



Dr. Ingo Müller graduated 1993 in Mineralogy (Diploma) at Ruhr-University Bochum, Germany. During his studies and until 1996, he already worked as preservationist of heritage buildings at Zollern Institute Bochum. He joined Hercules, Inc. Düsseldorf as scientist and earned his PhD in Mineralogy at Westphalian Wilhelm-University in Münster. Since 2008 he acts as project manager at Wacker Chemie AG (Wacker Polymer Systems).

Dr. Ingo Müller | Wacker Chemie AG | Burghausen, Germany

# Logistic Fitting – A mathematical Analysis of Ultrasonic Velocity-time-curves

## ABSTRACT

The measurement of the sonic velocity of an ultrasonic impulse is used to monitor the setting behavior of mineral binder systems such as cements, mortars and concretes. A data processing method by the means of mathematical analysis was developed by Wacker Chemie AG and UltraTest GmbH to retrieve more information from velocity-time-curves. A sum function of logistic terms is fitted to the curve and the 1<sup>st</sup> to 3<sup>rd</sup> derivative is computed to provide data of sonic acceleration and key parameters of setting processes. A cost and time effective software solution – the Logistic Fitting Module (LFM) – was developed in cooperation with d:Al:mond, a software developer.

This study investigates the utility of the Logistic Fitting Module using the examples of ordinary Portland cement (OPC) and a simple OPC-based tile adhesive. Results of ultrasonic measurements (US) are compared to those of alternative and complimentary test methods as heat flux calorimetry (HFC), X-ray diffractometry (XRD) and Vicat needle penetration tests. This investigation will show that ultrasonic measurements correlate well with those complementary test methods.

## INTRODUCTION

Using ultrasonic testing devices from UltraTest a sonic impulse is transmitted through the mortar samples over a distance of 30 mm. The travelling time of the impulse is measured and the sonic velocity calculated as distance divided by travelling time. The dynamic elastic modulus  $E_d$  – an important material constant in concrete industries – is a function of the sonic velocity and can therefore be determined by ultrasonic measurements [1]:

$$E_d = \frac{u^2 \rho (1 + \nu)(1 - 2\nu)}{(1 - \nu)}$$

$u$  = sonic velocity,  $\rho$  = sample bulk density,  
 $\nu$  = Poisson's ratio

In dry mortar industries the elastic modulus plays a minor role. Instead four different kinds of strength – compressive strength, flexural strength, tensile strength and shear bond strength are determined by classic mechanical test methods. Strength is a function of the elastic modulus which can be determined as a function of sonic velocity. So strength itself can be described as a function of sonic velocity, yet with unknown and probably non-linear correlation based on a variety of material parameters and thus depending on the used binder formulation. In the author's experience a correlation between sonic velocity at a given time point of hydration can be correlated with a certain absolute figure of achieved strength. But this correlation has to be determined for each binder formulation and

for each kind of strength separately. With myriads of formulations in the construction material market it is senseless to try to correlate all of them unless a limited portfolio of formulations has to be correlated. Nevertheless, there is a simple fact of the velocity-strength-relation: strength increases with rising sonic velocity – yet in a non-linear way – and decreases with declining velocity.

Looking at the time velocity curve of a setting OPC (fig. 1) we see that the inclination of the graph changes over hydration time with several inflexion points indicating that cement setting is a superimposition of several strength developing stages. The first derivative (sonic acceleration) illustrates the stages much better. At the very beginning of cement hydration there is a slight stiffening indicated by a sharp acceleration peak (A). After a dormant period of a local acceleration minimum a broad peak (2-5 h) indicates cement setting according to Vicat (B) followed by an even broader peak (6-12h) indicating the beginning of hardening (C).

But here is a problem: the velocity-time curve is just an x-y-plot of measured data not a derivable function. Instead of a real 1<sup>st</sup> derivative an approximative  $\Delta v/\Delta t$ -function with a  $\Delta t$  over 15 measurements is plotted in figure 1:

$$a(t_i) = \frac{\Delta u}{\Delta t} = \frac{u(t_{i+7}) - u(t_{i-7})}{t_{i+7} - t_{i-7}}$$

$a(t_i)$  = sonic acceleration at  $t_i$ ,  $t_i$  = time point of interest,  
 $u(t_{i\pm 7})$  = sonic velocity of the 7<sup>th</sup> measurement before respectively after  $t_i$ ,

The  $\Delta v/\Delta t$ -option is provided by the UltraTestLabsoftware, the data processing and device-controlling software by UltraTest. A disadvantage of  $\Delta v/\Delta t$  is that any little uncertainty of the velocity measurement is significantly amplified in the acceleration curve leading to signal loss in white noise at high velocities, reduced temporal resolution and inaccuracies of peak positions (climax points of acceleration) especially at early hydration times.

