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ÚSTAV CHEMIE MATERIÁLŮ

UTILIZATION OF LIGNOSULFONATE PLASTICIZER IN ALKALI-ACTIVATED MATERIALS

VYUŽITÍ PLASTIFIKÁTORU NA BÁZI LIGNOSULFONÁTU V ALKALICKY AKTIVOVANÝCH MATERIÁLECH

BACHELOR'S THESIS
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ABSTRAKT

Tato bakalářská práce se zabývá využitím plastifikátorů na bázi lignosulfonátu v alkalicky aktivovaných materiálech. Sledován byl vliv na směs pasty aktivované vysokopecní strusky za použití hydroxidu sodného, vodního skla o různých modulech a uhličitanu sodného. Pozorován byl vliv plastifikátoru na bázi lignosulfonátu při zamíchávání do různých směsí, na zpracovatelnost, mechanické vlastnosti a reologii směsi. Důležitým faktorem byly použité aktivátory ve směsích. Nejlépe reagující směs na lignosulfonát se ukázala být za použití NaOH jako aktivátoru. Při pokusech pochopit reologické vlastnosti sledovaných směsí, jako klíčového faktoru chování těchto směsí bylo měření zeta potenciálu. Hodnoty zeta potenciálu nám daly bližší náhled na povrchový náboj častic vysokopecní strusky. Ten se prokázal jako klíčový faktor při posuzovaní účinnosti plastifikátoru. Tato zjištění budou vzata v úvahu a dále diskutovány v této práci.

ABSTRACT

This bachelor thesis deals with the use of lignosulfonate-based plasticizers in alkali-activated materials. The effect on the paste mixture of activated blast furnace slag using sodium hydroxide, water glass with different modulus and sodium carbonate was monitored. The effect of a mixed lignosulfonate-based plasticizer into different mixtures, on workability, mechanical properties and rheology of the mixture was monitored. Activators in the mixtures were found to be an important factor. The mixture which showed the best reaction with lignosulfonate was using NaOH as activator. In attempts to understand the rheological properties of the studied mixtures, a zeta potential was observed as a key factor in the behaviour of these mixtures. It manifested interesting trends. The zeta potential values gave us a closer look at the surface charge of the blast furnace slag particles. This has been shown to be a key factor in assessing the effectiveness of the plasticizer. These findings will be taken into account and further discussed in this work.

KLÍČOVÁ SLOVA

Alkalicky aktivované materialy, alkalická aktivace, vysokopecná struska, plastifikátor
KEY WORDS

Alkali-activated materials, alkaline activation, blast furnace slag, plasticizer

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PROHLÁŠENÍ:

Prohlašuji, že jsem bakalářskou práci vypracoval samostatně a že všechny použité literární zdroje jsem správně a úplně citoval. Bakalářská práce je z hlediska obsahu majetkem Fakulty chemické VUT v Brně a může být využita ke komerčním účelům jen se souhlasem vedoucího bakalářské práce a děkana FCH VUT.

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Content

1 Introduction

The bachelor thesis deals with the influence of a lignosulfonate-based plasticizer on alkali-activated materials. In particular, blast furnace slag activated with commercially available activators such as sodium hydroxide, water glass and sodium carbonate was used.

Alkali-activated materials are binder materials that compete with today's commercially used binders such as Portland cement. Concrete made from ordinary Portland cement (OPC), including its mixtures with admixtures, is the second most used commodity of mankind after water. Global cement production in 2008 was approximately 2.6 billion tonnes, which conservatively contributes 5–8 % of global anthropogenic CO_2 emissions. The rapidly growing demand for developed civil infrastructure in China, India, the Middle East, and the developing world will significantly expand the cement and concrete industries. Such a situation calls for acceptable solutions. Alkali-activated materials could provide such a solution. [31]

Because most of the material in alkali-activated binder is generally obtained from industrial by-products, which are usually attributed very little or no environmental footprint, these binders have been identified as offering the potential for significant greenhouse gas savings compared to Portland cement [2]. Chemical admixtures, namely plasticizers and superplasticizers, are also an important part of the search for new solutions. In this work, we will monitor primarily a lignosulfonate-based plasticizer. Lignosulfonates are among the first dispersants used as concrete admixtures. These are substances which are considered as by-products of the chemical industry. It is also the second most widespread organic substance, so its ecological and economic importance cannot be neglected. [19]

2 Theoretical background

2.1 Alkali-activated materials

The use of alkali-activated materials as binders can be traced back to the first human civilizations. Studies dealing with this issue looked mainly at the possible use of materials in the construction of pyramids in Egypt, which would mean the use of alkali-activated materials 4,000 years ago. Other traces of use were discovered in the construction of monuments in Central and South America, as well as in constructions from the time of the Roman Empire.[1]

