Limestone Fillers Conserve Cement Part 2: Durability Issues and the Effects of Limestone Fineness on Mixtures

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Limestone Fillers Conserve Cement

Part 2: Durability issues and the effects of limestone fineness on mixtures

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Part 1 of this article used Powers' model to demonstrate the viability of increased limestone filler replacement levels in lower water-cementitious material ratio (*w/cm*) concretes.[1] Commonly cited potential negative impacts of increased limestone replacement levels typically center on two durability issues: increased susceptibility to carbonation and the potential for thaumasite formation.[2,3] One might conjecture that both of these would be dramatically reduced in the denser, lower water-cement ratio (*w/c*) concretes where increased limestone replacement levels may be most applicable. For the case of thaumasite formation, a recent review article highlights that damage is indeed controlled when a low effective *w/c* is employed.[4]

The topic of limestone fineness is also addressed by contrasting the performance of limestone substitutions of different median particle sizes. The topic of fineness becomes paramount when one considers differences between interground limestone and limestone that's added after the cement is ground. In the former case, the interground limestone powder will likely be finer than the interground cement clinker due to it being the softer of the two materials, while in the latter case, the limestone powder can be finer, as fine as, or coarser than the base cement, depending on the selection of the limestone powder itself.

AUTOGENOUS DEFORMATION

Autogenous deformation is of particular concern for lower *w/cm* concretes, mainly due to its potentially significant contribution to early-age cracking. Two recent studies have highlighted the importance of limestone fineness in providing some reduction in measured autogenous deformation of mortars.[5,6] Figure 1 presents results for mortars for which strength results are provided in Table 1 (also Table 1 in Part 1 of this article; repeated here for completeness).[5] While from a strength viewpoint there was little difference in performance between the two different fineness limestones, from an autogenous deformation viewpoint there is a considerable advantage in using the coarser of the two limestones.

Autogenous deformation is controlled by the amount of chemical shrinkage (self-desiccation) occurring in the specimen and the sizes of the pores being emptied during the self-desiccation process. Smaller, partially water-filled pores result in higher capillary stresses and greater deformation (and susceptibility to cracking). Limestone replacements can be performed with powders that are finer, as fine as, or coarser than the cement powder.

When the limestone particles are finer than the cement, they will reduce the interparticle spacing in the fresh paste and ultimately lead to higher capillary stresses and increased autogenous deformation, as exemplified by the finer of the two limestones in Fig. 1. If the limestone is of similar fineness to the cement, a small reduction in autogenous deformation might be expected due to the dilution effect (increased effective *w/c*) and the fact that the chemical shrinkage occurring per unit volume of material is decreased. Finally, when the limestone is coarser than the cement, it will result in an increase in interparticle spacing and may provide a substantial reduction in autogenous deformation, as exemplified by the coarser of the two limestones in Fig. 1.

Figure 1 also shows another set of recent experimental results[6] for cement mortar samples with 0.30 *w/cm*, 55%

TABLE 1
Compressive strength results for mortar cubes without and with a 10% by mass replacement of cement by limestone powder[5]

Mixture	$w/c = 0.35$	$w/cm = 0.357$ fine limestone	$w/cm = 0.357$ coarse limestone
1-day strength, MPa/psi	36.2 (1.4)*/5250	29.5 (1.0)/4280 18.5% reduction	25.8 (1.0)/3750 28.8% reduction
3-day strength, MPa/psi	55.6 (2.4)/8070	49.4 (2.7)/7170 11.2% reduction	48.8 (1.1)/7080 12.2% reduction
7-day strength, MPa/psi	64.8 (1.0)/9390	57.4 (0.2)/8320 11.4% reduction	56.4 (3.0)/8180 13% reduction
28-day strength, MPa/psi	78.5 (2.2)/11,380	72.9 (3.9)/10,580 7.1% reduction	73.3 (3.4)/10,630 6.6% reduction

*Numbers in parentheses indicate one standard deviation in MPa as determined for the three replicate specimens tested at each age.

