**A Review of research on the relationship between mechanical properties and chemical-morphological structure of the hydration products of hydraulic binders**
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# A REVIEW OF RESEARCH ON THE RELATIONSHIP BETWEEN MECHANICAL PROPERTIES AND CHEMICAL-MORPHOLOGICAL STRUCTURE OF THE HYDRATION PRODUCTS OF HYDRAULIC BINDERS

BY

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# PREFACE

One of the most interesting fields of activity in cement chemistry relates to the study of the factors that determine the strength development in the hardened cement paste. A combination of factors such as the chemical nature, surface forces, surface area, morphology, porosity and other characteristics may influence in a complex way the strength properties of the hardened paste.

Recent work has shown that the hydrated silicate in hardened cements exists not only as ortho but also as di, teri and poly-silicate chains. It appears therefore that the mechanical properties may also depend on the degree of condensation of the silicate structure. Rio and Saini have attempted to explain the variation in the mechanical property of cement hydrated under different conditions, by variations in the chemical nature, the morphology and the degree of condensation in the hydrated silicates.

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              (Prospettive di studio sulle relazioni
              esistenti tra caratteristiche meccaniche
              e struttura chimico-morfologica dei prodotti
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## A REVIEW OF RESEARCH ON THE RELATIONSHIP

## BETWEEN MECHANICAL PROPERTIES AND

## CHEMICAL-MORPHOLOGICAL STRUCTURE OF

## THE HYDRATION PRODUCTS OF HYDRAULIC BINDERS

Research has been going on for some time now in our laboratory on the hydration mechanism of portland cement with a view to determining the best properties of binders and the most suitable conditions of hydration for controlling the hardening process of the cement according to the various requirements of practice, especially with regard to the increase of initial strength.

An earlier paper[1] revealed the influence of the mineralogical composition of the clinker on the rate of hydration of the tricalcium silicate present as well as the influence of the calcium sulphate and its interaction with the ferric and aluminium phases in relation to a modification of the ionic equilibrium of the mixing solutions with the cement paste.

In the second paper[2] some observations were reported on the hydration mechanism of tricalcium silicate, and an attempt was made to describe the process of diffusion of the water through the layer of hydrated products towards the interior of the grain by means of a mathematical expression.

In a third paper[3] we studied the influence of sodium sulphate and calcium chloride on the reaction kinetics of the tricalcium silicate and the evolution of the mechanical strength.

The results of the research mentioned above and the investigations of other authors on the same subject recently encouraged us to carry on our study, at the same time bearing in mind the different aspects of the hydration process.

Undoubtedly, the development of the mechanical strength is linked to variations in the evolution of the chemical and

morphological structure of the hydration products while the latter, in turn, may depend essentially on the degree of condensation of the hydrosilicates present, so that an interpretation of the hydration process in polymolecular terms would also be interesting and worthwhile.

Our program, therefore, has as its aim the study of the relations existing between mechanical properties, degree of hydration and condensation of the hydrosilicates and relative morphological structure, as well as the effect that the presence of certain additives such as calcium sulphate and calcium chloride may have on these.

In this preliminary paper we think it opportune to outline the subject of our research and present a program of our activities.

\* \* \*

Some of the properties shown by the binary water-cement system have permitted reliable formulation in macromolecular terms of the nature of the hydration process of the binders and the structure of the compounds derived therefrom.

As is known, two types of mechanisms have hitherto been proposed for the hydration reaction of the silicates:

1.    solution-precipitation, "through solution"[4];

2.    direct solid-liquid reactions, "direct mechanism"[4].

According to the first mechanism[2], when the silicates come into contact with water the ions $Ca^{++}$, $SiO_4^{-4}$ and $O^{=}$ situated on the surface of the grains pass into solution at different rates in the form of hydrated ions, as shown by electroconductivity measurements. They then diffuse from the surface, interact to form the molecules of a hydrosilicate gel of varying composition, the X-ray diffraction spectrum being more or less that of natural tobermorite. These constitute nuclei which grow to form colloidal particles which then flocculate. According to Brunauer and Greenberg[5], the fact

that under the microscope the gels sometimes appear remote from
the initial grain either as coatings around particles of $Ca(OH)_2$
having separated in the course of hydration, or singly as such,
clearly indicates a mechanism of this type.

