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3D particle size distribution of inter-ground Portland limestone/slag cement from 2D observations: Characterization and distribution evaluation

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HIGHLIGHTS

- 2D PSD of limestone, slag, and OPC in PLC (-S) binders was determined by BSE.
- Using 2D data and a discrete stereology, the 3D PSD was reconstructed.
- Inter-grinding makes the binder particles coarser and distribution broader.
- Inter-grinding of PLC (-S) binders benefits the particle packing.

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ABSTRACT

In this research, the particle size distribution (PSD) of different components in inter-ground Portland limestone cement (PLC) and limestone-slag cement (PLC-S) was characterization by using an electron microscopy approach. Firstly, the 2D PSD of limestone, slag, and Portland cement (OPC) was determined by means of image analysis. Based on the 2D data and using a discrete stereology, the 3D size distribution was reconstructed. Finally, the PSD of inter-ground mixtures was assessed by using a compressible packing model. The results showed that the addition of limestone in cement makes the OPC component coarser and distribution broader; meanwhile, the limestone particles were found to be finer than the OPC particles. The addition of both limestone and slag (PLC-S) were found to further broaden the PSD of OPC component and limestone component with the mean size of particles increased in the following order (limestone < slag < OPC). Among the tested samples, the packing density of OPC was the lowest while the packing density of PLC-S was found to be the highest. Based on test results, it can be concluded that the addition of more components during inter-grinding makes the particle size of binder coarser and distribution broader, which in turn, benefits the particle packing and possibly improves the mechanical and durability performance of the cement based composites.

1. Introduction

The environmental impact and associated high energy consumption from the manufacturing of Portland cement has resulted in the use of various supplementary cementitious materials (SCMs) [1,2]. In this context, various SCMs such as pulversized fuel ash (PFA), silica fume (SF), rice husk ash (RHA), slag etc have been used as partial replacement of Portland cement in concrete [3,4] so as to improve the mechanical properties and durability of the concrete [5–9]. Fine limestone powder is one of the SCMs, which have been prescribed in worldwide standards. For example, EN 197-1 suggested the use of limestone in Portland limestone cement (PLC) up to 21–35% [4,10]; ASTM C595 recommends 15% as the maximum dosage of limestone [11], while the Chinese Standard JC/T 600-2010 suggests the dosage of limestone as 10–25% [12]. Moreover, during the last decade, the production of PLC has shown a rapid increase in the cement industry. Based on the available literature [4,13], it can be concluded that limestone is an effective SCM,

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which can be used to improve the mechanical properties and reduces the cost of concrete.

With the acceptance of PLC, viz. addition of limestone in Portland cement, some researchers have also introduced minerals admixtures (PFA, metakaolin, slags etc. [11,14]) in the PLC system to further improve the properties of the product. The functionality of the binary and ternary cementitious system is due to the reaction of aluminate minerals in the binders with limestone. This reaction results in the formation of carboaluminates, which can further densify the microstructure and thus improve the mechanical properties of the mixed concrete [15,16].

Inter-grinding of Portland cement clinker, limestone, and gypsum is a commonly used technology to produce PLC [17–20]. By doing this, the cementitious materials are homogenized during the grinding and only one silo is sufficient for the production of powder composites at the concrete plant. Furthermore, it is reported that the inter-grinding of powders benefits the formation of carboaluminate and improves the properties of concretes, e.g. decrease in porosity [15] and thereby improving the durability. It is also known that particle size distribution (PSD) of the cementitious materials influences the packing density, hydration process, and hydration related properties of concrete [3,4,10,21,22]. Moreover, in modeling assignment, the PSD of the SCMs is a key parameter that influences modeling accuracy [23–25]. For inter-grinding method, the composites that have various stiffness and dimension are mixed and ground together. Hence, the experience from grinding individual components for designated PSD does not suit for the inter-grinding regime.

Few methods such as thermal analysis [26] and sedimentation method [27] have been proposed to determine the PSD of limestone related components in the inter-ground mixture. However, the size fraction classification determined by these methods is relatively rough, especially for particles of sizes below tens of micron. Hence, the method cannot be reliably used to determine the PSD of ground limestone, which has high concentration of fine fraction particles. Therefore, the existing methods to determine the PSD of limestone components are only indirect methods. Moreover, no direct method has been used to observe limestone related cementitious materials with particle size ranging from microns to nanometers. The backscattered electron image and the energy dispersive X-ray analysis (EDX) modules of the scanning electron microscopy (SEM) is an alternative direct-observing technique that can identify different types of cementitious materials with particle size ranging from microns to nanometers, such as slag [28] and PFA [29]. However, as per authors' knowledge, this technique has not been used in measuring the inter-ground PLC and related additives. Hence, in this paper, the backscattered electron image along with the energy dispersive X-ray analysis modules of the scanning electron microscopy was used to identify the different components present in the PLC (with/without slag). The PSD of different components present in PLC (with/without slag) was compared and the influence of limestone/slag on the PSD of the inter-ground product was also examined.

