

Morphology of Calcium Hydroxide in Cement Paste

H. H. BACHE, G. M. IDORN, P. NEPPER-CHRISTENSEN, and J. NIELSEN,
Concrete Research Laboratory, Karlstrup, Denmark

The present article surveys literature on observations on the occurrence and morphology of crystalline calcium hydroxide in cement paste, carried out with a polarizing microscope on thin sections of concrete and mortar. A short description is given of deposits of natural calcium hydroxide (portlandite) and related natural minerals.

The chemical and physical conditions necessary for the formation of calcium hydroxide in fine-pored systems such as cement paste and concrete are discussed, and the effect of the external natural conditions on the crystallization is mentioned.

Recent observations are discussed and illustrated by means of microphotographs, and an attempt is made to explain these observations. Particular attention is paid to the presence of crystalline calcium hydroxide in air bubbles. Promising fields for future investigations are outlined.

THE MAIN solid constituents of hardened cement paste are cement gel, calcium hydroxide and unhydrated cement particles. The calcium hydroxide forms and crystallizes from the liquid phase of the cement paste as a reaction product during hydration. The solid phase may be macrocrystalline, microcrystalline, slightly crystallized, or even amorphous.

The content of crystalline calcium hydroxide in completely hydrated cement paste is of the order of magnitude of 15 percent by volume. This is such a considerable proportion that the calcium hydroxide must have a considerable effect on the physical and chemical characteristics of the cement paste.

A thorough knowledge of the structural composition of the cement paste and of the physical and chemical characteristics of its constituents is necessary in order to understand and describe the behavior of the paste under external physical and chemical influences. For our present knowledge of these conditions we feel indebted to the work of T. C. Powers and colleagues at the Portland Cement Association.

The part played by calcium hydroxide in the process of hydration has received the attention of many research workers. However, there are but few investigations into the influence of the formation, morphology and distribution of crystalline calcium hydroxide on the properties of the paste. The aim of the present paper is to encourage further studies of these factors.

EARLIER OBSERVATIONS

In the late twenties Sundius and Assarson (1) investigated the microstructure of concrete by means of thin section examinations. They ascertained the presence of unhydrated grains of cement (β - C_2S and C_3A), humic hydrates in the form of film on sand particles, and air bubbles. They found fibrous or spherulitic precipitates, believed to be calcite, and relatively large, rounded formations of a fine-threaded compound with low birefringence, found to be calcium aluminate sulphate.

Calcium hydroxide had crystallized (a) on the surfaces of sand grains, (b) in irregular spaces (pores) in the paste, (c) around air bubbles, and (d) in air bubbles (most air bubbles were found to be empty).

The formations of calcium hydroxide ranged in size from submicroscopic crystallites to aggregates of anhedral crystals having a diameter of 100 to 200 microns. The

investigation formed part of extensive studies of concrete deterioration due to the percolation of soft water.

McConnell et al. (2) mention several substances observed in petrographic examinations of concrete, including (a) calcium carbonate as calcite and aragonite; (b) calcium aluminate sulphate hydrate; and (c) calcium sulphate hydrate (gypsum).

The occurrence of calcium hydroxide is described as follows:

This compound is one of the normal products of hydration of portland cement, and occurs in all concrete. However, the manner of its occurrence varies considerably. It may be evenly distributed as minute crystals throughout the cement paste, or it may be found as segregations of larger crystals, occupying fractures or voids of various shapes, commonly concentrated in openings adjacent to aggregate particles. There seems to be little correlation between the amount and mode of occurrence of calcium hydroxide and the quality of the concrete. Segregations of calcium hydroxide at the periphery of aggregate grains should not be mistaken for products of interaction between aggregate and cement.

Samples which have been exposed to severe conditions of freezing and thawing often contain relatively large quantities of calcium hydroxide crystals in fractures. Apparently, repeated cycles of freezing and thawing favor the concentration of calcium hydroxide as secondary deposits, possibly through a process of solution and recrystallization, since calcium hydroxide is more soluble at 0 C than at higher temperatures.

From thin section examinations of undeteriorated concrete, K. Mather (3) found that relatively small sized crystals of calcium hydroxide were characteristic of concrete with limestone aggregates, whereas much larger crystals were found in concrete with granodiorite and diorite aggregates (siliceous).

B. Mather (4) mentions the occurrence of calcium hydroxide in concrete cores taken at a depth of 10 m in a monolithic concrete mass. Clear, colorless plates of calcium hydroxide, associated with calcium aluminate sulphate, were observed in voids, and it was indicated that "the growth of calcium hydroxide in crystals is a fairly common occurrence in the interior of structures."

Farran (5) states that in concrete (with "artificial cement," i.e., portland cement), the contact between aggregate particles and cement paste is largely constituted by crystalline calcium hydroxide, frequently accompanied by a gel substance. However, such "films" of calcium hydroxide were not found with carbonate aggregate. In carbonated areas of cement paste it was observed that secondary calcite had the same orientation as adjacent calcium hydroxide. It is suggested that the orientation of calcium hydroxide on the surface of carbonate aggregate particles is similar to that of the particle surface, thus establishing what is designated epitaxial contact growth. This kind of contact is believed to be the reason for stronger contact between cement paste and carbonate aggregate than between cement paste and siliceous aggregates.

Idorn (6) shows microphotographs of air bubbles containing calcite in Roman concrete from an aqueduct near Arles in Southern France (about 300 A. D.). The concrete seemed to have been manufactured with air entrainment. A large number of the bubbles, mainly the smallest (< 0.2 mm diameter), were found to be completely filled by the precipitate. In larger bubbles (about 0.5 to 1.0 mm diameter), both separate and aggregate crystals were found growing in from the walls of the bubbles towards the interior. The author suggests that similar phenomena may occur in modern air-entrained concrete under certain types of exposure, e.g., combined tidal and freezing-thawing exposure. The filling of air bubbles under such conditions may have an adverse effect on the frost resistance of concrete. The same paper contains a microphotograph of an air bubble occupied by a single crystal of calcium hydroxide in a mortar bar that had been stored for three years in a sodium sulfate solution. Calcite crystals growing on the walls of air bubbles in a Norwegian concrete are also shown; this concrete had been severely exposed to water rich in sulfates. Mention is made (7) of spherical,

compact formations of fibrous calcium aluminate sulfate ("tennis balls") in air bubbles on broken faces of severely deteriorated concrete. The same paper shows hexagonal, platy crystals in air bubbles, identified as calcium aluminate hydrate, similar to hydrocalumite (see Tilley 8). The presence of this rare compound was believed to be due to attack by aggressive carbon dioxide and sulfate dissolved in ambient ground water.

Bruere (9) observed crystalline calcium hydroxide in air bubbles in air-entrained cement paste. He mentions the possible importance of this phenomenon to frost resistance. However, the calcium hydroxide was chiefly found in the larger bubbles, which are considered to have the least influence on this resistance.

Idorn (10, 11, 12) presents further examples of the occurrence of secondary precipitates, e. g., calcium hydroxide, in sound and deteriorating concrete. Mention is made (10) of two-generation growth of calcium hydroxide completely filling some air bubbles, together with growth of fibrous calcium hydroxide in air bubbles. Microphotographs showing crystalline calcium hydroxide in mortar bars that had not been subjected to deleterious exposure were presented (11). The precipitate was found in the following locations:

1. In irregular spaces in the structure of the hardened paste, originating from water sockets in the freshly mixed mortar, from bleeding, or from voids due to insufficient compaction;
2. In the form of a film on the surfaces of grains of sand; and
3. Around and inside air bubbles.

Idorn describes (13) an examination of concrete exposed to freezing and thawing. In one case the concrete had been frozen while still green. The microfractures remaining from ice-lens had secondarily been occupied by calcium hydroxide, which had also formed seams along the aggregate particles. Larger, subhedral crystals predominated in the interior of the concrete mass. Larger and even more compact aggregates of calcium hydroxide were observed in thin sections of a concrete test slab from Greenland, which had been severely damaged through combined exposure to wetting/drying and freezing/thawing. Deep surface pitting (raveling) and carbonation inwards from the scarred surface characterized the deterioration. The unusual size of the calcium hydroxide crystal formation was thought to indicate repeated dissolution and recrystallization as a result of the exposure condition.

Lyubimova and Pinus (14) state that there is a contact layer of calcium hydroxide between aggregate particles (except carbonates) and cement paste. Reference is made to Skramtaev (15) and Pantelev (16).

Larsen (17) describes the use of point-counting in thin sections as a means of assessing the amount of calcium hydroxide in the cement paste. It is suggested that this measurement may give a quantitative "degree of deterioration."

Terrier and Moreau (18) present a comprehensive collection of observations on the microstructure of portland cement paste, including microphotographs of crystalline calcium hydroxide in air bubbles and as seams along grains of sand. They point out the effect of the presence and mode of occurrence of calcium hydroxide on the strength of the mortar.