The gel might form, however, as an ionic chemisorption
phenomenon followed by diffusion[6] over the surface of the
grains of the silicate, which would be seen to be coated with a
layer, the thickness of which increases with time, and of which
the permeability to water and to the ions in the more advanced
stages of hydration would constitute a system of the "rate
controlling" type.

The presence of the tobermoritic gel in the paste results
in a number of properties such as thixotropy, the phenomenon
of setting and subsequent hardening, and mechanical characteristics
that can be adequately explained when related to the chemical
and morphological structure of this gel.


Properties and morphological structure

According to the most recent theories[7], thixotropic gels
are made up of laminar or fibril particles which are in contact
with each other only at a few points. For example, Van Olphen[8]
proposed, for bentonite gels, points of contact between the
negative charges situated on the surface and attributable to
the presence of SiOH groups which become ionized in the alkaline
medium to $SiO^-$, and positive charges due to non-saturated $Al^{+++}$
ions situated alongside the lamellae. The electrostatic as well
as the Van der Waals forces operating in these systems are strong
enough for low concentrations to develop a network structure,
but not strong enough to prevent fracture under a certain shear
stress. It has also been seen experimentally that the forces
involved in thixotropic gels can change, altering either the pH
or the ionic strength of the solution in contact with solid
surfaces[9].

Now, a morphological structure suitable for the formation

of a thixotropic gel has been proposed[10] for tobermorite. It comprises stratified crystals; the central part of each layer having empirical composition $CaO_2$, can be described as an extremely distorted form of a lamina of $Ca(OH)_2$, completely deprived of its hydrogen atoms. This lamina is bounded on both sides by parallel strips of metasilicate chains of the type present in wollastonite (triple chains). Unlike the latter, however, where the $SiO_4$ tetrahedrons are linked to the $CaO_6$ polyhedrons by the common participation of O atoms, the tetrahedrons and polyhedrons in tobermorite are linked by means of common O-O bonds; the linkage, therefore, is not through vertices but through sides, which implies the characteristic distortion of the oxide layer mentioned above.

The composite strata which have empirical formula $Ca_4Si_6O_{18}$ are packed in a sandwich structure, the strips of each stratum passing directly over or under the next stratum. The remaining Ca ions along with four molecules of $H_2O$ are thought to be situated in the canalicular zones between the different strips, without, however, being definitely positioned. The position of the two remaining hydrogen ions has not yet been established either, but very probably they are linked to the metasilicate chains forming silanolic groups SiOH, with consequent presence of water, not only in molecular form, but also in hydroxy form. I.R. absorption spectra support the hypothesis that water is present interstitially in molecular form (6.2 $\mu$) and in hydroxy form (2.9 $\mu$)[11,12].

According to Brunauer and Greenberg[5] the phenomenon of setting of the paste might be due to transverse chemical bonds between the different molecular layers of the gel with consequent formation of a bidimensional and tridimensional structure. These bonds might be of the hydrogen type, or the ionic type involving the $Ca^{++}$ ions, or the covalent type deriving from the condensation of the silanolic groups with formation of siloxanic bonds Si-O-Si, and hence possibly of polymeric structure. The presence of these siloxanic bonds would explain, as Taylor emphasized at the recent Tokyo Congress[13], the anomalous thermodehydration behaviour shown by natural tobermorite in which,

for temperatures up to approximately 450°C, a contraction (from
11.3 to 9.3 Å) is followed in the recticular spacing (from 9.35
to 9.7 Å) for a further increase of temperature up to 650°C.
In addition, these bonds would justify both the otherwise un-
explainable plane of cleavage (100) shown by one type of natural
tobermorite (Loch Eynort) and the property shown by the above-
mentioned material of dehydrating without changing the recticular
spacing c.

The hypothesis of polymeric structure in hydrosilicates was
also supported by Brunauer[14] on the basis of many studies
having as their subjects such characteristics as surface develop-
ment, the water of hydration and the heat of hydration peculiar
to the paste. The experimental finding that both the surface
area and the heat of hydration are always proportional to the
water of hydration, and hence to the quantity of hydration
products, implies that in all stages of hydration the same type
of gel, with a constant composition of the copolymer type, is
always formed, to the constitution of which therefore, the
various constituents of the binders contribute. These binders do
not become hydrated independently at the same rate as when they
are isolated, but at fractional rates in constant or even equal
proportions, once the steady state of the process has been
reached[14,15,16]. The tendency towards fractional rates of
hydration at a constant or even equal ratio, may suggest the
setting up of a mechanism capable of balancing the various
hydration rates of the separate components.