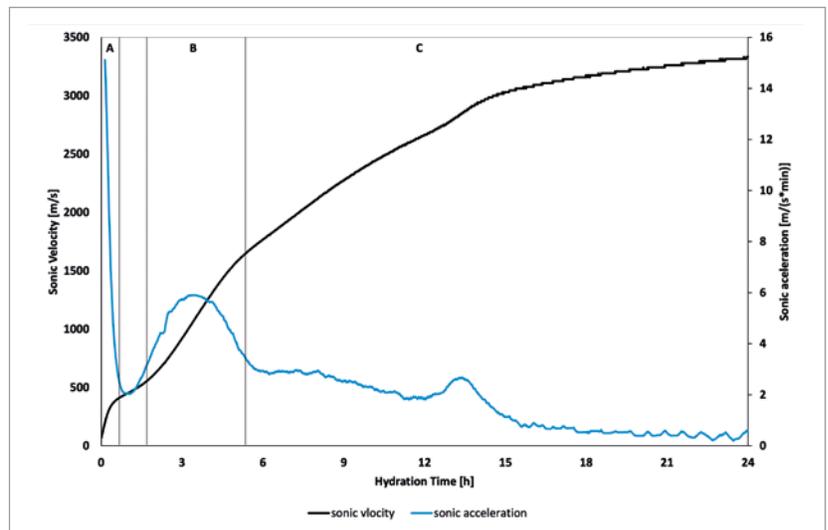


Fig. 1: Development of sonic velocity and acceleration of an ordinary Portland cement over the first 24 hours of hydration. The sonic acceleration illustrates the classic stages in which the setting cement changes its consistency from a creamy paste to a hard and brittle solid-state body: initial stiffening (A), setting according to Vicat (B) and hardening (C).

## LOGISTIC FITTING

To overcome the problems of the  $\Delta v/\Delta t$ -curve a mathematic method was developed at Wacker Chemie AG to fit a derivable function to the velocity-time curve. From that function the derivatives can be computed even for single processes and key data of acceleration peaks can be determined. In search of suitable functions two possible solutions were found: the trigonometric arcus tangent function and the exponential "logistic function". Both functions are equivalent and can be transcribed into each other. For the easier derivation the logistic function was chosen. By the way, the author had no idea what a trigonometric function has to do with cement setting.

The logistic function describes the growth of anything at limited resources [2] and is traditionally used by biologists and economists to describe the growth of a bacteria population respectively market growth:

$$P(t) = \frac{P_{max}}{1 + \left(\frac{P_{max}}{P_0} - 1\right) e^{-kP_{max}t}}$$

$P(t)$  = population (market share) at a given time  $t$ ,  $P_{max}$  = maximum population (market potential),  $P_0$  = population at  $t=0$  (start of experiment / product launch),  $k$  = kinetic proportionality factor

The fact that the logistic function describes a growth process may also serve as physicochemical justification for using it to describe cement set. Rising sonic velocity is at the end caused by crystal growth with the ion concentration in the pore solution as limited resource. Adopting the function to our needs and by eliminating some unnecessary marginal conditions the logistic function could be simplified to the following form:

$$u(t) = \frac{u_{max}}{1 + e^{-k(t-t_d)}}$$

$u_{max}$  = maximum sonic velocity,  $t_d$  = delay time

A single logistic function describes only one single growth process. Since cement hydration is a complex superimposition of several different processes the fitting function must be rewritten as a sum function of several logistic terms:

$$u(t) = u_0 + \sum_{i=1}^n \frac{u_i}{1 + e^{-k_i(t-t_i)}}$$

$u_0$  = integration constant

The number of terms  $n$  depends on the complexity of the formulation and the time frame of observation. A pure ordinary Portland cement demands 6 to 9 terms in 24 hours whereas a complex ternary system needs up to 16 terms in 4 days. Once the sum function is fitted to the time velocity curve the 1<sup>st</sup> derivative, the sonic acceleration  $a(t)$  can be computed.

$$a(t) = \sum_{i=1}^n \frac{u_i k_i e^{-k_i(t-t_i)}}{(1 + e^{-k_i(t-t_i)})^2}$$

$3n+1$  parameters have to be fitted resulting in 49 fitting parameters for the most complex formulation ever tested. To do that in a cost and time effective way a fitting software was developed in a cooperation of Wacker with UltraTest and d:Al:mond. The software is commercially available, is distributed by UltraTest and comes as an add-in module for the UltraTestLab software. The so-called Logistic Fitting Module (LFM) is designed for 20 terms. The accuracy of the fit achieved with the LFM is illustrated in figure 2.

Since the single peaks of sonic acceleration shall be traced back to single hydration processes it is worthwhile to look at the graphs of the single acceleration terms (fig. 3).

The Portland cement used in this study (Milke 52.5 R Premium) shows four distinct peaks of the global acceleration curve (sum function). This is typical for OPC but not each cement shows the broad 3<sup>rd</sup> peak (at 8 h) with such a clarity. This peak is often superimposed by neighbored peaks and shows up as a shoulder or even worth as an asymmetry of the previous or following peak.