Alkali-activated material is the broadest classification encompassing virtually any binder system derived from the reaction of an alkali metal, in solid or liquid state, and an aluminosilicate powder. It also includes materials called 'geopolymers'. Solid aluminosilicates can be calcium silicates, taken from the alkaline activation of common clinkers, or more aluminosilicate-rich precursors formed as intermediates in industrial production, including blast furnace slag, fly ash, and metakaolin. Concentrated aqueous solutions of alkali hydroxides, silicates, carbonates or sulfates are used as alkaline activators-practically any soluble substance capable of supplying alkali metal cations, raising the pH of the reaction mixture and accelerating the dissolution of the solid precursor. [2,3].

Based on the composition of the raw materials, these binders can be divided into two groups: alkaline binder systems $Me_2O–Me_2O_3–SiO_2–H_2O$ and alkaline earth binder systems $Me_2O–MeO–Me_2O_3–SiO_2–H_2O$. Subsequent alkaline activation of aluminosilicates results in the formation of aluminosilicate gels whose composition can be defined by the formulations $Mn[–(Si–O)_2–Al–O]n$. wH_2O where M is an alkali metal cation (Na^+, K^+, Ca^{2+}), n represents the degree of polycondensation and z is the ratio between SiO_2: Al_2O_3. It is thus an inorganic polymer system [3,4]. In some cases, the term 'geopolymer' has been introduced. Geopolymers are in many cases seen as a subset of alkali-activated materials, where the binder phase consists almost exclusively of highly coordinated aluminosilicate. Geopolymers were defined in the 70's of 20th century by Davidovits [5]. His definition said: *,,...27Al The NMR spectrum must show a peak only at about 55 ppm. Al can be present in the product structure only and exclusively in coordination 4..."*(Fig. 1.)[6,7] If the alkaline system does not meet this condition, it cannot be called a geopolymer, but an alkali-activated material. This narrow definition includes only materials achieved by alkaline activation of metakaolin.
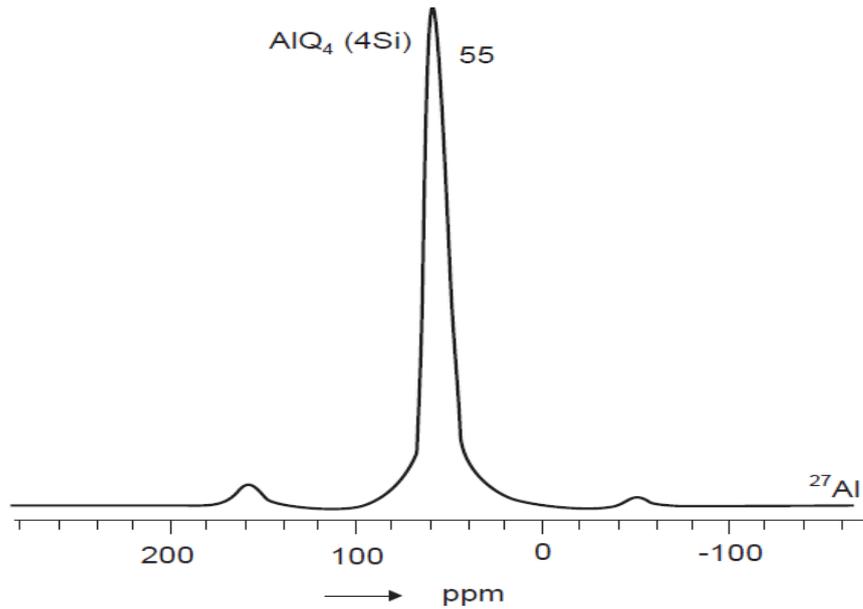
Fig. 1: NMR MAS ^{27}Al of "real" geopolymer [6,7]