This hypothesis is compatible with the idea that after the
initial fast reaction, hydration is controlled by diffusion
through the coating of hydration products around the grains, in
the formation of which there is abatement of the faster reactions
and a tendency towards equalization of the rates, or at least
towards a constancy in the relationship of the fractional rates
between the various hydration reactions. The mean rate of
hydration, therefore, would come to be controlled by the diffusion
of the water through the gelatinous layer of hydration products
that would form[17]. In this connection it is interesting to
note that an investigation into the hydration of pure silicates

carried out by Zur Strassen[18] showed that in the case of $C_3S$ the entire process is controlled by laws of diffusion according to which the rate at which hydration occurs varies inversely with the thickness of the layer; indeed, it is sufficient to exceed the limit of 25% in the hydration for the energy of activation to drop from values (9.3 kcal/mole) of the same order of magnitude as those given by Iler[19] for the polymerization of orthosilicic acid to values (6.3 kcal/mole) indicating a process controlled by the diffusion[20], whereas in the case of $\beta$ $C_2S$, which undergoes hydration much more slowly, the process is of the linear type for the whole time necessary for the formation of a coating having a thickness such as to render the effect of diffusion predominant.

The experimental finding that the hydration reaction of $C_3S$ undergoes a major abatement from that predicted simply on the basis of the increase of thickness of the gel has been convincingly explained by Rio et al.[21], assuming that the permeability of the layer of hydrated products does not remain constant, but decreases with time owing to a continuous modification not of its composition but of its structure. The dynamics of this structural modification was described by Lea[22] and by Jeffery[23] who stated that in the hydration process both the laminar structures of the gel at low C/S (CSH(I)) and its fibrous or fibre-textured structures of high C/S (CSH(II)) would fill both the interparticle and internal spaces of the gel itself with a relative increase in the number of contacts between the different structural elements, which would undoubtedly be favoured by the forces of cohesion which, as is known, become effective at a certain threshold distance. It is therefore possible, on the basis of this mechanism, to imagine the creation of directional and suitably oriented zones which would constitute true points of attachment, with the phenomenon of hardening being due to the increasing number of these points.

## Properties and chemical structure

A considerable contribution to the investigation of the chemical structure of the products deriving from the process of hydration was recently made by Lentz[24], who extended the technique of silication of silicate minerals[25] to hydrated pastes. As is known, this technique permits substitution for the bivalent metals, which join the various silicatic structures into a network by means of bridges of the metal oxide type, a more stable terminal group ($Me_3Si$) without (theoretically at least) modifying the original silicate structure.

From tests carried out on both anhydrous calcium silicate and pastes of various ages, Lentz was able to state that the structures which are comparatively prominent in these systems are not only of ortho-, but also of di-, tri- and polysilicate type, the latter being of still unknown molecular configuration, and that these structures vary their content during the process.

The existence of silicate structures at various degrees of condensation has already been assumed in a certain number of studies appearing in the literature. For example, to explain the constancy of the density of tobermoritic gels of different C/S ratio, Taylor and Howison[26] assumed the formation of pyrosilicate structure, $Si_2O_7$, for hydrates of high C/S ratio, which would be due to partial depolymerization and formation of dimers from the metasilicate chains. The unattached $SiO_4$ tetrahedrons in the central layer of $CaO_2$ (tetrahedral bridges) would gradually be removed, or, more precisely, only the $SiO_2$ group would be removed, the other two oxygen atoms belonging also to the neighbouring tetrahedrons.

The removal of the $SiO_2$ which results in rupture of the metasilicate chain is balanced by the entrance into the lattice of a $Ca^{++}$ ion which locates itself not in the layer at the position of the $SiO_2$, but between the layers. For the sake of the law of electrical neutrality the removal of the $SiO_2$ group, which is electrically neutral, is accompanied by that of two hydrogen ions, so as to balance the positive charge of

the Ca ions.  The substitution $Ca^{++}/SiO_4$ $2H^+$ with negligible influence on the weight of the pseudo cells would explain the constancy in the density with varying ratio C/S, and would also justify the decrease in thickness of the layers (lattice distance c) observed experimentally by Grüdemo[27].

