

## **Limestone Fillers to Conserve Cement in Low w/cm Concretes: An Analysis Based on Powers' Model**

Dale P. Bentz<sup>A</sup>  
Edgardo F. Irassar<sup>B</sup>  
Brooks Bucher<sup>C</sup>  
W. Jason Weiss<sup>C</sup>

<sup>A</sup> Building and Fire Research Laboratory  
National Institute of Standards and Technology  
100 Bureau Drive Stop 8615  
Gaithersburg, MD 20899-8615 USA  
E-mail: [dale.bentz@nist.gov](mailto:dale.bentz@nist.gov)  
Phone: (301)975-5865  
FAX: (301)990-6891

<sup>B</sup> Facultad de Ingeniería  
Universidad Nacional del Centro de la Provincia de Buenos Aires  
Av. del Valle 5737  
B7400JWI - Olavarría - ARGENTINA  
E-mail: [firassar@fio.unicen.edu.ar](mailto:firassar@fio.unicen.edu.ar)  
Phone: +54 2284 451 055 interno 212  
FAX: +54 2284 450 628

<sup>C</sup> Purdue University School of Civil Engineering  
550 Stadium Mall Drive  
West Lafayette, IN 47907 USA  
E-mail: [bebucher@purdue.edu](mailto:bebucher@purdue.edu)  
E-mail: [wjweiss@purdue.edu](mailto:wjweiss@purdue.edu)  
Phone: (765)494-2215  
FAX: (765)494-0395

### **Introduction**

“Green” concrete has become a rallying cry for the 21<sup>st</sup> century. In addition to field performance, concrete mixtures are now also judged by their energy consumption, carbon dioxide production, and waste stream utilization. While this problem is being attacked from many vantage points, perhaps one under-recognized opportunity is the replacement of a portion of the cement by an effectively inert filler in lower water-to-cement ratio (*w/c*) concretes. Although it is recognized and accepted that in many lower *w/c* concretes all of the cement is unable to hydrate due to space limitations and/or water deficiencies, much cement is still used each year in the role of a relatively expensive filler in these mixtures. Bonavetti et al. [1] have proposed that limestone powder substitution for cement makes perfect sense in these lower *w/c* concretes, saving money and energy and reducing carbon dioxide emissions.

Limestone powder additions to cements and concretes in the U.S. have developed along a much different path than that taken in Europe, where limestone/cement blends have been employed for many years. After years of discussion, it was only in 2004 that the ASTM International 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 [2]. An extensive survey of the literature available at that time conducted by the Portland Cement Association [3] concluded that “in general, the use of up to 5 % limestone does not affect the performance of portland cement.” Higher addition rates of 10 % to 15 % are currently being discussed, particularly in Canada where the Canadian Standards Association may supersede its American (International) counterpart in moving to higher levels [4]. In the U.S., some concrete ready-mix producers already add limestone powder above a 5 % level directly to their concrete mixtures. In the Netherlands and elsewhere, limestone powder is commonly employed as a filler in self-consolidating concretes (SCCs), once again at values well above the 5 % level [5]. 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 [3,4]. One might conjecture that both of these would be dramatically reduced in the denser, lower  $w/c$  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 [6].

This paper utilizes Powers’ model to analyze total capillary porosity in limestone-filled cement pastes to suggest appropriate replacement levels as a function of water-to-cementitious material ratio,  $w/cm$ . 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 limestones vs. limestone that is added after the grinding of the cement. 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.

### **Powers’ Model**

“Powers’” model, as originally presented by Powers and Brownyard [7], idealizes hydration as a reaction between cement particles and water to produce a single hydration product, cement gel. Based on adsorption/desorption measurements performed on numerous cement pastes of various  $w/c$  and degrees of hydration, they arrived at a quantitative interpretation of hydration for this simplified conceptualization. Here, their quantitative model is applied utilizing the following assumed values from Jensen and Hansen [8], all in mass units of water per mass unit of cement reacted: a non-evaporable water content of 0.23, a chemical shrinkage of 0.064, and a cement gel water content of 0.19. Based on these values, they provided the following estimates for volumetric phase fractions as a function of degree of hydration,  $\alpha$ , and starting water-to-cement ratio,  $w/c$ :

Chemical shrinkage:  $V_{cs} = 0.20(1 - p)\alpha$

Capillary water:  $V_{cw} = p - 1.32(1 - p)\alpha$

Gel water:  $V_{gw} = 0.60(1 - p)\alpha$  (1)

Gel solids:  $V_{gs} = 1.52(1 - p)\alpha$

Cement:  $V_c = (1 - p)(1 - \alpha)$

Volume balance:  $V_c + V_{gs} + V_{gw} + V_{cw} + V_{cs} = 1$

where  $p=(w/c)/(w/c+\rho_w/\rho_c)$  and  $\rho_w$  and  $\rho_c$  refer to the densities of water and cement, here assigned values of  $1000 \text{ kg/m}^3$  ( $1686 \text{ lb/yd}^3$ ) and  $3150 \text{ kg/m}^3$  ( $5310 \text{ lb/yd}^3$ ), respectively. The above equations can be applied in a variety of contexts of practical significance for concrete mixture proportioning. For example, by setting the cement, capillary water, and chemical shrinkage volumes to zero so that effectively all of the available volume is filled with gel water and gel solids, the maximum achievable degree of hydration for a given  $w/c$  under **saturated** curing conditions can be determined. According to this model, for  $w/c$  below about 0.356, there is insufficient space available for complete hydration of the cement. At a  $w/c$  of about 0.42, there is just sufficient water for complete hydration of the cement, if no additional sources of curing water are available (**sealed** curing, for example). It should be noted that this value of 0.42 is equal to the sum of the assumed non-evaporable and gel water contents at complete hydration (0.23 and 0.19) [8]. Powers' model is illustrated graphically in Figure 1 for a  $w/c=0.4$  cement paste at three different degrees of hydration.

