Limestone Fillers Conserve Cement

Part 1: An analysis based on Powers' model

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"Green" concrete has become a rallying cry for the twenty-first century. In addition to its field performance, a concrete mixture is now judged by its recycled material content, embodied energy, and carbon footprint. Bonavetti et al.[1] have proposed that limestone powder substitution for cement makes perfect sense in concrete mixtures with lower water-cement ratio (w/c) values, as space limitations or water deficiencies in these mixtures can make it impossible for all of the cement to hydrate. Because unhydrated cement is essentially expensive filler, limestone powder substitution can cut costs as it saves energy and reduces carbon dioxide emissions resulting from cement production.

While limestone/cement blends have been employed for many years in Europe, 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] and this was done only after an extensive survey of the available literature led to the conclusion that "in general, the use of up to 5% limestone does not affect the performance of portland cement."[3] Higher addition rates of 10 to 15% are currently being discussed in the U.S., and in 2009, the Canadian Standards Association has in fact approved Portland Limestone Cements with up to 15%.[4] In the U.S., some ready mixed concrete 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, once again at values well above the 5% level.[5]

In Part 1 of this article, we use Powers' model to analyze total capillary porosity in limestone-filled cement pastes to suggest appropriate replacement levels. We'll address durability issues[6] and the effects of limestone fineness on the performance of mixtures in Part 2.

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, a porous solid. 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 nonevaporable 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, α, and starting w/c:

$$
\begin{array}{ll}
\text{Chemical shrinkage:} & V_{cs} = 0.20(1-p)\alpha \\
\text{Capillary water:} & V_{cw} = p - 1.32(1-p)\alpha \\
\text{Gel water:} & V_{gw} = 0.60(1-p)\alpha \\
\text{Gel solids:} & V_{gs} = 1.52(1-p)\alpha \\
\text{Cement:} & V_{c} = (1-p)(1-\alpha) \\
\text{Volume balance:} & V_c + V_{gs} + V_{gw} + V_{cw} + V_{cs} = 1
\end{array}
\quad (1)
$$

where $p = (w/c)/(w/c + \rho_w/\rho_c)$ is simply the initial volume fraction of water in the mixture, and ρ_w and ρ_c refer to the densities of water and cement, here assigned values of 1000 kg/m³ (1686 lb/yd³) and 3150 kg/m³ (5310 lb/yd³),

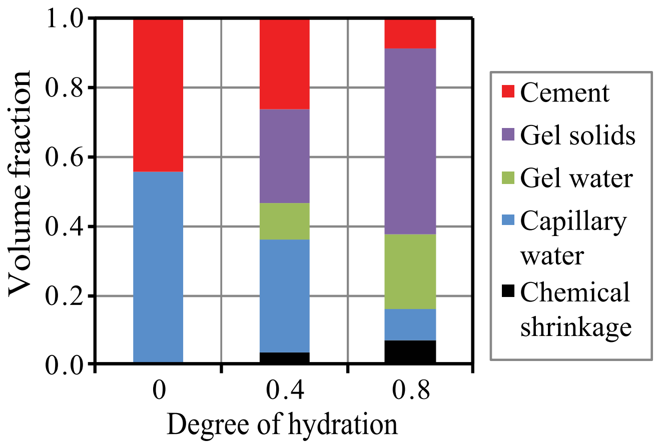

Fig. 1: Illustration of Powers' model for cement hydration for *w/c* = 0.4 cement paste at the indicated degrees of hydration

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 nonevaporable and gel water contents at complete hydration (0.23 and 0.19).[8] Powers' model is illustrated graphically in Fig. 1 for a *w/c* = 0.4 cement paste at three different degrees of hydration.

In recent years, a greater proportion of concrete is being produced with *w/c* of 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^3 [4550 lb/yd^3]) 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-cement mass ratio and not the water-(cement + limestone) ratio (*w/cm*), which would typically characterize a limestone-blended cement.

