

Activation of Calcium Aluminate Based Aqueous Suspensions

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INTRODUCTION

Besides the wide use of calcium aluminate cement (CAC) as a binder for refractory castables, the dispersion of its particles in water is still a challenge due to their fast hydration reaction. This effect inhibits using CAC in other applications, for instance for colloidal processing or direct foaming. Even with the use of additives that act retarding the hydration, the setting control is not sufficient for some new applications. For example, for direct ink writing additive manufacturing techniques, which are based on the printing of slurries, it's desired to have a feedstock that presents a viscous liquid behaviour when extruded and a solid one just after deposition [1]. The transition between the liquid feedstock into a solid should be well controlled in order to generate a ceramic layer with convenient mechanical strength, able to support the next one printed over it. A similar transition is desired for the production of ceramic foams by the direct foaming route. In order to avoid the destabilisation of the foam, which would result in undesired microstructures, fast solidification of the system is required [2]. Based on these demands, the possibility of stabilising CAC particles in water is attractive and could create new technological applications for this raw material.

Recently, a new technology was developed in order to stabilise CAC particles into an aqueous and non-toxic media. Based on that, it's possible to produce CAC-based suspensions with a range of stability up to 6 months at room temperature. Besides cement, other ceramic powders, as alumina, can be added to the suspension. After stabilisation, it is possible to reactivate the system, allowing the hydration reaction to take place.

The reactivation of CAC-based suspensions can be conducted by the increase of the system's pH. After adjusting this property to the basic range, the hydration of the refractory cement can occur normally. If a faster solidification is desired, hydration can be speed up by adding some lithium source [3] or increasing the temperature [4]. The presence of Li⁺ catalyses the formation of calcium aluminate hydroxides as it reacts with aluminium ions generating lithium aluminate [3]. Therefore, the amount of Ca²⁺ in the aqueous media increases and the particles of lithium aluminate act as nuclei to the growth of hydrates. The solubility of calcium aluminates also can be increased by adjusting the temperature [4].

In addition to the possibility of tailoring the setting kinetics of the CAC-based aqueous suspensions, other benefits are pointed out for this potential raw material. Among them, the dispersion of cement particles, the high mechanical strength after solidification and the generation of refractory phases at elevated temperatures, are further attractive to the refractory industry.

Considering the potential of application for CAC-based suspensions as refractory raw materials, the kinetics of solidification was studied in this work. The effects of pH, the amount of lithium and temperature in the solidification of CAC-based suspensions were characterised by rheometry, ultrasound speed and temperature measurements. With these techniques, the transition from a liquid to a solid was assessed and associated with the hydration steps of calcium aluminate cement.

MATERIALS AND METHODS

Two CAC-based stabilised suspensions produced by Kerneos (Vaulx-Milieu, France) were used in this work. The main general information is presented in the Tab. 1. Suspension A was comprised only by CAC, whereas the composition B contained 80% of alumina and 20% of cement. The same amount of water was used for both suspensions.

Tab. 1: Information about the CAC-based suspensions

Components (wt%)	Suspension	
	A	B
CAC	75	15
Reactive aluminas	0	60
Water	25	25
Volumetric fraction of solids, vol%	50	45

In order adjust the systems' pH and reactivate the suspensions, an aqueous solution of NaOH with 4 mol.L⁻¹ of concentration, was selected. The hydration reaction was speed up by using different quantities of an aqueous solution of Li₂SO₄ at 1.4 mol.L⁻¹.

The effect of the amount of base added in the systems was monitored by pH measurements, carried out by a pH meter SevenMulti S40 (Metler Toledo, Switzerland). Aqueous buffer solutions with pH 7, 9 and 12 were used to calibrate the electrode. The impact of the pH increase in the suspensions' rheology was also followed by the viscosity measurements at room temperature. These tests were carried out in a rheometer MCR 302 (Anton Paar GmbH, Austria). For the rheology tests, the cup-in-vane geometry was selected and the test was carried out at a shear rate of 1000 s⁻¹.