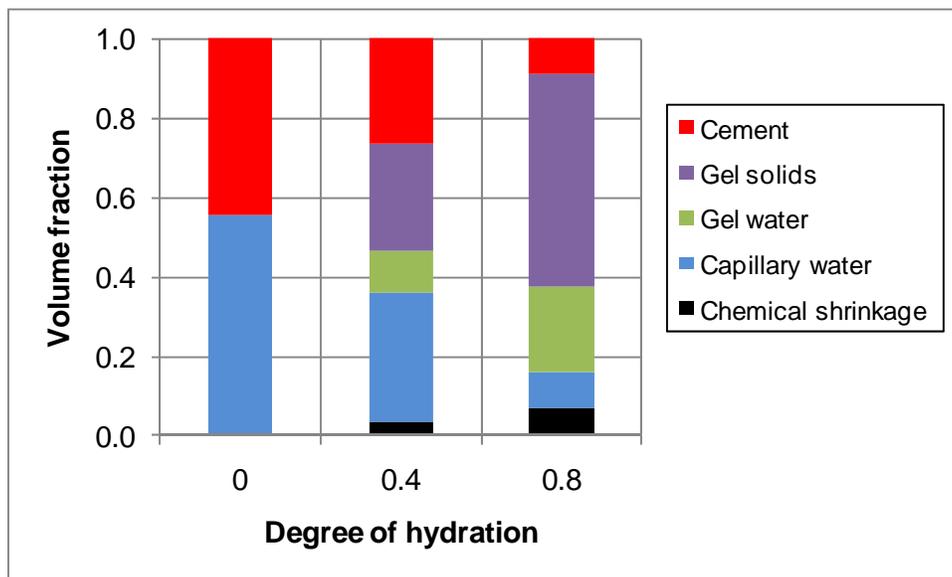


Figure 1 – Illustration of Powers’ model for cement hydration for  $w/c=0.4$  cement paste at the indicated degrees of hydration.

In recent years, a greater proportion of concrete is being produced with  $w/c$  less than 0.42, or even less than 0.356. Powers’ model implies that in these concretes, a portion of the cement is only functioning as an inert filler, as there is insufficient space and/or insufficient water for complete hydration to be achieved. It is in these concretes that the replacement of a portion of the cement with a less expensive and more environmentally friendly filler, such as limestone powder, is particularly attractive [1,9].

If, as a first order approximation, the limestone filler (density of about 2700 kg/m<sup>3</sup> or 4550 lb/yd<sup>3</sup>) is considered to be inert, equation set (1) for Powers’ model can be easily adapted to the cement/limestone blended pastes by simply multiplying all of the volume fractions by a term representing the volume fraction of (base cement and water) paste, or  $(1-V_{LF})$  where  $V_{LF}$  is the volume fraction of limestone filler in the blended paste. In this case, the volume balance becomes:

Volume balance with limestone filler: 
$$V_c + V_{gs} + V_{gw} + V_{cw} + V_{cs} = 1 - V_{LF}$$

When the equations are used in this form, it must be kept in mind that  $w/c$  in equation set (1) represents the *effective* water-to-cement mass ratio and not the water-to-(cement+limestone) ratio ( $w/cm$ ). As will be illustrated in the results section to follow, a simple analysis based on Powers’ model for limestone-filled cements yields valuable information concerning appropriate filler replacement levels as a function of  $w/cm$ .

## Results

### *Powers’ Model*

Powers’ model will be applied to the two limiting cases of saturated and sealed curing. For saturated curing, it is assumed that an adequate supply of additional water is consistently available to maintain all of the capillary (and gel) porosity within the cement paste under saturated conditions. This water could be available from an external source or from internal curing, for example. The amount of additional water necessary to maintain saturated conditions in the paste is conveniently given by the chemical shrinkage computed from equation set (1). In this case, according to the model, for  $w/c$  below about 0.356 for a base cement paste with no limestone filler, a final total capillary porosity of zero can be achieved, and there will thus be insufficient space for complete hydration of the cement. As the  $w/cm$  goes even lower, a greater fraction of the base cement in the system without limestone would remain unhydrated, providing the potential opportunity for ever-increasing limestone replacement levels, as shown in Figure 2. For a limestone replacement level,  $M_{LF}$ , of 5 % by mass, zero porosity is predicted for a  $w/cm$  of 0.338. For 10 %, 15 %, 20 %, and 25 % replacements by mass, the corresponding  $w/cm$  are 0.32, 0.303, 0.285, and 0.267, respectively, as described by the equation  $w/cm(\text{for porosity}=0)=0.356*(1-M_{LF})$ . These results suggest that for a  $w/cm=0.3$  concrete cured to maximum hydration under saturated conditions (if such curing is possible),

limestone replacements on the order of about 15 % by mass should be possible without sacrificing performance in terms of long term achieved total capillary porosity.

