



# The influence of filler type and surface area on the hydration rates of calcium aluminate cement



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## ABSTRACT

The addition of finely pulverized materials such as limestone and quartz has been observed to increase the reaction rates of ordinary portland cement. This study describes the effects of mineral fillers including: limestone, dolomite and quartz on the hydration rates of calcium aluminate cements. By detailed analysis of isothermal calorimetry data and application of a phase boundary nucleation and growth model, it is shown that finely ground minerals enhance reaction rates in relation to: (1) their surface area, which increases with increasing proportion of CAC replacement by a fine mineral filler, and (2) the increase in the amount of water available for CAC hydration, i.e., dilution, that occurs as the CAC is replaced by a filler. Unlike in the case of OPC, CAC hydration rates, and enhancements therein in the presence of fillers are independent of the mineral type and are only a function of available surface area.

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## 1. Introduction and background

Over the past several years, on account of its production related CO<sub>2</sub> emissions, significant efforts have been made to reduce the use of cement as the primary binding agent in concrete [1–4]. One topic of significant study has been the so-called *filler effect* [4–11], wherein the replacement of OPC by a suitable filler (i.e., quartz, limestone, rutile) results in enhanced reaction rates, allowing for reduction of the OPC content without compromising property gain at early ages. The filler effect results from the enhanced nucleation of hydration products as additional surface area is provided by fine filler agents. While a wide range of fillers have been evaluated, in OPC, carbonate-based fillers (e.g., limestone, dolomite) have been noted to show filler effects superior to other mineral agents on account of their superior surface properties, and chemical composition [6,7,12–15].

Unlike OPC, calcium aluminate cements (CACs) consist dominantly of monocalcium aluminate (CaO·Al<sub>2</sub>O<sub>3</sub>, CA) and gehlenite (2CaO·Al<sub>2</sub>O<sub>3</sub>·SiO<sub>2</sub>, C<sub>2</sub>AS)<sup>1</sup> [16–19]. In spite of several decades of use, the influence of fillers on CAC hydration has been lesser studied. Towards this end, the current study uses a combination of experiments and simulations to elucidate the effects of the filler content (i.e., CAC replacement level and w/c increase), filler type (i.e., CaCO<sub>3</sub>, CaMg(CO<sub>3</sub>)<sub>2</sub> and α-SiO<sub>2</sub>) and surface area (i.e., fineness of fillers) on CAC hydration kinetics. A boundary nucleation and growth model is used to explain the links between surface area, and mineral type on hydration rates [7,9]. The results suggest that CAC-based binders are far less sensitive to mineral filler type, than OPC-based systems.

## 2. Materials and experimental methods

A commercially available grey calcium aluminate cement (CAC, referred to as CAC or cement interchangeably, hereafter) Secar<sup>®</sup>51 produced by Kerneos Aluminate Technologies was used. The oxide composition (Table 1) of the CAC was determined by X-ray fluorescence (XRF). The mineralogical composition of the

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<sup>1</sup> Standard cement chemistry notation is used throughout this paper. As per this notation: C = CaO, A = Al<sub>2</sub>O<sub>3</sub>, F = Fe<sub>2</sub>O<sub>3</sub>, S = SiO<sub>2</sub>, T = TiO<sub>2</sub>, CS = CaSO<sub>4</sub>·2H<sub>2</sub>O and H = H<sub>2</sub>O.

CAC as determined using Rietveld refinement of X-ray diffraction (XRD) patterns is (by mass): 73.3% CA, 18.1% C<sub>2</sub>AS, 4.9% CT with minor phases in the form of 0.8% CaO, 0.6% C<sub>2</sub>F, 1.5% C<sub>3</sub>FT and 0.8% Fe<sub>3</sub>O<sub>4</sub>. The limestone and quartz powders used are commercially available size classified products produced by OMYA A.G. and U.S. Silica. The dolomite used was produced by Blue Mountain Minerals. Oxide compositions of CAC and as well as the main components for the fillers used can be found in Table 1.

