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Morphology and microstructure of hydrating Portland cement and its constituents II. Changes in hydration of calcium silicates alone and in the presence of triethanolamine and calcium lignosulphonate, both with and without gypsum

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MORPHOLOGY AND MICROSTRUCTURE OF HYDRATING PORTLAND CEMENT AND ITS CONSTITUENTS

**II. CHANGES IN HYDRATION OF CALCIUM SILICATES ALONE
AND IN THE PRESENCE OF TRIETHANOLAMINE AND CALCIUM
LIGNOSULPHONATE, BOTH WITH AND WITHOUT GYPSUM**

by
T.D. Ciach and E.G. Swenson

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MORPHOLOGY AND MICROSTRUCTURE OF HYDRATING
PORTLAND CEMENT AND ITS CONSTITUENTS
II. CHANGES IN HYDRATION OF CALCIUM SILICATES
ALONE AND IN THE PRESENCE OF TRIETHANOLAMINE
AND CALCIUM LIGNOSULPHONATE, BOTH WITH
AND WITHOUT GYPSUM

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ABSTRACT

Systematic sequential observations with the electron microscope were made of the morphological changes which occurred during hydration of C_3S^* and C_2S pastes, with and without the presence of gypsum. The specific effects of each of two admixtures were studied: triethanolamine and calcium lignosulphonate. Water to C_3S or C_2S ratio was 0.5 and admixture dosage was 0.5%. The admixtures had some effect on changes in microstructure, but they had a pronounced influence on the rate of the hydration processes.

SOMMAIRE

Des observations au microscope électronique ont été faites en séquence systématique pour observer les changements morphologiques qui prennent place au cours de l'hydratation de pâte de C_3S et de C_2S , en présence ou non de gypse. Les effets spécifiques de deux adjuvants ont été étudiés: le triéthanolamine et le lignosulfonate de calcium. La fraction eau: C_3S et eau: C_2S était de 0.5 et le dosage d'adjuvants, de 0.5%. Les adjuvants ont provoqué un certain effet sur les changements dans la microstructure, et ont de plus montré une influence considérable sur la vitesse du procédé d'hydratation.

*Standard cement nomenclature is used; $C_3S = 3CaO.SiO_2$; $C_2S = 2CaO.SiO_2$; $C_3A = 3CaO.Al_2O_3$; $C_4AF = 4CaO.Al_2O_3.Fe_2O_3$; w/c = water:cement ratio by weight.

This is the second of a series of papers reporting the results of long-term studies on the relationship between morphological changes in hydrating portland cement and its microstructure in the plastic and hardened states. The first one (1) dealt with tricalcium aluminate: the effects of triethanolamine and calcium lignosulphonate admixtures in the absence and in the presence of gypsum. This one is concerned with the tricalcium and dicalcium silicate components.

The method involves the observation and interpretation of a series of electron micrographs of various paste mixtures during hydration. Care is taken to select representative and characteristic structures and formations. X-ray is used to identify certain phases. When changes occur, the corresponding series of electron micrographs are shown, and when no change occurs, only one or two are presented. The formations shown are representative but of a qualitative nature.

Many micrographs showing morphology changes during hydration of cement compounds have been published. Usually these were taken only at advanced ages of hydration; often they represented cases of hydration in excess water, and too often they represented isolated examples of morphology rather than the dominant forms.

The present study, carried out on a systematic basis, is expected to fill a need for a sequential record of the characteristic microstructure and morphology of cement and its components when hydrating as a paste with various admixtures. An understanding of these changes and their effects, and the availability of a method of studying all such systems, are of practical value to the concrete technologist.

Like the first paper (1), this consists mainly of observations of changes in morphology. Parallel studies are designed to make possible a correlation between the microstructure and the mechanical and other properties of hardened portland cement paste (2).

