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Article

Effect of Plasticizer on Hydration and Rheological Behavior of Cement Pastes

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Abstract: Lignosulfonate-based admixtures (LS) obtained from sulfite pulping processes were the first dispersants added as a water-reducer to concrete. Less effective than the latest superplasticizers, the low cost and low environmental footprint of LS continue to allow these materials to compete in the building and construction market. In addition to the dispersion effect, LS is known to retard cement hydration. The aim of this paper is to characterize the effect of LS on the hydration and rheology of cement paste. The effect of the time at which the LS is added, either by immediate addition or after ten minutes of hydration, has been investigated. It appears that the immediate addition of LS is less effective than the delayed addition when it comes to dispersion of cement, likely due to the initial ettringite formation.

Keywords: lignosulfonate; yield stress; hydration; cement paste; ettringite



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1. Introduction

General use of admixtures allows the formulation of concrete that was previously impossible to produce. These types of concrete are, for example, of fluid consistency, although they have a low water-to-binder ratio (high-performance concretes, HPC) [1–3], or of a fluid consistency during casting, and are then cohesive as soon as they are poured into place (self-compacting concretes, SCC) [3,4]. This control of fresh behavior is based on the addition of admixtures (water-reducers or plasticizers, high-range water reducers or superplasticizers), which improves the workability of concrete by improving the dispersion of the cement particles. In fact, these admixtures can reduce the water content and thus enhance mechanical strength and durability, or they allow for increasing the fluidity of concrete without changing the water content.

Lignosulfonate-based admixtures (LS) were one of the first dispersants added as a water-reducer to concrete and have been used since the 1930s [5,6]. LS are water-soluble anionic polyelectrolyte polymers derived from the wood pulping industry. They allow for reducing the water content of cement by 5 to 15% [7,8]. They act via adsorption at the solid–liquid interface and induce electrostatic repulsion and steric hindrance [9,10], which enhance the dispersion of particles. Less effective than the latest superplasticizers, but with a more favorable environmental footprint [8,11], the low cost of LS continues to allow these materials to compete in the building and construction market.

Besides the dispersion effect, LS has an influence on cement hydration [12,13]. They are known to retard cement hydration [7,14,15], and have been used as retarders for many years. However, the real influence of lignosulfonate (LS) is difficult to establish due to complex interactions with cement. The first studies focused on simplified systems such as the tricalcium aluminate system (C₃A) [14–17]. By comparing purified and commercial lignosulfonate, Milestone [15] and Chatterji [17] concluded that the retarding effect was mainly due to the sugar acids such as aldonic acids present in the commercial LS. Sugar

acids inhibit the hydration of tricalcium aluminate (C_3A) of which a large amount remains unhydrated after 50 days of hydration [15]. However, at low concentrations, Ramachandran [18] found that the purified lignosulfonates were almost as effective as the unpurified material. As observed by Ramachandran and Feldman [14], at low concentrations, LS inhibits the hydration of C_3A via the formation of a C_3A -LS complex on the surface. At higher concentrations, there is the precipitation of a gel containing excess calcium and aluminate ions. The effect of lignosulfonate on the hydration of C_3S alone and in the presence of C_3A has been examined by Monosi et al. [19]. They found that in the presence of 0.3% LS, the C_3S hydration is strongly retarded, whereas by mixing 20% C_3A with C_3S , the retarding effect is significantly lower. Recent studies [12,20,21] showed that the hydration of C_3S and C_3A is retarded in the presence of LS. LS influences the sulfate phase in the system: It accelerates the initial dissolution of gypsum and the early aluminate reaction and retards the second formation of ettringite.

The mechanisms behind the retarding effect remain unclear, and several hypotheses have been formulated to explain it [7,9,13,20–24], such as the complexation of calcium ions, the perturbation of hydrate nucleation, surface adsorption, protective layer formation, and the dissolution–precipitation mechanism. Recently, Recalde Lummer and Plank [23] proposed a mechanism able to explain the retarding effect of lignosulfonate. According to these authors, the retardation of cement hydration in the presence of lignosulfonates is due to the formation of large agglomerates of LS-calcium ions complexes in the pore solution. By precipitating on the surface of the anhydrous cement, these agglomerates lead to the development of a diffusion barrier formed by a polymer layer of low permeability, which hinders the water accessibility of the non-hydrated cement.

