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Interactions of polysaccharide stabilising agents with early cement hydration without and in the presence of superplasticizers

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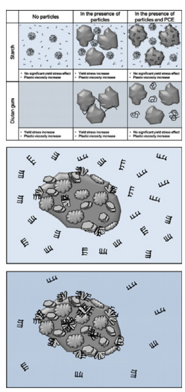
HIGHLIGHTS

- The effect of polysaccharide stabilising agents on rheology and setting was studied.
- Diutan gum affects yield stress in the liquid efficiently, while starch requires particles.
- In the presence of superplasticizers, starch and diutan gum have similar effects.
- Stabilising agents can reduce retarding effects of superplasticizer.

GRAPHICAL ABSTRACT



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ABSTRACT

Polysaccharides are incorporated into cement based systems in order to modify the rheological properties. Typically, cellulose ethers, sphingan gums, guar gum or starch ethers are applied. Depending upon their chemistry, molecular architecture, and adsorption tendency, polysaccharides interact differently with the entire cementitious system. Some stabilising agents like diutan gum mainly affect the cementitious paste; other stabilising agents like starch tend to interact with the sand fraction and even with the coarse aggregates. Cellulose and guar gum shows more diverse performances.

Typically stabilising admixtures like polysaccharides are used, when sophisticated rheological properties are adjusted. Therefore, polysaccharides are often used in combination with superplasticisers, which are added to reduce the yield stress of concrete. This can cause interactions, particularly when the stabilising agent shows a strong tendency to adsorb on particle surfaces. Adsorptive stabilising agents may reduce the amount of adsorbed superplasticisers, thus affecting both viscosity and yield stress, while non-adsorptive stabilising agents mainly affect the plastic viscosity independently of the superplasticiser. Due to the strong influence of superplasticisers on the yield stress, influences of the stabilising agent on the yield stress retreat into the background, so that their major effect is an increase of the plastic viscosity.

The paper provides a comprehensive overview of how different polysaccharide superplasticisers affect cementitious flowable systems and points out the challenges of the combined use of polysaccharides and superplasticisers. Based on rheometric experiments and observations of the hydration process, time dependent effects on the workability as well as of the hydration of cement are presented and discussed.

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1. Introduction

During the last 15–20 years, the use of stabilising admixtures in concrete has increased. In flowable systems they are often added supplementary to superplasticisers with the purpose of increasing the viscosity for better segregation resistance. Sometimes they are referred to as viscosity modifying or viscosity enhancing agents. As they typically affect both yield stress and plastic viscosity, here, they are referred to as stabilising agents (STA).

Polymeric STAs are typically based on polysaccharides [1,2]. Modified cellulose is often used as a linear polysaccharide. Through etherification, functional groups can be amended and charges can be incorporated. Other types of stabilising admixtures are sphingans such as welan gum or diutan gum, which are also linear polysaccharides like cellulose ethers. Their side chains consist of one or two monosaccharides and their backbone contains carboxylate groups providing an anionic charge [3–8]. Also guar gum STA has been matter of recent research [9,10]. Guar gum consists of a mannose backbone with randomly arranged branchpoints of galactose. For construction materials, it is typically hydoxy propylated. Another important STA type is modified starch. It can be retrieved from potatoes, cassava, maize, or rice [11,12] and needs to be modified to be cold-water soluble [13–15]. Starch is chemically similar to cellulose, however the glucose units are arranged pointing in the same direction, while the glucose units of cellulose are arranged alternating to each other at a 180° angle. Furthermore, starches consist of two types of macromolecules, the linear amylose (0%–30%) and the tree-like structured amylopectin (70%–100%). Starch based stabilising agents typically require higher dosages than sphingans to become effective [14,16,17]. However, they are much cheaper in price, which makes them attractive for the concrete market [18].

Typically, the mode of operation of STAs is explained by their capability to absorb water. The absorption capacity is assumed to increase with increasing molecular mass [19]. However, there is no linear correlation between molecular mass and water retention effect [20]. It is often assumed that most polysaccharides may be incompatible with the hydration of cement due to degrading in the high alkaline environment in the cement paste or loss of effectiveness due to shrinkage in the presence of metal ions [4,20,21], but there are also studies that show a high stability in alkaline environment for a variety of STAs [22]. Hence, the effect on yield stress and plastic viscosity can also depend strongly upon the degree of modification of the STA [9,10], which affects the alkaline stability.

