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A combined SEM–Calorimetric approach for assessing hydration and porosity development in GGBS concrete

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ABSTRACT

A combination of semi-adiabatic calorimetry and Scanning Electron Microscopy (SEM) is employed for characterising the hydration process and pore structure development of cementitious pastes. The efficiency of this method is investigated by obtaining hydration curve parameters for four different concrete mixes manufactured using varying combinations of limestone blended cement (CEM II/A-LL) and ground granulated blast-furnace slag (GGBS) over a period of six months after casting. Embedded thermocouples recorded the internal temperature development associated with heat of hydration released in the first hours after casting. Hydration monitoring was continued by analysing SEM images taken from broken concrete specimens at various time intervals. Reliable hydration quantification using this approach requires the aggregate particles to be identified and filtered out of the image; this is achieved using a semi-automatic image processing methodology developed for detection and segmentation of aggregates from the concrete paste. Grey-level thresholding and the inflection point method are employed to determine the area fraction of the void space and assess porosity. Hydration degrees are then determined by applying thresholding methods to distinguish the hydrated and anhydrous cement particles. Corresponding hydration curve parameters were obtained based on the experimental data, and the resulting curves were compared with those obtained based on commonly used cement composition models.

1. Introduction

The degree of hydration (α) is an indicator of progress of the reaction between cement grains and water, and is defined as the ratio of hydrated cement grains to the original quantity of cement grains available in the mix. Hydration curves are a useful tool for characterizing the hydration behaviour of concrete mixes at a reference temperature (T_r) [1].

1.1. Parametric modelling of hydration progress

The exponential formulation proposed in Equation (1) [2] is one of the most commonly used models of hydration progress and predicts hydration degree in terms of the equivalent rather than chronological age of concrete. This is to account for the combined effects of time and temperature, and has been reported to accurately represent the S-shape of hydration development curves [3].

$$\alpha(t_e) = \alpha_u \ \exp\left(- \left[\frac{\tau}{t_e}\right]^{\beta} \right) \qquad \text{Equation 1}$$

In the above equation, α indicates the degree of hydration of the mix, and t_e represents the equivalent age of a specimen cured at the reference temperature (T_r). The hydration time parameter (τ) and hydration shape parameter (β) determine the acceleration, retardation and rate of hydration in each mix [4]. The ultimate degree of hydration (α_u) expresses the maximum hydration degree a given mix is deemed to reach in practice. More information about these parameters and the detailed calculations involved in obtaining equivalent ages can be found in Refs. [1,5].

Considering the large number of influencing factors, e.g. water-cement ratio, mix composition, compaction, curing temperature, and humidity, degree of hydration of a mix at a certain age cannot be easily estimated using a pure mechanistic model. In order to

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obtain representative hydration curve parameters for defining the early age behaviour of a certain mix, the parametric model of Equation (1) should be fitted with a number of data points, and the mix-specific parameters determined. One of the approaches to obtain the data points in order to calibrate the curve, is direct measurement of the amount of cement gel that has formed in the paste over time. However application of this method is not always possible due to the equipment reqiured. Therefore, indirect approaches are often used, with estimation being based on the amount of chemically bound water or the heat released during hydration [1].

There are however difficulties in assessing degree of hydration based on the released heat of hydration. Total heat of hydration can be determined using adiabatic calorimetry, but that requires specialist equipment that is not commonly available. Alternately, knowledge of the exact cement composition is required, as is concrete temperature monitoring using embedded sensors. Furthermore, this method is only applicable before the internal concrete temperature has stabilised with the ambient temperature—a condition that only pertains to a few days after casting; any hydration progress beyond this period cannot be captured using this approach. Although this approach is unlikely to provide a precise estimate of the degree of hydration [1], it is still widely used. The need for a direct approach based on assessment of the amount of cementitious gel formed in the pore structure becomes more pronounced if hydration is used in predicting the secondary characteristics of the mixes, e.g. diffusivity and permeability.

