Evaluation of the influence of sodium and magnesium lignosulfonates on the hydration kinetics of cementitious paste

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Abstract

Motivated by their low cost, lignosulfonate-based water reducers are the most used type of admixture in the concrete industry worldwide. Due to the plurality of types of lignosulfonates (LSs) and the recent update to the Brazilian standard for admixtures for concrete, the objective of this work was to investigate the impact of sodium (Na-LS) and magnesium (Mg-LS) lignosulfonates, raw materials present in the Brazilian market, in pastes and concretes produced with cement type CP II F 40 under different dosages (0.40% and 0.80%). For this, the following tests were performed: adsorption curves, isothermal calorimetry, microanalytical tests (TGA/DTG and DRX), and application in the concrete according to NBR 11768-1 standard. The results showed different hydration evolutions among the pastes produced with these lignosulfonates. As a consequence, despite the similarity in water reduction, it was verified that Mg-LS was more suitable for RA1-R (water reducer-retarder, setting time 120-360 min), while Na-LS was more suitable for RA1 (water reducer, setting time 30-160 min).

Keywords: characterization, chemical admixture, hydration, lignosulfonate, Portland cement.

INTRODUCTION

It is a well-known fact that the concrete industry has developed rapidly because of technological advances and improvements, especially in the admixtures chain [1]. Currently, it is unthinkable to produce concrete without the use of chemical admixtures [2], as these promote the improvement of the fresh and hardened states and the durability of the concrete [3, 4]. Among several types, water reducers/plasticizers are those with the highest consumption volume [2]. Because they are more environmentally friendly, lignosulfonate-based admixtures form the highest percentage among water-reducing/retarding admixtures used in the concrete industry [3, 5]. Lignosulfonates are complex anionic polymers obtained together with cellulose during acid sulfite or bisulfite pulping of wood [6]. Depending on the neutralization, precipitation, and fermentation process, as well as the type (coniferous or hardwood) and age of the wood used as raw material, lignosulfonates can present themselves as complex structures combined with various types of positive ions (Ca^{2+}, Na^+, Mg^{2+}, etc.), different molar masses and also under the possible presence of sugars in their compositions, important when combined with Portland cement, as they considerably influence hydration kinetics, setting times and concrete fresh state [7-10]. It is important to highlight that the Brazilian admixtures standards [4, 11, 12], in force since 2019, do not comment on the possible and variable constituents of water reducers, much less mention

the existence of different types of lignosulfonates, which is corroborated by the lack of knowledge on the part of users in the Brazilian market, a fact confirmed by the authors of this study. Furthermore, the processes implemented in the manufacturing of lignosulfonates have undergone several modifications over time. Until the 1930s, calcium was the base typically used with sulfurous acid; magnesium and sodium have, however, become the dominant cooking agents [13, 14]. This trend can be attributed to its beneficial chemistry, better results with respect to pulp quality, and good chemical and heat recovery systems. Calcium has the disadvantage of its low solubility which restricts calcium sulfite pulping to low pH (<2) cooking only. The ammonium cation, on the other hand, is applicable over a wide range of operating pH (up to 11) but, since it produces darker unbleached pulps, more bleaching chemicals are required, which creates problems associated with the chemical recovery and regeneration.

Lignosulfonates have high molecular masses, in the order of 20,000-30,000 g/mol, with wide molecular weight distribution and varying degrees of sulfonation. Despite some divergences [15], there is a consensus that the adsorption and water-reducing capacity of lignosulfonates increase with their molecular weight [5-7]. The main mechanism of action of lignosulfonate is attributed to the phenomenon of adsorption on cement particles, which is a characteristic of sulfonated polymers, neutralizing surface charges and causing electrostatic repulsion in the cement paste. The adsorption of lignosulfonates is selective, being explained by the difference in the polarity of surface charges of the cement phases, being negative on the surface of C_3S and C_2S and positive on C_3A and C_4AF, since lignosulfonates have

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massive groups of anionic character [16-19]. The adsorption depends mainly on factors such as: type of cement, type, and content of mineral admixtures (decreasing order of adsorption: carbonate filler>fly ash>blast furnace slag); particle fineness (higher fineness increases adsorption); and mass ratio of phases (higher C_3S/C_2S and C_3A/C_4AF increase adsorption) [20-22]. The adsorption curve of a polymer, which correlates the amount of polymer adsorbed by the particles and the dosage of polymer introduced, generally presents, under isothermal equilibrium, the pattern followed by the Langmuir model, given by [16-27]:

$$m_{SA} = \frac{m_{SA}^{\infty}.k.C_A}{1+C_A} \tag{A}$$

where m_{sa} is the mass of the adsorbed polymer (mg), m_{SA}^{∞} is the mass of polymer adsorbed on the plateau (mg), k is the chemical equilibrium constant, and c_A is the polymer concentration in the solution (mg/g). However, the Langmuir model is cited as unsuitable for cementitious paste systems, since the specific surface changes with hydration and the polymer is not adsorbed equally in all cement phases, not attending to fundamental hypotheses that are the basis for the Langmuir model [23, 27]. With the increase in the doses of lignosulfonates, there is a consequent increase in the specific surface of cement hydrates (especially ettringite) that serve as preferred adsorption sites. Thus, the adsorption does not reach equilibrium and, therefore, the adsorption mechanism cannot be attributed exclusively to the monolayer type of phenomenon, indicating the possibility of the coexistence of other lignosulfonate consumption mechanisms.

The influence of lignosulfonates on the hydration of cement is quite complex and depends on several factors, mainly those related to the compositional characteristics of lignosulfonates and cement, which are increasingly diverse for environmental and technical reasons [28]. Lignosulfonates can contain significant amounts of by-products such as sugars, which are known to delay the hydration of the aluminate phases (C_3A and C_4AF in the early ages) and silicates (C_3S and C_2S up to 30 days) [29, 30]. However, sugars generally contribute to a significant increase in final strength, a fact attributed to slower hydration that produces a more dense and higher quality cementitious gel [31-35]. Varied effects of delay in setting time were observed with different dosages and types of lignosulfonates [36]. However, even if the delay intensity of lignosulfonate varies proportionally to its sugar content, the presence of C_3A-rich cement mitigates this effect [6]. Wang et al. [37] cite that lignosulfonates mainly affect the hydration kinetics of C_3S, which extend the dormant period of cement. This phenomenon is explained by the adsorption of anionic lignosulfonates through their sulfonate and hydroxyl groups, which coat the C-S-H gel with a layer that is less permeable to water, which hinders and delays further hydration.