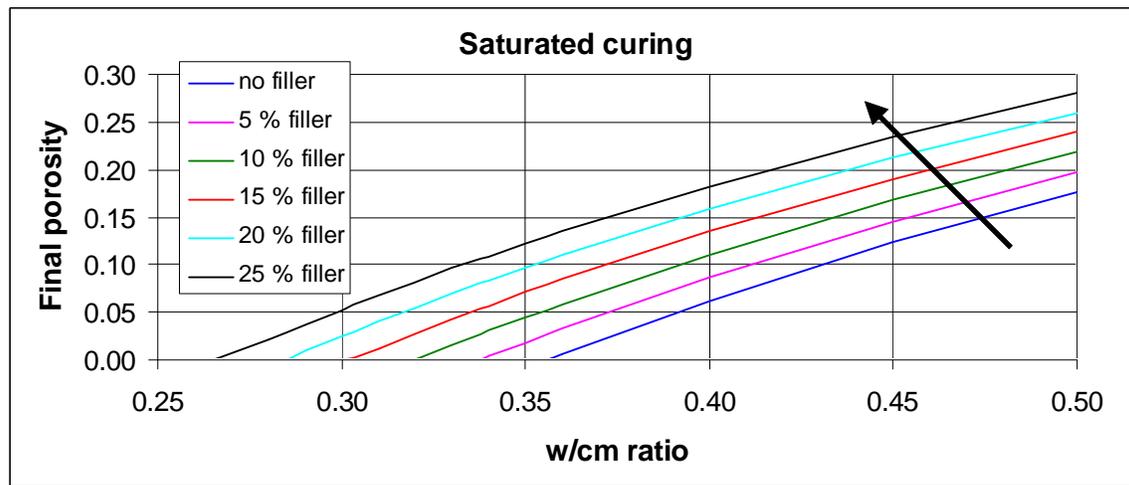


Figure 2 - Predicted final total capillary porosity as a function of  $w/cm$  ( $cm$ =cement+limestone) and limestone filler substitution (by mass) under saturated curing conditions according to Powers' model.

Next, the case of sealed curing conditions is considered based on Powers' model. Here, there is no additional water available for curing/hydration beyond that present in the original concrete mixture, so that a  $w/c$  of 0.42 is required to provide complete hydration for the paste with no limestone replacement. Even with complete hydration, a total capillary porosity of about 8.7 % (empty pores due to self-desiccation induced by chemical shrinkage as computed using equation set (1)) will be present in the final material. Once again, as shown in Figure 3, as  $w/cm$  is lowered below 0.42, increasing replacement levels of limestone for cement appear as viable. In the case of sealed curing, for example, a  $w/cm=0.35$  system should be able to incorporate a replacement level of limestone of about 17 % by mass while still ultimately achieving the "lowest possible" total capillary porosity.

The curing conditions of most concretes lie somewhere between these extremes of saturated and sealed curing. While it might be hoped that sealed curing would represent a worst case scenario in terms of water availability, improper curing could of course result in water loss due to evaporation and further limit achievable degrees of hydration with a concurrent increase in capillary porosity. But, returning to the assumption that most curing conditions would lie between the cases of saturated and sealed, the results in Figures 2 and 3 would suggest that limestone replacement levels well above 5 % could be utilized in a wide range of lower  $w/cm$  concretes.

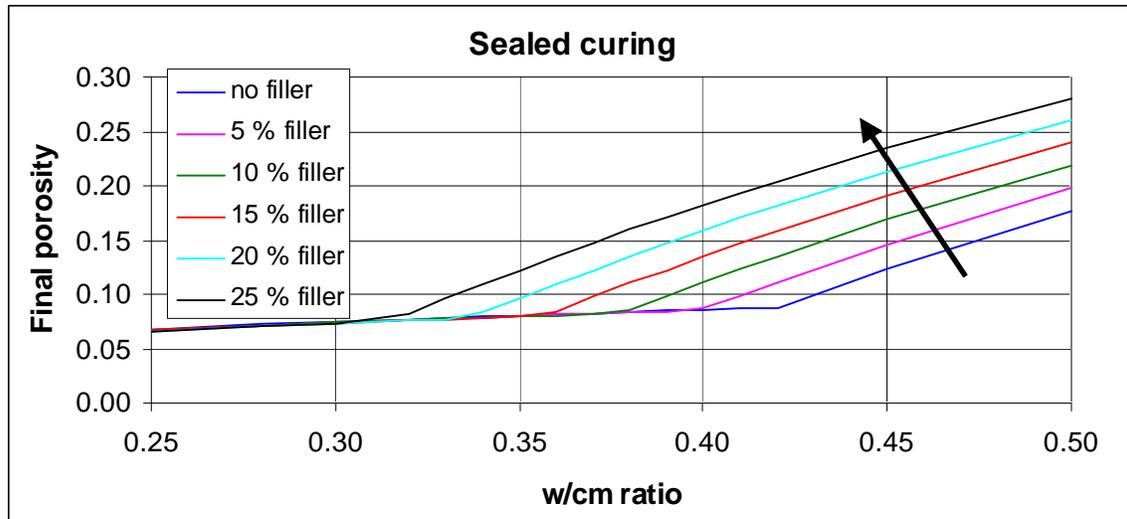


Figure 3 - Predicted final total capillary porosity (empty and water-filled) as a function of  $w/cm$  and limestone filler substitution under sealed curing conditions according to Powers' model.

