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Thixotropy of SCC—A model describing the effect of particle packing and superplasticizer adsorption on thixotropic structural build-up of the mortar phase based on interparticle interactions

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ABSTRACT

This article considers the thixotropy of SCC mortars and the responsible mechanisms. The objective is a model describing the thixotropic structural build-up based on interparticle interactions and hydration kinetics of the fresh binder paste. In the experimental studies, the formation of thixotropic structure in SCC mortars was varied by changing the composition of the binder paste and quantified rheologically. At the same time, the surface coverage of particles by superplasticizer polymers and the particle packing in the suspension were determined to characterize interparticle interactions. Based on the results, a qualitative model as well as a calculation method were developed to describe the thixotropic behaviour. It is shown that the contribution of colloidal surface interactions and hydration reactions to thixotropy both increase with decreasing surface coverage and therefore decreasing particle separation. In addition, thixotropy increases with increasing contact interactions resulting from a higher solid volume fraction or a lower maximum packing density.

1. Introduction

The instationary rheological properties due to interparticle interactions and the hydration reactions of cement present an essential feature of cementitious suspensions. This is made macroscopically evident by thixotropy and initial setting of concrete [1–4]. Thixotropy describes the reversible reduction in yield stress and viscosity under applied shear stress with subsequent regeneration after the removal of shear stress [5–8].

Self-compacting concretes exhibit pronounced thixotropic properties [9–21]. Thus thixotropy is of great importance for the workability of SCC. In particular, properties such as the ability to fill the formwork [22], formwork pressure [9,11,12,15,16,21,23–25] or segregation resistance [18,20,26] are mainly controlled by the thixotropic properties of concrete. In addition to the relevance for SCC, a general understanding of the thixotropic structural build-up in concrete is of great importance for additive manufacturing techniques in concrete construction as shown by Perrot et al. [27] and Wangler et al. [28].

Fresh concrete is subjected to high shear rates during production, transport in the mixing vehicle and handling at the construction site, Fig. 1. During these processes, self-compacting concrete has a low yield stress τ_0 and viscosity η, and therefore good workability properties, but possibly an insufficient segregation resistance. If the actual yield stress is below a critical yield stress τ_S segregation can occur. After pouring into the formwork and placement, the fresh concrete is no longer subjected to shear. Yield stress and viscosity increase steadily within a few seconds to minutes thus hindering the segregation of the coarse aggregate.

The thixotropic (re-)generation of yield stress and viscosity after removal of shear stress is therefore of particular relevance for formwork pressure and the segregation resistance of SCC. A pronounced thixotropic structural build-up can contribute to a reduction in formwork pressure while increasing segregation resistance. Thus, the workability properties of SCC can only be controlled by considering the instationary development of the rheological properties.

In order to control the thixotropic properties, it is necessary to determine the mechanisms responsible for thixotropy in cementitious suspensions. Consequently, the present work focusses on describing the thixotropic structural build-up in the mortar phase of SCC based on interparticle interactions and the hydration kinetics in the fresh paste phase.

2. Thixotropy and interparticle interactions

2.1. Mechanisms of thixotropy in cementitious suspensions

The thixotropic properties of cementitious suspensions originate in a change in the microstructure of the suspension in dependence of shear

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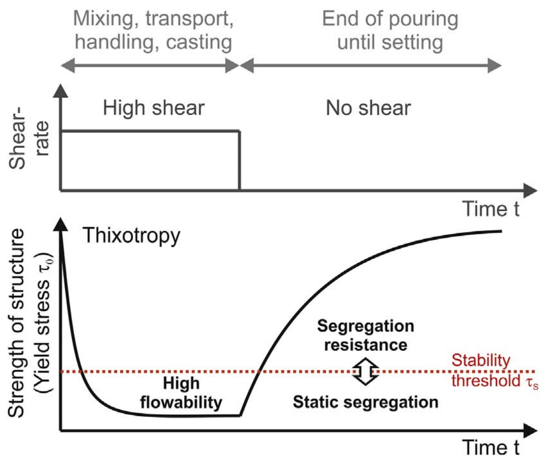

Fig. 1. Thixotropy during processing of SCC.

stress. It was therefore possible to demonstrate experimentally a decrease in size of the particle agglomerates in cementitious suspensions with increasing duration of applied shear stress and higher shear rates, [13,29]. An input of external energy leads to the progressive destruction of the microstructure and thus a reduction in viscosity and yield stress.

