# WET-GROUND CALCIUM ALUMINATE CEMENT AS A BINDER FOR MACROPOROUS REFRACTORIES DERIVED FROM ALUMINA-STABILISED FOAMS

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## ABSTRACT

Calcium aluminate cement (CAC) is broadly used as a binder for ceramic applications as it can provide suitable setting times, high mechanical strength and refractoriness. When applied to macroporous refractories, this binder can set the fresh foam before the aging phenomena take place, resulting in higher porosity. Nevertheless, its large particles induce bubble size enlargement, resulting in samples with coarser and wider-distributed pore sizes, which is undesirable for high-temperature thermal insulation. An alternative to overcome this issue is the grinding of CAC stable aqueous suspensions ($CAC_S$), which can be carried out by using sodium gluconate as a reversible hydration hindering additive. The efficiency of the $CAC_S$ grinding process was assessed as a function of time and the impacts of adding wet-ground CAC to macroporous refractories derived from $Al_2O_3$-stabilised foams were analysed. By using the wet-ground CAC, samples with a faster setting kinetics, higher mechanical strength and refined pores were attained.

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## 1 INTRODUCTION

Nowadays, directly-foamed ultrastable porous ceramics can be used to give rise to macroporous refractories with high porosity, low density and homogeneous microstructure[1,2]. These materials can find several applications, including high-temperature thermal insulation[1,2]. In this regard, computational simulations show that pore sizes ranging from 0.5 µm to 3 µm minimize the thermal conductivity of $Al_2O_3$-based porous ceramics in the range between 1000 °C and 1700 °C, improving their performance and enhancing energy saving[3]. Ceramics with pores lying in this size range are categorized as macroporous ceramics according to IUPAC. An essential feature to be considered in the production of these directly-foamed macroporous refractories is the proper selection of the binder, which must provide suitable setting times, mechanical strength after curing and refractoriness[4]. Although calcium aluminate cement (CAC) has been broadly applied due to its efficiency to provide such features, some authors pointed out that the large particles of this binder – coarser than those of the other raw materials in the composition – may induce bubble size enlargement in the liquid foam, resulting in macroporous samples with higher average pore size and wider cell size distribution[5,6], which is undesirable for the production of high-temperature thermal insulators.

An alternative to overcome this issue is the CAC milling, however, the dry process is ineffective, and the wet one looks unfeasible due to hydration[7]. In this regard, based on some of the authors previous study, the production of a calcium aluminate cement stable aqueous suspension ($CAC_S$) using sodium gluconate as a reversible hydration hindering additive can be a way to enable the CAC wet-milling[8]. Suspensions like these ($CAC_S$) have already been used to produce ultrastable ceramic foams, leading to macroporous refractories with high porosity and suitable mechanical strength, but still presenting pore sizes larger than the optimized range (0.5 µm – 3 µm)[5]. Therefore, the use of wet-ground CAC seems to be an alternative to refine the pore size distribution, bringing it closer to the desired range. In this work, the use of sodium gluconate was evaluated as reversible hydration hindering additive to allow the CAC wet-milling. The efficiency of the grinding process was assessed as a function of time and the impacts of adding wet-ground CAC to macroporous refractories derived from $Al_2O_3$-stabilised foams, were analysed.

## 2 MATERIALS AND METHODS

### 2.1 Materials

Macroporous samples were produced following the procedure described by Finhana *et al.*[6]. Firstly, $Al_2O_3$ suspensions containing 35 vol% of alumina A1000SG ($d_{50}$ = 0.6 µm, SA = 8.2 $m^2.g^{-1}$, Almatis, Ludwigshafen, Germany) were prepared. A1000SG was mixed in demineralised water, the system pH was adjusted to 5 with HCl 1 $mol.L^{-1}$ (diluted solution from hydrochloric acid 37 %, Synth, Diadema, Brazil) additions and the suspensions were kept under mechanical stirring for 1 h. Then, 10 µmol of L-leucine (Synth, Diadema, Brazil) per $m^2$ of $Al_2O_3$ surface area was added to the suspension and direct foaming by mechanical stirring was carried out using dispersing and *fouet* blades. After the foaming step, $CaCO_3$ (calcite, 99 %, $d_{50}$ = 7,38 µm, Imerys, Mogi das Cruzes, Brazil) was added to the system at the right content to enable 100 wt% of hibonite formation at the thermodynamic equilibrium (6 mol $Al_2O_3$: 1 mol $CaCO_3$). The *in situ* formation of this phase can partially counteract the undesirable high sintering-induced shrinkage of these macroporous ceramics[6].

