



On the effect of calcium lignosulfonate on the rheology and setting time of cement paste



A. Colombo^{a,*}, M.R. Geiker^a, H. Justnes^{b,c}, R.A. Lauten^d, K. De Weerd^a

^a Department of Structural Engineering, Norwegian University of Science and Technology, Trondheim, Norway

^b SINTEF Building and Infrastructure, Trondheim, Norway

^c Department of Materials Science and Engineering, Norwegian University of Science and Technology, Trondheim, Norway

^d Borregaard, Sarpsborg, Norway

ARTICLE INFO

Keywords:

Lignosulfonate
Admixture
Rheology
Setting retardation
Adsorption

ABSTRACT

The effect of softwood calcium lignosulfonate, LSs, on the rheology and setting time of cement paste has been investigated. Two Portland cements with different surface area and C_3A content were used. The lignosulfonate was added either immediately with the mixing water or delayed after 10 min of hydration. The cement pastes were characterized in terms of specific surface, rheology and heat of hydration. Extracted pore solutions were analysed for free lignosulfonate concentration and for changes in elemental composition. Immediate addition of LSs increased the specific surface, but not delayed addition. Correlations were found between rheology and surface coverage by LSs, as determined by adsorption isotherms, and between the setting time and the amount of free LSs in the pore solution. An increased setting retardation upon delayed addition related to an increased concentration of Al in the pore solution.

1. Introduction

Water-reducers, or plasticizers, are commonly used admixtures for concrete. Their addition to fresh concrete allows obtaining highly fluid concrete at low water-binder ratios, improving the mechanical properties and the durability of the hardened concrete [1,2]. The plasticizer used in this paper is a low-sugar softwood calcium lignosulfonate (LSs), commonly used in concrete in dosages 0.25–0.40 mass % of binder. Lignosulfonates are polyelectrolytes derived from lignins in the pulping industry. Lignin can be derived from various sources of biomass, and lignosulfonates of different molecular weight and amount of functional groups (carboxyl groups, phenolic-OH, sulfonic groups) can be produced.

The dispersing effectiveness of plasticizers on cementitious materials is, amongst others, a function of the degree of adsorption on the surface of the cement grains and hydrates. There are two main dispersing mechanisms: electrostatic repulsion and steric hindrance. Which of the mechanisms is dominant depends on the plasticizer type. During electrostatic repulsion the adsorbed plasticizer layer renders the particle surface negatively charged, *i.e.* with a negative zeta potential. As negatively charged particles approach each other, electrostatic repulsion prevents them from forming agglomerates. Additionally, when two surfaces approach close enough for their adsorbed layers to

overlap, a steric force develops. This will contribute in hindering particles to get close enough to form agglomerates. The key parameters that govern the steric repulsion are the adsorption layer thickness and its conformation at the solid liquid interface [3]. Lignosulfonate can disperse cement particles by both electrostatic repulsion and steric hindrance, as reported by Vikan [4], amongst others.

In addition to dispersion, the interaction between cement and plasticizer can potentially lead to retardation of the setting time of the cement paste. Several mechanisms of retardation are hypothesized in the literature, the main ones being: calcium complexation, nucleation poisoning of hydrates, surface adsorption on anhydrous cement particles, and presence of sugars in the plasticizer [5–8]. Calcium complexation involves the interaction between plasticizing polymers and calcium ions in the pore solution. This would slow down the build-up of calcium supersaturation needed for hydrates nucleation. However, according to Bishop et al. [5], and Marchon and Flatt [7], amongst others, the low dosages of plasticizers generally used limit the amount of calcium potentially complexed. Thus, calcium complexation does not appear likely as a main mechanism of setting retardation of cement. As stated by Thomas and Birchall [9] and Marchon and Flatt [7] amongst others, retardation by nucleation poisoning of hydrates is where the plasticizer poisons the nuclei of CH, preventing its growth. By suppressing CH precipitation, C_3S dissolution is delayed, as the degree of

* Corresponding author.

E-mail address: alessia.colombo@ntnu.no (A. Colombo).

calcium saturation in the pore solution is unaltered. Hence, C-S-H precipitation is hindered, which leads to prolongation of the induction period of the cement paste [7]. Surface adsorption of the plasticizer on unhydrated cement grains might reduce the dissolution of the clinker phases and cause retardation. This, in turn, retards the formation of hydrates, prolonging the induction period of the cement paste [7]. Finally, the sugars contained in the plasticizers generally delay the onset of the acceleration period, by adsorbing on anhydrous phases like C_3S , but also on cement hydrates, especially CH [10]. In conclusion, the mechanisms that most likely retard the cement setting appear to be related to (1) the plasticizers poisoning the nuclei of CH, retarding C_3S dissolution and C-S-H precipitation, (2) the reduced dissolution of clinker phases, and (3) the possible presence of sugars in the plasticizer.