The same rheometer and geometry were used for the oscillatory tests of the activated suspensions. The linear viscoelastic domain of the systems at 1 Hz was previously analysed and was found out to be in the strain range of 0.02% – 0.5%. Based on this, the evolution of storage (G') and loss (G'') moduli as a function of time was carried out at 1 Hz and 0.1% of strain. Whereas G' represents the solid behaviour of the viscoelastic material, G'' express its liquid features. Changes in G' and G'' as a function of time could suggest some microstructural evolution as the formation of a gel, for example [5]. These tests were carried out in the temperature range between 20°C and 50°C. In order to avoid evaporation, a thin layer of oil was placed over the suspensions during these experiments.

In situ ultrasound speed (US) and temperature measurements of CAC-based suspensions were also carried out for the systems kept at room temperature up to 48 hours after reactivation. The ultrasound speed evolution was measured by an ultrasonic measuring system IP-8 (Ultratest, Germany) and allowed the evolution of the percolation of the solid particles, which could be related to the solidification of the system [6]. The temperature evolution of the activated systems was monitored by a temperature measuring system comprised by a K thermocouple and a data recorder. Considering that the precipitation of calcium aluminate hydrates is followed by the

release of heat [7], this phenomenon could be detected by measurements of temperature. When these results are coupled with the US curves, it is possible to identify the share of hydration to the system solidification.

RESULTS AND DISCUSSION

As the increase in pH is the first step to reactivate the CAC-based suspensions, titration and viscosity evolution of the suspensions A and B were measured. The results are plotted in Fig. 1. Based on those, suspension A presented an initial pH slightly superior to that of the suspension B. It was also easier to increase the pH in the plain CAC suspension when compared to that containing CAC and alumina. For system B, part of OH⁻ was possibly adsorbed on the partially positive charged Al₂O₃ surface [8]. Due to this effect, more base solution was needed to increase the pH of the suspension B.

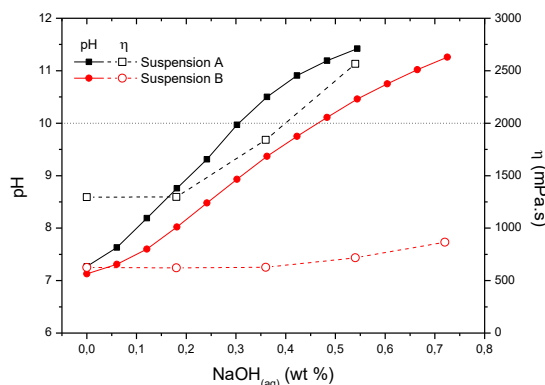


Fig. 1: pH and viscosity (η) of suspensions as a function of the amount of base added in the system. The curves are only guides to the eyes.

When both suspensions reached a pH value close to 10 (Fig. 1), it was observed the increase in the viscosity (η), suggesting that some change occurred in their microstructures. The different volumetric fraction of solids as shown in the Tab. 1 justifies the values of η before the addition of base solution to the system. However, the evolution of η around pH 10 was more intense in the composition A. Based on that, it is possible to conclude that the viscosity increase was caused by the presence of calcium aluminates that seems to be reactivated above pH 10. The hydration of CAC is divided into three stages: dissolution, nucleation and massive precipitation [4]. Considering that nucleation and precipitation would occur within a few hours after activation, the increase in viscosity presented in the Fig. 1 is associated with the period of dissolution of CAC particles. Thus, ionic strength could induce the viscosity increase in the systems.

In order to follow the kinetics of solidification with time, ultrasound speed (US) and temperature measurements were carried out for the suspensions with pH adjusted to 11. The results, presented in the Fig. 2, suggested that two main phenomena took place after reactivation. The first one, observed within the first hour of measurement for both the systems, was characterised by the increase of US value. When this result is compared with the previously discussed in Fig. 1, it is possible to infer that the increase in viscosity caused the percolation of solid particles, generating a gel. This transition was followed up by the reduction of temperature, which was due to the thermal equilibrium of the suspensions and the environment.