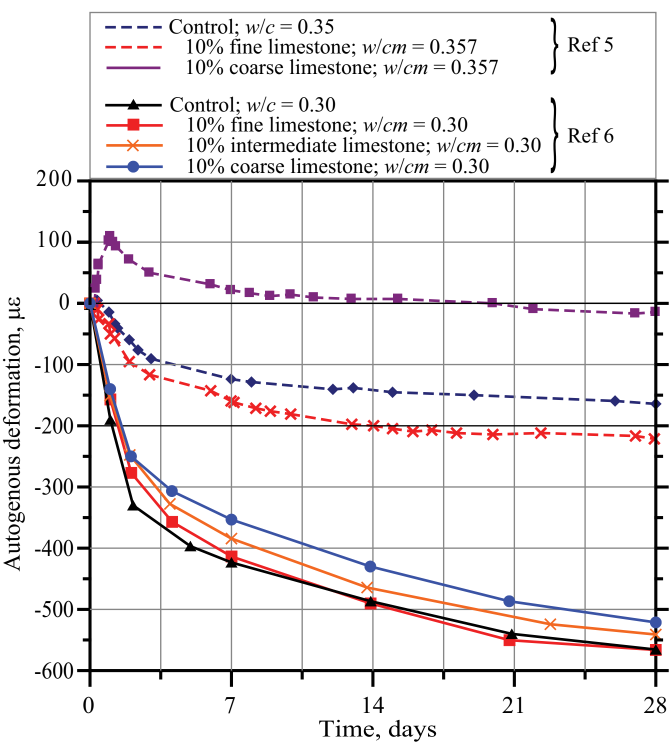

Fig. 1: Autogenous deformation versus time for mortars with and without a 10% limestone replacement by mass for cement[5,6]

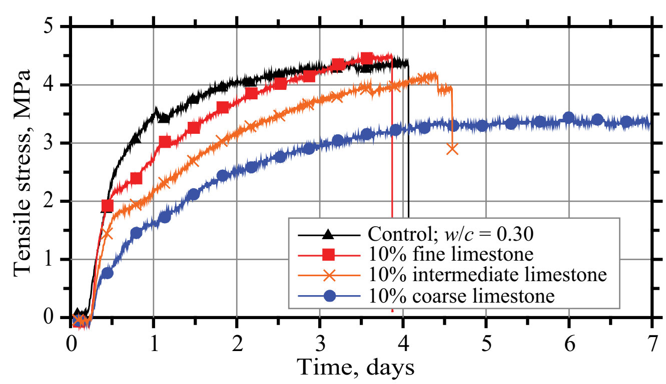

Fig. 2: Stress development versus time for a representative specimen of three specimens of plain mortar rings and mortar rings containing 10% replacement by mass of different fineness limestone powders.[6] All mixtures had $w/cm = 0.30$. A sudden decrease in the tensile stress indicates cracking

sand by volume, and 10% limestone replacement by mass. That study employed limestone of three different finenesses ranging from 3 to 100 μm for median particle diameters. The intermediate limestone powder has a similar fineness to that of the cement used, with a median particle diameter of 17 μm. The reduced autogenous deformation shown in Fig. 1 may also lead to a decrease in the potential for early-age cracking when using coarser limestone powders.[6] Cracking caused by only autogenous strains develops much sooner in mortars containing a finer limestone compared to mortars containing a coarser limestone, as demonstrated in Fig. 2 in which the same mortars from Fig. 1 (with $w/cm = 0.30$) were used in restrained shrinkage tests (ASTM C1581[7]). Results from one representative specimen of the three specimens tested for each mixture are plotted in Fig. 2.[7] For the coarsest limestone mixture, one specimen cracked after 161 hours, whereas the other two specimens did not crack during the course of the 8-day test.

Figure 3 presents the average time to cracking plotted against the median particle size for each of the three limestone finenesses. On average, the samples containing the coarse limestone cracked 82 hours after the samples

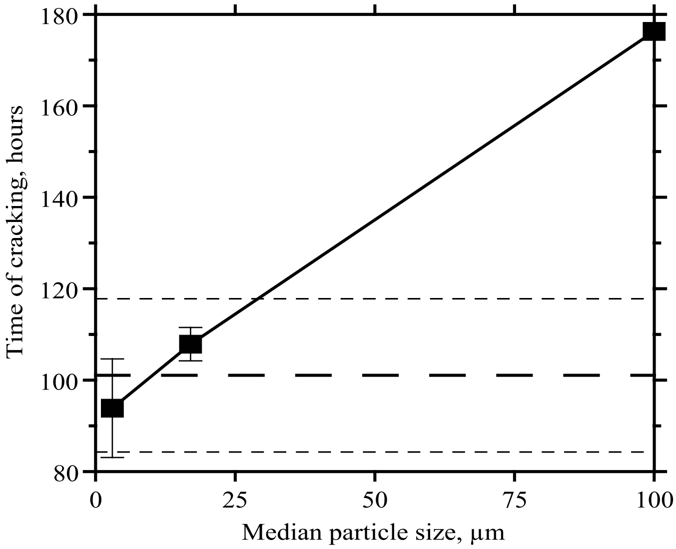

Fig. 3: Average time to cracking of limestone cement mortars versus median particle size of limestone replacement. The heavy dashed line indicates the time to cracking for the control base cement system with no limestone replacement, with its accompanying error bars as indicated by the two dashed lines[6]

containing the finest limestone. It should be noted that only one of the three samples with the coarse limestone cracked at the time the testing was complete. This further indicates a reduction in the cracking potential with the more coarse limestone grind.[8] Some benefits have also been observed in commercial cements with interground limestone.

