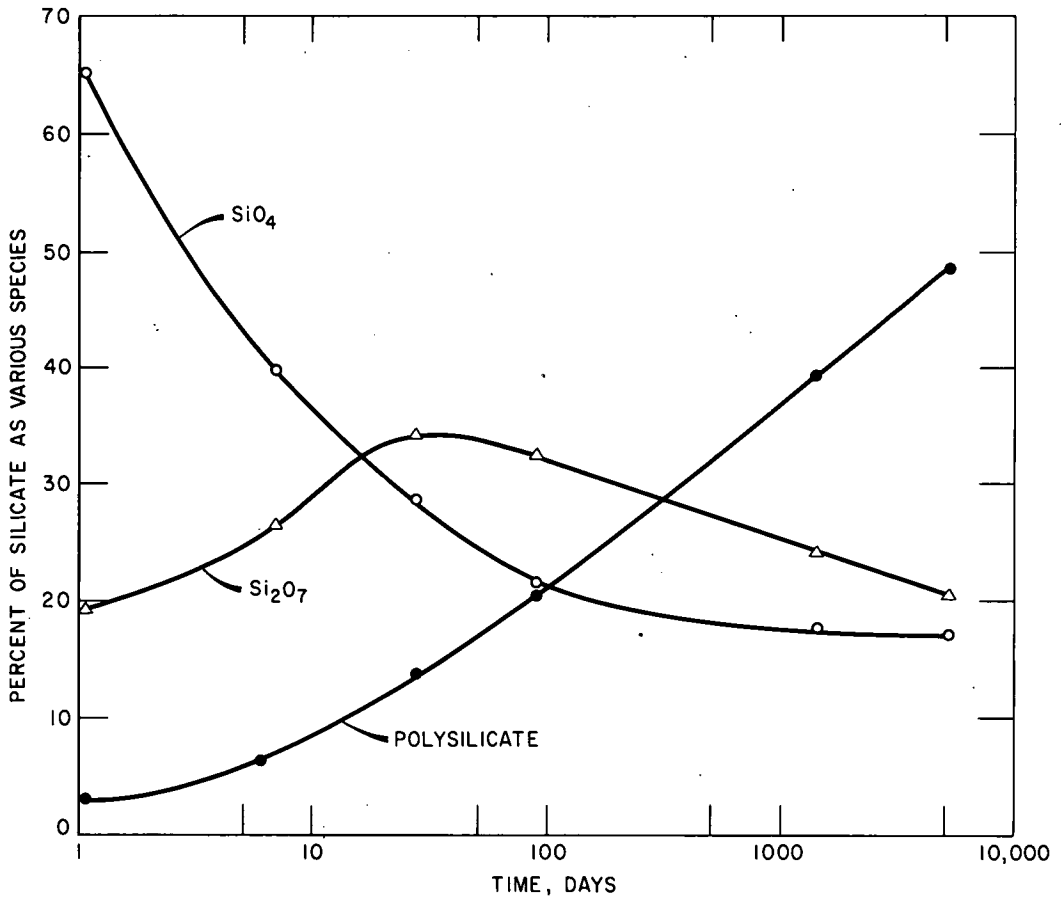


Figure 3. The major silicate structure changes in hydrated portland cement paste from one day of hydration to 14.7 years of hydration.

nonsilicate constituents in portland cement do not interfere with the TMS method of analysis. Another important point is that 99.5 percent of the silicate has been accounted for as various organosilyl derivatives.

Silicate Structure Changes During Hydration

The value of the TMS method of silicate structure analysis lies in the analysis of a series of samples representing different hydration times rather than in the analysis of the original portland cement. The distribution of silicate structures obtained with unhydrated portland cement is valuable as a starting point, but the changes that occur during hydration are the pertinent data. Various samples of hydrated cement paste ranging from one day of hydration to 14.7 years of hydration were analyzed for silicate structures using the TMS method. The major silicate structures found in these samples are an orthosilicate, a disilicate, and a polysilicate of unknown molecular configuration. There are also minor quantities of other silicate structures derived from the cement pastes. They are a trisilicate, a cyclic tetrasilicate, and a material tentatively identified as a cyclic pentasilicate.

The change in the silicate structure composition of the hydrated cement as the paste ages will be discussed for each structure. The data for the major silicate derivatives are shown in Figures 2 and 3. In Figure 2 the data are plotted for the first three

months of hydration with time represented on a linear scale. This figure illustrates the rapid changes that occur in a short period of time. In Figure 3 the data from one day of hydration to 14.7 years of hydration are plotted. Time is represented on a logarithmic scale for convenience only.