To be applied as a binder, stable suspensions containing 25 vol% of calcium aluminate cement ($CAC_S$) were also prepared as described by Finhana *et al.*[6]. To produce these suspensions, 0 - 1 wt% of sodium gluconate (SG, 99 %, Synth, Diadema, Brazil) was firstly dissolved in demineralised water, which pH was previously adjusted to ~ 3.8 whit HCl 1 $mol.L^{-1}$ additions. Then, CAC (Secar 71, $d_{50}$ = 24 µm, Imerys, Le Teil, France) was dispersed in the solutions and kept under mechanical stirring for 10 min. After that, xanthan gum (1.79 wt% relative to the mass of water, Rhodopol 23, Solvay Novocare, Paulínia, Brazil) was added to the system, followed by another 10 min of mechanical stirring. For the CAC wet-grinding evaluation, these suspensions were milled as described in section 2.2. Before incorporating these CAC-based suspensions into the foam, the wet-ground ($CAC_{S,G}$) or the unground ($CAC_S$) suspensions were reactivated by adding 4.9 mL of acetic acid (99.5 %, synth, Diadema, Brazil) for each 100 mL of suspension, followed by 10 min of mechanical stirring[8]. The resulting ultrastable foams (UF) were moulded (50 mm x 50 mm cylinders), cured at 50 °C for 48 h and dried at 110 °C for 24 h. Some samples were also fired at 1600 °C for 5 h.

### 2.2 Methods

To evaluate the feasibility of the $CAC_S$ milling, CAC suspensions containing 0 – 1 wt% of SG over the mass of binder were produced and ground. The latter process was carried out in a ball mill and the particle size distribution was assessed as a function of grinding time in a small volume automated wet dispersion accessory Hydro 2000S coupled to a Mastersizer 2000, both from Malvern Panalytical (Malvern, United Kingdom). The dry grinding of CAC raw powder ($CAC_P$) was also evaluated to compare its effectiveness with the wet process.

Aiming at evaluating the setting kinetics provided by the wet-ground CAC suspension ($CAC_{S,G}$) compared to the unground one ($CAC_S$), $Al_2O_3$-$CaCO_3$ compositions (ACC) were prepared according to Table 1. The produced samples had the speed of ultrasound waves going through them assessed as a function of time. The analysis was carried out at 25 °C in IP-8 equipment (UltraTest, Achim, Germany), following ASTM C597-16.

Table 1 - Composition of $Al_2O_3$-$CaCO_3$ suspensions

| Raw material or additive | wt% |
|---|---|
| $Al_2O_3$ CL370 ($d_{50}$ = 2,5 µm, SA = 3,0 $m^2.g^{-1}$, Almatis, Ludwigshafen, Germany) | 67.79 |
| $Al_2O_3$ CT3000SG ($d_{50}$ = 0,4 µm, SA = 7,5 $m^2.g^{-1}$, Almatis, Ludwigshafen, Germany) | 5.10 |
| $CaCO_3$ (calcite, 99 %, $d_{50}$ = 7,38 µm, Imerys, Mogi das Cruzes, Brazil) | 11.50 |
| FS 60 (Castament® FS 60, BASF, Trostberg, Germany) | 0.53 |
| Lutensol AT 50 (Lutensol® AT 50 Pulver, BASF, Trostberg, Germany) | 0.11 |
| Demineralised water | 14.07 |
| CAC Secar 71 ($d_{50}$ = 24 µm, Imerys, Le Teil, France) | 0.90 |

Green and fired macroporous samples were characterized according to their total porosity and cold crushing strength (CCS). The former was calculated using the relationship between the samples' volumetric density and their helium pycnometry (AccuPyc 1330, Micromeritics, Norcross, USA) density, whereas the latter was evaluated in MTS 810 equipment (MTS, Eden Prairie, USA) following the ASTM C133-97. Pore size distribution was evaluated by image analysis obtained in a stereomicroscope Stemi 2000-C, coupled to an AxioCam ERc5S camera (both from Zeiss, Oberkochen, Germany) and using the Software Digimizer® (version 4.6.1, MedCalc Software, Oostende, Belgium).

