

Modeling the influence of limestone filler on cement hydration using CEMHYD3D

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Abstract

The ASTM C150 standard specification for Portland cement now permits the cement to contain up to 5% of ground limestone. While these and much higher levels of limestone filler substitution have been employed in Europe and elsewhere for many years, changing the ASTM standard has been a slow process. Having computational tools to assist in better understanding the influence of limestone additions on cement hydration and microstructure development should facilitate the acceptance of these more economical and ecological materials. With this in mind, the CEMHYD3D computer model for cement hydration has been extended and preliminarily validated for the incorporation of limestone at substitution levels up to 20% by mass fraction. The hydration model has been modified to incorporate both the influence of limestone as a fine filler, providing additional surfaces for the nucleation and growth of hydration products, and its relatively slow reaction with the hydrating cement to form a monocarboaluminate (AFmc) phase, similar to the AFm phase formed in ordinary Portland cement. Because a 20% limestone substitution substantially modifies the effective water-to-cement ratio of the blended mixtures, the influence of limestone substitutions on hydration rates is observed to be a strong function of water-to-solids ratio (w/s), with significant acceleration observed for lower (e.g., 0.35) w/s , while no discernible acceleration is observed for pastes with $w/s = 0.435$.

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1. Introduction

After many years of discussion, in 2004, the ASTM C150 standard specification for Portland cement was modified to allow the incorporation of up to a 5% mass fraction of limestone in ordinary Portland cements [1]. An extensive survey of the literature conducted by the Portland Cement Association [2] concluded that “in general, the use of up to 5% limestone does not affect the performance of Portland cement”. Even higher contents of ground limestone could potentially be utilized in lower water-to-cement ratio (<0.45) systems, where a substantial fraction of the cement

clinker particles remains unhydrated, effectively acting as a rather expensive filler material [3–5].

Because concretes made with limestone-containing cements are often prepared at a water-to-solids ratio (w/s) similar to the water-to-cement ratio (w/c) of the concrete with no limestone, the effective w/c of the limestone-filled concrete can be substantially increased from that of the original mixture. This will naturally modify the hydration characteristics of the concrete. Further, the additional surface area provided by the limestone particles may provide sites for the nucleation and growth of hydration products, generally enhancing the achieved hydration. Finally, the ground limestone is slightly reactive with the Portland cement, mainly forming a monocarboaluminate phase [6–9]. Being able to predict the influence of a specific limestone substitution on the hydration behavior of a specific cement

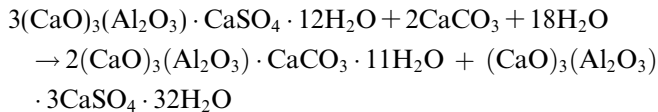
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paste (or concrete) should expedite the usage of these filled cements and allow for a priori design of concrete mixtures that meet desired performance criteria. In this paper, the CEMHYD3D hydration model developed by NIST will be extended to consider the above influences of limestone fillers on cement hydration and validated against experimental measurements.

2. CEMHYD3D modeling

The influence of limestone filler on cement hydration was modeled using a modified version of CEMHYD3D V. 2.0 [10,11]. Both the chemical reactivity and the “fine filler” effects of the limestone were considered. Based on experimental observations in the literature [2,6–9], the formation of a monocarboaluminate [AFmc—(CaO)₃(Al₂O₃)·CaCO₃·11H₂O] phase in preference to a monosulfoaluminate [AFm—(CaO)₃(Al₂O₃)·CaSO₄·12H₂O] phase was added by modifying the CEMHYD3D computer codes to include the following reaction:



This reaction favors the production of AFmc (and ettringite) over that of the conventional AFm phase in the presence of calcium carbonate. In the CEMHYD3D model, this reaction becomes active only when the initial calcium sulfate is depleted and the previously formed ettringite begins to convert to the AFm phase by reaction with more of the cement clinker aluminate phases. This is in general agreement with experimental observations [6,7]. While other reaction paths could be written for the formation of AFmc in a cement-based system, the above scheme was chosen for its simplicity in implementation in the CEMHYD3D codes and the fact that it does yield the desired effect: the formation of the AFmc phase at the expense of the AFm phase. The calcium carbonate generally has a rather low reactivity (because of its low solubility), and in typical simulations using the updated CEMHYD3D codes, for a 20% by mass fraction substitution of ground limestone for cement, only about 5% of the limestone present reacts during the first ≈180 d of hydration.