Orthosilicate.—The quantity of orthosilicate derivative obtained from the hydrated cement pastes decreases as the paste ages. The quantity of orthosilicate derived from the original portland cement represented 81.9 percent of the total silicate and after one day of hydration this quantity had decreased to 65.1 percent. After seven days the quantity of this species had decreased to 39.8 percent, or only about one-half of the orthosilicate structure remained. This monomer species continued to decrease at a reduced rate for a period of years (Fig. 3), but the major change had occurred in a matter of a few weeks. After a total time of 14.7 years of hydration the quantity of monomer silicate derived from the hydrated cement paste represented only 17 percent of the silicate in the specimen.

Since the orthosilicate quantity decreases in the manner shown (Figs. 2 and 3), it seems quite probable that this derivative represents the calcium silicates in the portland cement that have not entered into the hydration reaction. On the other hand, if an orthosilicate is one of the hydration products (5), this method of analysis would not differentiate between it and the original unhydrated calcium orthosilicates. Therefore, the orthosilicate derivative could represent either C_3S , β - C_2S , or a hydrated calcium orthosilicate. If one of the hydration products is a calcium orthosilicate, these data indicate that it must be an unstable or intermediate hydration product.

One of the orthosilicate hydrates that can occur in a $CaOSiO_2-H_2O$ system is afwillite. Megaw determined the crystal structure of this mineral and found that a system of hydrogen bonds exists among the independent SiO_4 tetrahedra (7). It is conceivable that when independent SiO_4 tetrahedra are in such close proximity that hydrogen bonding can exist they might polymerize into higher molecular weight species upon acidification before end-blocking with Me_3Si groups can occur. In that event, this type of orthosilicate hydrate would not be recovered as an orthosilicate derivative. Dr. Copeland of the Portland Cement Association supplied a synthetic specimen of afwillite that was analyzed by the TMS method. The orthosilicate derivative accounted for 64.0 percent of the silicate and the dimer only 12.2 percent. A polysilicate derivative representing 16.8 percent of the silicate was also obtained. Whether the polysilicate was present in the original specimen or whether it was a by-product of the TMS analysis is not known. Possibly this point could be clarified by analyzing a well-crystallized natural specimen. The primary conclusion that can be made from this analysis is that even in a silicate system where hydrogen bonding exists, the major product derived by the TMS analysis is representative of the parent structure.

Disilicate.—Bernal, Jeffery, and Taylor (8) concluded that the anhydrous silicates act only as a source of silicate ions from which the hydration products can be formed. This study shows that the amount of silicate structure representing the original silicate diminishes during hydration. Therefore, the hydration products have to be polymeric silicates. One of the polymeric substances found has a disilicate structure. The experimental data for this structure are also plotted in Figures 2 and 3. The quantity of disilicate structure obtained from a seven-day-old cement paste is two times the amount derived from the original portland cement. This species continues to increase in quantity for a period of about four weeks to a maximum of 34.3 percent of the silicate. After this time, the disilicate species gradually decreases and after 14.7 years of hydration only 20.6 percent of the silicate is accounted for as the dimer structure.

Earlier in the discussion it was shown that a disilicate structure was derived from portland cement even though the silicates in portland cement are orthosilicates. The explanation for the disilicate structure in that case is that it resulted from the polymerization of some of the orthosilicic acid, and is not necessarily representative of a disilicate structure in the portland cement. In the case of the hydrated cement paste, the disilicate derivative is believed to represent a parent calcium disilicate structure. The basis for this belief is that as the cement paste ages the orthosilicate quantity decreases, while at the same time the quantity of disilicate derivative increases. If the sole source of disilicate was due to some polymerization of orthosilicic acid (resulting from the

