



CAC bond refractory castables – when does the hydraulic reaction take place in LC-castables?

OLAF KRAUSE^{1*}, FLORIAN HOLLEYN¹, JOHANNES KASPER², CHRISTIAN DANNERT², DANIEL TISCHER³

¹Hochschule Koblenz, Höhr-Grenzhausen, Germany

²Forschungsgemeinschaft Feuerfest e.V., Höhr-Grenzhausen, Germany

³Mineralwerk Westerwald Horn GmbH & Co. KG, Weitefeld, Germany

*e-mail: krause@hs-koblenz.de

Abstract

This article contributes to a meaningful interpretation of results gathered by *in situ* measurements of sonic velocity, electrical conductivity and the formation of calcium-aluminium-hydrates during setting and curing of LC refractory castables. All said monitoring techniques are well known in the refractory community and are well documented in the literature. However, the time dependent changes of the said properties are not well correlated to mineralogical and in consequence technological changes of the material during setting and curing.

The basic interest of refractory users of course is to define the time at which the installation or the pre-shape construction element can be demoulded. This is in principle possible with the methods listed above. However, after water addition the time dependent changes of sonic velocity, electrical conductivity and temperature are as diverse as there are possible combinations of cements, microfines and surface-active additives. In further the ambient conditions, temperature and relative humidity have a strong influence on these properties and this does not only mean a simple time-shift. Up to now, the results are more confusing than helpful to determine the best time for demoulding pre-shapes and refractory linings.

Recent research at Koblenz University of Applied Science contributes to a deeper understanding of the setting behaviour, because besides the physical evolution of the said parameters the time dependent formation of hydrate phases is also investigated by means of a gravimetric method. The paper will show further insights in the evolution of refractory castables during setting and curing.

After a two years' research project performed with Forschungsgemeinschaft Feuerfest e.V. and Institute of Ceramics and Building Materials, Refractory Materials Division, we can contribute to the understanding as follows: The strength evolution recorded by means of ultrasonic velocity is mostly dependent on the dispersing agent that leads to typical time resolved strength patterns. However, gravimetric analysis of the water content bond to the hydrate phases determined by the freeze-drying method clearly show that, depending on the dispersing agent, the first increase of the sonic velocity does not correlate with the formation of hydrate phases. Additional measurements of the electrical conductivity assist the assumption that the said increase does not stand for the formation of hydrate phases. We suppose that, in the early stage of hardening, gelation or coagulation are the predominant reactions that occur. However, further investigations are necessary to gain a deeper understanding for this pre-setting reaction in highly dispersed refractory castables.

Keywords: Refractory castables, Setting kinetics, Mixing energy, Cement testing, Hydration process

OGNIOTRWAŁE MATERIAŁY ODLEWANE NA SPOIWIE CAC – KIEDY MA MIEJSCE REAKCJA HYDRAULICZNA W ODLEWACH LC?

Artykuł wnosi wkład w pełną treści interpretację wyników zgromadzonych za pomocą pomiarów *in situ* prędkości fali dźwiękowej, przewodności elektrycznej i powstawania hydratów glinokrzemianowych w czasie wiązania i dojrzewania niskocementowych betonów ogniotrwałych. Wszystkie wymienione techniki monitorowania znane są w środowisku technologów zajmujących się materiałami ogniotrwałymi i dobrze udokumentowane w literaturze. Jednakże, zależność zmian tych właściwości w czasie nie jest dobrze skorelowana ze zmianami mineralogicznymi, a w konsekwencji technologicznymi materiału w czasie wiązania i dojrzewania.