Introduction

Tricalcium silicate (C_3S) and dicalcium silicate (C_2S) together constitute some 75 per cent of portland cement. The hydration of these

mineralogical components leads to the formation of the calcium silicate hydrates which largely constitute the structure of the hardened paste.

Extensive studies have been made on the nature and reactions of C_3S and C_2S , and on the nature of their hydration products. Studies of the morphology and microstructure of the hydration products and how they are affected by various additives have been summarized in the international symposia on the chemistry of cement and concrete. The specific effects of the presence of gypsum have been treated therein by Copeland and Kantro (3) and by Taylor (4).

The presence of gypsum can have an accelerating or retarding effect on the hydration of C_3S depending on the concentration present, but both effects are rather small. Apparently gypsum does not form new phases with the calcium silicate hydrates, for only the usual phases of CSH and CH were present after hydration (5, 6, 7, 8). SO_4^{2-} ions can replace SiO_4^{4-} ions to an extent not exceeding 5 per cent. It appears that this has some influence on morphology because the rolled-up foils or sheets do not form under these conditions; only the fibrous particles in a cigar-like shape occur (6).

The extensive use of organic chemicals as admixtures in concrete and the variety of these in use make it important to understand the changes that take place due to their presence. The present paper describes experiments with combinations of C_3S or C_2S and dosages of triethanolamine or calcium lignosulphonate in the absence and in the presence of gypsum. These two organic chemicals are commonly used in many commercial admixture formulations. Systematic sequential observations are made with the electron microscope to determine morphological changes from a few minutes to 3 months. X-ray and other methods were used at times to identify certain phases. This study is part of a continuing, broad study of concrete admixtures at the Division of Building Research.

Materials and Procedures

The tricalcium silicate and dicalcium silicate samples used in these experiments were supplied by the Portland Cement Association Research Laboratories. Blaine surface areas were: for C_3S , 3310 sq cm per gram;

for C_2S , 2770 sq cm per gram. Corresponding free limes were, in per cent: for C_3S , 0.46; for C_2S , not determined. The C_3S was 99.2 per cent pure in terms of silica and lime.

The pastes were prepared on the basis of water to dry C_3S (or C_2S) by weight = 0.5. The gypsum was prepared from large, clear natural crystals which were ground to pass the 200 DIN sieve. The mixture of C_3S and 10 per cent by weight of gypsum was prepared by grinding them together in a porcelain-alumina ball mill.

Admixture dosages were 0.5 per cent by weight of dry C_3S and C_2S . The triethanolamine was of chemically pure reagent grade. The calcium lignosulphonate was a commercially prepared product, chemically treated to destroy excess sugars. Total sugars averaged 0.08 per cent and total reducing bodies about 4 per cent.

A description of methods and procedures used in preparing and examining test specimens is given in the first paper in this series (on tri-calcium aluminate) (1):

At intervals of 5 minutes, 1 and 4 hours, 1, 2, 3, and 7 days, and 1, 2, and 3 months, samples were taken and tested. Hydration was stopped by treating with acetone at about $-18^\circ C$, then drying of the frozen samples in a vacuum.

Single stage replicas of the broken surfaces of the paste were made using the platinum-carbon technique (9). The electron micrographs shown are those that depict the average and general morphology. Exceptional forms and structures were not considered.

Observations and Discussion

1. Hydration of C_3S and C_2S with neither Gypsum nor Organic Admixture Present

In the first 3 days, the hydration of C_3S began from the edge-like parts of the grains and also at the small particles formed by recrystallization. Very thin, semicrystalline crumpled films of hydration products were observed (Fig. 1). These sometimes formed a bridge-like structure between unhydrated grains of C_3S .

FIG. 1

The microstructure of C_3S with no admixture, $w/c = 0.5$. Age 3 days. Loosely crumpled foils of hydration products around unhydrated grains of C_3S .

FIG. 2

The microstructure of C_3S with no admixture, $w/c = 0.5$. Age 23 days. Plates of hydration products with three-dimensional fibres of CSH.