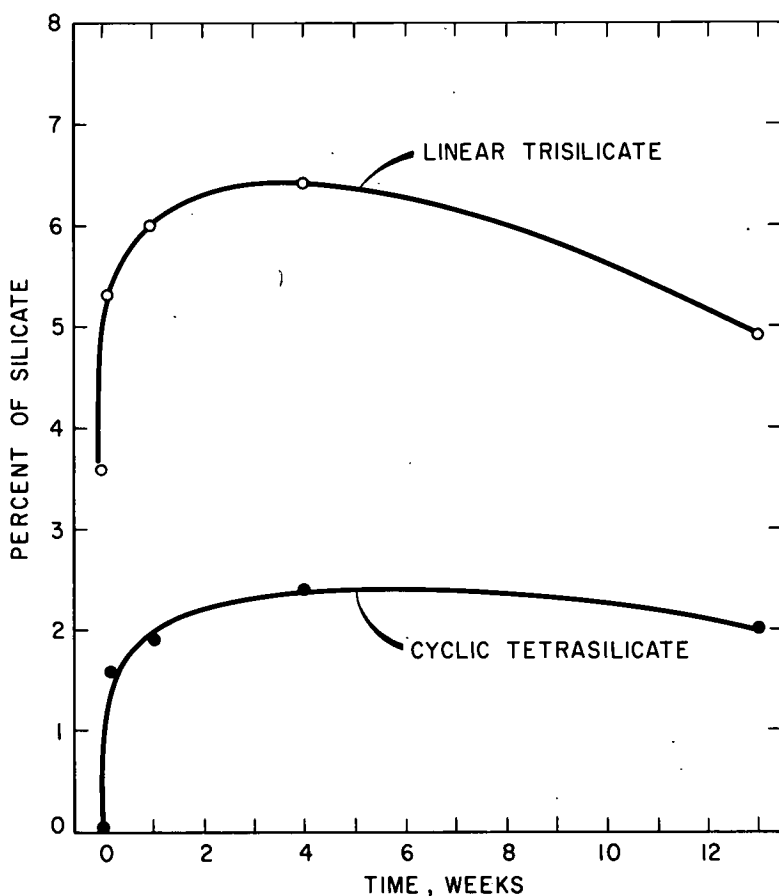


Figure 4. The silicate structure changes of the known minor species in hydrated portland cement paste to three months of hydration time.

acidification of a calcium orthosilicate), then the quantity of disilicate should decrease as the paste hydrates. The fact that a hydrated cement paste yields a larger quantity of disilicate structure than the portland cement, when less orthosilicate structure is present to act as its potential source, is good evidence that a calcium disilicate hydrate is produced by the hydration reaction.

Taylor and Howison (9) hypothesized Si_2O_7 structures for hydrates having high $\text{CaO}:\text{SiO}_2$ ratios. Their explanation was that a dimer structure would result from a breaking up of the metasilicate chain by replacement of the bridging tetrahedra with calcium. This description implies a depolymerization of a polysilicate. Since the quantity of disilicate structure increases during the early stages of hydration and decreases during the later stages, it seems improbable that this species results from a depolymerization of a higher structure. A change of this type indicates that the dimer is an intermediate structure or a building block in a polymerization process.

Flory published a theoretical treatise in 1936 which is pertinent to this discussion (10). He showed that in a condensation type polymerization a dimer is the first product of the reaction and therefore increases in quantity during the early stages of polymerization. As the reaction proceeds, the rate of formation of the dimer is less than the rate at which the dimer enters into the polymerization process as an intermediate for higher molecular weight species. Then the quantity of dimer decreases. Each subsequent polymeric species, such as the trimer, tetramer, etc., shows the same rise and fall pattern.

If the hydration of portland cement can be considered as a condensation type of polymerization, the increase and subsequent decrease of a dimer species is theoretically sound.

Trisilicate and Cyclic Tetrasilicate. —The trisilicate and cyclic tetrasilicate derivatives could possibly be written off as by-products of the trimethylsilylation reaction because they are present as minor constituents in the reaction product of all of the specimens analyzed. On the other hand, they may represent true structures and therefore provide important clues for the interpretation of the structure of the final hydration product.

There is some evidence that they are not strictly by-products of the analysis technique. For example, when hemimorphite, a naturally occurring disilicate mineral, was analyzed, the ratio of trimer species obtained as a by-product to dimer species obtained was 0.03 to 1 (1). The average ratio found in the cement work is about 0.2 to 1, which is a considerably larger quantity of trimer species than was obtained in the mineral work. Another potential source of the trisilicate structure as a by-product might be some acid degradation of a higher silicate structure. In that case the quantity obtained should increase in proportion to the formation of the polysilicate structure. The fact that it does not discounts the acid degradation hypothesis as a significant source of the trisilicate species.

Mehedlov-Petrosyan and Babushkin (11) proposed the theory that one of the structures produced in the second stage of hydration is trisilicate chains and that this species then polymerizes into bands of $[\text{Si}_6\text{O}_{17}]^{10-}$. If the trisilicate species found in this study is a real product of the hydration reaction, it must be even less stable than the disilicate species because a maximum quantity of only 6.4 percent of the total silicate as a trisilicate derivative was observed.