### *Hydration and Strength*

Because reactive cement is being replaced with a relatively inert limestone, it would be expected that some decrease in compressive strength would occur in systems with limestone replacement for cement. However, for the lower  $w/cm$  systems presented in Figures 2 and 3, this decrease might be quite minimal at later ages as the same total capillary porosity is achievable for a range of limestone replacement values. For example, for a  $w/cm$  of 0.3 under sealed curing conditions, a low capillary porosity (about 7 %) should be obtainable for limestone replacement levels from 0 % to 25 % by mass. In these cases, the long term strengths might be only slightly reduced in the systems with limestone replacement, due to limestone powder being weaker than (unhydrated) ground cement clinker.

While the results in Figures 2 and 3 are only theoretical as based on Powers' model, several studies have quantified the influence of limestone replacements on mortar and concrete compressive strengths. In a study initiated by Bentz and Conway [9], experimental measurements indicated no detectable difference in 56 d compressive strength between a control  $w/c=0.3$  mortar and one in which the coarsest cement particles (nominally those of diameter greater than 30  $\mu\text{m}$ ) had been replaced by a coarse limestone at a 15 % replacement level on a volume basis [10]. Compressive strengths from a more recent study [11] are summarized in Table 1, which compares a  $w/c=0.35$  control mortar to two mortars ( $w/cm=0.357$ ) with 10 % limestone replacement by mass, either by a fine (16  $\mu\text{m}$  median diameter) or a coarse (80  $\mu\text{m}$  median diameter) limestone. While the strength in the system with the coarser limestone is nearly 30 % below the value of the control at an age of 1 d, by 28 d, the two limestone replacement mortars both exhibit strengths that are within 7 % of the control mortar.

Table 1. Compressive strength results for mortar cubes without and with a 10 % by mass replacement of cement by limestone powder [11].

Mixture	w/c = 0.35	w/cm = 0.357 fine limestone	w/cm = 0.357 coarse limestone
<b>1 d strength (MPa/psi)</b>	36.2 (1.4) <sup>A</sup> / 5250	29.5 (1.0) / 4280 18.5 % reduction	25.8 (1.0) / 3750 28.8 % reduction
<b>3 d strength (MPa/psi)</b>	55.6 (2.4) / 8070	49.4 (2.7) / 7170 11.2 % reduction	48.8 (1.1) / 7080 12.2 % reduction
<b>7 d strength (MPa/psi)</b>	64.8 (1.0) / 9390	57.4 (0.2) / 8320 11.4 % reduction	56.4 (3.0) / 8180 13 % reduction
<b>28 d strength (MPa/psi)</b>	78.5 (2.2) / 11380	72.9 (3.9) / 10580 7.1 % reduction	73.3 (3.4) / 10630 6.6 % reduction

<sup>A</sup>Numbers in parentheses indicate one standard deviation in MPa as determined for the three replicate specimens tested at each age.

Additional results from Bonavetti et al. [1] indicate that the gel-space ratio expression of Powers' model can be used successfully to describe the compressive strength of concretes containing limestone filler. According to this expression, compressive strength,  $f_c$ , is related to the gel-space ratio,  $X$ , as shown in the following equation:

$$f_c = f_0 X^n \quad (2)$$

where  $f_0$  is an intrinsic strength that depends on the cement composition and particle size distribution, and  $n$  generally assumes a value between 2.6 and 3.0. The gel-space ratio,  $X$  is calculated as:

$$X = \frac{0.68\alpha}{0.32\alpha + \frac{w}{c}} \quad (3)$$

where  $\alpha$  is the mass-based degree of hydration of the cement and the  $w/c$  is the *effective* water/cement ratio (not including limestone as part of the cement) .

Table 2 summarizes compressive strengths of different concrete mixtures ( $w/cm = 0.30, 0.34$  and  $0.40$ ) determined on 100 mm x 200 mm (4" by 8") cylinders after curing for up to 28 d in water saturated with lime [1,12,13]. Experimental measurements were made using a cement without limestone (C0), and two portland limestone cements containing around 10 % (C10) and 20 % (C20) of limestone filler. For each concrete, the gel-space ratio was calculated using an  $\alpha$ -value estimated by determination of non-evaporable water content at different ages [1]. Figure 4 shows that the compressive strength/gel-space ratio expression obtained from a curve fitting of experimental data, and the fitted  $n$  coefficient agrees with the value found in the literature.

Table 2. Compressive strength results for concretes containing C0, C10 and C20 cements in MPa (psi) [1,12,13].