Idorn (19) shows a void in concrete, partly filled by adjacent individual crystals of calcium hydroxide growing inward from the wall of the void. The crystals are very small and granular closest to the wall, indicating a relatively rapid crystallization, the rate of which has decreased as the process proceeded. The larger crystals are very much alike in size, shape and orientation, thus indicating crystallization from a liquid phase. The same paper shows gypsum crystals, possibly a replacement of calcium hydroxide, deposited along sand grains in a concrete attacked by sulfate. Mention is also made of isolated areas of pure cement paste with extensive formations of calcium hydroxide in concrete in which most of the cement paste has been dissolved and distorted due to severe sulfate attack combined with alkali-aggregate reaction. It is stated that calcium hydroxide and unhydrated β -C₂S always seem to occur together—either they are both present or neither of them is found. The presence of both is considered to indicate soundness of the concrete, whereas their absence is thought to indicate severe chemical attack on the cement paste.

NATURAL MINERALS

Tilley (8) gives a report on calcium hydroxide as a natural mineral, found at Scawt Hill, County Antrim. The mineral was found as a constituent of aggregates composed mainly of afwillite, forming in fillings in larnite-spurrite rocks. Calcite and ettringite were also found together with the afwillite in cavities in these contact rocks. It is stated that

The manner of occurrence and association of these afwillite- $\text{Ca}(\text{OH})_2$ aggregates with larnite-spurrite assemblages makes it clear that both these minerals arise by hydration of these calcium orthosilicates. It was previously noted that afwillite was "derivated" by alteration of spurrite. The formation of $\text{Ca}(\text{OH})_2$ can be regarded as a further development of this hydration process in which hydrolysis of calcium orthosilicate has also played a part.

Tilley suggests the name "portlandite" for crystalline calcium hydroxide occurring naturally.

It is of interest that the natural mineral tobermorite and other hydrated calcium silicates have been found in cavities in olivine-dolerite dike rock traversing jurassic limestone near the town of Portree on the Island of Skye in West Scotland (see, e. g., Sweet et al., 20).

It seems that these natural mineral groups ought to be intensively investigated in relation to the chemistry and structural formation of cements and cement paste.

PHYSICS AND CHEMISTRY OF CALCIUM HYDROXIDE

Calcium hydroxide is precipitated as a slightly soluble substance in hardening cement paste. Its thermodynamic solubility product at 20 C is determined as $K_{\text{SP}} = 10^{-5.7}$ (Greenberg and Copeland, 21). Calcium hydroxide crystallizes in the hexagonal-rhombohedral system as hexagonal plates or short prisms with perfect basal cleavage. It is uniaxially negative with indexes of refraction, $n_{\omega} = 1.574$ and $n_{\epsilon} = 1.545$ (see, e. g., Lea 22).

The surface energy and entropy of calcium hydroxide crystals are 1180 erg/cm^2 and 18.2 e. u. , respectively (Brunauer and Greenberg, 23). The surface tension has been found by Hedin (24) to be 595 dyne/cm at 20 C, varying linearly with the absolute temperature. The specific weight is 2230 g/cm^3 (22), and the coefficient of thermal expansion is stated by Terrier and Moreau (18) to be of the order of magnitude of 7.5×10^{-6} per deg C.

When calcium oxide is dissolved in water, a solution supersaturated with respect to crystallized calcium hydroxide is quickly formed. A theory on the mechanism of hydration of calcium oxide in water has been put forward by Hedin and Thorén (25) and Hedin (26). According to this theory, primarily dissolved ions from the solid oxide phase are formed. Only secondarily do these ions "associate into undissociated calcium hydroxide molecules, so that the equilibrium of dissociation is reached." This results initially in a strongly supersaturated solution.

Ringquist (27) has measured the electrolytic conductivity of pure calcium hydroxide solutions and has tabulated the concentration as a function of the conductivity in the temperature range from 0 C to 100 C. Hedin (26) has measured the diffusion constants, rates of dissolution, and rates of crystallization for calcium hydroxide in solutions of varying concentration. It appears that at low supersaturations, crystal growth only proceeds at prism faces, while at high supersaturations, the rate of crystal growth is higher at the base than at prism faces.

When cement is mixed with water, a solution supersaturated with respect to calcium hydroxide is rapidly formed because the free CaO content of the cement dissolves, and the same happens to alkali-metals and sulfates. During the subsequent hydration of C_3S and C_2S , the solution is supplied with further calcium hydroxide, and it has been found that supersaturated solutions can exist for rather a long time (Brunauer and Greenberg, 23, and Greene, 28). Electrical resistance measurements on concrete

during steam-curing have indicated that maximum calcium hydroxide concentration occurs after $\frac{1}{2}$ to $1\frac{1}{2}$ hours' curing (Szuk, 29).

Differential thermal analyses of hardening cement paste, reported by Greene (28), show that crystalline calcium hydroxide begins to form after 4 hours' reaction. Thereafter, the crystallization proceeds rather rapidly.

The major part of the calcium hydroxide in cement paste is probably formed by precipitation from solution. According to Grudemo (30), however, it seems that some of the calcium hydroxide may be formed by topochemical reaction within the anhydrous calcium silicate crystals. Calcium hydroxide formed in this way has been characterized as almost amorphous.

Calcium hydroxide may be precipitated everywhere in the structure of mortar and concrete, in the early stages of hydration intermixed with CSH-gel (Taylor, 31), but later on in pores and voids as described in detail below. The crystals may grow to considerable size by slow segregation and accumulation processes (30), partly conditioned by the continuous formation of new calcium hydroxide during the hydration of the cement and partly due to dissolution of small crystals and precipitation on larger crystals.

Assuming the precipitation of calcium hydroxide in mortar and concrete to proceed qualitatively, in the same manner as in pure water, the course of reaction may be described as follows: A calcium hydroxide solution is formed, the concentration of which increases continuously up to a certain critical value, at which crystal nuclei are formed. Higher concentrations than the critical value may occur due to the great rate of solution of calcium oxide. The formation and growth of crystal nuclei then proceed until the concentration has fallen below the critical value below which new crystals cannot be formed and only the growth of existing crystals takes place. The calcium hydroxide thus formed is subject to dissolution and reprecipitation due, for instance, to changes in the composition of the solution caused by leaching and the addition of other substances, changes in temperature and concentration, and differences in crystal sizes. In pure water, the relationship between saturation concentration and crystal size is as follows:

$$\log c_{DT} = \log c_{\infty T} + \frac{k}{d}$$

where c_{DT} denotes the concentration at temperature T of a solution in equilibrium with crystals of diameter D , and $c_{\infty T}$ denotes equilibrium concentration at temperature T with crystals of "infinite" size. In the temperature range likely to be of interest, the latter concentration decreases linearly with the temperature. Hedin (24) has determined the constant k in the above equation empirically and has arrived at a value of 0.0136 microns, the units of the concentrations and the diameters being in grams CaO per liter and microns, respectively.

As the saturation concentration increases with decreasing size of crystal, there will be tendency toward the growth of large crystals at the expense of small ones. The rate of this transformation depends on the rate of diffusion of calcium hydroxide in the liquid-filled system. Thus, it is possible that many small crystals and only a few large ones will be present in concrete in which a dense structure is formed rapidly, whereas the opposite may apply in cases of less dense concrete.

The solubility conditions described above for pure water change when "foreign" ions are present. For instance, alkali-hydroxides reduce the solubility of calcium hydroxide appreciably. A table giving the solubility of calcium hydroxide as a function of the concentration of sodium hydroxide and potassium hydroxide is presented by Lea (22).

RECENT OBSERVATIONS ON THE MORPHOLOGY OF CALCIUM HYDROXIDE IN MORTAR AND CONCRETE

The above summary of earlier observations shows that calcium hydroxide may be found as a crystalline precipitate in the structure of portland cement mortar and concrete. On the basis of microphotographs, the various characteristic modes of occurrence can be described as follows:

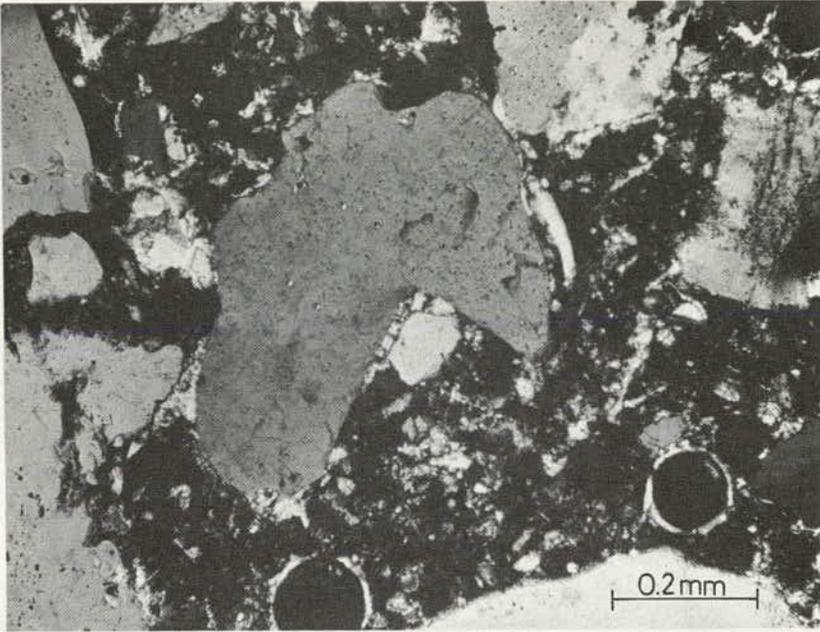


Figure 1. Calcium hydroxide formations in portland cement mortar. Calcium hydroxide (white parts) is seen precipitated as crystal aggregates in the paste, on the surfaces of quartz particles, in narrow spaces between adjacent quartz particles, and around air bubbles. Crossed nicols.

