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Influence of gypsum fineness in the first hours of cement paste: Hydration kinetics and rheological behaviour

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HIGHLIGHTS

- The gypsum surface area influence in the cement hydration.
- The physical characteristics of gypsum modify the dissolution and influenced in the ettringite formation.
- After the consumption of gypsum the formation of hydrates and the heat flow tends to equalize.
- Rheologically, the gypsum fineness influencia in the evolution of the resistance to the flow in function of the time.

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ABSTRACT

During the cement production process, gypsum and other additives are input in the clinker grinding and each component present different breakage characteristics. The final particles size depends of the difference of the grindability of their constituent. Thus, it is difficult to know precisely the effect of gypsum fineness in the hydration kinetics or rheological behaviour of the cement paste. Therefore, three gypsum particle size were analysed, classified as fine, medium, and coarse, as well as one clinker collected before grinding. The primary tests included heat flow by calorimetry, X-ray diffraction, and rotational rheometer. It was possible to evaluate how gypsum fineness altered the hydration kinetics in the first few hours and promoted different rheological behaviours from the clinker analysed.

1. Introduction

Gypsum is added to Portland cement during the clinker grinding stage along with other inputs, such as limestone, slags, and pozzolans. Without gypsum, any cement in contact with water rapidly loses its workability, and hardens [1]. This occurs because the hydration of C_3A causes the formation of small plates of calcium aluminate [2,3]. Gypsum is used to precisely control the hydration of C_3A and, subsequently, the setting time of the cementitious material.

Several studies [4–11] have evaluated the interaction between C_3A and gypsum phases in order to understand their hydration kinetics, as well as the influence of calcium sulphate types [4,5], gypsum contents [5–8], and other compound additions [6–8].

Gypsum also interacts with the C_3S phases, modifying the growth of C-S-H [9] and increasing heat flow during the early stages of the hydration process [10]. Both effects have been observed by Quennoz and Scrivener [11] for alite-gypsum samples. However, the acceleration effect was not observed for C_3S (pure phase), but only in systems with higher temperatures [11].

Other assessments were conducted in fresh and hardened states [12–16], but none of them have investigated the influence of gypsum fineness because the gypsum was ground together with the clinker.

The grinding method is fundamental for multicomponent cements, and their physical interactions are greatly influenced by the grindability difference [16]. Clinker grinding, in general, requires more energy than gypsum grinding, which is added at low levels [17].

One of the problems caused by the simultaneous grinding of different inputs, besides the different grindabilities, is the difficulty in optimizing the fineness of each component, which can lead to overgrinding [18].

Several studies have evaluated cement grindability [16–18] applied to the particle size distribution of bicomponent (clinker

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and gypsum) [16,17] or multicomponent (clinker, gypsum, and others) systems [16,18]. These analyses prioritized the distribution of particles [16,19], Blaine's fineness values [16,19], and grinding energy [17,19]; when assessing the interaction between cement and water, the analyses investigated the compressive strength [16,19].

Rheological analysis may help in the characterization of pastes during cement hydration [20]. The higher the mixing energy, the better the properties in the fresh state, the greater the dispersion of particles, and the lower the agglomeration force [21–23]. However, different testing configurations during the analysis may result in different rheological behaviour responses for the same cementitious paste [24,25]. In the present study, the rheology test was used to determine the influence of gypsum fineness in the first few hours of cement hydration.

The analysis of the hydration and rheological behaviour of cement pastes with the addition of fine, medium, and coarse gypsum made it possible to measure the influence of gypsum fineness on the cement paste.

2. Materials and methods

2.1. Gypsum and clinker

The gypsum phases used in this study are natural minerals with size dimensions between 3 and 6 cm.

The gypsum and clinker materials were characterized according to Brazilian standards as ignition loss by the Brazilian standardization (NBRNM 18) [26], insoluble residue (NBRNM 15) [27], specific mass (NBR 16605) [28], and specific surface area (NBR 16372) [29]. The particle sizes that were measured on a Malvern Instruments Laser Granulometer, Scirocco 2000 dry module, with obscuration ranging from 2% to 5% and weighted residual of approximately 0.5%.

Other tests conducted were X-ray fluorescence (XRF) and X-ray diffraction (XRD), and the phase proportions were obtained by the Rietveld method. The XRD patterns of the clinker and gypsum samples in the anhydrous and fresh states were executed on X 'PERT Pro MPD equipment from Philips, with the following instrumental conditions: Cu-Kα radiation (λ = 1.54187 Å); a generator of 40 mA, 40 kV; time per step of 40.640 s; and step of 0.017° 2θ. The anhydrous materials were analysed with a 0.5° fixed divergent slit and a 5°–70° 2θ angular range; the mineral concentrations were estimated by the Rietveld method with Bruker's TOPAS® software version 3.0.