Between 3 and 7 days, the C_3S hydration products took on the form of fibrous particles which "radiated" as a mesh-like structure on the surface of the C_3S grains. These fibrous particles were probably CSH, which are usually described as fibrous particles rolled up from semicrystalline, very thin foils or sheets (5, 10, 11).

Between 7 and 28 days the C_3S hydration products did show changes. Some aggregations displaying tabular and striated structures appeared to cover some of the fibrous particles of CSH observed in the earlier stages of hydration. Sometimes these tabular structures displayed a mesh-like fracture on the surfaces of the plates. This mesh-like structure probably acted as a nucleus for further formations of hydration products, or it may have been merely an indication of the appearance of the original pore system before filling began (Fig. 2). It was observed that the fibrous particles of CSH, which were oriented in three directions at angles of about 60° , had formed plates of a "felted," partly interlocking structure. A similar structure of C_3S hydration products was found by Grudemo (11), Copeland et al. (12) and Brunauer (13). These plates of "felted" structure form striated

FIG. 3

The microstructure of C_3S with no admixture, $w/c = 0.5$. Age 2 months. Pseudomorphs of C_3S grains; striated plate structure of hydration products; and some hexagonal crystals of CH.

FIG. 4

The microstructure of C_3S with no admixture, $w/c = 0.5$. Age 3 months. Fibrous interlocking and striated plate structure of hydration products between pseudomorphs of C_3S grains.

aggregations and often display the columnar cleavage as well.

Between 1 and 2 months of C_3S hydration the striated (plate) structure became bound as a coating around either the partly hydrated C_3S grains or pseudomorphs of them (Fig. 3). Single crystals of calcium hydroxide of very good hexagonal habit can also be observed.

At 3 months' hydration there were no further clearly defined changes in the microstructure of the C_3S paste. During this latter period the felted, partly interlocking structure of the plates of CSH was also observed (Fig. 4).

The hydration products of C_2S were found to be similar to those of C_3S when both were examined in the same way, except that the products of C_2S appeared later in age, as was expected. As compared with the hydration process of C_3S , the hydration of C_2S started more slowly, and the second form of CSH, which for C_3S appeared like long fibres, appeared rather needle-like in this case. The three-dimensional network which tended to form plates under these conditions had a less ideal arrangement than that for C_3S (see Figs. 2 and 4), and therefore was likened more to a felted structure (Fig. 5).

FIG. 5

The microstructure of C_2S paste with no admixture, $w/c = 0.5$. Age 3 months. Fibres of cigar-shaped CSH around pseudomorphs of grains of C_2S .

FIG. 6

The microstructure of C_3S paste with gypsum and no admixture. Age 6 hours. Large crystals of gypsum; unhydrated grains of C_3S ; and semicrystalline crumpled foils of hydration products.

The rather limited number of calcium hydroxide crystals observed in the hydration products of both C_3S and C_2S suggested that either they were obscured by other hydration products or that some form of accommodation of the CH in the CSH structures took place.

X-ray examination of the C_3S paste after two months of hydration revealed unhydrated C_3S and patterns that appeared to be closely related to those of tobermorite. There were also patterns similar to those of $Ca(OH)_2$.

2. Hydration of C_3S with Gypsum but no Organic Admixtures Present

The presence of gypsum did not greatly affect the products of hydration of C_3S but it did affect the rates of formation of these products. It also, when compared with the hydration of C_3S alone, affected the structure of C_3S paste.

The first products, observed at one hour of hydration, appeared as small, rounded particles on the surfaces of unhydrated grains of C_3S . At 6 hours there had formed, in addition, an amorphous film between the C_3S grains and the gypsum (Fig. 6).

FIG. 7

The microstructure of C_3S paste with gypsum and no admixture. Age 1 day. Fibrous particles of hydration products of CSH.

