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.

Keywords: limestone, dolomite, quartz, calcium aluminate cement, calorimetry.

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1.0 Introduction and background

Over the past several years, on account of its production related CO₂ emissions, significant efforts have been made to reduce the use of cement as the primary binding agent in concrete [1, 2, 3, 4]. One topic of significant study has been the so-called *filler effect* [5, 6, 7, 8, 9, 10, 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, 13, 14, 15].

Unlike OPC, calcium aluminate cements (CACs) consist dominantly of monocalcium aluminate (CaO·Al₂O₃, CA) and gehlenite (2CaO·Al₂O₃·SiO₂, C₂AS) [16, 17, 18, 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., CaCO₃, CaMg(CO₃)₂ and α-SiO₂) 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.

*** Standard cement chemistry notation is used throughout this paper. As per this notation: C=CaO, A=Al₂O₃, F = Fe₂O₃, S=SiO₂, T = TiO₂ CS= CaSO₄·2H₂O and H=H₂O.

2.0 Materials and Experimental Methods

A commercially available grey calcium aluminate cement (CAC, referred to as CAC or cement interchangeably, hereafter) Secar®51 produced by Kerneos Aluminate Technologies was used. The oxide composition (Table 1) of the CAC was determined by X-ray florescence (XRF). The mineralogical composition of the CAC as determined using Rietveld refinement of X-ray diffraction (XRD) patterns is (by mass): 73.3% CA, 18.1% C₂AS, 4.9% CT with minor phases in the form of 0.8% CaO, 0.6% C₂F, 1.5% C₃FT and 0.8% Fe₃O₄. 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.

Table 1: Oxide composition of CAC and Main components of fillers

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

The particle size distributions (Figure 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^2/m^3) of the material. By factoring in the density of each powder (i.e. 3150, 2700, 2650 and 2850 kg/m^3 for the CAC, limestone, quartz and dolomite respectively), the specific surface area is obtained in the units of m^2/kg . The uncertainty in the light scattering was determined to be $\approx 6\%$ 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_{50}) and the specific surface area (SSA) for all materials are presented in Table 2.

Table 2: The nominal specific surface area (SSA) and d_{50} of the solids as calculated using the measured particle size distributions.		
Materials	SSA (m^2/kg)	Size (d_{50}, μm)
Secar 51	504.85	8.15
Limestone 0.7 μm	2592.13	1.38
Limestone 3 μm	1353.29	2.92
Limestone 15 μm	399.29	14.26
Limestone 40 μm	228.62	39.78
Dolomite	297.25	11.83
Quartz-10 μm	1610.05	3.86
Quartz-40 μm	464.56	7.42
Quartz-75 μm	270.22	17.18

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70 Cementitious pastes were prepared using deionized water at a fixed water-to-solid (w/s = 0.60,
71 mass basis) ratio using a planetary mixer as described in ASTM C305 [21]. To better understand
72 the role of fillers, the CAC content was reduced at mass-based replacement levels ranging from
73 0-to-50% (mass-basis) by limestone, quartz or dolomite powders. The replacement levels were
74 selected to match the overall area of solids per gram of anhydrous cement across the different
75 fillers used. The additional surface area provided by the fillers was calculated using an area
76 multiplier (AM) proposed by Oey et al. [7] (see Equation 1):

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$AM = 1 + \frac{r SSA_{\text{filler}}}{(100 - r) SSA_{\text{cement}}}$	(1)
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79 where, r (mass %) is percentage of CAC replaced by a filler, SSA_{cement} and SSA_{filler} (m^2/kg) are the
80 specific surface areas of the CAC and filler respectively. The AM parameter accounts for both
81 the dilution effect (i.e., CAC replacement level) and the specific surface area of the solids (i.e.,
82 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_{cement} . 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. Figure 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 $\leq 50\%$. 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.

Table 3: The level of CAC replacement (%) calculated for each filler so as to maintain an equivalent value of the area multiplier (AM).				
Filler	AM=1.2	AM=1.5	AM=2	AM=3
Limestone 0.7 µm	3.50	8.75	16.25	28.00
Limestone 3 µm	6.75	15.50	27.00	42.50
Limestone 15 µm	20.00	38.50	N/A	N/A
Limestone 40 µm	30.50	50.00	N/A	N/A
Dolomite	25.25	45.75	N/A	N/A
Quartz 75µm	27.00	48.25	N/A	N/A
Quartz 40µm	17.75	35.00	N/A	N/A
Quartz 10µm	5.75	13.50	23.75	38.50

3.0 Experimental Results and Discussion

Due to the use of ambient temperatures and for $w/c \geq 0.60$, it is expected that CAH_{10} , C_2AH_8 and AH_3 hydrates form, and are present in the systems considered herein [18]. Representative X-ray diffraction (XRD) patterns shown in Figure 3 illustrate that at ages less than 2 days, CAH_{10} and C_2AH_8 are the primary hydration products independent of the filler present. In systems prepared without and with fillers, C_2AH_8 and CAH_{10} are the primary hydration products respectively. Formation of CAH_{10} , which is a water-rich hydration product, instead of C_2AH_8 , 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 Figure 3(a), wherein the weak intensities of monocarboaluminate indicate its presence in minute

quantities. Therefore, it is assumed that all fillers used in this study do not partake in reaction with the anhydrous CAC, and, as such, remain “inert” for the ages considered.

