EARLY-AGE STRENGTH DEVELOPMENT OF SILICA-GEL BONDED REFRACTORY CASTABLES: EFFECT OF HYBRID BONDING

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ABSTRACT

The 3D extrusion process offers a promising route for producing refractory components with less labour, shorter production times, and minimal waste. Its success relies on controlling early-age setting to ensure layer-by-layer deposition. Using calcium aluminate cement (CAC) as a binder can provide castables with good rheology and early mechanical strength for such applications but also increases the risk of explosive spalling and limits recyclability. This study compares a printable CAC-bonded castable with no-cement castables bonded with microsilica (MS) or colloidal silica (CS), both without and with small CAC additions. Setting was monitored via ultrasonic (US) wave velocity, and early strength by cold modulus of rupture (CMOR) tests. In CAC systems, strength develops concurrently with the US velocity increase. In MS and CS systems, the velocity rise corresponds to gelation, with strength developing later. CAC addition accelerates strength gain in both MS and CS systems. These findings provide insights for tailoring sustainable 3D refractory inks.

INTRODUCTION

Refractory castables bonded with calcium aluminate cement (CAC) remain widely used in high temperature industries due to their rapid setting and their ability to develop sufficient mechanical strength at an early age. These properties enable safe and fast demoulding of precast elements and early strength for *in-situ* installations before ceramic bonding. However, CAC-bonded castables suffer from several drawbacks, including:

- Sensitivity during drying, as the release of free and chemically bonded water can generate internal vapour pressure, leading to crack formation or explosive spalling;
- Reduced refractoriness due to the formation of low-melting phases in the presence of silica;
- High-temperature instability associated with the formation of CA_2 and CA_6 phases, which cause significant volume expansion and subsequent cracking.

To overcome these limitations, significant efforts have been made to develop cement-free bonding technologies, particularly colloidal silica (CS)-bonded castables. These systems offer:

- Improved drying performance, thanks to the absence of chemically bonded water and the development of a highly permeable microstructure after curing;
- Lower environmental impact due to the elimination of CaO-bearing phases.

However, CS-bonded castables still face challenges, notably their slow setting kinetics and low green strength, which make the demoulding and handling of large precast parts difficult [1]. In CS systems, setting is governed by the formation of a siloxane (Si–O–Si) three-dimensional network via the condensation of silanol groups (Si–OH), which entrap coarse aggregates and matrix, as water evaporates. This process can be accelerated by air drying, pH adjustment, or the addition of setting agents, such as CaO, which promote hydroxyl consumption through $Ca(OH)_2$ formation [2, 3]. But to qualify as no-cement castables (NCC) according to the EN ISO 1927-1 standard, the total CaO content, including the CaO added as the setting agent, must remain below 0,2 wt.%.

More recently, Elkem has developed a dry alternative to colloidal silica: the SioxX® product family, which consists of microsilica-based binders. These products contain particles approximately ten times larger than those in CS (≈150 nm vs. 8–15 nm) [4, 5], leading to the classification of these systems as microsilica (MS)-gel bonded castables. Recent studies have shown that an effective bonding network is formed through microsilica coagulation, via a mechanism similar to that of colloidal silica [5]. When small amount of CAC is added as a coagulating agent, Ca^{2+} ions, released upon dissolution, bond to the negatively charged microsilica surface, forming a 3D gel network. This approach has been shown to improve setting behaviour and green strength [4, 6-8].

In addition to performance, MS-gel bonded systems offer practical advantages such as an "all-in-the-bag" dry formulation, facilitating transport, storage, and on-site use. Despite these benefits, understanding of their early-age setting behaviour remains limited, as current studies mostly report ultrasonic velocity measurements to monitor the setting process while green strength values only after curing, and often in systems that include small amounts of CAC as a setting agent [4, 6–8]. To date, no study has clearly established a direct correlation between the evolution of ultrasonic wave propagation and the actual mechanical strength development throughout the setting process, whether in CS-bonded or MS-gel bonded castables. As a result, the early-age mechanical behaviour of these CAC-free systems remains poorly documented when assessed using a combined approach involving both non-destructive and destructive testing methods. Nevertheless, a deeper insight into early-age structuration is essential to optimise critical processing steps such as shaping, particularly in the context of advanced manufacturing techniques like 3D extrusion printing of refractory castables. In such layer-by-layer deposition process, where cement-free formulations are increasingly favoured for sustainability reasons, the success of the process relies on the material's ability to develop sufficient stiffness and cohesion over time, without requiring actual mechanical strength, to meet the buildability requirements of the technique.

