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Initial Hydration Reactions and Mechanisms of Delayed Ettringite Formation in Portland Cements

H.-J. Kuzel

Mineralogisches Institut der Universität Erlangen - Nürnberg, Schloßgarten 5a, 91054 Erlangen, Germany

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Abstract

The aluminate hydration reactions in Portland cements were followed by X-ray diffraction. Using a computerized focusing Huber–Guinier diffractometer, the patterns were obtained from the pastes directly, without preliminary drying or grinding. It is shown that the widely accepted theories on the hydration of C_3A *in the presence of calcium sulfate cannot be applied generally to commercial Portland cements. Only in cases of pastes nearly free of* CO_2 *will the ettlingite formed in the course of the induction period transform to monosulfate. In cement pastes containing more than about 0.5%* CO_2 *the conversion is prevented and monosulfate is replaced by hemicarbonate or monocarbonate. The quantity of* CO_2 *sufficient to replace monosulfate by carbonated AFm phases depends on the ratio of* SO_3 *to* C_3A *and the amount of available* Al_2O_3*. The results clearly show that with cements or concretes containing monosulfate the risk of delayed ettringite formation as a result of carbonation reactions should be taken into account. The interlayer sulfate groups in the crystal structure of monosulfate can be replaced by carbonate. This exchange results in increasing sulfate concentration in the pore solution and thus leads to delayed ettringite formation.* *© 1996 Elsevier Science Limited.*

INTRODUCTION

The initial setting of Portland cements is regulated by intergrinding with a calcium sulfate. According to the classical view of the C_3A-sulfate reactions the induction period of a cement paste is attributed to the formation of a protective layer of ettringite around the crystals of the highly reactive C_3A. In Portland cements the molar ratio of SO_3 to C_3A ranges from 0.7 to 1.2, suggesting that the final hydration product will not be ettringite but mainly monosulfate or a member of the solid solution series between monosulfate and hemisulfate.[1,2]

Hydration experiments made with pure compounds in the system $C_3A–CaSO_4 \cdot H_2O$ by many authors[3–7] indicated that formation of monosulfate occurs in two stages which may be described formally by the following equations:

$$C_3A + \underbrace{3CaSO_4 \cdot 2H_2O}_{\text{gypsum}} + 27H_2O \Rightarrow \underbrace{C_3A \cdot 3CaSO_4 \cdot 33H_2O}_{\text{ettringite}} \qquad (1)$$

$$2C_3A + \underbrace{C_3A \cdot 3CaSO_4 \cdot 33H_2O}_{\text{ettringite}} + 9H_2O \Rightarrow \underbrace{3C_3A \cdot CaSO_4 \cdot 14H_2O}_{\text{monosulfate}} \qquad (2)$$

The water contents of ettringite and monosulfate given in the above formulae were derived from recent Rietveld crystal structure refinements by the author on the basis of X-ray powder diagrams taken in the presence of water.

In the first stage (eqn (1)), one third of the available C_3A is used in the formation of the protective layer of ettringite around the C_3A particles. This probably causes the transport of H_2O and SO_4^{2-} to the C_3A surface to be controlled by diffusion. The second stage takes place after the solid calcium sulfate has been completely consumed and the SO_3 concentration in the pore solution has fallen to the value of 2.35 mg/l corresponding to the invariant point for the equilibrium ettringite + monosulfate + $Ca(OH)_2$ + solution, causing the ettringite to become unstable.[8,9] The coating is removed and the transformation to monosulfate proceeds according to eqn (2). The overall reaction is described by eqn (3):

$$C_3A + 3\underset{\text{gypsum}}{CaSO_4 \cdot 2H_2O} + 36H_2O \Rightarrow 3\underset{\text{monosulfate}}{C_3A \cdot CaSO_4 \cdot 14H_2O} \quad (3)$$

With the famous reports of Candlot,[10] Michaelis[11] and Lafuma[12] which appeared about one century ago it became evident that an excess amount of calcium sulfate in Portland cement could lead to delayed ettringite formation, and that attack by solutions containing sulfate, such as polluted ground water, could have a similar effect. Since the ettringite crystallized *in situ* has a larger volume than the parent solid phases, the generated stress may result in expansion, cracking or, ultimately, disintegration. The Al^{3+} needed for the formation of ettringite could be supplied by unhydrated C_3A or ferrite phase, but it is believed that the main source of aluminate in hardened concrete is monosulfate in accordance with a reaction of the type

$$\underset{\text{monosulfate}}{C_3A \cdot CaSO_4 \cdot 14H_2O} + 2\underset{\text{gypsum}}{CaSO_4 \cdot 2H_2O} + 15H_2O \Rightarrow \underset{\text{ettringite}}{C_3A \cdot 3CaSO_4 \cdot 33H_2O} \quad (4)$$

