It is well-known that the hardening behaviour of cementous systems essentially depends on the mineralogy of the cement type and the interactions between cement particles and related additives. With aspects to characteristically applied installation techniques of refractory castables, this fact emphasizes the assumption that different combinations of dispersing agents or plasticizers, which are based on polycarboxylateether (PCE) technology with commercially available calciumaluminatecements (CAC) lead to a variety of hardening profiles which also effects their drying behaviour. The presented study combines the results obtained by applying simultaneous measurement devices, named sonic velocity and electrical conductivity, over the first 48 h after casting and conventional measurement of the mechanical strength after defined hardening time intervals. Additional XRD measurements accomplished for a selection of pure cement slurries-additive combinations give a clear indication that the mineralogy of the cement hydrate phases reacts sensitively, when different dispersing agents are used. Over fifty different combinations of refractory castable compositions of the type low cement castable (LCC) were evaluated. A representative selection is envisaged. Although all applied cements show roughly equal chemical compositions, with an alumina content of 70 mass-%, the setting time varies within a wide time range: between 8 and more than 48 h – to be precise. Despite the mineralogy of the CAC, the characteristic relationship between setting kinetics and strength evolution is obviously essential controlled by the applied dispersing agents.

Experimental procedure
The strength evolution subjected to four different types of CAC in combination with varying dispersing agents was investigated by using a high pure, silica free tabular alumina based LCC model castable grained up to 3 mm. The model composition can be categorized as highly dispersed under consideration of micron and submicron scaled matrices used as alumina microfillers.
(Tab. 1). All samples were prepared under equal conditions by applying the regulations of EN 1402. The casting, setting and curing were performed under precisely defined ambient conditions (20 °C at 90% relative humidity). To assure constant conditions the measurements of sonic velocity and electrical conductivity were conducted in a climate cabinet. Sonic velocity was measured by using an ULTRATEST IP 8 standard device. The sonic emission and detection unit was also integrated in a climate cabinet. Background noise suppression was applied to reduce interferences caused by the climate cabinet. The results in meter per second are plotted versus time. The measurement of the electrical conductivity was executed with a 50 Hz AC impedance spectrometric setup. Therefore two corrosion resistant metal electrodes are casted into a 40 mm × 40 mm × 140 mm sample bar in a defined distance and coupled to an impedance spectrometer. The results in [mS/cm] are plotted versus time. Electrical conductivity and sonic velocity were measured over the first 48 h after casting. The evaluation of the strength development was finally conducted after exactly 24 h and 48 h after shaping the samples by machine moulding. This was conducted under the same temperature conditions (20 °C). The strength evolution was determined under consideration of the European Standard EN 1402. Both cold crushing strength (CCS) and cold modulus of rupture (CMOR) were recorded by using prisms of 40 mm × 40 mm × 160 mm size using Tony Technik testing equipment. The results are represented in [MPa] with respect to selected samples. Additional X-ray diffractometric experiments for the determination of the phase evolution in pure cement limes during the setting and curing period were carried out on a selection of CAC and two different PCEs at a constant ambient temperature of 20 °C. CAC-C and D were selected as they are corundum free what may affect the phase evolution during hydration of CA and CAα. PCE (III) and (V) were chosen because they cause the most divergent setting behaviour. For the determination of the phase transformations during hydration a SIEMENS D500 diffractometer with monochromatic wavelength (CuKα, λ = 1,5406 Å) was used within an angular range of 2Θ = 4°–57° with an increment of 0,04° 2Θ and a measuring time of 5 s per increment. Measurements were carried out for the dry cement and with addition of water (w/c = 0,7) after a setting period of 24, 48 h and one week. The cement slurries were moulded in plastic cups. For XRD preparation subsamples were extracted from the plastic cups and were ground thoroughly before the preparation of the XRD test specimens. In order to be able to compare the different CAC and additive combinations, the obtained diagrams were used for a peak area measurement so that relative differences in the phase compositions can be visualized.