## INVESTIGATION OF ORDINARY PORTLAND CEMENT

Pure OPC cannot be investigated by ultrasonics because shrinkage during hydration causes microcracks and loss of contact at the sender/receiver-specimen-interface. This leads to disturbed and interrupted signal transmission. Therefore a mixture of 35 % OPC and 65 % silica sand is used. The silica sand is supposed to be inert thus having no effect on the hydration kinetic. The absolute values of sonic velocity might differ from those of pure OPC because of the high silica volume. Since we focus on the temporal development of sonic acceleration this does not matter as long as the aggregates do not change hydration kinetics. This is also true for the heat flux where it does not matter if silica sand is added or not. The absolute values of heat development drop down because of the dilution of cement with sand but the temporal development of heat flux does not change. The basic mixture of cement and silica sand without any further additives is not regarded as mortar but as an equivalent substitute of pure cement for those test methods. Vicat needle penetration tests were done with this basic mixture as well because crack formation would falsify the results. XRD investigations were performed without aggregates because X-ray reflexes of quartz would superimpose those of cement phases and the dilution of cement will lead to an inferior signal-noise-ratio. The water/cement ratio was the same for all those investigations.

As demonstrated in figure 3 the sonic acceleration gives evidence of hydration processes effecting the consistency of mortars but does not reveal the nature of those processes. Therefore a correlation with complimentary test methods is needed.

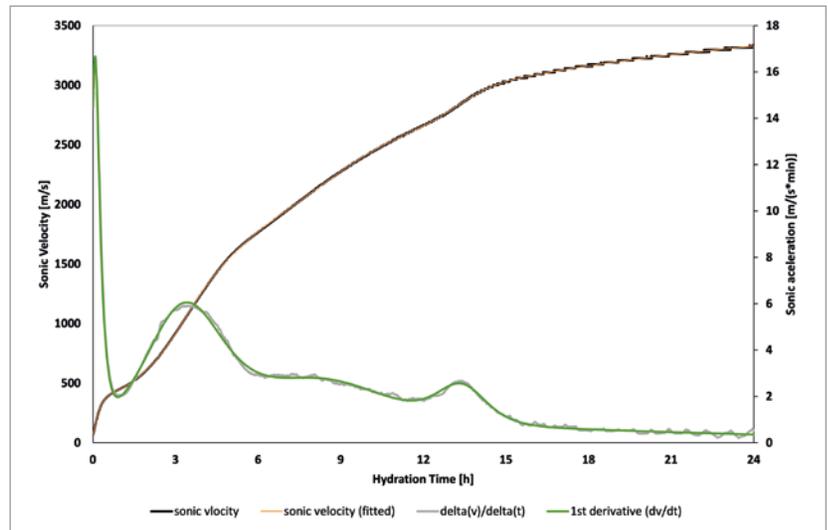


Fig. 2: Measured data versus fitted function. The logistic sum function is fits very well. Its thin yellow graph superimposes the black time velocity curve perfectly.

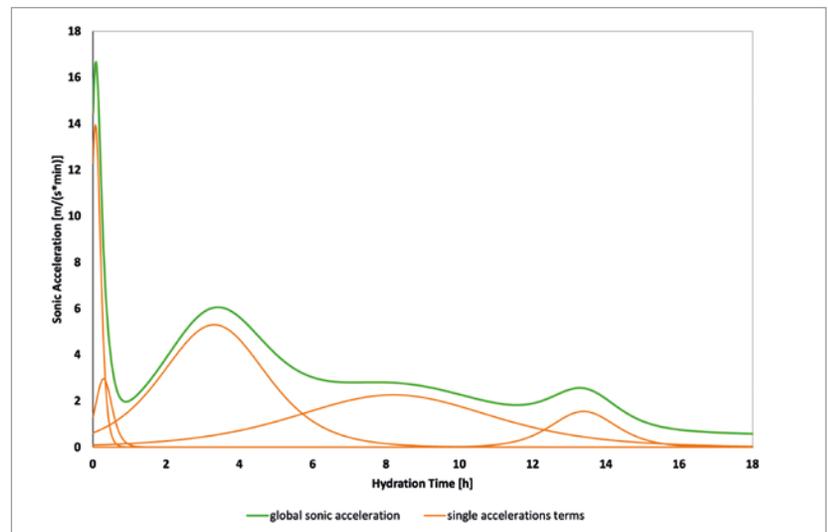


Fig. 3: The first derivatives of single terms give evidence of hydration processes leading to significant changes of the mortar consistence.

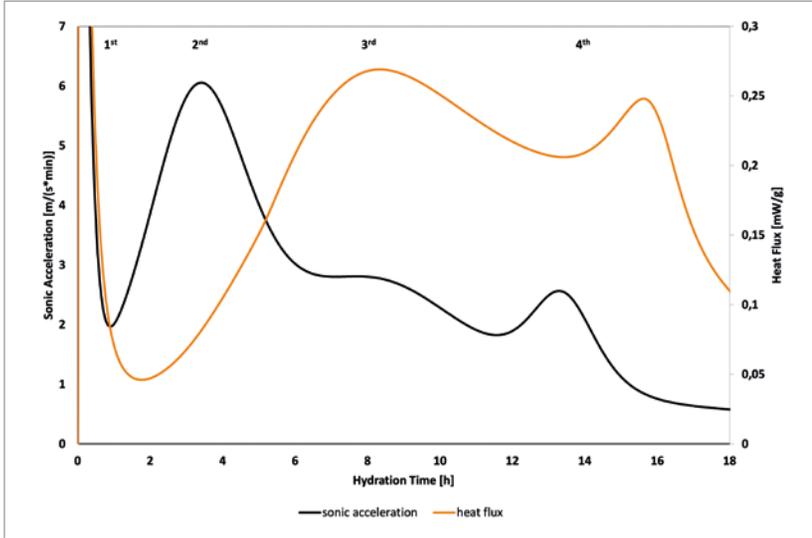


Fig. 4: Comparison of sonic acceleration and heat flux. Except of the 2<sup>nd</sup> one each sonic acceleration peak has a corresponding exothermal event.