Cement	Age, d	<i>w/cm</i>		
		0.30	0.34	0.40
C0	1	-.-	10.9 (1580)	6.3 (910)
	3	45.6 (6610)	33.7 (4890)	26.1 (3790)
	7	49.2 (7140)	40.5 (5870)	35.8 (5190)
	28	56.7 (8220)	56.2/ (8150)	47.3 (6860)
C10	1	-.-	23.9 (3470)	16.0 (2320)
	3	45.1 (6540)	36.0 (5220)	29.2 (4240)
	7	49.9 (7240)	39.0 (5660)	33.4 (4840)
	28	55.6 (8060)	52.7 (7640)	43.7 (6340)
C20	1	-.-	16.0 (2320)	15.8 (2290)
	3	43.7 (6340)	34.3 (4970)	30.2 (4380)
	7	44.5 (6450)	36.5 (5290)	34.9 (5060)
	28	50.1 (7270)	50.7 (7350)	41.6 (6030)

The results in Table 2 are somewhat different than those obtained for mortar cubes. Concretes with C10 cement produce compressive strengths that are similar to or higher than those of plain concrete up to 7 d, while the strengths of concretes containing C20 cements were similar to those of plain concrete up to 3 d. Thereafter, a reduction of the relative strength was observed. Compared with the concrete without limestone filler, the reduction of compressive strength at 28 d was in the range of 2 % to 8 % and 10 % to 12 % for the C10 and C20 cements, respectively. This behavior can be attributed to the design of the cement to achieve a similar strength at 28 d (> 40 MPa or 5800 psi) using an intergrinding process [12,13]. For achieving this purpose, portland limestone cements are generally finer overall, and have a smaller median grain size for the clinker particles, which therefore hydrate faster and produce higher early-age strengths (Table 2).

The close agreement of the experimental values with the fitted gel-space ratio expression confirms that the optimum level of limestone filler replacement will be a function of the mixture proportions, specifically the *w/cm* ratio. To obtain the same quality of paste, the percentage of limestone filler has to decrease when the *w/cm* ratio used in the system increases, as shown in Figures 2 and 3. Hence, for a *w/cm* in the range

of 0.30 to 0.35, it is theoretically possible to incorporate around 15 % of limestone filler in cement to obtain a paste with a similar or better gel–space ratio.

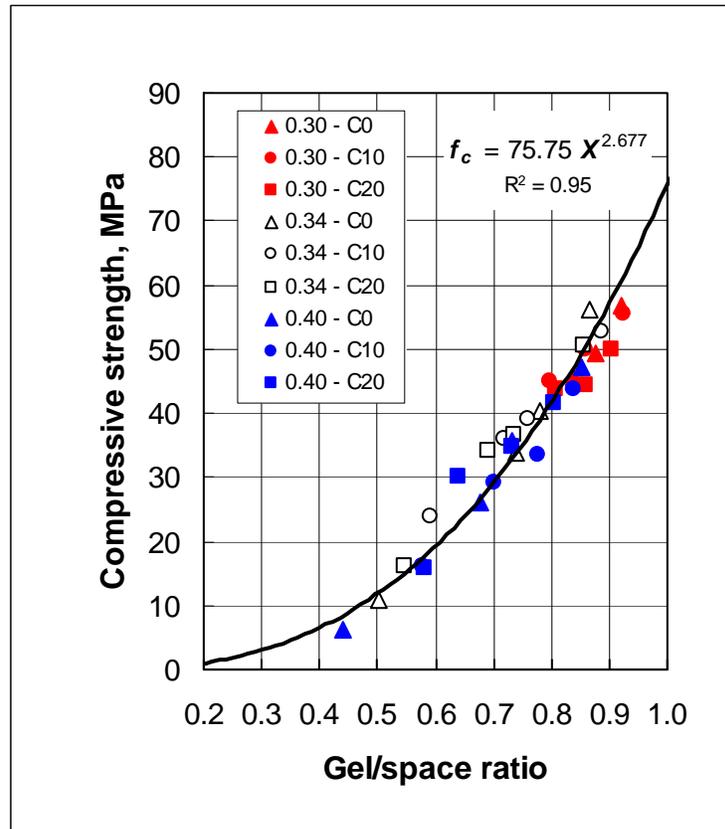


Figure 4 – Experimental and predicted compressive strength of concrete as function of gel-space ratio (1 MPa equals 145.04 psi) [1,12,13].

### *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 [11,14]. Figure 5 presents results for the same mortars whose strength results were provided in Table 1 [11]. 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 either 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 Figure 5. 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 Figure 5.

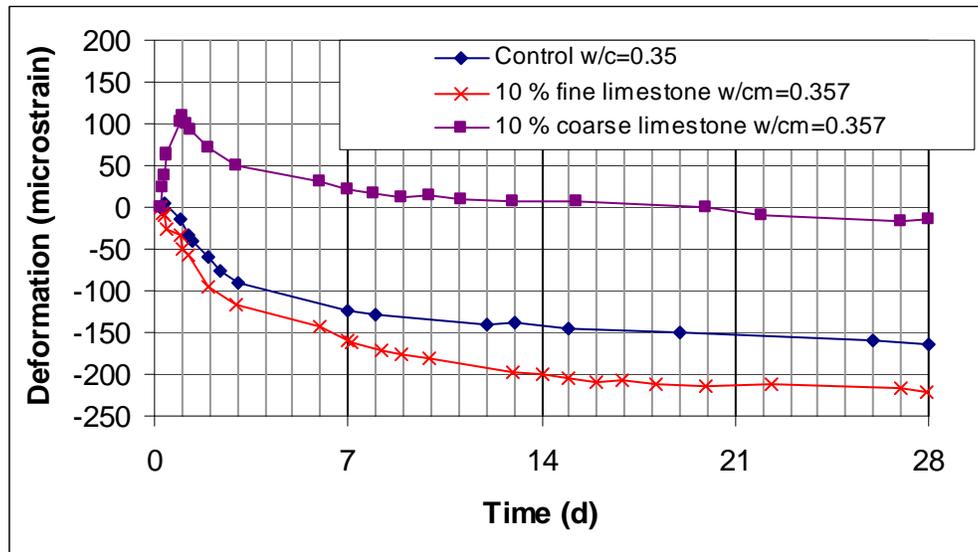


Figure 5 – Autogenous deformation vs. time for mortars with and without a 10 % limestone replacement by mass for cement [11].