## 3 RESULTS AND DISCUSSION

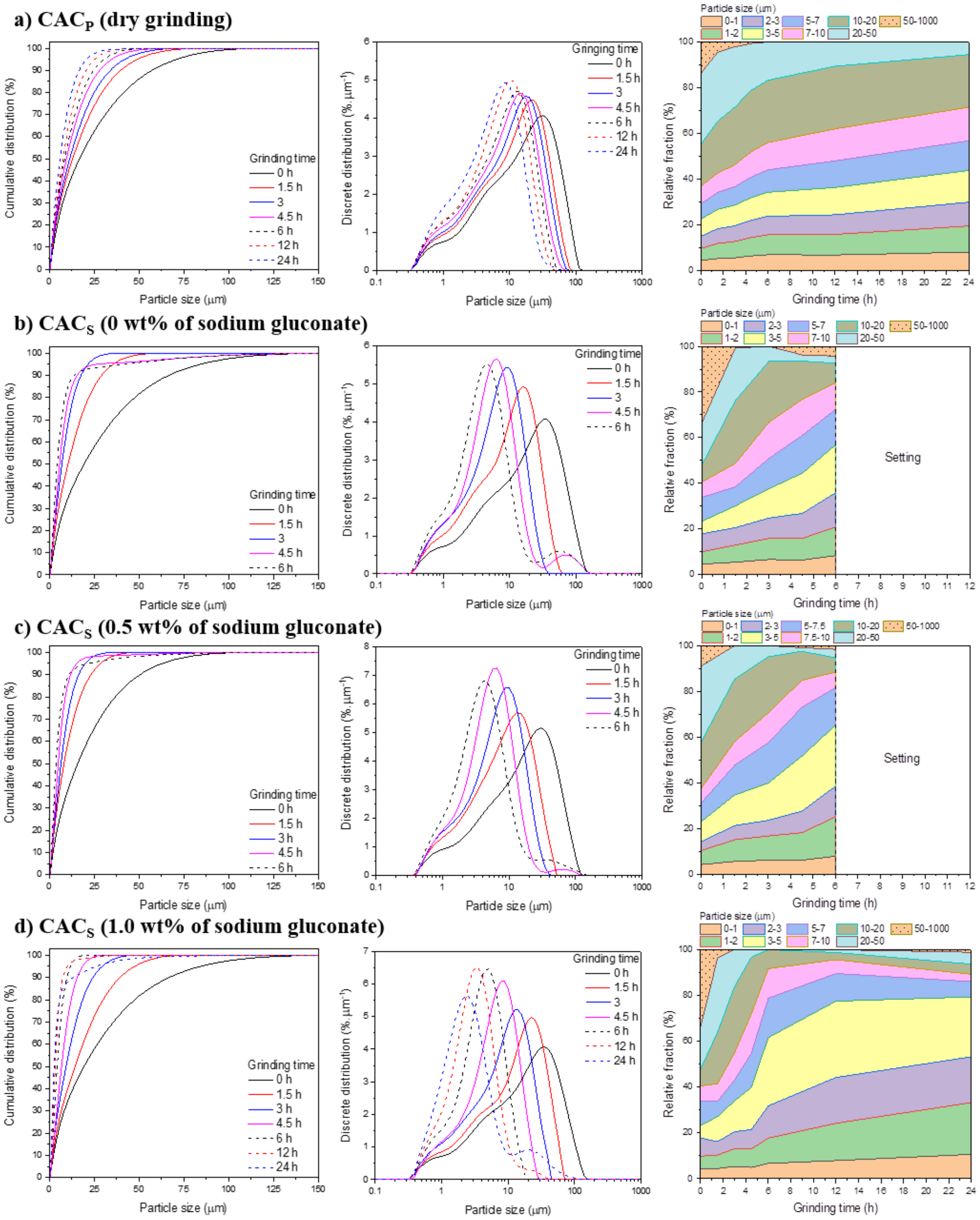
Figure 1 shows the particle size distribution (cumulative, discrete and by range size) as a function of grinding time for the CAC raw powder ($CAC_P$) or $CAC_S$ containing different amounts of sodium gluconate. It can be observed that the wet grinding is more efficient than the dry one, which is also shown in Table 2 that presents the percentual reduction of $d_{10}$, $d_{50}$, and $d_{90}$ particle size values for $CAC_P$ and $CAC_S$ (0 wt% of SG) between 0 h and 3 h of grinding. Nevertheless, the milling process becomes less effective after 6 h for both cases. Besides that, after 4.5 h of grinding for suspensions containing 0 wt% (CAC in water) and 0.5 wt% of SG, and after 12 h for the suspension containing 1 wt% of this additive, it can be observed that the reduction in particle size is accompanied by the rising of a coarser solids fraction. This phenomenon is attributed to the CAC hydration due to the absence ($CAC_S$ containing 0 wt% of SG) or deficiency ($CAC_S$ containing 0.5 or 1 wt% SG) of sodium gluconate molecules, which resulted in the setting of these suspensions, except for the composition containing the highest amount of sodium gluconate (1 wt%). This latter content had its hydration observed just after 12 h of grinding, but remained as a suspension throughout the evaluated period (24 h), proving to be the most promising suspension to be ground and applied as a binder. Thus, the suspension ground for 6 h was used to produce the macroporous samples.