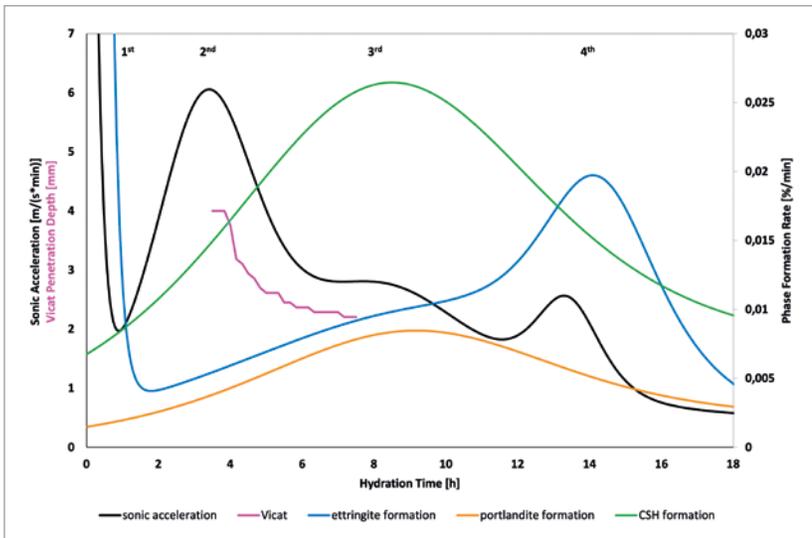


Fig. 5: Sonic acceleration compared to phase formation as determined by XRD and setting according to Vicat

## ULTRASONIC VERSUS HEAT FLUX

The heat flux peak pattern shows some similarity with that of ultrasonics (fig. 4) though with a significant difference: the second sonic acceleration peak has no corresponding heat flux event. Heat flux at this point of time is not down to zero but close to a local minimum. The 1<sup>st</sup>, 3<sup>rd</sup> and 4<sup>th</sup> acceleration peak correspond with heat flux events. Thus the changes in mortar consistency as indicated by sonic acceleration can be traced back to exothermal chemical or physical reactions except of the 2<sup>nd</sup> sonic acceleration event.

## ULTRASONIC VERSUS XRD

Quantitative phase analysis was performed by the Institute of Mineralogy at the University of Erlangen by the means of X-ray diffractometry and subsequent Rietveld analysis. The phase development in setting mortars was monitored in-situ over 24 hours with a temporal resolution of 30 minutes. The X-ray-amorphous CSH was quantified by mass balance from C<sub>3</sub>S-consumption. A logistic sum function can be fitted to the phase-content-time curve of each hydrated phase. Because of inaccuracies of XRD-Rietveld analysis the phase-content-time graph is quite rough. Nonetheless the logistic fitting method allows to determine the precipitation rate (R) of hydrated phases as 1<sup>st</sup> derivative of the phase content (C) over time. The achieved accuracy allows the correlation of XRD data with US and HFC results.

$$C(t) = C_0 + \sum_{i=1}^n \frac{C_i}{1 + e^{-k_i(t-t_i)}}$$

$$R = \frac{dC}{dt} = \sum_{i=1}^n \frac{C_i k_i e^{-k_i(t-t_i)}}{(1 + e^{-k_i(t-t_i)})^2}$$

As shown in figure 5 the first and fourth acceleration peak correlate perfectly with increased ettringite precipitation. Little ettringite is also formed during sonic acceleration of the third peak. The third sonic acceleration event is essentially triggered by portlandite and CSH formation during the main silicate hydration process. The second acceleration peak correlates best with the setting onset according to Vicat while hydrate phase formation is close to local minima albeit not down to zero. As expected, the phase formations monitored by XRD correlate with HFC data (compare fig. 5 with fig. 4) because hydrate phase precipitation is an exothermal process.

#### PORTLAND CEMENT HYDRATION

The four steps of sonic acceleration during OPC hydration correlate well with the findings in cement research of the last decades. The steps of hydration can be listed in the following way:

