



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

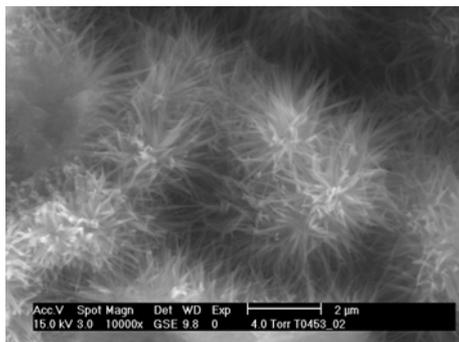
For the hydration studies, pastes were mixed and the admixture was added dissolved in the mixing water. The admixture amount was included in the calculation of the water content used. The hydration products were investigated by ESEM/EDX, Differential Scanning Calorimetry (DSC) and X-Ray Diffraction (XRD). 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  $300 \text{ kg/m}^3$  CEM I 32,5 R,  $1784 \text{ kg/m}^3$  Rhine gravelly sand (A32/B32),  $50 \text{ kg/m}^3$  coal fly ash and  $176 \text{ kg/m}^3$  water.

## 4. Test Results

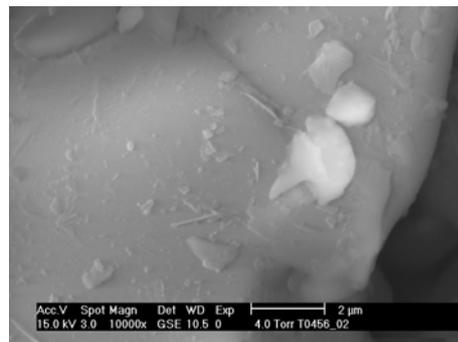
### 4.1. Influence of LTR on the hydration of synthetic clinker phases and of mixtures between clinker phases and calcium sulfate and/or calcium hydroxide

#### 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.



*Fig. 2  $w/C_3S = 0.50$ , at age of 28 days, normal hydration, development of C-S-H phases – paste hardened*



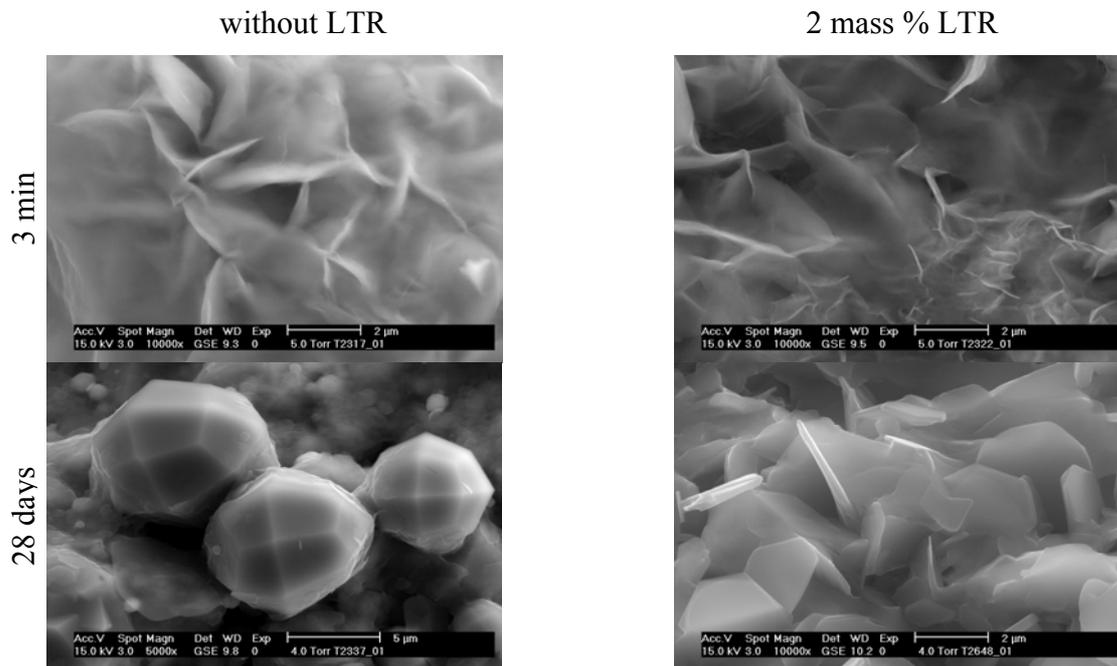
*Fig. 3  $w/C_3S = 0.50$ , 2 mass % LTR, at age of 180 days, no hydration products – paste can still be processed*

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  $C_3S$  particles were present.