The second phenomenon observed was the disturbance in the US curves followed by the heat release. This effect was associated with the massive precipitation of calcium aluminate hydrates. The formation of these hydrates most likely caused dimensional variations in the system, disturbing the path of the ultrasound waves. Fig. 2(b) presents a reduction in the US values observed among 15 and 24 hours. As the system B had a higher amount of alumina and considering the ternary solubility diagram of the system Al₂O₃-CaO-H₂O, it is possible that amorphous Al(OH)₃ was formed after reactivation [3]. The later crystallisation of this phase could generate defects in the microstructure, reducing the US speed.

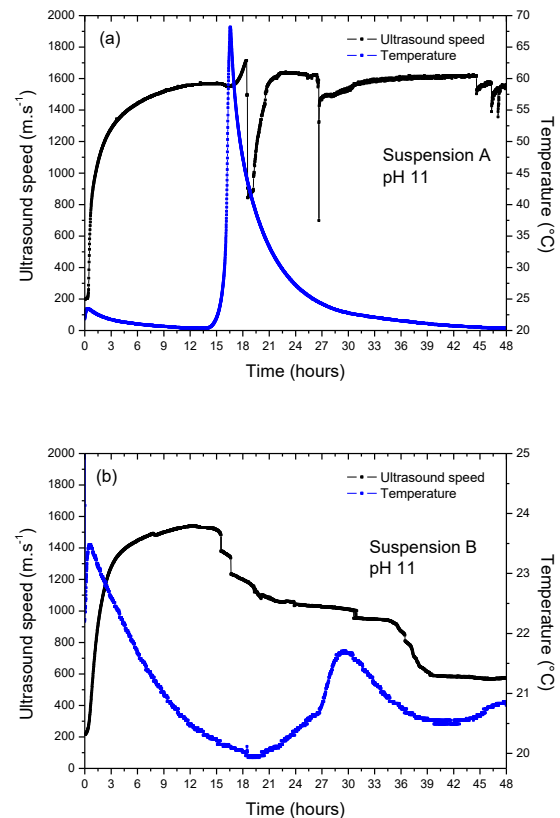


Fig. 2: Ultrasound speed and temperature evolution after adjusting the pH of suspensions to 11 with the NaOH aqueous solution.

Based on the results discussed before, it was concluded that CAC-based suspensions could be activated by increasing the pH. Besides the increase in viscosity and ultrasound speed recorded for the initial 3 hours, the precipitation of calcium aluminate hydrates took place after at least 15 hours. Aiming to reduce this time, additions of lithium sulphate were carried out to the systems, after adjusting their pH to 11 (for suspension A) or to 12.5 (for suspension B). The pH of suspension B was adjusted to a higher value in favour of speeding its solidification.

Initially, oscillatory tests were carried out to the suspensions. In Fig. 3, the evolution of G' and G'' can be observed as function of time. These measurements were accomplished immediately after adding the base and lithium sources, and stirring the suspensions at 1000 s⁻¹ for 1 minute. The initial increase of both G' and G'' was related to the reconstruction of the system's microstructure after the intense disturbing process. During the measurements, G' was higher than G'' . Besides that, both curves followed a parallel path up to an inflection point, where G' started to increase at a higher rate. At the same time, the storage modulus (G') reached a superior