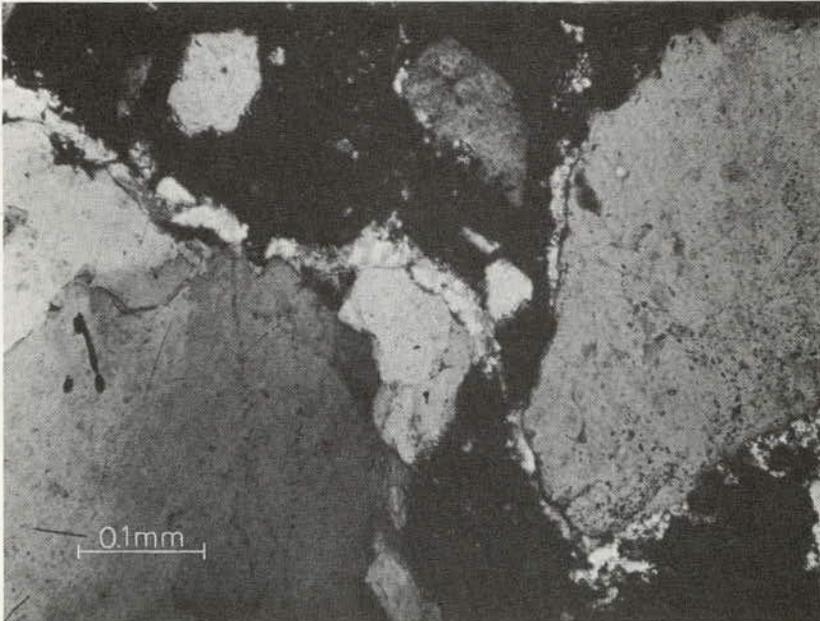


Figure 2. Band of crystalline calcium hydroxide in cement paste and along surfaces of quartz particles. Crossed nicols.

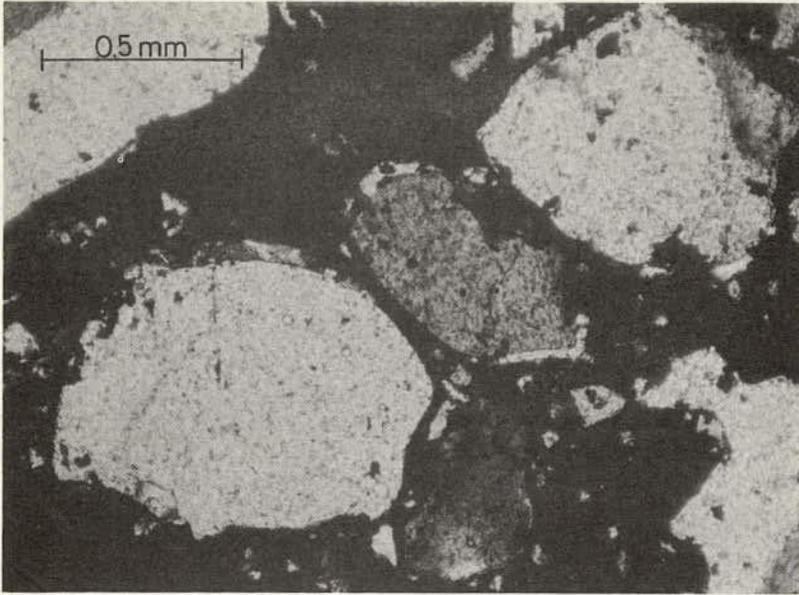


Figure 3. Calcium hydroxide coatings on surfaces of quartz particles in portland cement mortar. Crossed nicols.

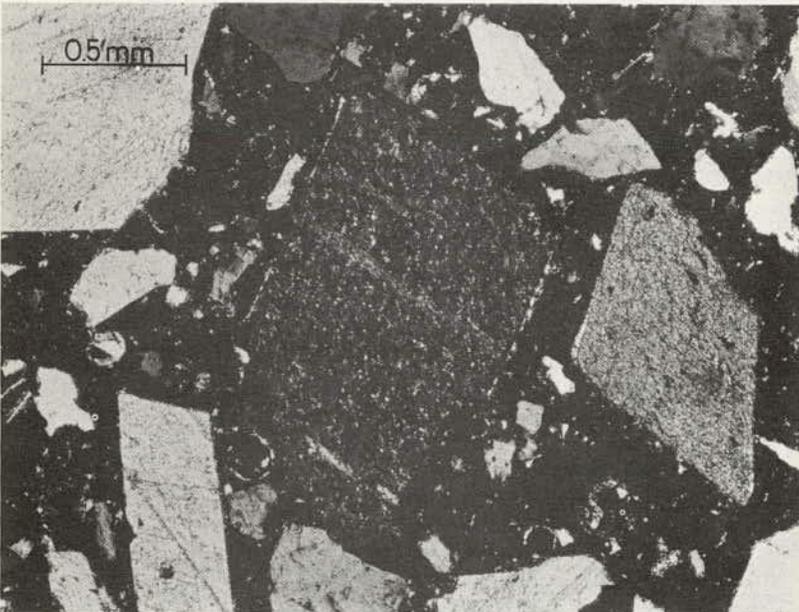


Figure 4. Calcium hydroxide coatings on surfaces of limestone (calcspars) particles in portland cement mortar. Particle in center is turned to extinct position to facilitate distinction of the brilliant calcium hydroxide rims. Crossed nicols.

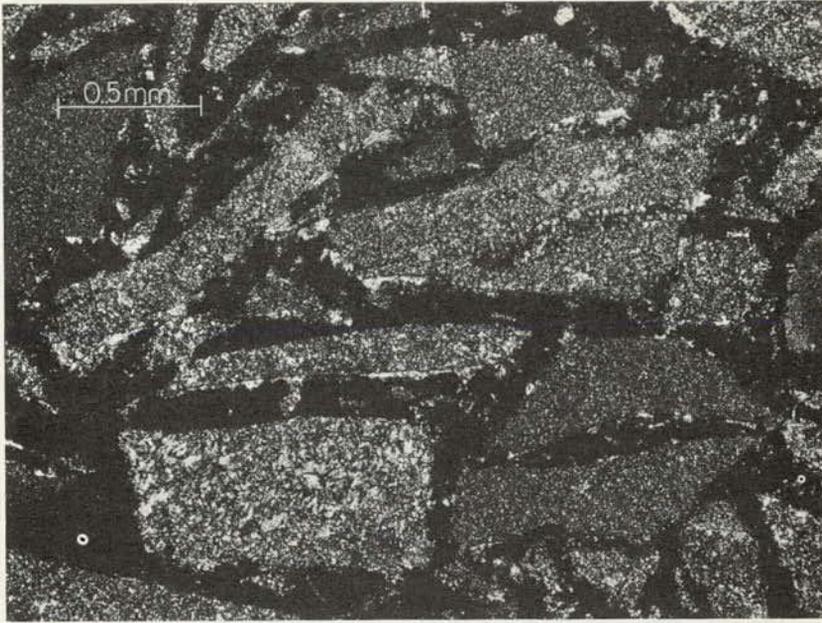


Figure 5. Calcium hydroxide precipitated as coatings on surfaces of flint particles and in liquid-filled spaces below horizontally oriented, long and flat aggregate particles. Crossed nicols.