**Results**

**Sonic velocity and electrical conductivity**

As shown in Fig. 1, the setting and hardening properties of refractory castables is strongly dependent on the cement-dispersing agent combination whereas the dispersing agent mainly controls the increasing curve progression of the sonic velocity that is caused by the ongoing hardening progress. The cement variety in use simply determines the starting point of the reaction and therefore is responsible for a time shift of the setting and hardening reaction. Hence, the cement is responsible for the total setting time. CAC-A and CAC-B appear to have a retarding effect while CAC-C and CAC-D show a faster setting and hardening reaction. The curve progressions as envisaged in Fig. 1 can be subdivided by three characteristic descriptions. By name, SHMP, which is defined as group 1, PCE (II), PCE (IV), PCE (V), summarized as group 2, and PCE (III) finally represents group 3. Within group 1, except CAC-B however, the SHMP containing castables show a certain primarily strength in combination with CAC which decreases after some hours and in further increases again till a plateau level of strength is attained. This certain setting behaviour is already described by Parr et al. [6] and is due to a primary calcium-phosphate formation. The electrical conductivity measurements of our work also indicate that the formation of calciumphosphate-complex-ions is the most likely reason for a primary strength increase. CAC-B in combination with SHMP only shows a decrease of the setting velocity at approximately seven hours after casting but no strength decrease is visible as in the other CAC. It appears to be most plausible that at the beginning CAC-B releases more calcium-ions into the hydrous solution in the first 7 h. In doing so a certain amount of calcium-ions is still available for the formation of hydrous cement phases. Except P (III) all PCE of group 2 show a similar setting behaviour. By applying PCE (II), PCE (IV) and PCE (V) as additives all formulations show a rapid hardening after mixing which is documented in a steep slope at the beginning of the hardening process. PCE (V) shows the steepest slope with a single inflexion point where the setting velocity is highest. Contrary to PCE (II) and PCE (IV), PCE (V) has a
retarding effect at the beginning of the reaction. In dependence of the CAC in use, during the first 8 to 16 h no setting and hardening is observed. For these polycarboxylates the CAC-species affect the late curing of the concrete. While applying CAC-D the hardening reaction is almost finished after the plateau is attained. CAC-A and CAC-B however still show an ascending slope that indicates an ongoing hardening process within the measurement time. As already reported for the cement-additive-combination CAC-B and SHMP, PCE (II) and PCE (IV) show a slight decrement of the setting and hardening velocity during the period of accelerated reaction. This is more pronounced for PCE (IV). Therefore PCE (II) and PCE (IV) show two inflexion points in the steep slope section of their curves whereas PCE (V) shows only one. Fig. 2 shows that the sonic velocity is correlated with the electrical conductivity and that the second inflexion point of PCE (II) and PCE (IV) is coeval with the point of massive precipitation of calcium aluminate hydrate-phases (CAH-phases) which is indicated by a significant decrease of the electrical conductivity. The first inflexion point of PCE (II) and PCE (IV) could be caused by a hampered ion dissolution indicated by a retarded increase of the electrical conductivity up until the second inflexion point of the sonic velocity is attained. PCE (V) only has one inflexion point coeval to a massive precipitation of CAH-phases as indicated by the electrical conductivity. It is assumed that this differing behaviour of PCE (V) in comparison to PCE (II) and PCE (IV) is due to the fact that the two latter operate as sodium containing cation exchange agents. PCE (V) is sodium free and does not operate as cation exchanging dispersant. Therefore for PCE (II) and PCE (IV) it is stated that a certain amount of Ca-ions are bond to the dispersing agent, which are in further not available for the hydraulic reaction. The apparent hardening may be due to a gelling process of the calcium-substituted dispersant.

Compared to the other polycarboxylates, PCE (III) shows an apparent hardening after six hours. However this is followed by a decrease in strength. The inflexion point, which correlates with a massive precipitation of CAH-phases, is retarded for approximately 15 h. As envisaged in Fig. 3, the time interval prior to the inflexion point is indicated by

Fig. 1 Setting velocities of four refractory castable compositions (CAC-A to CAC-D) subjected to various dispersing agents; PCE (II) circle, PCE (III) square, PCE (IV) triangle, PCE (V) asterisk are compared with SHMP diamond [12]
an almost constant electrical conductivity. No precipitation of CAH-phases and therefore no hydraulic bonding obviously takes place.