Cadix and James [38] cite that lignosulfonates adsorb strongly onto C_3A, reducing the amount of retarder available to inhibit C_3S hydration, while C_4AF adsorbs significantly fewer lignosulfonates than C_3A. Colombo et al. [39] comment that lignosulfonate retards the hydration of C_3S depending on its concentration in the pore solution and that several authors diverge on the hydration of C_3A, some have concluded that lignosulfonates delay it, while others have concluded that lignosulfonates do not delay or even accelerate slightly the C_3A hydration. Several studies highlight that lignosulfonate accelerates the formation of ettringite which induces a significant decrease in SO_4^{2-} concentration via greater solubility of the sulfate phase in the initial hydration time. Consequently, the increase in the amount of bound water is found and attributed to the accelerated formation of ettringite [40-43]. Danner et al. [44] reported a greater accumulation of heat at the age of 1 h, attributed to the facilitated formation of ettringite with the increase of lignosulfonates. However, the heat accumulated in the 10 to 44 h interval was less than the reference, equalizing in the final ages. Danner et al. [6] observed that higher doses of lignosulfonates increased the induction period in pastes. Although the calorimetry did not find significant differences between the studied lignosulfonates, the X-ray diffraction tests indicated differences in the morphology and crystallinity of portlandite and ettringite. In general, the heat accumulated in 44 h was reduced compared to the references. In another article, Danner et al. [44] also did not find considerable differences in the delay of low-sugar sodium and calcium lignosulfonates in cementitious pastes. However, differences were observed when analyzing pure pastes of C_3A and gypsum in combination with such lignosulfonates, confirming that the interaction of certain types of lignosulfonates with C_3A may have a less delaying effect than usual in the hydration of Portland cement pastes.

In view of this scenario of such diversity of concrete component materials, especially cementitious materials and admixtures, it is important to optimize the admixture-cement combination to achieve a certain property. Therefore, the general objective of this study was to investigate the impact of sodium and magnesium lignosulfonates in cement pastes and concretes produced with cement type CP II F 40, as they are fundamental raw materials with a strong presence in the Brazilian market for the manufacturing of water-reducing admixtures. The main hypothesis raised is that because both lignosulfonates come from different origins, there are basic differences in their structural and compositional characteristics (especially pH, molar mass, degree of sulfonation, and sugar content) which result in different performances in terms of adsorption and hydration kinetics of cementitious paste and, therefore, can influence in their final applications in concrete. Such details are often omitted in product data sheets and/or not commented on by the technical community at large. It is justifiable to carry out this work, as it aims to corroborate the additional care that manufacturers and users of admixtures must take in the selection of water-reducing admixtures, elucidating the importance and influence of those basic raw materials have on compatibility studies between cement and admixtures.

EXPERIMENTAL

Materials. *Portland cement*: a commercial Portland cement from a Brazilian manufacturer was used. The type is CP II F 40 conforming to NBR 16697 standard [45]. In addition to being commercially representative, this type of cement is normally adopted by Brazilian standards, such as NBR 11768-1 [4]. Representative batches were obtained using the Scoop method, in which the cement is mixed in a container with the aid of a spatula, removing the sample from the middle of the pot, preventing it from segregation and alterations such as carbonation [46]. A sample of cement obtained by the Scoop method and passing through a 200 μm sieve had its chemical composition obtained by X-ray fluorescence analysis (XRF), which was carried out in a spectrometer (Axios Max, PANalytical) and the results are shown in Table I. The mineralogical composition is shown in Fig. 1 and was determined by X-ray diffraction (XRD) and the Rietveld refinement method. A powder sample passed through the #200 sieve was analyzed in the range of 5°-70° 2θ, with a step of 0.02° 2θ and 0.5 s/step, under 30 kV voltage and 10 mA, using a diffractometer (D2 Phaser, Bruker) with monochromatic CuKα radiation (λ=1.5418 Å). The crystalline structure was identified using a software (X'Pert Pro, PANalytical) comparing the spectrum obtained with the Powder Diffraction File (PDF) database, provided and constantly updated by the International Center for Diffraction Data (ICDD). Rietveld analysis was performed using the TOPAS 4.4 software and the mineralogical relationships of fundamental components of the cement were determined, as shown in Table II.

Lignosulfonates: the study used two different types of commercial lignosulfonates commonly available in the Brazilian market containing sodium and magnesium. Sodium lignosulfonate (Na-LS) originated from the

process of pulping sodium sulfite from a controlled mixture of coniferous wood (fir, *Picea abies*, and pine, *Pinus sylvestris*). Magnesium lignosulfonate (Mg-LS) came from the pulping process of acid sulfite of magnesium from hardwood (eucalyptus, *Eucalyptus globulus*). The physical and chemical properties and elementary compositions were provided by the manufacturers of lignosulfonates (Table III). The structural characterizations of lignosulfonates were performed by Fourier transform infrared spectroscopy (FTIR) using an equipment (IRAffinity-1, Shimadzu) with an attenuated total reflectance (ATR) accessory module. The samples were scanned in the range of 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}. The association of wavenumbers of vibrational bands in the FTIR spectra (Fig. 2) is given in Table IV [49-53]. The FTIR analysis is an important method to demonstrate qualitatively or semi-quantitatively the differences in the presence and contents of functional groups of the studied LSs, which have a fundamental role in the adsorption mechanism and therefore in their performances and compatibilities with cement. With a few exceptions, in general, both lignosulfonates presented common bands with similar intensities, except for bands at 1330 and 1271 cm^{-1}, exclusive to Na-LS and Mg-LS, respectively. This can be explained since the spectral region below 1400 cm^{-1} is very difficult to analyze, because most bands are complex with various vibration contributions [54]. Furthermore, both lignosulfonates have different origins and treatment and manufacturing processes. However, it is important to highlight the existence and similarity of the intensity of the bands referring to the hydrophilic sulfonic groups (1192, 1044, and 655 cm^{-1}) for both lignosulfonates, in agreement with the similar sulfonation degrees presented in Table III. Such analysis is important for the present study because it is worth remembering that it is through the sulfonate groups that lignosulfonates adsorb and are incorporated into

Table I - Chemical composition (wt%) determined by XRF of CP II F 40 cement.

CaO	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	SO$_3$	MgO	TiO$_2$	SrO	P$_2$O$_5$	MnO	K$_2$O	Na$_2$O	LOI	Total	Na$_2$Oeq.
55.48	26.58	3.87	6.07	2.05	4.04	0.57	0.14	0.42	0.04	0.16	0.43	4.59	99.85	0.53

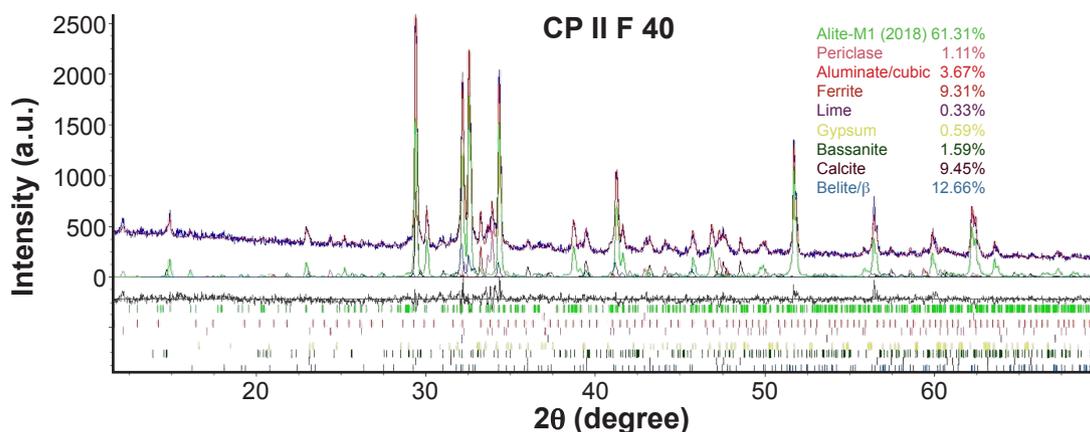*LOI: loss on ignition; Na$_2$Oeq.: Na$_2$O equivalent=Na$_2$O+0.658.K$_2$O.*

Figure 1: XRD pattern and mineralogical composition of cement CP II F 40 via Rietveld analysis.

