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Effect of particle size and slag content on the early hydration of interground blended cements

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ABSTRACT

Three blended cements prepared by intergrinding 6–35% slag with clinker and gypsum, and a control portland cement, were sieved to yield 0–10 μm, 10–30 μm, 30–50 μm, and >50 μm subgroups. Clinker/slag/gypsum contents, and oxide compositions of the subgroups differed significantly from the unsieved cements. Fine subgroups always contained more gypsum and had lower slag-to-clinker ratios than coarse subgroups. Heat evolution was investigated up to 48 h using isothermal calorimetry. Contribution of slag to early heat evolution was limited. 0–10 μm particles evolved up to 5–10% of their heat in the first 30 min. Particle size affected the peak rate of heat evolution but not its timing. A linear relationship was observed between heat evolved from 0 to 24 h and from 24 h to 48 h. Median size or slag content of subgroups affected the positions of data points on this line. Heat evolved up to 24 h (or 48 h) was found to be closely related to particle size. Rate of heat development does not appear to be strongly influenced by particle size above ~30 μm.

1. Introduction

For environmental, economical, and technical reasons, nearly 75% of cement produced in Europe now contains different proportions of one or more of ground granulated blast furnace slag, natural pozzolans, fly ash, silica fume, and limestone [1]. Incorporation of mineral admixtures modifies the hydration of cement which is affected by factors such as clinker phase composition and fineness of the cement, water-to-cement ratio, temperature, and amount of chemical and mineral admixtures [2]. The influence of partial replacement of portland cement with mineral admixtures on early hydration can be studied by measuring the changes in the rate and amount of heat evolution [3], among other methods [4–6].

Ground granulated blast furnace slag (slag) is a latent hydraulic material which, when mixed with hydrating portland cement, can be activated by the alkalis present and the calcium hydroxide produced. It can modify the structure of clinker hydration products [7], particularly their amounts [8]. 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 [9]. Pozzolan or slag incorporation is typically reported to retard and reduce the rate of hydration [8,10–12]. However, several investigations report enhanced early cement hydration caused by fine pozzolan or slag incorporation [13–18]. Conflicting results can be explained by differences in the types, compositions, and finenesses of the SCM used. It has been suggested that very fine cement particles can hydrate fully within 24 h [21] whereas particles larger than 45 μm hydrate slowly [22] and that particles with equivalent-volume sphere diameters greater than ~15 μm may not hydrate completely [23]. As such, the contribution of a cement particle to strength is closely related to its size [24,25]. However, these generalisations do not necessarily apply to interground blended cements. In almost all of these studies, the clinker (plus gypsum) and the SCM were ground separately, hence the particle size distribution (PSD) of the remaining portland cement was unchanged. Careful selection of SCM and clinker PSDs has been proposed for separately-ground blended cements. Pastes and mortars in which SCMs replace coarse clinker particles can give strengths equal to those made with portland cement only [26,27]. Zhang et al. [28–31] reported that replacement of fine clinker particles with slag and coarse particles with a less-reactive SCM can give high degrees of hydration and

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improved microstructure development, even at early ages and for SCM levels greater than 50%. However, intergrinding of slag and clinker is more common than separate grinding [9] and in the case of blended cements, differences in grindability can lead to significant changes in the relative proportions of the finer and coarser portions of the cement [19,20]. To the authors' knowledge, there are not any studies that present actual ratios of slag, clinker and gypsum in different size ranges of interground slag-blended cements. The work presented here is part of an extensive study, the aim of which is to investigate the effects of different SCMs interground with clinker (and gypsum) on the early heat of hydration of blended cements and to distinguish the contributions of different size ranges. Natural pozzolan-blended cements have been previously reported on [20]. In this part of the study, slag-blended cements of the types CEM II/A and CEM II/B [32] are studied. The effects of interground slag on early hydration are analyzed through determining the rate of heat evolution (using isothermal calorimetry), and chemical compositions of sieved 0–10 μm, 10–30 μm, 30–50 μm, and >50 μm subgroups of the original blended cements. Quantification of differences between component finenesses can provide valuable insight into their contributions to overall behavior in interground blended cements and complement studies on grinding of cement.

2. Materials and method

Blended cements were prepared by intergrinding a slag with a clinker and gypsum rock in a laboratory ball mill. A control portland cement (C) without slag was also prepared. The slag contents of the blended cements were 6% (S6), 20% (S20), and 35% (S35) of the combined clinker and gypsum. The amount of gypsum added to C and S6 was 5% (by mass of clinker + gypsum). It was reduced to 4% for S20 and S35 due to reduced amount of clinker. Table 1 shows the chemical compositions of the clinker, pozzolan and gypsum.