Głównym przedmiotem zainteresowania użytkowników materiałów ogniotrwałych jest określenie czasu, po którym szalunek lub forma odlewane elementu mogą być zdemontowane. W zasadzie jest to możliwe za pomocą przedstawionych powyżej metod, jednak po wprowadzeniu wody prędkość fali dźwiękowej, przewodnictwo elektryczne i temperatura są tak zróżnicowane jak możliwe kombinacje cementów, mikroziarna i dodatków powierzchniowo czynnych. Ponadto, warunki otoczenia, temperatura i wilgotność mają silny wpływ na te właściwości i nie oznacza to tylko prostego przesunięcia w czasie. Jak dotąd otrzymane wyniki są bardziej mylące niż pomocne w określeniu najkorzystniejszego czasu demontażu form lub oszalowania wyłożeń. Obecne badania przeprowadzone na Uniwersytecie Nauk Stosowanych w Koblenzji pozwalają na głębsze zrozumienie zachowania w czasie wiązania, ponieważ obok fizycznej ewolucji wspomnianych parametrów badano również metodą grawimetryczną tworzenie się hydratów w zależności od czasu. Artykuł pokaże dalsze rozzeznanie ewolucji betonów w czasie wiązania i dojrzewania. Po dwóch latach realizacji projektu wspólnie z Forschungsgemeinschaft Feuerfest e.V i Oddziałem Materiałów Ogniotrwałych Instytutu Ceramiki i Materiałów Budowlanych możemy wnieść następujący wkład w rozwiązanie problemu: Zmiany wytrzymałościowe rejestrowane metodą ultradźwiękową są zależne głównie od dodatku dyspergującego, co prowadzi do typowych zależności wytrzymałości od czasu. Jednakże analiza grawimetryczna ilości wody związanej przez fazy hydratów, przeprowadzone metodą suszenia przez zamarzanie, jasno pokazują, że zależnie od zastosowanego dodatku dyspergującego pierwszy wzrost prędkości ultradźwięków nie koreluje z tworzeniem się hydratów. Dodatkowe pomiary przewodnictwa elektrycznego prowadzą do wniosku, że ten wzrost wytrzymałości nie jest związany z powstawaniem hydratów. Przypuszczamy, że żelowanie lub koagulacja są dominującymi reakcjami, które występują we wczesnym stadium twardnienia betonu. Konieczne są jednak dalsze badania w celu głębszego zrozumienia reakcji wczesnego wiązania silnie zdyspergowanych betonów ogniotrwałych.

Słowa kluczowe: materiały ogniotrwałe odlewane, kinetyka osadzania, energia mieszania, cementu, badanie cementu, proces hydratacji

1. Introduction

The setting process of cement limes is dominated by the dissolution of calcium aluminates and the precipitation of hydrate phases and is basically investigated by Götz-Neunhoeffler [1]. The kind of hydrate phase (CAH_{10} , C_2AH_8 and C_3AH_6) is influenced by setting time and setting temperature and will finally lead to the stable C_3AH_6 phase [2, 3]. However recent results derived from LC refractory castables show that not only the said hydrous phases are formed [4]. Our research leads to the assumption that the water to cement ratio influences the amount of water that is bonded to the cement. Refractory castables are typically heated up as soon as they have a sufficient green strength. Therefore, it is unlikely that the stable hydrate phase, C_3AH_6 , is formed. Up to now it remains unclear how calcium aluminate in different hydration stages will influence the early green strength development (12 to 96 hours). However, it is clear that there will be certain differences, as they can be visualised by monitoring the setting kinetics by means of sonic velocity and electrical conductivity. The effect of the mixing energy on the hydrous phase formation was investigated in a previous project at Koblenz University of Applied Science (Hochschule Koblenz).

In industrial use, the setting and curing reaction is aborted when the refractory lining is dried and thereafter heated up to service conditions. Here the kinetic aspect of the hydration reactions is of major interest to predict the green strength evolution in the castable. Shortly after the installation on site, the concrete is going to be heated up for the first time. Thereby, it will be necessary to use monitoring tools to pursue the setting process.

