FROST EFFECT ON THE HYDRATION OF C_3S AND C_2S PASTES

by

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1. Introduction and survey of the literature

Hydration kinetics and mechanism of clinker minerals, among others of C_3S and C_2S, were much looked into. The results are, however, not agreeing in all respects. Our own results support statements by SCHWIETE and PETZOLD, according to whom — in the initial phase of hydration — a gel skin rich in calcium is forming topochemically on the surface of calcium silicates of non-stoichiometrical composition, containing crystal nuclei and pores, as proved by electron microscope tests. The hydration theory of POWERS supposes a transition zone between the C_3S crystal and the reaction zone, through which the material leaving the mother crystal must diffuse to get through the gel skin into the water-filled capillary space. Simultaneously, water molecules diffuse through the gel into the reaction space. Hydration products formed on both sides of the transition zone are not identical, the reason being a different diffusion rate of individual ions. Based on calculations, β C_2S has a hydration rate three times slower than C_3S.

LOCHER et al. proved by electron microscopy that at low reaction temperatures (5 °C) larger calcium silicate hydrates of different morphology are forming, constituting a three-dimensional stable space net, this is why C_3S pastes reach a higher final strength than in normal curing. Advantage of early frost effect is considered by MTSCHEDLOW-PETROSSIAN et al. to be the increased solubility of portlandite released during hydration, and with it the increasing specific volume of the silicate gel, though the rate of hydration is slowing down.

2. Effect of the hardening temperature on hydration kinetics of C_3S and C_2S pastes

For the tests, artificial "X-ray pure" C_3S and C_2S were used; paste cubes of 2 cm edge length were made with 30 and 22% of water, cured at room temperature (20 °C) and steam-cured at 50, 70 and 90 °C. After a self-curing of 2 hours, the specimens were steam-cured at a corresponding temperature, then stored at room temperature and 100% r.h. For studies of hydration kinetics, strength and derivatographic tests were carried out at 1, 2, 7, 28, 90, 180 and 360 days.

Comparison of cube strengths of silicate minerals hydrated under identical conditions (Fig. 1) shows strength values of C_3S pastes to be nearly 3 times higher than respective values of C_2S pastes. Fig. 1/a shows clearly that cube strenth of C_3S increases as a monotonic function of time — the steeper the increase, the lower the hardening temperature — whereas the strength of C_2S pastes hardly varies up to 28 days (at this time the C_3S strength is nearly 6 times higher than for C_2S) the monotonic increase begins only at 28 days.

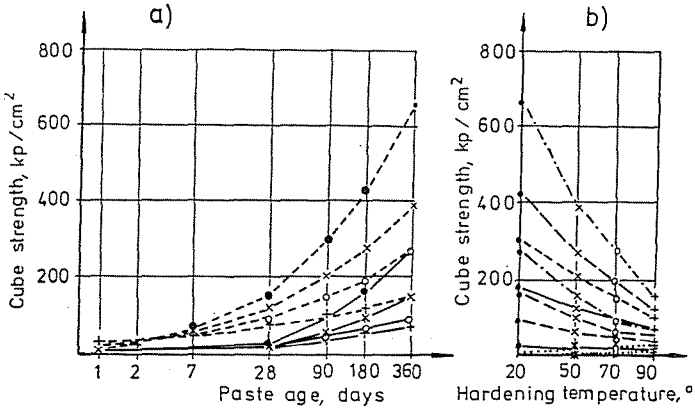

Fig. 1. Cube strength of C_3S and C_2S pastes hardened at:

— — — — C_3S
———— C_2S

a) ● 20 °C
x 50 °C
o 70 °C
+ 90 °C
b) .... 1 day
—— 28 days
- - - 93 days
— — 180 days
—·—·— 360 days

Of the cube strength data plotted vs. hardening temperature (Fig. 1/b) it is evident that until the 28th day the steam-curing temperature has no decisive effect; from this time onwards the strength values of specimens of the same age yield more and more steeply sloping sets of curves with the increase of the curing temperature.