Both Taylor's hypothesis and Lentz's experimental results on hydrated silicates were recently confirmed by Funk by the method of dissolving in methanolic HCl followed by reaction with a solution of molybdic acid[28].  From the tests that he carried out Funk was able to  draw a final conclusion concerning the existence in the hydrosilicates of polycondensate structures of various types, and hence a distribution of the degree of condensation.  Although he succeeded in defining only one curve of variability in the degree of condensation, being able to evaluate it only very approximately, Funk found that with an increase in the ratio C/S beyond 0.8-1.1, the degree of conden-sation decreases[29] whereas it increases with increasing temper-ature of the hydration process[30].

A later confirmation of the possible existence of polyconden-sate structures in the hydrosilicates present in the paste came from an interesting study presented by the Russian school at the 4th International Symposium in Washington in 1960[31].  The existence of the $SiO_3^=$ ion, which is thermodynamically possible, in an alkaline medium can be assumed experimentally only if these anions polymerize, as is logical to suppose in view of the unsaturated character of the double bond, and form complex mole-cules, the size and shape of which are controlled by the type of base cation present in solution and in the hydrosilicate. Taylor stated at the recent Tokyo Symposium[13] that the condensation of the $SiO_4$ tetrahedrons and of the metallo-oxygen polyhedrons of the central layer either  occur simultaneously, but not independently, the two processes affecting each other reciprocally, or, alternatively, there is prior formation of metallic hydroxide laminae which act as matrices for the sub-sequent condensation of the $SiO_4^=$, with formation of only structures that the matrix is capable of "accepting".  Therefore, before speaking merely of polymerization, in the formation of

complex silicates, for condensation of the silicate anions, the process should be considered as a polymerization for coordinated condensation in which the metallic cation plays a primary part.

In the presence of Ca ions in particular, the polymerization of the $SiO_3^=$ anion might lead to the formation of traces of the type $(Si_6O_{17})^{-10}$, as in xonotlite, a hydrosilicate of thermal origin, "crimps" $(Si_{12}O_{31})^{-14}$, a net structure $(Si_6O_{15})^{-6}$, all derived from the typical regrouping of wollastonite $Si_3O_9$[29,30]. Very probably the low crystallinity of the tobermorite present in the hydrated state is due to this inhomogeneity in the degree of condensation and to this myriad possibility of polycondensate structure in a more or less complex manner. Perhaps a more realistic representation of the structure of these semicrystalline or quasiamorphous tobermoritic phases would consist in the existence in the central Ca-O layer, essentially similar to that present in natural tobermorite (c = 11.3 Å), not of regular triple chains but of an entirely random sequence of more or less short chains interspersed with hydroxy groups[34,35]. The length of the chains can vary randomly up to the minimum limit of the isolated tetrahedron, and this randomness is reflected in variable degree of order with which the individual layers are packed in relation to each other, resulting in the poor definition or complete absence of the peak corresponding to the greater basal spacing (c or thickness of the layer). Both of these effects (shortening of the chains and their substitution by hydroxy ions) not only produce an increase in the ratio C/S above the value 0.8, but would confirm the hypothesis of a satisfactory structural similarity greater than that between natural tobermorite and hydrosilicates of the cement pastes, between these and jennite, calcium and sodium hydrosilicate of mineral origin, recently discovered and defined[13,37].

In the presence of condensable SiOH groups it might be possible to alter the properties of some calcium hydrosili-cates by producing substances with special mechanical character-istics[31], although in a nonexclusive way, in view of the pro-found influence exerted on these characteristics by the phenomena of structural intergrowth and interlinkage, as brought out at

the recent Tokyo Symposium[38].

## Relations between mechanical characteristics and chemical-morphological structure

The major contribution to our knowledge of the dependence of mechanical properties on the structure and the type of hydrosilicates present is derived from the series of studies which had as their object the treatment of the hydraulic bonds at high temperature and pressure. As we know, this technique was developed and elaborated for several reasons: in the first place, besides considerably accelerating the hydration reaction, the products obtained show chemical resistance and mechanical strength superior to the products normally obtained, and finally, there is the possibility of using products which, while inert at ordinary temperatures, display cementing properties at higher temperatures.