RESULTS

Theoretical limits

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/cm* (equivalent to *w/c* for a paste without limestone filler) below about 0.356 for a base cement paste with no limestone filler, a final total capillary porosity of zero can be achieved, thus, there will 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 (Fig. 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* (for porosity = 0) = $0.356*(1 - M_{LF})$. These results suggest that for concrete with a *w/cm* of 0.3 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.

In the case of sealed curing, there is no additional water available for curing/hydration beyond what's present in the original concrete mixture. So a *w/cm* of 0.42 is required to provide complete hydration for the paste with no limestone replacement (Fig. 2). 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 *w/cm* is lowered below 0.42, increasing replacement levels of limestone for cement appear viable. In the case of sealed curing, for example, a system with a *w/cm* of 0.35 should

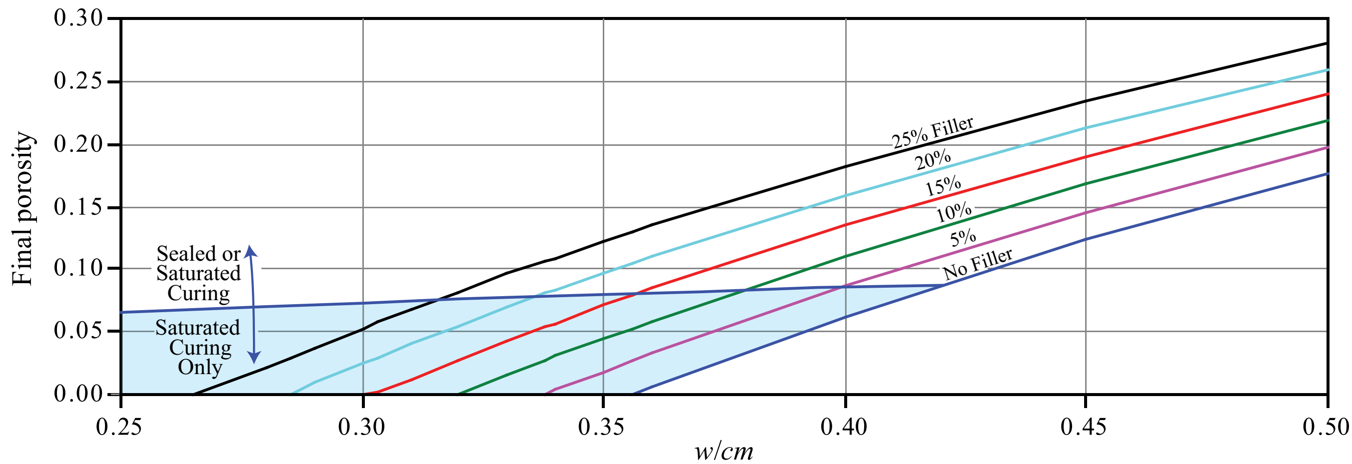

Fig. 2: Predicted final total capillary porosity (empty and water-filled) as a function of *w/cm* (*cm* = cement + limestone) and limestone filler substitution (by mass according to Powers' model)

be able to incorporate a replacement level of limestone of about 17% by mass while still ultimately achieving the "lowest possible" total capillary porosity (Fig. 2).

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 can result in water loss due to evaporation, further limiting 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 Fig. 2 would suggest that limestone replacement levels well above 5% could be used in a wide range of lower *w/cm* concretes.

Quantified effects

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. For the lower *w/cm* systems presented in Fig. 2, however, 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.

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
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.

