A NEW METHOD FOR ASSESSING CALCIUM ALUMINATES CEMENTS

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ABSTRACT

The final properties and service life of monolithic installations will partly depend on the initial conditions. In this context, the initial strength development is of primary importance and can contribute to reduce overall costs. The hardening and initial strength development of castables will condition the minimum time for demoulding. Decreasing the demoulding time can significantly reduce relining times, consequent equipment down times and improve the productivity in the case of a pre-cast operation.

Various classical techniques allow the various steps in the castable placing chain, from the loss of workability to the completely hardened state, to be followed. The major problem encountered with these methods is the sensitivity to external conditions and the inability to relate the data to the mechanical resistance.

For monolithic castables with complex formulations, external conditions, such as temperature or humidity, can significantly affect the strength acquisition kinetics. It is, in this context, difficult to obtain reliable information versus time. Furthermore, measures on simplified systems, such as neat cement paste or mortars, can differ significantly compared to real castables formulations due to the presence of fillers and aggregates. Thus, there is a clear need for practical and reliable methods, achievable for the whole castable, to follow the change in characteristics as function of time.

This paper aims to evaluate an original and non destructive method, in comparison with traditional techniques like Vicat-set in mortars or exothermic profiles. This method relies on following the propagation of ultrasonic waves and the paper demonstrates the experimental approach necessary to characterise the castable from the fresh state to the completely hardened state.

The interest of this non-destructive and “continuous” method is evaluated in the field of industrial control techniques and is compared with other classical methods.

1 Introduction

Accurate measurements of early-age properties of refractory castables are crucial to operations scheduling, and in-situ quality control of material. As the long-term behaviour of castables is closely related to the firsts steps of installation and hydration, the knowledge of the evolution of rheology, setting and hardening is essential to forecast the performance and achieve the targeted characteristics.

Calcium aluminate cement is widely used in most of the refractory castables which have evolved from conventional castables to low and ultralow cement castables. This continued evolution has been possible with the introduction of fine powders (fillers of alumina, silica fume, magnesia) which fill the gaps between the cement grains and the aggregates, reducing the water demand and globally increasing the global performance [1]. In LCC systems, the CAC is in consequence only a part **of** an interdependent and complex system. The properties, from the rheology to the final hardened state via the setting behaviour will depend on all these components.

In consequence, we need to study not only the behaviour of cement itself but also the entire binder system.

Various classical techniques allow the various steps in the castable placing chain, from the loss of workability to the completely hardened state, to be characterised. The major problem encountered with these methods is the sensitivity to external conditions and the inability to relate the data to the mechanical resistance. They generally only provide partial information, for a given time or period of time.

Thus, there is a clear need for practical and reliable methods, achievable for the whole castable, to follow the change in characteristics as function of time, from the fresh state to the final hardened state.

This paper will present an approach by which the hardening kinetics of the whole refractory castable can be continuously followed and monitored using an ultrasonic method. The technique is based on the propagation velocity of ultrasonic waves through a sample. It can be applied from the end of mixing to the complete hardened state of the castable. The principle can use both compressive and shear ultrasonic waves to calculate the elastic properties of the material. In this paper, only the compressive wave is used to follow the propagation velocity which is directly linked to the structured state of the material.

Ultrasonic methods have been firstly widely used in the field of Porland based civil concretes, and specially for the control of the final hardened state: strength estimation, thickness measurements, elastic modulus or crack locations in the dense structure [2-5]**.** This method has also been successfully used to follow the evolution of elastic modulus of refractory concrete during heating up, from 20°C to 1600°C [6]. More recently**, the** RILEM organization has set up a Technical Committee on “advanced testing of cement based materials during setting and hardening (TC 185-ATC) which deals with methods detecting changes in the electrical and physical properties of early age concrete, including the ultrasonic wave propagation method. This method has already been applied to continuous monitoring of setting and hardening of mortars and concrete [7-8] and specially to follow the hydration of calcium aluminate cements [9,10,17]. It allows to provide information about all the hydration steps from early age to the final hardened state.

