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Cellulose ethers and cement paste permeability

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ABSTRACT

Cellulose ether (CE) admixtures are used to improve the water retaining properties of cement-based materials in order to ensure their homogeneity during casting operations. Water permeation through concrete is usually quantified by permeability. In this study, an oedometric cell has been adapted to investigate the influence of CE dosage on the permeability of fresh cement pastes. The purpose-designed device has to allow the filtration of CE aggregates through the oedometric filters and retain cement particles. Simultaneous rheological shear flow measurements have been carried out to evaluate the viscosities of the initial interstitial liquid and the percolated fluid that has filtrated through the fresh cement paste. Comparison of both viscosities allows the evaluation of the amount of CE adsorbed by the cement particles over a wide range of CE dosage. Moreover, the analysis of experimental results confirms previous studies concerning the improvement of water retaining ability due to CE that in turn limits the amount of bleed water. Comparison of an apparent viscosity computed from permeability measurements and viscosity computed from rheological measurements shows that CE strongly modifies the particle networks above the overlap concentration. The results of this study suggest that CE aggregates are formed and plug part of the cement paste porosity. As a result, the apparent viscosity increases and leads to a strong decrease in the material's apparent permeability. Finally, apparent permeabilities are reported for CE dosages ranging from 0% to 0.5%. The results of the study show that combination of rheological and permeability measurements offers a promising method to analyze how CE acts on fresh cement pastes, that are subjected to a hydraulic gradient induced by casting processes.

1. Introduction

Nowadays, stability of fresh concrete is a major concern in mix design of highly fluid and self-compacting concrete (SCC). The freshly made mix has to remain homogeneous during the casting operation and the amount of bleed water has to be limited. It has recently been shown that cement grains in highly flowable concrete or SCC are not close enough to form a stable network that is able to sustain gravitational forces [1]. Consequently, these types of mixes are susceptible to bleeding. In order to slow down and prevent bleeding, viscosity modifying admixtures (VMA) are used, such as cellulose ether, superabsorbent polymer or welan gum [2–4]. These admixtures increase the water retaining properties of the freshly mixed concrete. It is worth noting that VMA are used for pre-cast processes such as extrusion, to prevent liquid drainage during production [5].

The improvement in material stability is due to different physical phenomena, which depend on the chemical nature of the admixtures. For all types of admixtures like VMA or superplasticizers [6], the viscosity of the interstitial liquid is largely increased and thus the bleeding or filtration rate is decreased. For cellulose ethers, another phenomenon is involved: the formation of aggregates of polymeric particles that plug part of the cement grain porosity [7]. Cellulose ethers tend to form aggregates during their dispersion due to hydrophobic interactions [7,8]. The particles' pore plugging induces a decrease in the water transport properties of the cement matrix. The size of these aggregates increases with the cellulose ether dosage and may reach more than a tenth of a micron [7–9]. It appears that this phenomenon predominates when the polymer dosage is higher than a critical dosage known as the overlap concentration [10,11].

This study focused on cellulose ethers and more precisely on the use of permeability measurements to assess their efficiency in improving the water retaining properties of fresh concrete. Permeability measurements were used to quantify the liquid filtration rate under a given pressure gradient. The device used to determine permeability consisted of a constant head measurement apparatus as described in Picandet et al. [12] and used in other studies [12,13].

This technique was used to estimate the hydraulic conductivity (here simply referred to as permeability) of fresh cement pastes. The permeability is very useful in evaluating the interstitial fluid transport properties as it links the liquid flow rate to the pressure gradient. This parameter is used to predict the amount of bleed water using consolidation theory [14–18] and to give drainage criteria for various concrete casting and pre-casting procedure [19].

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The efficiency of cellulose ethers in improving concrete stability is often determined using empirical tests that do not involve material parameters (imbibition, sieve stability test…[7]). It is therefore of value to use an apparent permeability coefficient that better describes the effectiveness of the cellulose ethers for improving water retaining properties.

Firstly, this paper describes the adaptation of the permeability measurement device to cement pastes containing cellulose; this adaptation was necessary to prevent plugging of the device filters due to the formation of polymer aggregates. Two tests were then simultaneously carried out: permeability measurements on cement pastes and rheological measurements on the interstitial fluid before and after its percolation through the cement pastes. The permeability measurements were used to evaluate the apparent permeability and apparent viscosity; these were then compared with the results obtained from the rheological measurements.

The comparison of the apparent viscosities (from permeability measurements and from rheological measurements, before and after percolation) yielded the quantity of adsorbed polymer on cement grain surface. Moreover, the amount of CE in the interstitial solution of the cement suspensions has been estimated using Total Carbon Organic measurements. Both methods provide the same adsorption ratio and give information about the underlying physics involved in the improvement of the water retaining properties of cement pastes due to cellulose ethers.

