

ENGINEERING CALCIUM ALUMINATE HYDRATION TO MAKE CASTABLE SETTING LESS DEPENDENT ON AMBIENT TEMPERATURE

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ABSTRACT

Setting behavior of calcium aluminate bonded refractory castables can vary in different environments, due to different dissolution and hydrate precipitation rates, as well as different mineralogical structure of hydrates that form as a function of temperature. It is quite common that a given castable will have an excessively long setting time at low temperatures, while inversely, having a too short workability and setting at high temperatures.

In this paper, a mineral based deflocculating active compound is used in an alumina spinel type castable that stabilizes the setting behavior over the temperature range 5°C to 35°C. A comparative study with a non-doped reference material is conducted, revealing the impact from the active compound on the hydration mechanisms across the temperature range.

Exothermic measurements, X-Ray Diffraction and Thermo-Gravimetric Analysis are used to describe the different hydration behavior of the reference and doped castables, and to understand how the temperature stabilizing effect is achieved.

INTRODUCTION

The hydration of calcium aluminate phases is dependent on time and temperature. This dependence is shown in Table 1 [1].

Table 1: Hydration mechanisms of CAC as function of temperature

Temperature	Hydration	Reaction
< 10°C	CA + 10H	→ CAH ₁₀
10 – 27°C	2CA + 11H	→ C ₂ AH ₈ + AH ₃
	CA + 10H	→ CAH ₁₀
>27°C	3CA + 12H	→ C ₃ AH ₆ + 2AH ₃
f(T°C + time)	2CAH ₁₀	→ C ₂ AH ₈ + AH ₃ + 9H
	3C ₂ AH ₈	→ 2C ₃ AH ₆ + AH ₃ + 9H

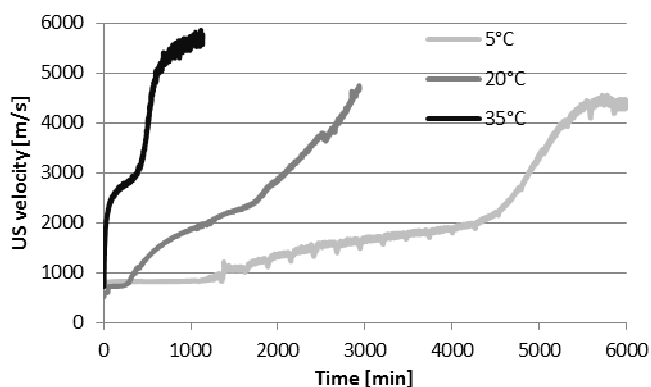


Fig. 1: Impact of temperature on the velocity profile of an ultrasonic measurement on a refractory castable [5]

The different hydration mechanisms have in turn an impact on the setting behavior and the mechanical strength development of deflocculated refractory castables containing calcium aluminate phases [2, 3].

The temperature dependent setting translates into difficulties while casting on work sites or on pre-cast shop floors, either due to extended demoulding times in cold countries or flash setting in warm countries.

There are several ways for observing the setting, one useful method and instrument, is the measurement of the speed of propagation of an ultrasonic wave through the castable. This was more extensively used and presented in an earlier papers [4, 5] and an example of this type of measurement is shown in Fig. 1. Measuring the temperature of the exothermic reaction is also a common way of observing when the massive precipitation of hydrates take place, this is particularly exploited in the work presented in this paper.

In many cases it's possible to influence the setting with retarders or accelerators, but this requires the additional time and effort of re-adjusting the castables. In an earlier study, presented in 2016 [5], an additive named REFPAC 500 (RP500) was developed, with the effect of stabilizing the setting behavior over the temperature range 5°C to 35°C. The advantages of this Active Compound is to create a stable setting time without the need of reformulation of recipes for different temperatures.

In this paper, further analysis of RP500 is presented, aiming at understanding more in depth the mechanisms that permit the stabilization of the setting behavior over the temperature range.