and constant value and the loss modulus (G'') started to fall. The physical meaning of this transition, where the solid behaviour was intensified and the liquid one reduced, is the formation of a gelled microstructure. As Fig. 3(a) shows, this transition occurred within 9 minutes for suspension A with pH adjusted to 11 and no lithium sulphate. Additions of $\text{Li}_2\text{SO}_4(\text{aq})$ accelerate the gel formation, reducing the time where this event occurred. The same effect was observed for suspension B, as seen in the Fig. 3(b). Lithium additions speed up the formation of the gel, but the times for this transition were higher than those observed for the plain CAC suspension. For suspension B without lithium, this time was longer than 20 min, whereas 0.62 wt% of this additive reduced the transition time to 12 min. As mentioned, the reaction of Li^+ with aluminium ions due to the precipitation of lithium aluminate particles, followed by an increase in the quantity of Ca^{2+} present in the aqueous media. The formation of lithium aluminate seems to be the main cause of the gel transition observed, as the release of heat due to precipitation of calcium aluminate hydrates occurred later, as presented in the Fig. 4. In this figure, the US and temperature curves measured for the suspensions A and B with pH adjusted to 11 or 12.5, and 0.35 wt% or 0.62 wt% of $\text{Li}_2\text{SO}_4(\text{aq})$, are plotted, respectively.

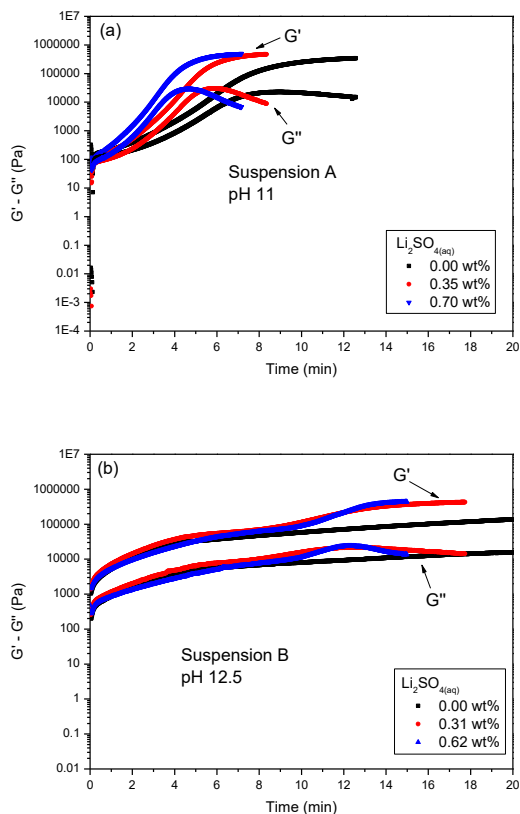


Fig. 3: Storage (G') and loss (G'') moduli measured after adjusting the pH and adding different amounts of lithium sulphate to the suspensions.

Conversely to the results in Fig. 2, the exothermic event occurred earlier for both systems containing lithium, as seen in the Fig. 4. The addition of Li^+ led to the acceleration of solidification, which was characterised by the increase in the US values. As observed in Fig. 4, US speed reached the maximum value in 3 hours for suspension A and 10 hours to the suspension B. Considering the temperature values attained when the lithium source was added and comparing them with those registered in the Fig. 2, it is noticed that Li^+ induced a stronger

release of heat. It could be supposed that a higher amount of hydrates were formed in this case. Additionally, no disturbances were identified in the US curves of Fig. 4 (a) and (b), suggesting that dimensional changes or cracking were minimised. Taking into account that the elastic modulus is proportional to the value of ultrasound speed [9], stronger microstructures were generated, highlighting the importance of this technique.

Besides the higher amount of $\text{Li}_2\text{SO}_4(\text{aq})$ added to the suspension B, the volume of activators was relatively small when considering the volume of the system. Therefore, higher quantities of this accelerator could be added to the suspension in order to speed up the transition from liquid to solid. However, it is important to keep in mind that, with the increase of Li^+ added, low melting phases could be generated in the system, depending on the composition. Deleterious effects could be observed at high temperatures, limiting the application range of the material.