In this context, this study aims to advance the understanding of the setting process and early-age strength development in MS- and CS-bonded castables, through a comparison with a conventional CAC-bonded formulation. The setting evolution is monitored in real time using ultrasonic wave velocity measurements, while cold modulus of rupture (CMOR) tests are performed at selected time points to quantify strength development throughout the setting stage. The results are expected to provide valuable insights for assessing the printability and early handling potential of NCC.

MATERIALS AND METHODS

Raw materials and mix design

Tabular alumina (TA) aggregates with various size fractions (1–3 mm, 1–0,5 mm, 0,5–0 mm, 0,6–0,2 mm, and 0,2–0 mm; all from Almatis, Germany) were used as the coarse and intermediate fractions. As fines, tabular alumina (≤ 45 µm, Almatis) and reactive alumina (RG4000, D_{50} ≈ 0,8–1,2 µm, Almatis) were incorporated. Three different binder systems were employed: CAC (Secar 71, Imerys, France), MS (SioxX-Zero, Elkem, Norway) and CS (Ludox HS-40, Merck, Germany). All particle size distributions (PSDs) were designed according to the Andreassen model with a q-value of 0,26. Table 1 summarises the overall mix formulations. To investigate the strength development during the setting process of MS- and CS-bonded castables, a conventional CAC-bonded mix, known to exhibit good printability for 3D extrusion process [9], was used as a reference, with a CAC content set at 5 wt.%. This reference formulation also included polycarboxylate ether (PCE) setting additives with both short and long side chains (FS10 and F60, BASF, Germany). For the CAC-free formulations, equivalent binder volumes were maintained by replacing 5wt.% of CAC with 3wt.%

of MS or the solid fraction of CS, based on their respective densities (≈ 2,2 g/cm³ for MS and solid part of CS vs. ≈ 3,0 g/cm³ for CAC).

To evaluate the effect of hybrid bonding strategies, small amounts of CAC were also introduced into MS- and CS-based formulations. The overall CaO content in these hybrid mixes was kept below 0,2 wt.% to preserve the NCC character of the system.

Finally, the water content of CS- and MS-bonded castables was adjusted to achieve comparable flowability to that of the CAC-bonded one.

Tab. 1: Composition of CAC-, MS- and CS-bonded castables

Material reference*	REF-CAC	MS-0CAC	MS-0,25CAC	MS-0,5CAC	CS-0CAC	CS-0,5CAC
Aggregates						
TA (0–3 mm)	70,00	71,50	71,25	71,00	71,50	71,00
Matrix						
TA (≤ 45 µm)	13,00	13,25	13,25	13,25	13,25	13,25
RG4000	12,00	12,25	12,25	12,25	12,25	12,25
CAC	5,00	0,00	0,25	0,50	0,00	0,50
MS	–	3,00	3,00	3,00	–	–
CS**	–	–	–	–	3,00	3,00
Additives						
PCE	0,03	–	–	–	–	–
Water content	7,0	5,25	5,25	5,25	5,25	5,25

* REF-CAC = CAC-bonded reference; MS = Microsilica-gel bonded; CS = Colloidal silica bonded; 0CAC / 0,25CAC / 0,5CAC= wt.% of CAC added.

** For CS formulations, the wt.% reported corresponds only to the solid content in the commercial suspension. The added water from the CS suspension was included in the total water content.

Ultrasonic (US) wave velocity measurements

The setting process was continuously monitored by measuring the propagation velocity of the US wave through the sample, with data acquisition every 30 seconds. Since US wave velocity is proportional to the square root of the material's Young's modulus, tracking its evolution over time provides a reliable and non-destructive means of evaluating stiffness development during setting [10]. The measurements were performed using an Ultratest IP-8 device (Ultratest GmbH, Germany), which includes a specially designed mould embedding piezoelectric transducers in direct contact with the sample. This configuration enables transmission and reception of US signals throughout the setting process. A temperature probe is also integrated for real-time monitoring of the sample temperature evolution.