Another set of recent experimental results [14] is provided in Figure 6 that shows the shrinkage of cement mortar samples with a  $w/cm$  of 0.30, 55 % sand by volume, and 10 % limestone replacement by mass. That study employed limestone of three different finenesses ranging from 3  $\mu\text{m}$  to 100  $\mu\text{m}$  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  $\mu\text{m}$ . The reduced autogenous deformation shown in Figures 5 and 6 may also lead to a decrease in the potential for early-age cracking when using coarser limestone powders [14]. Cracking caused by autogenous strains only, develops much sooner in mortars containing a finer limestone compared to ones containing a coarser limestone, as demonstrated in Figure 7 in which the same mortars from Figure 6 were used in restrained shrinkage tests (ASTM C1581 [15]). Results from one representative specimen of the three specimens tested for each mixture are plotted in Figure 7 [14]. For the coarsest limestone mixture, one specimen cracked after 161 h, while the other two specimens did not crack during the course of the 8 d test.

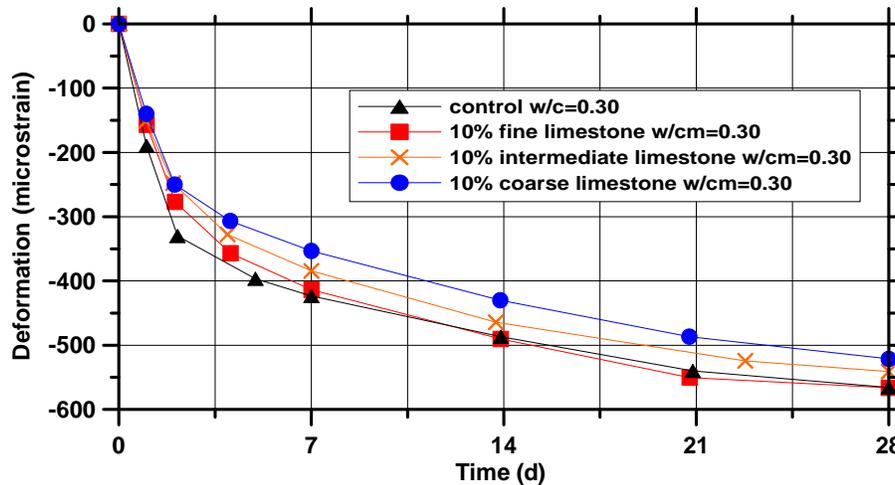


Figure 6 – Autogenous deformation vs. time for plain mortars and mortars containing 10 % replacement by mass of different fineness limestone powders [14].

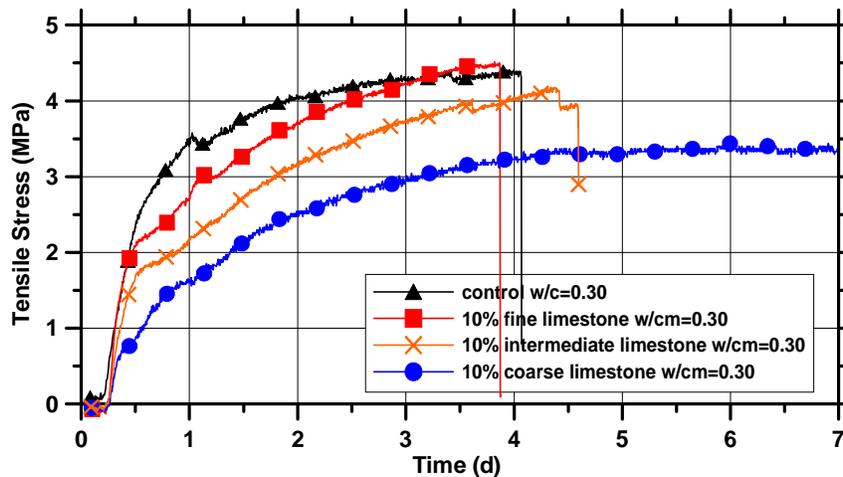


Figure 7 – Stress development vs. time for a representative specimen of three specimens of plain mortar rings and mortar rings containing 10 % replacement by mass of different fineness limestone powders [14]. A sudden decrease in the tensile stress indicates cracking.

Figure 8 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 h after the samples 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 [16]. Some benefits have also been observed in commercial cements with interground limestone. Research conducted at Purdue University [17] on cement mortars containing 5 % and 10 % interground limestone with a  $w/cm=0.30$  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 h

in comparison to the results in Figure 8 for blended (as opposed to interground) limestones [14].