In conclusion, lignosulfonate was found to retard cement hydration. According to Ramachandran et al. [25], the retarding effect of lignosulfonate depends on the water-to-cement ratio, temperature, the composition of cement, and the time at which LS is added. This last point is important and has been the subject of several studies [13,26–30]. Flatt and Houst [28] found that the effect of time of addition depends on the type of polymer and should have an influence on workability. It can affect the polymer consumption of cement paste and thus the retarding effect. According to Chiochio and Paolini [27], maximum workability is obtained when the admixture is added at the beginning of the induction period of cement hydration. Aiad [26] and Hsu et al. [29] suggest that the optimal addition time of the superplasticizer in concrete should be between 10 and 15 min, which corresponds to the beginning of the induction period of cement hydration. Recently, Colombo et al. [13,24,31] investigated LS consumption of two different types of cement where LS was added either with immediate (IA) or delayed (DA) addition after 10 min of hydration. They also studied the impact of LS addition on rheology and hydration. They observed a lower efficiency of the LS to improve cement paste fluidity in the case of IA compared to DA. They ascribed this to the formation of finely dispersed additional ettringite during the first 10 min of hydration when LS was added by IA. The additional ettringite was not observed for DA or in the absence of LS. The additional finely dispersed ettringite led to a considerable increase in the available surface for LS adsorption, thereby causing a considerable increase in LS consumption in the case of IA and a lower efficiency compared to DA.

The effect of LS on the early development of hydration during the dormant period remains unclear and requires deeper investigation. Furthermore, the early development of hydration can strongly affect the rheological behavior of cement paste and the effectiveness of LS. According to the literature review, the time at which LS is added appears to be a key parameter. The aim of this paper is to examine the effect of LS on the early development of hydration by varying the time at which it is added. Then, the impact of early hydration on the dispersive action of LS is investigated. The time at which the lignosulfonate (LS) is added is investigated through immediate (IA) and delayed (DA) addition (at 10 min of hydration). The development of hydration is examined using the calorimetry

test and in situ XRD. The dispersive action is assessed by rheological measurement and consumption of LS.

2. Materials and Methods

2.1. Materials

The experiments were carried out using ordinary Portland cement CEM I 52.5 R produced by Cemex (called CX) with a density of 3.1 g/cm³. The chemical composition of this raw material is given in Table 1.

Table 1. Composition of the raw material in [%wt].

Chemical Analysis ^a	CX	Phase Composition ^c	CX
Na ₂ O	0.20	alite	54.3
MgO	2.40	belite	18.8
Al ₂ O ₃	4.60	aluminate cubic	4.7
SiO ₂	20.00	aluminate ortho	2.4
P ₂ O ₅	0.23	ferrite	6.5
SO ₃	3.60	periclase	1.1
K ₂ O	1.00	calcite	3.6/3.7 ^b
CaO	64.00	portlandite	2.6/2.5 ^b
TiO ₂	0.25	anhydrite	2.1
Fe ₂ O ₃	2.60	hemihydrate	1.8
		arcanite	0.6
		aphtthalite	0.7
		thenardite	0.8
CO ₂ ^b	1.6		
Ignition loss (900 °C) ^b	3.3		

^a XRF data, ^b TGA, ^c XRD Rietveld.

The particle size distribution is measured with a diluted cement suspension ($w/c = 3.2$) using a laser granulometer (LS 13,320—Beckman–Coulter, Brea, CA, USA) with an adapted optical cement model (real part of the refractive index of 1.7 and imaginary part of 0.1). These measurements were completed by SEM observations using an FEI Quanta 200 FEG scanning electron microscope and specific surface measurements using Micromeritics Tristar II Plus 3030. The Blaine-specific surface of the cement is 5400 cm²/g, and the BET-specific surface is approximately 1.35 m²/g.

SEM observations show an angular morphology of the cement particles, which can be expected as it is ground. The laser granulometric measurements show a particle size distribution ranging from 0.07 to 52 μm with a median particle diameter of 13 μm.

Two plasticizers were used. The first one was a standard calcium lignosulfonate (LS1) and the second one was a modified calcium lignosulfonate (LS2). The properties of these plasticizers are given in Table 2.

Table 2. Properties of plasticizers.

Plasticizer	Mw (g/mol)	Mn (g/mol)	Total Sugar (%)
LS1	29,000	2100	8.3
LS2	6400	500	14.8

2.2. Sample Preparation

Samples are prepared with the same procedure as Colombo et al. [13]. Cement (278.8 g) and water were mixed in a Braun mixer MR530 (intensity 6) with a water-to-cement ratio w/c of 0.4, according to the following sequence: 30 s mixing, scraping the mixer walls to homogenize the mix, 5 min resting, and 1 min mixing. The effect of the time at which LS is introduced was investigated by applying two different procedures: Immediate addition of LS with the mixing water (IA) and delayed addition of LS at 10 min of hydration (DA).

For IA, the binder was mixed with deionized water containing lignosulfonate according to the above procedure. For DA, the binder and 85% of the total water were mixed according to the following mixing procedure used by Colombo et al. [13]: 30 s of mixing and scraping the mixer walls to homogenize the mix, followed by 10 min of resting. LS and the remaining 15% of the needed water were then added to the mix, which was mixed for 1 min.