1. Directly after water addition the pore solution is undersaturated in any aspect and clinker phases dissolve quickly.  $C_3A$  as the most active clinker phase reacts immediately with sulfates forming ettringite. This leads to a slight stiffening of the mortar paste and is recorded as sonic acceleration of the first peak. Ettringite precipitation can also be determined easily by XRD. It also contributes to heat release as recorded by HFC. But at this early stage the first heat flux peak is a superimposition of exothermal ettringite crystallization and clinker dissolution heat.
2. The ion concentration in the pore water increases rapidly. Especially the calcium ion concentration reaches saturation level soon.  $C_3A$  becomes less soluble in this saturated pore solution and ettringite crystallization nearly dies on starvation for aluminum [3]. Yet the pore solution does not reach supersaturation in respect of portlandite and CSH precipitation. Crystallization processes, heat flux and sonic acceleration come to a local minimum.
3. The silicate dissolution slows down in Ca-saturated solution but does not stop completely. Juilland et al. [4] showed that  $C_3S$ -dissolution turns from a rapid diffusion-controlled process to a slow surface-controlled one where unit cell step retreat at the surface of  $C_3S$  plays a critical role. Despite of the high ion concentration Ca- and silicate ions dissolve slowly from disadvantageous atom positions at the edges of unit cell steps. Thus the ion concentration in the pore solution still increases slowly and steadily. Eventually supersaturation in respect of portlandite and CSH is reached and both hydrate phases start to precipitate slowly at first. The onset of CSH and portlandite precipitation correlates with a local maximum of sonic acceleration (2<sup>nd</sup> peak). Ettringite precipitation was never down to zero and accelerates slightly at this stage. Although  $C_3A$  should be insoluble at this Ca-concentration level the author assumes that surface-controlled dissolution as observed and proofed for  $C_3S$  is probably also true for  $C_3A$ . The little hydrate phases formed at this stage is obviously responsible for a significant change in the mortar consistency as observed in Vicat needle penetration tests and ultrasonic measurements.
4. Ettringite, portlandite and CSH precipitation serves as a Ca-ion sink for the pore solution. The Ca-ion concentration decreases during main hydration as Rothstein et al. reported [5]. Portlandite and CSH precipitation accelerate with decreasing ion concentration. The coalescence of tiny CSH needles in the mortar matrix affects the sonic acceleration (3<sup>rd</sup> peak). Eventually undersaturation is reached in respect of  $C_3A$ . Aluminate dissolution and ettringite precipitation accelerate significantly and is detected by XRD, HFC and ultrasonic (4<sup>th</sup> peak).

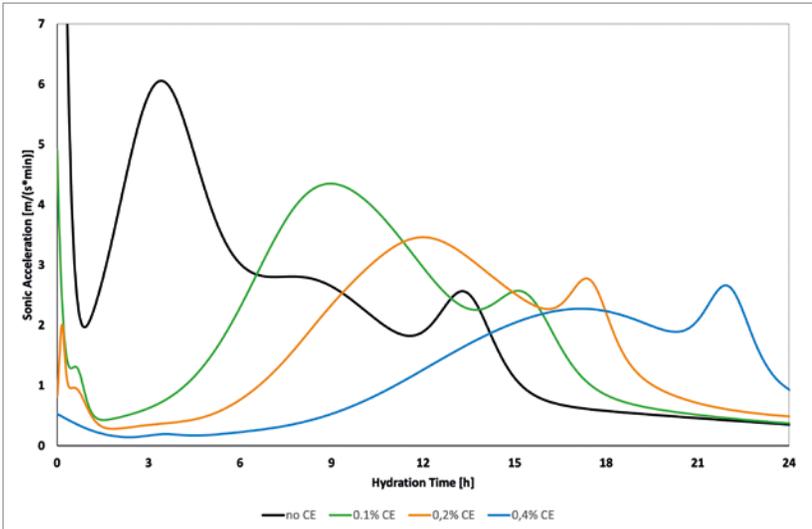


Fig. 6: Sonic acceleration in CE-modified mortar at difference addition levels of CE-type 1

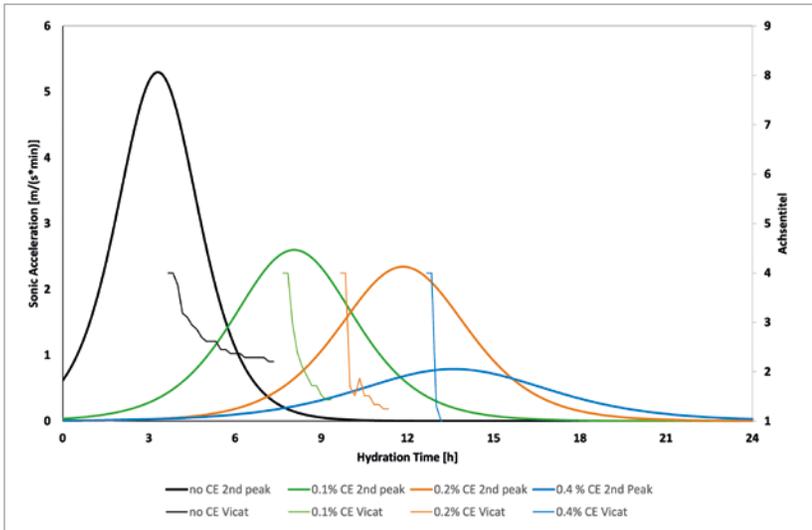


Fig. 7: Vicat setting times of mortars modified with CE-type 1 at different dosages in comparison with the second sonic acceleration event

## RETARDING EFFECTS OF CELLULOSE ETHERS MONITORED BY ULTRASONIC MEASUREMENTS

The target of this study was not to determine the interactions of OPC with cellulose ether (CE). This has been described in detail 15 years ago [3]. The aim was to proof the merit of ultrasonic measurements not only in pure binder formulations but in applicable mortar formulations, too. Logistic fitting applied on ultrasonic data can only persist as suitable test method in dry mortar application if the effects of additives are reflected in LFM data output. As a first step a primitive cementitious tile adhesive was used to demonstrate the utility of ultrasonic testing. A primitive tile adhesive for thin-bed application is a mixture of 35 % OPC, 65 % silica sand and +0.4 % CE on top. Three different grades of unmodified (i.e. pure) CE with different degrees of substitution (DS) from Ashland were used. Those types were chosen because they are best known by the author in contrast to competitive products.