EXPERIMENTAL SETUP

Model formula

In order to perform comparative measurements with the Active Compound RP500 and a reference system, we used a model formula based on alumina and a calcium magnesium aluminate binder, presented in Table 2.

To improve the precision of the measurements (particularly the exothermic reaction and X-Ray Diffraction), the model formula was transposed from its standard version (1) into a μ -concrete (2) by removal of the coarse grain fractions larger than 1mm.

Table 2: Model formula for refractory castable

Raw Material	Spec.	1		2	
Tab. Alumina	0-6 mm	47		0	
Tab. Alumina	0-1 mm	20		38	
Fine filler		15		28	
Binder	CMA 72	18		34	
PCE	Al200/300	0.1	0	0.2	0
T°C Stabilizer	RP500	0	1	0	2
Water		5		9.5	

As reference, the castable was deflocculated using a mix of PCE (AL200) and an accelerated PCE (AL300). The ratio between AL200 and AL300 was chosen to reach the same setting time as with RP500 at 20°C in order to observe the variations at 5°C and 35°C. It's important for the understanding of the results in this paper to emphasize that the reference system is already slightly accelerated by a lithium accelerator included in AL300, while the RP500 deflocculated formula is lithium free and only accelerated via its mineralogical composition.

Trials were done to ensure that the μ -concrete had an equivalent

setting behavior as the model formula. For the sake of clarity: The word “setting time” is here a direct reference to the exothermic event during the precipitation of hydrates and which is in depth measured and studied in this paper.

Exothermic analysis

Exothermic analysis is made with a thermally insulated container in which the castable is poured, and a thermocouple measures the temperature variations over time. The μ -concrete (number 2 from Table 2) was used for these measurements.

Sample Preparation for XRD and TGA

The μ -concrete is manually mixed for 2 minutes with water, the material is casted in 20x20x160mm molds. Parts of the 20x20x160mm rods are cured for 3h, 6h, 18h, 24h, 48h and 72h in chambers with different temperatures (5°C, 20°C and 35°C). The hydration of the samples is stopped at the given time interval by use of acetone and ether solutions. The samples are then sieved to below 315 μ m to minimize the effect of coarser particles and improve the characterization of the hydrates.

X-Ray Diffraction (XRD)

The X-ray Diffraction analyses were performed on a Bruker D8-Advance diffractometer under Cu-K α radiation in the 2 θ range 5°-80°. Samples were then quantified by Rietveld analysis with Bruker TOPAS software.

Thermo Gravimetric Analysis (TGA)

The TGA analyses were performed on a NETZSCH_STA449F3 Jupiter in which, around 50mg of sample was placed into an open alumina crucible under 80%N₂/20%O₂ atmosphere, and investigated from 30°C to 1000°C with a heating rate of 10°C/min.

RESULTS

Exothermic analysis

Exothermic measurements were done using the μ -concrete as indicated in Table 2 formula (2). The results can be observed in Fig. 2 and Fig. 3 for the reference with AL200/300 and RP500 respectively.