The results obtained by numerous experimenters can be summarized as follows: for typical treatment times of 12-14 hours it is known that while the compressive strength of the paste of $\beta$ $C_2S$ increases continuously with the temperature at least up to about $230^{\circ}C$, that of $C_3S$, on the contrary, increases at first and then decreases definitely for temperatures about $180-200^{\circ}C$ until a value below that of $\beta$ $C_2S$ is reached[36]. This phenomenon was readily explained by taking into account the fact that development of mechanical compressive strength depends on the formation of an adequate amount of the gelatinous matrix. Now, in both cases this matrix, because of the hydration reaction, is first formed and then destroyed. However, whereas $\beta$ $C_2S$ reacts so slowly that the process of formation is dominant even after many hours of treatment at about $200^{\circ}C$ (with mechanical strength consequently higher than that attainable at lower temperature), the $C_3S$ reacting more rapidly proceeds so that the process of destruction (or transformation) of the original matrix occurs chiefly after a few hours above $180-200^{\circ}C$. This brings about a decrease of mechanical strength with values

distinctly below both those of $\beta$ $C_2S$ and those found in $C_3S$
paste kept at room temperature for an equal length of time.

The change of compressive strength with varying processing
conditions also observed in portland cement of industrial origin
has led to closer study of the hydrothermal reaction with regard
both to its mechanism and the product obtainable from it. In
an interesting study by the Russian school[40] it was shown how,
in the case of portland cement, the process carried out in an
autoclave resulted in the formation of hydrosilicates of more
crystalline structure which increased the mechanical strength,
provided the process of the crystallization is limited in its
entirety; otherwise, an initial improvement is followed by a
distinct decrease in mechanical strength owing to coarsely
crystalline formations of fragile structure. It follows from
this that only a proper ratio between essentially amorphous gel
and crystalline components will assure optimum mechanical strength,
hence, the possibility, as well as the necessity of careful
control of heat and pressure throughout the entire process.

Both the chemical and morphological nature of the thermally
obtainable hydrosilicates have been and remain the subject of
investigations and studies which undoubtedly find support, in
view of the similarity of the processes, in studies of the hydro-
thermal behaviour of lime-silica and cement-silica mixtures.
The experimental findings that the addition of certain quantities
of reactive silica (finely divided quartz or silicic acid) results
in an increase of compressive strength both in pure and in
cement silicate pastes, has been the subject of studies and
research by many experimenters.

Kalousek[41] and Sanders and Smothers[42] using first calcium
and silica mixtures, then portland cement-silica systems, both
noted that the resulting hydrosilicates undergo a change in
the X-ray diffraction spectrum which becomes more pronounced and
meaningful, first when proceeding in the time of the reaction
to 175°C with mixtures of definite C/S ratio (about 0.8), and
secondly by varying the C/S ratio of the initial mixture for
a given hydrothermal processing time. In both cases a very
distinct and intense line appeared at 11.4 Å, the line 3.03 Å

resolved into a doublet at 3.07 and 2.96 $\overset{o}{A}$, and there was a slight increase in the distance of the line at 1.82 $\overset{o}{A}$.

From comparison of the diffraction spectra of hydrosilicates of known structure, we note a close similarity with that of natural tobermorite (c $=$ 11.4 $\overset{o}{A}$), which is known to have laminar structure. At the same time, both authors noted how the intensity and the form of the paste at 11.4 $\overset{o}{A}$ varies with varying ratio C/S of the mixture or with different processing conditions. For a ratio C/S $=$ 0.8 at a given interval of time at the processing temperature, the maximum intensity of this peak is accompanied by maximum mechanical strength.

Definition of the area of possible existence of the phases involved in the process[43] made it possible to clarify satisfactorily the entire course of the hydrothermal reaction. Initially the hydration of the binder, even if carried out at higher than room temperature, leads to the formation of a matrix consisting of tobermoritic gel and cryptocrystalline $Ca(OH)_2$ so intimately mixed as to be difficult to distinguish one from the other. At approximately $130^{o}C$ there is a gradual transformation of the gel into $\alpha$ $C_2SH$ hydrosilicate of known chemical structure $(Ca_2(HSiO_4)OH)$ appearing in the form of orthorhombic crystal flakes, which are almost certainly formed by internal rearrangement of the gel without, therefore, depending on the possible presence (and possible reactions) of $Ca(OH)_2$ crystals.