Fig. 1 presents the flowchart of the different types of grinding processes used to obtain coarse, medium, and fine particles of gypsum and clinker.

For the gypsum, free water and the water of crystallization were also evaluated. The amount of water present in the gypsum was measured via two methods, according to NBR 12130 [30] and by thermogravimetric analysis (TGA) with heating rate of 10 °C/min, synthetic air atmosphere, mass of 10 mg, and at temperatures 30–500 °C.

2.2. Cementitious pastes

The cementitious pastes were composed of clinker and gypsum with a proportion of 4% by mass with coarse, medium, and fine granulometric distributions. The final dosages were fulfilled with clinker content of 96% (by mass) and water/solids (w/s) of 0.46. The samples are referred to as C + CG (clinker + coarse gypsum), C + MG (clinker + medium gypsum), and C + FG (clinker + fine gypsum). The analyses were conducted to identify the influence of the gypsum on the reactivity of the cement paste.

The paste mixtures were prepared on a Fisatom bench mixer at a minimum rotation of 400 rpm for 30 s; distilled water was added to the dried sample and then the rotation was set at 1000 rpm for 2 min. Thereafter, the mixer was stopped for 30 s, and the edge and bottom of the mixing vessel were scarified. Finally, the rotation was set at 3000 rpm for 2 min for a total mixing time of 5 min. The temperature of the laboratory remained in equilibrium with the temperature of the experiments, 23 °C ± 1.

The heat flow by isothermal calorimetry was obtained using TAM Air equipment of TA Instruments at a temperature of 23 °C. The calorimeter test started at 10 min after the of paste mixing and the test duration was for a total time of 40 h. The heat flow curve presented is the mean curve of the three repetitions.

The XRD patterns of the paste sample were determined by the automatic divergent slit at 10 mm, and the angular range was 7°–70° 2θ; the development of the hydrated products and consumption of the anhydrous compounds were realized in High Score Plus software, version 3.0d. To avoid the loss of water to the environment and shrinkage, a plastic film (Kapton) was used on the surface of the sample. The sample mixed in the same way as in the rheological tests.

The rheological analyses were conducted on a Haake RheoStress 600 rotational rheometer and the following plate-plate configuration: 35 mm diameter with 1 mm gap and smooth surface. A temperature of 24 °C was controlled by Haake's Thermocontrol and a DC 30 thermal circulator. The first rheological analysis of the flow test was completed 20 min after mixing; the test was then repeated after 1, 2, and 3 h of mixing. The first rheological analysis of the flow test was completed 20 min after mixing; the test was then repeated after 1, 2, and 3 h of mixing. Each sample was taken from the mixer bowl which remained at rest, in this way the on the shear history was not changed and the process of hydration and segregation of the samples as a function of time was analysed. The result is a flow curve for each time analysed, where the shear rate ranged from 0 to 150 s^{-1} rpm for 1 min, followed by deceleration for another 1 min until a zero-shear rate is obtained.

3. Results and discussion

3.1. Influence of gypsum fineness on cement particle size distribution

The particle size distributions of the gypsum and clinker phases are shown in Fig. 2. The clinker has a granulometric distribution

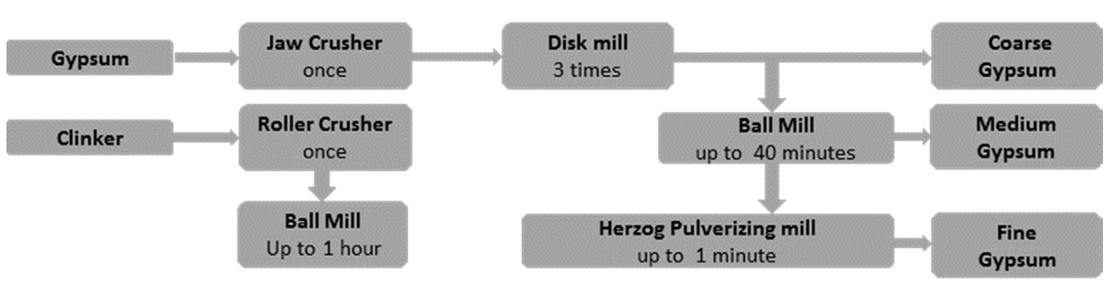

Fig. 1. Gypsum and clinker grinding flowchart methods.