Cold Modulus Of Rupture (CMOR)

The bending strength was determined by cold modulus of rupture (CMOR) tests in accordance with ISO 1927-6, using format D specimens. Prior to testing, the samples were stored in sealed plastic bags to maintain a relative humidity of approximately 95%. Tests were performed at 1, 2, 4, 9, 18 and 24 hours after the water addition when demoulding was possible and the material had sufficiently hardened. At each time point, three specimens were tested.

RESULTS

Reference CAC-bonded castable (REF-CAC)

The REF-CAC castable exhibits a characteristic three-stage evolution in the US wave velocity curve (Fig. 1):

- _Stage 1 (approx. 0–4 h after water addition):_ the initial rise in US velocity is likely related to early coagulation phenomena, potentially induced by interactions between the short side chain PCE (FS10) present in the formulation and Ca^{2+} ions released at early age. The resulting Ca^{2+}–PCE complexation reduces fluidity (i.e. increases viscosity), inducing an apparent stiffening without mechanical strength development [11].
- _Stage 2 (approx. 4–12 h):_ a second, more pronounced increase in US velocity begins with the temperature rise in the sample and gradually stabilises around the exothermic peak. This second stage is attributed to the exothermic hydration reactions of CAC phases
- _Stage 3 (beyond 12 h):_ After the exothermic peak, both US velocity and mechanical strength continue to increase at a slower rate. This hardening phase is associated with the progressive conversion of metastable hydrates (CAH_{10} and C_2AH_8) into stable phases (C_3AH_6), further enhancing the castable's stiffness.

These interpretations are supported by CMOR measurements (Fig. 2), which show that mechanical strength begins to develop with the onset of Stage 2. No measurable strength was observed during Stage 1 (i.e., at 1 h and 2 h), as the samples remained soft.

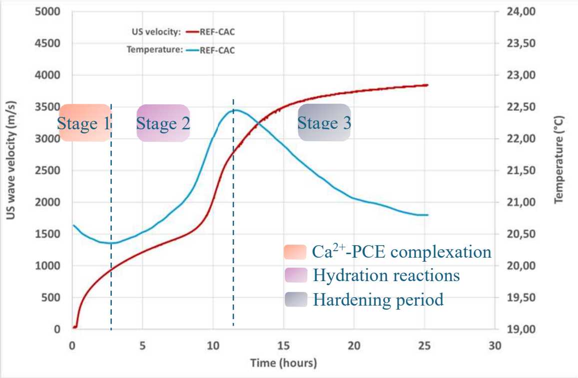

Fig. 1: US velocity and temperature vs. time for REF-CAC

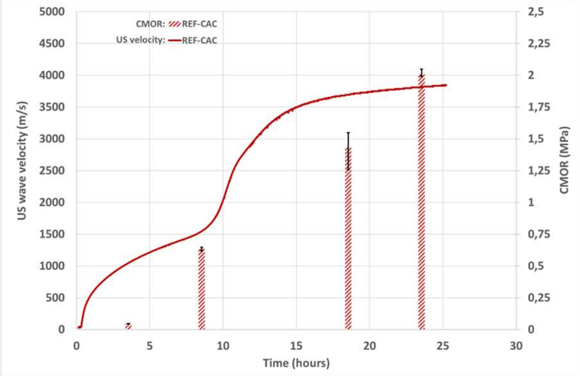

Fig. 2: US velocity and CMOR vs. time for REF-CAC

Effect of binder system on setting and strength development

US velocity curves and CMOR values of MS-0CAC and CS-0CAC castables were plotted alongside the REF-CAC castable (Fig. 3). No significant temperature rise was observed for MS- and CS- bonded systems, confirming the absence of exothermic hydration reactions. Therefore, temperature curves are not shown on Fig. 3 for clarity.

Compared to the REF-CAC castable, both MS-0CAC and CS-0CAC castables exhibit only a single sharp rise during the monitoring period. This single increase in US velocity is not directly correlated with early mechanical strength development. Indeed, for the MS-0CAC castable, no measurable strength is observed at 9 hours because the material is still soft, whereas a significant strength is reached at 18 hours, suggesting that strength development begins between 9 and 18 hours, without any corresponding change in US velocity. In the CS-0CAC castable, mechanical strength becomes measurable only at 24 hours and remains relatively low.