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2 Experimental

Different castable systems were used in conjunction with a 70% alumina cement, Secar® 71. Castable formulations are presented in table I along with the raw materials used in each system. The particle size distribution were calculated using the Dinger and Funk model with a q value of between 0.25-0.35. The systems were designed for vibration placing. Three Low Cement Castables are used, based on tabular alumina, bauxite and andalusite, all containing fume silica and calcined alumina as the fine fillers,

Two additives systems were used either with Na-TPP (**S1**) or with a 3 additives system (**S2**). (can you not be more specific and at least list the components?)The additive systems ensure a good compromise between fluidity and working time to allow proper placing of the castable. The two additives systems were chosen for their different mechanisms of action. Na-tripolyphosphate relies on a pure ionic dispersion mechanism whereas S2 incorporate an electrosteric component for dispersion.

Material	LCC-AT5	LCC-B5	LCC-AND5
Tabular alumina 0-6mm	80		
Bauxite 0-6mm		85	
Andalousite 0-5mm			80
Calcined alumina	10	5	10
Fume silica 971U	5	5	5
70% CAC (Secar71)	5	5	5
Water content	5.5	5.5	5.5

Table I. Castables composition.

Measurement of placing properties

Placing properties for each system were characterized through the flow profile and working time.

Flow value: determined using a cone with 100mm base diameter, 50 mm high and 70 mm top diameter. The cone is placed on a vibrating table (according to the ASTM norm 230C) filled with the castable, then taken away and subjected to 20 seconds of vibration. Flow value resulting of the “cake” is calculated as a percentage as follows:

FV (%) = (cake diameter – initial diameter) / initial diameter * 100

Working time: time after mixing at which the castable will not flow under vibration.

Measurement of castable hardening kinetics

Hardening kinetics were followed by exothermic profile, mechanical resistance, dynamic elastic modulus and a new original method based on the propagation of ultrasonic waves. Results were compared to the standard Vicat-setting method on equivalent mortars.

Exothermic profiles: determined at 20°C with castable samples placed in an insulated chamber. A thermocouple, imbedded in the cast sample, is linked to a data capture system and the temperature recorded as a function of time [11].

Dynamic elastic modulus: based on the frequency resonance of sonic waves in longitudinal mode. The sample is hit with a little hammer, the frequency resonance is directly related to the material elastic properties. The method is applicable as soon as the material begins to harden.

Mechanical resistance: Cold Crushing strength were measured on 30*30*160 mm prisms cured at 20°C/100% relative hygrometry between 0-24 hours.

Ulrasonic measurement:

Only the compressive wave is used to follow the propagation velocity which is directly linked to the structured state of the material. The apparatus is presented figure I.

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The wet mixed castable, with a maximum grain size of 6mm is placed in the mould, then vibrated during one minute to ensure that no air bubbles will perturbe the signal [13,14]. Classical demoulding oil is used to facilitate the demoulding of hardened castable. Since the shrinkage of the castable could lead to a decoupling of the material and the mould, silicon grease is used to ensure a good interface between the cells and the castable.

A compressive wave is generated from a piezoelectric transducer through the material with a 25kH frequency.

Figure I: Ultrasonic apparatus (8 channels)

The measurements are performed during very short time periods (a few µs) which are converted from the electrical signals by the two piezoelectric transducers (transmitter and receiver). After amplification the signal is recorded as the wave velocity.

The change in velocity as a function of time is then used to follow the structure development of the castable from the fresh state to the completely hardened state.

3 Results and Discussion

Based on the analysis of the experimental results, and for the simplest case, three characteristic stages can be distinguished in the evolution of ultrasonic wave velocity (figure II). The first stage goes from a suspension of cement particles partially dissolved and ultrafines to the first solid phase percolation. In this first stage, the velocity remains low and stable.

The values are smaller than the velocity in water (around 1400 m/s) and even smaller than in the air (330 m/s). According to previously studies [12,13], this phenomenon can be caused by entrapped air in the castable, playing a dominant role compared to the low amount of hydrates formed.