The particle size distributions (Fig. 1) of the solids were measured using a Beckman Coulter static light-scattering (SLS) analyzer (LS13-320) using isopropanol/sonication for dispersing the powders to primary particles. This methodology allows the quantification of volume fractions of the particles corresponding to each size class ranging between 0.04 μm and 2000 μm using the Mie theory for analysis of light scattering data. Assuming spherical shape of the particles, the total surface area of the particles belonging to each size class is calculated and, ultimately, added to estimate the cumulative surface area per unit volume (m<sup>2</sup>/m<sup>3</sup>) of the material. By factoring in the density of each powder (i.e. 3150, 2700, 2650 and 2850 kg/m<sup>3</sup> for the CAC, limestone, quartz and dolomite respectively), the specific surface area is obtained in the units of m<sup>2</sup>/kg. The uncertainty in the light scattering was determined to be ≈6% based on multiple measurements performed on six replicate samples. Given the irregular, angular nature of the particles considered, the spherical particle assumption results in an underestimation of the solid surface area by a factor of 1.6-to-1.8 [20] for typical pulverized powders. The median diameter (*d*<sub>50</sub>) and the specific surface area (SSA) for all materials are presented in Table 2.

Cementitious pastes were prepared using deionized water at a fixed water-to-solid (*w/s* = 0.60, mass basis) ratio using a planetary mixer as described in ASTM C305 [21]. To better understand the role of fillers, the CAC content was reduced at mass-based replacement levels ranging from 0% to 50% (mass-basis) by limestone, quartz or dolomite powders. The replacement levels were selected to match the overall area of solids per gram of anhydrous cement across the different fillers used. The additional surface area provided by the fillers was calculated using an area multiplier (AM) proposed by Oey et al. [7] (see Eq. (1)):

$$AM = 1 + \frac{rSSA_{\text{filler}}}{(100 - r)SSA_{\text{cement}}} \quad (1)$$

where, *r* (mass %) is percentage of CAC replaced by a filler, *SSA*<sub>filler</sub> and *SSA*<sub>filler</sub> (m<sup>2</sup>/kg) are the specific surface areas of the CAC and filler respectively. The AM parameter accounts for both the dilution effect (i.e., CAC replacement level) and the specific surface area of the solids (i.e., CAC and filler). As such, AM increases with CAC replacement level and filler fineness. Therefore, the total area of the solids per gram of anhydrous CAC can be simply calculated as the product of the AM and *SSA*<sub>filler</sub>. AM serves as a direct measure of additional surface area available for product nucleation. By matching AMs, several mixtures were proportioned with an equivalent surface area of solids per gram of anhydrous CAC, i.e., for AM = 1.2, 1.5, 2.0, 3.0. Fig. 2 shows the replacement level required to achieve each AM value for all the fillers used, so long as the CAC replacement level was maintained at ≤50%. Table 3 shows the level of CAC replacement required by each filler to ensure the targeted AM values. It should be noted that AM = 3.0 means that this mixture shows a solid surface area which is 3x larger than the pure CAC mixture (i.e., where AM = 1.0).

The influence of cement replacement on the rate of CAC reaction was tracked using isothermal conduction calorimetry. A Tam Air isothermal calorimeter (TA Instruments, New Castle, DE) was used to determine the heat evolved during hydration at a constant temperature condition of 25 °C. The rate and extent of heat release are normalized by the mass of CAC and, as such, the heat evolution profiles serve as direct indicators of hydration kinetics of CAC.

### 3. Experimental results and discussion

Due to the use of ambient temperatures and for *w/c* ≥ 0.60, it is expected that CAH<sub>10</sub>, C<sub>2</sub>AH<sub>8</sub> and AH<sub>3</sub> hydrates form, and are present in the systems considered herein [18]. Representative X-ray diffraction (XRD) patterns shown in Fig. 3 illustrate that at ages less than 2 days, CAH<sub>10</sub> and C<sub>2</sub>AH<sub>8</sub> are the primary hydration products independent of the filler present. In systems prepared without and with fillers, C<sub>2</sub>AH<sub>8</sub> and CAH<sub>10</sub> are the primary hydration products respectively. Formation of CAH<sub>10</sub>, which is a water-rich hydration product, instead of C<sub>2</sub>AH<sub>8</sub>, at early ages, can be explained due to a higher water-to-cement ratio (*w/c*) in systems prepared with fillers. It should be noted that due to the very low dissolution rates of limestone and dolomite [22,23], substantial reaction between CA and carbonate provided by carbonate based fillers is not expected [24,25]. This is corroborated by the XRD patterns shown in Fig. 3 (a), wherein the weak intensities of monocarboaluminate indicate its presence in minute quantities. Therefore, it is assumed that all