A review of the very extensive literature on sulfate attack is given by Taylor.[13]

Recently evidence has been published that the reactions observed in the system C_3A–$CaSO_4$–H_2O probably do not occur in the hydration of commercial Portland cements.[14–16] In contrast to the classical theory, X-ray diffraction experiments on pastes using a "wet cell" indicated that ettringite persists in mortars and concretes even after years. Neither monosulfate nor hemisulfate was detected, and the authors concluded from a consideration of the calorimetric and X-ray data that the transformation of ettringite to monosulfate is suppressed in the presence of small amounts of CO_2 in the paste and that hemicarbonate or monocarbonate is formed instead. It was shown that monosulfate occurred only in cases where the Portland cement contained less than about 0.5% of CO_2. Further evidence was given that the instability of monosulfate in the presence of CO_2 will result in delayed ettringite formation as a first step in carbonation reactions.

In the present paper additional experimental results supporting the new theory of the mechanisms of the initial hydration reactions of Portland cements and of delayed formation of ettringite in concrete will be presented.

EXPERIMENTAL PROCEDURES

Hydration experiments were carried out with a series of commercial German Portland cements. In the present paper only the results obtained with a typical example, a PZ45F cement, will be given. The chemical analyses and the calculated mineralogical compositions of three samples of this cement are shown in Table 1. The CO_2 contents were determined by the standard procedure given in DIN 1164. Cement PZ45F(A) was taken from a customer's silo a few days after production. Sample PZ45F(B) came from the same kiln but was collected directly after the finish grinding and showed a considerably lower CO_2 content. The specific surface area

Table 1. Compositions of the Portland cements

Cement	*PZ45F(A)*	*PZ45F(B)*	*PZ45F(C)*
CaO	63.2	63.2	63.2
Al_2O_3	6.1	6.2	6.2
Fe_2O_3	2.5	2.5	2.5
K_2O	1.2	1.2	0.9
SiO_2	19.8	20.2	20.0
SO_3	3.9	4.0	4.4
CO_2	0.9	0.4	<0.1
C_3A	11.8	12.1	12.1
C_3S	53.7	53.9	53.6
C_2S	16.1	16.2	16.2
C_4AF	7.8	7.8	7.8

was 415 m^2kg^{-1} (Blaine). The nearly CO_2-free cement PZ45F(C) was prepared in the laboratory by grinding the freshly burned clinker of the PZ45F, which already contained 0.4% SO_3, with 8.6% $CaSO_4 \cdot 2H_2O$ (=4.0% SO_3) to a specific surface area of 433 m^2kg^{-1}.

Attempts to follow the hydration reactions with X-ray diffraction using a conventional Bragg–Brentano diffractometer do not give reliable results since drying and grinding of the hydration products may cause uncontrolled dehydration and disordering of the crystal structures of the AFm and AFt phases. These effects usually lead, not only to complications in the identification of the compounds, but frequently also to incorrect interpretation of the data. To avoid them a method was developed to obtain X-ray diffraction diagrams from the pastes without drying and grinding of the samples. A thin layer of the cement paste, about 0.2mm in thickness, is made with the desired water to solid ratio and uniformly distributed between two Mylar films. This sample is tightly sealed in a special specimen holder so that loss of water and attack by atmospheric CO_2 are prevented. With this arrangement the diffraction patterns of one and the same sample can be periodically recorded. The scans were taken at 25°C with the flat samples in asymmetric transmission position using a computerized focusing Huber–Guinier diffractometer and $CuK_{\alpha 1}$ radiation.