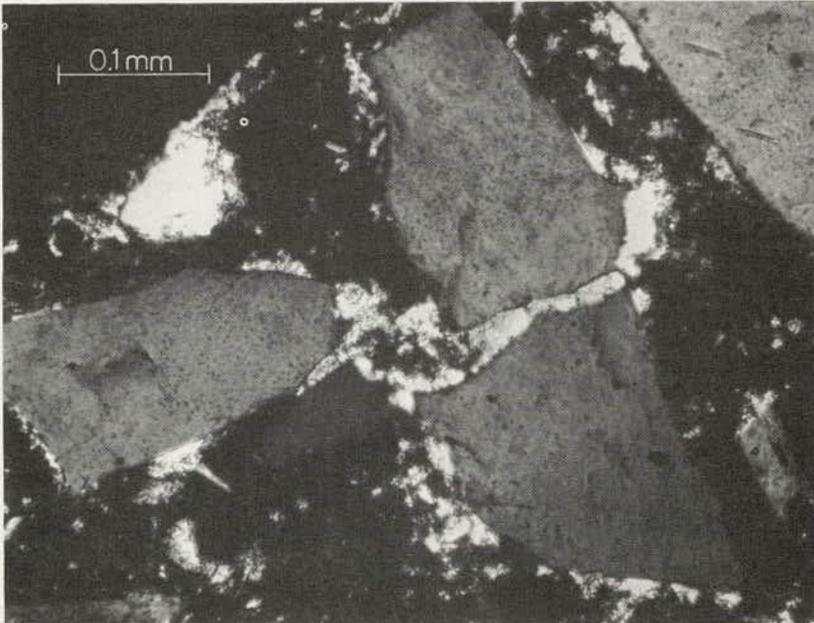


Figure 6. Calcium hydroxide precipitated in narrow spaces between adjacent quartz particles in portland cement mortar. Crossed nicols.

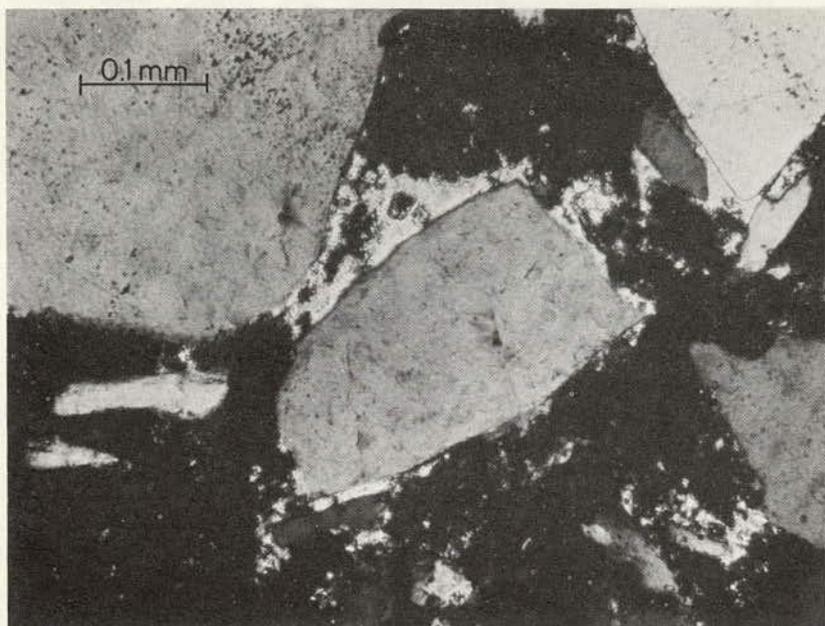


Figure 7. Crystalline calcium hydroxide in narrow space between two quartz particles in portland cement mortar. Crossed nicols.

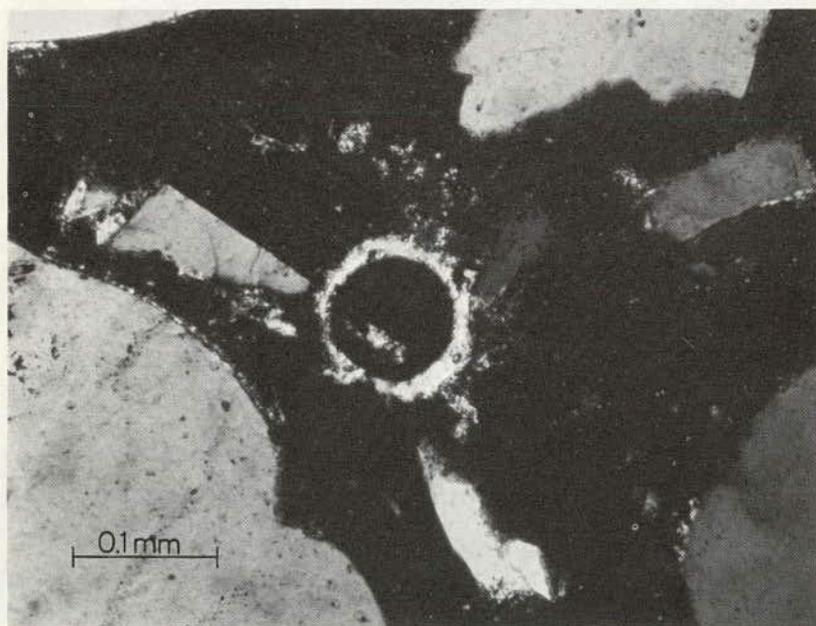


Figure 8. Air bubble in portland cement mortar, surrounded by a coronate shell of calcium hydroxide. Crossed nicols.

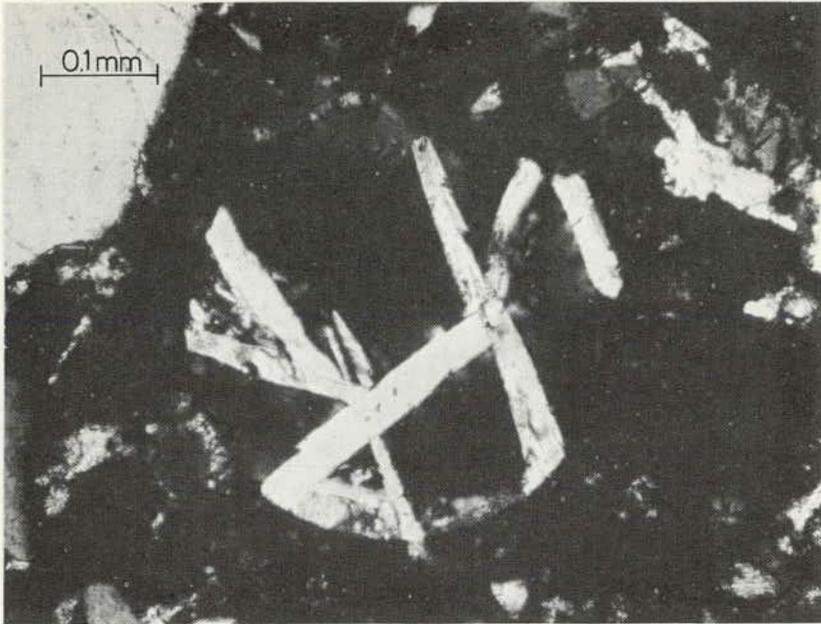


Figure 9. Air bubble in portland cement paste, partly filled with euhedral and subhedral calcium hydroxide crystals. Crossed nicols.

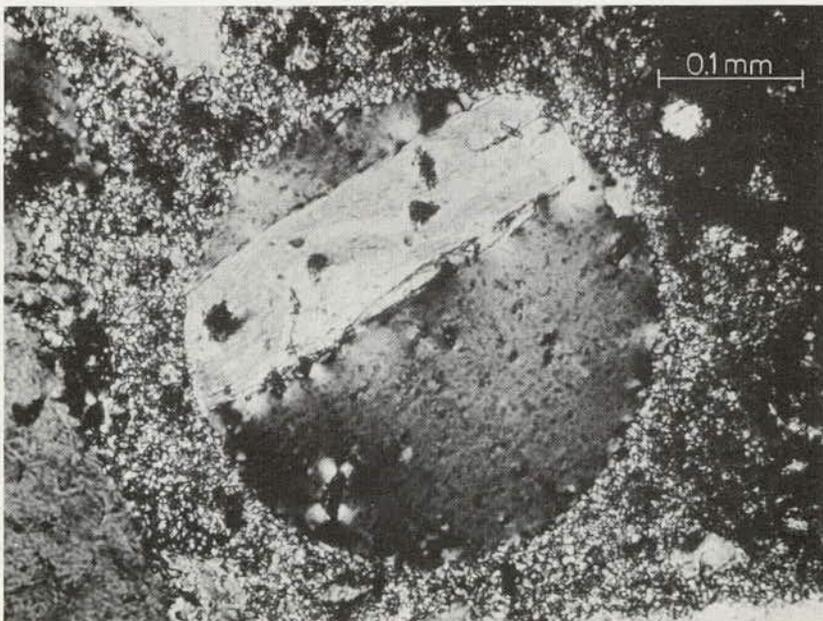


Figure 10. Originally air-filled bubble with one calcium hydroxide crystal in carbonated area of portland cement mortar. Crossed nicols.

