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Physico-chemical kinetics of structural build-up of neat cement-based suspensions

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ABSTRACT

The rate of structural build-up of cement-based suspensions at rest is a result of combined physical and chemical structuration processes. The non-destructive dynamic rheometry was used to investigate the influence of cement fineness and content, alkali sulfate content, and temperature of the suspension on the percolation time and rigidification rate of neat cement suspensions. Zeta potential, calorimetric, and spectrometric measurements were performed to explore the corresponding microstructural changes in cement suspension. Test results showed that the percolation time is controlled by the frequency of Brownian collisions, the distance between dispersed particles, and intensity of cohesion between cement particles. On the other hand, a high rigidification rate can be secured by increasing the number of contact points per unit volume of paste, nucleation rate of cement hydrates, and intensity of inter-particle cohesion. A semi-empirical model correlating the build-up indices and the microstructural characteristics was developed and validated.

1. Introduction

The build-up of cement suspensions is a time-dependent phenomenon reflecting the growth rate of apparent rheological properties, such as static yield stress, zero-shear rate viscosity, and storage modulus with time [1,2]. The degree of structural build-up is a key property that affects the macroscopic behavior of cement-based materials after casting [3–8]. Indeed, in the case of casting tall wall elements, it is preferred to use concrete with high kinetics of structural build-up to reduce the lateral pressure exerted on the formwork and allow faster pressure decay after casting [3,9,10]. Furthermore, in the case of a layer by layer construction in the 3D–printing of cement-based materials, it is crucial to optimize the degree of structural build-up to ensure successful casting. In fact, high kinetics of build-up can affect the bond between cast layers within the printed structure [6]. Meanwhile, an adequate structuration rate is required to allow gaining a sufficient strength level capable of sustaining the weight of subsequently extruded layers [11].

The structural build-up of cement suspensions is a complex phenomenon associated to the combined effect of both physical structuration due to inter-particles colloidal interactions and chemical rigidification resulting from cement hydration [12]. When a cement suspension is allowed to rest after shearing, cement particles flocculate and form a three-dimensional structure due to the induced van der Waals and electrostatic forces [13,14]. The change in size of cement clusters of concentrated cement suspensions has been recently monitored using a laser backscattering technique. It has been confirmed that the kinetics of aggregation are highly influenced by shear history, paste ingredients, and rate of shear strain [15,16]. In addition to the aggregation of cement flocs at rest, an additional time-dependent process occurs due to nucleation of cement hydrates [17–19]. Through this process, the nucleated C-S-H at the pseudo contact points between cement particles can rigidify the formed network, leading to increasing the stress-bearing capacity of formed structure.

The kinetics of build-up of cement-based suspensions is affected by several mixture parameters, including mixture composition, characteristics of its constituents, temperature of suspension, and shear history. For example, it was reported that neat cement pastes proportioned with a water-to-cement ratio (*w/c*) of 0.36 is more thixotropic than those made with a *w/c* of 0.42 [20]. Furthermore, a significant effect of *w/c* on the variations in lateral pressure and thixotropy of self-consolidating concrete (SCC) mixtures proportioned with a similar initial slump flow was observed [21]. It was shown that 0.46 *w/c* mixtures exhibited greater initial lateral pressure and lower thixotropy compared with those proportioned with *w/c* of 0.40 and 0.36. Additionally, for a given *w/c*, the increase in binder content from 400 to 550 kg/m^3 resulted in a higher degree of restructuration of concrete equivalent-mortar (CEM) mixtures [22].

The change in binder type was also reported to affect the time-dependent behavior, where CEM and SCC mixtures prepared with Type 30 CSA cement exhibited higher thixotropy than those prepared with binary or ternary cement [22]. Additionally, some studies have reported the change in both rheological and thixotropic properties of cement mixtures with the change in cement properties, such as specific

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surface area, C_3A and alkalis contents [23–26]. For example, the increase in specific surface area of cement has shown to increase the energy needed to breakdown structure of cement pastes [25]. On the other hand, the effect of alkalis content has shown to depend on the reactivity of clinker in cement pastes. Higher alkalis content was found to change the shape of hysteresis loops of clinker suspensions from thixotropic into anti-thixotropic, but did not alter the hysteresis loop in the case of cement suspensions [26]. Besides, many studies have reported the considerable influence of type and dosage of various chemical and mineral admixtures on the level and rate of structural build-up and consequently on the lateral pressure of cementitious systems [21,27–31].

The structural build-up of cementitious systems has been shown to be temperature dependent [32–34]. Indeed, a nonlinear increase in yield stress and storage modulus values was observed when the temperature of cement paste varied between 20 and 45 °C [34]. The coupled effect of time and temperature on the variations of static yield stress for mortar mixtures extracted from SCC is shown to be greatly affected by the type and dosage of HRWR [32].

