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Simple methods to estimate the influence of limestone fillers on reaction and property evolution in cementitious materials

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ABSTRACT

A commercial interest in sustainable cementing materials is driving efforts to reduce the use of cement in concrete. Limestone fillers are a promising direction towards achieving such cement use reductions. In spite of increasing filler use, little information is available to rapidly estimate the influences of limestone fillers, and more importantly filler fineness on reaction and property development. This work develops simple models to predict the effect of particle size classified limestone on hydration reactions and compressive strength development. The method builds on a relativistic basis, such that enhancements and alterations in reactions and properties are described in relation to a given control (pure cement) mixture. The prediction method considers aspects such as: (1) accelerations in reactions, (2) changes in inter-particle spacing as linked to the limestone filler's fineness and (3) a porosity increase with increasing cement replacement. The predictive power of the approach is demonstrated for a variety of mixtures composed using three ASTM C150 compliant cements and forwards a basis for developing mixture proportioning strategies, such that *apriori* estimations of the mixture response (reaction rate and mechanical properties) can be used to optimize binder proportioning and thus strategize new methods to limit cement use in concrete construction applications.

1. Introduction and background

CO_2 emissions resulting from cement production are a cause of considerable concern to the concrete construction community [1]. To limit the CO_2 impact of cement production and use, the construction industry is making ever more substantial efforts to reduce and optimize the use of cement in concrete. Substantial amongst these efforts are initiatives to utilize high volumes of mineral substances (e.g., fly ash, limestone, quartz, etc.) to replace portland cement in concrete [2–8]. While much desired from a sustainability basis, large reductions in the portland cement content can be detrimental due to their role in delaying and/or depressing property development (e.g., setting, strength gain), and hence the constructability of low cement content binders [9]. Such reductions in constructability are a substantial obstacle to the commercial use and deployment of low-cement content binder systems.

In spite of substantial advances, concrete mixture proportioning is yet an empirical, parametric process in which a large number and combinations of materials require evaluation before an optimum mixture proportion is achieved. Clearly, as any parametric process, this approach is laborious and time-consuming. Thus, to ease the proportioning of sustainable mixtures, it would be beneficial if a cement or concrete producer may be able to virtually estimate the response of a mixture's mixture's binder fraction in relation to hydration and property development – as the cement content is systematically reduced.

Towards satisfying both of these needs, i.e., developing sustainable cementing materials and improving strategies for their proportioning, this research advances simple relationships based on chemical and physical indicators which can be used to predict the influence of size classified limestone additions on hydration and strength development in these materials. Based on a large experimental dataset, the approach is developed and applied for three ASTM C150 compliant cements, for cement replacement levels ranging between 0–50% (by mass) by limestone filler. Special attention is paid to limestone as its ability to serve as a "*mineral*

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Table 1
The phase compositions of the ordinary portland cements used in this study.

ID	Phase	Mass%	ID	Phase	Mass%	ID	Phase	Mass%
OPC I/II	C_3S	63.10	OPC II/V	C_3S	62.60	OPC III	C_3S	63.30
	C_2S	12.89		C_2S	11.76		C_2S	10.31
	C_3A	3.67		C_3A	4.58		C_3A	3.93
	C_4AF	10.83		C_4AF	13.92		C_4AF	14.22
	Na_2O Equivalent	0.38		Na_2O Equivalent	0.55		Na_2O Equivalent	0.47

