



The effect of calcium lignosulfonate on ettringite formation in cement paste

A. Colombo^{a,*}, M. 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, NTNU, Norway

^b SINTEF Building and Infrastructure, Trondheim, Norway

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

^d Borregaard, Sarpsborg, Norway



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ABSTRACT

The effect of a softwood calcium lignosulfonate, LSs, on the ettringite formed in cement paste was investigated. Two Portland cements, mainly differing in surface area and C₃A content, were used. The effect of LSs addition time was studied, by adding either the LSs immediately with the mixing water or after 10 min of hydration. After 30 min of hydration of both cement pastes, the immediate addition of LSs caused the formation of numerous small ettringite crystals. The ettringite crystals had similar shape in pastes with and without LSs addition: cubic or cuboidal shape with length between 0.1 and 0.4 μm. These small particles caused an increase in surface area, which in turn increased the LSs adsorption by the cement paste. This could potentially lead to incompatibility issues between cement and plasticizer.

1. Introduction

Water-reducers, or plasticizers, allow obtaining highly fluid concrete with low water-to-binder ratios, additionally improving the mechanical properties and the durability of the hardened concrete.

In this paper, a low-sugar softwood calcium lignosulfonate (LSs) is investigated. LSs is commonly used in concrete in the dosage of 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, which allows producing lignosulfonates with different molecular weight and amount of functional groups, as explained by Gelardi et al. [1], amongst others.

Amongst the clinker phases, C₃A is the one with the highest hydraulic reactivity, reacting immediately upon water contact. In the presence of gypsum, the first stable hydration product from C₃A is ettringite (AFt). Ettringite forms as long as there are enough sulfate ions in solution. When gypsum is depleted, ettringite will start further reacting with the residual C₃A, forming monosulfoaluminate hydrate (AFm) [2].

The dispersing effectiveness of a superplasticizer on cementitious materials is, amongst others, a function of its degree of adsorption on the surface of cement grains and hydrates. The two main dispersing mechanisms are electrostatic repulsion and steric hindrance. The plasticizer type determines which of the two mechanisms will be dominant. During electrostatic repulsion the adsorbed plasticizer layer renders the particle surface negatively charged. 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.

The amount of substrate surface which is covered by adsorbed polymer is referred to as surface coverage. As both major dispersion mechanisms rely on surface coverage, it will be a dominating parameter with regard to the dispersing efficiency of plasticizers. In a previous paper [5], the authors showed that the rheological behaviour relates to the degree of polymer coverage of the available surface for adsorption. In particular, the achievement of high or full surface coverage was found to correspond to a drop in yield stress and viscosity of the cement paste.

The polymer is not adsorbed equally on the four main cement phases. According to Yoshioka et al. [6], a much higher adsorption occurs on aluminate and ferrite than on the silicate phases. According to Zingg et al. [7] and Plank et al. [8], the plasticizer will be adsorbed also on the cement hydrates, ettringite being the hydrate adsorbing the most.

It is known that plasticizers can cause changes in hydrates morphology, especially for ettringite. Prince et al. [9] studied a system of

* Corresponding author.

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

calcined kaolin, lime and anhydrite and found that sodium polynaphthalene sulfonate blocks the development of needle-like ettringite crystals. Instead, ettringite formed in small massive clusters. Hekal and Kishar [10] found that the size of the ettringite crystals formed in a C_3A - $CaSO_4$ system decreased as the dosage of a sodium naphthalene sulfonate-formaldehyde polycondensate increased. Cody et al. [11] synthesized ettringite in presence of a commercial lignosulfonate. They found that a large amount of ettringite formed in the form of small spherical crystals. Danner et al. [12] observed that the addition of calcium and sodium lignosulfonate led to the formation of small ettringite crystals with rounded oval shape. On the other hand, Kerui et al. [13] investigated a fly ash cement, reporting that a mixture of calcium lignosulfonate and sodium bicarbonate caused a change in ettringite formation from a large number of tiny crystals into a limited number of large needle-like crystal particles. In conclusion, generally [9–12] plasticizers have been reported to cause the ettringite crystals to be smaller in size and to deviate from the typical needle-shape, taking a spherical or cubic morphology, except for Kerui et al. [13], who found that ettringite formed in few large needle-like crystals. However, it should be kept in mind that the results might have been influenced by the fact that lignosulfonate was combined with $NaHCO_3$.