The basic methods to monitor the setting process are discussed by Proske [5] as the temperature measurement of the sample, sonic velocity measurement and the measurement of the electrical conductivity. The combination of these methods is helpful for the microstructural interpretation of the setting process [6–8]. Further examples for the application of single measurements (temperature or sonic velocity) show distinct influences on the setting kinetics [9–14]. Up to a few years ago, measurements of the electrical conductivity were only performed on plain calcium-aluminate pastes [15, 16]. Krause *et al.* performed the first measurements for the electrical conductivity on ready-to-use refractory castables in combination with sonic velocity measurements [4].

2. Analytical methods

At Koblenz University of Applied Science, four methods for analyzing the setting kinetics are in use. The sonic velocity measurement in combination with the temperature evolution is tested with a commercially available device. The electrical conductivity method as developed at HS-Koblenz was validated several times. The freeze-drying method was recently developed within the research project on which we report here on fundamental aspects.

2.1. Setting velocity by means of sonic velocity and temperature increase

Detecting the sonic velocity and the temperature is a standard method to determine the hardening of refractory concrete during the setting process. By sending an ultrasonic signal through the castable and measuring the transit time, the velocity can be calculated and is proportional to the Young's modulus of the sample. The used testing device is produced and distributed by UltraTest GmbH Dr. Steinkamp & Büssenschütt, and includes a thermocouple to detect and simultaneously record the sample temperature as a further indicator for the hydration processes due to the released crystallization heat.

2.2. Setting velocity by means of electrical conductivity

The measurement of the electrical conductivity of pure and low concentrated calcium aluminate suspensions is frequently published. Systematic studies of Krause *et al.* show that the measuring method of the electrical conductivity can also be applied to ready to use refractory castables [4]. Several examinations on refractory castables have already been performed with variations of the cements and types of dispersing agents. The measuring cell is based on a simple capacitor. The electrodes are rectangular and coplanar. The dielectric medium is the castable. The sample length is about 72 mm, the width is 40 mm, and the height is from 40 mm to 50 mm. The variation of the resulting curve of the setting process can be assigned to the dissolution of ions into water of pores or nucleation processes during the hydration. Here it is worth to mention that the focus of this method clearly lies on the change of electrical conductivity as a function of setting time. The absolute values are neglected.

2.3. Direct quantification of the hydrate-bonded to pore water ratio by means of the freeze-drying method

An approach to analyse the setting of refractory castables is the gravimetric detection of the pore and hydrate water contents. By drying out the remaining pore water at different stages of the setting process, the quantity of pore water and of water bonded by hydrate phases can be determined and therefore the hydration progress can be recorded. To prevent further reaction of water with the cement during the drying process, the samples are frozen rapidly in liquid nitrogen whereby the remaining iced pore water is dried out by a freeze-drying process. This means that the iced water is removed by sublimation at a prevailing pressure of 0.1 mbar. Therefore, no remaining pore water can react with cement to hydrates and distort the results if the pore water is dried out completely. 30 to 40 samples are collected during the first 48 hours after mixing.

The freeze-drying process therefore is valuable to distinguish between pore water and chemically-bonded hydrate water. The values are both obtained gravimetrically by weighing.

The pore water w_p and the hydrate water contents w_h are calculated by equations 1 and 2 where m_f is the weight of the frozen sample before the freeze-drying process, m_d the

sample weight after the freeze drying, and m_h after heating to 850°C. w_p and w_h are determined independently and should sum up to the total amount of water addition.

$$w_p = \frac{m_f - m_d}{m_h} \quad (1)$$

$$w_h = \frac{m_d - m_h}{m_h} \quad (2)$$

3. Experimental setup

The castable compositions are shown in Table 1. They were mixed in an EIRIC R05 in 32 kg batches using a pin agitator rotating directionally with 10 m/s tool velocity. Samples for ultrasonic tests and electrical conductivity were taken. In further, 30 to 40 samples for the freeze-drying method were derived from the said batch and treated as described above. The ambient conditions were set to constant 20°C and 95% relative humidity in a climate cabinet to enable constant setting and curing conditions over 48 hours. For both castables, three attempts V1 to V3 are documented in the results.