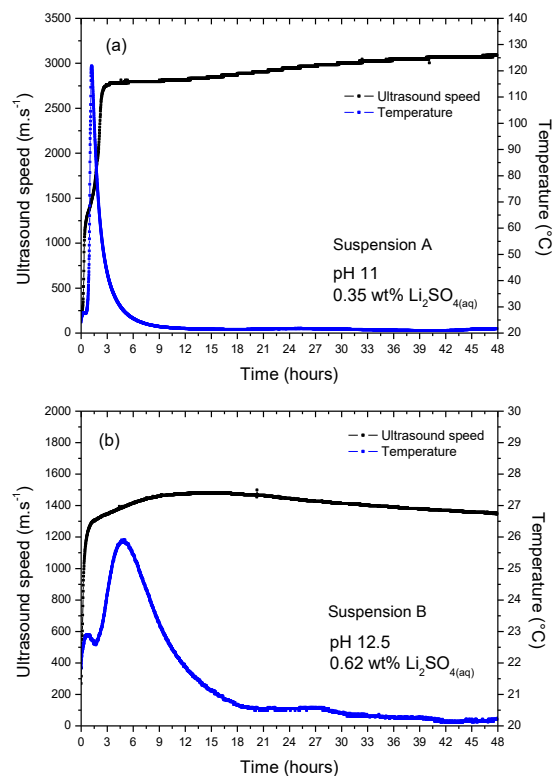


Fig. 4: Evolution of ultrasound speed and temperature of suspensions activated with NaOH solution and lithium sulphate.

The acceleration of the liquid-solid transition could be attained by increasing the temperature of the systems. In order to evaluate the effect of temperature on the solidification of reactivated suspensions, oscillatory tests were carried out in suspensions A and B with pH adjusted to 11 or 12.5 and 0.35 wt% or 0.62 wt% of lithium source added, respectively. The curves showing the evolution of storage and loss moduli with time, for temperatures of 20°C , 40°C and 50°C , are presented in the Fig. 5.

For both the suspensions, the evolution of the viscoelastic moduli showed the same behaviour. Initially, it was identified the increase in the values of G' and G'' , related to the microstructure recovery after discontinuing the stirring. The storage modulus was higher than the loss one, and they increased up to the inflection point where G' augmented in a higher rate, reaching a superior and constant value. At this point, G'' started to fall, indicating that the liquid behaviour of the suspensions was continuously reduced. This transition occurred in shorter times when the temperature was increased and was

more prominent for suspension B. For this system, it was detected a reduction in the gelling time from about 12 minutes at 20°C down to 2 minutes at 50°C. System A also presented the reduction in the gelling, from 5 minutes down to 1 minute when the temperature was raised from 20°C to 50°C. Very likely the increase in the calcium aluminates solubility with temperature enriched the aqueous media with Ca^{2+} . When these ions were exposed to an environment with homogeneous nuclei, the hydration could take place earlier. By this mechanism, it was possible to avoid the excessive addition of lithium sulphate to the systems, and a faster solidification was achieved. The increase of temperature above 27°C also induces the formation of more stable and denser calcium aluminate hydrates [4]. The risk of damages due to the transition with time of less stable phases to more stable ones would be reduced and a stable microstructure could be attained.

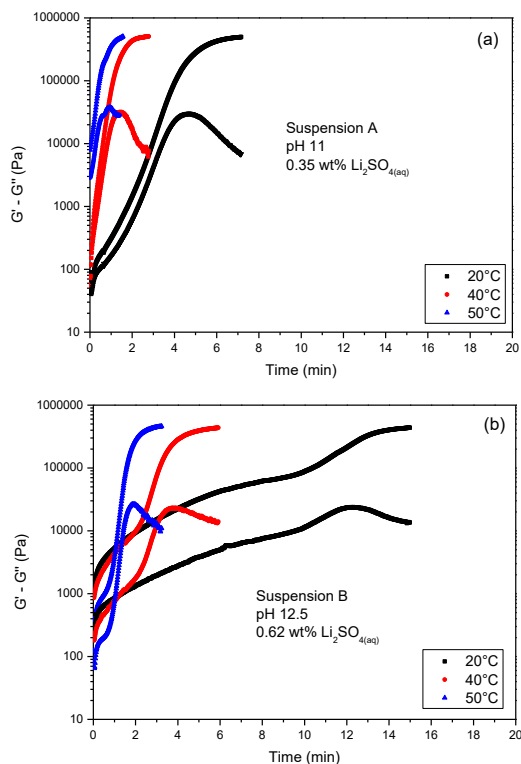


Fig. 5: Temperature effect in the evolution of storage and loss moduli of the activated suspensions.