Table II - Mineralogical relations, in mass, of fundamental components of cement CP II F 40.

Determination	Content (%)
Silicates (C_3S+C_2S)	73.97
Aluminates (C_3A+C_4AF)	12.98
Calcite ($CaCO_3$)	9.45
Total sulfates ($Ca_2SO_4.2H_2O+Ca_2SO_4.1/2H_2O$)	2.18
Others	1.42
C_3A/sulfates	1.68

C_3S: $3CaO.SiO_2$; C_2S: $2CaO.SiO_2$; C_3A: $3CaO.Al_2O_3$; C_4AF: $4CaO.Al_2O_3.Fe_2O_3$.

Table III - Physical-chemical characteristics and elementary compositions of lignosulfonates in their original forms as raw materials supplied commercially.

Characteristic	Na-LS	Mg-LS
Aspect	Fine brown powder	Dark brown viscous liquid
pH at 20 °C	6±1	3±1
Solid content (%)	97	51
Density (g/cm³)	-	1.3
Ash (%)*	28.9	10.0
Insoluble material (%)*	<0.1	-
Total sugar (%)*	2.00	12.80
Molar mass M_w (g/mol)	10482	2400
Na (%)*	9.00	0.28
Mg (%)*	-	4.1
N (%)*	-	<1.0
C (%)*	-	44.00
H (%)*	-	3.00
S (%)*	8.50	8.00
SO_3H (%)*	10.8[a]	11.2[b]
Ca (%)*	0.12	0.11
Chloride (%)*	0.01	0.16
Sulfate (%)*	7.50	4.50

*: percentage by mass/mass of total dry solids; [a]: data from [47]; [b]: data from [48].

the C-S-H gel, which changes its morphology and makes it more impermeable, which further delays the hydration [42]. As sulfonic groups are essential for the adsorption of lignosulfonates, the degree of sulfonation determines the amount of free lignosulfonate in the pore solution, which directly impacts the hydration kinetics of the cement. Several studies have shown that there is an increase in setting time when the amount of free lignosulfonate is increased, which has been attributed to the increase in Al concentration in the pore solution that causes C_3S poisoning and the consequent formation of C-A-S-H (calcium aluminum silicate hydrate)
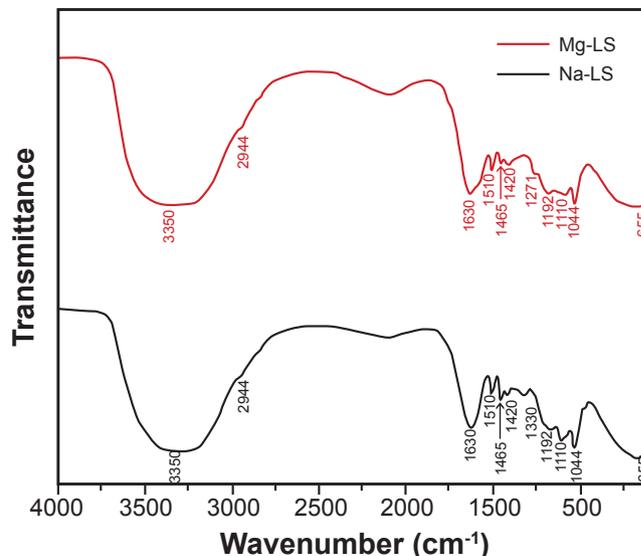

Figure 2: FTIR spectra of sodium lignosulfonate (Na-LS, black line) and magnesium lignosulfonate (Mg-LS, red line).

instead of C-S-H (calcium silicate hydrate) [39, 43].

As the studied lignosulfonates had different physical aspects and solid contents in their forms originally supplied as raw materials, it was decided to prepare homogeneous aqueous solutions of both with a solid content standardized at 40±1%. It is important to highlight this action since the study intended to evaluate separately the influence of different types of lignosulfonates on the hydration of Portland cement, without the synergistic interference of the most varied raw materials also present in lignosulfonate-based water-reducing admixtures for concrete normally available on the market, such as accelerators and retarders. A small and equal amount of defoamer (0.1% by mass of tri-isobutyl phosphate) was added to avoid foam during sample preparation and excessive air entrainment. The physical-chemical characteristics of each aqueous solution of lignosulfonates are shown in Table V. It is possible to observe a considerable difference in pH values of the LS solutions, which can influence their adsorption characteristics on cement particles. Several studies have shown that when pH value is increased, there is an increase in surface charge on LS molecules and also an increase in the degree of loose aggregation due to ionization of functional groups, especially sulfonic and phenolic hydroxyl groups [55-57].

Water: due to its greater sensitivity, deionized water was used in the studies of lignosulfonate-cement interactions and hydration kinetics of cement pastes.

Preparation of paste samples - TGA/DTG and XRD: for the thermogravimetric analysis/derivative thermogravimetry (TGA/DTG) and X-ray diffraction (XRD) techniques, 5 families of cement pastes were made with a constant water/cement (w/c) ratio (in mass) of 0.40. In addition to the reference, the other ones had aqueous solutions of lignosulfonates added at dosages of 0.40% and 0.80% in relation to the cement mass. These dosages were chosen because they are commonly used in concrete, and they are

Table IV - Selected FTIR bands of sodium and magnesium lignosulfonates.

Assignment of vibrational band	Wavenumber (cm^{-1})
(OH) ν - axial deformation of H_2O in lignosulfonates	3350 (Na-LS, Mg-LS)
(C-H)$_x$ ν - axial deformation (aliphatic+aromatic)	2944 (Na-LS, Mg-LS)
(C-C) ν - deformation (aromatic ring)	1630 (Na-LS, Mg-LS)
(C=C) ν - deformation (aromatic ring)	1510 (Na-LS, Mg-LS)
(C-H) δ - bending (CH$_3$+CH$_2$)	1465 (Na-LS, Mg-LS)
(C-O) ν - ester stretching	1420 (Na-LS, Mg-LS)
(C-H) δ$_{ang}$ - angular bending of methyl group (CH$_3$)	1330 (Na-LS)
(C-O) ν - ester stretching	1271 (Mg-LS)
(S=O) ν - stretching SO$_2$OH (sulfonic group)	1192 (Na-LS, Mg-LS)
(C-O) ν - stretching	1110 (Na-LS, Mg-LS)
(C-OH + C-O-C) ν - stretching (OH aliphatic+ether, sulfonic group)	1044 (Na-LS, Mg-LS)
(C-S) δ - vibration SO$_2$OH (sulfonic group)	655 (Na-LS, Mg-LS)

Table V - Basic physical-chemical characteristics of admixtures (aqueous solutions of lignosulfonates).