Once the shear stress is no longer applied, reconstruction of the microstructure occurs. In cementitious suspensions, structure formation is attributed to the flocculation of the fine flour particles of the cement and additions as well as the first hydration products [3,30]. The phenomenon of thixotropic structural build-up is controlled by both colloidal surface interactions [6] and hydration reactions [4,31–33]. According to Roussel [33] the thixotropic structural build-up may be divided into three stages.

i. Colloidal network percolation - Formation of a network due to colloidal surface interactions

The investigations of Roussel [33] show that this physical process takes only a few seconds. During this stage, the strength of the particle network is determined by the colloidal surface interactions.

ii. Rigid percolation - Formation of bridges by the nucleation of early hydration products

Owing to the nucleation of early hydration products on the particle surfaces during the dormant period, bridges form between the particles via the first metastable C-S-H phases and other early hydration products such as ettringite. This process is controlled by the early hydration reactions and can take up to 100 s, [33].

iii. Rigidification - Strengthening of the particle network

Concurrent the particle structure is further strengthened as the number and size of the bridges increase. This stage continues until the processes responsible for initial setting produce an irreversible structure.

During the first minutes, the nucleation of early hydration products induces a linear increase in yield stress with time [11,18,20,34]. However, the increase in yield stress becomes non-linear after a longer time period (before initial setting), [27,35–38]. After longer resting times, a larger fraction of the structural build-up is irreversible, i.e. non-thixotropic. This can be explained by the formation of permanent particle bridges and an increase in the solid volume fraction due to cement particle nucleation, [4,36,38].

2.2. Interparticle interactions in cementitious suspensions

The basic structure of the particle network is thus determined by colloidal surface interactions in the first seconds at no shear conditions. In addition to surface interactions, contact interactions between particles contribute significantly to the strength of the particle network. Owing to the special conditions in cementitious suspensions (i.e. the effect of hydration reactions, the high ionic strength of the aqueous phase, the comparatively low coverage of particles with superplasticizer polymers and the high solid fraction) a quantitative description of the interparticle interactions is far from trivial. However, various studies show that such an approach is applicable and relevant to cementitious materials with regard to their rheological properties, [38–45].

On applying the DLVO theory, surface forces are considered which are due to (a) repulsive electrostatic double-layer interactions, (b) attractive van der Waals interactions, and (c) repulsive steric interactions due adsorbed polymers [20,32,42,46,47]. Ion correlation forces due to divalent ions can also contribute to the attractive interaction [43,48–51]. If the ion correlation forces are neglected, the van der Waals attraction dominates the other surface interactions in cementitious suspensions and thus determines the attraction between the colloidal particles [32,43]. The maximum attraction between two particles can be described by

$$F_{att} = \frac{A_S \cdot a^*}{12(h + 2\delta_0)^2} \tag{1}$$

where A_S is the screened Hamaker constant [47,52], a^* is the radius of curvature of the "contact" points [53], h is the surface to surface separation at the contact points and δ_0 the distance between the surface and nucleus of the surface atoms [20,43,54,55]. If a superplasticizer is added to the suspension, the particle separation h is essentially determined by the degree of coverage θ of the particles with superplasticizer polymers as well as the conformation of the adsorbed superplasticizer. The interparticle separation h increases with surface coverage θ.

Contact interactions occur in a suspension with increasing solid volume fraction Φ when the particles are no longer dispersed in the liquid phase and begin to form a particle network at the percolation volume fraction Φ_{perc}. The strength of the particle network is determined by the number of particle contacts and crowding effects [32]. It is possible to describe this quantitatively from the packing of the particles which is simplified by using the solid volume fraction Φ of the suspension, the percolation volume fraction Φ_{perc} and the maximum solid fraction Φ_m of the suspension at random close packing, i.e. maximum packing density, compare [32,45,53]. The strength of the particle network increases with increasing solid volume fraction and decreasing maximum packing density. Since contact interactions and particle packing determine decisively the rheological properties of particulate suspensions, it is possible to write both the viscosity and the yield stress as a function of the solid volume fraction and maximum packing density, Eqs. (2) and (3), [43,53,56–60].

$$\eta_S \sim \left(1 - \frac{\Phi}{\Phi_m}\right)^{-\Phi_m} \tag{2}$$

$$\tau_0 \sim \frac{\Phi^2(\Phi - \Phi_{perc})}{\Phi_m(\Phi_m - \Phi)} \tag{3}$$

It is worth noting that the yield stress of cementitious suspensions depends on the percolation volume fraction Φ_{perc} as shown by Perrot et al. [45]. However, at high solid volume fractions the effect of the percolation fraction decreases and Eq. (3) can be simplified to Eq. 4, [53].

$$\tau_0 \sim \frac{\Phi^3}{\Phi_m(\Phi_m - \Phi)} \tag{4}$$