The following abbreviations will be used:

F =Ferrite phase
E =Ettringite, $C_3A \cdot 3CaSO_4 \cdot 33H_2O$
Ms-14 =Monosulfate $C_3A \cdot CaSO_4 \cdot 14H_2O$
Ms-16 =Monosulfate $C_3A \cdot CaSO_4 \cdot 16H_2O$
Mc =Monocarbonate $C_3A \cdot CaCO_3 \cdot 11H_2O$
Hc =Hemicarbonate $C_3A \cdot 1/2CaCO_3$ $1/2Ca(OH)_2 \cdot 11.5H_2O$
CH =Portlandite, $Ca(OH)_2$
G =Gypsum, $CaSO_4 \cdot 2H_2O$
C =Calcite, $CaCO_3$

RESULTS

Hydration reactions of the Portland cement PZ45F(A)

Although Portland cements generally contain less than 12% of C_3A, the hydration reactions of the aluminate phase can be easily tracked by the Huber–Guinier method mentioned above. Figure 1 shows some selected patterns of a paste made with cement PZ45F(A) and a water to solid ratio of 0.6. The intensity data were collected in the step scan mode with a preset time normally of 5 s, advancing the goniometer in steps of 0.01°θ, and stored as ASCII files which were then imported directly into the worksheet of a commercial graphics program.

The diagrams clearly demonstrate the sequence of reactions as functions of time. In the course of the induction period, after a

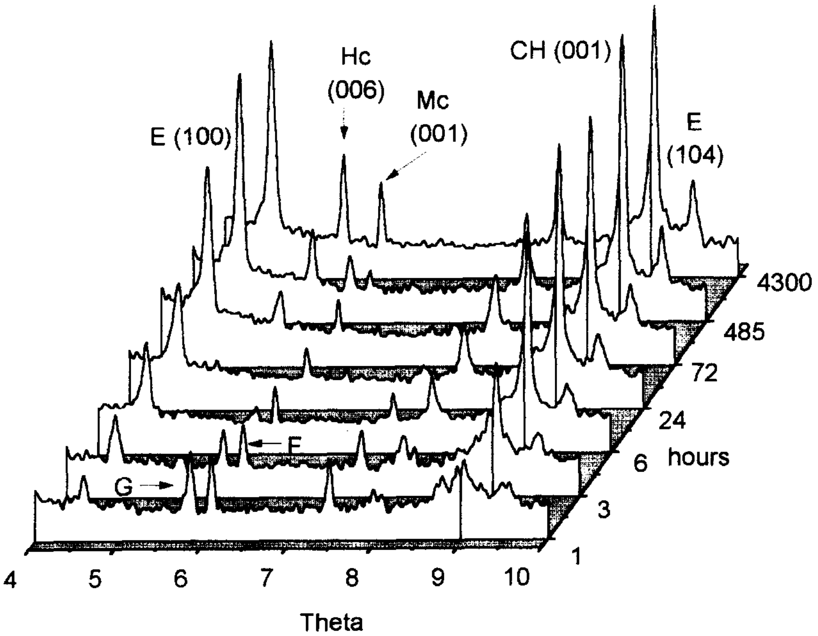

Fig. 1. X-ray Huber–Guinier diagrams for a paste of the cement PZ45F(A); w/c = 0.6, T = 25°C, $CuK_{\alpha 1}$ radiation.

hydration time of about 1 h, a small amount of distinctly crystalline ettringite, probably forming the protective layer around the C_3A particles according to eqn (1), was observed. In the following hours the content of ettringite increased gradually and a considerable amount of $Ca(OH)_2$ was produced due to the high reactivity of the alite.

After the 020 reflection of gypsum ($\theta = 5.85°$) had disappeared and sulfate ions in solution became depleted at about 24 h hydration time, the ettringite coating was probably removed and lost its function as a diffusion barrier. At this point, if eqn (2) correctly represents the course of events, the ettringite should start to convert to monosulfate. In actual fact, the ettringite persisted; instead of the monosulfate peaks, the 006 peak of hemicarbonate appeared at $\theta = 5.39°$, indicating that reaction had occurred between the remaining C_3A, the CO_2 in the pore solution and the $Ca(OH)_2$ to produce hemicarbonate, ($C_3A \cdot 1/2CaCO_3 \cdot 1/2Ca(OH)_2 \cdot 11.5H_2O$).