Different amounts of LS were used: 0–0.2–0.4–0.6–0.8–1.0–1.2–1.5 mass% of cement.

2.3. Isothermal Calorimetry

Hydration kinetics of the cement pastes was explored with an isothermal calorimeter TAM Air from TA Instruments. Pastes were prepared by external mixing at $w/c = 0.4$ and then introduced into the device. The calorimeter measures the difference in heat flow between 5 g of cement paste and a reference (deionized water) at 25 °C. Cement hydration is an overall exothermic reaction, therefore the rate of the heat of the reaction or thermal power curves can provide information regarding the different stages of the hydration reactions of ordinary Portland cement [32]. The results are presented in Section 3.1.

2.4. X-ray Diffraction Analysis

Some admixed cement pastes were also analyzed by X-ray diffraction (XRD). First, 30 min after the end of the mixing process, cement hydration was stopped by immersing the paste in isopropanol with a volume ratio of 1:5. After centrifugation at 10,000 rpm for 5 min and removal of the solvent by evaporation with ether under an extractor hood for the night, the hydrated cement powder was recovered. Then, it was analyzed with a diffractometer BRUKER D8 Advance (Cu $K\alpha$, $\lambda = 1.54 \text{ \AA}$) with a LYNXEYE detector. The angle of the incident beam varies between 5° and 70°, with a measurement duration of 30 min and a step size of 0.01°. The software X'Pert High Score was used to process diffraction patterns, and crystals were identified using the PDF (Powder Diffraction File) database. The results are presented in Section 3.1.

2.5. Consumption of Lignosulfonate LS

The amount of consumed LS is determined by the depletion method [33] using total organic carbon measurements. This amount is calculated by subtracting the measured amount of LS remaining in the pore water from the total amount of LS initially introduced. After the mixing process, the pore water was extracted by centrifugation at 7000 rpm for 10 min and the supernatant liquid was filtered with a 0.45 μm PTFE filter. Then, 30 min after the water addition, a volume of 4 mL of the supernatant was diluted with 16 mL of deionized water and acidified with drops of concentrated hydrochloric acid. The change in the pore water volume due to the bound water was not considered. Measurements were then carried out using the Vario TOC cube from Elementar. All the tests were performed in triplicate. The TOC analyzer was calibrated with neat cement paste to account for organic carbon in the cement due to grinding agents. The results are presented in Section 3.2.

2.6. Rheological Protocol

Rheological measurements were carried out using an experimental Couette rheometer AR2000 ex from TA instruments equipped with a four-blade vane geometry (internal diameter = 28 mm, the outer cup diameter = 30 mm). The geometry constants were calibrated using the Couette analogy [34].

The performed measurement procedure started 5 min after the end of the mixing process. It consisted of two steps (Figure 1). The first step (stress growth) allowed measuring the yield stress [35,36]. The yield stress is the minimum shear stress required to induce the flow. It is a very relevant parameter to describe the effect of superplasticizers on workability [37]. The stress growth procedure starts with a strong pre-shear (100 s^{-1} during 30 s) followed by a resting time of 120 s, and then a small rotational velocity corresponding to a shear rate of 10^{-2} s^{-1} is applied to the vane geometry for 200 s. On the shear rate vs. strain curve obtained

for the yield stress measurement, the stress increases linearly with the strain to reach a peak followed by a slow decrease corresponding to the structural breakup of the suspension [37]. The peak defines the static yield stress. The second step consists of the measurement of viscosities by applying a constant shear rate (100, 50, and 10 s^{-1}) during the time required to reach steady-state flow. The results are presented in Section 3.2.

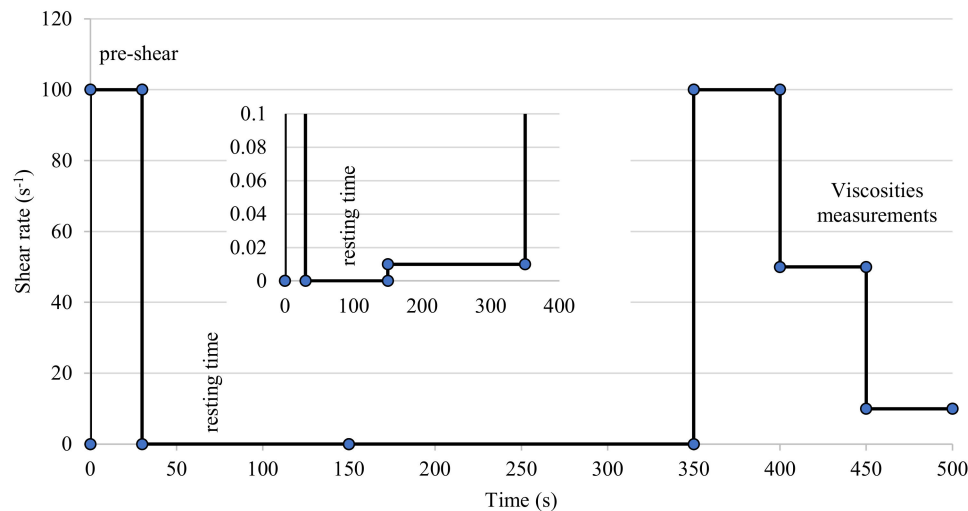


Figure 1. Protocol of rheological measurements.