After the strength tests, the specimens were prepared for derivatographic tests by crushing to less than 60 μ grain size, stopping the hydration with the usual method of isopropanol treatment. Because of resemblance of the derivatograms in Fig. 2, only the thermal curves of 1-year C_3S and C_2S pastes, steam-cured at 50 °C, are shown, as an example. It is apparent that in the case of C_3S also an important quantity of $Ca(OH)_2$ develops, the thermal dehydration of which takes place at about 500 °C, whereas for C_2S pastes, presence of crystalline portlandite could be concluded on, on hand of the thermograms, only at the age of 1 year from a small deflexion, hardly to be called a peak.

The reaction equation of C_3S hydration was supposed as follows, according to TAYLOR's tobermorite formula:

$$6\ C_3S + 18\ H \rightarrow C_5S_6HH_4 + 13\ CH\,.$$

In case of complete hydration the system's water demand is 23.67%. The structural water percentage (CO_2 converted to H_2O) read off the derivatograms in the temperature interval of 300 to 900 °C, expressed in the percentage of water necessary for complete hydration (14 mol = 18.41%) is named "hydration degree." Data derived from the measured data are given in Fig. 3. It is noted that hydration degrees calculated from tobermorite and portlandite contents, respectively, according to the above reaction equation, are well agree-

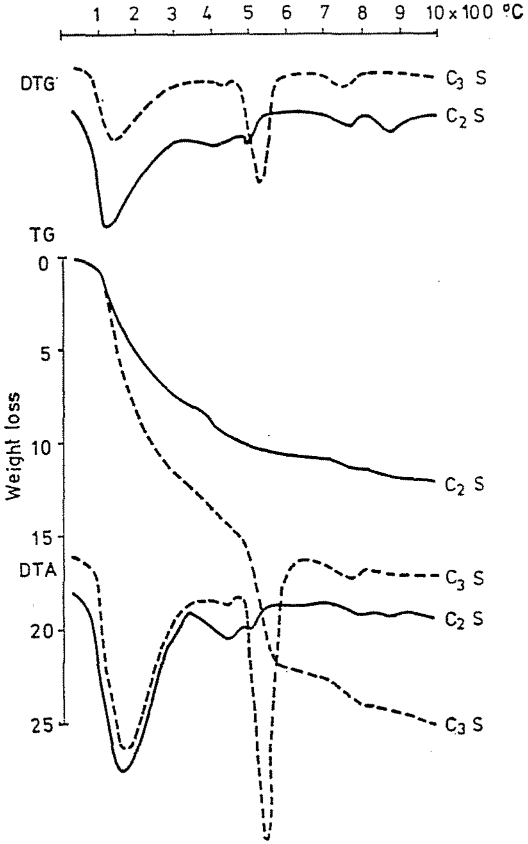

Fig. 2. Derivatograms of 1-year C_3S and C_2S pastes steam-cured at 50 °C, then stored at room temperature in humid atmosphere

ing with those calculated from the mentioned structural water content, supporting the correctness of the reaction equation.

According to the reaction equation supposed for the hydration of C_2S:

$$7\,C_2S + 10\,H \rightarrow C_5S_6HH_4 + C_2SH_2 + 3\,CH + 4\,C$$

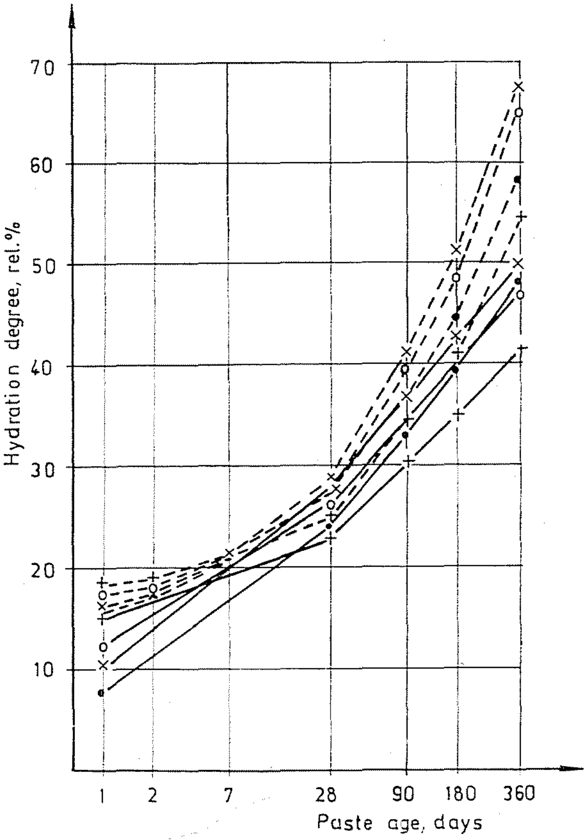

Fig. 3. Degree of hydration of C_3S and C_2S pastes, hardened at:

— — — — C_3S
———— C_2S

● 20 °C
x 50 °C
○ 70 °C
+ 90 °C

for complete hydration 14.94% of water is wanted, in relation to which the degree of hydration is calculated (6 mol = 8.96% of $H_2O_{struct.}$). As C_2S is a mineral of much denser structure than C_3S, it becomes much slower hydrated, i.e. the gel skin on the surface of the grains takes a much longer time to become saturated. Because of the dense structure of C_2S the developing hydrates fill any possible space and pore, therefore the portlandite released during hydration cannot crystallize and is present amorphously as an inordinate gel.

This view is supported by the well-known fact that in hydrated C_2S pastes portlandite crystals can be detected neither by X-radiography nor by electron microscopy. Due to the microcrystalline structure of the hydrates and the amorphous state of portlandite, at present evaluation of the derivatograms is impossible, therefore only the structural water quantity can be taken into consideration, without assigning it to each of the hydration products.

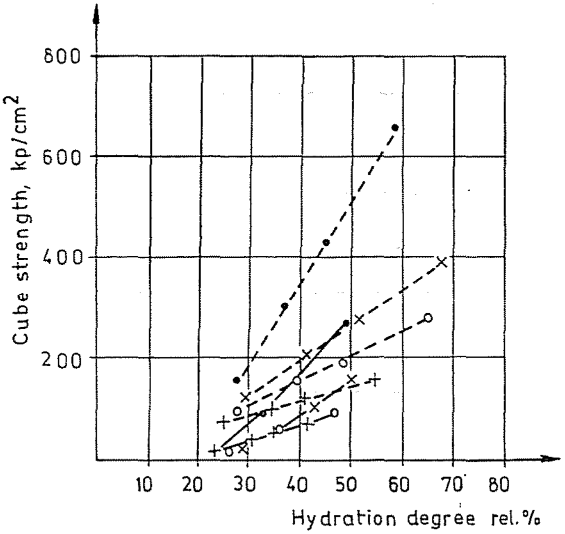

Fig. 4. Relation between cube strength and hydration degree of C_3S and C_2S pastes, hardened at:

— — — — C_3S
———— C_2S

● 20 °C
x 50 °C
○ 70 °C
+ 90 °C

The structural water quantity is essentially greater in the hydration of C_3S and increases much steeper as a function of the paste age than for C_2S. For both silicate minerals, a hardening temperature of 50 °C has proved to be the optimum (up to 1 year); further increase of the steam-curing temperature reduced the percentage of structural water.

Time curve of hydration degrees calculated on the basis of structural water content is shown in Fig. 3. There is no essential deviation between corresponding values of the two silicate minerals but later, at the age of 1 year ($\sim 18\%$).