4. Results

4.1. Setting and hardening kinetics of the RTE-castables

The hardening of RTE starts between 7.5 and 9 hours and is mostly finished between 12.5 and 14 hours. In this stage, the sonic velocity increases to approximately 5000 m/s. All three attempts, as depicted in Fig. 1, show almost this end value. However, the starting point of the hardening varies around 1.5 hours, as a result of slight

Table 1: Compounds of two tabular-alumina based castables. The first contains microsilica (MS) and the second is free of microsilica (RTE).

Raw material	MS	RTE
Tabular 0–3 mm	78	78
Calcined alumina	10	10
Reactive alumina	4	7
Microsilica	3	0
CAC	5	5
Dispersant FS20	FS 20/0.15	FS 60/ 0.15
Water	5.1	4.5

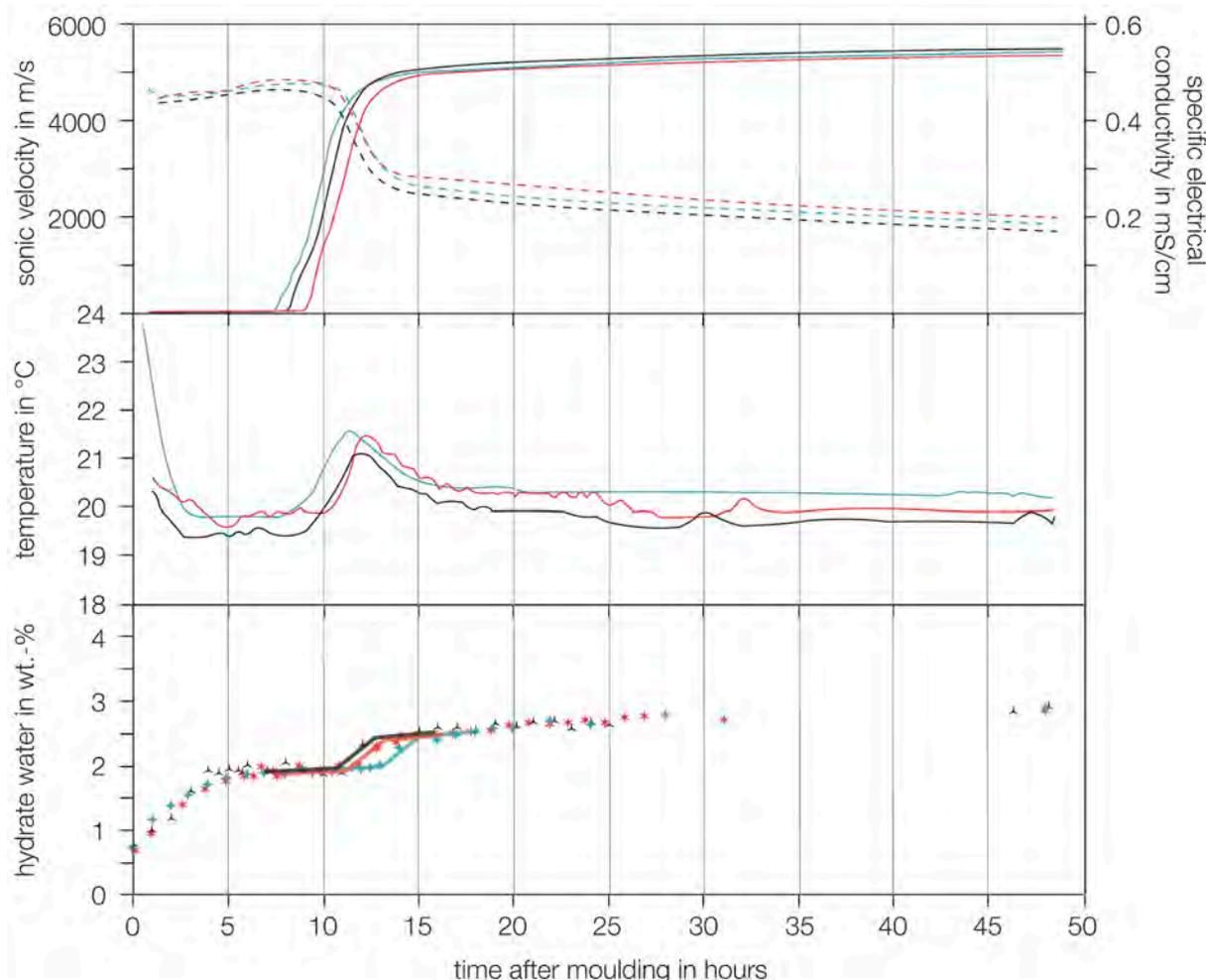


Fig. 1. Setting kinetics of the RTE castable (Table 1). Different colours indicate three single measurements of the same material. The upmost diagram show the evolution of the sonic velocity and the electrical conductivity (dashed line). The diagram in the middle the temperature progression and in the diagram below, the gravimetric measurement of the hydrate phase content is shown.

variations of the mixing process. This indicates that concrete setting is sensitive to the mixing procedure. Especially V1 shows an initial temperature that lies approximately 5°C higher than for V2 and V3. This primarily indicates deviations in mixing energy input, because all mixes were stabilized to a temperature of 19.5°C to 19.9°C before the mixing process was initiated. Secondly the higher initial temperature for V1 leads to an earlier temperature peak at 11.5 hours that indicates the maximum crystallization rate of the hydrate phases. Different to that, V2 and V3 show a temperature peak after 12.5 hours. This is remarkable because all mixtures are stabilized to 20°C in the climate cabinet approximately 5 hours after mixing. This indicates that the initial temperature increase caused by mixing significantly influences the setting kinetics.