In the following days the phase composition of the paste became even more complex. As the hydration of alite and belite proceeded and C–S–H gel was formed, the background intensities of the X-ray diagrams increased. After about 300 h the 001 peak of monocarbonate ($C_3A \cdot CaCO_3 \cdot 11H_2O$) appeared. Even after a hydration time of 180 days the transformation of ettringite to monosulfate did not occur and ettringite, hemicarbonate, monocarbonate and $Ca(OH)_2$ coexisted with solution. As was observed earlier with other Portland cements,[14] the ferrite had not disappeared at a hydration time of 600 h, indicating poor reactivity of that phase.

Hydration reactions of the Portland cement PZ45F(B)

The initial reactions of cement PZ45F(B), which contained less CO_2, were similar to those of cement PZ45F(A), as is shown in Fig. 2. Hydration again started with the formation of ettringite from the C_3A and of $Ca(OH)_2$, but after more than 50 h the reactions became significantly different from those observed with cement PZ45F(A). On the right hand (high angle) flank of the 100 peak of ettringite at $\theta = 4.53°$, the 003 reflection of the hydrate $C_3A \cdot CaSO_4 \cdot 14H_2O$ appeared at $\theta = 4.64°$, indicating that transformation of ettringite to monosulfate had started in accordance with eqn (2). In the following hours the intensities of the monosulfate reflections increased slowly at the expense of ettringite. After about 200 h hydration time the transformation came to a halt and the broadened 006 peak of hemicarbonate appeared. With increasing time no further changes in phase composition were observed

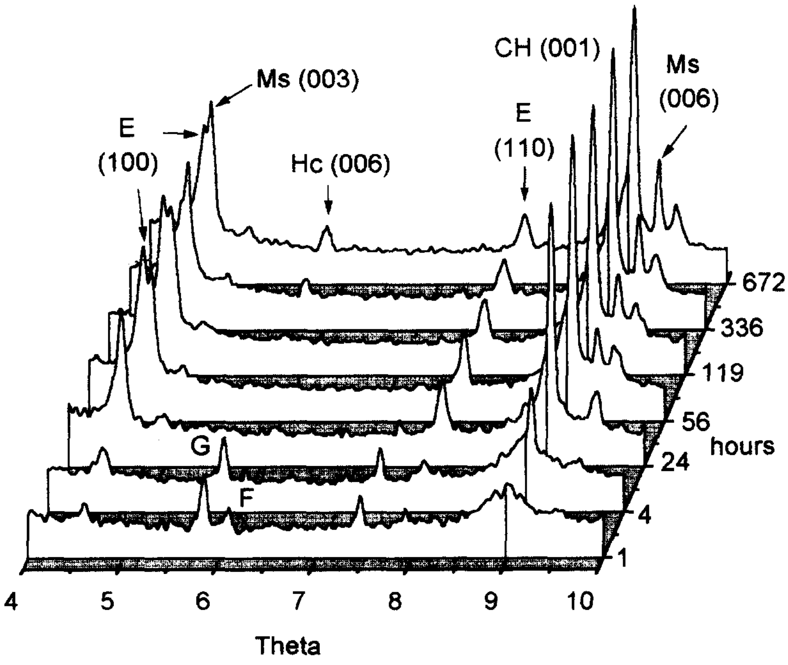

Fig. 2. X-ray Huber–Guinier diagrams for a paste of the cement PZ45F(B); w/c = 0.6, $T = 25°C$, $CuK_{\alpha 1}$ radiation.

and ettringite, monosulfate-$14H_2O$, hemicarbonate and $Ca(OH)_2$ appeared to be in equilibrium with solution.

Hydration reactions of the Portland cement PZ45F(C)

The X-ray diagrams shown in Fig. 3 were obtained with a preset time of 10 s to achieve better smoothing of the intensity data.

The hydration reactions of the aluminate phase in the nearly CO_2-free cement, PZ45F(C), were completely different from those observed with the CO_2-containing commercial cements. After 12 h relatively large amounts of ettringite and $Ca(OH)_2$ were present. Only a small quantity of gypsum and some ferrite phase were left. In the diagram obtained after 26 h, new and broadened peaks centred at $\theta = 4.23°$ and $\theta = 8.46°$ appeared with high intensity. These were shown to be due to monosulfate-$16H_2O$. In the following 24 h the reflections of this hydrate and those of ettringite weakened rapidly and after 50 h only monosulfate-$14H_2O$, $Ca(OH)_2$ and a very small amount of residual ettringite coexisted. In this case reaction(2) had occurred nearly to completion. Even with very long treatment of the paste in the presence of water and under strict exclusion of CO_2, no major phase changes occurred. This observation indicates that monosulfate is either a thermodynamically stable, or at least an extremely persistent phase in the system under the given conditions.