Characteristic	Na-LS	Mg-LS
Aspect	Brown liquid	Brown liquid
pH at 20 °C	5.01	3.39
Solid content (%)	40.38	40.21
Density (g/cm³)	1.03	1.03

similar to those highlighted by Colombo et al. [23]. Exclusive samples were made for each evaluation at the age of 90 min, 6 h, 12 h, 24 h, 7 days, and 28 days. It is worth noting that the choices for these ages were limited by operational issues in the sample preparation stage, where the use of a special humidity and controlled temperature chamber would be more appropriate, as used by Scrivener et al. [58], for continuous study of the evolution of phases during hydration for the same sample. Therefore, unfortunately, this was a limitation of the present work being possible the occurrence of preferential orientation during the temporal analysis via XRD for ettringite and portlandite. Despite all care, carbonation was also possible, and the occurrence of this phenomenon is important, because, in addition to the initial formation of ettringite, there may also be the formation of hemi-carbonates that gradually convert into mono-carbonates when CO_2 from different sources is sufficiently present [59-61]. The mixing procedure specified by NBR 16606 standard [62] was adopted. With the mixer stopped, the water was poured into the bowl with subsequent dosing of the lignosulfonate solution, followed by the addition of cement which was allowed to rest for 30 s. Afterward, it was mixed at low speed for 30 s. Subsequently, the mixer was turned off for 60 s, where in the first 30 s the bowl was scraped with the aid of a rubber spatula. Finally, the mixer was turned on at a fast speed for 60 s. After mixing, the pastes were molded in cylindrical polystyrene tubes (H=62 mm, Ø=31 mm, V=30 mL) and sealed with plastic film. The curing was carried out under sealed conditions at 27±2 °C and humidity greater than 50%. A release agent was not used to avoid any influence on cement hydration. The samples were identified as y-LS-z, where y refers to the type of lignosulfonate and z refers to the dosage of lignosulfonate. For example, a sample denoted as Na-LS-0.40 indicated the use of sodium lignosulfonate under 0.40% dosage on the mass of the cement. The samples remained in these curing conditions until the age of analysis, where thin central slices of the sample were obtained, avoiding areas that may have suffered bleeding, through mechanical cutting with a circular diamond saw blade and spraying of mineral oil and isopropyl alcohol as cooling lubricants. Soon after, hydration was stopped according to the appropriate methods.

Hydration stoppage - TGA/DTG and XRD: for thermogravimetric analysis (TGA) and X-ray diffraction (XRD), hydration was stopped with the use of isopropyl alcohol and later removal with diethyl ether [63-65]. At the selected ages, slices of hardened paste with 3 to 5 mm thickness were manually and gently ground with a mortar and pestle. The obtained powder was immersed in isopropanol for 15 min and then washed with diethyl ether in a Buchner funnel, and then dried in an oven for 8 min at 40 °C. The proportion of 5 g of ground paste to 50 mL of isopropanol and 10 mL of diethyl ether was used. Finally, the dried samples were sieved (200 mesh), stored in Eppendorf tubes, and directed to the TGA/DTG and XRD analysis.

Thermogravimetric analysis: TGA/DTG analysis was performed on samples with 7.0±0.3 mg in a thermal analyzer (DTG-60H, Shimadzu). The heating rate adopted was 20 °C/min, starting from room temperature to 1000 °C and an alumina crucible was used. The inert purge gas was nitrogen (N$_2$) at a flow rate of 40 mL/min. The results were expressed as a percentage by mass. The curves of the contents of portlandite and chemically combined water were

plotted using Eqs. B and C [66-71]:

$$BW = \frac{m_{total} - m_{500}}{m_{500}} \cdot 100 \qquad (B)$$

$$CH = \frac{m_{H_2OCH}}{m_{500}} \cdot \frac{M(Ca(OH)_2)}{M(H_2O)} \cdot 100 = \frac{m_{400} - m_{470}}{m_{500}} \cdot \frac{74}{18} \cdot 10 \quad (C)$$

where BW is the chemically combined water (%), CH is the Portlandite content (%), m_{total} is the total mass of paste after hydration stoppage by solvent exchange (mg), m_n is the dry mass of the sample in n °C (mg), m_{H2OCH} is the loss of mass due to Portlandite dehydroxylation, given by the difference between m_{400} and m_{470} (mg), and M is the molar mass.

X-ray diffraction (XRD): to monitor hydration and to qualitatively determine the mineralogical composition of the paste samples, the same diffractometer and experimental parameters used in the characterization of the cement were used.

Isothermal conduction calorimetry: for the isothermal calorimetry of the pastes, an equipment (I-CAL 8000, Calmetrix) was used under 25 °C and a total duration of 72 h. The w/c=0.40 and the following mass dosages for each lignosulfonate were also fixed: 0, 0.40% and 0.80% in relation to the cement mass. The mixtures of the pastes were made manually outside the calorimeter, weighing constituents in the calorimeter vial and mixing manually with a spatula for around 1 min. The measurements were started immediately. The accumulated heats of cement pastes were determined at the following ages: 1.5, 6, 12, 24, and 48 h. The setting times were estimated as the time needed to reach half the maximum thermal energy of the main hydration peak with an accuracy of 0.1 h [72].

Adsorption isotherms: to determine the adsorption curves, samples were prepared by mixing 20 g of cement and 40 g of aqueous lignosulfonate solution, which contained the following increasing doses, by mass, of LS: 0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.5, 1.7, 2.0, 2.5, 3.0, 3.5, and 4.0 wt%. The mixing was made in a shaker incubator (SPLabor) for 30 min at 25 °C and rotation of 250 rpm. Afterward, the suspensions were centrifuged for 15 min at 25 °C and 3000 rpm in a centrifuge (K3 Series, Centurion Sci.). Finally, the separated liquid phase was extracted with the aid of a micropipette and the total organic carbon (TOC) content was determined using a portable photometer (Pastel UV, Secoman). The contents of adsorbed lignosulfonates were obtained by the difference between the amount initially added and the amount present in the liquid phase measured by TOC, after centrifugation. It was necessary to determine auxiliary calibration curves for Mg-LS and Na-LS, shown in
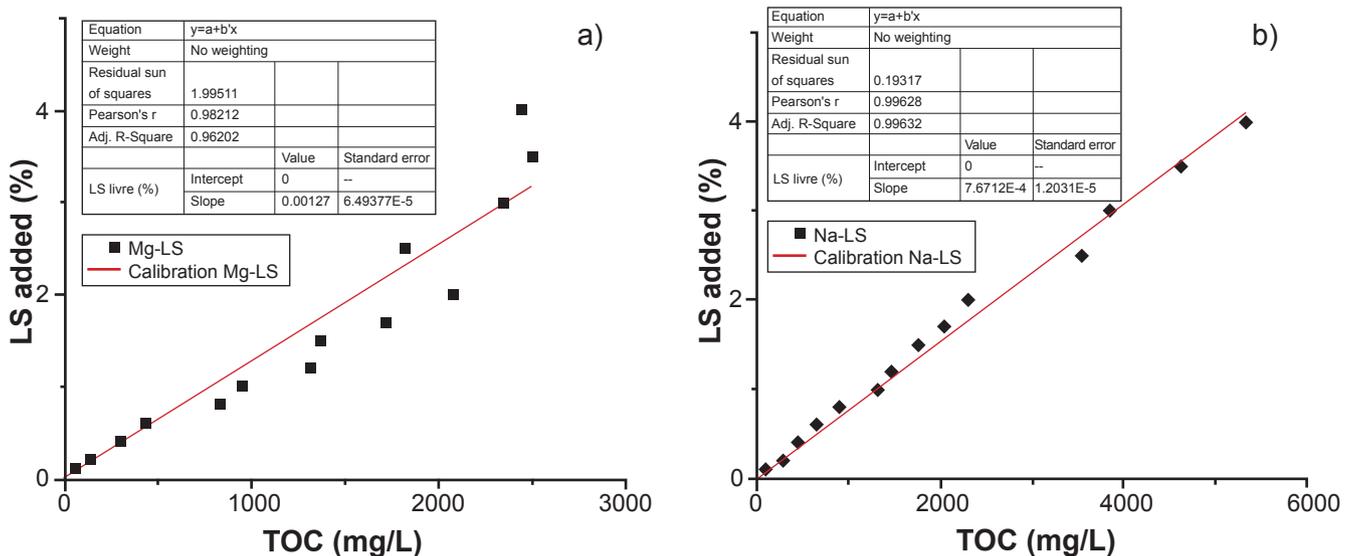

Figure 3: Calibration curves of adsorbed lignosulfonate for: a) Mg-LS; and b) Na-LS.