Several studies reported that also the amount of formed hydrates might change upon plasticizer addition. Zingg [14] found that some polycarboxylate-type superplasticizers (PCE) had a limited influence on the amount of ettringite formed in Portland cements. This was confirmed by Dalas et al. [15], who found only a slight decrease in the amount of ettringite precipitated in a C_3A - $CaSO_4$ system, though its specific area was strongly increased. Hekal and Kishar [10] investigated a similar system of C_3A and $CaSO_4$ reporting that the ettringite formation was increasingly retarded in the first 24 h of hydration as the dosage of a sodium naphthalene sulfonate-formaldehyde polycondensate increased. Lignosulfonate was, on the other hand, found to accelerate ettringite formation in cement by Bishop and Barron [16]. The amount of ettringite formed by a fly ash cement was found to increase in presence of a mixture of calcium lignosulfonate and sodium bicarbonate by Kerui et al. [13]. Danner et al. [17] investigated three different cements in combination with a calcium-lignosulfonate and reported that the initial formation of ettringite was accelerated. In conclusion, the amount of ettringite formed has both been observed to increase and decrease depending on the plasticizers used.

The aim of this paper is to understand the effect of a calcium lignosulfonate (LSs) on the formation of ettringite in Portland cement paste. Two Portland cements mainly differing in surface area and C_3A content were chosen. The effects were studied both by adding the lignosulfonate immediately with the mixing water (IA), and by adding it after 10 min of hydration (DA). Changes in composition and amount of cement hydrates after 30 min of hydration caused by the addition of the LSs were investigated with thermogravimetric analysis (TGA) and X-ray powder diffraction (XRD). The effect of LSs on the hydrates of hardened cement was also studied with TGA after 28 days of hydration. The hydrates morphology was observed with scanning electron microscopy (SEM) after 30 min of hydration, and their chemical composition was analysed with energy dispersive spectroscopy (EDS). The elemental composition of the pore solution extracted from the cement paste samples after 30 min of hydration was analysed with inductive coupled plasma – mass spectroscopy (ICP-MS). In addition, the effect of LSs on the solubility of the different calcium sulfates, i.e. anhydrite, hemihydrate and gypsum, was investigated by determining the soluble Ca and S by ICP-MS in calcium sulfate suspensions containing increasing LSs dosages. The adsorption isotherms and BET measurement presented in a previous paper by the same authors [18] were combined with the new results reported in the present paper. In the present paper, the authors succeeded in observing the morphology of ettringite in real cement paste with and without the LSs, and not as a pure synthesized phase. The results of this paper are connected to those discussed in a previous paper by the same authors [5], which was more focused on the

Table 1

Main phases in cement ANL and CX from XRD-Rietveld analysis^a: results obtained with TGA analysis.

Phase composition (mass % of powder)	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

effect of LSs on setting time and rheology of cement paste. The results of the present paper give further insight on the effect of LSs on the formation of cement hydrates, and thus contribute to a deeper understanding of the mechanisms behind the interactions between lignosulfonate and cement paste.

2. Experimental

2.1. Materials

The experiments were performed on two different cements: a CEM I 52.5 N (ANL) produced by Norcem, and a CEM I 52.5 R (CX), produced by Cemex, as defined by the European Standard EN197-1. The content of the main clinker phases of the cements quantified by XRD Rietveld, according to Le Saoût et al. [19], 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 surface area, density, and BET surface area are given in Table 3.

A sugar-reduced softwood calcium lignosulfonate (LSs), produced by Borregaard, was used as plasticizer. Fractionated lignosulfonate samples with low polydispersity indices and known molecular weight were used as calibration standards for determination of molecular weight. Its weight average molecular weight (M_w), as measured with gel permeation chromatography (GPC), was 29,000 g/mol and the number average molecular weight (M_n) was 2100 g/mol, giving broad molar-mass dispersity (\mathbb{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 [20]. 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 product by

Table 2

Chemical composition of the cements given by the producers.

Chemical compound (mass % of powder)	ANL	CX
CaO	62.7	64.0
SiO ₂	20.6	20.0
Al ₂ O ₃	4.4	4.6
Fe ₂ O ₃	3.5	2.6
SO ₃	3.3	3.6
MgO	1.6	2.4
K ₂ O	0.4	1.0
Na ₂ O	0.3	0.2
TiO ₂	0.2	0.2
P ₂ O ₅	0.2	0.2
LOI (%) 1000 °C	1.6	1.7
Sum	97.2	98.9

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