Furthermore, the viscosity at shear rates of 50 ($1/\text{s}$) was measured as a function of time. The results are presented in Section 4.

3. Results

3.1. Effect of LS and Addition Time on Hydration

The aim of calorimetry tests is to investigate the effect of two lignosulfonates (LS1 and LS2) and their addition time on the hydration kinetics of CX cement paste. The heat development as a function of time for the studied systems is shown in Figure 2. These thermal power curves show the rate of the heat of hydration at 20 °C [7]. The typical thermal curve of ordinary Portland cement is similar to that of CX cement without LS (Figure 2). In general, this curve exhibits several periods: The initial period, the induction period, and the main period. During the main period, two peaks of the heat of hydration occur. The first peak corresponds to the silicate reaction, while the second peak, detectable as a shoulder of the main peak, can be attributed to the acceleration of the aluminate reaction (dissolution of C_3A and the final formation of ettringite) [38]. The position of the second peak depends on the sulfate content of the cement and takes place after sulfate depletion [39].

For cement paste without LS, the silicate peak occurs earlier (6 h) than for cement paste with LS (up to 24 h for cement paste with 1.5% LS2). This peak is not even observed after 48 h in cement paste with 1.5% LS1. This indicates that adding LS1 and LS2 retards the silicate reaction. In addition, the measured thermal power in the main peak increases for LS dosages of 0.4 and 1% and decreases for an LS dosage of 1.5%. It should be noted that for a low dosage (0.4% LS in Figure 2), no shoulder of the main peak is observed. The only peak detectable could be attributed both to the silicate and aluminate reactions. In fact, these reactions could occur simultaneously, leading to a single peak of heat release (Figure 2).

In addition to its effect on the silicate reaction, LS retards the occurrence of the sulfate depletion peak. The second formation of ettringite seems to be delayed as the LS dosage increases. The time between the main peak and the shoulder is also influenced by the presence of LS.

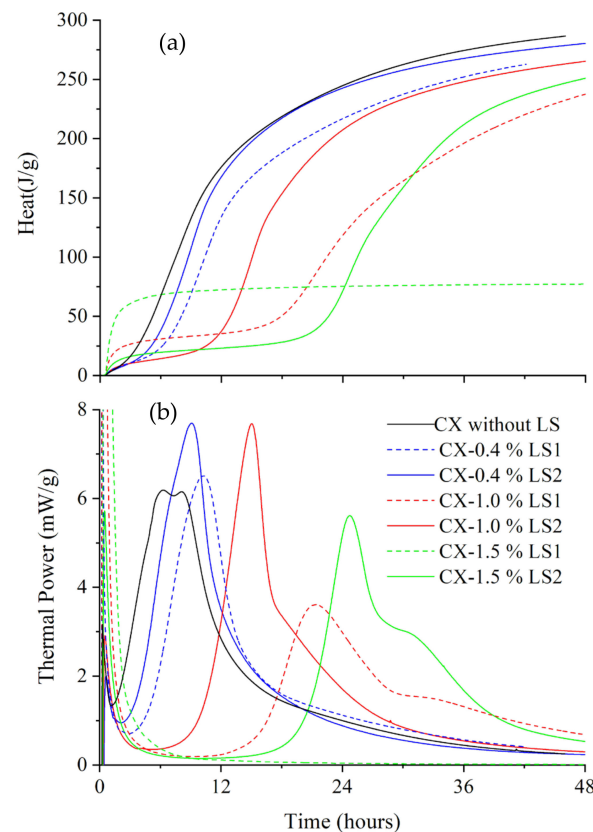


Figure 2. Heat development between 0 and 48 h for the CX cement with immediate addition (IA) of LS1 and LS2: (a) Cumulative heat, (b) thermal power.

These results show that the addition of LS retards both the silicate and aluminate reactions. During the main period, the presence of LS strongly retards the dissolution of C_3A and the formation of ettringite. Many observations [12,15,17,19] confirm that lignosulfonate retards cement hydration, and several hypothesized mechanisms of retardation were proposed [7,9,20–23].

In order to discuss the retarding effect, the setting time was determined according to the ASTM standard C1679-14, which defines the setting time as the time to reach half of the average maximum power of the main hydration peak in the calorimetric curve. The setting retardation time was calculated as the setting time measured with calorimetry, from which the setting time of the sample without the admixture was subtracted. The setting retardation as a function of the LS dosage is shown in Figure 3. The delay induced by the addition of LS seems to strongly depend on the LS dosage and the addition time, but very little on the kind of LS. Comparing LS1 and LS2, no significant difference can be observed for dosages less than 1%. The differences appear for an LS dosage of 1.5% (Figure 3).