FIG. 8

The microstructure of C_3S paste with gypsum and no admixture. Age 1 month. The fibrous sieve structure of hydration products with parallel cleavage.

After 1 day's hydration small fibres in a rosette pattern had developed; they appeared on the surface of tabular crystals of gypsum and C_3S grains. At the same time, small, rounded particles on the grains of C_3S appeared (Fig. 7). These looked similar to those resulting from nucleation of CSH fibres between the third and seventh day of hydration.

Between 1 day and 1 month the hydration products developed as a massive, partly striated or fibrous structure. Fibres of CSH assembled into aggregates of sieve-like and partly columnar form between the unhydrated C_3S grains or the pseudomorphs of these (Fig. 8). After an etching treatment with ethylene glycol for 30 minutes, part of the hydration products were removed; the microstructure then had a fibrous network in which these CSH fibres displayed a rosette-like or brush arrangement. In the areas where the glycol had almost completely removed the hydration products of C_3S , there appeared fractures that continued through the unhydrated grains of C_3S and the fibrous network between them (Fig. 9).

FIG. 9

The microstructure of C_3S paste with gypsum and no admixture. Age 1 month. Treated with glycol. Fibrous hydration products show bundle-like arrangement.

FIG. 10

The microstructure of C_3S paste with triethanolamine, $w/c = 0.5$. Age 4 hours. Semicrystalline crumpled foils of hydration products.

3. Hydration of C_3S and C_2S in Absence of Gypsum but with Triethanolamine Present

In the presence of this admixture, the hydration process of C_3S appeared to proceed more rapidly than it did with no admixture present. After only 4 hours the grains of C_3S were covered by very thin, crumpled films which displayed bridge-like bondings similar to those that had formed, at 3 days hydration of C_3S alone (Fig. 1). Along with these semicrystalline foils were single fibrous particles of CSH (Fig. 10). After 1 day these small fibrous particles of CSH radiated over the grains of unhydrated C_3S . At 7 days the microstructure appeared as unoriented, partly rolled sheets and plates between fibrous particles and unhydrated grains (Fig. 11). Many of these plates showed some degree of fracture on the surfaces.

At later ages, up to 3 months, no significant change in the microstructure of C_3S products occurred (Fig. 12).

Apart from the rate of hydration, the only differences between the products formed in the absence and in the presence of triethanolamine were

FIG. 11

The microstructure of C_3S paste with triethanolamine, $w/c = 0.5$. Age 7 days. Unoriented plates of hydration products usually show an interlocking fibrous structure.

FIG. 12

The microstructure of C_3S with triethanolamine, $w/c = 0.5$. Age 2 months. Loose plates and fibrous microstructure of hydration products.

that in the presence of the admixture, the felted, fibrous structure of the plates was clearer, and many plates formed in an unoriented structure, only occasionally displaying striated cleavage (Fig. 12).

The X-ray examination at 2 months showed the presence of unhydrated C_3S and a CSH closely related to tobermorite; this had also been the case when no admixture was present. From a comparison of these two systems it was found that the size of the fibrous particles of CSH was greater in the paste with triethanolamine present than in the paste with no admixture. In both cases X-ray revealed patterns similar to those of calcium hydroxide, although only a few single crystals of CH of good hexagonal habit were observed by electron microscope. These results are similar to those reported in many other investigations (12, 14, 15, 16, 17); in all of these studies, apparently, not all of the CH produced during hydration can be accounted for by available methods. This situation is attributed by some to the formation of CSH with a very high C/S ratio, and by others to the highly amorphous state of the CH which can readily be absorbed on the surfaces of CSH.

The hydration of C_2S and C_3S in the presence of triethanolamine were very similar. The process was, however, more rapid when the admixture was present, and the microstructure was less compact; the needle-like particles of CSH appeared separately and more often as imprints on surfaces of hydration products. The platy forms of the hydration products were rather unoriented.