Numerous researchers have noted an acceleration of the hydration of cement due to the addition of fine limestone or other fine particles [3,12–14]. Apparently, the surfaces of the individual filler particles provide sites for the nucleation of cement hydration products such as the calcium silicate hydrate gel (C–S–H)¹ that is the dominant hydration product in most hydrated Portland cements. Thus, the first modification to CEMHYD3D to incorporate this effect has been to allow the precipitation of both C–S–H and calcium

hydroxide (CH) hydration products on the surfaces of the limestone particles.

In Version 2.0 of the CEMHYD3D model [11], the “induction” period of cement hydration has been modeled by making the initial dissolution probabilities of all four of the major cement clinker phases (C₃S, C₂S, C₃A, and C₄AF) proportional to the volume of C–S–H that has formed (an autoacceleratory type of behavior [15]). The best fit to available experimental degree of hydration data for ordinary Portland cements is obtained when these initial dissolution probabilities are proportional to the normalized volume of C–S–H (the volume of C–S–H formed divided by the volume of the initial cement present) raised to the second power [11]. To model the “fine filler” effect in pastes with limestone substitutions for cement, the early time dissolution probabilities in CEMHYD3D have been further modified to be also proportional to the ratio of the initial total (cement clinker and limestone) surface area divided by the initial cement clinker surface area, once again raised to the second power. Modeling the influence of the substituted filler in this manner implies that hydration during the induction period is “accelerated” (or the length of the induction period is decreased) when a thinner C–S–H layer is formed over a larger surface area. It could also imply that less time is needed for the calcium (and hydroxide) ions to build up to some critical concentration in solution when the initial C–S–H is “dispersed” over a larger surface area than that provided by the initial cement particles. While neither of these mechanisms were included directly in the CEMHYD3D model, making the initial dissolution rates proportional to the ratio of the surface areas as described above would be consistent with either of them, and would provide a simple approach for obtaining the desired effects. One could also consider a proportionality based on filler and cement clinker volumes, instead of surface areas. However, utilizing surface areas has the advantage that the fineness of the substituted filler, as well as its overall volume fraction, can influence the hydration.

3. Experimental

Cement and Concrete Reference Laboratory (CCRL) Portland cement proficiency sample 152 [16], issued in January of 2004, was used to assess the hydration rates of cement pastes cured under saturated and sealed conditions. Portland cement pastes initially with $w/c = 0.35$ and $w/c = 0.45$ by mass were prepared by mixing the water and cement in a temperature-controlled high-speed blender for several minutes at 20 °C. For both w/s mass ratios (0.35 and 0.45), cement 152 was also blended with a “fine” limestone powder replacing 20% of the cement by mass. The limestone powder was obtained by using an air classifier to separate a commercially available material with a cutoff diameter of approximately 30 μm [5], and retaining the finer of the two fractions (which contained approximately 65% particles finer than 30 μm). Based on its measured loss on ignition, the limestone powder was estimated to be 97%

¹ Conventional cement chemistry notation is used from this point forward in this paper: C=CaO, S=SiO₂, A=Al₂O₃, F=Fe₂O₃, and H=H₂O.

CaCO₃. Freshly cast wafers (≈5 g) of cement paste were placed in small pre-weighed capped plastic vials to be cured under either saturated (water ponded on top) or sealed conditions at 20 °C. It should be kept in mind that these small samples will hydrate under nearly isothermal conditions and will not experience any auto-acceleratory effects that might be experienced in larger samples hydrating under adiabatic or semi-adiabatic conditions.

After about 4 h of curing, any accumulated bleed water was removed from the vials using a pipette, to assess the true effective w/c or w/s of the pastes. The containers of the sealed paste specimens were simply resealed after removing the bleed water; for the saturated paste specimens, after removing the bleed water and reweighing the vials, a small amount of a fresh supply of distilled water was added to the top of the wafers to maintain saturation, before resealing the vials. While the volume of accumulated bleed water was negligible for the $w/s = 0.35$ pastes, for the $w/s = 0.45$ pastes, the measured effective ratio after removing the accumulated bleed water was found to be about 0.435. At ages of (1, 3, 7, 28, 92, and 182) d, specimens were removed from their vials, crushed to a fine powder using a mortar and pestle, flushed with methanol in a thistle tube connected to a vacuum, and divided between two crucibles. The non-evaporable water content (W_N) of each crucible sample was determined as the mass loss between 105 °C and 1000 °C divided by the mass of the ignited sample, corrected for the measured loss-on-ignition of the unhydrated cement (or of the unhydrated cement/20% limestone blend). Previously, the expanded uncertainty in the calculated W_N had been estimated to be 0.001 g/g cement, assuming a coverage factor of 2 [10]. W_N values were converted to estimated degrees of hydration based on the phase composition of the cement and published coefficients for the non-evaporable water contents of the various hydrated cement clinker phases [17]. Based on a propagation of error analysis, the estimated uncertainty in the calculated degree of hydration is 0.004.