As reported [3] CE has a direct phase-specific retarding effect on the silicate hydration of OPC depending on the degree of substitution and the addition level, of course. The retardation is caused by adsorption of CE on the surface of hydrate phases leading to surface intoxication and reduced crystal growth. The mass values of adsorbed CE-molecules depend on the degree of substitution: the lower the DS the higher the amount of adsorbed CE. The sequence of average DS-values for the three CE-types are as follows:

$$DS_{\text{Type 1}} \ll DS_{\text{Type 2}} < DS_{\text{Type 3}}$$

CE provided with kind support by Ashland.

That the retarding effect of cellulose ether depends on the addition level as shown in figure 6 for CE-type 1 is no surprise. Yet the question is posed if the relation between sonic acceleration, Vicat penetration and phase development as found for pure OPC is still valid for CE-modified mortars. Figure 7 shows the correlation of the second sonic acceleration peak with Vicat penetration depth. Vicat setting time is a little short for a CE-dosage of 0.2 % but correlates very well with the second major sonic acceleration event for all other samples.

The correlation between sonic acceleration and phase formation (fig. 8 and 9) is still valid, too.

The very early ettringite formation according to XRD-Rietveld analysis in the CE-modified mortar is stronger than supposed by sonic acceleration. At least there is no significant time shift neither of the precipitation peak nor of the weak first acceleration peak. HFC would not help in this case because in this time frame the precipitation heat from ettringite formation is strongly superimposed by the dissolution heat of the primary clinker phases. Theoretically cellulose ether should not have a strong, direct retarding effect on ettringite formation because CE does not adsorb on ettringite and thus surface intoxication is not the case. Therefor the relatively strong precipitation peak fits into the scheme. A weaker unspecific retarding effect might come from the increased pore solution viscosity slowing down ion diffusion. The author assumes two possible effects that keeps the consistency of the CE-modified mortar less stiff despite of ettringite formation: Cellulose ether stabilizes air voids. CE is not a pronounced air entraining agent but it stabilizes the air voids entrained by stirring. This gives ettringite more space to grow without coalescence. Cellulose ether dissolved in the pore water might also serve as a lubricant that allows ettringite crystals to slide. Both effects would lead to a less rigid texture than in unmodified mortar. However, this issue has to be subject of future investigations.

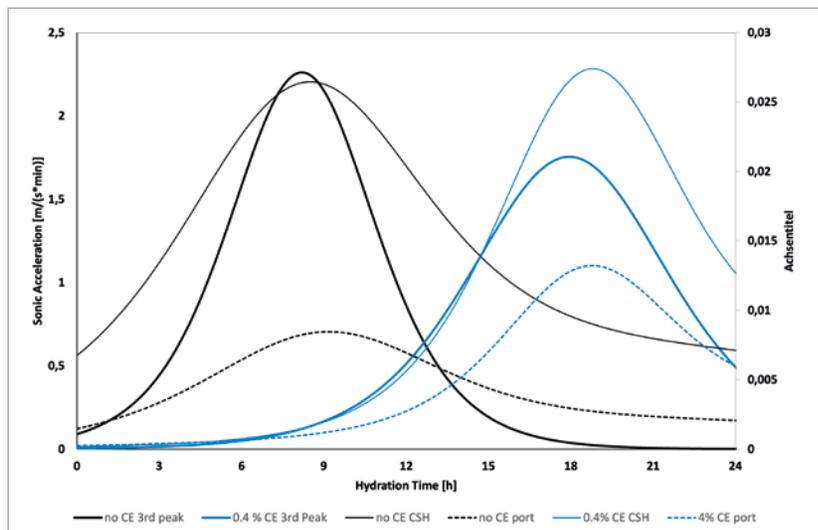


Fig. 8: 3<sup>rd</sup> major sonic acceleration events of mortars modified with CE-type 1 at different dosages in comparison with portlandite and CSH-precipitation

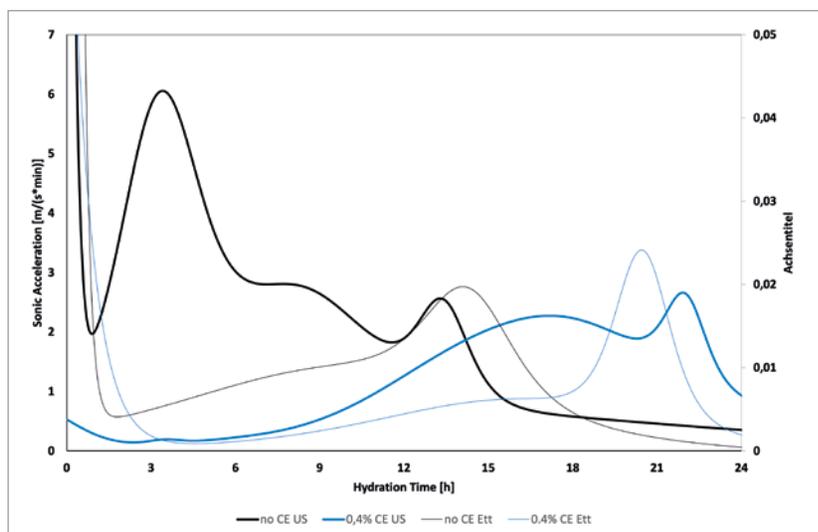


Fig. 9: Sonic acceleration of mortars modified with CE-type 1 at different dosages in comparison with ettringite precipitation