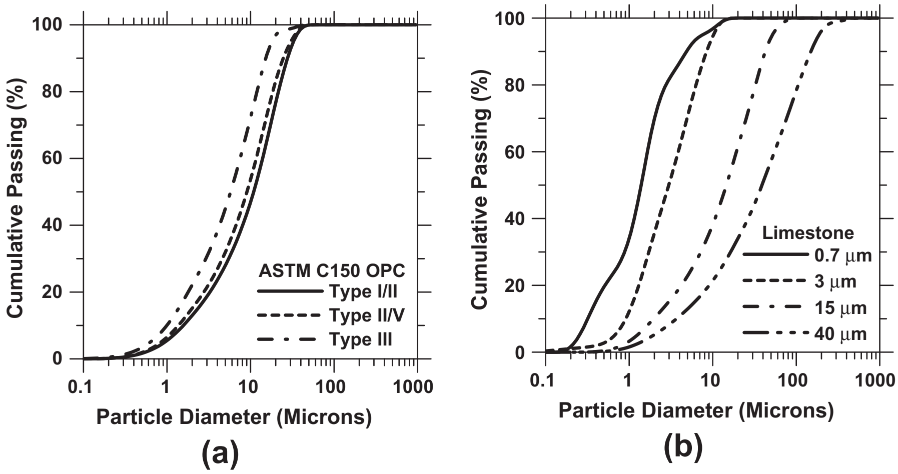

Fig. 1. Particle size distributions for the: (a) cement and (b) limestone used in this study.

acceleration agent" advances opportunities to reduce the cement content in a binder, by accelerating hydration product formation at early ages [10]. Thus the work advances: (1) simple strategies for concrete technologists to virtually estimate the influence of the cement replacement level and limestone fineness on reactions and property development and (2) enables a means to limit the need for time consuming, parametric mixture evaluations as are common today. The results have broad implications on refining mixture proportioning strategies, and introducing new approaches which can be used to proportion the next generation of binders with a reduced cement content.

2. Materials, mixing procedures and methods

Three ASTM C150 compliant cements were used in this study [11]. The phase compositions of the cements used are provided in Table 1. The limestone powders used are, nominally pure, commercially available, particle size classified products produced by OMYA A.G[2]. The particle size distributions (PSD, Fig. 1) of all the solids were measured using light scattering using isopropanol and sonication for dispersing the powders to primary particles. The uncertainty in the scattering measurements was determined to be 6% based on measurements performed on six replicates assuming the density of cement and limestone to be 3150 kg/m^3 and 2700 kg/m^3 respectively. Cementitious paste mixtures were prepared using de-ionized (DI) water at a fixed water-to-solids ratio ($w/s = 0.45$) as described in ASTM C305 [11]. To better understand the role of the limestone filler, the cement content was progressively reduced, by replacement in 10% increments, from 0–50% (mass-basis) by limestone powders of varying median particle (d_{50}, Table 2) sizes. Other mixtures were prepared with w/c equivalent to those obtained for the cement replaced systems, ranging from $w/c = 0.45$-to-0.643.

The influence of powder additions (cement replacement) on the solid surface area of the system is described using an area multiplier (AM, unitless) as shown in Eq. (1):

$$\mathrm{AM} = \frac{100 + \frac{(r.\mathrm{SSA_F})+((100-r).\mathrm{SSA_C})}{((100-r).\mathrm{SSA_c})}}{100} \quad (1)$$

where: r (mass%) is the percentage replacement of cement by limestone filler and $\mathrm{SSA_C}$ and $\mathrm{SSA_F}$ (m^2/g) are the specific surface areas of the cement and limestone respectively - – calculated using the particle size distribution of the powder materials, while assuming spherical particles. Thus, the AM is a scaling factor that describes the change in solid surface area induced by filler addition in comparison to the surface area provided by a unit mass (1 g) of cement (reactant). In other words, AM is the surface area of filler per unit surface area of cement in the system. The greater this quantity is, either because the filler is finer or because it is present in greater amounts, the more AM will exceed unity. It should be noted that the calculation of the AM is subject to uncertainties that stem from measurements of the particle size distributions and the assumption of spherical particle shape.

Table 2
Nominal d_{50} and specific surface area (SSA) values for the cement and limestone powders, calculated using their measured particle size distributions shown in Fig. 1.

	ASTM C150 OPC		Size classified limestone		
Powder ID	d_{50} (μm)	SSA (m^2/kg)	Powder ID (μm)	d_{50} (μm)	SSA (m^2/kg)
Type I/II	9.83	486.00	0.7	1.40	2592.10
Type II/V	8.94	538.02	3	2.98	1353.20
Type III	5.61	780.27	15	14.87	399.20
			40	40.10	228.60

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[2] Certain commercial materials and equipment are identified to adequately specify experimental procedures. In no case does such identification imply recommendation or endorsement by the University of California, Los Angeles or Arizona State University, nor does it imply that the items identified are necessarily the best available for the purpose.