Virtual cement pastes were created using CEMHYD3D to match each of the experimental mixtures. Densities of 3200 kg/m³ and 2700 kg/m³ were assumed for the cement and limestone, respectively. The measured particle size distributions, as shown in Fig. 1, were utilized for cement 152 and for the limestone filler. The w/c and w/s in the virtual pastes were selected to match those in the real prepared pastes, after accounting for removal of the accumulated bleed water. The chemical composition of cement 152, as measured by scanning electron microscopy (SEM) [18], is provided in Table 1. In addition, the cement contained 6% calcium sulfates by volume, distributed as approximately 44% gypsum (dihydrate), 52% hemihydrate, and 4% anhydrite, as determined by X-ray diffraction measurements. For all of the simulations conducted using the modified CEMHYD3D software, a conversion factor of 0.00035 h/cycle² was used to convert between model cycles and real time [10,11]. The same value was used throughout

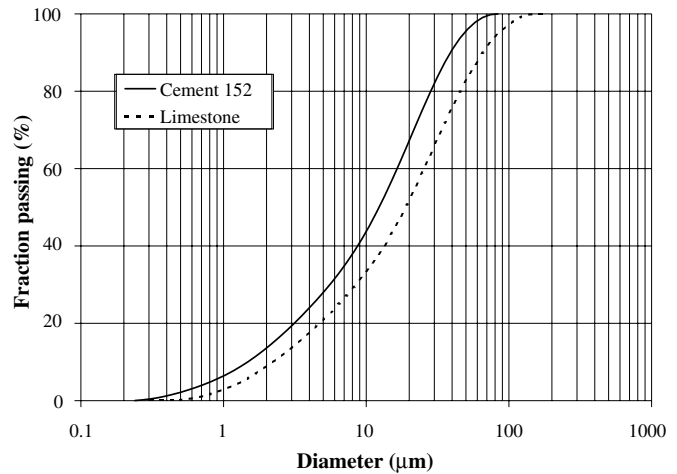


Fig. 1. Particle size distributions for the materials used in this study as measured by laser diffraction techniques.

Table 1
Measured volume and surface area fractions for CCRL cement 152

Clinker phase	Volume fraction	Surface area fraction
C ₃ S	0.7344 (0.0085)	0.6869 (0.0211)
C ₂ S	0.0938 (0.0063)	0.1337 (0.0123)
C ₃ A	0.1311 (0.0084)	0.1386 (0.0121)
C ₄ AF	0.0407 (0.0030)	0.0408 (0.0047)

Numbers in parentheses indicate standard deviations derived from a set of six SEM/X-ray map images [18].

for different w/s (0.35 or 0.435), limestone contents (0% or 20%), and curing conditions (saturated or sealed).

4. Results and discussion

Fig. 2 presents the CEMHYD3D model and the experimental results for the degree of hydration for cement pastes with and without 20% limestone substitution, with a “final” $w/s = 0.435$ and cured under saturated conditions. For this higher w/s , the CEMHYD3D model

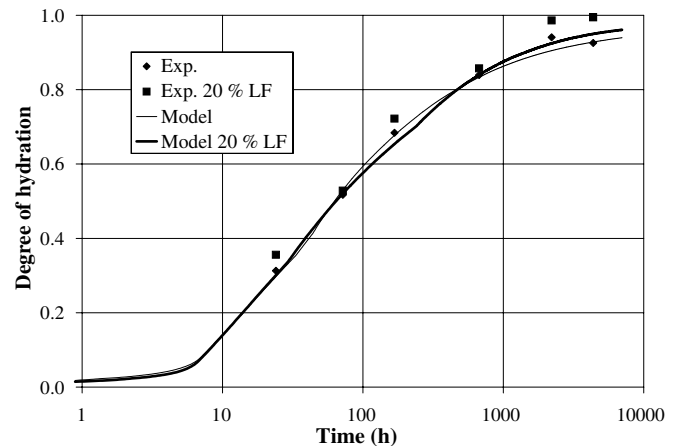


Fig. 2. Experimental and model estimated degrees of hydration for cement 152 with and without 20% by mass fraction limestone substitution for $w/s = 0.435$, cured under saturated conditions.

predicts basically no acceleration of the cement hydration by the substitution of limestone and this is what is in fact observed experimentally. At hydration times of 90 d and beyond, there is a slight increase in the amount of hydration achieved in the pastes with the 20% limestone substitution, most likely due to the higher effective w/c (0.544 vs. 0.435) in the filled system. Similar results are displayed for the pastes exposed to sealed curing conditions as shown in Fig. 3. Even under sealed conditions, there is sufficient water initially present in the two pastes for hydration to continue at its “nominal” maximum rate.