Relation between cube strength and hydration degree of the silicate minerals hydrated at different temperatures is shown in Fig. 4. The similar trend of the respective curves (for C_3S and C_2S pastes hydrated at an identical temperature) permits to suppose an identical correlation, meaning that only the hydration kinetics of the two silicate minerals are different (due to the different densities of the two initial structures) but the mechanism of the hydration is similar, irrespective of the hardening temperature.

3. Effect of continuous freezing on the hydration of steam-cured paste specimens

C_3S and C_2S pastes steam-cured at 70 and 90 °C, resp. were kept from the age of 1 day to 28 days constantly in a freezing chamber at —20 °C, subsequently stored at room temperature with 100% r.h. until testing. Cube strength and structural water percentages read off the derivatograms are plotted in Fig. 5.

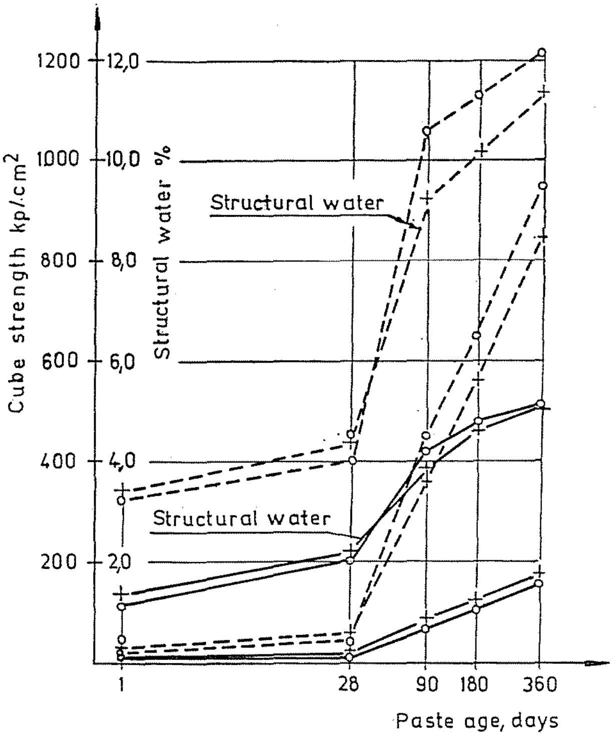

Fig. 5.

— — — C_3S
——— C_2S

○ 70 °C
+ 90 °C

It could be stated that during the continuous freezing period neither the strength, nor the structural water percentage, i.e. the degree of hydration increased substantially. After the freezing effect ceased — especially in case of C_3S pastes — a sudden increase in strength occurred, whereas there was a marked hydration degree increase only between 28 and 90 days, followed by a period of moderate increase. Comparing the cube strengths after freezing of C_3S and C_2S paste specimens hydrated under identical conditions it was found that the strength increase of the former was nearly twice as high as of the latter.

Temperature of preliminary steam-curing is also influencing the development of strength. As mentioned above, strength of both silicate minerals decreases for a higher steam-curing temperature. After a continuous freezing effect, however, C_2S pastes — steam-cured at higher temperature — not only exhibited a greater increase of strength, but also their strength was higher than that of specimens steam-cured at 70 °C.

No anomalies similar to that of strength data were observed for the structural water and the degree of hydration. After the end of the freezing effect, the structural water quantity increased nearly at the same rate in both silicate minerals — irrespective of the previous steam-curing temperature. Accordingly, similarity of the hydration degree diagrams calculated from the structural water contents permits to conclude on the similarity of the effect of continuous freezing at −20 °C.

As the increase in strength of the frozen specimens cannot be taken even approximately proportional to the increase in the hydration degree of the corresponding specimens, the effect of continuous freezing at −20 °C is considered to create a possibility for the formation of a few well developed crystal nuclei in consequence of the rate decrease or of stoppage of ion-diffusion promoting hydration. When the water present in the pores froze, the capillary volume of the system increased, providing space for growth of crystalline hydrates after the freezing effect ceased.