While the results in Fig. 2 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 the 56-day compressive strength between a control mortar with a *w/c* of 0.3 and one in which the coarsest cement particles (nominally those of diameter greater than 30 µm) had been replaced by a coarse

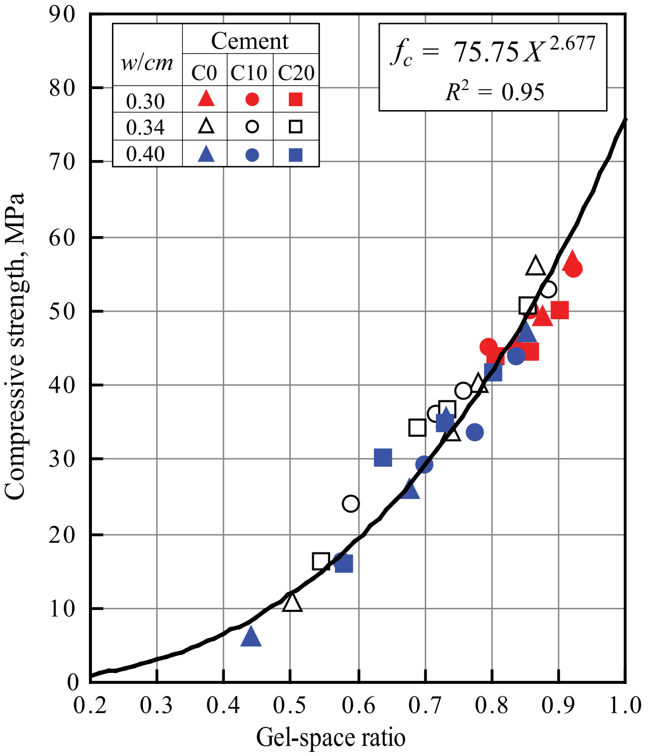

Fig. 3: Experimental and predicted compressive strength of concrete as function of gel-space ratio (1 MPa = 145.04 psi)[1, 12, 13]

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 control mortar with a *w/c* of 0.35 to two mortars (each with a *w/cm* of 0.357) with 10% limestone replacement by mass, either with a fine (16 µm median diameter) or a coarse (80 µm 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 day, by 28 days, the two limestone replacement mortars both exhibit strengths that are within 7% of the control mortar.

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

$$f_c = f_0 X^n \tag{2}$$

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

$$X = \frac{0.68\alpha}{0.32\alpha + w/c} \tag{3}$$

where α is the mass-based degree of hydration of the cement.

Table 2 summarizes compressive strengths of different concrete mixtures (with *w/cm* of 0.30, 0.34, and 0.40) determined on 100 x 200 mm (4 x 8 in.) cylinders after curing for up to 28 days in water saturated with lime.[1, 12, 13] Experimental measurements were made using a cement without limestone (C0) and two portland limestone cements containing about 10% (C10) and 20% (C20) limestone filler. For each concrete, the gel-space ratio was calculated using an α-value estimated by determination of nonevaporable water content at different ages.[1] Figure 3 shows the compressive strength/gel-space ratio expression obtained from a curve fitting of experimental data. The fitted value for n agrees with the range of values found in the literature.

The results in Table 2 are somewhat different than those obtained for mortar cubes. Concretes with

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

Cement	Age, days	w/cm		
		0.30	0.34	0.40
No limestone filler (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)
10% limestone filler (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)
20% limestone filler (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)

C10 cement produce compressive strengths that are similar to or higher than those of plain concrete up to 7 days, while the strengths of concretes containing C20 cement were similar to those of plain concrete up to 3 days. Thereafter, a reduction of the relative strength was observed. Compared with the concrete without limestone filler, the reduction of compressive strength at 28 days 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 days (greater than 40 MPa [5800 psi]) using an intergrinding process.[12, 13] Because it is softer than clinker, interground limestone powder will likely be finer than the accompanying cement. Also, interground 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*. To obtain the same quality of paste, the percentage of limestone filler has to decrease when the *w/cm* used in the system increases, as shown in Fig. 2. 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 to obtain a paste with a similar or better gel-space ratio.

SUMMARY

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.

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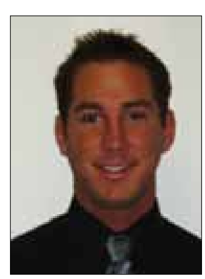

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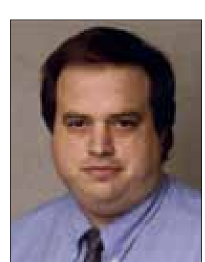

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