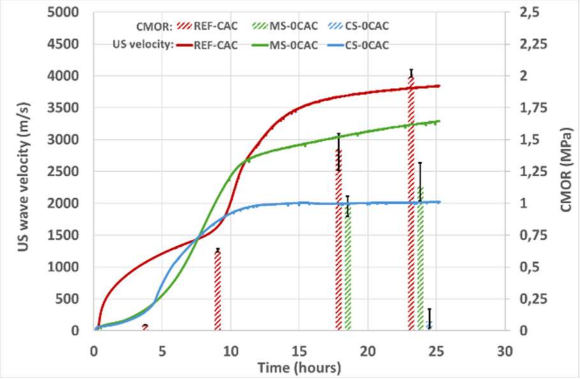

Fig. 3: Comparison of US velocity and CMOR for REF-CAC, MS-0CAC and CS-0CAC castables

This delay between the evolution of US velocity and mechanical strength, unlike the behaviour observed in the REF-CAC system, highlights a different setting mechanism in CAC-free castables. This setting mechanism can be described as follows:

- *<u>Stage 1 – Dormant period:</u>* Initially, colloidal silica particles bearing silanol groups (Si–OH) remain stable in suspension. No significant change in stiffness or mechanical properties occurs during this phase.
- *<u>Stage 2 – Gelation period:</u>* Destabilisation of the silica particles leads to their aggregation and the formation of a three-dimensional physical network via hydrogen bonding and Van der Waals forces. This results in increased viscosity and apparent stiffening of the system, as reflected by the sharp US velocity rise. However, no covalent bonding or mechanical strength is developed at this stage. This behaviour could be confirmed by oscillatory rheology measurements, where the gelation point corresponds to the crossover between storage (G′) and loss (G″) moduli, already observed for pure colloidal suspensions [12].
- *<u>Stage 3 – Hardening period:</u>* As drying progresses, silanol groups condense to form siloxane bonds ((Si–OH + Si–OH → Si–O–Si + H_2O), progressively building a covalently bonded network. This process is much slower and diffuse than CAC hydration reactions, which explains the absence of a second sharp US velocity increase. The moderate US velocity rise in this stage may be analogous to the hardening period in CAC systems but is driven here by polymerisation rather than hydrate conversion.

To better visualise the setting behaviour in CAC-free systems, Fig. 4 summarises the typical three-stage evolution observed in MS-0CAC and CS-0CAC castables. However, for the CS-0CAC castable, although the gelation likely occurs at a similar time as in the MS-0CAC system, the polycondensation appears more delayed. The reason for this delay is not yet understood. A plateau in US velocity is observed between the end of the initial rise and the onset of mechanical strength development, possibly reflecting a second dormant period. Beyond 24 hours, a slight increase in US velocity suggests that polycondensation reactions may be starting (Fig. 5).

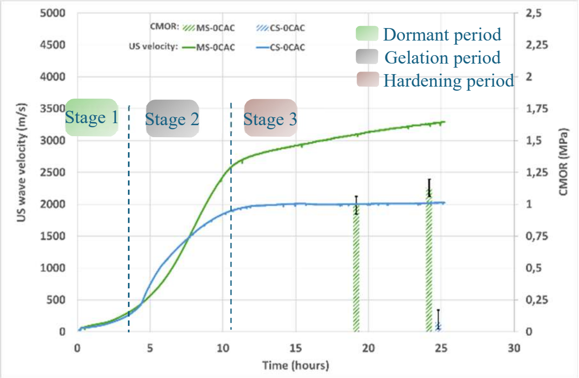

Fig. 4: US velocity and CMOR for MS-0CAC and CS-0CAC castables

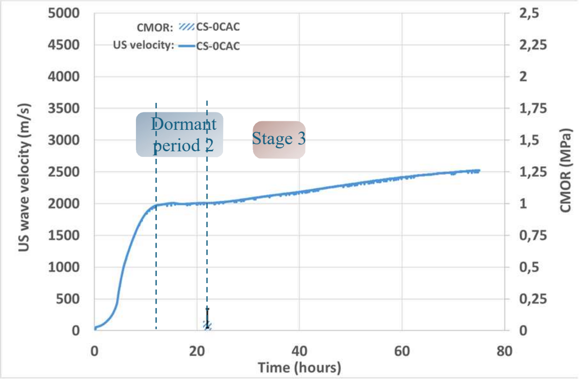

Fig. 5: Delayed polycondensation in CS-0CAC castable: US velocity and CMOR over extended monitoring period