4. Effect of cyclic freezing on the hydration of steam-cured paste specimens

C_3S and C_2S paste specimens steam-cured previously at 70 and 90 °C were stored from 1 day to 28 days, alternately per diem in a freezer at −20 °C and in water at +20 °C, subsequently at room temperature of 100% r.h. Slope of the strength diagrams in Fig. 6 shows that development of hydration is also inhibited by cyclic freezing and when stopped, increase of the cube strength of C_3S pastes is about three times higher than that of the identically treated C_2S pastes. Sloping curve of the hydration degree indicates that hydration kinetics of C_2S is almost linear, whereas corresponding curves for C_3S are essentially steeper from 28 to 90 days than subsequently or during cyclic freezing.

In case of a higher initial steam-curing temperature both measured and calculated values (structural water content, degree of hydration) are always lower than when curing was carried out at a lower temperature, except for the cube strength of C_2S pastes, for which the increase of initial steam-curing temperature resulted in a strength increase.

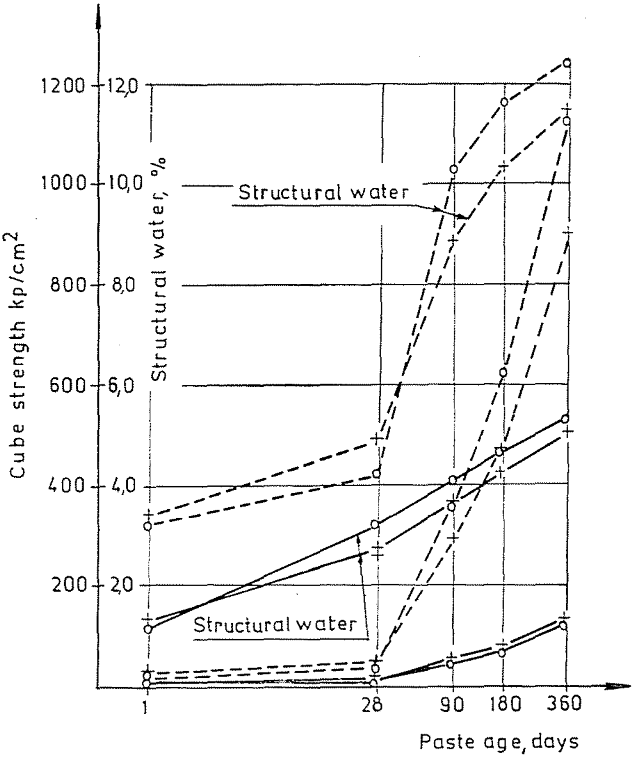

Fig. 6. Cube strength and structural water of C_3S and C_2S pastes, previously steam-cured at 70 and 90 °C, subsequently subjected to cyclic freezing at —20 °C up to 28 days

5. Effect of cyclic freezing temperature on the hydration of C_3S pastes

C_3S paste specimens previously steam-cured at 70 °C were exposed up to 28 days to daily cycles of alternating storage in a freezer at —5 and —20 °C, in water at +20 °C, and then at room temperature of 100% r.h. Strength values and measured and calculated derivatogram data are shown in Fig. 7. It was found that during the effect of freezing at —5 °C, cube strength of the pastes was lower than if subjected to steam-curing only, though higher than those exposed to freezing at —20 °C. Both structural water content and the hydration degree calculated are hardly affected by the temperature of cyclic freezing, the quantity of structural water in freezing at —5 °C being always a little higher.