The temperature peaks of all attempts correlate properly with the steep increase of the sonic velocity. More precisely, the time of the temperature peaks superposes with the second turning point of the steep slope of the ultrasonic curve progressions. The first turning point was already indicated as the first setting that must be correlated with the interlacing of the organic dispersing agent chains [4].

The development of electrical conductivity typically behaves vice-versa to the ultra-sonic signal over the monitored 48 hours. In all attempts, the electrical conductivity increases systematically till the temperature peak indicates

the time of the highest hydrate formation. In this period, the electrical conductivity decreases rapidly, due to a significant loss of pore water that is now bond to the hydrate phases.

For the determination of the hydrate phase content, the first sample was taken 5 minutes after the mixing process. At this time, the admixtures already show a significant amount of hydrate phases. Within the first 6 hours, the amount of hydrate phases increases rapidly and remains almost at a constant value between (1.8–2)% hydrate water for the next 6 hours. Between 11.5 and 12.5 hours, a significant increase of the hydrate phase content is visible that lasts for about one hour. This period is in good correlation with the instant of time at which electrical conductivity, sonic velocity, and temperature indicate the maximum formation rate of hydrate phases. Thereafter the crystallization rate fades out to an end value of approximately 2.9%.

4.2. Setting and hardening kinetics of the MS-castables

Fig. 2 envisages the curve progressions for the sonic velocity, temperature, electrical conductivity, and the hydrate formation of the MS-castables. In this case, the castable composition contains 3% microsilica and FS 20 replaces FS 60 as it was used in the plain RTE-composition.