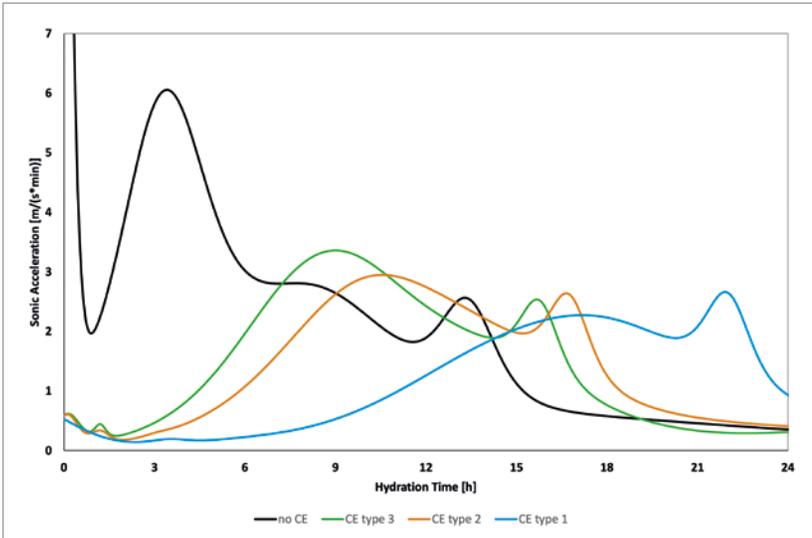


Fig. 10: Unmodified mortar in comparison to mixtures containing three different CE-types. The retardation effect depends on the degree of substitution. The lower the DS-value the stronger the retardation.

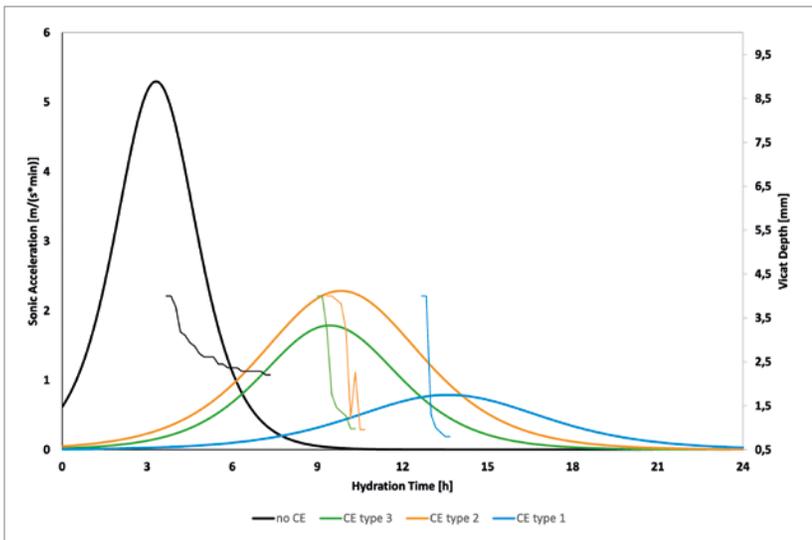


Fig. 11: Comparison between the second sonic acceleration peaks (bold lines) and Vicat depths (thin lines) for mortars modified with different CE-types

The second ettringite formation after hours is tremendously retarded by cellulose ether. This is an indirect effect controlled by ion-equilibria in the pore solution. CE affects the portlandite and CSH precipitation directly and efficiently by adsorption and surface intoxication. Retarded precipitation of those hydrates means less calcium consumption and a high Ca-concentration level in the pore water in which  $C_3A$  remains insoluble for a longer time. This is in accordance with the delayed second ettringite formation and fourth major sonic acceleration peak.

As mentioned above the adsorption values of cellulose ethers depend on the degree of substitution. Cellulose is a polysaccharide that consists of an unbranched chain of polymerized anhydro-glucose rings each of them carrying 3 hydroxyl groups. These groups form hydrogen bonds to neighbored cellulose molecules. These hydrogen bonds make cellulose insoluble in water. To transform cellulose into water-soluble cellulose ether a part of those hydroxyl groups is substituted by side chains of ethylene oxide or propylene oxide and methyl groups. The remaining hydroxyl groups on the anhydro-glucose ring are responsible for CE-adsorption on portlandite and CSH. The less hydroxyl groups are substituted the stronger is the adsorption. The degree of substitution (DS) is the average number of substituted hydroxyl groups per anhydro-glucose ring. The larger the DS-value the less the adsorption and the weaker the retarding effect of CE. Does the correlation between logistic fitting, phase development and Vicat penetration depth persist in this case, too?