Quite different results, however, are observed for the $w/s = 0.35$ pastes as shown in Figs. 4 and 5. For this lower w/s , the additional water (relative to the amount of Portland cement, 0.4375 vs. 0.35), along with the additional surfaces provided by the limestone for precipitation of reaction products, results in a significant acceleration of the cement hydration in the filled systems. This trend is observed both for saturated (Fig. 4) and for sealed

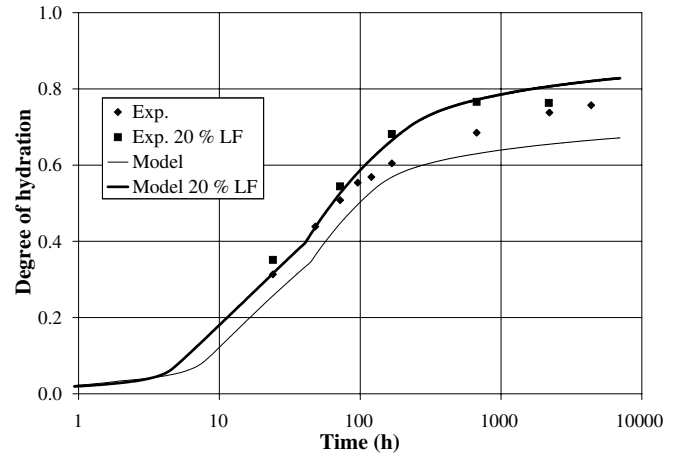


Fig. 5. Experimental and model estimated degrees of hydration for cement 152 with and without 20% by mass fraction limestone substitution for $w/s = 0.35$, cured under sealed conditions.

(Fig. 5) curing conditions, and is consistent with previous observations that lower w/s pastes, mortars, and concretes can achieve equivalent performance with higher levels of limestone substitutions than their higher w/s counterparts [3,4,19].

In general, the results in Figs. 2–5 indicate that the modified CEMHYD3D model provides a good prediction of the influence of limestone substitution on the hydration rates of these blended materials. While the model does underpredict the observed hydration for the pastes without fillers cured under *sealed* conditions, in each of the four cases (two different w/s and two different curing conditions), the *relative* effects of the limestone substitution on achieved degree of hydration are modeled within the experimental error in the degree of hydration measurements.

The CEMHYD3D model was further employed to project the acceleration of cement hydration for a 20% limestone substituted blend with a $w/s = 0.3$. The results

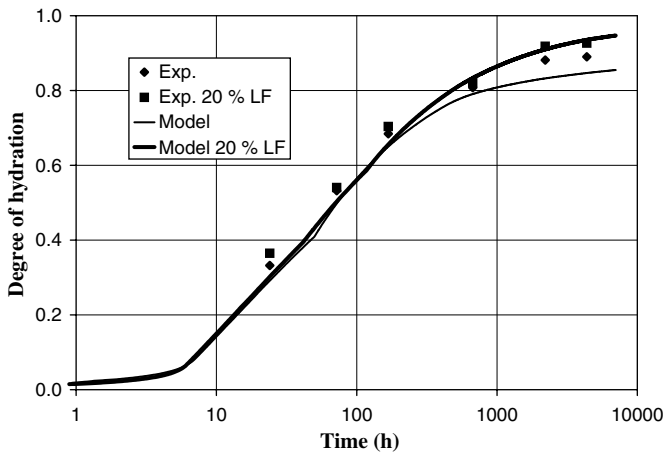


Fig. 3. Experimental and model estimated degrees of hydration for cement 152 with and without 20% by mass fraction limestone substitution for $w/s = 0.435$, cured under sealed conditions.