2.1.1 Structure of alkali-activated materials

The structure of alkali-activated systems is closely connected with the reaction of aluminosilicate material when the original chemical bonds are broken, and new ones are formed. This is mainly the decomposition of Si–O–Si bonds and the penetration of Al tetrahedra into the bond. This is followed by the formation of aluminosilicate gels (zeolite precursors), which can be defined with polycondensation reactions. Forming gel, partially amorphous or crystalline substances may be formed depending on the nature of the starting materials and the reaction conditions. The most common crystalline precursors of the zeolite type (analcemia, hydro-sodalite and others) are formed primarily in extremely diluted suspensions (w> 1 ... 10). In the case of the above-mentioned amorphous bodies, Davidovits proposed the terminology of "polysialates", which considers the Si-to-Al ratio (Fig. 2.). [4,8].
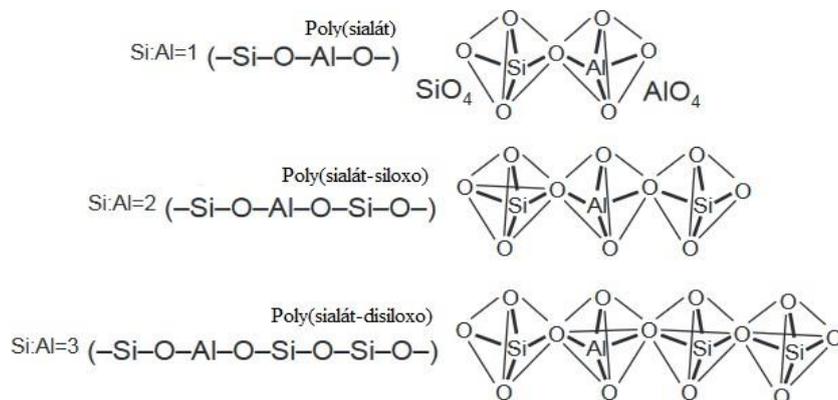

Fig. 2: Poly(sialate) structure as proposed by Davidovits [8]

Polysialates form a three-dimensional aluminosilicate network which can be characterized by an epirical formula Na, Kn {–(Si–O)z–Al–O}n ·wH_2O where M is representing atoms K, Na or Ca, n –level of polycondensation. This network is configured by SiO_4 and AlO_4 tetrahedrons connected via an oxygen bridge. Chains or rings connected by Si–O–Al bridges are formed. The presence of positively charged ions is required (Na$^+$, K$^+$, Ca^{2+}) which balance the negative charge of aluminum which it acquires in coordination 4 [4,8].
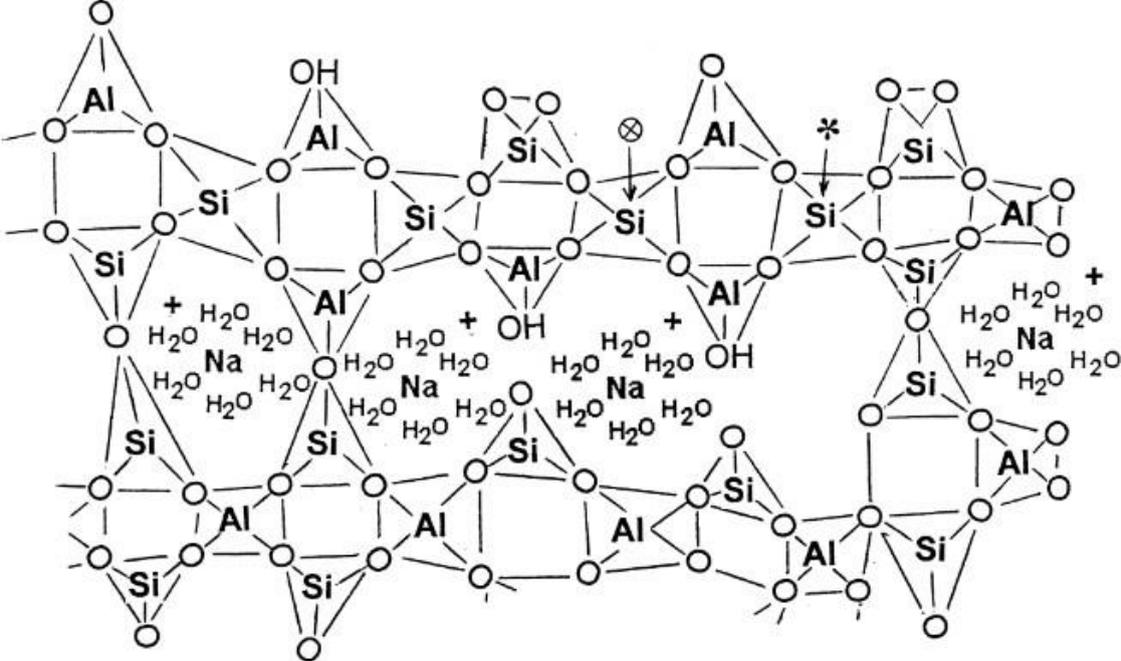

Fig. 3: Barbarosian model of geopolymer alkali-activated material [4]