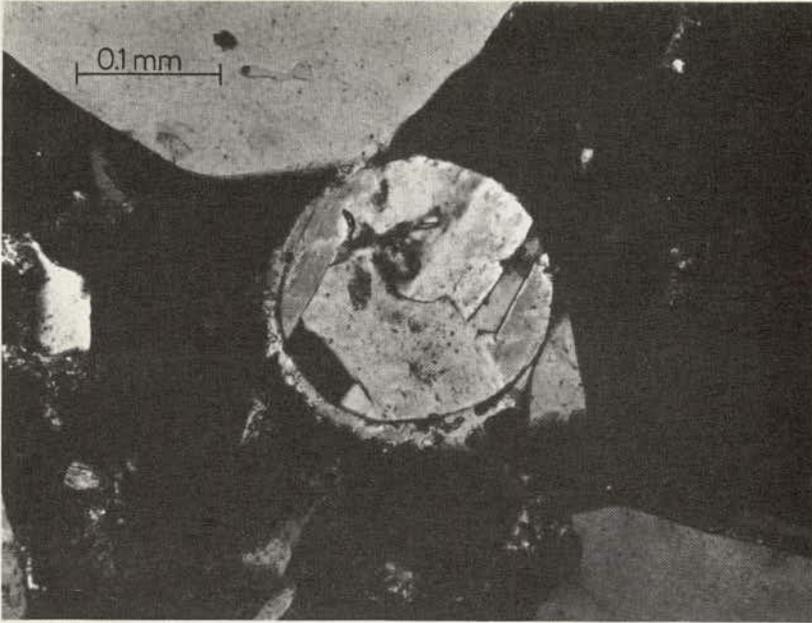


Figure 11. Subhedral calcium hydroxide crystals filling an originally air-filled bubble in portland cement mortar. A thin calcium hydroxide shell can also be seen surrounding part of the bubble. Crossed nicols.

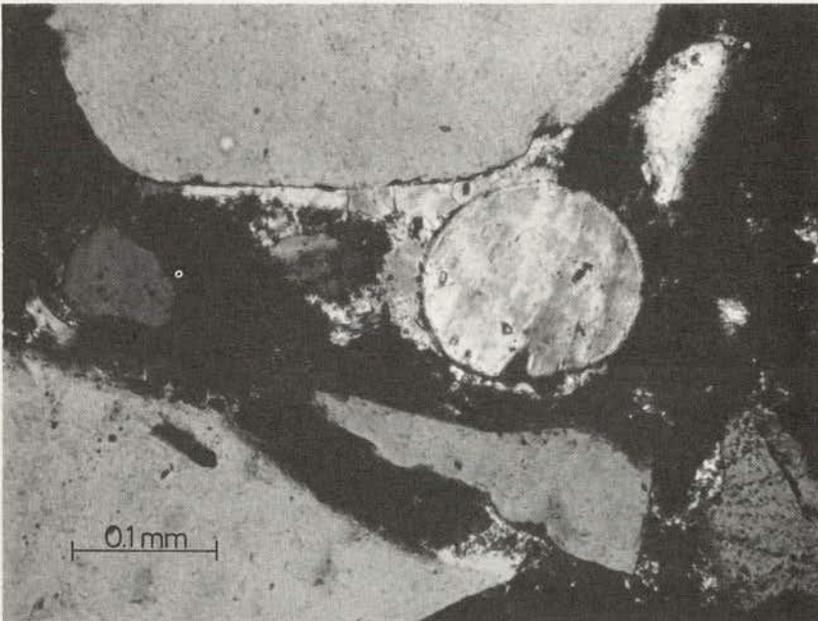


Figure 12. Originally air-filled bubble in portland cement mortar, now nearly filled with calcium hydroxide. Calcium hydroxide also surrounds part of bubble and is precipitated in narrow space between bubble and adjacent quartz particle. Crossed nicols.



Figure 13. Air bubble in portland cement mortar with thin, plate-shaped, subhedral calcium hydroxide crystals. Hexagonal shape of crystals is clearly visible. Reflected light.

1. Separate or aggregate crystals and crystallites scattered in the cement paste, sometimes as more or less continuous, twisted, band-like formations (Figs. 1 and 2).
2. Layers covering the surfaces of aggregate particles and in surface depressions on aggregate particles (Figs. 2, 3, 4 and 5).
3. In sockets below aggregate particles (Fig. 5).
4. In narrow spaces between aggregate particles (Figs. 6 and 7).
5. As coronas around spherical air bubbles (Fig. 8).
6. Inside originally air-filled bubbles, frequently as large, well-developed crystals (Figs. 9, 10, 11, 12 and 13).

Besides these modes of occurrence, crystalline calcium hydroxide must be expected to exist in submicroscopic distribution in the capillaries and gel pores of the hardened paste, and some authors have even asserted that an amorphous phase exists, although they have not described its morphology.

The microphotographs show that examination of thin sections is a suitable method in morphological studies. Magnifications up to 400 times were used, and this is sufficient for recognition of the majority of calcium hydroxide crystals occurring in concrete. Thin sections of 20 to 30 microns thickness in axis parallel sections of calcium hydroxide crystals yield interference colors of first and second order. These make calcium hydroxide easily distinguishable from almost all other components in mortar and concrete. The basal cleavage is frequently recognizable, and when growing in voids, the crystals may assume an elaborate idiomorphic character.

The microphotographs were part of thin section examinations of various types of mortar carried out by the Concrete Research Laboratory, Karlstrup. Observations have been made on mortars made with different types of cement (portland cements both with and without pozzolan), and different types of fine aggregate (quartz, limestone, flint), and on both air-entrained and non-air-entrained mortars. The curing conditions (water-curing, both with and without subsequent air-curing) and the age at the time of thin section preparation were also varied.

In these mortars all the modes of occurrence of calcium hydroxide mentioned earlier were recorded, some being more marked than others. A more detailed description of these, together with the results of some supplementary quantitative investigations, follows.

1. During the early stages of hydration, calcium hydroxide crystallizes in voids and capillaries in the cement paste. In thin sections, the calcium hydroxide is seen either as aggregates of crystallites or, if the section lies in the plane of a capillary, as irregular crystal bands (Figs. 1 and 2).

2. Calcium hydroxide can be deposited on the surface of aggregate particles in layers of thickness varying from a few microns to about 50 microns or more. This has been observed on quartz particles (Figs. 2 and 3), limestone particles (Fig. 4), flint particles (Fig. 5), and feldspar particles. It has been ascertained by comparison of mortars 7 days and 90 days old that the thickness of the coating increases with age. Thin layers of calcium hydroxide on sand grains were recorded within 24 hours after mixing.

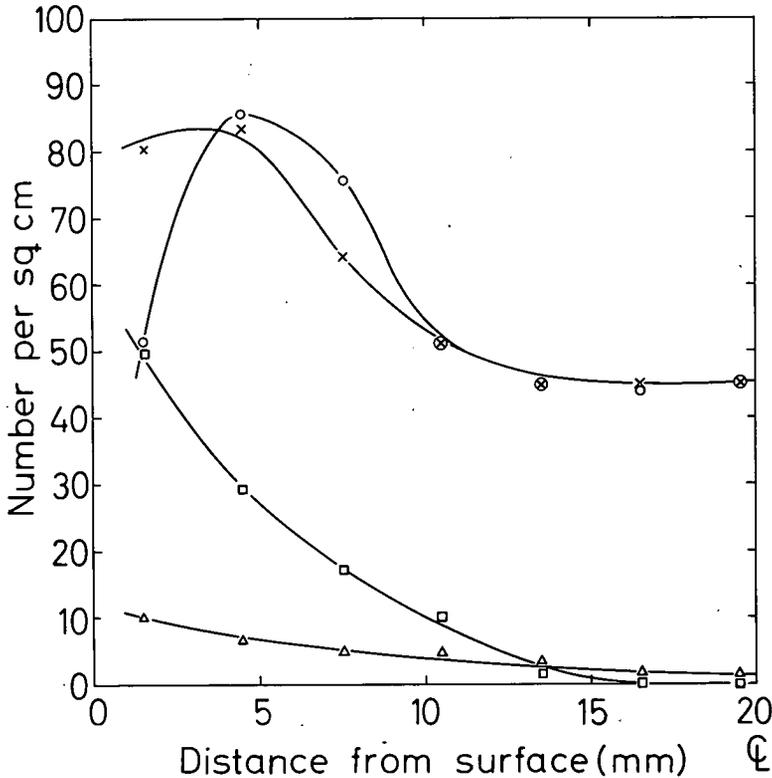


Figure 14. Number of calcium hydroxide-filled air bubbles per square centimeter in cross-sections of various water-cured mortar specimens vs depth from surface.

- x Air-entrained mortar with portland cement (3500 cm²/g Blaine), cured in stagnant water.
- o Air-entrained mortar with portland cement (3500 cm²/g Blaine), cured in running water.
- Δ Ordinary mortar with portland cement (3500 cm²/g Blaine), cured in stagnant water.
- Ordinary mortar with portland cement (5000 cm²/g Blaine), cured in stagnant water.

3. In experiments with long or flat sand grains, such as crushed flint, which became horizontally oriented during compaction of the mortar, concentrated formations of calcium hydroxide were observed in cavities under the sand grains, apparently originally water pockets (Fig. 5).