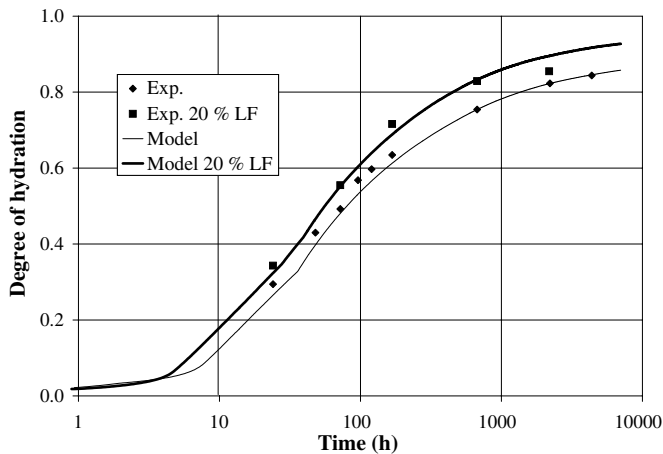


Fig. 4. Experimental and model estimated degrees of hydration for cement 152 with and without 20% by mass fraction limestone substitution for $w/s = 0.35$, cured under saturated conditions.

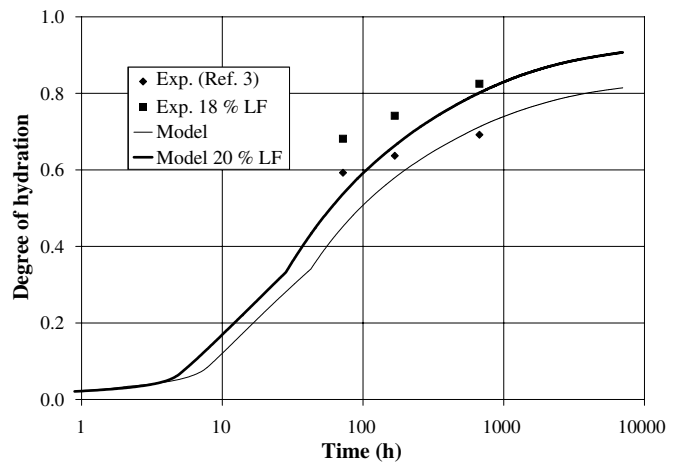


Fig. 6. Model predicted degrees of hydration for cement 152 with and without 20% by mass fraction limestone substitution for $w/s = 0.3$, cured under saturated conditions. Experimental data for similarly-cured (concrete) systems from Ref. [3] are shown for comparison.

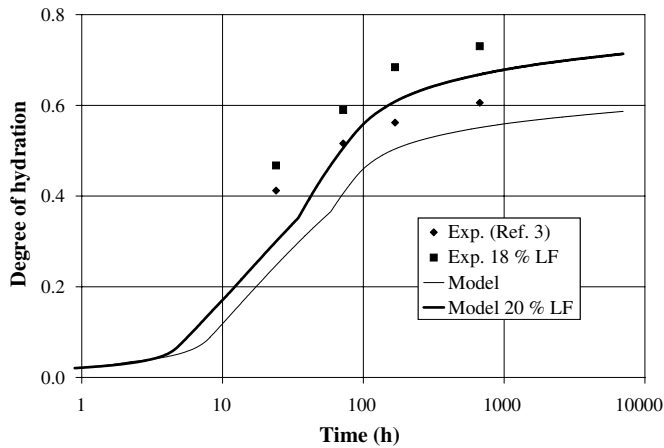


Fig. 7. Model predicted degrees of hydration for cement 152 with and without 20% by mass fraction limestone substitution for $w/s = 0.3$, cured under sealed conditions. Experimental data for similarly-cured (paste) systems from Ref. [3] are shown for comparison.

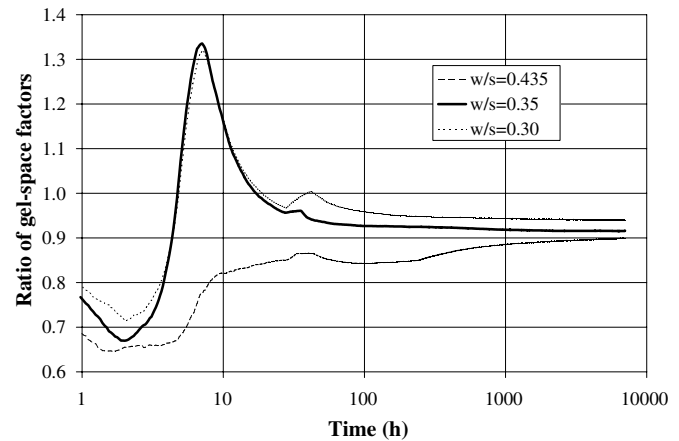


Fig. 8. Model ratios of gel-space factors for cement paste with 20% by mass fraction limestone substitution to cement paste without limestone plotted vs. hydration time for saturated curing conditions.