A cyclic tetrasilicate structure has also been found in the crude reaction product derived from hydrated cement paste. The quantity of this species is even less than the amount of trisilicate found. None of it was found in the original portland cement. The maximum amount is only 2.4 percent of the total silicate which was found in the 28-day-old cement paste. Examination of the data shows that it varies in proportion to the quantity of disilicate structure. This correlation suggests that the cyclic tetrasilicate could be a by-product resulting from the dimerization of the disilicic acid produced upon acidification of the calcium disilicate. The work mentioned previously with the mineral hemimorphite is not in agreement with this interpretation.

The data for the trisilicate and tetrasilicate derivatives are plotted in Figure 4. How much significance can be attached to these data is not known, but it is interesting to note that as the cement paste ages the amounts of these species rise and fall much the same as the dimer species does.

Unidentified Derivatives. —Some of the compounds that appear on the g.l.c. chromatogram have not been identified. All of them represent minor amounts and therefore do not significantly affect the quantitative results reported. The largest of these, which is peak No. 10 in Figure 1, has been tentatively identified as a cyclic pentasilicate. On the basis of the g.l.c. values only, which are not necessarily weight percent values, this species increases from a zero quantity in portland cement to 3.4 percent of the chromatogram in the three-month-old cement paste. Although this is a minor quantity, it probably has some significance because of its regular appearance in the cement paste derivatives. Another reason it is believed to be a real product of the hydration reaction is that it is difficult to visualize how a cyclic pentasilicate could have resulted from a side reaction during the trimethylsilylation step.

Polysilicate. —The derivative referred to in this paper as the polysilicate increases steadily from 3 percent of the silicate in the one-day-old cement paste to 48.4 percent of the silicate in the 14.7-year-old specimen. This derivative may be the most important one obtained from hydrated portland cement paste because it is the only silicate derivative found that continues to increase in quantity as the hydrated cement ages. Therefore, it eventually becomes the major product in hydrated cement paste, and it may be the derivative of tobermorite gel.

Various attempts to determine the structure of the polysilicate derivative have not been successful, but information has been obtained which does provide some description.

The carbon analyses of the derivatives vary only slightly from a high of 29.9 percent to a low of 28.86 percent. There appears to be some regularity in this variation. The source of this carbon is the methyl groups in the trimethylsilylating agent. Using the carbon analysis to calculate the molar ratio of $\text{Me}_3\text{SiO}_{1/2}$ substituents to $\text{SiO}_{4/2}$ in the silicate structure, a value ranging from a minimum of 1.38 $\text{Me}_3\text{SiO}_{1/2}:\text{SiO}_{4/2}$ is obtained. This ratio can be used as a guide to help in the interpretation of the structure. For example, if the parent polysilicate structure is a single linear chain, it should yield a derivative having a 2:1 ratio. Since the ratio is considerably less than 2:1, a polymeric structure more complex than a metasilicate chain is suggested.

The molecular weight of the trimethylsilyl polysilicates derived from the three-month-old paste and 14.7-year-old paste was determined with a vapor pressure osmometer. The molecular weights were 2110 and 2700 respectively. Part of this weight is contributed by the trimethylsilyl end-blocking. In order to obtain a value that is characteristic only of the silicate portion of the polymer it is necessary to calculate the quantity of $\text{Me}_3\text{SiO}_{1/2}$ in the derivative and subtract it from the measured value. Using the carbon assay to determine the $\text{Me}_3\text{SiO}_{1/2}:\text{SiO}_2$ ratio, which is 1.46 for the polysilicate derived from the three-month-old paste, the equivalent weight of each silicate unit is 178 $[(1.46 \times 81) + (1 \times 60)]$. Dividing the measured molecular weight by this equivalent weight, a value of 11.85 silicate units per mol of polysilicate is obtained. The polysilicate derived from the 14.7-year-old cement paste has 15.8 silicate units per mol of polymer. It should be realized that the measured molecular weight is a number average molecular weight and it is very probable the polysilicate is not a single species, but like most polymers, it is composed of a variety of sizes of species. Therefore, the measured values represent averages, and it is not surprising to obtain fractional numbers. The most significant feature of this part of the study is that the average size of the silicate polymer has increased by about four silicate units between three months and 14.7 years. Here is evidence that not only does the quantity of polysilicate increase with time, but also the average size of the polysilicate increases with time. Therefore, the derivative that is referred to as a polysilicate in this paper does not represent a singular species, but rather it is a species composed of various sizes of molecules that changes with the age of the cement paste. The same is true with organic polymers, i. e., the composition of an organic polymer changes in respect to molecular size throughout the period of polymerization.

