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Influences of limestone particle size distributions and contents on blended cement properties

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HIGHLIGHTS

- We developed limestone cement with high packing density to maximize binder properties.
- Limestone powders with three main particle diameters were examined.
- Combinations of limestone powders with several different particle sizes were studied.
- Increasing surface area and packing density improve blended cement performances.
- Blended cement with a combination of several particle sizes performed the best.

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ABSTRACT

Limestone cement with high packing density was developed to maximize binder properties in spite of increased limestone contents. Limestone powders with three main particle diameters relative to the clinker particles were used. Cements with a single-size limestone particle and with combinations of several particle sizes were compared. It was concluded that the replacement of an active material with an inert additive can improve cement paste performances by increasing the surface area and the packing density of the cement-based particles, mainly when limestone powders with a combination of several different particle size distributions were used due to increased packing density.

1. Introduction

Due to environmental and energy efficiency concerns, there is growing interest in the development of a blended Portland cement in which the amount of clinker is reduced and partially replaced with mineral additives. There are three principal motivators behind these efforts: (1) ecological benefits, as a result of lower CO_2 emissions to the atmosphere, (2) economic benefits, since reduced clinker cement is cheaper to produce, and (3) scientific/technological benefits, based on improved cement and concrete performance. There are two main types of mineral additives commonly used: (1) pozzolanic additives such as fly ash, slag, and metakaolin [1–3] and (2) materials which are not considered pozzolanic, generally having low reactivity with cement minerals. Of the latter type, limestone is one of the most attractive additives because it is considered natural, available, and economical. Several studies have reported that cement blended with limestone had improved initial compressive strengths with lower setting times compared to the original cement, i.e., without added limestone [4–6]. The addition of fine inert limestone powder, whose surface area was greater than that of the clinker, increased the hydration rate at early age and the generated heat of hydration [5]. However, the final strength of the blended cement after 28 days was less than that of the original cement paste.

Cement properties have been explained by the effect of packing density, which is defined as the ratio between the solid phase volume and the total volume of the system (Fig. 1). The inclusion in the system of particles with improved particle size gradation confers on it increased packing density and, thus, decreased porosity, as was also described by the linear packing density model of grain

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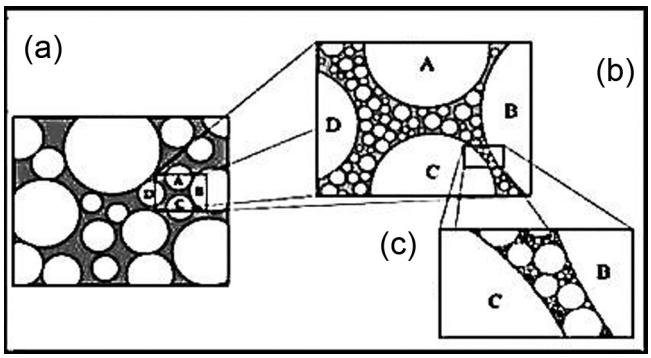

Fig. 1. Packing density theory (hierarchical approach) [8].

mixtures by Stovall et al. [7]. Fig. 1a schematically illustrates the packing density of a system in which the presence of small particles reduces the unoccupied spaces between the larger particles (A, B, C, and D) [8]. Fig. 1b and c shows that the space between the smaller particles is filled by even smaller particles (i.e., a hierarchical approach).

The addition of fine limestone powder as clinker replacement has also been shown to increase the number of nucleation centers, an outcome elicited by its high surface area [5]. The greater the number of nucleation centers during the hydration process, the higher its hydration rate and early age strength. According to Voglis et al. [9], to obtain a limestone–cement blend of similar strength to that of cement alone (without limestone) at day 28 after blending, the surface area of the limestone cement must be higher than that of the cement. Kumar et al. [10,11] showed that an increase in the cement fineness, filler fineness, or filler content acts to increase chemical reactions. Oey et al. [12] also showed the influence of powder addition (limestone and quartz) on the solid surface area of the system by an area multiplier (AM) and its effect on the reaction rate.

Although limestone is considered an inert additive, there is substantial evidence that it is not completely inert, and during the hydration process, additional products are formed by the reaction of the limestone and the C_3A phase [13–16]. Several researchers have reported that partial replacement of clinker with mineral additives influenced the flow and workability of fresh cement paste [17–21]. The flow behavior of clinker with mineral additives is affected by several factors such as the particle shape, reactivity of the additives, the content, and the packing density of the particles. In systems with higher packing density, less water is trapped between the particles, making more water available to lubricate the particles, increasing the flow and workability of the fresh cement paste.