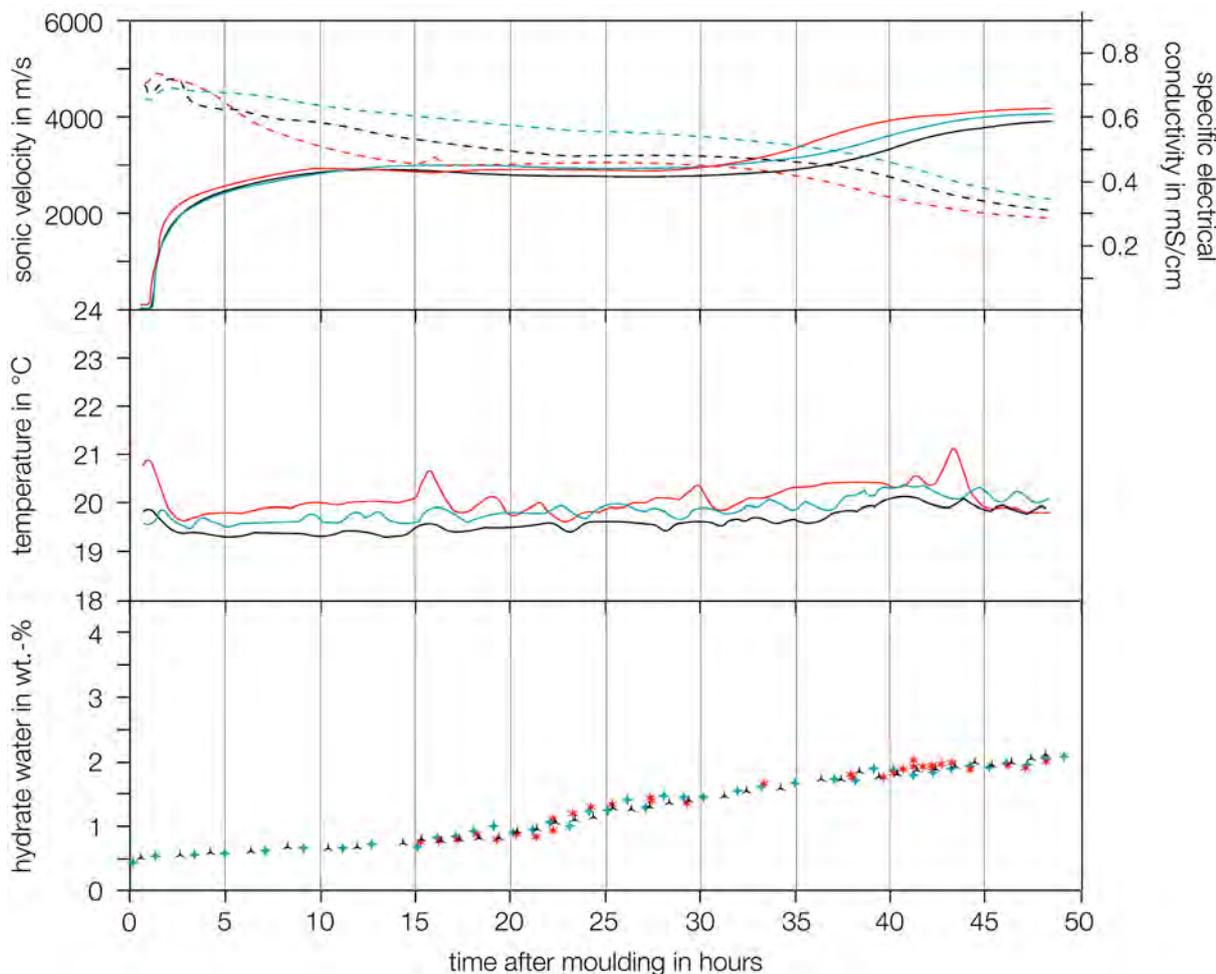


Fig. 2. Setting kinetics of the MS castable (Table 1). Different colours indicate three single measurements of the same material. The upmost diagram show the evolution of the sonic velocity and the electrical conductivity (dashed line). The diagram in the middle the temperature progression and in the diagram below, the gravimetric measurement of the hydrate phase content is shown.