Table 2: Percentual reduction of $d_{90}$, $d_{50}$, and $d_{10}$ particle size values between 0 and 3 h of grinding for $CAC_P$ and $CAC_S$.

| | Reduction of $d_{10}$ (%) | Reduction of $d_{50}$ (%) | Reduction of $d_{90}$ (%) |
|---|---|---|---|
| $CAC_P$ (dry grinding) | 18,35 | 32,50 | 40,36 |
| $CAC_S$ (0 wt% of sodium gluconate) | 30,23 | 63,77 | 73,51 |

Figure 2(a) shows the evolution of ultrasound speed through $Al_2O_3$-$CaCO_3$ (ACC) suspensions (described in item 2.2) containing $CAC_S$ (ACC + $CAC_S$) or $CAC_{S,G}$ (ACC + $CAC_{S,G}$). It can be seen that the latter one presented a faster setting kinetics, solidifying in less than 15 h. Figure 2(b) shows a plain $CAC_{S,G}$ sample ~ 30 min after its activation, highlighting the effect arising from the grinding as the sample was already solid after this short time. Thus, as the particle size decreased, CAC reactivity increased, allowing a faster setting kinetics. On one hand, this feature is desirable to speed up the porous ceramic production, on the other, it implies a narrow workability window.

Figure 1: Particle size as a function of grinding time for (a) CAC$_P$ (dry grinding), (b) CAC$_S$ in water containing 0 wt% of sodium gluconate, (c) CAC$_S$ in water containing 0.5 wt% of sodium gluconate, and (d) CAC$_S$ in water containing 1 wt% of sodium gluconate.



a) CAC$_P$ (dry grinding)

b) CAC$_S$ (0 wt% of sodium gluconate)