Our work has developed blended limestone cement with higher packing density and optimal surface area related to the original cement to maximize the properties of the binder. The limestone particles were grinned separately and then added to the original cement. Limestone powders with several different particle sizes were used to partially replace the original cement. Single particle size distributions of limestone were compared with systems containing multiple combinations of limestone particle size distributions. The amount of water required to obtain a hydraulic binder having a normal consistency and the hydration degree were examined using penetration depth vs. time measurements until reaching final setting. Also compressive strength measurements, scanning electron microscopy, and Rietveld quantitative phase analysis of X-ray diffraction were used to examine the blended cement properties.

2. Material and methods

CEM I 52.5 R was partially replaced with limestone powders (>99.8% $CaCO_3$) with varying particle size distributions. The chemical composition of the original cement is presented in Table 1. Three different limestone powders representing several particle diameters—smaller than, larger than, or similarly sized to the original CEM I with a mean particle size of 17 μm—were tested. The limestone powders with the smaller and similarly sized particles to the original cement were fractions of the same source, while the limestone with larger size was from a different source. However, the purity and the density of the limestone powders were similar. Two different powder systems were prepared and investigated:

(i) *Single-particle-size distribution system*: The original cement was partially replaced with limestone with a single-particle-size distribution—either smaller than, larger than, or similarly sized to the cement particle. Cement replacement effects were investigated using several limestone–cement mixtures in which the limestone powder comprised 5%, 10%, 20%, or 30% of the mixture (by mass).
(ii) Combined-particle-size distribution system: The original cement was partially replaced with limestone powder containing a combination of particles that were larger than and smaller than the cement particles. Several mixtures were tested, in which the ratio of large to small limestone particles was varied (1/4, 3/2, or 4/1). All mixtures contained only 5% limestone.

Several testing methods were used to study the properties of the powders, the fresh cement pastes, and the hardened cement pastes.

2.1. Powders

Surface area and particle size distribution (PSD) were examined for the powders. The surface area of each individual powder was determined using the BET technique with N_2. Cement and limestone powder surface areas were calculated by multiplying the cumulative relative weight of each powder by the surface area of the individual component in the powder mixture. Particle size distribution was determined by laser diffraction scattering (CSI-100, Ankersmid).

2.2. Cement pastes

The workability of each cement paste was determined based on normal consistency. Each cement powder—blended or original—was mixed with the amount of water needed to obtain a normal consistency according to EN 196/3. After each sample (i.e., original cement or original cement + limestone) was mixed to normal consistency according to the standard, the sample was placed in water at 20 ± 1 °C, and the penetration depth was measured until the final setting time was obtained by an automatic Vicat Needle Apparatus (Toni Technik). The bulk density of the different fresh cement pastes was measured following Wong et al. [19]. For this measurement, the original cement and blended cement pastes with 20% limestone composed of three different particle sizes (53 μm, 25 μm, and 3 μm) were prepared all to normal consistency. The weight of three samples of each paste type was measured in a container with a volume of 250 ml. First the container was half filled with the fresh paste and then was compacted using a vibration table for 1 min. After the compaction of the first layer, the container was completely filled and compacted for another minute. The average bulk density value of each paste type was then calculated.

2.3. Mortar hardening

Following EN 196-1 to evaluate compressive strengths, the cement pastes discussed above were mixed with standard sand with a maximum particle size of 1.60 mm and water to obtain a water:powder:sand weight proportion of 0.5:1:3, such that the cementitious material (original cement + limestone powder) content was 450 g. The specimens were mixed and cast in molds measuring 40 × 40 × 160 mm. After curing the specimens for 24 h at 20 ± 1 °C, they were demolded and immersed in water at 20 ± 1 °C until the compressive strength was tested. The compressive strength of each sample was measured in a press (Toni Technik) 1 d and 28 d after casting, and each sample's strength was based on an average of six specimens.

Fragments of the hardened mortar blends obtained after testing the compressive strengths were prepared for microstructure mineral content analysis and image analysis. To that end, the fragments were immersed in acetone for 1 h to remove the water and then kept in a stove for 120 min at 60 °C. Immediately after this procedure, the specimens were vacuum impregnated with low viscosity epoxy. After 24 h, the samples were ground with # 220, # 500, # 1200, and # 2400 sandpapers, after which they were polished with 3-μm alumina oxide paste on a lap wheel.

The microstructures of these polished specimens were observed using a TESCAN VEGA3 scanning electron microscope (SEM). Energy dispersive X-ray spectroscopy (EDX) was used to provide elemental identification and compositional