Research conducted at Purdue University[9] on cement mortars containing 5 and 10% interground limestone with a *w/cm* of 0.30 showed that these mixtures provided minor benefits in decreasing autogenous deformation and total deformation for early ages and long term, particularly at the 10% replacement level. The study also concluded that mixtures containing interground limestone may decrease the susceptibility to cracking at early ages, but by less than 10 hours compared with the results in Fig. 3 for blended (as opposed to interground) limestones.[6]

TRANSPORT AND DURABILITY

The ingress of aggressive ions occurs by several transport mechanisms, including the flow of the solution throughout the connected pores of concrete by permeability, capillary suction, and the diffusion of ions. For structures continuously soaked in an aggressive medium, diffusion is the main transport mechanism in low *w/cm* concrete. Among aggressive ions, the ingress of chlorides can produce the corrosion of reinforcement in concrete structures. It is generally agreed that the rate of chloride ingress into concrete is highly dependent on the capillary porosity.

According to one model-based study,[10,11] the capillary porosity becomes disconnected (depercolated) when its value is around 18%, and the relative diffusion coefficient of an ion can be expressed as[11]

$$D/D_0 = 0.001 + 0.07\phi^2 + 1.8(\phi - 0.18)^2 H(\phi - 0.18) \qquad (1)$$

where D is the diffusion coefficient for an ion through cement paste, D_0 is the diffusion coefficient of this ion in water, ϕ is the capillary porosity per Fig. 4 (also Fig. 2 in Part 1 of this article; repeated here for completeness), and H is the Heaviside step function, here with $H = 0$ for $\phi < 0.18$ and $H = 1$ for $\phi \geq 0.18$. From Fig. 4, it can be observed that final porosity depends on both *w/cm* and the limestone filler replacement level. For cement without filler, disconnected porosity can be attained using a *w/cm* near 0.50, while a reduction of *w/cm* to 0.42 is needed for cement containing 20% limestone filler replacement by mass.

Figure 5 shows the variation of the relative diffusion coefficient D/D_0 calculated for cements containing 0, 10, and 20% replacement levels of limestone filler, at complete hydration. It can be observed that for *w/cm* greater than 0.4, a significant increase of D/D_0 is predicted for those systems with limestone replacement, corresponding to a faster penetration of chloride ions into the concrete. For the C0, C10, and C20 cements described in Part 1, an experimental study[12] carried out on concretes (with a *w/cm* of 0.40 and a unit cement content of 350 kg/m^3 [590 lb/yd^3]) exposed to chloride solution (3% NaCl by mass) revealed that the chloride penetration was deeper at 45 days for the mixtures with increased limestone contents.

After 1 year, the apparent diffusion coefficient value was 5.0×10^{-12} m^2/s (7.8×10^{-9} $in.^2/s$) for the C0 cement and two times greater for both cements containing limestone filler (C10 and C20), while no differences were observed in the chloride content at the surface for the three materials.[13] For *w/cm* greater than 0.4, at complete hydration, the total porosity (Fig. 4) increases due to the replacement of a part of the cement by the same quantity of limestone filler. Consequently, there is an increase of D/D_0 that could be compensated for in practice by a slight reduction of *w/cm*. As shown in Fig. 5, for *w/cm* less than 0.35, low ion diffusivities would be expected in all three concretes.