Delayed ettringite formation in the paste of cement PZ45F(C)

In the next stage of the investigation the cement systems were 'opened', and the changes in phase composition of the hydration products of cement PZ45F(C) were followed in the presence of atmospheric CO_2. As described earlier, the Huber–Guinier X-ray diagrams were taken from layers of the cement paste about 0.2 mm thick, which were contained between two Mylar films and then tightly sealed in the specimen holder. To allow slow access of CO_2 to the paste an opening about 0.2 mm in diameter was made in one of the films. The sample was then placed above the water surface in a glass beaker partly filled with water and covered only with filter paper, so that reaction with CO_2 at high relative humidity was possible. To avoid drying up of the paste the opening was always closed when the sample was removed from the beaker to take X-ray diagrams.

X-ray diffraction diagrams of the same specimen were periodically recorded as before, with the results given in Fig. 4. To provide a basis for comparison, the first scan shows the coexisting crystalline phases monosulfate-$14H_2O$ and

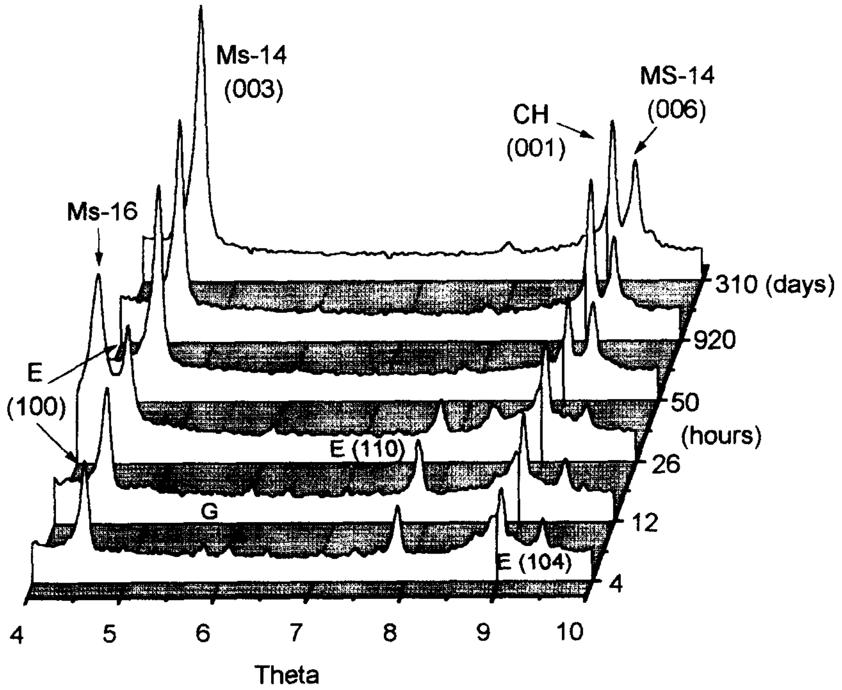

Fig. 3. X-ray Huber–Guinier diagrams for a paste of the CO_2-free cement PZ45F(C), w/c = 0.6, $T = 25°C$, $CuK_{\alpha 1}$ radiation.