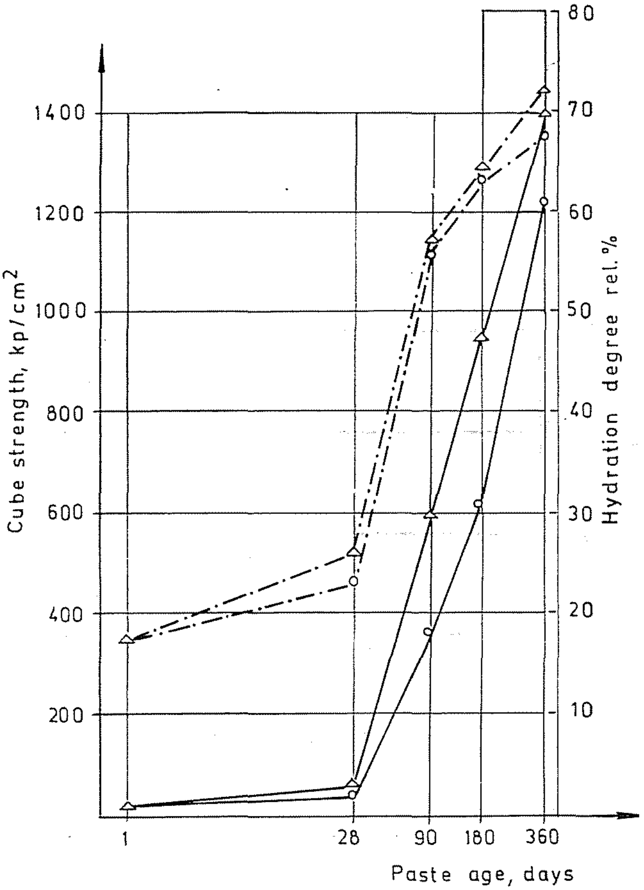

Fig. 7. Cube strength and hydration degree of C_3S pastes, previously steam-cured at 70 °C, then subjected to cyclic freezing at —5 (△) and —20 °C (○) up to 28 days
—— cube strength —·—·— hydration degree

6. Effect of cyclic immersed storage on the hydration of steam-cured paste specimens

C_3S pastes, previously steam-cured at 50, 70 and 90 °C, were stored up to 28 days alternately in water at 20 °C, at room temperature and in a humid atmosphere. Comparing curves of Fig. 8 with corresponding curves in Fig. 1, it can be stated that as an effect of cyclic immersed storage, with rising steam-curing temperature the cube strength of C_3S pastes is increasing proportionally to the previous steam-curing temperature. At the same time, the structural water content and the character and order of the curves representing the hydration degree remain unaffected from the variation of the storage, only the values are higher than for specimens stored from the age of 1 day in humid atmosphere.

The higher the temperature of previous steam-curing, the steeper the lines representing the relation between cube strength and hydration degree.