Effect of hybrid bonding on setting and strength development

MS-based systems with CAC addition

Compared to the reference MS-0CAC system, the incorporation of small amounts of CAC significantly alters the setting behaviour by accelerating the structuration of the silica network. In the MS-0,25CAC and MS-0,5CAC systems, the US velocity increases sharply within the first 2 to 3 hours, whereas it takes between 4 and 10 hours for MS-0CAC. This indicates that CAC addition induces a much faster transition from a liquid or soft material to a stiffened one (Fig. 6). The dormant period observed in the MS-0CAC system is shortened or even eliminated for MS-0,25CAC and MS-0,5CAC.

This acceleration is also reflected in the mechanical strength development. Measurable CMOR values are observed as early as 1 hour for MS-0,5CAC and 4 hours for MS-0,25CAC, whereas no strength is detected before 18 hours in the MS-0CAC. For MS-0,5CAC, the development of mechanical strength closely matches the US velocity increase, with a maximum CMOR value reached as the US velocity stabilises. In contrast, for MS-0,25CAC, strength development appears to lag slightly behind the acoustic signal stabilisation: the material remains soft during the velocity rise, implying that the gelation is not finished or the polycondensation reactions had not started yet. However, once mechanical strength emerges, it appears to stabilise quickly, similarly to MS-0,5CAC. After 24 hours, all systems reach comparable CMOR values, confirming that the main effect of CAC lies in accelerating the kinetics of setting and structuration process of the silica network rather than changing the final mechanical performance.

As a result, the addition of CAC into the MS-based system leads to the elimination of the dormant period (Stage 1), and to the overlapping, or even merging, of the gelation (Stage 2) and hardening (Stage 3) phases.

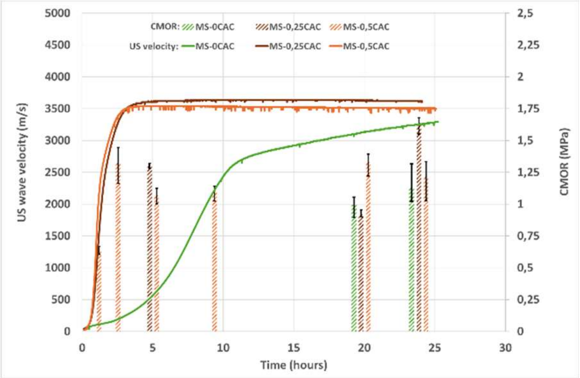

Fig. 6: US velocity and CMOR for MS-0CAC, MS-0,25CAC and MS-0,5CAC castables

This behaviour can be attributed to the hybrid bonding mechanism. The addition of small amounts of CAC leads to Ca^{2+} ions dissolution which react with hydroxyl species in the system (from free water and silanol groups promoting the early structuration of the silica network through the formation of $Ca(OH)_2$ [1]. By reducing free water, these ions favour the proximity and interaction of silanol groups (Si–OH), thereby accelerating their polycondensation into a covalently bonded siloxane network. The higher the CAC content, the stronger this catalytic effect, resulting in a faster development of stiffness and mechanical strength.

CS-based systems with CAC addition

Compared to the reference CS-0CAC system, the addition of 0,5wt.% of CAC delayed the gelation process as the US velocity rise appears between 8 and 15 hours while between 4 and 10 hours for CS-0CAC (Fig. 7). However, CAC addition seems to accelerate the hardening period as the slow rate in US velocity after the sharp rise is directly present.

Regarding mechanical strength development, both systems show low CMOR values at 24 hours, but the strength measured for CS-0,5CAC is slightly higher, and correlates with the ongoing increase in US velocity. This indicates that structuration and mechanical reinforcement are still progressing. In contrast, the plateau in US velocity observed for CS-0CAC implies that the material remains in a poorly structured state, consistent with the weak strength achieved.