Then, a solid percolation path is formed in the paste creating an hydrates network: the ultrasonic wave propagates through a solid instead of through the liquid phase. At this critical time, some authors [4] have shown that the shear wave begins to propagate through the material. A sharp increase of velocity is observed. Just before this critical time, some authors [14] have detected a slight decrease of the velocity corresponding to an increase of tortuosity in the paste due to a growing hydrates network but not yet connected. It is believed that the increasing velocity is controlled by the amount of the connected solid phase [4,15].

A plateau is then reached in the third stage, without big changes over the time.

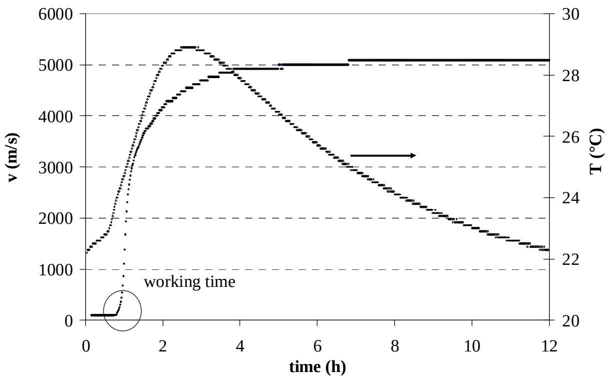

Figure II: Velocity and exothermic profile for castable AT5, S2

During the first stage when castable is fluid, the flow can be measured under vibration (figure III). This corresponds to the installing period. The end of the first stage, marked by a sharp increase of ultrasonic velocity approximately corresponds to the end of workability, called here working time, corresponding with a great loss of flow under vibration. At this point, a sharp increase is marked on the exothermic profile.

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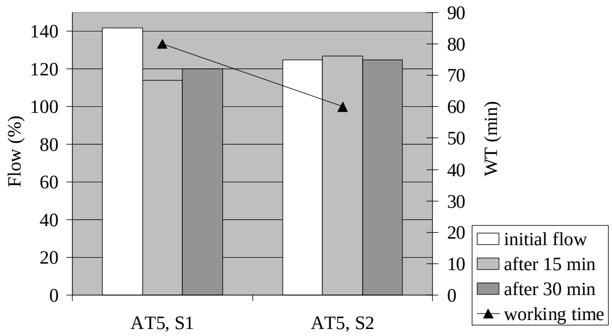

Figure III: Flow profile and working time for castable AT5

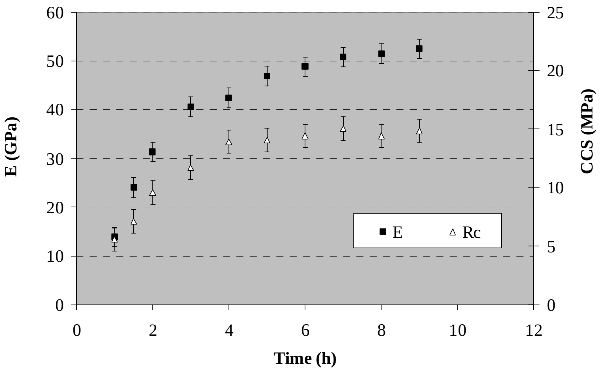

Figure IV: Evolution of strength and elastic modulus over the time for castable AT5_S2

The second period with increasing velocity corresponds to the global hardening kinetics. The classical setting times measured by the Vicat method are localized as follow: at the beginning of increasing velocity for initial setting time and soon after for the final setting time.

In this second stage, both elastic modulus and strength increase, in parallel the main exothermic peak occurs (figures III, IV). This period corresponds to the growth of hydrates content and solid phase portion. The comparison with the massive precipitation observed by conductimetry is difficult because the situation in a diluted system is significantly far from a concentrated solution.

When the velocity remains stable, both elastic modulus and strength reach a plateau, faster for mechanical resistance (figure IV). Many attempts have been maid to try to rely the ultrasonic compressive wave velocity to the compressive strength, but the relation is not trivial and depends on the castable formulation [12,16].

Influence of admixtures type

Depending on the type of admixtures, the profile of the velocity curve can be different (figure V). It is characterized by several steps and curvatures which are not all well identified today. It is therefore more difficult to compare with parameters issues from traditional methods.