4. Narrow spaces between aggregate particles are frequently partly or completely filled with calcium hydroxide (Figs. 6 and 7). This probably indicates areas where liquid separation (bleeding) has taken place in the plastic phase of the concrete.

5. A calcium hydroxide shell of varying thickness is usually precipitated around spherical voids, i.e., voids that already exist as air-filled bubbles surrounded by liquid in the plastic phase of the concrete. This kind of precipitation occurs around the bubbles, not inside, which can be concluded from the fact that the outside of the shell is irregular, while the inside has a smooth, circular shape (Fig. 8).

6. Air bubbles are sometimes more or less filled with calcium hydroxide crystals (Figs. 9 to 13). The crystals are frequently so big and well developed that their hexagonal shape is easily recognized when ruptured surfaces of mortar are examined in reflected light (Fig. 13).

It has not yet been possible to ascertain whether the formation and growth of crystals is caused by surface diffusion in a liquid film on the walls of the bubbles or by precipitation from a saturated solution. The latter hypothesis implies that the originally air-filled bubbles become filled with liquid.

Some quantitative measurements have been carried out on thin sections of mortar in order to clarify this question. In a series of thin sections, the number of air bubbles per square unit that were completely or partly filled with calcium hydroxide were counted and recorded as a function of the depth from the original outer surface of the mortar specimen. Averages of the results are shown in Figure 14.

It appears from this figure that, except in the case of curing in running water, the number of calcium hydroxide-filled bubbles decreases with increasing depth from the surface. When cured in running water, the number increases over a few millimeters near the surface and then decreases. It should be noted that no conclusions can be drawn from Figure 14 regarding the proportion of the total number of air bubbles that is filled with calcium hydroxide in the various types of mortar investigated. In order

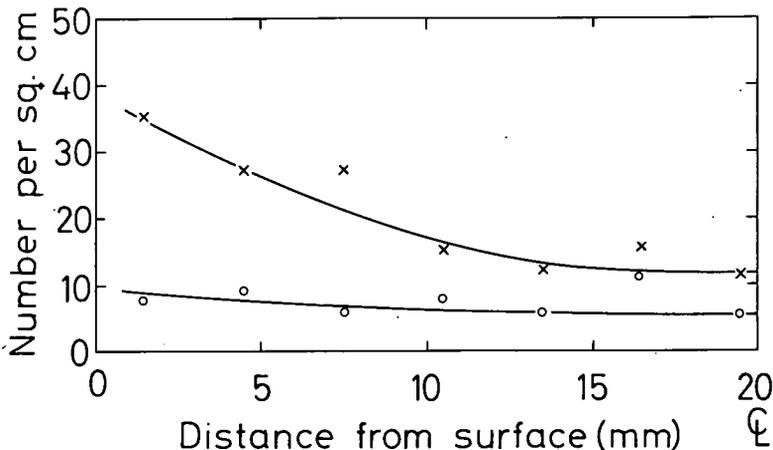


Figure 15. Number of calcium hydroxide-filled air bubbles per square centimeter in cross-sections of various water-cured mortar specimens vs depth from surface.

- Ordinary mortar with portland cement (2600 cm^2/g Blaine), cured for 7 days in stagnant water.
- x Ordinary mortar with portland cement (2600 cm^2/g Blaine), cured for 90 days in stagnant water.

to make such a comparison, the air content and the size of the bubbles must be measured.

Assuming a uniform distribution of the air bubbles over the entire cross-section, Figure 14 does, however, illustrate the fact that the concentration of calcium hydroxide-filled bubbles decreases toward the center of the cross-section, and that the decrease in concentration is most pronounced in the most rapidly hardening mortar. Thus, the crystallization of calcium hydroxide in originally air-filled bubbles is a surface phenomenon that may be conditional upon the fact that the mortar specimens have been cured in water. No calcium hydroxide-filled bubbles were observed in a concrete that had been steam-cured for 48 hours and then cured in air.

In a mortar prepared with ordinary portland cement (2600 cm²/g Blaine), air bubbles completely filled with large subhedral calcium hydroxide crystals were observed after 7 days of curing in water. Figure 15 shows the effect of the time on the rate of filling. It will be seen that the concentration of calcium hydroxide-filled air bubbles increases with time, and that the character of this filling as a surface-conditioned phenomenon becomes more pronounced with age.

In the air-entrained mortars examined, it is mainly bubbles having a greater diameter than 75 microns that are filled with calcium hydroxide. Only exceptionally does calcium hydroxide occur in bubbles of a diameter less than 50 microns. (The diameters of the bubbles seem to be uniformly distributed in the range from about 25 microns to about 150 microns.)

DISCUSSION

When a solution is present in a fine-pored system such as cement paste, a certain permanent supersaturation is thermodynamically possible, the equilibrium concentration being so displaced that it increases with decreasing size of pore. The reason is that, whereas crystallization is normally only conditional upon the transformation of a certain quantity of liquid to a solid, in fine pores it also involves the formation of additional surface, for which extra energy is required. The smaller the pores, the greater will be the surface formed per unit volume of transformed material and the greater the energy required. This means that the finer the pores, the greater the concentration that is required to bring about the transformation, as expressed in the above equilibrium equation. Thus, concentration gradients are established within the pore system, leading to the transport of calcium hydroxide from the finer pores to the coarser pores and voids.

Coatings on Surfaces of Aggregate Particles

During the mixing of a mortar or concrete, the individual aggregate particles are wetted, thereby becoming surrounded by a liquid film. As this film must be expected to have a relatively great thickness, greater concentrations of calcium hydroxide than that corresponding to a saturated solution at the given temperature cannot be maintained for any length of time. Whether or not the formation and growth of crystals then starts up presumably depends on whether the film immediately becomes so greatly supersaturated that the spontaneous formation of nuclei takes place (Hedin and Thorén, 25), or whether the particle surface can itself function as crystal nuclei.

The latter question has been investigated by Hedin (26), who measured the increase in weight of various types of minerals with different surface characteristics when these minerals were used as crystal nuclei in supersaturated calcium hydroxide solutions. He found that crystals grew more rapidly on feldspar, calcite, mica and quartz than on portlandite and natural sand. The first four types of minerals were crushed materials, while the portlandite consisted of pure crystals and the sand of round, polished grains. Hedin suggests as an explanation of the phenomenon that irregular surfaces with many edges and corners facilitate crystallization.

Martin (32) has measured the increase in weight of thin, polished plates of marble, magnesite, quartz and quartz glass in supersaturated calcium hydroxide solutions. He found that the greatest increase in weight took place in the case of marble and magnesite.

Farran (5) has observed calcium hydroxide coatings on glass, quartz and feldspar in 15-day old mortar. The layers did not increase in thickness from the 3rd to the 12th month.

Assarson and Sundius (1) have observed that calcium hydroxide coatings are more marked on grains of sand that are covered with reddish-brown films of iron-oxide and humus than on clean grains.

In the present investigation, coatings have been observed on quartz, calcspar, feldspar and flint, and it seems reasonable to assume that it is not the type of mineral that determines whether or not calcium hydroxide will be deposited on the surface, but rather the actual surface texture.

Regardless of whether the crystallization starts by the spontaneous formation of nuclei or whether the aggregate particles themselves act as crystal nuclei, it is certain that the formation of calcium hydroxide on particle surfaces is a normal phenomenon in mortar and concrete, and that the coatings form rather rapidly. Thus, a thin coating can be observed after only 24 hours. When crystallization has started, the concentration in the liquid film around the aggregate particles will, as mentioned above, fall to saturation concentration. Thereafter, it will be possible for the transport of calcium hydroxide to take place by diffusion from and through adjacent, fine, liquid-filled pores, where the calcium hydroxide concentration is higher and where calcium hydroxide is still being formed by continued hydration, so that the thickness of the coatings will increase. How long this increase will continue and how thick the layers become presumably depend on many factors, such as the surroundings and density of the concrete. Farran's investigations and the present work have shown that growth may continue for about three months and that thicknesses of up to about 50 microns may be reached.

Under and Between Aggregate Particles and Around Air Bubbles

In areas in the concrete mass where liquid is present or concentrates during the plastic phase, the formation and growth of calcium hydroxide crystals will also be able to take place as described above, i.e., by diffusion of calcium hydroxide from fine, supersaturated pores to accumulations of liquid where supersaturation is not thermodynamically possible.

Such accumulations of liquid can occur under aggregate particles as a consequence of bleeding provided the liquid cannot escape. The occurrence of calcium hydroxide in such locations has been ascertained under long and flat flint particles in the present investigation, and has also been reported by Terrier and Moreau (18).

Liquid may also accumulate in spaces between adjacent grains of sand where the cement grains suspended in the fresh concrete have difficulty penetrating. It must be presumed that this type of liquid accumulation can occur due to penetration of water into concrete that is insufficiently compacted, or by sedimentation (bleeding) in concrete with surplus mixing water. Calcium hydroxide has been observed in such locations.