Concerning the effect of the time at which the LS is added, Figure 3 shows that the delayed addition of LS induces more retardation. For the delayed addition, the retarding effect is more pronounced as the LS dosage increases. It is well known that the retarding effect is affected by the addition time of admixtures [27,30,32]. According to Taylor [7], the retarding effect is more pronounced if the polymer is added 2–4 min after mixing because the aluminate has, by that time, reacted to some extent with the gypsum and less polymer is consumed. Flatt and Houst [28] emphasize that delayed addition can reduce the polymer consumption by the cement components and thus the formation of the organo-mineral phase. In fact, polymers are generally trapped in the organo-mineral phase and become less effective. Aitcin [40] noted that the delayed introduction of the polymer provides time for the sulfate ions, originating from, e.g., gypsum, to impede the C_3A reaction.

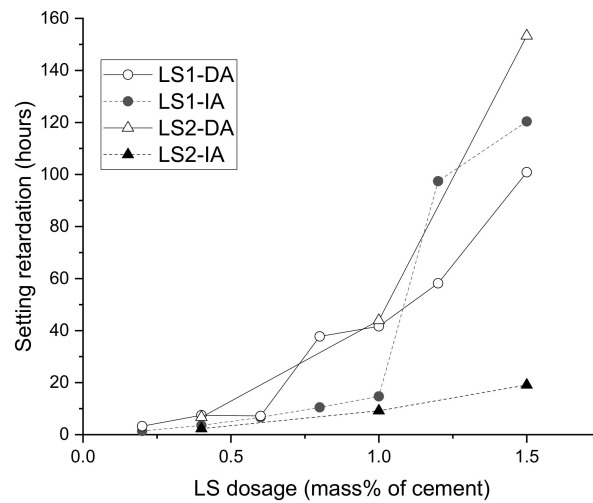


Figure 3. Setting time retardation as a function of LS dosage with immediate and delayed addition.

The effect of the addition time of lignosulfonate on the cement after 30 min of hydration was investigated with X-Ray Diffraction (XRD). The analysis was performed on CX cement pastes with different dosages of LS2 both for immediate addition (IA) and delayed addition (DA). Figure 4 shows the XRD patterns obtained. It can be observed that the peaks corresponding to ettringite in the cement paste without LS after 30 min of hydration are less pronounced than in cement pastes with LS. The addition of LS leads to an increase in ettringite formation. Furthermore, it could be noted that the peak corresponding to ettringite is much higher for immediate addition than delayed addition, which indicates more ettringite formation. The peak (at $2\theta = 25.7^\circ$) representing anhydrite remains roughly constant. By analyzing these results it appears that immediate addition leads to a larger amount of ettringite in the paste after 30 min of hydration. This is in line with Colombo et al. [13] and Danner et al. [12] who found that the presence of LS in the cement paste accelerates the initial formation of ettringite.

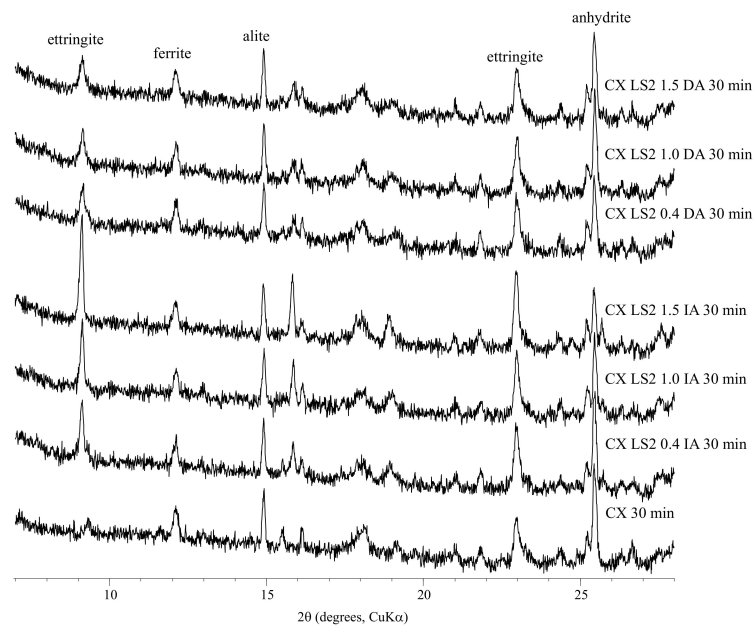
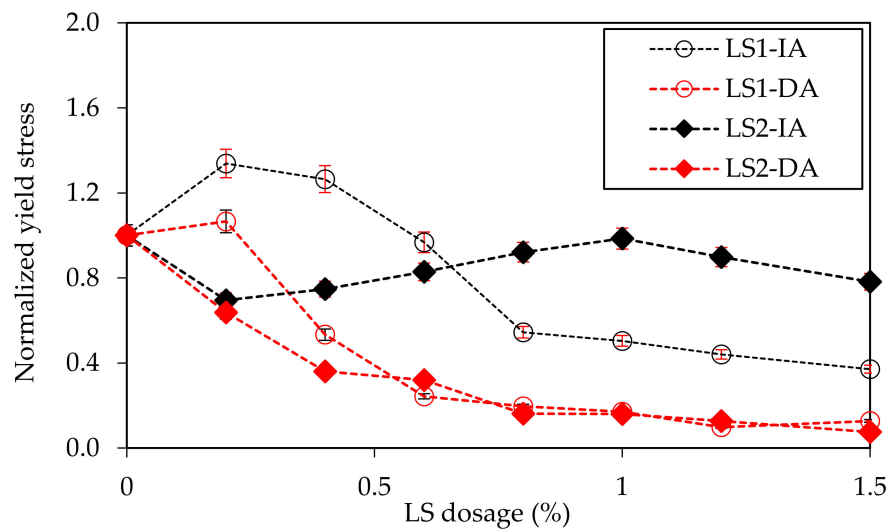