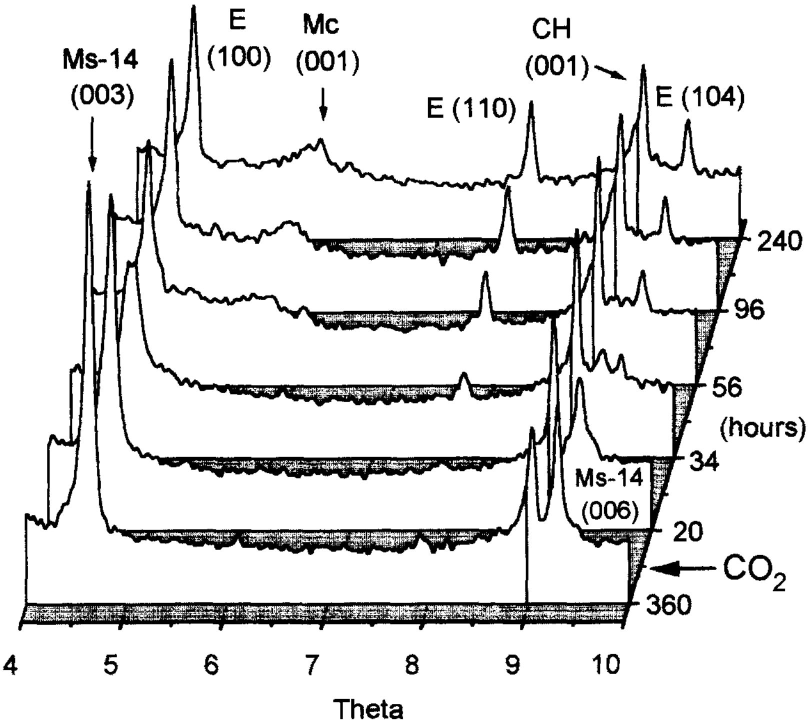

Fig. 4. X-ray Huber–Guinier diagrams. Delayed ettringite formation in a paste of the cement PZ45F(C); w/c = 0.6, $T = 25°C$, $CuK_{\alpha 1}$ radiation.

$Ca(OH)_2$ in a paste of the nearly carbonate-free cement PZ45F(C) at 360 h hydration time. Twenty hours after penetration of the film and the exposure of the cement paste to atmospheric CO_2 the intensities of the monosulfate lines had decreased slightly. Later on the reactions with CO_2 proceeded faster and after 34 h attack a considerable amount of ettringite had crystallized, clearly at the expense of monosulfate. In the following hours the content of ettringite in the paste increased continuously and the reflections of monosulfate-$14H_2O$ weakened. Finally, peaks of monocarbonate appeared; they were broadened, indicating a structurally imperfect phase.

It is important to point out that in this stage of carbonation no formation of crystalline $CaCO_3$ could be detected. The pore solution thus still had a high pH value. Only after prolonged treatment of the paste with CO_2, there occurred decomposition of hemicarbonate and monocarbonate, reaction of $Ca(OH)_2$ to form $CaCO_3$ and, finally, carbonation of ettringite.

The amount of ettringite formed in the 'open' cement systems after more than 500 h hydration appeared to be higher than would have been expected from the SO_3 content. A similar observation was made earlier[14] in the course of experiments with other types of Portland cement. As the hk0 reflections of the ettringite were significantly shifted towards higher Bragg-angles the author believes that SO_4^{2-} was partly replaced by other anions in the crystal structure.

DISCUSSION

Hydration products of the C_3A

The hydration experiments clearly support the earlier results obtained in systems with pure components and Portland cements of different types and from different producers.[14–16] Evidently the reactions of C_3A with calcium sulfates are controlled by the CO_3^{2-} available in the cement paste. The ettringite crystallizing in the course of the initial hydration will transform to monosulfate according to eqns (1), (2) and (3) only under CO_2-free conditions; thus, hydration would proceed in the manner generally described in textbooks of cement chemistry only if the paste is nearly free of CO_2 and if no limestone has been added.

If a cement paste contains a sufficient amount of reactive $CaCO_3$ added by intergrinding limestone or introduced via CO_2 in the course of grinding, storage, or pneumatic transport of the cement powder, or with the aggregate or the mixing water, the hydration of C_3A follows another sequence of reactions. If the molar C_3A/SO_3 ratio of the cement is near to 1 this may be described by the equation

$$\begin{gathered}3C_3A+3CaSO_4{\cdot}2H_2O+2Ca(OH)_2\\ +CO_2+49H_2O \Rightarrow \underset{\text{ettringite}}{C_3A{\cdot}3CaSO_4{\cdot}33H_2O}\\ +\underset{\text{hemicarbonate}}{2C_3A{\cdot}1/2CaCO_3{\cdot}1/2Ca(OH)_2{\cdot}11.5H_2O}\end{gathered} \tag{5}$$

In the presence of more CO_3^{2-}, the hemicarbonate in eqn (5) is partially or completely replaced by monocarbonate. The $Ca(OH)_2$ required in either case is supplied by the hydration of alite and belite. The ettringite persists, the formation of monosulfate is suppressed and, instead, the AFm phases hemicarbonate, monocarbonate or both will crystallize.