Also, apparent permeabilities are reported for a range of CE dosage and have been used to evaluate the fraction of the fluid stopped due to the CE clusters bridge from the comparison of the obtained percolated volume and the percolated volume computed with the Darcy law. Finally, a statistical approach has been adapted to compute the probability that CE aggregates block the numerous sieves made by the cement particle assembly to highlight the trend of the jamming phenomenon induced by the use of CE in cement pastes.

2. Materials and sample preparation

2.1. Materials

A Cement CEM 1 52.5N CE CP2 NF from St Pierre La Cour (Lafarge, France) was used in this study. The largest grain size was less than 100 μm and the average grain diameter was approximately 15 μm; the specific density of the cement was 3.15.

CEs are polymers derived from cellulose and can be used in mortar or cement with the following derivatives: hydroxypropylmethyl cellulose (HPMC), hydroxymethyl cellulose (HEMC) and hydroxyethyl cellulose (HEC). These admixtures are known to form CE aggregates of different sizes, depending on their concentration [7]. According to the technical data sheet, 90% of the particle size is less than 180 μm. The CE used, trade name Tylose® MH 4000 P2 is a hydroxyethoxy methoxy cellulose (HEMC) supplied by ShinEtsu (Japan), having a degree of substitution (DS) of 1.6 and a molar degree of substitution (MS) of 0.15. Dynamic light scattering measurements (DLS) were carried out at a constant temperature of 25 °C using a Zetasizer nano S from Malvern Instruments. The value of the hydrodynamic radius was computed at 39.4 nm from the average of seven independent measurements on dilute solution with a dosage of 0.07% of CE in distilled water. The molar mass of the polymer M_w is 150,000 g mol^{-1}. The chemical structure of this additive is shown in Fig. 1.

2.2. Sample preparation

Cellulose ethers are soluble in water but tend to form powder lumps during dispersion in water at room temperature [7]. To ensure a complete dispersion, the CE powder was dispersed and dissolved for 2 min in a blender. The solution was then slowly stirred with a magnetic stir bar for 24 h at room temperature, in a closed recipient, until a transparent homogenous solution was obtained.

Cement pastes were prepared by mixing the previously prepared CE solution with the dry cement. Dry cement and CE solutions were firstly mixed for 30 s in a planetary Hobart mixer. The paste was then mixed by hand to ensure that no dry particles remained on the mixer wall. Finally, to obtain a homogeneous material the mixture was stirred for a further 1 min 30 s. All cement pastes tested were prepared with a water cement ratio of 0.4. The CE dosage ranged from 0.01% to 0.5% of CE to cement by weight. No sedimentation and bleeding were noticed after the sample preparation procedure.

3. Measurement procedures

3.1. Permeability measurement

A special device (Fig. 2) previously presented in Picandet et al. [20] was used for the permeability measurement of the cement pastes. This simple method consists in measuring a volume of fluid percolating through a cement paste sample located in a closed cell submitted to a pressure gradient. The cell was connected to an air pressure regulator, which had a 1 kPa accuracy. Two different filtration systems were used to avoid migration of the solid through the drainage system: i) the commonly used thin Fisherbrand® filter papers, 8 μm mesh size and 0.16 mm thick, which were located on the upper and lower sides of the sample, with a porous stone located on the lower side of the sample; ii) a 5 mm thick geotextile material filter made of entangled plastic fibers with a 200 μm mesh size. Each filtration system was firstly saturated with the interstitial fluid used to prepare the cement paste; this ensured that the percolated flow was effective at the beginning of the test. To control the height of the cement paste, the weight of the sample placed into the cell was measured before the test. The height of the sample was measured with a rule and the material which adhered to the rule was then replaced to re-establish the initial height. The cell was then vibrated to ensure that entrapped air was removed from the sample. Sample heights ranged from 2 to 6 cm depending on the cellulose ether content. For the highest CE content, the sample had to be thin enough to result in a hydraulic gradient high enough to accurately measure the percolated volume [20]. A perforated plate was carefully placed on the cement paste and the cell was filled with the percolating fluid. The fluid was the same composition as the interstitial fluid used to prepare the cement paste. Air pressure was then applied on the top of the cell and adjusted as a function of the CE content. At the end of the test, the height variation of the sample due to consolidation was measured

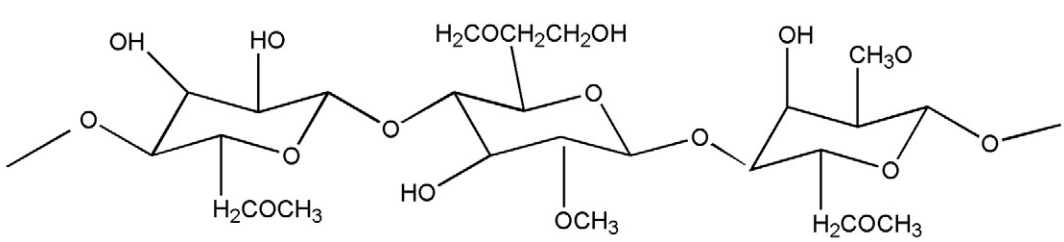

Fig. 1. Schematic structure of the CE studied.