**Strength development**

First of all it can be anticipated that a correlation between sonic velocity and strength evolution should be evident. As emerged in Fig. 4 and Fig. 5, the determined values for CCS (primarily influence through particle size distribution of coarse aggregates) and the emor (primarily influence through matrix effects) basically show the same results as obtained by the measurement of the sonic velocity. For group 1 which stands for a classical SHMP dispersed system, a strength increase between 24 and 48 h is obvious. For CAC-B the highest strength increase is visible in Fig. 4, which excellently corresponds to Fig. 1 in which CAC-B is the only cement that shows no strength decrease due to the described accelerated dilution of CA phase. However, the effectiveness of PCE (III) obviously doesn’t have any crucial dependence on the combined CAC. The application of the PCE represented by group 2 in principle shows a higher strength level than visible for SHMP and PCE (III). After 24 h of curing the PCE of group 2 almost already achieve the strength level as visible after 48 h. A remarkable exception is evident if PCE (V) is combined with CAC-A. In this case a significant increase in strength is recorded that may be explained by a higher degree of hydration of the CAC phases. This result is coherent with those obtained with the sonic velocity (Fig. 1) where CAC in combination with P (V) show the highest values.

**Phase evolution in pure cement compositions mixed with water and PCE**

By means of XRD analysis six principal phases were determined. CA and CA2 are the main constituents of the dry CAC products C and D. Due to the high detection limits, as they are typical for XRD measurements, the expected mayenite (C12A7) could not be identified. CAC D shows a by 7 % remarkable higher CA concentration than CAC C but a by 50 % significant lower CA2 concentration. After adding water they show a steep decrease in concentration if the data illustration is time-resolved. This is because of the cement dissolution in water that is more distinct for the CA phase than for CA2. If the CA concentration is higher, basically more CA is dissolved. That means that the residual CA concentration is higher after one week of curing. This is most evident for additive free CAC D formulation. If PCEs are added to the watery suspension CAC D show a higher residual CA phase after one week of curing. It appears to be evident that the addition of PCEs affects the dissolution of CA. This fact is obvious for the CA rich CAC D. In contrast, the residual CA concentration in CAC C shows no effect to PCE (III) but PCE (V) significantly lowers the residual CA content. In case of CA2, the addition of PCE hampers the dissolution in CAC D but accelerate it in CAC C. After one week the...
Strength development of four refractory castable compositions (CAC-A to CAC-D) subjected to dispersing agents represented by group 1 and group 3; SHMP on the left side is compared with PCE (III), right side.

Fig. 4

Strength development of four refractory castable compositions (CAC-A to CAC-D) subjected to various dispersing agents of group 2; PCE (II) on the left side is compared with PCE (IV), middle, and PCE (V), right side.

Fig. 5
residual CA$_2$ concentration shows a broader scatter for CAC D than for CAC C. While the concentration of CA and CA$_2$ decreases after adding water, the hydrous phases CAH$_{10}$, C$_4$AH$_{18}$, AH$_3$ and C$_3$AH$_6$ increase. However, as visible in Fig. 6 all hydrous phases show a broad scatter in concentration in dependence on the CAC – PCE combination. In all formulations CAH$_{10}$ is developed but not in the PCE free CAC D where this phase was not detected. In the other cases after 48 h the CAH$_{10}$ concentration decreases due to a dewatering process of the hydrous phases. CAC D with added PCE (V) shows an exceptional curve progression. It remains unclear why the curve describes an increasing slope. The appearance of C$_4$AH$_{18}$ over the time can be discussed similar to that of CAH$_{10}$. Again there is a remarkable scatter of the concentration and again the additive free formulation of CAC D only shows minor amounts of C$_4$AH$_{18}$ during the first 24 h. The decreasing slopes after 48 h can be again discussed with a stepwise

**Fig. 6** Phase evolution of CAC C and D over the first week after moulding. Pure cements were analyzed and in further combined with dispersing agents P (III) and P (V). For the initial value, the dry cement compositions were analyzed, wherein CAC D contains about 7 % more CA but about 50 % less CA$_2$. Abbreviations in use: Cw = CAC C with water addition, CwP (III) / CwP (V) = CAC C with water addition and with additional PCE (III) and PCE (V) respectively, Dw = CAC D with water addition, DwP (III) / DwP (V) = CAC D with water addition and with additional PCE (III) and PCE (V) respectively (if lines are not visible as in the diagram of C$_3$AH$_6$ then no peak could be determined in the XRD diagrams)
dewatering of $C_4AH_18$. As already described by many authors e.g. Götz Neunhoffer and Parr [7, 8] water rich CAH phases dewater under the formation of $AH_3$ and $C_3AH_6$. The concentration of both phases increases with progressing time. However, their concentrations are very low with the additive free CAC D formulation as an exception. The latter shows a five times higher concentration of $AH_3$ and even a 10 times higher concentration of $C_2AH_8$ already after 24 h of curing.