A steep increase of the sonic velocity is already visible at about one hour after mixing. Between 10 and 15 hours, the sonic velocity proceeds with an almost constant velocity for the next 20 hours. Thereafter, all admixtures show again a significant increase from about 2900 m/s to 4000 m/s.

In contrast to the RTE castable, the electrical conductivity exhibits no significant increase at the initial time of the setting process. In all cases this increase is only visible for a short period of about one hour. Thereafter the electrical conductivity decreases mirroring the curve progression of the sonic velocity. The temperature profile shows no significant peak over the entire monitoring time of 48 hours.

The hydrates formation, as it can be directly observed by plotting the hydrate pore water against time (Fig. 2), starts immediately after mixing with a shallow slope till 20 hours. Thereafter the hydrates formation continues with a slightly increased formation rate. There is no indication that the hydrates formation is already finished after 48 hour, because there is still an increase visible following the same slope of the curves that is already apparent after 20 hours. The derived hydrate phase concentration as a function of time is mirrored by the evolution of the electrical conductivity.

Over all monitored parameter it should be obvious, that the first strength increase derived from the sonic velocity should not be correlated with a strength formation based on the hydration progress. It should be correlated with the interlacing of the organic dispersing agent chains or a coagulation process.

5. Conclusions

The envisaged methods for the investigation of the setting behaviour of hydraulic bond refractory castables show in combination a detailed view on the reactions occurring during setting, hardening and curing.

The setting, hardening, and curing process is very sensitive to the mixing conditions. Even under strictly controlled mixing conditions as they were defined for the presented formulations, minor time shifts of the setting and hardening reaction are unavoidable. Minor time shifts already influence the green strength if tested after 48 hours.

The gravimetric determination of the hydraulic bond water content over the setting and curing time by the freeze-drying method clearly show reliable results that enables to approximate the hydrate phase concentration at any time during setting and curing. For a precise determination, the prevailing phases should be known and can be additionally determined e.g. by XRD methods.

The freeze-drying method depicts that it is necessary to clearly distinguish between setting and hardening of hydraulic bond refractory castables. Both castables show that the first strength evolution does not correlate with the formation of hydraulic phases. This behaviour is more obvious for the microsilica containing material and is typical for all castables in which FS 20 is used. It should be correlated with a setting period where predominantly coagulation takes place.

Therefore, a prescribed terminology will help to prevent misapprehension. We propose to use setting, hardening, and curing in a very strict way whereby setting should sole-

ly document the first development of strength, hardening should apply for the formation of hydrate phase, and curing for the late hydrate phase evolution due to the formation of Katoit, the stable cubic phase C_3AH_6 .

Monitoring the electrical conductivity delivers results that can be best correlated with the formation of the hydrate phase. A drop of the specific electrical conductivity always correlates with a diminution of pore water due to the formation of hydrate phases. Therefore, this method does better apply for monitoring the hydrate phases formation in the concrete than the sonic velocity.

The curve pattern of the sonic velocity describes the physical state of the concrete which does not directly correlate with the formation of hydrate phases. However, a distinct dispersing agent leads to a curve pattern that makes different dispersing agents distinguishable. Therefore, curve patterns of the sonic velocity allow determining the nature of the dispersing agent.

In conclusion, all discussed monitoring methods provide a more detailed insight on the reaction kinetics in CAC based refractory castables, whereby the monitoring tools deliver complementary results that really show the physical and chemical processes that occur after the addition of water. However, all mentioned methods are simply descriptive methods that cannot shed light on the reactions that occur in the castables. Further research is necessary to gain a basic knowledge which processes lead to the early strength that is clearly entailed by the nature of the dispersing agent.

Acknowledgement

We would like to thank the German Federation of Industrial Research Associations (AiF) for its financial support of the research project IGF-No. 119 EN. This project was carried out under the auspices of AiF and financed within the budget of the Federal Ministry of Economics and Technology (BMW) through the programme to promote collective industrial research (IGF).

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Received 29 August 2017, accepted 6 September 2017.