Figure 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 Figure 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 (Figure 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 (Figure 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. Figure 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.

Figure 5: Heat release curves for CAC mixtures for: (a) 27% replacement of CAC and (b) 38.5% replacement of CAC, by limestone and quartz fillers. The reference designates a cementitious blend containing no filler agents, i.e., pure CAC for w/s = 0.60.

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 surface, this water is not uniformly available to partake in hydration – and should be discounted from consideration [28]. The consolidation of the paste in the vertical direction during the plastic state also alters the packing of particles – resulting in a reduction in the solid-solid separations in the material. To better quantify bleeding effects, the bleed water exhausted to the sample surface was removed

and its mass determined for all mixtures considered herein, over the first 8 hours of hydration. This data was used to quantify the actual w/s and w/c for each mixture to understand any possible impact on CAC hydration rates. Expectedly, the high w/c systems (i.e., those containing a higher quantity of mineral filler) expel more water; an effect which exacerbates as the filler particle size increases (i.e., when filler particles coarser than the CAC are introduced; as shown in Figure 6).

The heat evolution profiles presented in Figures (3-5) were processed to extract calorimetric parameters indicative of CAC hydration kinetics including: (a) slope during acceleration regime, (b) inverse of time elapsed from initial water contact to the main heat peak, and (c) amplitude of the heat peak (i.e., the heat flow value at the main peak). These quantities were analyzed in the context of the actual w/c and the surface area of the solids, presented in the form of the AM. Figure 7 shows the calorimetric parameters as function of the actual w/c for each mixture. It is seen that as w/c increases, CAC hydration is enhanced, as indicated by the broadly linear correlation between the calorimetric parameters and w/c. It is also noted that at equal w/c, the acceleration induced by all fillers is comparable to each other.

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175

176 In addition to water availability, the amount of surface area available and its relation to CAC
 177 hydration kinetics was also examined (Figure 8). CAC hydration is enhanced as the amount of
 178 surface area provided by the fillers increases. It is noted that all three fillers: quartz, limestone
 179 and dolomite, enhance hydration of CAC equivalently – a significant conclusions which indicates
 180 that all fillers, at equivalent surface areas, contribute equally towards enhancing CAC hydration.
 181 In light of results shown in Figure (7-8), it is postulated that in CAC binders both carbonaceous
 182 and quartz fillers have equivalent acceleratory effects because: (a) the primary hydrates formed
 183 in CAC systems are not sensitive to the uptake of carbonate ions and (b) neither of these fillers
 184 provide a desired surface (i.e., more desired than the CAC grains themselves) for the nucleation
 185 of the CAC hydrates. It should be noted that the scatter in the datasets presented in Figures (7-
 186 8) can be attributed to: (a) bleeding, which cannot be remediated during isothermal calorimetry
 187 measurements and (b) differences in surface morphologies of the fillers, which may contribute
 188 to some differences in reaction rates. The morphologies of the filler can indeed have an impact

in the density of product nuclei that form on the surface of the fillers. Some of the morphological features that can vary amongst the fillers are distribution of defects, etc. Such features, however, cannot be detected precisely, by means of light scattering or BET surface area determination methods. In the particular case of bleeding, it is possible that even after the CAC paste has hardened, bleed-water could progressively permeate into the sample and, consequently, affect hydration of CAC and heat evolution profiles.

Figure 8: The correlation between the area multiplier (AM) and: (a) heat flow at peak, (b) slope of the acceleration regime, (c) inverse of time to main peak. The solid lines show a best fit line to the data set while the dashed lines represent a $\pm 10\%$ bound to the best fit line.

4.0. Numerical Simulations of the Heat Release Response

The hydration of OPC's and pure cement phases has widely been studied using phase boundary nucleation and growth (BNG) models [29, 30, 31, 32, 33, 34]. These models simulate the nucleation and growth of a single product phase that starts at the solid phase boundaries. However, these models can incorporate different assumptions about the nucleation process (i.e., homogeneous or heterogeneous), frequency of nucleation (i.e., site saturation or continuous nucleation) and mechanisms of product growth (i.e., isotropic or anisotropic growth of product). Due to their

flexibility, BNG models have been successfully extended to study the effects of various process parameters including addition of chemical admixtures [35, 36] and mineral filler additions [7, 11].