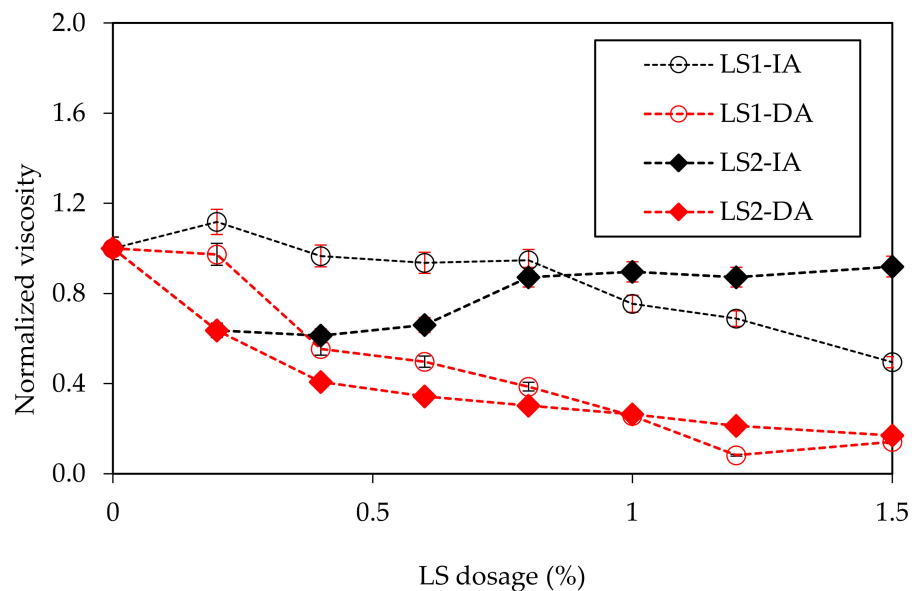
Figure 4. X-ray diffraction patterns for CX cement pastes with 0.4, 1, and 1.5 of LS2 (mass % of binder) with IA or DA after 30 min of hydration.

3.2. Effect on Rheological Behaviour

As shown in Figure 5, the normalized yield stress (the reference is the cement paste without LS) and viscosity measured at a shear rate of 100 s^{-1} decrease with increasing LS dosage, except for LS2 with immediate addition. It should be noted that for LS with both IA and DA, the normalized yield stress and viscosity increase for a dosage of 0.2%. The measurements have been repeated several times. Moreover, the addition time seems to have a considerable impact. The decrease in both the yield stress and viscosity, and thus the increase in fluidity, is more significant with delayed addition. Concerning the effect of the type of LS, LS1 appears to be more efficient than LS2 with immediate addition, but no marked difference is observed between these polymers with delayed addition.



(a)



(b)

Figure 5. Normalized yield stress (a) and viscosity (b) (at 100 s^{-1}) as a function of LS dosage.

Therefore, if we consider the consumption curves in Figure 6, it is clear that the significant decrease in yield stress (or viscosity) concerns the samples that reached a plateau.

In fact, reaching a plateau could signify that the surface of cement particles is “completely” covered with LS. This leads to a better dispersion of cement particles, visible in the decrease in both yield stress and viscosity. It is well known that the optimum dispersion is reached when the total surface of cement particles is covered by the plasticizer (at the plateau) or sometimes before the plateau in the adsorption isotherm [41].