The DS-depending retardation of mortar hydration as monitored by sonic acceleration is clearly demonstrated in figure 10. The correlation of Vicat penetration depth with the second acceleration peak is nearly perfect (fig. 11). The CSH-precipitation

correlates fairly with the second sonic acceleration peak (fig. 12). A mismatch occurs for the mortar modified with CE-type 3. The CSH-precipitation runs ahead of sonic acceleration. A very good agreement persists for ettringite crystallization and the fourth acceleration peak (fig 13).

The relation between sonic acceleration and physicochemical hydration processes is valid for formulated mortars. The effect of single additives on cement hydration can be investigated by stepwise addition as shown in figure 6 where the time shifts of single acceleration peaks in dependence of the dosage level is observed.

### USEFULNESS OF ULTRASONIC MEASUREMENTS IN COMPARISON TO ALTERNATIVE AND COMPLEMENTARY METHODS

Ultrasonic as a professional laboratory device is relatively cheap, easy to learn and easy to handle. It does not have test limitations like Vicat (200 measurements maximum) and is less sensitive to sample preparation than HFC. In comparison to HFC ultrasonics supply additional information while HFC correlates better with silicate hydration monitored by in-situ XRD. XRD-Rietveld supply additional information that cannot be achieved by ultrasonics or HFC and is therefore a useful complimentary method yet not easy to perform. XRD analysis demands a fulltime job of experienced personal while ultrasonics is easy to operate along the way. By the author's experience ultrasonic is a very useful and cost-effective method.

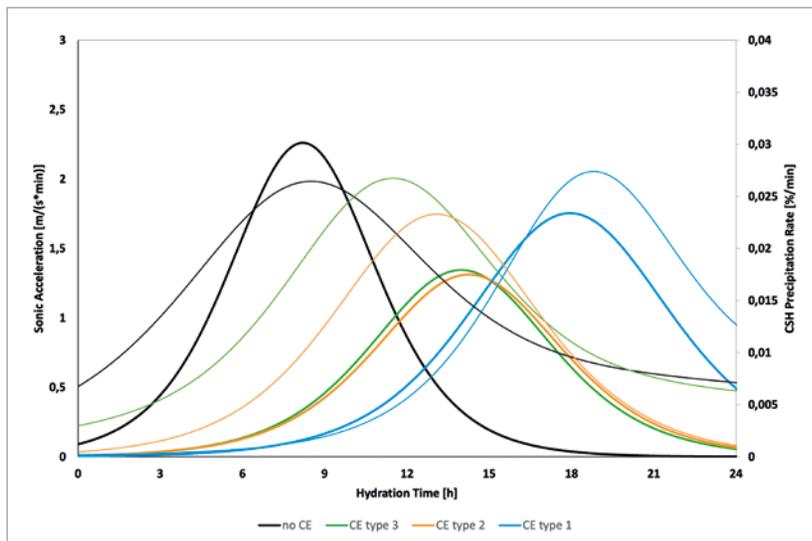


Fig. 12: Third major sonic acceleration events (bold lines) and CSH-precipitation rates (thin lines)

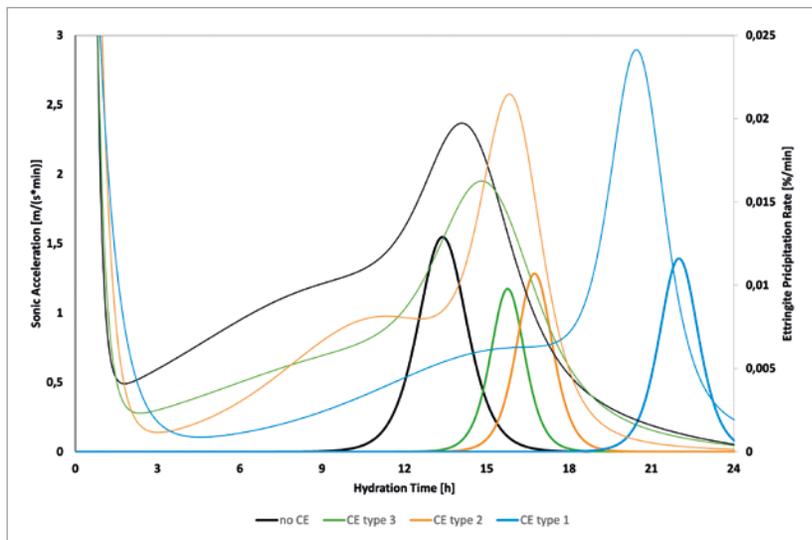


Fig. 13: Fourth major sonic acceleration events (bold lines) and ettringite-precipitation rates (thin lines)

**Table 1: Method comparison in a nutshell**

Performance	ultrasonic	Vicat	HFC	XRD
Costs	0	0	0	-
Information content	+	-	+	++
Simpleness of operation	+	+	-	--
Workload	+	+	+	-
Operator's skill requirements	+	+	0	-
Reproducibility	+	0	+	0
Observation time limitation	+	-	+	+
Temporal resolution	+	-	+	--
Sensitivity to sample preparation	+	+	-	-
Sensitivity to lab environment	-	+	+	+

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