Few studies have applied BNG models to describe hydration of CAC-based systems. Ukrainczyk [37] applied a combination of three different mechanisms: i.e., nucleation and growth, chemical interaction and mass transfer to simulate CAC hydration. This study applies a modified BNG formulation, described previously to describe the influences of different fillers on the kinetics of reactions in CAC based systems [7, 11, 29, 32, 35, 38, 39]. A filler is assumed to accelerate CAC reactions, the extent of which is calculated from Eq. (2), by providing only additional surface area for product nucleation, without any impacts on the nature of the CAC hydration products, in terms of their properties or composition, i.e., the filler is assumed to be inert (see Figure 3).

$$\text{Extent of Transformation (X)} = 1 - \exp \left[-2a_{BV} \int_0^{G_{out}t} (1 - \exp(-A_f)) dy \right] \quad (2)$$

where: X is the volume fraction of the reactant transformed to product, G_{out} is the isotropic outward growth rate of the product phase, y is a variable of integration, a_{BV} is the boundary area per unit volume, t is the simulation time (h) and A_f is the extended area of the transformed product phase described in Equations (3-4).

$$A_f = \pi \left[I_{density} \cdot G_{par}^2 \cdot \left(t_r^2 - \frac{y^2}{G_{out}^2} \right) + I_{rate} \cdot G_{par}^2 \cdot \left(\frac{t_r^3}{3} - \frac{y^2 t_r}{G_{out}^2} + \frac{2y^3}{3G_{out}^3} \right) \right] \text{ if } (y \geq G_{out} \cdot t_r) \quad (3)$$

$$\text{and, } A_f = 0 \text{ if } (y < G_{out} \cdot t_r) \quad (4a)$$

$$\text{Here, } (t_r = (t - t_0)) \quad (4b)$$

The model formulation is discussed in detail elsewhere [7, 11, 35]. The parameters used in the model include: (a) I_{density} (μm^{-2}), the nucleation density of the product, that is, the number of supercritical nuclei per unit surface area formed at the time of nucleation event (t_0), (b) I_{rate} ($\mu\text{m}^{-2} \cdot \text{h}^{-1}$), the nucleation rate, (c) G_{par} ($\mu\text{m} \cdot \text{h}^{-1}$), the growth rate parallel to the particle surface, (d) G_{out} ($\mu\text{m} \cdot \text{h}^{-1}$), the outward growth rate perpendicular to the particle surface and (e) a_f (unitless), the simulation analogue of the area multiplier (AM) which represents in the increase the in solid surface area provided by fine fillers. The w/s , specific surface area of the CAC and the fillers ($\text{SSA}_{\text{cement}}$ and $\text{SSA}_{\text{filler}}$) and CAC replacement level (r , %) are used as inputs. The cumulative heat evolved by the reaction of the CAC is computed using a scaling parameter, A (kJ/mole), as shown in Equation (5):

$$\text{Rate of heat evolution} = \frac{dH}{dt} = A \cdot \left(\frac{100}{100-r} \right) \frac{dX}{dt} \quad (5)$$

where: X is the volume fraction of reactant transformed to product, r (%) is the mass-based percentage replacement level of mineral filler (when present) which accounts for the effects of dilution (i.e., a reduction in the CAC content). In addition, since the simulations begin only at the end of the induction period which varies slightly from one mixture to the another, the simulation time is mapped to real time by using a parameter t_0 (hours).

For all simulations, I_{rate} , G_{out} and G_{par} are fixed; taking values of $0.00 \mu\text{m}^{-2} \cdot \text{h}^{-1}$, $0.054 \mu\text{m} \cdot \text{h}^{-1}$ and $0.027 \mu\text{m} \cdot \text{h}^{-1}$ respectively. The 2:1 ratio of the outward product growth rate with respect to the parallel one is representative of dendritic growth of the product [40]. Since, the growth rates of

the hydration products in CAC systems have not been measured, the value of the outward growth rate is drawn from simulations of other cementitious systems [7]. It is pointed out that the assignment of $I_{\text{rate}} = 0.00 \mu\text{m}^{-2} \cdot \text{h}^{-1}$ corresponds to nucleation site-saturation, implying that growth of the product phases begins from nuclei that are initially present, or form at very early ages, and no further nuclei are permitted to form after the initial nucleation burst. To fit the reaction response of the mixtures, a simplex algorithm was applied, which iteratively varies the values of the I_{density} , a_{factor} , A and t_0 , within pre-defined constraints, to minimize the difference between the simulated and measured heat evolution profiles [7].