4. Hydration of C_3S with Gypsum and Triethanolamine Present

The microstructure of the hydration products of C_3S in this combination was observed to be quite similar to that of C_3S alone, or of C_3S with gypsum, except that fibres of calcium silicate hydrate displayed an arrangement that was mainly a three-dimensional, felted plate structure. At times one observed also the rosette or brush arrangement (Fig. 13).

5. Hydration of C_3S and C_2S without Gypsum but with Calcium Lignosulphonate Present

The presence of this admixture appeared to retard drastically the hydration processes of both C_3S and C_2S . The only hydration products formed in 3 months were semicrystalline films or crumpled foils; in the case of C_3S , fibrous-like particles of CSH, which usually take the form of bundle-like aggregations, also developed. These products all appear to be similar to those that occurred in the early stages of hydration without an admixture or with triethanolamine.

In 23 days of hydration of C_3S , the only product formed was a very thin and crumpled amorphous film. After 23 days there was an observable increase in the amount of this product, which sometimes manifested itself as bridge-like particles between unhydrated grains of C_3S (Fig. 14). Between 1 month's and 2 months' hydration there could be observed single, fibrous-like particles of hydration products on the surfaces of C_3S grains, and bundle-like aggregations of CSH which apparently had been formed from the small fibrous particles between the unhydrated C_3S grains (Figs. 15 and 16).

These products were still to be observed up to 3 months' hydration, but one also observed small, rounded aggregations of amorphous material,

FIG. 13

Microstructure of C_3S paste with gypsum and triethanolamine, $w/c = 0.5$. Age 1 month. Fibrous, three-dimensional, interlocking plates, and a radial arrangement of fibrous hydration products.

FIG. 14

The microstructure of C_3S paste with calcium lignosulphonate, $w/c = 0.5$. Age 23 days. Unhydrated grains of C_3S with crumpled foils of hydration products.

FIG. 15

The microstructure of C_3S paste with calcium lignosulphonate, $w/c = 0.5$. Age 1 month. Single, needle-like particles of hydration products (CSH) on surfaces of grains of partly hydrated C_3S .

FIG. 16

The microstructure of C_3S paste with calcium lignosulphonate. Age 2 months. Bundles of fibres and small rounded particles of hydration products on the surfaces of partly hydrated C_3S grains.

FIG. 17

The microstructure of C_3S paste with gypsum and calcium ligno-sulphonate, $w/c = 0.5$. Age 1 hour. Small rounded particles of hydration products between unhydrated grains of C_3S .

FIG. 18

The microstructure of C_3S paste with gypsum and calcium ligno-sulphonate, $w/c = 0.5$. Age 6 hours. Large crystals of gypsum and small rounded particles of hydration products.

FIG. 19

The microstructure of C_3S paste with gypsum and calcium ligno-sulphonate, $w/c = 0.5$. Age 3 days. Large, thin plates of parallel cleavage, and rounded particles of hydration products.

FIG. 20

The microstructure of C_3S paste with gypsum and calcium ligno-sulphonate, $w/c = 0.5$. Age 7 days. Some large hexagonal-like particles of hydration products and unhydrated grains of C_3S and gypsum.

which was probably CH (Fig. 16). The paste had not yet hardened at this time. The hydration of C_2S in this combination evinced quite similar behaviour.

Results of X-ray examinations of C_3S paste at 2 months showed only the presence of unhydrated C_3S , CSH of very poor crystal form and some patterns similar to those of $Ca(OH)_2$. The fibrous particles were a form of CSH closely related to tobermorite but, in this case, they had retained the semi-amorphous habit. The X-ray diagrams for all three cases (with no admixture, with triethanolamine and with the lignosulphonate), are very similar, except that in the last case the patterns are weaker.

6. Hydration of C_3S in Presence of Gypsum and Calcium Lignosulphonate

At 1 hour the hydration products appeared as small rounded particles on the surface of C_3S grains; amorphous films also occurred. These were still the dominant forms at 3 days hydration (Figs. 17 and 18), although one also observed in the hydration products some plate-like forms of parallel cleavage covered by small precipitations (Fig. 19).