2. Materials and methods

2.1. Materials

In this research, OPC, PLC, and PLC with slag (PLC-S) manufactured by Lafarge Ltd. and complying with ASTM C595 were used. PLC was obtained by inter-grinding the composite of limestone, gypsum, and cement clinker. The dosage of limestone in PLC was 10% by mass while the dosage of limestone and slag in PLC-S was kept as 8% and 10% by mass respectively.

2.2. XRD testing

The X-ray Diffraction (XRD) was used to determine the phase changes in materials before and after inter-grinding. The test was conducted using a Bruker D8 instrument with a CuKα source (λ = 1.54 Å) at 40 kV and 40 mA.

2.3. Preparation of samples for SEM

In order to clearly identify different elements and minerals present in the tested samples, the following procedure was adopted. At first, the slurry was prepared by mixing 8 g of sample powder with 7 g of epoxy resin. The prepared slurry was injected into a plastic cylindrical mould (Φ 22 × 55 mm) followed by placing the sample at room temperature for 24 h. Thereafter, the sample was cut into small slices using a precision diamond saw operated at low speed. After cutting, the samples were polished in following succession (9 μm, 6 μm, 3 μm, 1 μm, and 0.25 μm) on Texmet polishing clothes. Finally, the surface of the samples was coated with a thin platinum film so as to avoid the charging effect during observation.

2.4. Parameters setting for SEM

The micro morphology of prepared samples as well as elemental mapping was examined by FEI Quanta 3D equipped with a field emission gun. In backscattered electron detection mode, an accelerating voltage of 12 kV and a beam current of 2.8 nA was used. The samples were observed at a magnification of ×800 while mapping images obtained had a resolution of 256 × 256 pixels. For each mapping scan, the duration of test was kept as 30 min. Moreover, for each sample, 10 different areas were observed and statistical analysis was carried out to reduce the random error due to limitation of the relatively small observation area.

2.5. Analysis of particle size distribution

The 2D PSD was obtained using a so-called discrete PSD approach [30]. For each of the considered 2D particle size representation, it calculates the radius of an equivalent circular particle having the same area. Thereafter, for the whole analyzed dataset, the areas corresponding to a certain equivalent radius are integrated. The images of the particle distribution obtained from the analysis were processed with the following procedure: Firstly, the area S of individual particles was obtained. Subsequently, it was assumed that all the particles were spherical in shape and the diameter D of the assumed particles was calculated according to the following formula ($D = 2 \times \sqrt{S/\pi}$). This formula was used to represent the dimension of particles. For each specimen, 10 randomly distributed figures were statistically analyzed. Hence, for the PLC specimen, there were 6850 OPC and 1265 limestone particles, whereas for the PLC-S specimen, there were 2853 OPC, 477 slag and 524 limestone particles.

Based on the 2D PSD and by using discrete stereology [31], the 3D PSD was reconstructed. The method is based on the assumption that when isolated spherical particles are intersected by a plane and after dividing the size distribution into size classes (discrete system), the equivalent radius corresponding to the class of the largest circular cross-sections is equal to the radius of the largest sphere class. In practice, the number of spheres per unit volume of size class i can be expressed as

$$\mathrm{N_{vi}} = \frac{1}{\mathrm{P_{i1}}\bar{H}'_{\mathrm{i}}}\left(\mathrm{N_{Ai}} - \sum_{\mathrm{j=1}}^{\mathrm{i-1}} \mathrm{P_{(i-j)(j+1)}}\bar{H}'_{\mathrm{i-j}}\mathrm{N_{v(i-j)}}\right), \quad (1)$$

where j is the 2D size class of profile; $\mathrm{N_{Ai}}$ is the number of spheres per unit volume of cross-section of size class i; $\mathrm{P_{ij}}$ is the probability of all 2D cross-sections produced by the 3D particles of size class i which fall into the 2D cross-section class j and can be described as

$$\mathrm{P_{ij}} = \frac{1}{\mathrm{R_i}}\left(\sqrt{\mathrm{R_i^2 - r_{j-1}^2}} - \sqrt{\mathrm{R_i^2 - r_j^2}}\right) \quad (2)$$

$\bar{H}'_{\mathrm{i}}$ is the mean projected height (mean height of the shadow cast by a particle spinning about constantly changing randomly oriented axes) and is described by

$$\bar{H}'_{\mathrm{i}} = \frac{\mathrm{D_{mi}}}{\mathrm{k}}, \quad (3)$$

where $\mathrm{D_{mi}}$ is the diameter of the 3D spheres of size class i and k is the number of classes [32].

The cumulative frequency of the 3D particles of class i can then be written as

$$\mathrm{a_i}\% = \sum_{\mathrm{m=1}}^{\mathrm{i}} \frac{\mathrm{N_{vm}}}{\sum_{\mathrm{l=1}}^{\mathrm{k}} \mathrm{N_{vl}}} * 100\% \quad (4)$$

3. Particle packing assessment

The compressible packing model (CPM) [33] was used to calculate the packing density of OPC, PLC, and PLC-S particle mixtures so as to assess the distribution superiority of particles obtained from inter-grinding technique. The model is described as follows:

$$K = \sum_{i=1}^{n} \frac{y_i}{\beta_i} / \left(\frac{1}{\Phi} - \frac{1}{\gamma_i}\right) \quad (5)$$