Influence of a long-term retarder on the hydration of clinker and cement

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Summary
This paper summarises the results of investigations on the effects of a long-term retarder (LTR) based on phosphonic acid (PBTC) on the hydration of several clinker phases (C₃S, C₃A, C₄AF), Portland cement clinker and Portland cement. It could be shown that long-term retardation is due to a thin sparingly soluble layer of calcium phosphonate on the particle surface. The formation of sparingly soluble calcium phosphonate requires 2.5 moles Ca²⁺ per mole PBTC. If enough Ca²⁺ is available sparingly soluble calcium phosphonate precipitates and forms a layer around the cement particles which retards further hydration immediately. In the contrary a lack of Ca²⁺ causes a short-termed acceleration in hydration of the reactive clinker phase C₃A. The investigations show that a controlled long-term retardation can only be achieved if the cement shows an optimal “natural” setting retardation, hence when the sulphate ingredient is fully compatible with the reactivity of C₃A.

Keywords: C₃A, C₄AF, C₃S, hydration, long-term retarder, PBTC, Portland cement clinker, Portland cement, retardation

1. Introduction
Long-term retarders (LTR) are organic retarders, which on account of their composition are capable of inhibiting the hydration of cement very strongly. During their use as recycling aids for wash water or residual concrete, they facilitate the cleaning of truck mixers and concrete mixers, and enable the recycling of the wash water or the residual concrete at sites which have no recycling water reservoir. Long-term retarders allowed in Germany as recycling aids consist of phosphonates and mainly contain 2-phosphono-butane-1,2,4-tricarboxylic acid (PBTC) [1,2]. PBTC shown in Figure 1 affects the hydration reactions of the cement with the mixing water very strongly. In addition to wash water and residual concrete recycling, long-term retarders are also used directly to control the hydration of the cement, e.g. in combination with accelerators for shotcrete in the wet-spray process in tunnel construction and in the deep drilling technology field, and in the production of bore piles and roller compacted concrete [3-6].

Fig. 1 PBTC-deprotonated
The knowledge concerning the interactions between the long-term retarding active component and cement is still inadequate [7]. Depending on the temperature and the time of addition, inverse reactions can occur with particular cements. For example, retarders may suddenly act as setting...
accelerators and/or severely impair the strength development of the concrete [7-11]. In practice, this can lead to costly chisel off and cleaning work, the loss of the mixing truck drum or even the destruction of entire bridge spans.

2. Aim and Extent of the Investigations

The aim of the investigations was to extend systematically knowledge concerning the effects of the PBTC-based long-term retarder on the hydration of clinker phases, clinker and cement. Firstly, the effect of the long-term retarder on the hydration of individual clinker phases (C_3A, C_4AF and C_3S) and on the hydration of mixtures of clinker phases, sulphate carriers and/or calcium hydroxide was studied chemically and mineralogically. The question as to whether and how the “natural” setting retardation, due to the reaction of C_3A or C_4AF fractions with dissolved sulphate to give ettringite, is influenced by the long-term retarder, was investigated by comparative studies between two industrial clinkers and on cements produced from them by the addition of sulphate. The chemical compound which leads to the long-term retardation was synthesised separately and chemically and mineralogically analysed. A model with which the mechanisms of action of this long-term retarder can be elucidated was derived. At some concretes with different amounts of LTR the compressive strength after 2, 7 and 28 days were tested.

3. Experimental procedures

For the hydration studies, pastes were mixed and the admixture was added dissolved in the mixing water. The admixture amount was included in the calculation of the water content used. The hydration products were investigated by ESEM/EDX, Differential Scanning Calorimetry (DSC) and X-Ray Diffraction (XRD). The sorption behaviour of the long-term retarder on clinker and cement was determined on suspensions (w/c = 3.75) over a period of 7 days by determination of the content of organic phosphorus in the solution. Pore solutions were filtered off from fresh cement paste with a vacuum pump, and pressed out in the case of hardened cement paste. Concretes composed of 300 kg/m³ CEM I 32,5 R, 1784 kg/m³ Rhine gravelly sand (A32/B32), 50 kg/m³ coal fly ash and 176 kg/m³ water.

4. Test Results

4.1. Influence of LTR on the hydration of synthetic clinker phases and of mixtures between clinker phases and calcium sulfate and/or calcium hydroxide

4.1.1. C_3S-hydration

Figure 2 shows an ESEM micrograph of unretarded C_3S paste at age of 28 days. Figure 3 displays a micrograph of C_3S paste with 2 mass % LTR at age of 180 days.