The effect of STA on rheological properties of mortar and concrete is extensive, depending on the type and modification of STA. Major influences are linked to the molecular weight, the molecular architecture, and the dosage [23,24] as well as to mixture parameters such as the water cement ratio and the pore solution chemistry. For cellulose derivatives and sphingans, Khayat distinguished between different modes of operation, depending on the type and concentration: fixation of water molecules through adsorption, immobilization of water through association, and intertwining of polymers [1,25]. The influences therefore mainly take place in the liquid phase. Due to the nature of the STA effect, the effectivity of the stabilising agent is dependent upon the shear rate, and thus the shear regime can have a strong effect on the observations [26]. According to Simonides and Terpstra the stabilising mechanism of starches differs. According to the authors, starch molecules, particularly the amylopectin, spreads out between the particles, thus maintain a stable distance [27]. This means, starches affect yield stress, particularly at rest, rather than plastic viscosity. Consequently, the stabilisation mechanism thus involves the whole system, including fines and aggregates. From these observations, two stabilising modes can be distinguished: stabilisation of the fluid (sphingans) and stabilisation of the particles in the fluid (starch). Therefore, this study focuses on diutan gum and starch based STA. Cellulose and HPG are likely to act in between these mechanisms depending upon the structure and modification.

Furthermore, supplementary admixtures can interfere with STAs. In particular, the combination with adsorptive superplasticisers can cause complex interactions. Flowable concrete systems with complex rheological behaviour typically contain high amounts of SPs, typically PCE. STAs and PCEs distinguish strongly from each other in their nature. PCEs may have molar masses between 10,000 and 200,000 g/mol and typically radii of gyration between a few and 150 nm [28–33], while for different polysaccharide STAs molar masses between 300,000 and 5,000,000 g/mol and radii of gyration between several tenth and 500 nm are reported [4,12,21,34]. Admixtures such as cellulose, welan and diutan gum are known to adsorb on particles [1,4,34–37]. Also adsorption of starch was reported by Palacios et al. [38], however, in comparison to welan gum, the adsorption was low. Adsorptive STAs may reduce the amount of adsorbed superplasticisers, thus affecting both viscosity and yield stress, while non-adsorptive STAs mainly affect the plastic viscosity independently of the superplasticiser [19]. However, it is also reported that the adsorption of present superplasticisers prevents the adsorption of diutan gum on particles [4]. Since adsorption is not the sole stabilising mechanism of diutan gum, this lack of adsorption in the presence of PCE does not inhibit a stabilising effect, but it assures no negative influence on the efficiency of PCE. The tendency for STA to adsorb competitively with PCE also strongly depends on the order at which PCE and STA are added. However, there are results that suggest that adsorption always takes place to a certain amount also in the presence of superplasticisers [3]. A delayed addition of STA was found to cause less STA adsorption, since adsorption sites were already blocked by PCE [38].

Choosing a type of STA and a specific amount offers the possibility of adjusting the rheology according to specified performance criteria. However, besides rheological effects, STA also affects hydration. Particularly accelerated or retarded setting can be observed [1,16,21,39,40]. These effects are not yet fully understood. It is said that retarded setting may be caused by adsorption of STA on cement particles, modifying the precipitation of minerals [1]. Furthermore, it is reported that the grade of retardation depends upon the C_3A content of the clinker: lower C_3A content causes less retardation [24]. The individual composition of stabilisers is reported to be a factor. According to Pourchez et al. the calcium binding capacity, that causes complexation, and a possible chelation due to alkaline instability, might cause set retardation [22]. Results with cellulose ethers, however, only showed a negligible calcium binding capacity and a high stability against high alkaline media. For the sphingan diutan gum it is also reported that the double rhamnose side chains sterically shield the carboxylate backbone, thus avoiding cross-linking by calcium ions [4] so that calcium binding is supposedly not the only effect for retardation. The effects of polysaccharides on rheology and setting are not thoroughly understood at this date.

The present paper shows some significant effects that polysaccharide stabilising agents based on starch and sphingan can incorporate into flowable cementitious systems with focus on systems without superplasticiser and with superplasticiser. Starch and sphingan were chosen because of their characteristic difference of their stabilising effect. Rheometric results of cement and limestone filler pastes and self-compacting concrete (SCC) are presented. Furthermore, the influences of stabilising agents on the early hydration are discussed without and in the presence of polycarboxylate ether based superplasticizer.

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