CONCLUSIONS

CAC-based stabilised suspensions comprising plain CAC or CAC and Al_2O_3 could be reactivated by increasing the system's pH to values above 10. After adjusting the pH, the suspensions presented two main steps of solidification: the first one occurred within the first hour after activation and was related to the formation of a gel. The second step, which took place after 17 hours for the suspension A and 30 hours for the suspension B, was characterised by the heat release and disturbance of ultrasound speed curve profile. This later step was associated with the precipitation of calcium aluminate hydrates.

The viscoelastic behaviour after reactivation was evaluated by rheology oscillatory measurements. These tests indicated that the addition of lithium sulphate speed up the gel formation, which was identified by the increase in the storage modulus up to a constant value followed by the continuous decrease of loss modulus. The effect of lithium additions as an accelerator was also observed in the ultrasound speed and temperature curves. Suspensions with pH and lithium sulphate amount adjusted

presented earlier solidification steps. For the alumina-rich suspension, higher additions of accelerator were needed in order to speed up the liquid-solid transition. The temperature effect was tested in order to reduce the amount of lithium added. It was observed that increasing the temperature of the activated systems acted as an accelerator for solidification, due to the earlier gel formation.

This set of results indicates that it is possible to adjust the kinetics of solidification of the CAC-based suspensions for very short times, as those demanded by feedstock for additive manufacturing or the production of ceramic foams. Considering the other benefits of calcium aluminate cements, these suspensions are pointed out as potential raw materials to be applied in new processing refractory routes. Nevertheless, further efforts are needed for the development of systems and devices that regulate the reactivation of the suspensions *in situ*, in order to apply them as feedstock to additive manufacturing. A careful study of the generated phases after activation and the related properties at high temperatures should also be carried out.

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BIBLIOGRAPHY

- [1] Lewis JA, Smay JE, Stuecker J, Cesarano J. Direct ink writing of three-dimensional ceramic structures. *J. Am. Ceram. Soc.* 89 (2006) 3599–3609.
- [2] Krauss JF, Gonzenbach UT, Elser P, Studart AR, Gauckler LJ. Microstructural control of self-setting particle-stabilized ceramic foams, *J. Am. Ceram. Soc.* 94 (2011) 77–83.
- [3] Rodger SA, Double DD. The chemistry of hydration of high alumina cement in the presence of accelerating and retarding admixtures, *Cem. Concr. Res.* 14 (1984) 73–82.
- [4] Parr C, Simonin F, Touzo B, Wöhrmeyer C, Valdelièvre B, Namba A. The impact of calcium aluminate cement hydration upon the properties of refractory castables, *TARJ Meet.* (2004) 1–17.
- [5] Rouyer J, Poulesquen A. Evidence of a fractal percolating network during geopolymerization, *J. Am. Ceram. Soc.* 98 (2015) 1580–1587.
- [6] Sayers CM, Dahlin A, Propagation of ultrasound through hydrating cement pastes at early times, *Adv. Cem. Based Mater.* 1 (1993) 12–21.
- [7] Klaus SR, Neubauer J, Goetz-Neunhoffer F. Hydration kinetics of CA2 and CA—Investigations performed on a synthetic calcium aluminate cement, *Cem. Concr. Res.* 43 (2013) 62–69.
- [8] Yopps J, Fuerstenau D. The zero point of charge of alpha-alumina, *J. Colloid Sci.* 19 (1964) 61–71.
- [9] Wachtman JB, Cannon WR, Matthewson MJ, *Mechanical properties of ceramics*, 2nd ed., John Wiley & Sons, Inc., 2009.

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