Conclusions

The introduced study aims to compile the setting and hardening process in refractory castables. Four commercially available calciumaluminate cements that have a similar chemical composition were subjected to different dispersing agents. First and foremost it has to be stated, that this paper follows a most practical approach to disclose that cement-dispersing agent combinations are not arbitrarily exchangeable. Different combinations result in different setting and hardening properties and should be tested carefully before they are exchanged in praxis. This study derives results for the setting behaviour of refractory castable model compositions by applying ultrasonic and electrical conductivity measurement simultaneously within the first 48 h after casting at constant ambient conditions. Corresponding strength profiles (CCS and CMOR) were determined after 24 and 48 h of curing. In addition X-ray diffraactometric investigations were carried out for pure cement additive combinations in order to determine the time dependent phase evolution during the first week of curing. It is clearly shown that different cement – additive combinations lead to drastic variations in the composition of the hydrous cement phases that are responsible for the strength evolution during setting and curing. However it should be mentioned that the results of the strength evolution (sonic velocity, electrical conductivity CCS and CMOR) are not one to one comparable as the setting and curing properties are strongly influenced by the dilution effect in force for concrete formulation in which the hydraulic inactive aggregates represent the major components. But the phase analysis gives a good indication that the strength evolution in concretes is closely related to the phase evolution during setting and curing. Möhmel [9] already published fundamental investigations related to this subject. His works clearly show that alumina rich CAC products (70 % $Al_2O_3$), which are comparable to those used for this study, develop to different hydrous phases in water if different PCEs are added.

From the analytical point of view, a major outcome of this study is that the in-situ measurement of the electrical conductivity in concrete formulations is a powerful extension of the established ultrasonic measurements. Both show a perfect correlation and are suitable to determine the real instant of time for a hydraulic reaction that is taking place. A change of the electrical conductivity...
is always linked to the amount of the ionic dissolution in the watery suspension of the mixing water. An increase of the electrical conductivity always indicates ionic dissolution and is linked relevantly to the dissolution of CAC. In combination electrical conductivity and sonic velocity measurements are powerful tools to determine the mode of function of different dispersing agents that could be indicated by measurements of selected strength profiles. A smoother curve progression as it is most pronounced for PCE (III) and denoted for PCE (II) and PCE (IV) might be correlated to the formation or decay of gel-like structures. In further it can clearly be stated that CAC products of different suppliers that appear to be chemically identical show divergent setting behaviours. Minor deviations in the mineralogical composition of the dry CAC may cause these disparities. However, the dominant causer for the hydration behaviour and strength development of CAC bonded matrices is the applied PCE with their generic characteristics.

**Outlook**

The envisaged investigations of the first 48 h setting and curing behaviour put focus on highly dispersed low cement castables (LCC). In dependence on the hydratable bonding system and the applied dispersant agent, a broad scatter of results is evident even at constant ambient conditions. Further tests in alternative ambient conditions may give more insights into the reaction mechanisms of highly dispersed castable systems as already remarked by Cölle [10]. Obviously, structural specifications and characteristics of the PCE molecules open various possibilities to control the hardening kinetics of CAC-bonded refractory castables by influencing its hydraulic reaction. Consequently PCE are indispensable ingredients with a key-function in design, development and manufacture of advanced refractory castables. In context of the present subjects both investigation and analysis of the applied PCE will be carried out in continuing works focussing on the interaction between PCE and surrounding matrix particles.

The presented results ultimately underline the basic mechanism already described by Dennis R. Dinger and opens up its meaning in context of the present work: “Dispersants want to be dispersed, but in concentrated forms, dispersants can cause local flocculation if they are not dispersed sufficiently and quickly. (...) mixing is stopped as soon as the bodies look sufficiently homogeneous. It is not possible to visually tell whether mixing is complete in most systems. For this reason, I believe most process engineers stop mixing processes prematurely” [11]. At present a project funded by the Stiftung Rheinland Pfalz für Innovation/DE is in progress to determine the dependence of the rheological properties of fresh concretes, the setting and curing velocity as a function of the mixing procedure.

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**References**