Although various studies have been conducted on the build-up of cement-based suspensions and its variation with the change in mixture composition and casting conditions, there is limited data regarding the effect of mixture parameters on the physical and chemical kinetics of structural build-up. The objective of this study is to evaluate the effect of *w/c*, cement fineness, alkali sulfate content, and temperature of the mixture on physical and chemical components of structuration at rest. The non-destructive dynamic rheometry was used to monitor the evolutions of viscoelastic properties of cement suspensions, including storage modulus (G′) and phase angle (δ). Two independent indices of build-up describing the rest time needed to form the structural colloidal network and its chemical rigidification rate were used to quantify build-up [35]. The corresponding microstructural changes, including interparticle cohesion, Brownian interactions, and nucleation intensity were evaluated and discussed. Furthermore, a model that can predict the build-up indices knowing the microstructural characteristics of fresh cement pastes was proposed.

2. Research significance

The present study provides quantitative data on the physical and chemical kinetics of structuration of neat cement suspensions at rest and their variations with the mixture parameters, such as *w/c*, fineness of cement, alkali sulfate content, and temperature of the suspension. The provided data can contribute in enhancing the fundamental knowledge related to the kinetics of structural build-up of cement-based suspensions. This can lead to better understanding and adequate control of the degree of structural build-up of cement-based materials at rest given the application on hand.

3. Experimental program

3.1. Materials, mixture proportions, and mixing sequence

Cement paste mixtures investigated in this study were systematically proportioned using General Use (GU) and Low Alkali (LA) cements complying with ASTM C150M. The chemical characteristics of used cements are summarized in Table 1. In addition, the GU cement was ground in a Hosokawa Alpine 100 AFG jet mill to produce various GU cements with different fineness values. The grinding levels were varied by controlling the grinding speeds at 4000 rpm, 8000 rpm, and 12,000 rpm, while keeping a constant feeding rate. The produced ground GU cements will be referred to as GU-4000, GU-8000, and GU-12000. The particle size distributions (PSDs) of GU and LA cements are summarized in Fig. 1. On the other hand, the Blaine and BET surface areas, as well as particles distribution characteristics are presented in Table 2.

In order to identify and capture the microstructural parameters governing the kinetics of structural build-up of neat cement suspensions, four different groups of cement mixtures were prepared (Table 3). The first group of mixtures was proportioned to evaluate the effect of solid concentration on the kinetics of build-up. Various mixtures were made using a GU cement and different water-to-cement ratios (*w/c*) varying from 0.35 to 0.55. These mixtures were tested at a constant temperature of 23 °C. In the second group, the effect of cement fineness was evaluated. The mixtures were made with various ground GU cements and three different *w/c* of 0.45, 0.50, and 0.55. The investigated mixtures had a constant temperature of 23 °C. On the other hand, the third group consisted in evaluating the effect of temperature of the suspension on the kinetics of build-up of 0.40 *w/c* mixtures. Different temperature values of 3, 13, 23, and 33 °C were evaluated. The mixtures investigated in the fourth group aimed to evaluate the effect of different additions of alkali sulfate (Na_2SO_4), by mass of cement, on the kinetics of build-up of 0.35 *w/c* cement suspensions made with LA cement.

All the investigated cement mixtures were mixed using a high-shear mixer according to the procedure described in ASTM C1738M. The temperature of mixing water was controlled to compensate for heat generation during mixing. Following the end of mixing, all mixtures had the targeted temperature with a precision of ±2 °C. The mixing sequence consisted in introducing the binder gradually over 1 min while the mixer is turned on. After a rest period of 150 s, the mixing was presumed for a total mixing time of 4 min and 30 s. Immediately after mixing, the sample was conserved in a sealed container to prevent water evaporation. The rheometric measurements were determined after 20 min from the first contact between water and cement. This was selected to allow performing measurements after the occurrence of early hydration reactions.

Table 1
Chemical characteristics of used GU and LA cements.

Composition (%)	GU	LA
CaO	63.7	65.2
SiO_2	19.9	19.8
Al_2O_3	3.5	3.4
SO_3	3.8	3.2
Fe_2O_3	2.7	3.1
MgO	2.0	1.6
Na_2O	0.19	0.13
K_2O	0.78	0.50
$Na_2O_{eq.}$	0.71	0.46

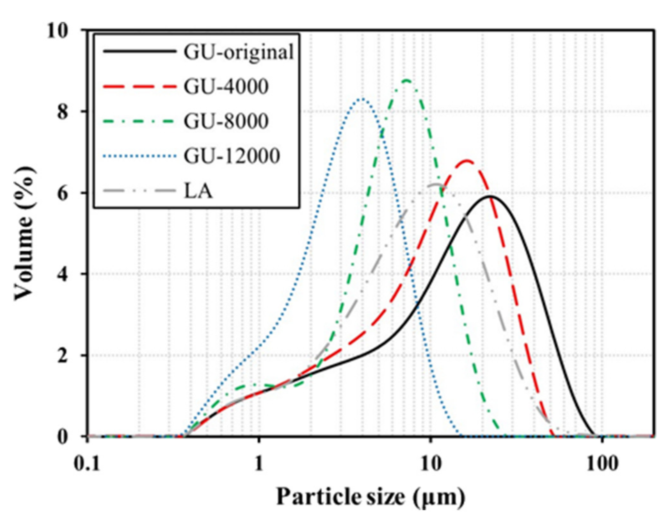

Fig. 1. Particle size distributions of used cements.