The quantity of CO_3^{2-} in a paste that is sufficient to replace monosulfate by hemicarbonate depends on the SO_3/C_3A ratio of the cement and on the available amount of C_3A. If a paste is made with a cement containing, for example, 12% of C_3A and a w/c ratio of 0.45, the presence of not more than 0.45% of CO_2 or 1.0% of $CaCO_3$, referred to the mass of paste, will prevent the formation of monosulfate completely. The value of 0.45% CO_2 is calculated on the basis of the following assumptions and approximations:

All the C_3A, but none of the C_4AF has reacted,
The clinker phases have the compositions C_3S, C_2S, C_3A and C_4AF, ionic substitutions thus beeing ignored,
The molar ratio $SO_3/C_3A = 1$, so that all the Al_2O_3 from the C_3A was used for the formation of monosulfate.

Because of the simplifying assumptions, the result is only approximate, though unlikely to be seriously in error.

If the molar ratio $SO_3/C_3A > 1$, some ettringite will persist from the initial reaction, and the amount of CO_2 needed to complete the formation of ettringite and hemicarbonate will be correspondingly reduced. In case of a molar ratio $SO_3/C_3A < 1$ less ettringite and more hemicarbonate will be formed in the paste in accordance with the appropriately modified eqn (5).

In a paste with less than 0.45% CO_2, the hydration experiments shown in Figs 2 and 3 indicate that hemicarbonate and monosulfate or monosulfate alone will form according to eqn (3).

Delayed ettringite formation

In the case of the CO_2-free cement PZ45F(C), the reaction of the hydrated paste with CO_2 leads to delayed ettringite formation (Fig. 4). This may be formally described by the following equation

$$\begin{gathered}3\ \underset{\text{monosulfate}}{C_3A{\cdot}CaSO_4{\cdot}14H_2O}+CO_2\\ +2Ca(OH)_2+13H_2O \Rightarrow\\ \underset{\text{ettringite}}{C_3A{\cdot}3CaSO_4{\cdot}33H_2O}\\ +\underset{\text{hemicarbonate}}{2C_3A{\cdot}1/2CaCO_3{\cdot}1/2Ca(OH)_2{\cdot}11.5H_2O}\end{gathered} \tag{6}$$

As large quantities of $Ca(OH)_2$ are still present in the paste (Fig. 4) the reaction occurs at $pH > 12$. The maximum amount of ettringite will be formed if the SO_3/C_3A ratio is equal to 1. In an undersulfated cement a member of the solid solution series between monosulfate and hemisulfate will crystallize;[15] hence less SO_3 is available for crystallization of ettringite and more hemicarbonate or monocarbonate would appear.

Knowing the densities of the solid reactants the change of volume accompanying delayed ettringite formation in the open system according to eqn (6) can be estimated. In a hardened CO_2-free paste made with w/c = 0.45, a cement containing 12% of C_3A and a given molar ratio of $SO_3/C_3A = 1$ the sulfate is bound in monosulfate-$14H_2O$. If the monosulfate is completely transformed to ettringite and hemicarbonate in accordance with eqn (6) the resulting increase in volume will be approximately 4%.

For a Portland cement mortar or concrete in which monosulfate is present, delayed ettringite formation according to eqn (6) is the first step in carbonation. In the second step CO_3^{2-} reacts with Ca^{2+} to $CaCO_3$, the AFm phases, ettringite and C–S–H are decalcified, and finally the pH drops to 8.5 or below.

The effect of CO_2 concentrations in cement pastes on the hydration reactions of the C_3A is summarized by the schematic diagram given in Fig. 5.

Two different reaction mechanisms are responsible for delayed ettringite formation:

Portland cement concrete is attacked by solutions containing sulfate according to the generally accepted classical view. The $Al(OH)_3$ needed is supplied by monosulfate, hemicarbonate, monocarbonate or unhydrated aluminate or ferrite phases (eqn (4)).

Portland cement concrete containing monosulfate is attacked by CO_2. The interlayer SO_4^{2-} groups in the crystal structure of monosulfate are replaced by CO_3^{2-} (Fig. 6). As a result, the sulfate concentration in the pore solution increases and ettringite is reformed (eqn (6)).