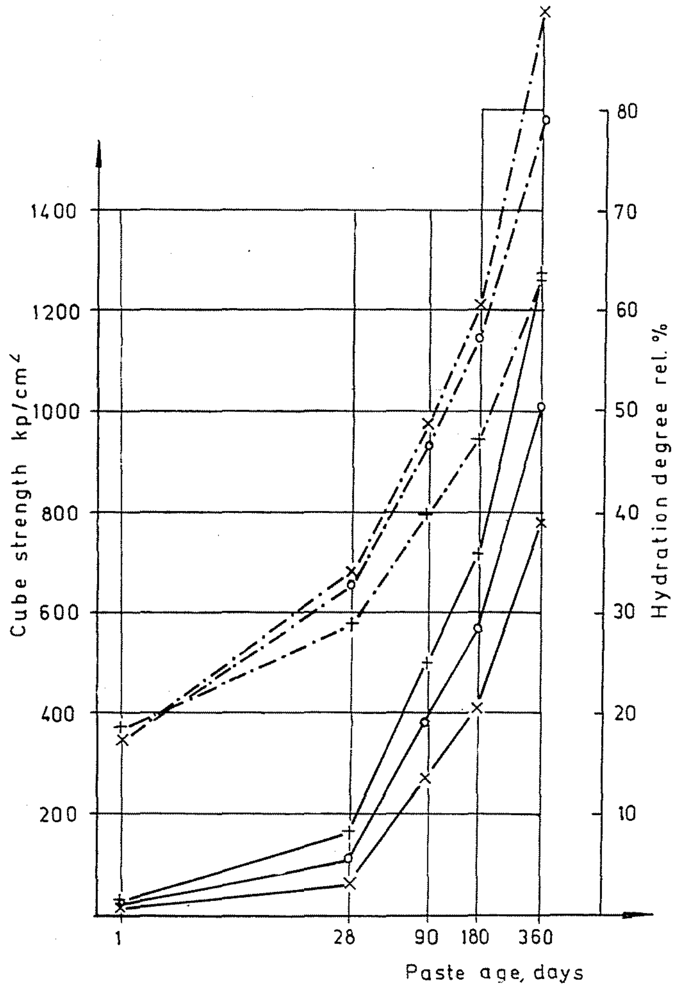

Fig. 8. Cube strength and hydration degree of C_3S pastes, previously steam-cured at different temperatures, then subjected to cyclic immersed storage up to 28 days

—— cube strength × 50 °C

—·—·— hydration degree ○ 70 °C

\+ 90 °C

7. Conclusions

In testing *the influence of hardening temperature* on hydration of silicate pastes it was found that with the increase of the hydrating temperature, strength of specimens of the same agè, i.e. the hydration kinetics was decreasing. From the observation that deviation percentages relative to normal curing strength data — from the age of 28 days — were nearly similar, identity of the hydration products and of the mechanism of hydration could be concluded. The similarity of hydration mechanisms of the two silicate minerals could be deduced also from the identical direction of the curves for the correlation between the cube strength and the hydration degree at identical hardening temperatures.

An essential difference between derivatograms of the two silicate minerals consists in the presence (or lack) of portlandite dehydrating at about 500 °C. During the hydration of C_3S pastes, an important quantity of portlandite (13 mols) develops beside tobermorite. As C_2S is a much denser mineral than C_3S, it hydrates much slower, i.e. more time is needed for saturation of the gel skin on the grain surface. C_2S being of a dense structure, the forming hydrates fill any possible place and pore, therefore portlandite released during the hydration cannot crystallize and is present as an unorganized gel, in an amorphous condition. This view is supported by the well-known fact that neither X-radiography nor electron microscopy can detect crystalline portlandite in the hydrated C_2S pastes.

In testing the hydration of silicate paste specimens steam-cured at 70 and 90 °C previous to *sustained freezing at —20 °C* up to 28 days, it was observed that during the freezing period neither the strength nor the structural water, or the hydration degree increased substantially. After, however, the effect of freezing ceased, the cube strength — especially of C_3S pastes — increased abruptly, with a moderate increase of the hydration degree. Higher previous steam-curing temperatures influenced only the development of C_2S paste strength; namely, steam-curing at 90 °C caused both hardening rate and final strength to increase, as compared to curing at 70 °C. Continuous freezing at —20 °C seems to facilitate the formation of a few well developed crystal nuclei as an effect of decrease or stoppage of the ion diffusion promoting hydration. When the water in the capillaries froze, the capillary volume of the system increased, providing space for the development of crystalline hydrates after the freezing effect ceased. Thus, with suitable curing and storage, even a lower hydration rate may correspond to a high strength.

From *cyclic freezing tests* on silicate specimens previously steam-cured at 70 and 90 °C, by storage for 28 days alternately per diem at —20 °C and at +20 °C, it could be established that development of hydration was also inhibited; after the cyclic freezing effect stopped, the cube strength increased rapidly and the rate of hydration moderately. Raising the previous steam-curing temperature the strength increase rate of C_3S pastes decreased, that of C_2S pastes increased, the rate of hydration, however, decreased for both silicate minerals.

Comparing the effect of both continuous and cyclic freezing at —20 °C on the strength of C_2S pastes it can be stated that continuous freezing — irrespective of the previous steam-curing temperature — results in a higher strength than does cyclic freezing. In our opinion this is due to the fact that the effect of prolonged cold storage to increase pore volume is absent in cyclic freezing and only the strength-increasing effect of intenser crystal nucleus formation prevails, due to the decrease of hydration rate.