Table VI - Technical requirements for type 1 water reducer admixtures (RA1) - NBR 11768-1 standard [4].

Admixture type@	IM coefficient*			Setting time (min)	
	1 day	7 days	28 days	Initial	Final
Water reducer, type 1 (RA1)	-	≥1.10	≥1.15	≥30	≤160
Water reducer, type 1 retarder (RA1-R)	-	≥1.10	≥1.15	≥120	≤360
Water reducer, type 1 accelerator (RA1-A)	≥1.15	≥1.10	≥1.00	≤30	-

@: for all types, minimum water reduction ≥8.0% and increase in air content ≤2.0%; *: calculated by the ratio between the compressive strength results of the concrete with lignosulfonate and the strength of the reference concrete.

Fig. 3, with pure aqueous solutions of LSs.

Impact of lignosulfonates on the fresh and hardened states of concrete: to evaluate the impact of aqueous solutions of lignosulfonates on the fresh and hardened states of concrete, the results obtained in a previously published paper were referenced [73]. Thus, the compliance of such admixtures with the requirements presented in Table VI and established by NBR 11768-1 [4] for water reducers type 1 was verified.

RESULTS AND DISCUSSION

Thermogravimetric analysis (TGA/DTG): the impact of sodium and magnesium lignosulfonates on the continuous hydration of CP II F 40 cement was observed by the changes in the TGA/DTG profiles. The TGA/DTG results showed that the hydration products were mainly ettringite (water loss around 100 °C) and C-S-H (water loss around 50-200 °C), which overlapped, and portlandite (weight loss by dehydroxylation at around 450 °C). There was also a global weight loss between 550 and 750 °C due to the decomposition of existing calcium carbonate in CO_2, which confirmed this component in its composition, according to Rietveld's analysis. Despite all care and the fact that the curing step was carried out in a sealed container, the occurrence of carbonation in the samples during the cutting and preparation process, even if minimal, is not dismissible. Obviously, the TGA/DTG curves indicated the same types of phases for hydrated cement in the absence or presence of the addition of Na-LS or Mg-LS. This was explained by the fact that both lignosulfonates did not affect the types of hydration products formed, being only influential in the hydration kinetics and/or physical state/degree of crystallinity, which can be confirmed later by the calorimetry and XRD.

As reported in several studies [6, 28-44], lignosulfonates have a strong influence on the evolution of hydration, reflected in the current work by the difference in the rate of evolution in ettringite, C-S-H, and portlandite contents, as shown in Fig. 4. At this age (t=12 h) and under the same dosages, Mg-LS triggered a lower hydration rate and a consequently reduced release of portlandite, being a strong indicator of its greater delay power compared to Na-LS, mainly attributed to its higher sugar content. Also, greater sensitivity regarding the impact on hydration and delay was observed for higher dosages of the same LS type. Consequently, it was possible to infer that there was a smaller loss of mass attributed to C-S-H with the increase in the dosages of lignosulfonates, with a global emphasis on Mg-LS-0.80. It is important to highlight the additional care in interpreting the results obtained in the temperature range for C-S-H and ettringite, since there was an overlapping of peaks related to the water loss of these compounds, which may even have the contribution of remaining calcium sulfates, leading to variations in the results observed with underestimation or overestimation of their quantities. However, as highlighted by Colombo et al. [43], this is acceptable since such analysis estimates the potential impact of lignosulfonates

on hydration, mainly in the quantification of portlandite contents, which serves as a complementary basis for other microanalytical analysis. Qualitatively, in general, it was possible to state that the addition of lignosulfonates to the cement paste led to an increase in mass loss in the range attributed to $CaCO_3$ between 550 and 750 °C. This fact was also observed in other studies [23, 43] and is explained and attributed mainly to the decomposition of lignosulfonates, in addition to the contribution, even if minimal, of a possible occurrence of carbonation during sample preparation.
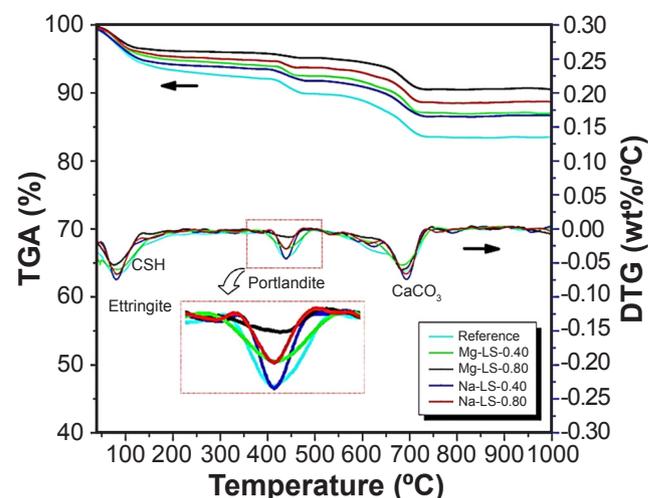

Figure 4: TGA/DTG curves for CP II F 40 (Reference), Mg-LS-0.40, Mg-LS-0.80, Na-LS-0.40, and Na-LS-0.80 pastes at the age of 12 h.

Table VII shows a summary of the temporal evolution of the quantified levels of chemically combined water and portlandite. An increase in the content of chemically combined water in the first 90 min was observed for pastes with lignosulfonates, being slightly higher for Mg-LS-0.80, probably related to the acceleration in the initial formation of ettringite, probably caused by the increase in the dissolution of sulfates by lignosulfonates. This inference is later correlated with the XRD results obtained. At 28 days, there was a tendency to equalize the contents of portlandite and combined water, which was expected, since the impact of lignosulfonates was more limited to the first ages with an emphasis on hydration and kinetics rates of formed products. However, the reference paste showed higher content of portlandite at 28 days, suggesting a higher remaining content of C_3S and C_2S in pastes made with lignosulfonates.

X-ray diffraction (XRD): the continuous hydration of cement combined with lignosulfonates was observed qualitatively from changes in the peak intensities of the crystalline phases in the XRD patterns, shown in Fig. 5. It should be noted that the marked time of 0 min refers to the non-hydrated cement sample. As in TGA/DTG, diffractograms indicate that the addition of lignosulfonates affected only the first ages, with the formation of the same phases being observed, although at different speeds, indicating almost the same behavior throughout the evolution of hydration. The progress of hydration is reflected by the formation and

Table VII - Results from TGA/DTG analyses: chemically combined water (BW) and portlandite (CH) contents.