SUMMARY AND PROSPECTUS

In low *w/cm* systems, it has been demonstrated that the autogenous deformation and propensity for related early-age cracking can be significantly reduced by judiciously using coarser limestones as a cement replacement to significantly reduce capillary stresses and decrease the number of reactive particles. In terms of durability, for concretes with *w/cm* greater than 0.4, limestone replacements will lead to increased diffusion rates. However, for lower

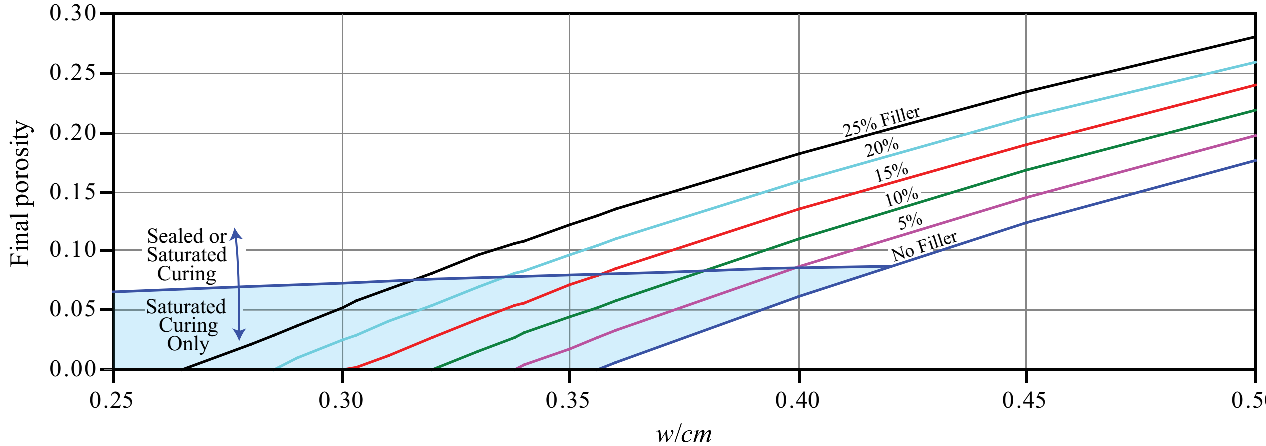

Fig. 4: Predicted final total capillary porosity (empty and water-filled) as a function of *w/cm* (*cm* = cement + limestone) and limestone filler substitution (by mass according to Powers' model [see Reference 1])

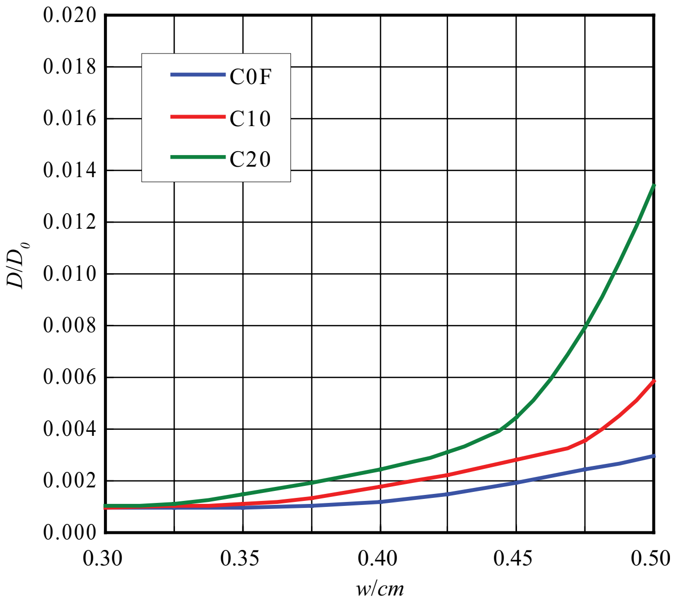

Fig. 5: Variation of relative diffusion coefficient (D/D_0) calculated from Eq. (1) as a function of *w/cm* for paste hydrated to its maximum extent and containing approximately 0% (C0F), 10% (C10), and 20% (C20) of limestone filler by mass

w/cm concretes, similar diffusion coefficients will be expected, as costly unreacted cement is being replaced by limestone filler. ACI and much of the concrete community as a whole are currently focused on sustainable solutions for construction. Based on the results presented in Parts 1 and 2 of this article and elsewhere, increased limestone replacement for cement in low *w/cm* concretes appears to be one viable, but currently underused, option.

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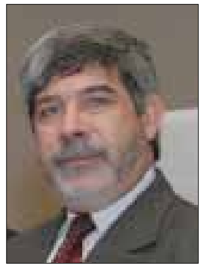

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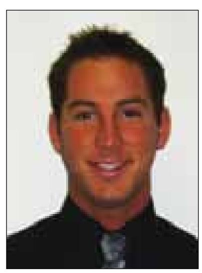

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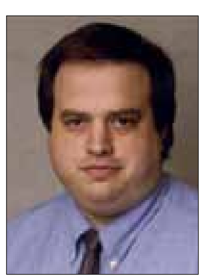

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