Both continuous and cyclic freezing at —20 °C affect similarly the correlation between strength and hydration rate: this can be deduced of the character of the corresponding curves.

The effect of *cyclic freezing temperature* was studied on C_3S pastes previously steam-cured at 70 °C. It was found that hydration slowed down also in cyclic freezing at —5 °C, but after ceasing of the freezing effect the strength increased at a higher rate than after freezing at —20 °C. Temperature of cyclic freezing hardly influenced the hydration rate calculated from the structural water. Efficiency of the above curing method is attributed to the fact that hydration slows down only to permit formation of crystal nuclei which can continue growing next day during immersed storage, namely heat transfer is faster, and part of the portlandite released during hydration furthers the hydration progress.

Testing the effect of *cyclic immersed storage* on hydration of C_3S pastes previously steam-cured at 50, 70 and 90 °C up to 28 days, it was found that the cube strength of the specimens was lower at this period than that of pastes only steam-cured, but increased the more rapidly, the higher was the temperature of previous steam-curing. The quantity of the structural water i.e. the rate of hydration decreased for a higher previous steam-curing temperature, similarly to that of only steam-cured specimens, though it was always higher numerically. The cause of this seems to be that because of both thermal movement of the molecules and increased ion-diffusion during steam-curing, the capillaries became gel-saturated, but in the humid atmosphere there was little possibility for crystalline hydrates — strength representatives — to form. In cyclic immersed storage, part of the strength-reducing portlandite was released, next day when air stored the water evaporated from the surface pores, starting the diffusion from the interior to the surface. Above process was repeated 14 times, with the result that gel was loosened up, permitting the formation of crystal nuclei which could further develop during storage in the humid atmosphere, resulting in increased cube strength. Structural water content decreased obviously with increasing curing temperature because the increased molecular heat movement due to thermal effect inhibited topochemical reactions.

Summary

Hydration kinetics of C_3S and C_2S pastes steam-cured at different temperatures, exposed to continuous and cyclic freezing at —20 °C up to 28 days was studied for 1 year. Cube strength and derivatography tests showed hydration to be inhibited during freezing periods — irrespective of previous steam-curing temperature and mode of freezing, — but after the freezing effect ceased, cube strength increased rapidly, and hydration rate moderately. At a

higher cyclic freezing temperature (−5 °C), cube strength increased at a higher rate than in any other case. With increasing steam curing temperature the hydration kinetics of C_3S pastes decreased but in immersed cyclic storage of steam-cured specimens the cube strength was found to increase the faster, the higher was the previous steam curing temperature.

Correlations between cube strength and hydration rate for both silicate minerals permit to suppose identity between hydration mechanisms, meaning that only hydration kinetics differ.

References

1. SCHWIETE, H. E.: Zementchemische Arbeiten aus dem Institut für Gesteinhüttenkunde, Zement-Kalk-Gips, 1961, 400—409.
2. PETZOLD, A.—GÖHLERT, I.: Differentialthermoanalyse hydratisierter Klinkerminerale, Tonindustrie Ztg. **86,** 1962, 228—232.
3. POWERS, T. C.: Einige physikalische Gesichtspunkte zur Hydratation von Portlandzement. Zement-Kalk-Gips, 1961, 81—87.
4. LOCHER, F. W.: Die chemische Reaktionen der Zementerhärtung. Tonindustrie Ztg. **88,** 1964, 40—43.
5. RICHARDZ, W.—LOCHER, F. W.: Ein Beitrag zur Morphologie und Wasserbindung von Kalziumsilikathydraten und zum Gefüge des Zementsteines. Zement-Kalk-Gips, 1965, 449—459.
6. MTSCHEDLOW-PETROSSIAN, O. P.—TSCHERNJAWSKY, W. L.: Einfluß niedriger Temperaturen auf den Hydratationsprozeß. Silikattechnik, **18,** 1967, 72—76.

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