For example, during the first stage, the dissolution of calcium aluminate cement can be blocked (with system S2) or characterized by a reaction between cement, ultrafines and admixtures: it is the case with Na TPP (system S1) for which we observe a first structural effect even in the fresh state. It may be explained by the reaction between phosphate and CAC which create very fine calcium phosphate compounds. In opposition, with the admixtures system S2, the first stage seems to be longer and more stable.

Further experiments will be conducted to explain these phenomena.

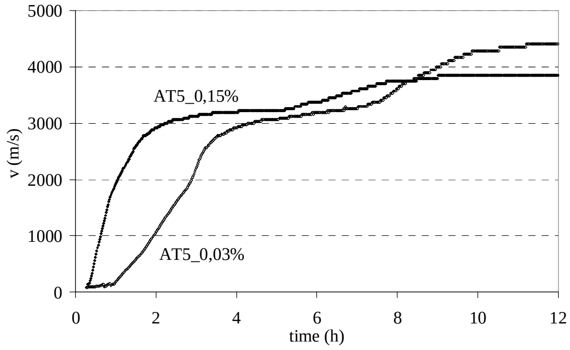

Figure V: Velocity for AT5 castable with different phosphate contents

Influence of raw materials

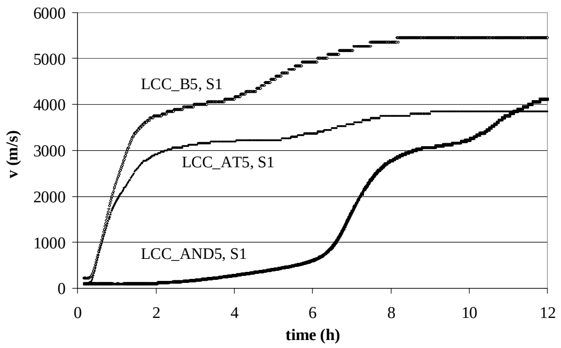

Figure VI: Velocity for the different castables (S1)

Depending on the type of raw materials (tabular alumina, bauxite, andalousite), the profile of the velocity curve can be different. The increase of velocity is achieved in several steps as seen in figure VI.

Influence of ambient temperature and ageing

The impact of temperature or ageing of the whole castable could be detected in the wave propagation curves. In both cases, for decreasing temperature or ageing, the first stage is longer and the velocity increase, delayed (□T in figure VII).

The ultrasonic method is very interesting to measure the impact of temperature or ageing on hardening kinetics, as previously shown by C. Parr and al. [17].

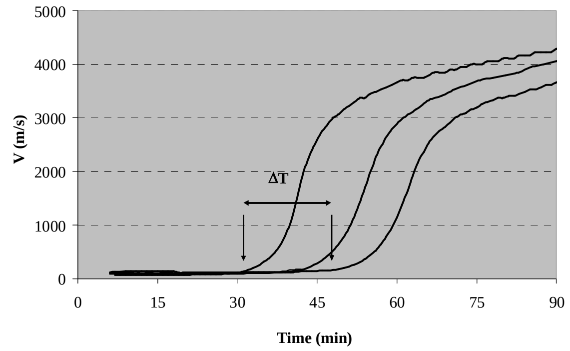

Figure VII: Example of variations in the ultrasonic velocity curve due to external parameters (castable AT5_S2)

The following of the ultrasonic propagation velocity is a promising method, with many advantages:

- in-situ, continuous and non-destructive method
- simple with numerical recording
- adapted with the whole castable and reproducible
- usable from fresh state to finally hardened state
- sensitive to each parameter

4 Conclusion

The record of ultrasonic wave propagation velocity is a reliable method to allow the various steps in the castable placing chain, from the loss of workability to the completely hardened state, to be followed. It is sensitive to different parameters, like the castable formulation, the admixtures type or the fillers nature. In particular, it allows to detect variations with ambient temperature or ageing. It has to be pointed out that different castables show different curves: there is no unique profile.

The hardening kinetics can be precisely followed by this method more on a qualitative manner.

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Relations with parameters issued from classical methods could be made but need to be studied in more details, as the relation depends greatly on the castable types.

Two main applications are emphasised: development of new castables formulation or quality control of products based on a same castable formulation, as the reproducibility is good.

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