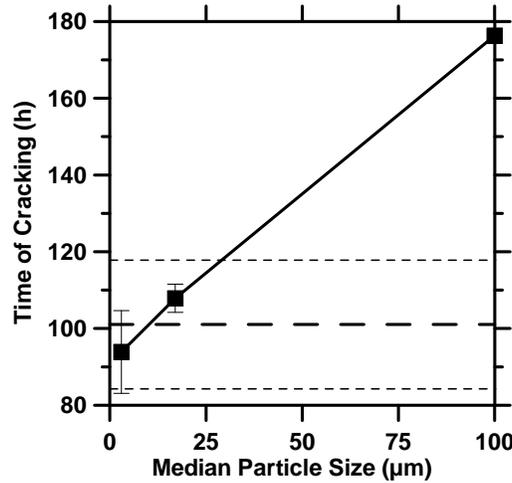


Figure 8 – Average time to cracking of limestone cement mortars vs. median particle size of limestone replacement. The heavy dashed line indicates the time to cracking for the control base cement system with no limestone replacement, with its accompanying error bars as indicated by the two dashed lines [14].

### *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 and capillary suction, and the diffusion of ions. For structures continuously soaked in an aggressive media, 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 [18,19], the capillary porosity becomes disconnected (depercolated) when its value is around 18 %, and the relative diffusion coefficient of an ion can be expressed as [19]:

$$D/D_0 = 0.001 + 0.07 \phi^2 + 1.8 (\phi - 0.18)^2 H(\phi - 0.18) \quad (4)$$

where  $D$  is the diffusion coefficient for an ion through cement paste,  $D_0$  is the diffusion coefficient of this ion in water,  $\phi$  is the capillary porosity (Figure 2), and  $H$  is the heaviside function with  $H=1$  for  $\phi \geq 0.18$  and  $H=0$  for  $\phi < 0.18$ . From Figure 2, 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 9 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  $w/cm > 0.4$ , 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 earlier, an experimental study [20] carried out on concretes ( $w/cm = 0.40$ , unit cement content =  $350 \text{ kg/m}^3$  or  $590 \text{ lb/yd}^3$ ) exposed to chloride solution (3 % NaCl by mass) revealed that the chloride penetration was deeper at 45 d for the increased limestone contents. After one year [13], the apparent diffusion coefficient value was  $5.0 \times 10^{-12} \text{ m}^2/\text{s}$  ( $7.8 \times 10^{-9} \text{ in}^2/\text{s}$ ) 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. For  $w/cm > 0.4$ , at complete hydration, the total porosity (Figure 2) 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 Figure 9, for  $w/cm < 0.35$ , low ion diffusivities would be expected in all three concretes.

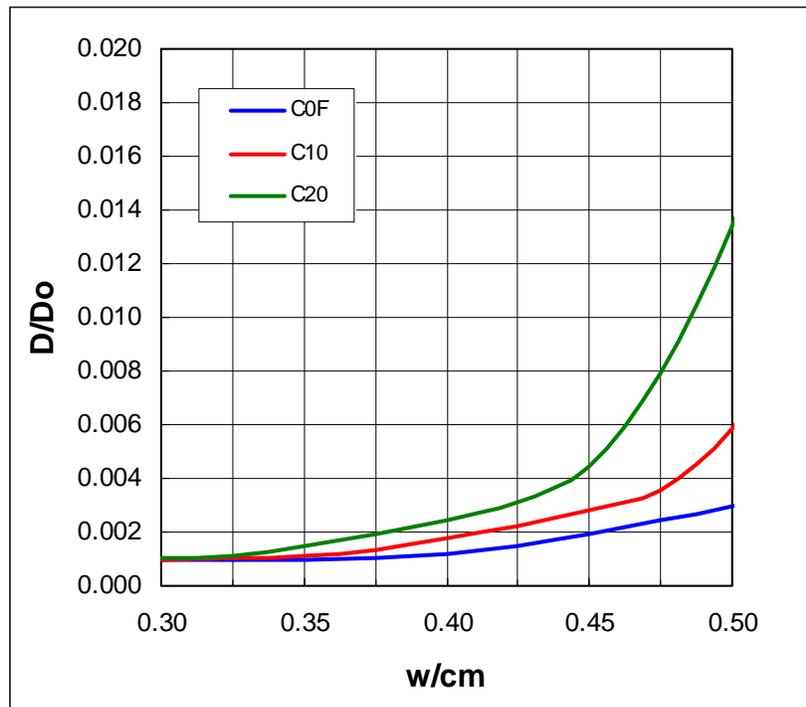


Figure 9 – Variation of *relative diffusion coefficient* ( $D/D_0$ ) calculated from equation (4) with  $w/cm$  ratio for paste hydrated to its maximum extent and containing approximately 0 % (C0F), 10 % (C10), and 20 % (C20) of limestone filler by mass.

### Summary and Prospectus

An analysis based on Powers' model has suggested that many currently produced low  $w/cm$  concretes offer a viable opportunity for limestone replacement of cement, at replacement levels well above the current 5 % allowed for in the ASTM C150 specification. Experimental results indicate compressive strength decreases on the order of 7 % for a replacement level of 10 % and on the order of 12 % for a 20 % replacement

level. If critical to performance (specifications), these strength losses could be compensated for by a slight reduction in  $w/cm$  for the concretes containing the limestone filler. In low  $w/cm$  systems, it has been further 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  $w/cm > 0.4$ , limestone replacements will lead to increased diffusion rates. However, for lower  $w/cm$  concretes, similar diffusion coefficients will be expected, as a more 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 this paper and elsewhere, increased limestone replacement for cement in low  $w/cm$  concretes appears to be one viable, but currently underutilized, option.

