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Influence of slag fineness on the strength and heat evolution of multiple-clinker blended cements

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HIGHLIGHTS

- Cements are made by blending multiple clinkers and ground slag.
- Replacing fine or coarse clinker with slag gives different cement performance.
- Cements with better strength/heat can be tailored.
- A general relation is found between 24-h and 48-h heat of hydration.
- A strong linear relation exists between same-day heat and strength measurements.

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ABSTRACT

Three clinkers and a blast furnace slag, ground separately, were combined to produce 27 cements. Each cement consisted of 35% fine (~6000 cm^2/g), 25% intermediate (~4000 cm^2/g), and 40% coarse (~2500 cm^2/g) particles. Slag made up the fine or intermediate particles in the blended cements, clinkers making up the remainder. Compressive strength was measured up to 28 d on mortars and heat evolution was investigated up to 48 h using isothermal calorimetry. Portland cements with different rates of strength gain and heat evolution could be obtained by mixing different clinkers. By combining clinkers, cements with lower early heat but higher strength could be prepared. The fine particles in the cements are responsible for strength gain up to 3 d, but the intermediate fraction is crucial for 28-d strength. Slag increasingly contributes to hydration after the 3–7 d period. Fine slag particles decrease early strength but allow high later-age strengths while intermediate slag particles allow smaller drops in early strength but yield lower 28-d strengths. Similarly, replacement of fine clinker particles with slag decreases 12-h heat more than replacement of intermediate particles but the difference diminishes beyond about 24 h. A strong linear relation exists between the 24-h and 48-h heats of the cements and could be useful for modelling the hydration rate of Portland or blended cements. Moderate relations exist between 12–48-h heat, and 1–7-d strength. A strong linear relation is observed between strength and heat measurements made at the same age. Strengths of the cement mortars are mostly within 20% of that estimated by the developed relation.

1. Introduction

Efforts to reduce the environmental impact of concrete are ever increasing. Blended cements containing one or more of ground granulated blast furnace slag, natural pozzolans, fly ash, silica fume, and limestone in different proportions, currently make up nearly 75% of all cement produced in Europe [1]. In addition to their environmental and economic benefits, mineral admixtures can also offer technical advantages by modifying the hydration of cement. The amount, composition, and fineness of the admixture can influence the rate of hydration, leading to changes in the rate of strength development and heat evolution. As such, the influence of partial replacement of Portland cement (PC) on early hydration can be studied by measuring the changes in the rate and amount of heat evolution [2], as well as other methods [3–5].

It is generally accepted that supplementary cementing materials (SCMs) reduce early heat evolution due to the dilution effect. Strength is lowered at early ages, particularly at high cement-replacement levels, and even up to 28 days, but ultimate degree of hydration and strength can be higher than for a cement-only mixture [6]. The incorporation of a pozzolan or slag is typically

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reported to retard and reduce the rate of hydration [7–10] but several studies report enhanced early cement hydration caused by fine pozzolan or slag incorporation [11–16]. Conflicting results can be explained by differences in the types, compositions, and finenesses of the SCM used. The contribution of a cement particle to strength is closely related to its size [17,18]. It has been suggested that very fine cement particles can hydrate fully within 24 h [19] whereas particles larger than 45 μm hydrate slowly [20] and that particles with equivalent-volume sphere diameters greater than ~15 μm may not hydrate completely [21]. Similarly, the contribution of a slag particle would be related to its size. Slag is a latent hydraulic material which, when mixed with hydrating PC, can be activated by the alkalis present and the calcium hydroxide produced. It can modify the structure of clinker hydration products [22], particularly their amounts [7]. Regourd et al. [23] noted that although slag particles don't immediately form hydration products upon contact with water, their surfaces are modified, hence their hydration in the presence of cement is quite complex.

Careful selection of SCM and clinker particle size distribution (PSD) are being investigated for separately-ground blended cements in an effort to deliver "tailor-made" cements that meet the market requirements [24]. Pastes and mortars in which SCMs replace coarse clinker particles have been shown to give strengths equal to those made with PC only [25,26]. Zhang et al. [27–30] reported that replacement of fine clinker particles with slag and coarse particles with a less-reactive SCM can give high degrees of hydration and improved microstructure development, even at early ages and for SCM levels greater than 50%. Albeit less practical, it could also be possible to control strength development of mortars by replacing clinker with one or more different clinkers. If matched properly (chemically and physically), slow-reacting and faster-reacting clinkers could be mixed to yield a greater drop in heat of hydration than in strength, at early ages, as well as other desirable properties. This, in turn, could lead to more environmentally-responsible concrete mixtures with lower cement dosages. This study looks at the strength development and heat evolution of mixtures incorporating up to three clinkers, as well as mixtures in which slag replaces different size fractions of the clinker.