The polysilicates derived from a C_3S paste (described later in this paper) and the hydrated cement pastes ranging in age from one month to 14.7 years were also studied by infrared spectroscopy. All of them gave nearly identical spectra. A complete interpretation of these spectra has not been possible because there has not been enough variety of pure trimethylsilyl silicate species prepared and studied by infrared to characterize the various absorption peaks. Nevertheless, the identical nature of the spectra suggests a consistency of molecular structural features of the polysilicate throughout the hydration period studied. Even though the molecular weight of the polysilicate increases as the paste ages, the basic structure does not change.

Unfortunately, it has not been possible to decipher the structure or molecular configuration of the polysilicate derivative using the $\text{Me}_3\text{SiO}_{1/2}:\text{SiO}_2$ ratio, molecular weight, and infrared analysis.

How representative is the polysilicate derivative of the parent structure? If the parent structure is degraded by the acid treatment, then the monomer, dimer, and other low molecular weight silicates found in the 14.7-year-old cement could result from such a degradation. In that case the polysilicate derivative would not be completely representative because it would be a residue of the degradation. If acid degradation of the calcium polysilicate does not occur to any appreciable extent, then the monomer and dimer obtained from the 14.7-year-old cement paste must be considered as derivatives of parent structures having the same silicate structures.

If a known polysilicate structure could be analyzed by the TMS method, then it would be possible to assess how representative the derivative is of the parent structure. Unfortunately, this author is not aware of any such material that fits the requirements of such an analysis, i. e., known structure and acid solubility of the released silicic acid. Wollastonite has some relationship to the study of cement, and it has been studied in

an attempt to partially resolve the above question. Although it does not meet the requirement of acid solubility, the information obtained may have some relevance.

Wollastonite

Wollastonite is similar to tobermorite in that both of them contain single Drierketten silicate chains (12). Wollastonite is decomposed by acid, but the silica released is insoluble in the acid medium (13). Tobermorite gel, on the other hand, yields a soluble silica in acid. The acid solubility characteristics of the mineral tobermorite are unknown to the author.

When wollastonite was subjected to the TMS method of analysis, 93 percent of the silicate was recovered as insoluble silica, 2.9 percent was converted to a trimethylsilyl polysilicate derivative that was soluble in the hexamethyldisiloxane phase, and only 0.05 percent of it was accounted for as the orthosilicate derivative. The infrared spectrum of the polysilicate derived from wollastonite is different from the spectra obtained on the polysilicates derived from hydrated cement. If the assumption is made that the mineral specimen was free of any imperfections in its structure, which is not necessarily true, these data show that only about 3 percent of the metasilicate chain was degraded to the extent that soluble silicate species could be derived from it. It should be borne in mind that this mineral was completely leached free of its calcium, which means that the acid was in liberal contact with the silicate portion of the structure. Even so, a very low quantity of soluble derivative was obtained. The major derivative was the insoluble silica, which is in agreement with the literature (13). To what extent this information satisfactorily answers the question about the acid degradation of the calcium polysilicate structure in hydrated cement paste can only be surmised.

The similarity in silicate structure between the minerals wollastonite and tobermorite and the difference in acid solubility between wollastonite and tobermorite gel have been pointed out. The analogy between the mineral tobermorite and tobermorite gel has been discussed in many papers and does not need to be reviewed here. However, an important question is raised by the anomaly of acid solubility. Why is the tobermorite gel acid soluble while wollastonite is not? The answer may simply be that there is a large difference in the molecular weight of the silicate portion of these two materials. The solubility of organic polymers is at least partially dependent upon their molecular weight. Lower molecular weight polymers are more soluble in some solvents than are the higher molecular weight polymers having the same chemical composition. Since the tobermorite gel in hydrated cement paste is a poorly crystallized material and is composed of very small particles, possibly its molecular weight is low enough that the silicate portion is either acid soluble or forms a colloidal suspension. Conversely, the lack of solubility of the metasilicate chain derived from the well crystallized wollastonite specimen may be due to its high molecular weight. In other words, the difference in acid solubility between wollastonite and tobermorite gel may be a function of molecular weight rather than a function of molecular configuration.

Wollastonite was not an ideal choice for this study, but at least the data show that a high molecular weight silicate does not yield an appreciable quantity of soluble silicate derivatives.