#### 4.1.2. $C_3A$ -, $C_4AF$ -hydration

Figures 4 and 5 show ESEM micrographs of  $C_3A$  paste without LTR and  $C_3A$  paste with 2 mass % LTR each at the ages of 3 min (top) and 28 days (bottom) respectively.



*Fig. 4  $w/C_3A = 1.00$ , at age of 3 min: formation of hexagonal and cubic C-A-H, at an age of 28 days: conversion of hexagonal C-A-H to cubic C-A-H ( $C_3AH_6$ -hydrogarnet)*

*Fig. 5  $w/C_3A = 1.00$ , 2 mass % LTR, at age of 3 min and 28 days: hexagonal C-A-H predominantly, no conversion after 28 days*

Whereas in the case of  $C_3A$  without LTR (Fig. 4) cubic calcium aluminat 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  $CAH_{10}$ ,  $C_2AH_8$  and  $C_4AH_{11-13}$ , 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  $C_4AF$  in the presence of LTR. X-ray diffraction studies at the age of 28 days showed that overall LTR increased the  $C_3A$  hydration. On the other hand, the hydration of  $C_4AF$  was decreased by LTR.

In mixtures composed of three parts  $C_3A$  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  $C_3A$  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  $C_4AF$ .

At all trials with calcium aluminates no organic compounds due to LTR like on the surface of  $C_3S$ , 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  $C_2AH_8$  and  $C_4AH_{11-13}$ . 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  $C_3S$  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.

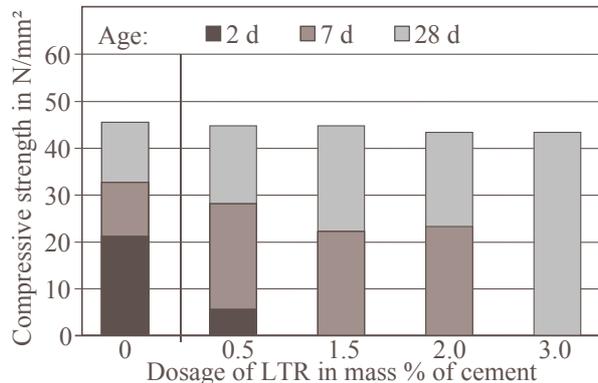


Fig. 6 Compressive strength of concretes with different dosages LTR after 2, 7 and 28 days

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 identical 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 ( $C_7H_{11}O_9P$ ) releases 5 protons and is present in completely dissociated form ( $[C_7H_6O_9P]^{5-}$ ). For the immediate formation of sparingly soluble calcium phosphonate ( $Ca_{2.5}[C_7H_6O_9P]$ ), 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 C<sub>3</sub>A. This causes an increased formation of hexagonal C-A-H and results in a marked stiffening or setting.

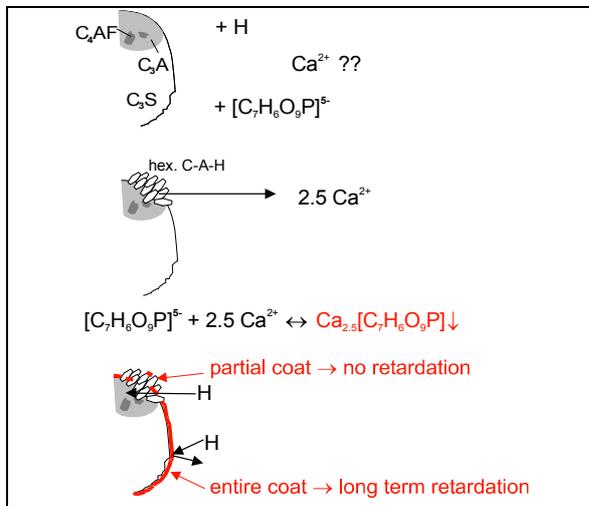


Fig. 7 Effect of LTR on hydration of Portland cement clinker without or with non-optimised supply of CaSO<sub>4</sub>

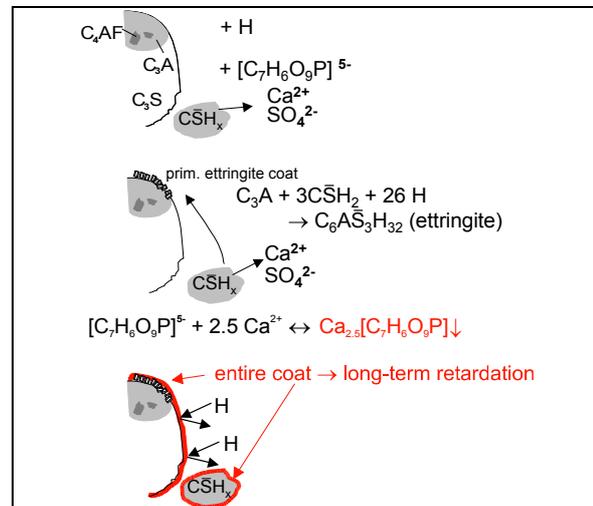


Fig. 8 Effect of LTR on hydration of Portland cement with optimised supply of CaSO<sub>4</sub>