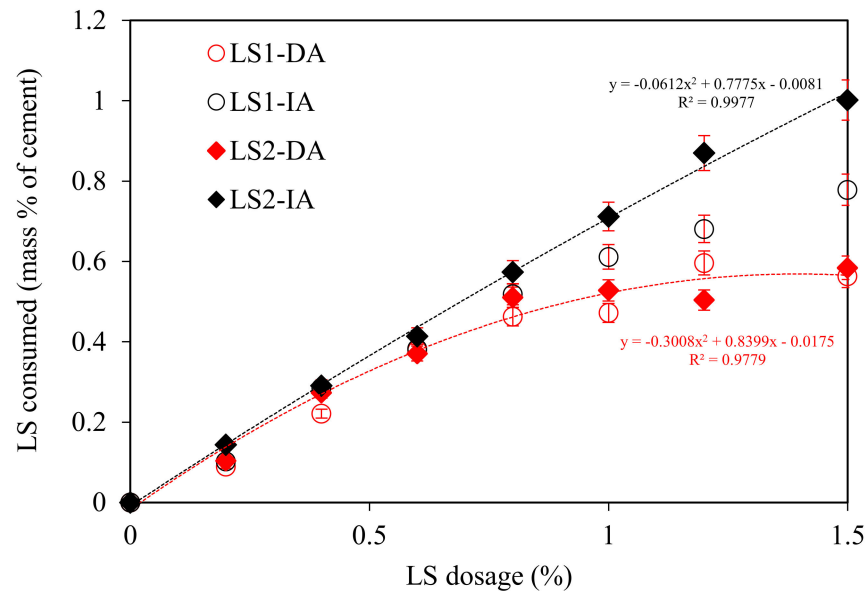


Figure 6. Amount of consumed lignosulfonates as a function of dosage.

It could be argued that the continuous consumption curve and the increase in yield stress with immediate addition (especially for LS2) could be related to the amount of ettringite in the case of IA (Section 3.1, Figure 4). This has also been observed in other studies [13,31,42] where the formation of a large amount of ettringite leads to a loss of fluidity and an increase in the surface area [31]. The accelerated formation of ettringite in the presence of lignosulfonate with the associated increase in surface area may account for the increase in normalized yield stress at some intermediate lignosulfonate dosages. In fact, there is simply an insufficient amount of dispersant in the system to properly reduce the yield stress.

4. Discussion

In addition to the retarding effect, LS was found to cause additional ettringite formation during the low activity (or dormant) period, especially when it was added immediately. In fact, in a previous article, Colombo et al. [31] found that the immediate addition (IA) of LS resulted in additional ettringite formation and an increase in the particle surface area. For delayed addition (DA), this effect was not observed. The same result is obtained in this study, as shown in Figure 4. This effect can explain the difference in LS consumption between IA and DA. In fact, as shown in Figure 6, the consumed amount of both LS1 and LS2 with delayed addition seems to reach a plateau, while no plateau is detected with immediate addition. LS1 and LS2 with IA continue to be consumed progressively with increasing dosage. These results are in accordance with the results obtained by Vikan [10] and Colombo et al. [13]. The increasing consumption observed for IA could be associated with the formation of additional surface area from the additional ettringite formed. It has to be kept in mind that the amount of consumed LS is not entirely adsorbed and also includes LS trapped in organo-mineral phases not taking part in the dispersion. Colombo et al. [31] explained the difference between IA and DA by the dissolution of C_3A , which is limited in the absence of LS by a protective hydrate layer.

From a practical point of view, the additional ettringite formation during the dormant period could also lead to a loss of workability. In order to assess this effect, viscosity monitoring was performed. For a non-reactive material (calcite), viscosity (measured at a constant shear rate) should slightly change. As shown in Figure 7, the viscosity of cement paste remains constant for 5 to 15 min after water addition. It can be noted that the viscosity of cement paste with the immediate addition of LS is greater than that of cement paste with a delayed addition of LS. This is consistent with the results presented in Figure 5.