When the simplex algorithm converges, the values of the fitting parameters are extracted and noted as the optimum values. Amongst the variable parameters, a_f and I_{density} , are most critical as they can be combined with SSA_{Cement} to calculate the number of supercritical product nuclei produced per gram of CAC as shown in Equation (6).

$$Product\ Nuclei(\#/g_c) = (SSA_c \cdot a_f) \cdot I_{density} \quad (6)$$

Figure 9 shows representative heat evolution profiles obtained via BNG simulations, compared against experiments. There is good agreement between the experiments and simulations across systems containing different fillers and CAC replacement levels. Excellent agreement is noted between the simulation parameter, t_0 , and the time to the main peak (see Figure 10a). This is expected because systems in which the onset of product formation is accelerated, values of t_0 are low. The values of the supercritical product nuclei formed at the end of the induction period were examined. As seen in Figure 10(b), with increasing w/c, the number of the product nuclei formed increases in a linear manner. This trend is in good agreement with observations from Figure 7, suggesting that the hydration of CAC is enhanced when there is more space (i.e., water, or porosity per unit mass of CAC) available in the microstructural volume [26]. It should be clarified here that a higher water content per unit mass of cement (w/c) does not necessarily translate to a higher solid-to-solid (i.e., inter-particle) distance, as explained later in this section.

This increase in the number of product nuclei is also noted with an increase in the AM (Figure 10c), suggesting that the availability of water and surface are both important contributors to CAC reaction rates. It is uniformly noted, no preference to a given filler is seen, with all fillers provided the same acceleration in CAC hydration – for equivalent AM, and w/c.

Figure 11: The average centroidal solid-to-solid distance calculated for various CAC systems prepared at a w/s = 0.60 with CAC replaced by: (a) carbonate and (b) quartz fillers at replacement levels ranging from 0 to 50% (by mass). The distances are calculated by averaging the distances between the center of a particle with respect to its nearest neighbors, packed within a three-dimensional virtual cube for an edge length (of the cube) of 1000 μm. (c) A 2D slice of a 3D-microstructure for a system prepared at w/s = 0.60 with 10% of the CAC (red spheres) replaced by dolomite (green).

Figure 11 shows the inter-particle distance calculated at the time of mixing of the solids with water calculated using a microstructural model [9], for all three mineral fillers across different CAC replacement levels. It is seen that fillers which are finer than CAC, cause a progressive decrease in the inter-particle distance with increasing replacement levels. On the other hand, coarser fillers cause an increase in the inter-particle distance, more so as the replacement level of CAC by a coarse filler increases. It is seen that at the same replacement level, (i.e., equivalent w/c) the quartz, limestone and dolomite filler produce widely different inter-particle distances

on account of differences in their particle size distributions. However, as shown in Figure 10(b), at the same w/c, all three fillers enhance hydration of CAC similarly. These trends show that the enhancement in CAC hydration depends on the effective w/c, i.e., a measure of the total space available in the microstructure per unit mass of cement, but not necessarily the inter-particle (i.e., solid to solid) distance so long the amount of available surface area remains consistent.

Figure 10(c) shows that the number of product nuclei, formed at the end of the induction period, is linearly proportional to additional surface area provided by the fillers. This suggests that CAC hydrated is enhanced by the provision of additional solid surface area for the heterogeneous nucleation of products. For equivalent (incremental) surface areas provided by the different fillers, the enhancement in CAC hydration remains broadly similar. This supports the idea that all three filler types used in this study promote the nucleation of products onto their surfaces equivalently, and rules out the possibility of the carbonaceous fillers participating in any substantial chemical interaction with the anhydrous or product phases present in CAC systems, especially so at early ages (i.e., less than 7 days, see Figure 3).

5.0. Summary and Conclusions

The hydration kinetics of CAC-based mixtures has been examined in the presence of both carbonate (i.e., limestone and dolomite) and quartz fillers. By using the concept of an area multiplier (AM), the increased surface area provided by the fillers has been correlated with noted increases in CAC reaction rates. In addition to surface area, CAC reaction rates are also dependent on w/c, i.e., the amount of space available in the microstructure. Unlike the case of

OPC, CAC's show no preference for filler chemistry, or type – as such, for an equivalent increase in surface area, all fillers provide equivalent enhancements in reaction rates. This equivalence in acceleratory effects amongst the three fillers examined herein is attributed to: (a) their inert nature, i.e., their inability to partake in chemical reactions with the CAC, especially at early ages and for the temperatures considered, and, (b) equivalent affinity for heterogeneous nucleation of hydration products onto their surfaces. These conclusions are supported by the outcomes of phase boundary nucleation and growth modeling applied to CAC hydration. It is also shown that the enhancement in hydration of CACs is related to the increase in w/c (i.e., dilution effects) but not necessarily the inter-particle distance between the solid particles at the time of mixing.

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