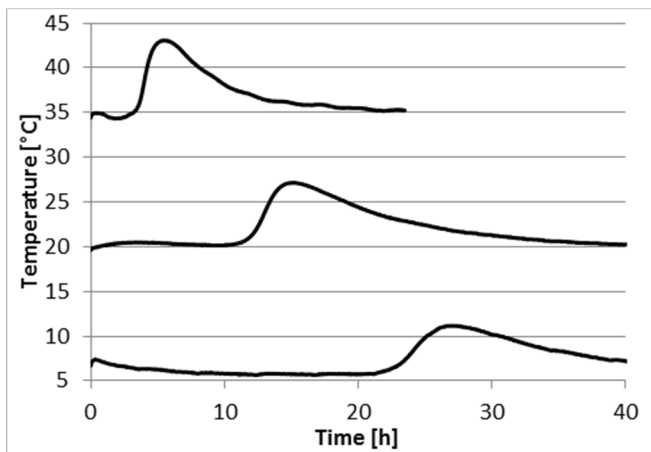


Fig. 2: Exothermic f(T°C) μ -concrete with AL200/300

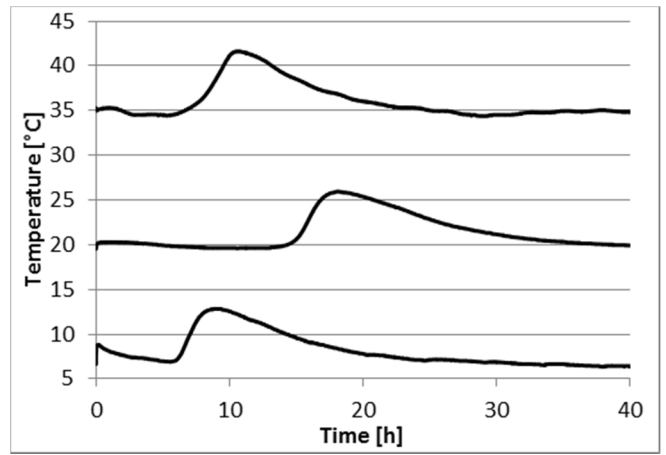


Fig. 3: Exothermic f(T°C) μ -concrete with RP500

The difference in setting behavior as function of temperature is clearly observed via the exothermic analysis of the reference system deflocculated with AL200/300 compared to the Active Compound RP500. While the standard deflocculated system shows a typical quick setting at 35°C and long setting at 5°C with an approximate time difference of 20 hours between these extremes, the RP500 system has an exothermic peak within a time interval of less than 10h independently of the temperature.