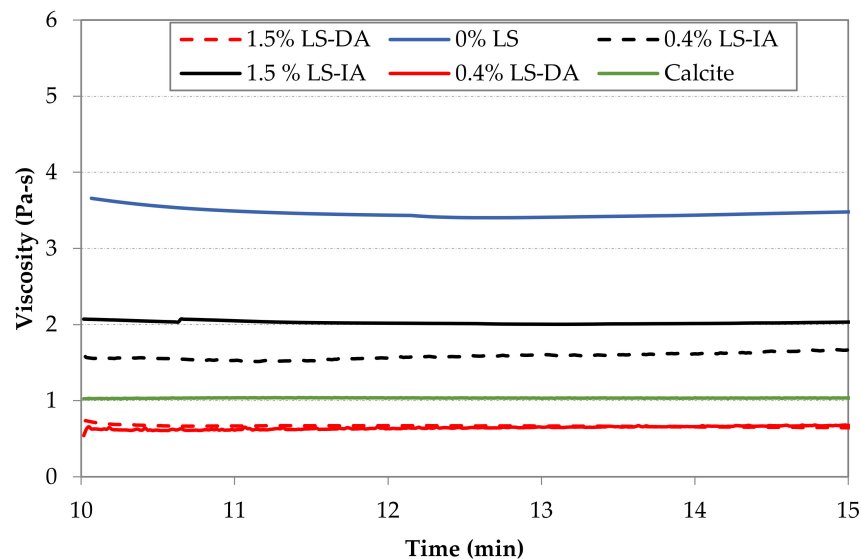


Figure 7. Evolution of viscosity measured at 50 s^{-1} . The time 0 corresponds to water/cement contact.

Furthermore, 15 min after water addition, viscosity begins to gradually increase except for cement paste with 1.5% LS with DA (Figure 8). The viscosity of calcite remains almost constant. This variation is thus due to the chemical evolution induced by hydration. In fact, during the dormant period, the formation of hydrates can lead to an increase in viscosity [42]. However, given the characterizations carried out, it cannot be concluded that this increase is due only to ettringite formation. Further investigations are required to explain the effect of chemical evolution during the dormant period on the viscosity of cement paste.

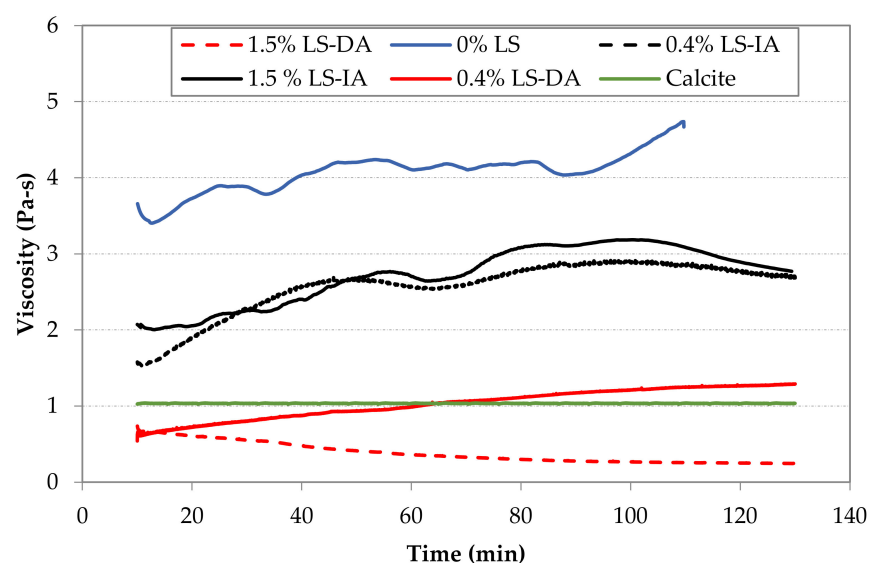


Figure 8. Evolution of viscosity measured at 50 s^{-1} . The time 0 corresponds to water/cement contact.

5. Conclusions

The impact of lignosulfonate (LS) on the hydration and rheology of cement paste has been characterized. Two types of LS with dosages of up to 1.5 mass% of cement were tested. The LS was added either with the mixing water (immediate addition) or 10 min after water addition (delayed addition).

Calorimetry results showed that the addition of LS retards both the silicate and aluminate reactions. During the main period, the presence of LS strongly retards the dissolution of C_3A and the second formation of ettringite. Moreover, according to XRD results, it appears that the initial formation of ettringite is enhanced in the presence of LS, in particular, when the latter is added immediately. The setting retardation time is more pronounced with the delayed addition of LS.

LS consumption measurements showed that for the delayed addition, the consumption plateau is almost reached at 0.8% of LS, whereas a continuous consumption of LS for immediate addition is observed. The delayed addition of LS improves particle dispersion and decreases the yield stress and viscosity more efficiently than the immediate addition. It should be noted that the maximum fluidity is reached when the available surface is almost completely covered by LS. In the case of delayed addition, the full surface coverage is reached at the plateau. The continuous consumption of LS with immediate addition could be due to the increasing surface available due to the formation of additional ettringite.

Finally, it seems that the delayed addition of LS allows for good maintenance of the workability compared to the immediate addition, which is very interesting from a practical point of view.

Author Contributions: Y.E.B.: Conceptualization, methodology, investigation, writing—original draft preparation, visualization. N.A.: Conceptualization, methodology, investigation, review, visualization. G.L.S.: Conceptualization, methodology, investigation, review, visualization. R.A.L.: Conceptualization, methodology, investigation, review, visualization. K.D.W.: Conceptualization, methodology, investigation, review, visualization. All authors have read and agreed to the published version of the manuscript.

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