Sample	Age	BW (%)	CH (%)
CP II F 40-Reference	90 min	1.74	0.91
	6 h	4.83	3.39
	12 h	11.29	9.10
	24 h	14.33	12.25
	7 d	18.99	16.97
	28 d	21.04	19.39
Mg-LS-0.40	90 min	2.28	0.20
	6 h	3.20	1.17
	12 h	8.15	6.37
	24 h	11.82	9.29
	7 d	19.25	16.74
	28 d	19.78	18.99
Mg-LS-0.80	90 min	2.63	1.05
	6 h	3.30	1.59
	12 h	5.00	2.50
	24 h	10.42	4.02
	7 d	18.84	15.55
	28 d	19.22	18.06
Na-LS-0.40	90 min	1.79	0.68
	6 h	3.34	1.87
	12 h	9.03	6.91
	24 h	10.79	11.01
	7 d	14.76	16.55
	28 d	19.65	19.23
Na-LS-0.80	90 min	2.10	1.18
	6 h	2.77	1.76
	12 h	6.74	4.08
	24 h	12.22	10.61
	7 d	19.40	16.17
	28 d	19.45	18.42

increase in the amounts of ettringite, C-S-H, and portlandite. As mentioned by Snellings [74], the particular difficulty in decomposing and associating hydrated cements is making a suitable peak model for the C-S-H, which is an amorphous phase and varies according to the cement composition. For this reason, it was preferred not to mark the C-S-H phase in the diffractograms in the present study.

A close inspection of the diffractograms shows the dissolution of phases C_3S, C_2S, C_3A, and C_4AF. When the dosage of lignosulfonates was increased from 0.40% to 0.80%, the dissolution of such phases occurred at later ages, being more pronounced when Mg-LS was used, confirming its greater retarding potential compared to Na-LS, so the combination Mg-LS-0.80 showed only slight

signs of portlandite at the age of 12 h. Such behavior should be reflected in the extension of the dormancy period of the pastes when observing the calorimetric regimes and also converged to the results obtained in the TGA/DTG analysis. Fig. 6 exposes the number of typical peak counts related to ettringite (d=9.7 Å, 2θ=9.1°) normalized to the highest values of the references that do not use lignosulfonates, during the first 24 h of hydration. It was evident that lignosulfonates contributed to the acceleration in the initial formation of ettringite at 90 min of hydration, being more pronounced for the highest dosages of 0.80% and when Mg-LS was used. In general, the similarities of dissolution kinetics of bassanite reflected by the temporal evolution of peak intensities in XRD analysis were qualitatively verified. Therefore, the increase in ettringite formation was attributed to the enhancement and acceleration of the C_3A reaction when lignosulfonates were added and not to a greater dissolution of calcium sulfates. In pure systems, Colombo et al. [43] found that the addition of lignosulfonate can even suppress the dissolution of calcium sulfate phases, especially anhydrite and bassanite, the latter being the main source of sulfates present in the CP II F 40 cement under study, which reinforced this analysis.

CP II F 40 presented gypsum and bassanite in their constitution, according to Rietveld's analysis. In the pastes, the conversion of bassanite into gypsum was expected, which was not found in the XRD analysis for combinations with CP II F 40, which can be explained by the instant dissolution of bassanite caused by its high solubility. In general, peaks related to the presence of hemi-carbonates (d=8.1 Å, 2θ=10.9°) and mono-carbonates (d=7.5 Å, 2θ=11.7°) were observed, which partially explained the variations in peaks related to $CaCO_3$ observed in the TGA/DTG analysis, which also underwent variation due to the influence of the decomposition of the added lignosulfonates, in addition to the possibility of carbonation, not discarded, as mentioned in the topic of sample preparation. However, this fact did not affect the conclusions obtained via XRD analysis.

Isothermal conduction calorimetry: greater setting delay was obtained with the addition of Mg-LS, which can be attributed to its higher sugar content (12.80%). An increase in the setting times was obtained with the increase in the doses of both lignosulfonates, resulting in smaller heat accumulations between the ages of 6 and 24 h. Such behavior reflects the impact of Na-LS and Mg-LS on the release rate of portlandite via consumption by dissolution and hydration of C_3S and C_2S phases demonstrated by the TGA/DTG and XRD tests. Evaluating the initial accumulated heat (Table VIII) up to 90 min there was a general slight increase when in the presence of greater amounts of LS. The main reason for this can be explained by the enhancement and acceleration of the C_3A reaction promoting the initial formation of ettringite, corroborating the results obtained in TGA/DTG and XRD at 90 min. Systematically, there was a tendency for equalization of heat accumulated in 48 h.

Adsorption isotherms: the adsorption curves of sodium and magnesium lignosulfonates on the CP II F 40 cement
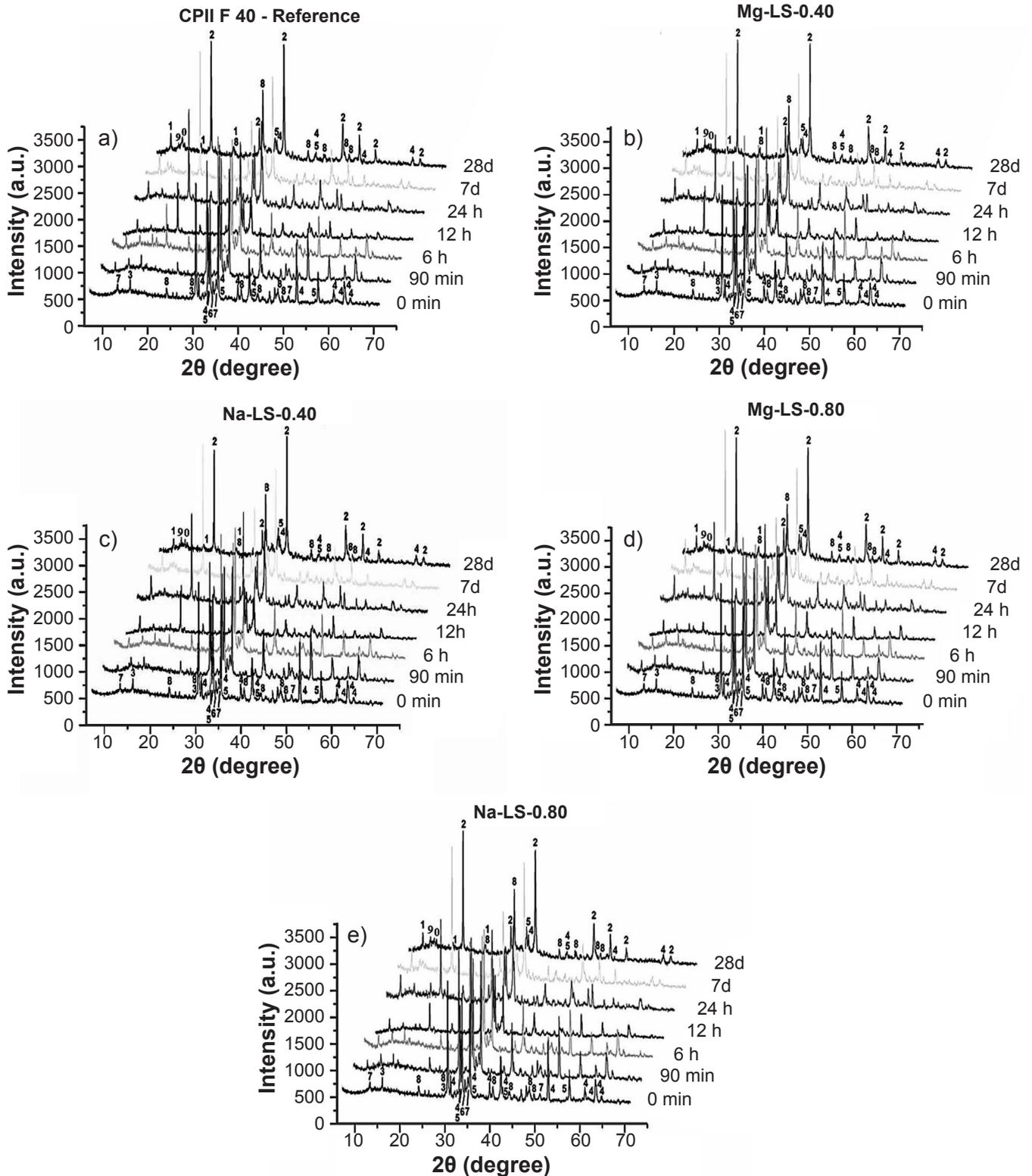
Figure 5: XRD patterns of the pastes: a) CP II F 40-Reference; b) Mg-LS-0.40; c) Mg-LS-0.80; d) Na-LS-0.40; and e) Na-LS-0.80. [1: ettringite (00-041-1451), 2: portlandite (00-004-0733), 3: bassanite (00-041-0224), 4: C_3S (00-042-0551), 5: C_2S (00-033-0302), 6: C_3A (00-038-1429), 7: C_4AF (00-030-0226), 8: $CaCO_3$ (00-005-0586), 9: hemi-carbonate (00-041-0221), 0: mono-carbonate (01-087-0493).]