XRD

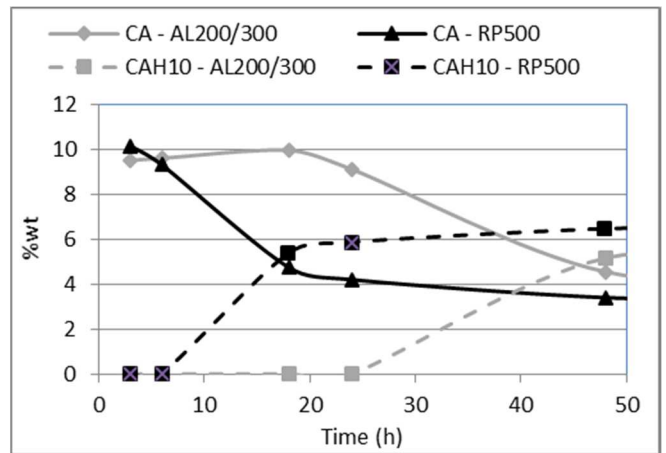


Fig. 4: Graph of mineralogical composition f(time) at 5°C

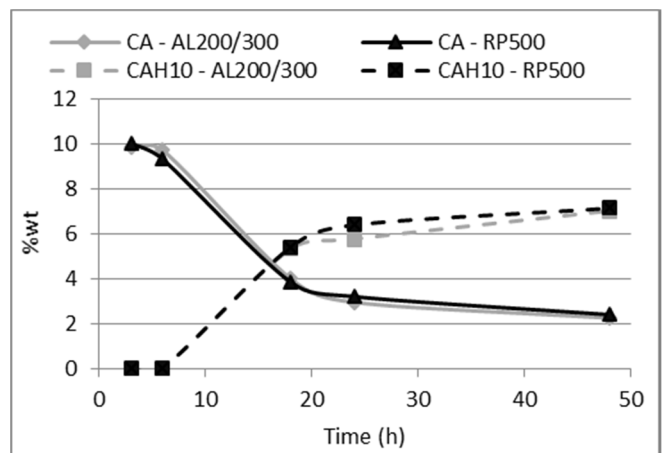


Fig. 5: Graph of mineralogical composition f(time) at 20°C

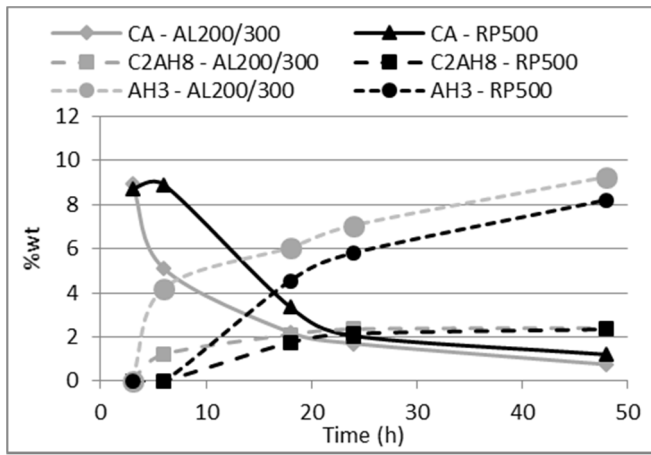


Fig. 6: Graph of mineralogical composition f(time) at 35°C

X-ray diffraction analysis and results are coherent with the observations from the exothermic measurements. The massive hydration is observed at time intervals corresponding to the exothermic peak measurements. The CA phase disappears while different hydrated phases are formed. We can identify that principally CAH₁₀ is formed at 5°C and 20°C while C₂AH₈ and AH₃ are formed at 35°C. In other words, the hydration mechanism in terms of what type of hydrates are formed, is not impacted by RP500. Only the kinetic behavior has been changed with a clear acceleration of the hydration at 5°C while having only a slight impact at 20°C, and none or minimal impact at 35°C.

TGA

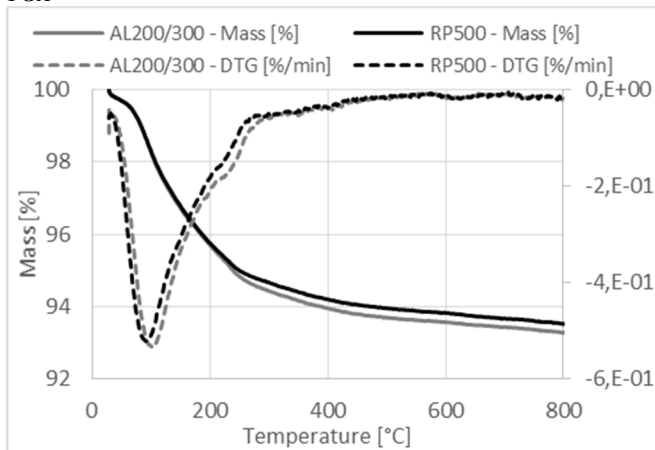


Fig. 7: TGA after curing 48h at 20°C, AL200/300 and RP500

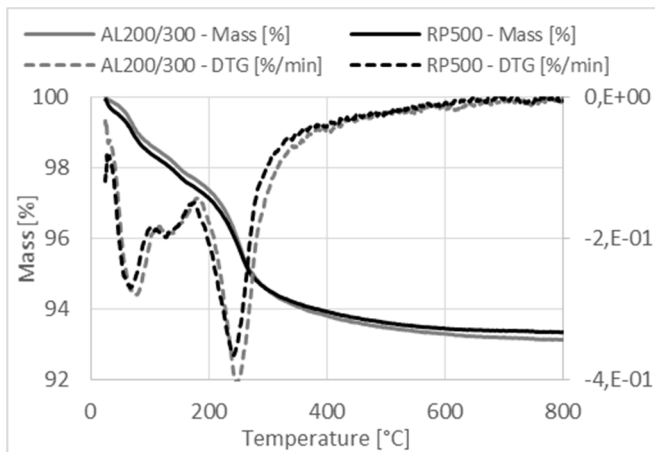


Fig. 8: TGA after curing 48h at 35°C, AL200/300 and RP500

The TGA measurement where done at different time intervals and at different temperatures. Given in Fig. 7 and Fig. 8, are the results from

48h curing at 20°C. The results shows a nearly identical behavior. This most probably means that we are dehydrating materials containing similar amount and type of hydrates. In other words, it is further indication that RP500 is only impacting the kinetic behavior, and not the actual hydration mechanism and hydrates that are formed

DISCUSSION

Solubility of hydrates

To explain how the kinetic behavior of the hydration is changed, we need to look at the solubility of hydrates depending on the calcium and alumina contents of a solution and how these vary with temperature.