Application of adiabatic calorimetry in assessing the hydration progress of the mixes requires measurement of mix-specific data points. This is most effective during the first few days after casting of the specimens, when the internal temperature is considerably different to the ambient surroundings, allowing clear calculation of the heat generated. On the other hand, this is the period when direct assessment of the cementitious pore structure is of less interest, since the concrete microstructure is far from its final configuration. The aim of this study is to propose a methodology for combining the indirect and direct methods, in order to monitor the pore structure development of mixes over a six months period after casting, with the indirect method being employed during the early age and the direct method covering the later stages of hydration and pore structure refinement.

Semi-adiabatic calorimetry and Scanning Electron Microscopic investigation of concrete specimens were adopted as the testing methodologies. The data points corresponding to the early age of specimens are obtained using calorimetry; while SEM has been employed for determining the amount of cement gel formed in the pore structure over an extended period of time up to six months after casting. A method has been introduced for determination of the hydration curve parameters to provide a suitable fit to the above data. The efficiency and constraints of this approach are explained and investigated through an experimental program.

Mixes of blended limestone cement (CEM II/A-LL) and Ground Granulated Blast-furnace Slag (GGBS) were considered in the experiments, since limited guidance is currently available for characterising the hydration behaviour of these mixes. The experimental data obtained from investigation of the selected mixes with the direct and indirect approaches are combined and used in developing characteristic hydration curves. The appropriate parameters resulting in the best-fit mathematical model for each mix are then calculated using a nonlinear multivariate regression. The resulting hydration characterisation curves are then compared with those obtained using a numerical model based on the cement composition.

1.2. Scanning Electron Microscopy (SEM)

SEM images are monochromatic displays of the difference in the electron flux of the backscattered signals that indicate the atomic number of the material under investigation [6]. This allows components of the concrete matrix to be distinguished and identified on a micro scale, based on the grey colour level they display. SEM is also capable of radiating X-ray signals, which may be collected using an Energy Dispersive X-ray Spectroscopy (EDX) system. The resulting image can be represented in the form of either a map of element distribution or a continuous spectrum, and is capable of displaying both the location and concentration of the elements present in the corresponding frame [7]. The elemental distribution maps provide an informative analysis tool that can be used together with the SEM images in the interpretation of the material under study.

Analysis of SEM images has frequently been employed to investigate various characteristics of cement and concrete paste, including investigation of the pore structure [8–10], quantification of porosity and phases such as anhydrous and hydrated cement paste [8,11–14], detection of cracks [15], determination of degree of hydration [16–18] and characterization of the structure of fresh cement paste [19].

1.2.1. Pore size distribution

Porosity of concrete influences both strength and transport properties. Pores, other than air voids, range in size from <10 nm (e.g. gel pores mainly contained within the hydrated cement paste) to 10 μm (e.g. capillary pores) [20].

The range of pore sizes detectable by SEM imaging is mainly a function of image resolution, with the smallest detectable size being in the range of 0.2 μm, dependent on equipment and setting conditions [21]. This method however is quite efficient in detecting the larger capillary pores and air voids, which are considered to be the more influential phase when it comes to modelling the transport properties of concrete [20].

1.2.2. Hydration assessment

SEM can be used for assessing the degree of hydration of concrete at any age, and contrary to the indirect method of heat evolution monitoring, does not require previous knowledge of the exact concrete composition. The difference in the mean atomic number of hydrated and anhydrous cement particles allows the user to determine the surface area corresponding to each phase on the SEM image. An estimate of the degree of hydration of the concrete samples can then be made based on the ratio of the area of hydrated cement to the total cement area in the image. The accuracy of this method depends on the quality of sample preparation and image acquisition, efficiency of the methodologies employed for aggregate segmentation, image processing and threshold determination among others.

2. Experimental program

In this study, four different concrete mixes were investigated. Each contained limestone aggregates and limestone blended cement (CEM II/A-LL) as the basic cementitious material. Varying GGBS replacement levels were employed (0, 30, 50 and 70% of the total binder content), and water-cement ratios in the range of 0.5–0.56.

2.1. Indirect assessment: semi-adiabatic calorimetry

Profiles of temperature build-up in the concrete mixes under investigation were monitored, utilising embedded thermocouples