At high initial C/S ratios ($C_3S$ or pure portland cement), if the temperature is raised to $160-170^{o}C$ we note the appearance, although limited with respect to that of $\alpha$ $C_2SH$, of tricalcium silicate hydrate (TSH), $Ca_6(Si_2O_7)(OH)_6$, a disilicate of fibrous structure, which would form by reaction of crystals of $Ca(OH)_2$ with the gel of the matrix or with $\alpha$ $C_2SH$. By lowering the C/S ratio with the addition of small quantities of active silica we note a progressive appearance both of $Ca(OH)_2$ and TSH accompanied by an increase in the production of $\alpha$ $C_2SH$, which has a decidedly unfavourable effect on the mechanical strength. Further additions of $SiO_2$, causing the appearance of increasing quantities of hydrosilicate of low C/S ratio and the progressive decrease, and

ultimately the disappearance, of the α C₂SH, results in an increasing mechanical strength, reaching a maximum for a ratio C/S of approximately 0.8-1.0, as reported in the literature by numerous other authors[44,47].

The thermodynamically possible existence of natural tobermorite of the crystalline type (11.4 Å) at the temperature and composition conditions at which the above hydrosilicate appears, has led some experimenters to contend that the formation of such a crystalline phase would guarantee high mechanical strength. In this connection, although it was definitely shown that the negative effect exerted by the α C₂SH on the mechanical strength[48] brings about coarse crystallinity and results in failure to bind the different parts of the structure strongly into a firm whole of considerable force, the effects on these properties both of tobermorite 11 Å (crystalline) and of CSH I (quasi amorphous or semicrystalline) both essentially laminar structure and at about the same ratio C/S, have been and still are the subject of dispute. Besides papers[40] in which the necessity of an adequate ratio in the binding material between the amorphous and the crystalline parts is emphasized in order to obtain optimum mechanical strength, widely differing results are found which lead us to think that the presence of tobermorite 11 Å is only of restricted benefit, and if present in limited quantities it may be directly dangerous as soon as it appears[49,50].

It has been ascertained experimentally that maximum mechanical compressive strength can be achieved only in the presence of phases of a laminar type with high dimensional stability (i.e., absence of shrinking) and high specific areas[41,47,49,51] capable of ensuring a sufficient number of points of contact between individual crystals, although fibrous or needle structure (TSH) would ensure high tensile strength values[36].

When we add to the series of studies concerning the straight morphological structure of the hydrosilicates of thermal origin the contribution to the chemical structure made by Funk[29], who determined experimentally the manner in which the degree of condensation of these structures increases continuously during

the hydrothermal process, eventually becoming virtually inesti-
mable, it can be reliably assumed that the optimum mechanical
strength (at least compressive strength) is associated with the
presence of very definite macromolecular morphological structures
with a quasi threshold degree of condensation (high but, at
least for the present, underminable) beyond which the formation
of phases would be favoured which, when crystallizing coarsely,
would determine the zone of fragility within the binder.

Unlike the results obtained with the hydrothermal process,
those so far obtained in the hydration process at room temperature
are less definite and accurate because of the virtual amorphous-
ness of the hydrosilicates obtained, which makes identification
of possible structures particularly difficult. The hydrosilicates
formed in this case show a lower degree of condensation, which
in part can be calculated[29], but the type of morphology mainly
involved in the mechanical properties is still the subject of
controversy and study, although from studies of the hydration
of calcium silicates in the presence of additives[52-55], and
those involving possible isomorphous substitutions in the
tobermoritic lattice[56,57], there is reason to believe, in this
case as well, that the essentially laminar structure and low C/S
ratio is mainly responsible for the mechanical properties.

In this connection it is interesting to recall how the
hydration characteristics of the calcium silicates in the presence
of substances of the type $CaSO_4 2H_2O$, $CaCl_2$, $CaSO_4 0.5H_2O$ may
change, producing a morphological change in the product which
tends to lose its fibrous character in favour of a flatter structure
with an increase of compressive strength, whereas the morphological
change produced by the introduction of the Al ion into the
tobermoritic lattice at the calcium or silicon position results
in an increase of flexural strength and a decrease of shrinkage[48].

With a view to clarifying the relation existing between
the chemical-morphological characteristics (degree of condensation,
surface development, degree of hydration) and the mechanical ones
(flexural and compressive strength) an experimental investigation
of the hydration of calcium silicates was begun some time ago at

the Central Cement Standards Laboratory* both in the absence
and in the presence of additives of the type $CaSO_4.2H_2O$ and $CaCl_2$.