Comparison of the micrographs shows clearly that the LTR addition of 2 mass % (Fig. 3) led to complete blocking of the hydration of C_3S. While in the case of the unretarded sample (Fig. 2) a compact structure of sharp needle-shaped C-S-H phases had formed as a result of hydration, no hydration products could be observed on the surfaces of the long-term retarded sample (Fig. 3) even...
after 180 days. After this time, the pastes displayed a soft consistency, like that directly after the addition of water. The light areas on the particles in Figure 3 display a higher content of oxygen and also carbon and phosphorus, compared to the remaining particle surface. This points to a phosphorus-containing organic compound on the particle surface. In this region, the carbon/phosphorus ratio was between 2.7 and 2.9 and thus approximately corresponded to the carbon/phosphorus ratio of the LTR, of about 2.7. It must be presumed that this is a region in which the admixture has become concentrated. After a hydration period of one year, the sample with 2 mass % LTR had hardened. At this age, the microstructure, in addition to the very compact structures due to the progression of the hydration, also sporadically displayed relatively porous regions. In these regions, poorly hydrated C₃S particles were present.

4.1.2. C₃A-, C₄AF-hydration

Figures 4 and 5 show ESEM micrographs of C₃A paste without LTR and C₃A paste with 2 mass % LTR each at the ages of 3 min (top) and 28 days (bottom) respectively.

Whereas in the case of C₃A without LTR (Fig. 4) cubic calcium aluminium hydrates (C-A-H) could mainly be seen, in sample with 2 mass % LTR (Fig. 5) in particular hexagonal C-A-H, such as for example CAH₁₀, C₂AH₈ and C₄AH₁₁-13, were formed. The formation of cubic C-A-H or the conversion of the hexagonal C-A-H into cubic C-A-H was strongly impeded by the LTR. The same was observed with the hydration of C₄AF in the presence of LTR. X-ray diffraction studies at the age of 28 days showed that overall LTR increased the C₃A hydration. On the other hand, the hydration of C₄AF was decreased by LTR.

In mixtures composed of three parts C₃A and one part hemihydrate and anhydrite respectively the formation of primary ettringite was initially accelerated by LTR for a short time. The further progress of the hydration of C₃A was strongly retarded. After 28 days the long-term retarded sample still displayed unhydrated hemihydrate. Samples which contained additional calcium hydroxide showed a normal formation of primary ettringite and a strong retardation of further hydration reactions. A similar situation was observed in the samples with C₄AF.
At all trials with calcium aluminates no organic compounds due to LTR like on the surface of C$_3$S, could be detected by EDX. This is due to the enlarged specific surface area caused by the hexagonal C-A-H.

4.2. Influence of LTR on the hydration of Portland cement clinker and Portland cements and on the compressive strength of concretes

Investigations of the sorption behaviour shows clearly that already 30 seconds after addition 93% of LTR was sorbed on the surface of cement particles. After 7 days LTR was sorbed completely.

With Portland cement clinkers or with Portland cements without calcium sulphate, LTR caused a short-term increase in the formation of hexagonal calcium aluminate hydrates, such as for example C$_2$AH$_8$ and C$_4$AH$_{11-13}$. As a result, the stiffening or setting of the pastes was accelerated. Portland cements weren’t accelerated by LTR. The coat of primary ettringite always formed on the Portland cements particles gained the retarding action of LTR. The hydration of the silicate phases was particularly strongly retarded by LTR.

The pore solutions of the retarded clinker pastes displayed higher contents of calcium and pore solutions of retarded cement pastes higher sulphate contents in addition. This was attributable firstly to the briefly intensified hydrolysis of the calcium aluminates and secondly to the stabilisation of submicroscopic crystal nuclei, e.g. of CaSO$_4$ or ettringite, by the residual LTR present in solution. After the retardation period, the calcium and sulphate concentration in the pore solution in question decreased as hydration recommenced [7]. Whereas with pure C$_3$S the LTR resulted in complete blocking of the hydration up to 180 days, at age 28 days all pastes and mortars produced with clinker and cement showed approximately the same hydration progress as the corresponding unretarded reference sample. This means that after the retardation a more rapid hydration set in.

Figure 6 shows the development of the compressive strength of normal Portland cement concretes with different dosages of LTR. The concretes were stored at 20 °C/100 % rel. humidity for 28 days.

![Figure 6 Compressive strength of concretes with different dosages LTR after 2, 7 and 28 days](image)

The concretes with LTR showed hardly any hardening at age of 2 days. With an increasing LTR-dosage the compressive strength after 7 days decreased corresponding to the extended retardation times. Moist curing up to 28 days resulted in a nearly identic compressive strength regardless of the LTR-dosage. Shorter curing led to a considerable loss of compressive strength in particular at LTR-dosages higher than 1.5 mass %.