During the plastic phase of the concrete, when the cement paste consists of a suspension of cement grains in liquid, spherical voids—air bubbles—must be surrounded by liquid in which the surface tension can act. As this liquid layer must be expected to have a relatively great thickness, the calcium hydroxide concentration cannot for any length of time be greater than the value corresponding to saturation. A concentration gradient is thus established that permits the transport of calcium hydroxide from surrounding fine pores and the segregation around air bubbles.

Calcium Hydroxide in Air Bubbles

On the basis of the present observations and general ideas on mass transport and thermodynamics in respect to porous materials, the following hypothesis is suggested to explain the formation of crystals in air bubbles:

The precipitation of calcium hydroxide crystals in air bubbles occurs in the liquid phase, the bubbles being completely or partly filled with liquid during the formation of crystals. The transport of calcium ions occurs by diffusion through fine liquid-filled pores that are supersaturated with calcium hydroxide to large completely or partly

liquid-filled bubbles where the crystallization takes place since supersaturation is not thermodynamically possible here.

The filling of air bubbles with liquid comes from the supply of liquid from the surroundings driven by capillary forces. Such a process requires the removal of the air locked in the bubbles, and this occurs by a process of solution and diffusion whereby the air in the bubbles, which is under a certain super-pressure, is dissolved in the liquid and diffuses to the surroundings.

The observations and ideas leading to this hypothesis are as follows:

1. The calcium hydroxide crystals observed are often large and regular, which indicates that the precipitation occurs during a liquid phase that is so slightly supersaturated that the influence of the concentration gradients does not outweigh the tendency toward regular lattice arrangement. The fact that the crystals usually have the shape of thin, hexagonal plates points in the same direction, as shown in the investigations by Hedin (26) into the dependence of the growth of crystals on the concentration. If it were a question of surface diffusion along adsorbed liquid film, the crystal formation would hardly result in such a regular lattice arrangement in large crystals.

2. Experience both from others, e.g., Helmuth (33), and the writers' investigations (not published) indicate that a certain filling of air bubbles with liquid, determined by weighing water-saturated test specimens, can take place.

3. It can be shown by theoretical calculations for perfectly porous materials with air bubbles that a filling process consisting of the capillary flow of liquid from the surroundings into air bubbles and the dissolution of air and diffusion of dissolved air to the surroundings is possible. The rates of this process thus calculated are of the same order of magnitude as those observed.

4. It has been observed that the number of air bubbles per unit volume that contain calcium hydroxide crystals is greatest near the surface, and that the number decreases with increasing distance from the surface. This is in agreement with the view that the filling of air bubbles with liquid is the basis for a considerable crystal development, and that this filling is dependent upon liquid transport from the surroundings.

5. The transport of calcium hydroxide through fine liquid-filled pores to the completely or partly liquid-filled air bubbles, where crystallization takes place, is thermodynamically possible. Such transport of calcium ions requires a concentration gradient since the transport goes from a higher to a lower concentration. As the concentration in the air bubbles at least corresponds to the saturation concentration, the concentration in the pores must be higher, and there must be a certain supersaturation in the pores for the transport to take place. Such supersaturation is, as previously stated, thermodynamically possible.

As can be proved by simple thermodynamic calculations, these considerations imply that small air bubbles become filled with liquid more rapidly than larger bubbles, but the observations show that calcium hydroxide mainly occurs in the largest bubbles. This has also been ascertained by Bruere (9). However, it is not considered necessary to reject the hypothesis purely on this basis. On the contrary, it is probably better to consider that the assumption that the cement paste is a homogeneous, perfectly porous system needs revising. Variations in the density of the pore structure, perhaps with a greater average permeability factor around large bubbles than around small ones, may thus be considered to play a dominant part.

The hypothesis further assumes that the filling of air bubbles with liquid and subsequent precipitation of calcium hydroxide only occur in concrete and mortar that are or have been in contact with water. This seems a reasonable assumption in view of the fact that calcium hydroxide has only been observed in bubbles in water-cured concrete and mortar, and that under these conditions, the crystallization is a surface phenomenon. On the other hand, this implies that the density of the pore structure at the time the concrete surface comes into contact with water must be decisive for the rate at which the bubbles become filled. This condition has been demonstrated in the present investigation by the fact that the concentration of bubbles filled with calcium hydroxide fell more sharply with increasing distance from the surface in a mortar produced with

a very rapidly hardening cement than in a mortar produced with a cement that hardened at a moderate speed. Both these types of mortar were immersed in water 24 hours after they were mixed.

The Effect of Variations in the Surroundings

The above considerations regarding the transport of calcium hydroxide in porous materials have only been concerned with transport due to structurally conditioned differences. However, other factors can create gradients in the chemical potential, e.g., the temperature and foreign ions.

The temperature has an effect because the solubility of calcium hydroxide varies with the temperature. For example, a lowering of the temperature, whereby the solubility of calcium hydroxide is increased, is presumed to accelerate the processes of dissolution of calcium hydroxide crystals in the finest pores, diffusion, and recrystallization in coarser pores. McConnell et al. (2), for instance, discuss the effect of repeated freezing and thawing on the crystallization processes, and Idorn (13) has observed unusual crystal growth in concrete exposed to severe freezing and thawing.

The solubility of calcium hydroxide can also be affected by foreign ions. Other hydroxides, as for instance alkali hydroxides, reduce the solubility, while certain organic materials can increase it very considerably. If such materials penetrate the concrete (sea water, de-icing agents, etc.), the dissolution-diffusion-recrystallization processes for calcium hydroxide may be affected as described above. Hansen (34) has described the effect on these processes of glycerine (used for de-icing concrete pavements), which increases the solubility of calcium hydroxide very considerably.

It should finally be mentioned that temperature gradients in a concrete body, moisture gradients, gradients in hydrostatic pressure, and differences in the thermal expansion coefficients of water, calcium hydroxide and cement gel, must be assumed to have a similar, more or less marked "pumping" effect.

Effect on Physical Characteristics

The importance of the mode of occurrence and distribution of calcium hydroxide in concrete, i.e., its morphology, to the strength characteristics of the concrete is not apparent because data on the strength of calcium hydroxide are not, as far as is known, available. Wischers (35) suggests that calcium hydroxide formations in cement paste have the effect of reducing the strength of the paste. It hardly seems likely that calcium hydroxide in a comparatively limited number of air bubbles, which are moreover most frequently only partly filled, can have any great influence on the strength. It seems more probable that calcium hydroxide coatings on the surfaces of aggregate particles may play some part, either by increasing or by reducing the adhesion between cement paste and aggregate particles. There are two contributions to this adhesion, namely the adhesion between cement paste and calcium hydroxide on the one hand and the adhesion between calcium hydroxide and aggregate particles on the other. The latter contribution may possibly vary greatly, depending on the type of aggregate. It has thus been suggested by Farran (5) that adhesion of an epitaxial nature may occur between calcium hydroxide and carbonate minerals. In concrete subjected to 680 freezing-thawing cycles, Terrier and Moreau (18) observed that the calcium hydroxide coating had loosened from the surfaces of the aggregate particles.

In the foregoing it has been shown that it is probable that in concrete immersed in water, liquid penetrates a number of the air bubbles closest to the surface. This reduces the frost resistance that is aimed at by means of air-entrainment. Observations of calcium hydroxide deposits indicate that it is especially the larger bubbles that become filled with liquid, and in this case, the frost resistance is hardly reduced very much. However, it has not yet proved possible to determine whether the absence of calcium hydroxide from air bubbles is synonymous with the fact that these have not been filled with liquid. It has frequently been observed that concrete structures standing in water, e.g., bridge piers, are attacked by frost at the waterline despite the use of air-entrained concrete, and this may possibly be related to the filling of air bubbles with liquid in areas below and about the waterline. Thus tidal exposure

of concrete may, in particular, call for the use of concrete with high air content air-entrainment.

It should also be mentioned that the morphology of calcium hydroxide in mortar and concrete plays a part in such phenomena as carbonation, as described by Powers (36), and the corrosion of reinforcement. Calcium hydroxide coatings on reinforcement have been observed by Farran (5) and are discussed by Idorn (11).

CONCLUSIONS

In concrete and mortar, calcium hydroxide is precipitated in the following locations: (a) as large or small crystal aggregates and in banded formations in the cement paste; (b) on the surfaces of aggregate particles; (c) in cavities under aggregate particles; (d) in narrow spaces between aggregate particles; (e) around air bubbles; and (f) inside originally air-filled bubbles.

The precipitation of calcium hydroxide in these locations, where supersaturated calcium hydroxide concentrations cannot exist for any length of time, takes place by diffusion from surrounding fine pores, where supersaturation is thermodynamically possible.