Lignosulfonates are known to have a retarding effect on cement hydration [11–13]. The sugars naturally contained in lignin contribute to longer setting times of cement, in particular the hexoses. The sugars can be almost completely removed, however also sugar-reduced LS can cause retardation [14]. Several studies concluded that the addition of calcium lignosulfonate changes the hydration of C_3S and C_3A [13,15–19]. According to Ramachandran [18], a strongly surface-bound calcium lignosulfonate complex could be detected for both C_3A and C_3S , which could cause retardation of C_3A and C_3S hydration. In another paper [15], Ramachandran stated that the retardation effect of calcium lignosulfonate depends on its concentration in solution and not on its proportion with respect to C_3S . C_3S hydration was delayed in proportion to the concentration, and it practically stopped for concentrations above 3 g/l of water. On the contrary, C_3S hydration was found to speed up for lignosulfonate concentrations under 1 g/l of water. Monosi et al. [16] found that, in a C_3A - C_3S system, the addition of calcium lignosulfonate led to a strong retardation in C_3S hydration, while C_3A hydration was slightly accelerated. The retardation in the C_3A - C_3S system was lower than that in pure C_3S systems. In fact, the lignosulfonate adsorption by C_3A decreases the concentration of polymer available to retard the C_3S hydration. Moreover, the arrest in C_3S hydration is partially counterbalanced by the increase in rate of hydration of C_3A , as stated by Collepardi et al. [17]. In conclusion, lignosulfonate was found to retard C_3S hydration [13,18] depending on its concentration in the pore solution [15]. C_3A hydration was found to be retarded by lignosulfonate by some authors [13,18,19], while not retarded [20] or slightly accelerated [16,17] by other authors.

As described by e.g. Flatt and Houst [21], the addition time of the plasticizer to the cement paste greatly affects the amount of plasticizer consumed by the cement paste and the extent of retardation. It has to be noted that the influence of the addition time was found to be lower for admixtures like polycarboxylic superplasticizers [22,23]. Several studies, amongst others Uchikawa et al. [24], Chiochio and Paolini [25], Aiad et al. [26], found that, at equal plasticizer dosage, the flow of cement paste prepared by delayed addition is higher than that of cement paste prepared by immediate addition. Moreover, the setting is further retarded in case of DA. Chiochio and Paolini [25] found that the optimum addition time of plasticizer to achieve the maximum workability corresponds to the beginning of the dormant period of the cement hydration without admixture. Hot [27], Hsu et al. [28], and Aiad [29] found that the optimum addition time was between 10 and 15 min after water addition.

The rheological behavior of fresh cementitious materials is generally characterized by yield stress (τ) and viscosity (μ). As described by e.g. Roussel et al., the yield stress corresponds to the energy needed to break down a network of interaction between particles in a cementitious system. Its origin lays in colloidal and contact interactions between particles. Viscosity results from hydrodynamic, colloidal and contact forces involved in the motion of the suspended cement grains. The yield stress is often considered as the most relevant parameter to describe workability and the ability of a material to properly fill a mold under its own weight. However, the viscosity also seems to be a very relevant parameter to describe cement or concrete workability,

especially for systems with low water-binder ratio [30,31]. Plasticizing admixtures can change both yield stress and viscosity by adsorbing on cement particles and changing the flocculation state of cement paste [31].

The subject of this paper is to investigate the effect of LSs on the rheological properties and setting time of two Portland cements with different physical and chemical properties (e.g. surface area, C_3A content). The samples were studied both by adding the lignosulfonate immediately with the mixing water (IA) and by adding it after 10 minutes hydration (DA). The results were compared to the adsorption isotherms presented in a previous paper by the same authors [32]. The amount of polymer consumed by the cement paste was related to the changes in rheological properties and hydration kinetics of the cement pastes due to LSs addition. Changes in the surface area of the hydrated cement particles were investigated by BET. The elemental composition of the pore solution extracted from the cement paste samples was analysed with ICP-MS. The results of this paper will contribute to a deeper understanding on the physical and chemical mechanisms behind the changes in rheological properties and setting time of cement paste with lignosulfonate.

2. Experimental

2.1. Materials

The experiments were performed on two different cements: a CEM I 52.5 N (ANL) and a CEM I 52.5 R (CX), as defined in the European standard EN197-1. The content of the main clinker phases of the cements quantified by XRD Rietveld, according to the technique described in [33], are given in Table 1. The chemical composition of the cements determined by XRF and the loss of ignition at 950 °C are reported in Table 2. The particle size distribution (d_{10} , d_{50} , d_{90}), Blaine and BET surface area, and density are given in Table 3.

A sugar-reduced softwood calcium lignosulfonate (LSs) was used as plasticizer. Its mass weighted molecular weight (M_w), as measured with gel permeation chromatography (GPC), was 29,000 g/mol and the number weighted molecular weight (M_n) was 2100 g/mol, giving broad molar-mass dispersity (\mathcal{D}_M) equal to 13.8. The molar-mass dispersity, also called polydispersity index, is defined as the ratio between M_w and M_n [34]. Additional physical and chemical properties of the lignosulfonate are listed in Table 4. For the lignosulfonate used in the present investigation, the sugars were removed from the polymer molecule by fermentation and resulting alcohol by distillation. The LSs was dissolved in deionised water to concentrations varying from 1 to 45% to ease dosing, and the water content was included in the calculation of the water-to-binder ratio (w/b).

Table 1
Main phases in cement ANL and CX from XRD-Rietveld analysis.

Phase composition (mass %)	ANL	CX
Alite	60.5	54.3
Belite	14.2	18.8
Aluminate cubic	1.3	4.7
Aluminate orthorhombic	0.9	2.4
Ferrite	14.0	6.5
Periclase	0.4	1.1
Quartz	0.3	–
Calcite	3.2/3.8 ^a	3.6/3.7 ^a
Portlandite	1.1/1.4 ^a	2.6/2.5 ^a
Anhydrite	–	2.1
Hemihydrate	2.6	1.8
Gypsum	1.0	–
Arcanite	–	0.6
Aphthalite	0.4	0.7
Thenardite	–	0.8

^a Results obtained with TGA analysis.

Download English Version:

<https://daneshyari.com/en/article/5437040>

Download Persian Version:

<https://daneshyari.com/article/5437040>

[Daneshyari.com](https://daneshyari.com)