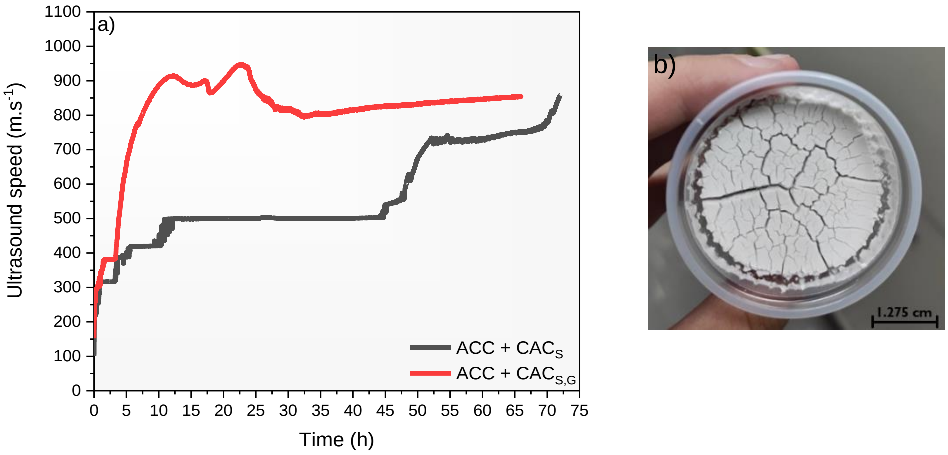
c) CAC$_S$ (0.5 wt% of sodium gluconate)

d) CAC$_S$ (1.0 wt% of sodium gluconate)

When applied as a binder to macroporous refractories, CAC$_{S,G}$ (UF + CAC$_{S,G}$) gave rise to green samples (110 °C) with lower total porosity compared to CAC$_S$-containing ones (UF +

CAC$_{S}$), resulting in higher green CCS (Table *3*). This reduction of the total porosity is assigned to a faster and more intensive mixing process required to incorporate the CAC$_{S,G}$ into the liquid foam, as its workability window was reduced due to the faster setting kinetics provided by the ground binder.

Figure 2: Evolution of ultrasound speed through $Al_2O_3$-$CaCO_3$ (ACC) suspensions containing CAC powder (ACC + CAC$_{P}$) or CAC suspension (ACC + CAC$_{S}$) or CAC ground suspension (ACC + CAC$_{S,G}$); (b) CAC$_{S,G}$ sample ~ 30 min after activation.



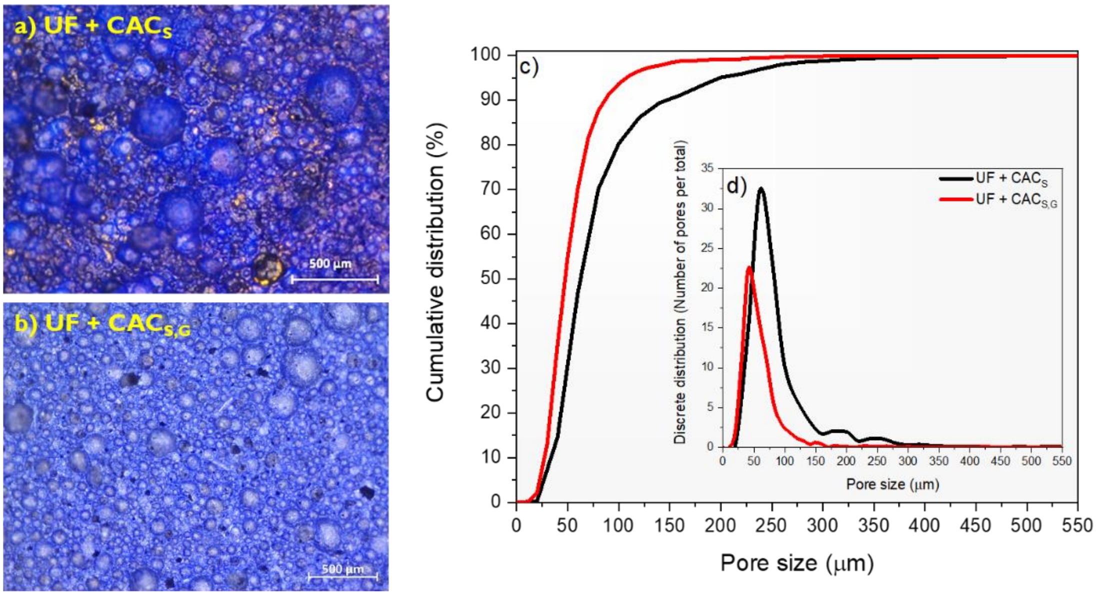
After firing (1600 °C / 5 h), sintering and densification were noticed for both macroporous compositions, as indicated by the reduction of total porosity and by the increase in CCS (Table *3*). Although the decrease of the total porosity was a bit lower for UF + CAC$_{S,G}$, which resulted in its higher porosity after firing, the samples of this composition also presented CCS values ~ 83 % higher than for the CAC$_{S}$-containing ones (UF + CAC$_{S}$). This result can be attributed both to the higher densification of the struts of UF + CAC$_{S,G}$ rather than pores densification, as well as a smaller pore size of this composition, which reduced the size of the mechanical critical flaw. Thus, using finer and more reactive CAC particles (CAC$_{S,G}$) favoured enhanced sinterability of the samples' struts and avoided small bubbles destabilisation in the fresh ceramic foam.