particles are given in Fig. 7. No curve fitted the Langmuir model, not reaching a plateau value. The adequacy of the linear model was notorious, where the increase in the dosage of Mg-LS and Na-LS led to an increase in the adsorbed quantities,

which can be explained by what was reported by Colombo et al. [23], who verified by BET analysis an increase in the specific surface area of the hydrates with the increase in the LS dosage. Such behavior was correlated to the accelerated

Ettringite (PDF41-1451)

$y=0.3952e^{0.2764x}$
$R^2 =0.7999$

$y=0.2981e^{0.5317x}$
$R^2 =0.9745$

$y=0.2627e^{0.378x}$
$R^2 =0.9064$

$y=0.1717e^{0.5162x}$
$R^2 =0.9846$

$y=0.2809e^{0.3043x}$
$R^2 =0.8135$

Legend:
- CP II F 40 - Reference
- Mg-LS-0.40
- Mg-LS-0.80
- Na-LS-0.40
- Na-LS-0.80
- Expon. (CPII F 40 - Reference)
- Exponential (Mg-LS-0.40)
- Exponential (Mg-LS-0.80)
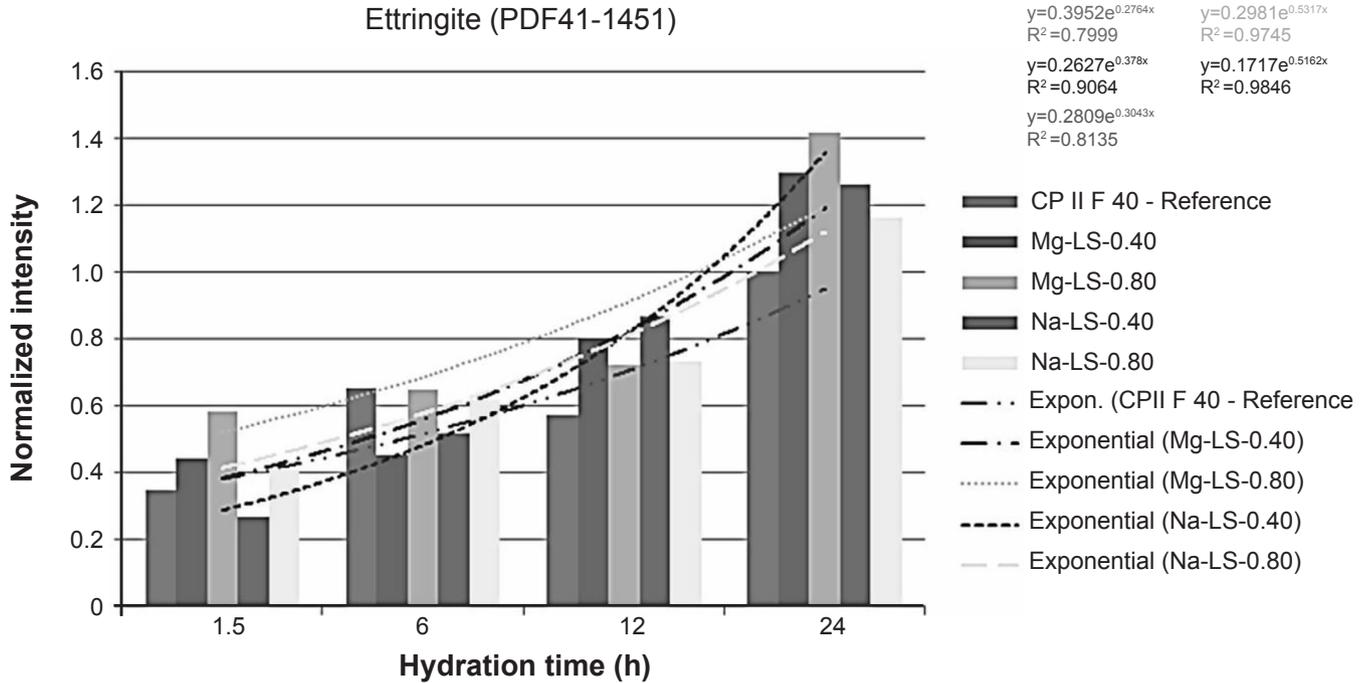- Exponential (Na-LS-0.40)
- Exponential (Na-LS-0.80)

Figure 6: Comparative evolution of normalized peaks of ettringite during hydration in the first 24 h of CP II F 40 pastes under different combinations.

Table VIII - Setting time and heat of hydration at different age times for the paste samples.

Sample	Setting time (h)	Heat accumulated (J/g cement)				
		1.5 h	6 h	12 h	24 h	48 h
Reference	4.5	12	39	103	178	243
Mg-LS-0.40	7.1	16	24	55	159	244
Mg-LS-0.80	10.5	19	25	35	123	234
Na-LS-0.40	6.2	13	28	75	170	241
Na-LS-0.80	8.2	14	26	48	153	244

formation of ettringite crystals provided by the addition of lignosulfonates, which corroborated the previous analysis of XRD, TGA/DTG, and calorimetry, in addition to what was reported by the cited studies [23, 43]. However, for both lignosulfonates, the adsorption rates were similar, although higher rates were expected for Mg-LS (lower relative content of free sulfates and its considerably lower molar mass), which was attributed to the similar degrees of sulfonation of both LSs. As mentioned in the introduction, as an adsorption plateau was not reached, the adsorption mechanism cannot be exclusively attributed to the phenomenon of surface saturation of the monolayer type, indicating the possibility of the coexistence of other mechanisms of consumption of lignosulfonates, such as the formation of organominerals, aggregation/ disaggregation, and molecular conformation [55, 56]. For this reason and to simplify the interpretations, several studies do not adopt Portland cement and/or are complemented with the evaluation of the adsorption of lignosulfonates in pure representative inert systems, such as the use of MgO [18] or

calcium sulfate [43], which was a limitation of the present study. The knowledge of this phenomenon is important as it has practical importance on the compatibility between lignosulfonates and cement, where the acceleration in the formation of ettringite causes an increase in the monolayer adsorption of LSs and can cause less delay in setting and early hardening [43]. For the present study, as both lignosulfonates showed similarity in terms of adsorption, the greater retarding power of Mg-LS was attributed to the significant presence of sugars in its composition.