All four cements were ground to a Blaine fineness of ~375 m2/kg. The cements were subsequently sieved using an ultrasonic sifter that combines vertical and mechanical shaking with ultrasound application to agitate the particles and prevent blocking/blinding of the mesh. Four “subgroups” were obtained from each cement: 0–10 μm, 10–30 μm, 30–50 μm, and >50 μm. So, a total of 20 cement powder samples (16 sieved and 4 unsieved) were obtained. Samples were named to reveal whether they were obtained from a control cement (C) or a cement containing 6, 20, or 35% slag (S), and the sieve interval they were sieved to, as explained with the following examples: 0 C is the control cement sieved to 0–10 μm; 30S6 is the cement containing 6% slag sieved to 30–50 μm; US35 is the “unsieved” cement containing 35% slag; etc.

A comparison of the grinding times required to achieve the target fineness gave an idea about the relative resistances of the original materials to comminution. While the control cement (C) took 45 min of grinding in the ball mill to achieve the desired Blaine, S35 took slightly over 60 min, indicating an increased difficulty in grinding due to the addition of slag. The clinker, slag, gypsum contents of the sieved subgroups were determined using CEN/TR 196-4 [33], and oxide compositions were determined using inductively coupled plasma mass spectrometry. The amount and rate of heat of hydration evolution was investigated up to 48 h using isothermal calorimetry at 23 °C. Heat flow data were integrated to obtain the total heat evolution in time and analyzed to determine the combined effect of particle size and slag content on early hydration. A water-to-powder ratio (W/P) of 0.4 was used for the paste samples of all size subgroups of all cements, except the 0–10 μm subgroups for which W/P was 0.6. This increase was needed to achieve adequate mixing of these fine samples. The effects of this change on properties are discussed in subsequent sections. The particle size distributions (PSDs) of the samples were determined using low-angle light scattering (laser diffraction).

Table 1
Chemical compositions of the clinker, slag and gypsum used.

Oxide (%)	Clinker	Slag	Gypsum
SiO_2	20.49	40.94	1.85
Al_2O_3	4.49	13.54	0.05
Fe_2O_3	4.29	0.95	0.19
CaO	66.41	32.64	32.40
MgO	0.97	7.38	0.21
SO_3	0.77	2.19	44.47
Na_2O	0.21	0.24	0.07
K_2O	0.80	1.23	0.05
Loss on Ignition	1.10	<0.01	20.89

3. Results and discussion

3.1. Sieving and particle size

Before any subsequent analysis could be performed, it was necessary to check that the sieving was successful. This was done first by visual observation of the different sieved subgroups using scanning electron microscopy (SEM). Although only 2-D, SEM images can show the presence of particles finer or coarser than the bottom and top sieve openings. Fig. 1 shows SEM images of 10 C and 50 C.

The particles in Fig. 1a are mostly uniformly sized and have diameters equal to or slightly larger than the 30-μm scale bar. Although the top sieve for 10 C has a 30-μm opening, particles sprinkled onto a flat surface tend to have their longer dimensions parallel to the surface so this result is logical. Fig. 1b shows that 50 C particles have reasonable sizes but some finer particles are also present due to these very fine particles adhering to the surfaces of larger particles. The efficiency of ultrasonification to break up agglomerates composed of particles with similar size is possibly greater than to break up smaller particles stuck to a coarse particle (with greater surface contact). Laser diffraction PSD analysis allows the determination of the amounts of particles of a subgroup within and outside of the expected size range. Fig. 2 reveals that the sieving is quite successful.

The subgroups have most of their particles between the top and bottom sieves used to obtain them. For example, 0 C has $D_{90} = 10.4$ μm (90% of the particles are smaller than this size). ~87% of the 0 C particles appear to be in the 0–10 μm range. ~65% of the 10 C particles appear to be in the 10–30 μm range, ~58% of the 30 C particles appear to be in the 30–50 μm range, and ~60% of the particles in 50 C appear to be larger than 50 μm. There can be two reasons why these values are lower than 100%. The first is imperfect sieving and is rather obvious. The second is that laser diffraction makes several assumptions to measure PSD [34]. The main assumption of sphere particle shape leads to errors for particles obtained by crushing. It has been suggested that laser diffraction PSD results show better agreement with the longest dimension of particles, rather than the intermediate (width) dimension of the particles which influences the sieve analysis results [35,36]. As such, some larger-than actual particles can be reported by LD. While it is easy to understand that particles smaller than the smaller sieve (the lower limit of the size range) could remain due to inefficient sieving, it is less probable for particles larger than the top size limit (the larger sieve) to be present. In Fig. 2a, 15–20% of the 0 C and 10 C particles, and ~22% of the 30 C particles are larger than the top size. Hence, it could be estimated that the sieving operation yields subgroups with ~80–95% of the particles having the correct