Table 3: Total porosity and cold crushing strength (CCS) of macroporous samples bonded with CAC$_{S}$ or CAC$_{S,G}$ after 110 °C for 24 h (green condition) or 1600 °C for 5 h (fired).

| | After 110 °C / 24 h | | After 1600 °C / 5 h | |
|---|---|---|---|---|
| Composition | Porosity (%) | CCS (MPa) | Porosity (%) | CCS (MPa) |
| UF + CAC$_{S}$ | 79.6 | 0.30 | 71.4 | 6.8 |
| UF + CAC$_{S,G}$ | 77.7 | 0.37 | 73.6 | 12.6 |

Figure 3 shows optical micrographs of (a) UF + CAC$_S$ and (b) UF + CAC$_{S,G}$ macroporous samples after firing (1600 °C / 5 h), and their (c) cumulative and (d) discrete pore size distributions. It can be noticed that using wet-ground CAC (UF + CAC$_{S,G}$) led to smaller average pore size and a narrower pore size distribution. This result is in tune with the hypothesis proposed by Santos *et at.*[5], in which the CAC larger particles induce topological changes in the foam structure in order to be accommodated, resulting in macroporous ceramics with higher average pore size. Thus, when the CAC$_{S,G}$ was applied (UF + CAC$_{S,G}$), its smaller particles did not affect significantly the bubbles' size of the fresh foam, giving rise to macroporous samples with smaller pores.

Figure 3: Optical micrographs of a) UF + CAC$_S$ and b) UF + CAC$_{S,G}$ macroporous samples after firing (1600 °C / 5 h) and their c) cumulative and d) discrete pore size distributions.



A better evaluation of the CAC$_{S,G}$-use on the energy saving related to the macroporous compositions analysed in this article is under development. Additionally, the ground CAC aqueous suspension presented in this paper will be used to produce surfactant-stabilised ceramic foams, which are simpler systems that can give rise to macroporous refractories with total porosity and CCS suitable for high-temperature thermal insulation[9]. Furthermore, the literature reports that adding $CaCO_3$ to these surfactant-stabilised materials can provide the total elimination of their sintering-induced shrinkage, which is highly desired[9]. Nevertheless, although the pore sizes of these ceramics are still far from the optimized range, using CAC$_{S,G}$ could be a way to bring them closer to the target.

## 4 CONCLUSIONS

The production of CAC aqueous suspensions using sodium gluconate as a reversible hydration hindering additive proved to be an efficient path to allow the CAC wet grinding. By using the wet-ground binder, ceramic foams with faster setting kinetics and smaller bubbles were attained. These features are assigned to the higher reactivity of the $CAC_{S,G}$ smaller particles and to their better accommodation inside the foam structure, which hindered significant topological changes in the foam structure leading to less small-bubbles destabilisation. After firing (1600 °C / 5 h), these foams gave rise to macroporous ceramics with smaller pores and cold crushing strength ~ 83 % higher when compared to the $CAC_S$-containing composition samples. Finally, the pore sizes tuning can improve the potential for energy saving of these materials, which implies that its use would lead to lower operating costs for high-temperature processes and, consequently, lower environmental impacts.

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