From the seventh until the fourteenth day of hydration, large grains of hexagonal-like cleavage were observed. These must be distinguished from the tabular, monoclinic grains of gypsum (Fig. 20).

After 1 month's hydration the paste was not yet hardened. At this time the 30-minute treatment with glycol destroyed all hydration products. Observations just prior to etching treatment showed that the component present had been the unhydrated C_3S grains, partly dissolved crystals of gypsum and semicrystalline films, and needle-like particles of hydration products on the surface of unhydrated C_3S (Figs. 21 and 22).

X-ray diffraction patterns made at 1 month of hydration showed the presence of the following phases: unhydrated C_3S , gypsum, and calcium hydroxide of very poor crystallinity.

Discussion

In general, the findings of these studies agree well with reported observations by others.

FIG. 21

The microstructure of C_3S paste with gypsum and calcium lignosulphonate, $w/c = 0.5$. Age 1 month. Eroded surfaces of a large crystal of gypsum and grains of C_3S with amorphous hydration products on the surface.

FIG. 22

The microstructure of C_3S paste with gypsum and calcium lignosulphonate, $w/c = 0.5$. Age 1 month. Crumpled foils and a single cigar-shaped fibrous particle of hydration products.

The presence of gypsum without the organic chemical admixtures appeared to accelerate the nucleation of particles of CSH in the hydration of C_3S . Observations in these studies did not make it possible to clearly determine the reported first hydration products of C_3S of very high C/S ratio (4,7). This form probably adheres very strongly to the C_3S grains (4) and cannot be distinguished from them by electron microscopic examination (7). One possibility is that this form constitutes the zonal structure of CSH around unhydrated grains of C_3S of very similar optical properties.

The earliest structure observed consisted of the semicrystalline films described during hydration of C_3S in the absence of gypsum.

After 3 days' hydration in the absence of gypsum, and 1 day's in the presence of gypsum, fibrous particles were observed which often radiated in a mesh-like structure.

At later stages of hydration when no admixture, or only triethanolamine, was present, the first amorphous CSH developed as pseudomorphs of C_3S

grains; the latter were surrounded by other hydration products of fibrous and plate-like forms. In the presence of calcium lignosulphonate this amorphous CSH, along with semi-amorphous crumpled foils around pseudomorphs of grains of C_3S , were the dominant forms of CSH during the whole time of hydration. The fibres or needle forms of CSH appear only as single particles.

It is notable that in all these observations, crystals of lime were almost entirely absent. A possible explanation is that the lime, liberated by hydration of the calcium silicates, remains attached in some manner to the CSH product when the proportion of water present is low. With high water contents, as in the case of suspensions, the lime may be detached and crystals may then form. Under the latter conditions a product of low C/S is formed (4). It has also been observed that the C/S ratios of the final products increases as the water-cement ratios decrease (17). The experiments with ethylene glycol revealed a marked difference in rates of etching on CSH surfaces. It may be argued that if Mg^{2+} , Al^{3+} , and Fe^{3+} can penetrate the CSH structure in other than displacement reactions, it should be possible for Ca^{++} to do so also. This accommodation of lime in the CSH structure under conditions of limited water content is worthy of further study.

The initial presence of a large proportion of $Ca(OH)_2$ as, for example, in the experiments of Copeland and Kantro (3) in which lime was premixed with the C_3S , can be expected to affect at least the rate of hydration. Taylor (4, p. 60) points out that the C/S ratio is considered a rate-governing factor due to differences in diffusion rates. In the present studies, no lime was premixed with the C_3S or C_2S .

Summary and Conclusions

This study provides a sequential record of the morphological and microstructure changes which accompanied hydration of C_3S and C_2S with and without gypsum present, and with and without the presence of two organic admixtures: triethanolamine and calcium lignosulphonate. It contributes to the possibilities of identification and classification, and provides a basis for relating the morphological changes of cement hydration to the properties of plastic and hardened concrete.