Both reactions can occur only in thermodynamically 'open' cement systems because either sulfate-containing solutions or CO_2 and water have to be added. The reaction sequences can be understood on the basis of the phase assemblages stable in the system $C_3A{\cdot}Ca(OH)_2{\cdot}18H_2O$–$C_3A{\cdot}3CaSO_4{\cdot}32H_2O$–$C_3A{\cdot}3CaCO_3{\cdot}32\ H_2O$ examined by the author in the course of the last years.[14] Delayed ettringite formation according to eqn (6) is clearly a consequence of the fact that the composition points of monosulfate or hemisulfate and monocarbonate in the system are not connected by an Alkemade line, whereas those of monocarbonate and ettringite are connected. Thus monosulfate and monocarbonate cannot coexist and, with increasing absorption of CO_2, monosulfate is replaced by the stable phase assemblages ettringite + hemicarbonate or ettringite + monocarbonate.

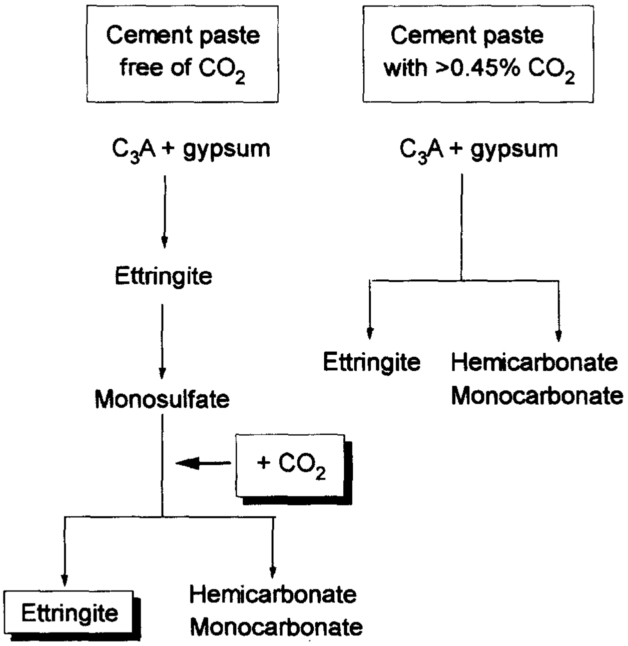

Fig. 5. Influence of CO_2 on C_3A hydration reactions in Portland cements.

It is not clear yet whether delayed ettringite formation by carbonation according to eqn (6) is merely of theoretical interest or whether it also affects the durability of concrete in practice, because only very limited information on the hydrates present in field concretes and mortars is available. In the course of the last few years the author has examined many commercial Portland cements and concretes. As he could neither find a cement with less than 0.5% CO_2 nor identify monosulfate with certainty in an ordinary mortar or concrete, he tends to believe that monosulfate generally does not occur unless the material was steam cured at more than 80°C, the limiting temperature for the stability of ettringite.[17]

However, to be on the safe side, it is recommended that a Portland cement should contain some reactive calcium carbonate in order to avoid the formation of monosulfate and consequent delayed ettringite formation as the first step of carbonation.

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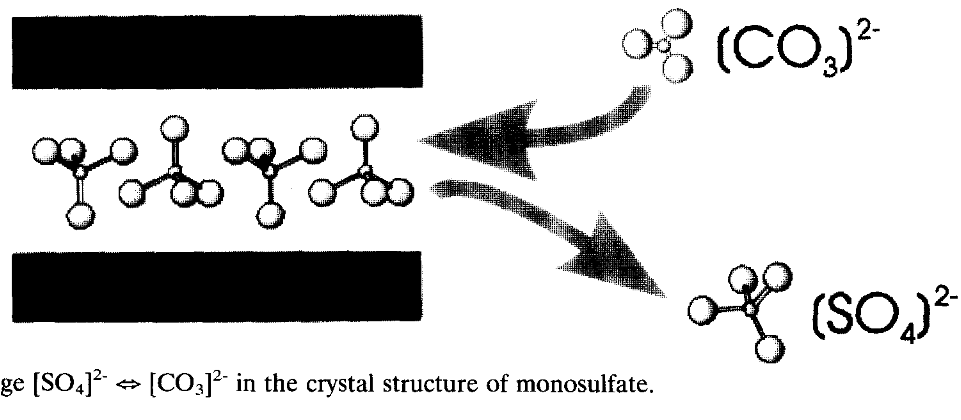

Fig. 6. Exchange $[SO_4]^{2-} \Leftrightarrow [CO_3]^{2-}$ in the crystal structure of monosulfate.

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