As indicated in Table 1, CAH₁₀ and C₂AH₈ can form at medium range temperatures and CAH₁₀ is formed exclusively at temperatures lower than 10°C. At temperatures above 27°C, CAH₁₀ is no longer formed and instead C₂AH₈ forms together with AH₃, or C₃AH₆ can even precipitate directly. These different hydrates and their precipitation at different temperatures can be explained by their solubility which we discuss here, and which has been extensively studied earlier [6].

At 5°C

CAH₁₀ has a very low solubility at low temperatures, meaning it is the most likely to form and the most thermodynamically stable. The reason why the setting time is long at 5°C is probably because of a long nucleation time required for this hydrate to form.

Two possible mechanisms can accelerate the setting at low temperatures; either by speeding up the dissolution of the calcium aluminate in the solution, or shortening the nucleation time of CAH₁₀ hydrates.

Dissolution or nucleation?

Since the mineralogical phase CA can be observed over time and that it disappears in a close to simultaneous manner compared to the formation of hydrates, we can assume that the limiting factor for the precipitation is the nucleation time rather than the dissolution speed.

The dissolution of CA is relatively quick in theory, and this is supported by conductivity measurements of pure phases in bibliography [7]. But those measurements are done with pure powders dissolved in large quantities of water. In a real castable system we can imagine that the CA may very well dissolve quickly on the surface. But on a microscopic level, close to the cement grains, this will quickly lead to an oversaturated solution and thereby stopping further dissolution. The nucleation will start and take whatever time it requires. When the nucleation reaches a critical point, the massive precipitation of hydrates start, the concentration of Ca²⁺ and Al(OH)₄⁻ ions will reduce and consequently the CA can continue to dissolve. The dissolution speed may or may not be a limiting factor during the precipitation but that should have little effect on the setting time since the entire event in any case is relatively short in comparison to the setting times we are registering.

At 20°C

When the temperature increases, the solubility of CAH₁₀ increases and its precipitation becomes more and more unlikely while the precipitation of C₂AH₈ becomes possible. At this temperature range, from 10°C to 27°C according to bibliography, it's possible to precipitate both hydrates.

It's possible that RP500 is still accelerating the CAH₁₀ formation, but since the solubility has increased and the precipitation occurs at higher ionic concentrations, the accelerating effect is reduced. Our exothermic measurement show an equivalent setting time at 20°C between the two systems, but one need to remember that we are comparing with AL200/300, a deflocculating system that contains a lithium based accelerator. This is why we should assume that an

accelerating effect at 20°C is existent even if not particularly strong.

At 35°C

At high temperature, the solubility of CAH₁₀ increases further. Meanwhile, the solubility of C₂AH₈ remains stable. A point is reached when the solubility of CAH₁₀ becomes higher than that of C₂AH₈. From this point on, the CAH₁₀ does no longer precipitate, but only C₂AH₈ and/or C₃AH₆ can form. According to literature and given in Table 1, this happens above 27°C.

Our exothermic measurements indicate that the acceleration effect of RP500 at 35°C is inexistent. This would be coherent with the idea that it only acts as an accelerator for the formation of CAH₁₀, but not for other hydrates. Again, since CAH₁₀ does not, and cannot precipitate at 35°C, it follows that its precipitation cannot be accelerated.