Another silicate sample studied was an aged C_3S paste. It fits the qualification of acid solubility, but the molecular structure probably should be classified as uncertain.

Hydrated Tricalcium Silicate Paste

A 2.7-year-old C_3S paste having a w/c ratio of 0.7 was analysed by the TMS technique. This specimen of paste is tobermorite gel (14). An acid-insoluble silica was recovered from it representing 7.6 percent of the total silicate, which is about the same as was found in an unhydrated C_3S specimen. If the insoluble silica is present as free silica and has not been a part of the hydration reaction, then the soluble silica derivatives should be calculated on the basis of the acid-soluble silicate only. These data are given in Table 2 along with the data obtained from the 14.7-year-old cement paste for comparison.

TABLE 2
COMPARISON OF ACID-SOLUBLE
SILICATE PERCENTAGE

Test Specimen	SiO ₄	Si ₂ O ₇	Si ₃ O ₁₀	(SiO ₃) ₄	(SiO ₄ /2) _x
2. 7-year-old C ₃ S paste	9.5	22.4	3.8	1.9	50.8
14. 7-year-old cement paste	17.0	20.5	3.8	1.7	48.4

There is considerable similarity between the derivatives obtained from the 2. 7-year-old C₃S paste and the 14. 7-year-old cement paste, except for the amount of ortho-silicate.

The C₃S paste used in this study should have been completely hydrated by the time it had aged 17 months (5). Complete hydration means that none of the original C₃S is detectable. It does not necessarily mean the completion of the hydration reaction. Bogue and Lerch (15) studied the hydration and compressive strength of C₃S paste. Their results show that even though hydration was complete after one year, the strength of the paste increased about 10 percent during the second year. A significant change occurred in their paste even after "complete hydration." Whether the completely hydrated C₃S paste used in this study has reached its final composition or not is not known. A more extensive study would be required in order to determine the age at which a C₃S paste has a stable composition.

The lower molecular weight species found in the C₃S paste by the TMS analysis could be an indication of the imperfections in tobermorite gel, which reportedly is a poorly crystallized substance, or they could be representative of specific calcium silicate hydrates. The former possibility means that the low molecular weight derivatives could have resulted from fragments of silicate that have not become an integral part of the larger crystal lattice. In the latter case the distribution of products would be an indication of the equilibrium state of the various calcium silicate hydrates.

The most significant difference between the C₃S paste and 14. 7-year-old paste is the amount of orthosilicate derived from them. Only 9.5 percent of the silicate in the C₃S paste is an orthosilicate, while 17 percent of the silicate derived from the 14. 7-year-old cement paste is an orthosilicate. The difference could be due to the presence of β-C₂S in the portland cement paste which may not be completely hydrated after 14. 7 years. Another explanation might be that Al has substituted for some of the Si in the silicate structure. Kalousek (16) showed that isomorphous substitution of Al can occur. This condition would provide a discontinuity in the silicate structure which could result in lower molecular weight derivatives because the Al-O-Si linkage is readily cleaved by acid (1).

SUMMARY

Various investigators have proposed that the products in the early stages of hydration of portland cement paste are different from those in the later stages (5) or that certain hydrates are intermediate products (17). In this study the hydration was followed by converting the various calcium silicates into stable trimethylsilyl derivatives. The quantitative analysis of these derivatives shows that the silicate structure composition of hydrated portland cement paste changes continually for at least fifteen years.

The orthosilicate content decreases by about 50 percent during the first seven days of hydration. It diminishes thereafter at a continually reducing rate until it represents only 17 percent of the total silicate after 14. 7 years of hydration. The loss of ortho-silicate is accompanied by the formation of a disilicate species which reaches its maximum quantity in about four weeks. After this time it too diminishes in quantity and

therefore appears to be an intermediate stage in the polymerization process. There is some evidence that a trisilicate and a cyclic tetrasilicate are also produced as minor hydration products. Throughout the entire hydration period studied a polysilicate of unknown structure is produced which represents 48.4 percent of the silicate in the 14.7-year-old paste specimen. The polysilicate may be composed of a consistent molecular configuration, but it probably contains a variety of molecular sizes rather than a singular species. The evidence for these conclusions is based on the infrared study and the fact that the molecular weight of the polysilicate increases as the paste ages.

The data obtained in this study support the hypothesis that the hydration of portland cement is a condensation type polymerization, that there are intermediate polymerization states, and that equilibrium has not been reached even after 14.7 years of reaction time.

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