5. Mechanisms of action of the PBTC-based LTR

From the information gained in these studies, the main mechanisms of action of the LTR can be derived. By way of example, Figure 7 and Figure 8 respectively show the mechanisms of action of the LTR on Portland cement clinker and Portland cement schematically. In an alkaline medium, PBTC (C$_7$H$_{11}$O$_9$P) releases 5 protons and is present in completely dissociated form ([C$_7$H$_6$O$_9$P]$^-$). For the immediate formation of sparingly soluble calcium phosphonate (Ca$_{2.5}$[C$_7$H$_6$O$_9$P]$_2$), 2.5 moles of calcium are needed per mole of PBTC. A molar ratio Ca/PBTC below 2.5 leads to soluble calcium phosphonate complexes of lower calcium content.
If LTR is added to Portland cement clinker without calcium sulphate carrier (Fig. 7) the calcium content in the pore solution is not sufficient to form sparingly soluble calcium phosphonate. Because of the calcium demand of the PBTC, there is generally a short-termed accelerated hydration of reactive clinker phases such as for example C₃A. This causes an increased formation of hexagonal Cₐ-H and results in a marked stiffening or setting.

The calcium ions released during this brief acceleration phase are bound by PBTC. The sparingly soluble calcium phosphonate (Ca₂(C₇H₆O₉P)₅) thus formed coats the surfaces of the individual clinker particles differently. On the surfaces of relatively unreac tive clinker phases such as for example C₃S and C₂S, which are still largely free from hydration products when the sparingly soluble compound is formed, essentially complete coating with calcium phosphonate can take place. As a result, the further access of water (H) or further ion exchange are markedly hindered and the hydration is retarded. Already hydrated surfaces, such as for example that of the C₃A, display a relatively large specific surface area, which cannot be completely covered with sparingly soluble calcium phosphonate. The access of water and ion exchange cannot be completely blocked. For this reason, compared to the less reactive clinker phases, the hydration of reactive calcium aluminates is mostly only slightly retarded by calcium phosphonate formed from LTR.

Because of the sulphate carrier (C₅SHₓ) contained in the Portland cement (Fig. 8), the concentration of calcium and sulphate in the pore solution is much higher than in the system containing only clinker. A thin layer of primary ettringite can form on the surface of the calcium aluminate. Moreover, sufficient calcium ions are available for the immediate formation of sparingly soluble calcium phosphonate. The calcium phosphonate coats both the surfaces of the clinker particle and also those of the still undissolved sulphate carrier. As a result, further hydration is strongly blocked.

The formation of primary ettringite and the coating of the surfaces with sparingly soluble calcium phosphonate constitute the precondition for planned prolongation of the workability by the long-term retarder. This means that sulphate carrier optimisation is not only the basis for the control of the setting of the cement, but also a precondition for the desired mode of action of the admixture.

6. Conclusion

By systematic studies, the state of knowledge concerning the effects of a long-term retarder (LTR) based on 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC) on the hydration of clinker phases (C₃S, C₃A and C₄AF), clinker and cement has been substantially extended. The following conclusions were drawn from the research results:

In the hydration of pure C₃A and C₄AF the retarder results in an increased formation of hexagonal calcium aluminate hydrate (Cₐ-H). Apart from this, the conversion of hexagonal Cₐ-H into cubic hydrates is strongly retarded. The conversion of C₃A is increased, and that of C₄AF decreased.
The hydration of pure C₃S was completely blocked for up to 180 days. The retarder action is attributable to the formation of sparingly soluble calcium phosphonate (Ca₂.₅[C₇H₆O₉P] ⋅ xH₂O). The formation of sparingly soluble calcium phosphonate requires 2.5 moles Ca²⁺ per mole of PBTC. If enough Ca²⁺ is available in the pore solution, sparingly soluble calcium phosphonate precipitates and forms a closed layer around the cement particles which retards further hydration immediately. Conversely, a lack of Ca²⁺ causes a short-term acceleration in hydration of the reactive clinker phase C₃A. Due to the formation of C-A-H the specific surface area increases. Therefore the formation of a closed layer of calcium phosphonate is impeded and the hydration of the calcium aluminates progresses.

With Portland cements, owing to the content of calcium sulphate, sufficient quantities of dissolved calcium are present for the direct formation of calcium phosphonate. The formation of primary ettringite and the coating of the surfaces with sparingly soluble calcium phosphonate are the precondition for planned prolongation of the workability by the long-term retarder. If calcium sulphate is absent or present in insufficient amount, for example in the case of Portland cement clinkers, the calcium demand of the LTR active substance PBTC results in a short-term acceleration of the hydration of reactive clinker phases, e.g. C₃A.

The direct formation of an ettringite layer on the cement particle and the simultaneous supply of calcium ions are not only important for controlling the setting of the cement but also for the desired mode of action of the long-term retarder. Therefore the retarder can’t take over the regulation of setting of cement instead of calcium sulfate optimisation.

Long-term retarded concretes, moist cured during the retardation time, developed the same compressive strength like unretarded concretes.

7. References