The formation of calcium hydroxide in air bubbles also takes place by precipitation from solution; investigations have shown that a number of the air bubbles closest to the surface in mortar and concrete cured in water become filled with liquid. However, it has not been possible to ascertain whether the absence of calcium hydroxide from air bubbles means that the bubbles have not been filled with liquid. This should be made the subject of a further investigation since a possible filling of all bubbles with liquid implies that the frost protection of air-entrained paste is lost. The question seems to be of particular importance for structures exposed to repeated wetting and drying in connection with freezing and thawing, e.g., marine structures, bridge piers and pavements.

The formation of calcium hydroxide on the surfaces of aggregate particles does not seem to depend very much on the actual type of mineral in aggregates. The surface texture (roughness) of the particles may be of greater importance.

The effect of the calcium hydroxide coatings on aggregate particles on the strength characteristics of concrete needs further study. Data on the strength and rheological properties of calcium hydroxide would be of particular interest. The effect of the coatings on the chemical reactions between cement paste and aggregate particles, especially during aging of the concrete and in connection with autoclaving, provides a profitable field for research.

The influence on the system $\text{Ca}(\text{OH})_2\text{-H}_2\text{O}$ of foreign ions in the viscous phase of the cement paste must also be pursued further. Within this field of investigation important technical problems such as the resistance of concrete structures to chemical attack from aggressive waters and to the application of de-icing salts can be pointed out.

A more detailed theoretical treatment and determination of the rates at which the physical and chemical processes determining the crystallization of calcium hydroxide in cement paste take place require knowledge of diffusion coefficients for calcium hydroxide and dissolved air in porous materials. Deeper studies are also called for concerning micro-variations in the permeability of hardened cement paste. Investigations into these phenomena are sparse.

REFERENCES

1. Assarson, G., and Sundius, N. Redögörelse för undersökningar angående orsakerna till forstorelse av betong i vattenbyggnader. Tekniska Meddelanden från Kungl. Vattenfallsstyrelsen. Series B, No. 16, July 1929.
2. McConnell, D., Mielenz, R. C., Holland, W. Y., and Greene, K. T. Cement-Aggregate Reaction in Concrete. Jour. ACI, Vol. 19, No. 2, pp. 93-128, Oct. 1947.
3. Mather, K. Applications of Light Microscopy in Concrete Research. Symposium on Light Microscopy. ASTM Spec. Publ. 143, pp. 51-69, New York, 1952.
4. Mather, B. Cracking of Concrete in the Tuscaloosa Lock. Proc. HRB, Vol. 31, pp. 218-233, 1952.

5. Farran, J. Contribution minéralogique à l'étude de l'adhérence entre les constituants hydratés des ciment et les matériaux enrobés. *Revue des Matériaux de Construction*, Nos. 490, 491 and 492, 1956.
6. Idorn, G. M. Mikroskopiske glimt af betonteknikkens historie. *Beton-Teknik*, No. 4, pp. 119-141, 1959.
7. Idorn, G. M. Concrete Deterioration of a Foundation. *Acta Polytechnica*, Civil Engineering and Building Construction Series, Vol. 4, No. 3, pp. 1-48, Copenhagen, 1957.
8. Tilley, C. E. Portlandite, a New Mineral from Scawt Hill, County Antrim. *Mineralogical Mag.*, pp. 419-420, 1933.
9. Bruere, G. M. The Relative Importance of Various Physical and Chemical Factors on Bubble Characteristics in Cement Pastes. *Australian Jour. of Applied Science*, Vol. 12, No. 1, pp. 78-86, March 1961.
10. Idorn, G. M. Studies of Disintegrated Concrete, Part II. Committee on Alkali Reactions in Concrete, Progress Report N3, pp. 1-47, Copenhagen, 1961.
11. Idorn, G. M. Nogle nye tendenser i betonforskningen. *Igenioren*, Vol. 72, No. 20, 1963.
12. Idorn, G. M. Studies of Disintegrated Concrete, Part III. Committee on Alkali Reactions in Concrete, Progress Report N4, pp. 1-66, Copenhagen, 1964.
13. Idorn, G. M. Studies of Disintegrated Concrete, Part IV. Committee on Alkali Reactions in Concrete, Progress Report N5, pp. 1-45, Copenhagen, 1964.
14. Lyubimova, T. Y., and Pinus, E. R. Crystallization Structure in the Contact Zone Between Aggregate and Cement in Concrete. *Colloid Jour.* Vol. 24, No. 5, pp. 491-498, 1962.
15. Skramtaev, B. G., Astreeva, O. M., and Lopatnikova, A. Y. *Tsment*, No. 5, 1955.
16. Panteleev, A. S. *Khim. nauka i prom-st'*, Vol. 3, p. 22, 1958.
17. Larsen, G. Microscopic Point Measuring: A Quantitative Petrographic Method of Determining the $\text{Ca}(\text{OH})_2$ Content of the Cement Paste of Concrete. *Mag. of Concrete Research*, Vol. 13, No. 38, pp. 71-76, 1961.
18. Terrier, P., and Moreau, M. Examens au microscope de pâtes de ciment portland. *Revue des Matériaux de Construction et de Travaux Publics*, No. 584, pp. 129-137, May 1964.
19. Idorn, G. M. Studies of Disintegrated Concrete, Part V. Committee on Alkali Reactions in Concrete, Progress Report N6, pp. 1-80, Copenhagen, 1964.
20. Sweet, J. M., Bothwell, D. I., and Williams, D. L. Tacharanite and Other Hydrated Calcium Silicates from Portree, Isle of Skye. *Mineralogical Mag.*, Vol. 32, No. 253, pp. 745-753, June 1961.
21. Greenberg, S. A., and Copeland, L. E. The Thermodynamic Functions for the Solution of Calcium Hydroxide in Water. *Jour. Phys. Chem.*, Vol. 64, pp. 1057-1059, July 1960.
22. Lea, F. M. *The Chemistry of Cement and Concrete*. London, 1956.
23. Brunauer, S., and Greenberg, S. A. The Hydration of Tricalcium Silicate and β -Dicalcium Silicate at Room Temperature. Fourth Internat. Symposium on Chem. of Cement, Washington, 1960. Proc., pp. 135-165.
24. Hedin, R. Saturation Concentration of Calcium Hydroxide. Swedish Cement and Concrete Research Inst., Royal Inst. of Technology, Stockholm. Proc. No. 27, pp. 1-14, Stockholm, 1955.
25. Hedin, R. and Thorén, P. -Å. Lime Research at the Chemical Department of the Swedish Cement and Concrete Research Institute. *Bull.* No. 16, Stockholm, 1949.
26. Hedin, R. Processes of Diffusion, Solution and Crystallization in System $\text{Ca}(\text{OH})_2\text{-H}_2\text{O}$. Swedish Cement and Concrete Research Inst., Royal Inst. of Technology, Stockholm. Proc. No. 33, pp. 1-92, Stockholm, 1962.
27. Ringquist, G. Concentration of Pure Calcium Hydroxide Solutions as a Function of Electrolytic Conductivity in the Temperature Range from 0 to 100 C. Tables. Swedish Cement and Concrete Research Inst., Royal Inst. of Technology, Stockholm. Proc. No. 19, Stockholm, 1952.

28. Greene, K. T. Early Hydration Reactions of Portland Cement. Fourth Internat. Symposium on Chem. of Cement, Washington, 1960. Proc., pp. 359-374.
29. Szuk, G. Setting and Hardening of Hydraulic Materials. Determination of Optimal Steam Curing of Prestressed Concrete Railway Sleepers by the Conductimetric Method. Acta Techn. Hung., Vol. 44, No. 3/4, pp. 329-377, 1963.
30. Grudemo, Å. Electron Microscopy of Portland Cement Pastes. In The Chemistry of Cement. H. F. W. Taylor, ed. Vol. 1, pp. 371-389, London and New York, 1964.
31. Taylor, H. F. W. Hydrothermal Reactions in System $\text{CaO-SiO}_2\text{-H}_2\text{O}$ and the Steam Curing of Cement and Cement-Silica Products. Fourth Internat. Symposium on Chem. of Cement, Washington, 1960. Proc., pp. 167-190.
32. Martin, H. Die Bindung im Beton. Betonstein-Zeitung, No. 11, pp. 549-533, 1963.
33. Helmuth, R. A. Dimensional Changes of Hardened Portland Cement Pastes Caused by Temperature Changes. Proc. HRB, Vol. 40, pp. 315-336, 1961.
34. Hansen, W. C. Crystal Growth as a Source of Expansion in Portland-Cement Concrete. Proc. ASTM, Vol. 63, pp. 932-945, 1963.
35. Wischers, G. Physikalische Eigenschaften des Zementsteins. Beton Herstellung Verwendung, Vol. 11, No. 7, pp. 481-486, 1961.
36. Powers, T. C. A Hypothesis on Carbonation Shrinkage. Jour. of PCA, Vol. 4, No. 2, 1962.