From the preliminary but significant results so far obtained
it is clear that the above characteristics are interrelated,
although sometimes the additives may affect the degree of inter-
relationship.  It is also evident that the hydrated part con-
stitutes a system with a very variable degree of condensation
with respect both to the modality with which hydration occurs
(still or in agitation) and of the type of additive present,
the latter being mainly responsible for determining a system with
a more or less disperse and heterogeneous degree of condensation.

In the particular case of $CaCl_2$, the investigation is also
intended to clarify the effect of the concentration of salts on
the character of the hydrated product obtainable in the first
curing and on the possible modifications that the latter may
undergo in the course of hydration.  The investigation has also
been extended to portland cements and pozzolan type cements of
industrial origin in order to determine the nature of the
particular hydrosilicates produced following  hydration.

The results obtained so far, which form the subject of
the next publication, and which, however slight, clearly show
that the morphological and structural characteristics of a
tobermoritic gel and the modification which it undergoes in the
presence of additives by various mechanisms, continue to con-
stitute a rich field for both basic and applied research into
the process of hydration of hydraulic binders.

It also appeared obvious that the mechanical characteristics
depend substantially on the morphological and structural ones
which the products of hydration may assume as a consequence both
of the different conditions of curing, and of the modifying
effects which the presence of certain substances may produce
in the course of hydration.

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* Laboratorio Centrale Cementisegni - Colleferro, Italy (Transl.).

# References

[1] A. Rio, A. Celani, M. Collepardi: Ind. Ital. Cemento, 35, 275 (1965).

[2] R. Turriziani, A. Rio, M. Collepardi: Ind. Ital. Cemento, 35, 635 (1965).

[3] A. Celani, M. Collepardi, A. Rio: Ind. Ital. Cemento, 36, 669 (1966).

[4] R. Kelly: Canadian J. of Chemistry, 38, 1209-1216, 1218-1225, (1960).

[5] S. Brunauer, S. A. Greenberg: Proceedings of the Fourth International Symposium, 135-163, Washington (1960).

[6] W. C. Hansen: Proceedings of the Symposium on Chemistry of Cement, London, 318-321 (1952).

[7] E. J. W. Vervey, J. Th. Overbeeck: « Theory of stability of lyophobic colloid », Elsevier Publ. Co. New York (1948).

[8] H. Van Olphen: « Rheological Phenomena of clay sols connection with the charge distribution on the micelles », Discus. Faraday Soc. II, 82-89 (1951).

[9] H. R. Kruyt: Colloid Science Vol. I, 1-57, Elsevier Publ. Co. New York (1952).

[10] H. D. Megaw, C. H. Kelsey: Crystal structure of tobermorite, Nature (London) 177, 390-1 (1956).
Proc. Symp. Int. Union of Crystallograph, Madrid (1956).

[11] G. L. Kalousek, R. Roy: J. Am. Ceram. Soc., 40, 236-329 (1957).

[12] C. M. Hunt: Proceedings of the Fourth Int. Symp., 297-305, Washington (1960).

[13] H. F. W. Taylor: « The calcium silicate hydrates » Principal Paper, Fifth Intern. Symp. Tokyo (1968).

[14] S. Brunauer: Some aspects of the physics and chemistry of cement, chapter 16, The Science of Engineering Materials, Edited by E. Goldman, J. Wiley and Sons Inc. New York (1957).

[15] Portland Cement Association, Yearly Report of the Research and Development Div., June 1957, 23-25.

[16] T. C. Powers: « The physical structure and engineering properties of concrete », P. C. A. Res. Depart. Bull. 90, July 1958.

[17] K. T. Greene: Proceedings of the Fourth Intern. Symposium, 359-373, Washington (1960).

[18] H. Zur Strassen: « The problem of non-selective hydration of cement minerals », Zement u. Beton, 16, 32-34, July 1959.

[19] R. K. Iler: « The colloid chemistry of silica and the silicates », Cornell University Press, Ithaca, N. Y. (1955).

[20] L. E. Copeland, D. L. Kantro: « Hydration of portland cement », Principal Papers, Fifth Intern. Symp., Tokyo (1968).

[21] R. Turriziani, A. Rio, M. Collepardi: Ind. Italiana del Cemento, 10, 1965.

[22] F. M. Lea: « The chemistry of cement and concrete » St. Martin's Press, Inc. New York (1956).

[23] J. W. Jeffery: Chem. and Ind. 1756-1763 (1955).