### **Acknowledgements**

The authors gratefully acknowledge support received from the Portland Cement Association Education Foundation Research Fellowship Program (Project F07-05), as well as materials provided by Holcim Cement, the Lehigh Portland Cement Company, and OMYA. The contents of this paper reflect the views of the authors, who are responsible for the facts and accuracy of the data presented. The contents do not necessarily reflect the views of the Portland Cement Association.

## References

- 1) Bonavetti, V., Donza, H., Menédez, G., Cabrera, O., and Irassar, E.F., “Limestone Filler Cement in Low  $w/c$  Concrete: A Rational Use of Energy,” *Cement and Concrete Research*, **33**, 865-871, 2003.
- 2) ASTM Annual Book of Standards, Vol. 04.01 Cement; Lime; Gypsum, West Conshohocken PA: American Society for Testing and Materials, 2004.
- 3) Hawkins P., Tennis P., and Detwiler R., The use of limestone in Portland cement: A state-of-the-art review. EB227, Skokie IL: Portland Cement Association, 2003, 44 pp.
- 4) Hooton, R.D., Nokken, M., and Thomas, M.D.A., “Portland-Limestone Cements: State-of-the-Art Report and Gap Analysis for CSA A 3000,” report prepared for St. Lawrence Cement, 2007.
- 5) Domone, P.L., “A Review of Hardened Mechanical Properties of Self-Compacting Concrete,” *Cement and Concrete Composites*, **29** (1), 1-12, 2007.
- 6) Irassar, E.F., “Sulfate Attack on Cementitious Materials Containing Limestone Filler – A Review,” *Cement and Concrete Research*, **39** (3), 241-254, 2009.
- 7) Powers, T.C., and Brownyard, T.L., “Studies of the Physical Properties of Hardened Portland Cement Paste,” *Journal of the American Concrete Institute*, **43** (multiple parts) 101, 249, 469, 549, 669, 845, 993, 1947, also published as PCA Bulletin 22, Research Laboratories of the Portland Cement Association, Chicago, 1948.
- 8) Jensen, O.M., and Hansen, P.F., “Water-Entrained Cement-Based Materials I. Principle and Theoretical Background,” *Cement and Concrete Research*, **31** (4), 647-654, 2001.
- 9) Bentz, D.P., and Conway, J.T., “Computer Modeling of the Replacement of “Coarse” Cement Particles by Inert Fillers in Low  $w/c$  Ratio Concretes: Hydration and Strength,” *Cement and Concrete Research*, **31** (3), 503-506, 2001.
- 10) Bentz, D.P., “Replacement of “Coarse” Cement Particles by Inert Fillers in Low  $w/c$  Ratio Concretes II: Experimental Validation,” *Cement and Concrete Research*, **35** (1), 185-188, 2005.
- 11) Bentz, D.P., and Peltz, M.A., “Reducing Thermal and Autogenous Shrinkage Contributions to Early-Age Cracking,” *ACI Materials Journal*, **105** (4), 414-420, 2008.
- 12) Bonavetti, V.L., Donza, H., Rahhal, V.F., and Irassar, E.F. “High Strength Concrete with Limestone Filler Cements,” *Proc. International Conference on High-Performance Concrete and Performance and Quality of Concrete Structures*, V.M. Malhotra, et al.

Eds., ACI SP-186, American Concrete Institute, Farmington Hills, MI, 1999, pp. 567–580.

13) Irassar, E.F., Bonavetti, V.L., Menendez, G., Cabrera, O., and Donza, H., “Mechanical Properties and Durability of Concrete made with Portland Limestone Cement,” *Proc. International Symposium on the Sustainable Development and Concrete Technology*, V.M. Malhotra Ed., ACI SP 202-27, Farmington Hills, MI, 2001, pp. 431-450.

14) Bucher, B., “Shrinkage and Cracking and its Relation to Cement Composition,” MSCE Thesis, Purdue University, West Lafayette, IN, To be completed 2009.

15) ASTM Annual Book of Standards, Vol. 04.02 Concrete and Aggregates, West Conshohocken PA: American Society for Testing and Materials, 2004.

16) Radlinska, A., Bucher, B., Weiss, W. J. (Accepted, to Appear 2008) “Assessing the Repeatability of the Restrained Ring Test, *Journal of ASTM International*,” JAI101944, **5** (10), 2008, pp. 11.

17) Bucher, B., Radlinska, A., and Weiss, J., “Preliminary Comments on Shrinkage and Shrinkage Cracking Behavior in Cement Systems that Contain Limestone,” Proceedings from NRMCA Concrete Technology Forum: Focus on Sustainable Development, 2008.

18) Bentz, D.P., and Garboczi, E.J. “Percolation of Phases in a Three-dimensional Cement Paste Microstructural Model,” *Cement Concrete Research*, **21** (2–3), 325–344, 1991.

19) Garboczi, E.J., and Bentz, D.P., “Computer Simulation of the Diffusivity of Cement-Based Materials,” *Journal of Materials Science*, **27**, 2083-2092, 1992.

20) González, M., Rahhal, V., Bonavetti, V. , Donza, H., and Irassar, E.F. “Effect of Curing on Early Chloride Diffusion of Filler Cement Concrete,” *Proc. International Conference on Infrastructure Regeneration and Rehabilitation, Improving the Quality Life Through Better Construction: A Vision for the Next Millennium*, R.N. Swamy Ed., Sheffield Academic Press, England, 1999, pp. 137-148.