2. Materials and method

Blended cements were prepared by combining a granulated blast furnace slag (S), three different clinkers (A, B, C), and gypsum (G), in various proportions. Portland cements containing only clinker and gypsum were also made, using either a single clinker or all three. Each cement contained 35% "fine", 25% "intermediate", and 40% "coarse" particles. Fine, intermediate, and coarse particles had target Blaine finenesses of about 6000 cm^2/g, 4000 cm^2/g, and 2500 cm^2/g, respectively. The materials were ground separately in a laboratory ball mill. Slag was used as the fine-size group or as the intermediate-size group in the blended cements. The clinkers and gypsum made up the remainder of these cements. The clinkers were commercially used products obtained from different cement producers. The slag was obtained from a steel plant in Karabük. The gypsum was obtained from a quarry near Ankara. Oxide compositions of the materials, determined using X-ray fluorescence spectrometry, are provided in Table 1.

The particular finenesses of the fine, intermediate, and coarse fractions of the cements were chosen based on work by Zhang et al. [27,28] who suggested that the PSD of a cement has a significant influence on its initial packing density and hydration, affecting the amount and composition of hydration products in the paste. At higher initial packing densities, less hydration product is needed to fill the inter-particle voids. Thus, the same amount of PC can give higher strength than in a mixture with a less-favorable PSD. Similarly, large drops in strength can be avoided when replacing cement with pozzolans, by choosing wisely the size range of the cement to be replaced. Smaller inter-particle distances also allow lower shrinkage. Upon studying various distributions suggested to achieve close packing of particles [31–34], Zhang et al. [27,28] proposed a "gap-graded" PSD for cements containing both high-activity powders like PC and lower-activity powders like slag. Assuming a maximum particle size of 80 μm, they selected the diameters of three size groups to make up the cement with the "ideal" packing, as 45 μm, 16 μm, and 6 μm, and suggested dividing the material into three fractions as <8 μm, 8–32 μm and >32 μm. In this study, Blaine finenesses of the fine, intermediate, and coarse fractions of the cements (~2500 cm^2/g, ~4000 cm^2/g, ~6000 cm^2/g) were chosen using Blaine fineness-mean particle size relations previously reported for PC and similar powders [35–37]. Also, they calculated the volume percentage of particles in each size fraction to be 36%, 25%, and 39%. As such, considering the rather similar specific gravities of slag and Portland cement, the mass percentages of 35%, 25%, and 40% were selected for the fine, intermediate, and coarse particles of the cements in this study.

Blaine fineness vs. grinding time curves drawn for each clinker and the slag gave an idea about the relative resistances of the original materials to comminution. As expected, the slag was the hardest material taking ~240 min to reach a Blaine of ~3000 cm^2/g, clinkers A and B somewhat softer taking ~110 min, and clinker C the softest, taking ~50 min. Based on these observations grinding times required to prepare fine, intermediate, and coarse particles of each clinker and the slag were chosen. Table 2 shows the D10, D50, and D90 values for the fine, intermediate, and coarse fractions of each material and Fig. 1 gives their measured Blaine fineness values.

While the PSD data indicates that different ground clinkers and slag in a given supposedly identical size group are mostly similar in size, there are some cases where a difference is marked, such as the D_{90} for coarse particles of clinker B. Fig. 1 shows that the comminution was not perfect. For instance, coarse particles of clinker A had Blaine ~3200 cm^2/g but coarse clinker B had ~2500 cm^2/g. Notably, clinker A always had slightly higher fineness than B or C, in all three size fractions. The possible influence of this situation on performance is addressed in the discussion section. The gypsum used in all cements had the same fineness, ~1250 cm^2/g. Fig. 2 shows the PSD curve for the cement made with A, B, and C in its fine, intermediate, and coarse portions (cement ABC). The combination of particles actually yielded a cement similar to the modified Fuller distribution with a maximum particle size of 80 μm, indicating high packing. PSDs of the cements were determined using low-angle light scattering (laser diffraction).

A total of 27 cements were prepared by combining the clinkers, the slag, and the gypsum. The naming scheme for the Portland, and blended cements can be explained as follows: If X represents any one clinker (either A, or B, or C) in a cement, Y represents a second (different) clinker in the same cement, Z represents a possible third clinker in the same cement, and S represents slag, then three single-clinker cements (XXX), six three-clinker mixtures (XYZ), and eighteen slag-containing cements (nine SXX/SXY, and nine XSX/XSY) were prepared. The first, second, and third letters in each cement name represents the material used as the fine, intermediate, or coarse particles, respectively. The combination of clinker and slag to produce the cements is summarized in Table 3.

Then, for example, cement ABC contains 35% of fine particles of clinker A, 25% intermediate particles of clinker B, and 40% coarse particles of clinker C, and no slag. SBC contains 35% fine slag particles. 5% gypsum by mass of its clinker content was added to each cement. Hence, the gypsum content was highest for the Portland