[24] C. W. Lentz: Proc. Symp. Structure of Portland Cement Paste and Concrete, 1965, 269-283 (1966).

[25] C. W. Lentz: Inorg. Chem., 3, 574-579 (1964).

[26] H. F. W. Taylor, J. W. Howison: Clay Minerals Bull., 3, 98-111 (1956).

[27] Å. Grudemo: Swedish Cement and Concrete Res. Inst. Proc. n. 26 (1955).

[28] H. Funk, R. Frydryck: Proc. Symp. Structure of Portland Cement Paste and Concrete, 1965, 284-290 (1966).

[29] H. Funk: Proc. Symp. Autoclaved Calcium Silicate Building Products, 1966, 122-124 (1967).

[30] H. Funk: Proc. Fifth Intern. Symposium, Tokyo (1968).

[31] O. P. Mchedlov-Petrosyan, W. I. Babushkin: Proc. Fourth Intern. Symp. Washington (1960), 533-544.

[32] N. V. Belov: Mineral. Transaction of the Geological Soc. of 1956 n. 10; 1959 n. 13.

[33] Kh. S. Mamedov, N. V. Belov: Rep. of Ac. Sc. URSS 1954, 40, 4; 1956, 107, 3; 1958; 121, 4/5; 1958, 123, 1/4.

[34] H. F. W. Taylor: Prog. in Ceram. Sci. 1, 89 (1961).

[35] Å Grudemo: Proc. Fourth Intern. Symp., 615, Washington (1960).

[36] H. F. W. Taylor: Proc. Symp. Autoclaved Calcium Silicate Build. Prod. 1966, 195-205 (1967).

[37] A. B. Carpenter, R. A. Chalmers et Others: Am. Mineral, 51, 56-74 (1966).

[38] R. Feldman, P. J. Sereda: Written Discussion - Session III, 1, 106 - Fifth Int. Symp., Tokyo (1968).

[39] H. F. W. Taylor: « The Chemistry of Cement » 1, 424, Academic Press, New York (1964).

[40] P. I. Bozhenov, V. I. Kavalerova, V. S. Salnikova, G. F. Suvorova: Proc. Fourth Int. Symp., 327-348, Washington (1960).

[41] G. L. Kalousek: Proc. Am. Concr. Inst. 51, 989 (1954-55).

[42] L. D. Sanders, W. J. Smothers: Proc. Am. Concr. Inst. 54, 127 (1957-58).

[43] A. Aitken, H. F. W. Taylor: J. Appl. Chem. Lond. 10, 7 (1960).

[44] V. R. Garashin, G. V. Sizov: Stroitel'nye Materialy, 12, 1, 33-35 (1966).

[45] Y. M. Butt, L. N. Rashkovich: « The hardening of binders at elevated temperatures » 2nd Edit., Moscow, Stroiizdat (1965).

[46] H. F. W. Taylor, W. F. Cole, D. R. Moorehead: Nature 201, 4922, 918-919 (1964).

[47] M. J. Purton, J. M. Coldrey: Proc. of Second Intern. Symp. on Autoclaved Silicate Building Materials N. 59, Hannover (1969).

[48] G. L. Kalousek: « High temperature steam curing of concrete at high pressure » Princip. Papers, Fifth Intern. Symp., Tokyo (1968).

[49] R. Kondo: Proc. of Symp. on Autoclaved Calcium Silicate Buildings Products, 92, London (1965).

[50] Y. Butt et Others, Sborn. Trud. Resp. Nauchno-issled. Inst. Stroitel Materialov 17, 66 (1960).

[51] A. V. Volzhenskii, G. V. Sizov: Stroitel'nye Materialy 13, 6, 17-19 (1967).

[52] H. Funk: Proc. of the Fourth Int. Symp. 291-295, Washington (1960).

[53] H. Kurczyk, H. Schwite: Tonindustrie Zeitung, 84, 24, 585 (1960).

[54] A. Celani, M. Collepardi, A. Rio: Ind. Italiana del Cemento, 11, 669 (1966).

[55] R. J. Dyczek: Written Discussion - Session II - 1-25 Fifth Int. Symp. Tokyo (1968).

[56] G. L. Kalousek: J. Am. Ceramic Soc. 40, 74-80 (1957).

[57] L. E. Copeland, E. Bodor, T. N. Chang, C. H. Weise: J. PCA Research and Development Laboratories 9, 61-67 (1967).