**Table 1**  
Oxide composition of CAC and main components of fillers.

| Sample                              | CAC: Secar 51 | Limestone | Dolomite | Quartz |
|-------------------------------------|---------------|-----------|----------|--------|
| SiO <sub>2</sub>                    | 4.71          | ~         | 0.70     | 100.00 |
| Al <sub>2</sub> O <sub>3</sub>      | 51.04         | ~         | ~        | ~      |
| Fe <sub>2</sub> O <sub>3</sub>      | 2.22          | ~         | ~        | ~      |
| CaO                                 | 38.94         | ~         | ~        | ~      |
| MgO                                 | 0.59          | ~         | ~        | ~      |
| SO <sub>3</sub>                     | 0.00          | ~         | ~        | ~      |
| Na <sub>2</sub> O                   | 0.07          | ~         | ~        | ~      |
| K <sub>2</sub> O                    | 0.31          | ~         | ~        | ~      |
| TiO <sub>2</sub>                    | 2.02          | ~         | ~        | ~      |
| P <sub>2</sub> O <sub>5</sub>       | 0.11          | ~         | ~        | ~      |
| CaCO <sub>3</sub>                   | ~             | 100.00    | 19.30    | ~      |
| CaMg(CO <sub>3</sub> ) <sub>2</sub> | ~             | ~         | 80.00    | ~      |
| Sum                                 | 100.00        | 100.00    | 100.00   | 100.00 |

fillers used in this study do not partake in reaction with the anhydrous CAC, and, as such, remain “inert” for the ages considered.

Fig. 4 shows representative heat evolution profiles for the plain and binary pastes (i.e., CAC + filler) prepared for AM = 1.2, 2.0 and 3.0. The reference system corresponds to a pure CAC (no filler) paste prepared at *w/s* = *w/c* = 0.60 (*w* = water, *s* = solids, *c* = CAC, on a mass basis). It is important to clarify that, in this study; *w/c* refers exclusively to the relation (mass basis) of water to CAC without consideration of the filler. On the other hand, *w/s* refers to the mass relation of water to all the solids present in the binder (i.e., CAC + filler). In cases where no filler is present *w/c* = *w/s*. From Fig. 4 it is observed that CAC hydration is accelerated in the presence of fillers as compared to the reference system. The enhancement in hydration is noted qualitatively in terms of the increase in the value of the main heat-flow peak. Increasing the filler replacement level induces a shortening of the induction period and left-shift of the main heat-flow peak (Fig. 4a). This is interesting because in mixtures having equivalent AM's (but not CAC replacement), the total solid surface area available for the nucleation of the hydrates is the same, but the effective *w/c* is different and scales with the replacement level. This relationship between the hydration kinetics and *w/c* thus, suggests that independent of surface area, a higher *w/c* leads to enhanced hydration of CAC's. To verify this hypothesis, the hydration kinetics of pure CAC pastes prepared at different *w/c* were examined (Fig. 4d). Indeed, increasing the *w/c* results in enhanced reactivity. Similar results have been reported by Gosselin et al. [26] and Siddiqui et al. [27], wherein enhanced reactivity of CA was attributed to the enhanced growth of the CAC hydrates when additional space is available in the microstructure. It is however postulated that hydration of CAC with increasing *w/c* is enhanced only up to a limiting *w/c* value, after which no further enhancement is noted.

In order to distinguish the effects of surface area from water availability, mixtures having the same level of CAC replacement constituted using different mineral fillers were compared. These mixtures showed different solid surface areas, albeit at the same CAC (mass) replacement level and thus *w/c*. Fig. 5 shows the heat evolution profiles for systems containing 27% and 38.5% of the CAC replaced by limestone and quartz fillers. It is seen that at the same replacement level (i.e., same amount of water available for CAC hydration), the reaction rate enhances with AM on account of a higher surface area being available for product phase nucleation. These results indicate that two factors i.e., surface area availability and water availability both exert controls on the CAC reaction rates.

While discussing water availability it should be pointed out that some of the filler containing mixtures considered herein, showed a tendency to bleed. It is important to quantify the content of such bleed water as if the mixture is to set with bleed water on the

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