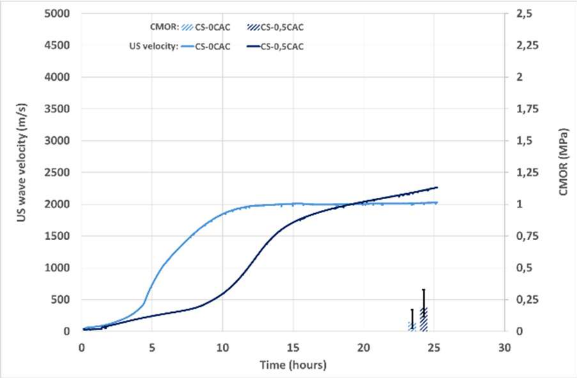

Fig. 7: US velocity and CMOR for CS-0CAC and CS-0,5CAC castables

Interestingly, this delayed gelation in CS-0,5CAC is absent when no CAC is used, as both MS-0CAC and CS-0CAC exhibit similar gelation times. This suggests that the interaction between Ca^{2+} ions and silica particles depends on the initial form of the binder, whether introduced as submicronic silica powder (MS) or as a stabilised colloidal suspension (CS).

In colloidal silica suspensions, particles are typically stabilised by monovalent cations such as Na^+ adsorbed onto their surface, which is the case for the colloidal silica suspension used in this study. Upon CAC addition, divalent Ca^{2+} ions can substitute Na^+ in the electrical double layer due to their higher valence and temporarily reinforce colloidal stability. As a result, these Ca^{2+} ions become engaged in surface charge compensation and are no longer available to react with hydroxyl groups or reduce the amount of free water in the system, both of which are crucial for initiating gelation.

After the gelation period, the CS-0,5CAC castable exhibits a slow increase in US velocity compared to the CS-0CAC one which exhibit a plateau, suggesting that once the physical network is formed, the subsequent polycondensation reactions proceed more rapidly in the presence of CAC in the CS system. This behaviour may result from a catalytic effect of Ca^{2+} ions, which, after the gelation period must be released and become available to interact with silanol groups and promote the polycondensation reactions. However, despite this apparent acceleration of the polycondensation step, the overall mechanical strength developed in the CS-0,5CAC system remains significantly lower than that observed in the MS-based systems. This discrepancy may be attributed to a lower degree of siloxane network crosslinking in the CS system. Thus, although CAC accelerates the hardening of CS system, it fails to achieve the same mechanical reinforcement observed in MS-based castables.

CONCLUSIONS

Understanding the early-age setting behaviour of refractory castables is essential for adapting them to 3D printing technologies. In this context, controlling the early-age setting mechanism is a key to achieve the required balance between pumpability and buildability. The castable bonded with calcium aluminate cement (CAC), used as a reference system in this study, has already demonstrated this balance, thanks to an initial stiffening phase, likely governed by calcium ion (Ca^{2+}) complexation with short side chain polycarboxylate ether (PCE) setting additives. This transient stiffening, which precedes mechanical strength development, ensures sufficient viscosity to support successive layers during printing, while maintaining adequate pumpability.

However, a shift toward more sustainable refractory castables involves the substitution of CAC, either partially or fully, through the introduction of alternative binder systems. Such systems enhance recyclability and reduce the risk of explosive spalling during drying or initial heat-up, contributing to a lower environmental footprint. In this context, CAC-free formulations based on colloidal silica suspension or microsilica powder represent a promising direction. Yet, their successful implementation in 3D printable formulation requires a precise control of their setting mechanism at early stages, as it directly influences the printability properties and ultimately the quality of printed parts.

From this perspective, the present study provides valuable insights into the setting and hardening mechanisms of no-cement castables bonded with silica-gel systems, with a particular focus on the effects of hybrid bonding through small additions of CAC. It highlights how such hybrid bonding can significantly modulate the setting behaviour by influencing the gelation and polycondensation phases, driven by Ca^{2+} ions interacting with silica particles and hydroxyl groups. These effects are strongly dependent on the nature of the silica source (microsilica vs. colloidal silica), underlining the importance of binder selection and formulation strategy. The findings pave the way for engineering sustainable refractory inks with tailored setting behaviour, specifically adapted for 3D extrusion process.

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