for saturated and sealed curing are shown in Figs. 6 and 7, respectively. The experimental results of Bonavetti et al. [3] are shown for comparison. It should not be expected that the CEMHYD3D model results would exactly match these experimental values as a different cement (composition, fineness, interground limestone, etc.) was employed in the studies in [3]. Rather, the experimental results are provided as a benchmark to evaluate the relative acceleration provided by the limestone substitution in the CEMHYD3D model systems. The magnitude of the observed acceleration for the two different curing conditions using the model is quite similar to that observed experimentally [3]. Because “free” water is at a premium when sealed curing conditions are employed, the relative “acceleration” of cement hydration provided by limestone substitution is always greater at later ages in the systems with sealed as opposed to saturated curing.

Care must be taken to not interpret the accelerated hydration provided by the limestone substitution in low w/s systems as a projected increase in compressive strength. While hydration is indeed accelerated, this increase in the production of cement hydration products must be considered in light of the initial dilution of the active cement component of the mixture by the limestone substitution [3]. A more proper interpretation in terms of projected compressive strengths is provided by considering the gel-space ratio of the two systems. Bonavetti et al. [3] have shown that the gel-space ratio concept of Powers provides an adequate description of the compressive strength development of concretes with and without limestone substitutions. The gel-space ratios of cement pastes with and without limestone, as computed by the CEMHYD3D model for saturated curing conditions, are compared in Fig. 8, which provides plots of the ratios of the values for systems with a 20% limestone filler substitution to those for unfilled systems. At very early ages of less than 1 d, a strength enhancement is projected in

the $w/s = 0.3$ and $w/s = 0.35$ systems containing the limestone filler, due to its significant acceleration of the initial cement hydration. However, in the long term, there is about a 5–8% reduction in the gel-space ratio in the filled systems with $w/s = 0.3$ and $w/s = 0.35$, as the dilution effect of the limestone substitution eventually overcomes the benefits of the accelerated cement hydration. These reductions in gel-space ratio would project to compressive strength reductions of between 15% and 20%, in general agreement with experimental observations [3]. The reduction in gel-space ratio is less for the $w/s = 0.3$ system than for the $w/s = 0.35$ one, suggesting once again that the lower the w/s , the higher the limestone substitution that can be made without sacrificing performance. On the other hand, for the higher $w/s = 0.435$ systems, a higher long term strength reduction on the order of 25% would be projected (with an even greater strength reduction projected at 28 d), so that a 20% limestone substitution level simply may be too high to maintain equivalent long-term performance in this blended material.

It is not surprising that the acceleration of cement hydration by limestone substitution is strongly influenced by the w/s of the paste. It is well known that, for w/c below about 0.36, there is insufficient (water-filled) space available in the three-dimensional microstructure to allow for complete hydration of the original cement. In this case, some of the cement clinker is acting as inert (and rather expensive) filler. With the advances in the development of high-range water-reducing agents and superplasticizers, and the concurrent movement towards high-performance concrete, the fraction of concretes with $w/s < 0.36$ being placed is increasing. In the long term, the efficiency of cement usage in such mixtures must be addressed. Limestone substitutions at levels above the 5% currently permitted in the ASTM C150 standard specification appear to provide an opportunity to economize on cement in these lower w/s concretes. Of course, durability aspects, particularly those relevant to thaumasite formation [20,21], must be given

proper consideration. Still, as summarized by Bonavetti et al. [3], “The use of limestone filler in this (low w/c concrete) mixture is a more rational option from the energy consumption, emission reduction, and economic point of view”.

5. Conclusions

The CEMHYD3D computer model has been modified to consider the influence of limestone substitutions, allowing a priori prediction of the effects of various limestone substitutions on achieved degree of hydration, microstructure, and strength development. Both the chemical and fine filler effects of limestone on cement hydration have been addressed. The revised model provides good agreement with experimental results, predicting a significant acceleration of cement hydration only in lower w/s (e.g., 0.35) ratio blended cement pastes. Thus, limestone substitutions are projected to be particularly advantageous in lower w/s (<0.4) mortars and concretes, where the cement clinker being replaced may only be serving the function of a relatively expensive filler material. In these systems, up to 20% of the cement could potentially be substituted by limestone (or other fillers) to economize on the usage of Portland cement clinker and to reduce the energy and the deleterious emissions associated with its production.

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