In the hydration of C_3S under the conditions of these experiments, the presence of gypsum did not appear to have any significant effect, except in providing some acceleration of nucleation of particles of CSH.

The first product of hydration, the semicrystalline film, appeared to convert directly to the needle-like or cigar-shaped, structures of calcium silicate hydrate.

The admixture triethanolamine appeared to have an accelerating effect when no gypsum was present in C_3S or C_2S paste. With C_3S and gypsum such acceleration was either very small or absent. In the latter case the fibrous particles were generally smaller than in the cases where no triethanolamine was present, and etching experiments indicated a higher C/S ratio.

Lignosulphonate retarded hydration in all cases: C_3S and C_2S with no gypsum, and C_3S with gypsum. To ages up to 1 month the only distinguishable products were an amorphous film surrounding unhydrated grains of calcium silicate, and a few rounded particles on the surfaces.

From 7 days on, depending on the rate of hydration in each case, the fibrous, or cigar-shaped, particles developed into a three-dimensional network which tended to form plates. These plates often had a felt-like appearance with a striated surface. Where such striations were not initially present, they could be made to appear by etching with glycol.

In all cases there was a remarkable absence of an appreciable quantity of $Ca(OH)_2$. This suggested an accommodation within the CSH lattice of CaO .

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References

1. T.D. Ciach and E.G. Swenson, Submitted to Cement and Concr. Res., 1, (1971).
2. T.D. Ciach, J.E. Gillott, E.G. Swenson, and P.J. Sereda, Cement and Concr. Res., 1, 13 (1971).
3. L.E. Copeland and D.L. Kantro, Fifth Int. Symp. on the Chem. of Cement, Tokyo, II, 387 (1968).
4. H.F.W. Taylor, Fifth Int. Symp. on the Chem. of Cement, Tokyo, II, 1 (1968).
5. S. Diamond, Tobermorite and Tobermorite-like Calcium Silicate Hydrates: Their Properties and Relationships to Clay Minerals. Ph. D. Thesis, Univ. Microfilms Inc., Ann Arbor, Michigan (1963).
6. L.E. Copeland, E. Bodor, T.N. Chang and C.H. Weise, J. Res. Dev. Labs Portld Cem. Ass. 9, 61 (1967).
7. J.G.M. de Jong, The Interaction of Tricalcium Silicate and Tricalcium Aluminate during their Hydration. Ph. D. Thesis, Technische Hogeschol, Eindhoven (1968).
8. G.L. Kalousek, ASTM, Mater. Res. Stan. 5, 292 (1965).
9. L.E. Copeland, E. Bodor, T.N. Chang and C.H. Weise, J. Res. Dev. Labs Portld Cem. Ass. 9, 61 (1967).
10. H.F.W. Taylor, The Chemistry of Cements. Academic Press, London (1964).
11. A. Grudemo, K. Tek. Högsk. Handl. Nr. 242 (1965).
12. L.E. Copeland and E.G. Schulz, Bull. Portland Cem. Ass. 135 (1962).
13. S. Brunauer, Proc. 8th Conf. Silicate Industry, Budapest (1966).
14. S. Brunauer and S.A. Greenberg, 4th Int. Symp. Chem. of Cem., Washington, 135 (1960).
15. H.G. Kurzyk and H.E. Schwiete, 4th Int. Symp. Chem. of Cem., Washington, 349 (1960).
16. F.W. Locher, Symp., Structure of Portland Cem. Paste and Concr Washington, H.R.B., Spec. Rept 90, 300 (1966).
17. D.L. Kantro, C.H. Weise and S. Brunauer, Symp. Structure of Portland Cem. Paste and Concr., Washington, H.R.B., Spec. Ref 90, 300 (1966).