Impact of lignosulfonates on the fresh and hardened states of concrete: Table IX shows a summary of the

Adsorption curves

Equation	y=a+b'x			
Weight	No weighting			
Residual sun of squares	0.36977	0.29064	0.19278	0.07255
Pearson's r	0.99421	0.994	0.99768	0.99917
Adj. R-Square	0.98764	0.98718	0.99502	0.99822
		Value	Standard error	
CPIILSNa	Intercept	0	--	
	Slope	0.85672	0.01564	
CPIILSMg	Intercept	0	--	
	Slope	0.8794	0.00959	

Legend:
- Mg-LS
- Na-LS
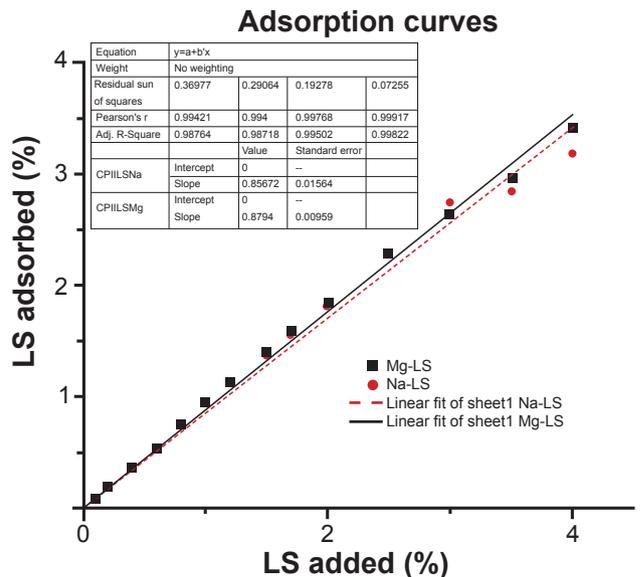- Linear fit of sheet1 Na-LS
- Linear fit of sheet1 Mg-LS

Figure 7: Adsorption curves obtained for combinations Mg-LS and Na-LS.

Table IX - Summary of the performance of aqueous solutions of lignosulfonates applied in the concrete according to NBR 11768-1 standard [4].

Sample	Water reduction (%)	Air content relative deviation (%)	IM 1 day	IM 7 days	IM 28 days	Setting time relative deviation (min)
Mg-LS-0.40	7.69	-0.3	1.00	1.10	1.00	156
Mg-LS-0.80	8.64	-0.4	0.85	1.10	1.13	360
Na-LS-0.40	7.69	+0.4	0.92	1.05	0.99	102
Na-LS-0.80	10.0	+0.3	0.82	1.10	1.07	222

IM: ratio between the compressive strength of the concrete with lignosulfonate and the strength of the reference concrete.

performance of aqueous solutions of lignosulfonates studied according to the technical requirements for water reducer admixtures type 1 (RA1) - NBR 11768-1 standard [4]. Regardless of dosage, none of the lignosulfonates met all the necessary requirements for the type 1 water reducer according to NBR 11768-1 [4]. However, for the same dosage, both lignosulfonates showed similar potentials in terms of water reduction, despite slight variations that were attributed to different levels of incorporated air. Only Mg-LS-0.80 and Na-LS-0.80 showed water reductions greater than 8.0%, a fundamental requirement for type 1 water reducers. These results were corroborated by the similarity of the adsorption curves obtained and also the degrees of sulfonation presented by both lignosulfonates. Regarding setting time, there was an increase in delay when the dosage of both lignosulfonates was also increased. However, the more pronounced retarding effect for Mg-LS was evident, which was attributed to the higher content of sugars present in its composition, since both lignosulfonates showed similar adsorptions and, consequently, similar amounts of free lignosulfonates. The higher mechanical performance obtained and reflected by the IM indexes, especially for Mg-LS-0.80 at 28 days, is also attributed to the greater presence of sugars in Mg-LS, similar to that obtained in other papers [31-35]. So far, it is worth noting that as mentioned by Mantellato et al. [75], commercial chemical admixtures are composed not only of lignosulfonates but also of a wide range of raw materials, such as accelerators, retarders, and strength activators, aiming to improve certain properties.

CONCLUSIONS

The impact of sodium (Na-LS) and magnesium (Mg-LS) lignosulfonates on pastes and concretes produced with cement type CP II F 40 at different dosages (0.40% and 0.80%) was investigated. From the results obtained, it can be concluded that both Na-LS and Mg-LS influenced the hydration kinetics of the pastes, but at different intensities. The TGA/DTG analysis showed that the increase in the dosages of LSs, regardless of type, caused a greater delay in setting, evidenced by the lower quantitative and comparative evolution of portlandite and by the calorimetry results too. In general, the effect

was more pronounced for the Mg-LS-0.80 combination. Furthermore, both LSs caused a similar increase in the chemically combined water content at 90 min, which was attributed to accelerated ettringite formation and confirmed by XRD and calorimetry analysis. The XRD analysis qualitatively showed the similarity of dissolution of bassanite, reinforcing that the acceleration in the formation of ettringite was a result of the optimization of the C_3A reactions, a fact also observed in the literature. The adsorption curves were similar and linear for both lignosulfonates and none fitted the Langmuir model reaching a plateau. The increasing adsorption rates were attributed to the acceleration of ettringite formation which caused an increase in specific surfaces and adsorption sites. The similarity of adsorption was explained by the similarity of the sulfonation degrees of both, which had a greater preponderance when compared to other characteristics, such as molar mass. The greater retarding power of Mg-LS was mainly attributed to the greater presence of sugars in its constitution since the amount of ettringite and free LSs in the pore solution, which can interfere with the hydration of other phases such as C_3S, were similar for both. When applied to concrete, both lignosulfonates did not cause rheological or compatibility problems and early stiffening. Confirming the adsorption results, both lignosulfonates presented similar performances in terms of water reduction, requiring a minimum dosage of 0.80% to meet the minimum requirements for the water reducer type 1 of NBR 11768-1 standard. However, the application in concrete corroborated the microanalytical analysis confirming the main difference in the performance of Mg-LS over Na-LS: higher setting delay and final strengths at 28 days. Therefore, it was possible to conclude that Mg-LS is more suitable for RA1-R (retarder), while Na-LS is more suitable for RA1. This conclusion clearly demonstrated the performance differentiation between Mg-LS and Na-LS when applied to CP II F 40 cement, corroborating the importance of selecting and differentiating lignosulfonates that normally constitute commercial admixtures, especially nowadays when quality robustness is sought for modern concrete, which is composed of a complex system of admixtures and supplementary cementitious materials.

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