The calcium ions released during this brief acceleration phase are bound by PBTC. The sparingly soluble calcium phosphonate (Ca<sub>2.5</sub>[C<sub>7</sub>H<sub>6</sub>O<sub>9</sub>P]) thus formed coats the surfaces of the individual clinker particles differently. On the surfaces of relatively unreactive clinker phases such as for example C<sub>3</sub>S and C<sub>2</sub>S, 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 C<sub>3</sub>A, 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 ( $\overline{CSH}_x$ ) 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 (C<sub>3</sub>S, C<sub>3</sub>A and C<sub>4</sub>AF), clinker and cement has been substantially extended. The following conclusions were drawn from the research results:

In the hydration of pure C<sub>3</sub>A and C<sub>4</sub>AF the retarder results in an increased formation of hexagonal calcium aluminate hydrate (C-A-H). Apart from this, the conversion of hexagonal C-A-H into cubic hydrates is strongly retarded. The conversion of C<sub>3</sub>A is increased, and that of C<sub>4</sub>AF decreased.

The hydration of pure  $C_3S$  was completely blocked for up to 180 days.

The retarder action is attributable to the formation of sparingly soluble calcium phosphonate ( $Ca_{2.5}[C_7H_6O_9P] \cdot xH_2O$ ). The formation of sparingly soluble calcium phosphonate requires 2.5 moles  $Ca^{2+}$  per mole of PBTC. If enough  $Ca^{2+}$  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  $Ca^{2+}$  causes a short-term acceleration in hydration of the reactive clinker phase  $C_3A$ . 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.  $C_3A$ .

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

- [1] BAYER AG, *BAYHIBIT-Anwendungen, Wirkungen, Eigenschaften*, Bayer AG, Anorganische Industrieprodukte, Leverkusen, Germany, 4/1998
- [2] DEUTSCHE BAUCHEMIE E.V., *Betonzusatzmittel und Umwelt, Sachstandsbericht*, Mai 1999, 3. Ausgabe, BAUCOM, Boehl-Iggelheim
- [3] BOBROWSKI, G. S., GUECIA, G.C.J., LUPYAN, D.A. and KINNEY, F.D., *Wiederaufbereitung von Betonmischungen*, German Patent DE 3727907, 1996
- [4] WENQUAN, L., HUIZHEN, L., ZHEN, H. and YAJIE, L., *Use of high range Retarder-Plasticizer for Roller-Compacted Concrete of the Three Gorges Project in China*. Fifth CANMET/ACI Superplasticizers and Other Chemical Admixtures, Italy, 1997, pp. 835-845
- [5] PAOLINI, M. and KHURANA, R., "Admixtures for Recycling of Waste Concrete", *Cement Concrete Composites*, 1998, Vol. 20, No. 2/3, pp. 221-229
- [6] OKAWA, Y. ; YAMAMIYA, H. and NISHIBAYASHI, S., "Study on the reuse of returned concrete", *Mag. of Concr. Res.*, 2000, Vol. 52, No. 2, pp. 109-115
- [7] RICKERT, J., *Zum Einfluss von Langzeitverzögerern auf der Basis von Phosphonsäure auf die Hydratation einzelner Klinkerphasen, Portlandzementklinker und Portlandzemente*, Bauhaus-Universität Weimar, Dissertation, (publication expected in 2004)
- [8] RICHARTZ, W. "Einfluss von Zusätzen auf das Erstarrungsverhalten von Zement" *Beton*, 1983, Vol. 33, No. 11, pp. 425-429 and No. 12, pp. 465-471
- [9] LIPUS, K., RICKERT, J. and SYLLA, H.-M., *ESEM-Untersuchungen zur Hydratation von Portlandzement unter Einfluß von verzögernden Zusatzmitteln*. 14<sup>th</sup> ibausil, Weimar, Bauhaus-Universität Weimar, 2000, pp. 301-313
- [10] RICKERT, J. "Influence of Retarders on the Hydration of Clinker and Cement", *Concrete Technology Reports 2001-2003*, Verlag Bau+Technik, Duesseldorf (publication expected in 2004)
- [11] RICKERT, J. and THIELEN, G. "Influence of a long-term retarder on the hydration of clinker and cement", *Cement, Concrete, and Aggregates*, ASTM Intern. (publ. expected in 2004)