With a close look at the exothermic profiles, there seem even to be a slight retardation of the μ -concrete at 35°C with RP500 compared to AL200/300. But again we must remember that we are comparing with a system that includes a lithium based accelerator. Most likely, rather than a retarding effect from RP500, we see the accelerating effect from AL300, which accelerates the reference castable at all temperatures, including 35°C

It is known that for CAC, there can be a delayed setting at temperatures around 28°C [7]. This is usually explained by this same change in precipitation mechanisms linked to the solubility of hydrates; but that there is a gap between the moment when CAH₁₀ becomes difficult to precipitate, but before the temperature where the rapid precipitation of C₂AH₈ is reached. This leads to a delay in the setting at this particular temperature. A verification of the behavior of the systems investigated in this paper in that particular temperature interval is ongoing.

SUMMARY

In this work, it was shown how a new Active Compound can stabilize the setting behavior of alumina-spinel cement based castables by offering a time interval of setting inferior to 10h over a temperature range from 5°C to 35°C. This was compared to a reference castable deflocculated with a standard PCE and accelerator mix, which obtained an equivalent setting behavior within a larger than 20h time difference over the same temperature range.

It has been shown that the massive precipitation of hydrates can be well observed via both the exothermic profile and at the same time observed via XRD. At 5°C and 20°C, principally CAH₁₀ is formed while C₂AH₈ and AH₃ is formed at 35°C. This corresponds well with earlier studies on the topic. The conclusion for this work is that the type of hydrates that are formed is not impacted by the new Active Compound. But only the kinetics of the hydration mechanisms are influenced by the additive. Further proof that the actually formed hydrates are not different between the reference system and RP500 was obtained via TGA measurements which were identical on samples cured for 48h at 20°C.

The main impact from the evaluated additive is a very efficient acceleration of the setting at 5°C, a slight acceleration at 20°C and no measurable impact at 35°C. This is contrary to a lithium based accelerator which has an accelerating effect at all temperatures. In this paper it was observed that the PCE and accelerator mix AL200/300 had a quicker setting than RP500 at 35°C. Most probably, this is only the accelerating effect of the lithium accelerator included in AL300. RP500 on the other hand is lithium free and does, as shown, only accelerates at low temperatures.

It is suggested that RP500 only has an accelerating effect on the formation, and particularly the nucleation, of CAH₁₀ hydrates. Because this hydrate precipitates exclusively at low temperatures, the accelerating effect is observed as very strong in the 5°C

measurements. At 20°C, the solubility is such that both CAH₁₀ and C₂AH₈ can precipitate simultaneously. In this case the accelerating effect is measured as relatively low. At high temperatures, no accelerating effect is observed, and this is consistent with the fact that only C₂AH₈ and/or C₃AH₆ forms at this temperature.

REFERENCES

- [1] Lea's Chemistry of Cement and Concrete, Fourth Edition, Chapter 13: Calcium Aluminate Cement.
- [2] Parr C et al. The impact of castable composition and calcium aluminate cement type on the rheology and mechanical properties of LCC at low ambient temperature. Institute Refractory Engineers annual Conference, Rotherham, England, 2005.
- [3] Cardoso F, Innocentini M, Akiyoshi M, Pandolfelli V. Effect of curing conditions on the properties of ultra-low cement refractory castables. Refractory Applications and News, Volume 9, Number 2, 2004.
- [4] Simonin F, Wöhrmeyer C, Parr C. A new method for assessing calcium aluminate cements UNITECR, Orlando, USA, 2005
- [5] Zetterström C, Frier E, Szepizdyn M, Wöhrmeyer C. A mineral based active compound with temperature stabilizing effect on setting properties in alumina-spinel castables EUROGRESS, Aachen, Germany, 2016
- [6] Lothenbach B, Pelletier-Chaignat L, Winnefeld F. Stability in the system CaO-Al₂O₃-H₂O. Cement and Concrete Research. 2012.
- [7] Mangabhai R.J. (edited by), Calcium Aluminate Cements, Proceedings of the International Synopsium held at Queen Mary and Westfield College, University of London, 9-11 July 1990.