The structural development of alkali-activated blast furnace slag-based materials has a highly heterogeneous character, controlled mainly by four processes. Dissolution of glass precursor particles, nucleation and growth of the initial solid phase, interaction, and mechanical binding at the boundary of the formed phases and subsequent successive reactions based on changes in dynamic equilibrium [3,9]. The main product of the activated blast furnace slag is an aluminum-substituted C–A–S–H type gel with a disordered C–S–H (I) structure similar to tobemorite. Using a number of characterization techniques such as nuclear magnetic resonance (NMR), it was possible to create a model describing the structure of alkali-activated blast furnace slag. [10]. The model was developed by Myers [11] based on the limitations associated with crosslinking and non-crosslinking of various tobemorite-like structures (Fig. 4.) allowing us to calculate the chain length, Al/Si ratio and the degree of crosslinking of these more complex structures.
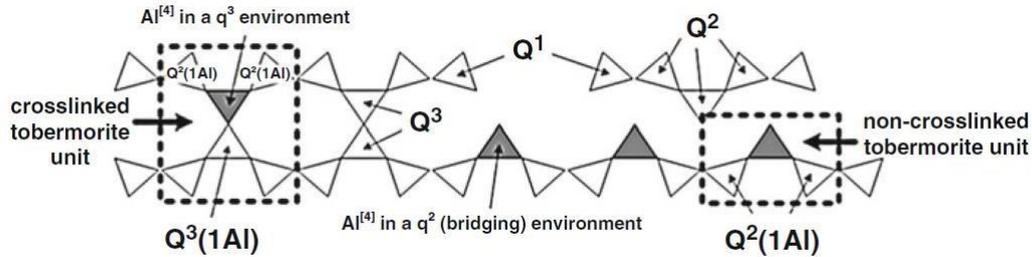
Fig. 4.: *Myers model of alkali-activated blast furnace slag [3]*

2.2 Primary raw materials to produce alkali activated materials

The raw materials most used to produce alkaline cement and concrete are blast furnace slag and fly ash. Metakaolin is also one of the raw materials that can be used in the alkaline activation process, but the production of cements and concrete is difficult to implement due to its high costs.

The chemical composition of these materials is very similar to that of commercial cements, where the main components are oxides of calcium, silicon and aluminum. However, the percentages of the other components vary considerably. Another important difference is their structure: cement contains crystalline silicates (e.g. alite , belite), while slag and ash are essentially glassy. [10]

2.2.1 Blast furnace slag

Ground granulated blast furnace slag is most used for the formation of alkali-activated materials, because its chemical composition and highly amorphous nature promotes the formation of reaction products developing high mechanical strength in good curing time with relatively low water consumption. [13] In recent years, granulated blast furnace slag has been successfully used as a total replacement for Portland cement. Pastes, mortars, concretes created by alkaline activation of blast furnace slag provide materials with a lower environmental profile, higher mechanical performance, and better durability than Portland cement. [12]

Blast furnace slag, formed as a by-product material in the production of iron, is formed by mixing acid clay tailings from iron ore and sulphur ash from coke with calcium and magnesium in limestones or dolomites used as fluxes. Slag obtained by combining acidic (SiO_2) and basic oxides (CaO a MgO) at high melting points (1600 °C), which is then cooled sharply to T < 800 °C, is later grounded and stored. The slag thus obtained has an average of 90 to 95 % glassy content, the network being formed mainly by [$(SiO_4)^{4-}$, $(AlO_4)^{5-}$, $(MgO_4)^{6-}$] and modified by (Ca^{2+}, Al^{3+}, Mg^{2+}) ions. Minor crystal structures are then formed from a solid solution of two melilite crystals, gehlenite and acermanite, forming a tetragonal system. [10]

Granulated slag with a high glass phase content, which has latent hydraulic properties, is most suitable for the alkaline activation process. On the contrary, slag with a large volume of crystalline phases has no hydraulic properties and is therefore suitable as an aggregate. [14]

2.3 Alkaline activators

Alkaline activators are, as the name suggests, substances responsible for the alkaline activation of the aluminosilicate system. The most commonly used compounds include hydroxides, especially sodium hydroxide (NaOH) and potassium hydroxide (KOH), water glass as well as primarily sodium or potassium and alkali salts. (M_2CO_3, M_2SO_4 where M = K, Na). Furthermore, strong mineral acids or aluminosilicates are used in smaller amounts [15].

Commercially used sodium and potassium hydroxides are produced by electrolysis of their brine. In addition to the liquid, the hydroxides are available in the form of solids, flakes, beads. Their chemical composition is the same, differing only in particle size.

Water glass is the common name for a series of compounds with the formula $Na_2O \cdot nSiO_2$. Theoretically, the ratio n can be any number, which gives the water glass different properties. Commercial liquid water glasses have a ratio n between 1.60 - 3.85. Outside this range, water glass has limited stability and is not practical. It is obtained by melting primary sand and sodium carbonate at 1350 - 1450 °C. Subsequently, the glass is dissolved in an autoclave at 140 - 160°C at a suitable vapor pressure. NaOH is added to the high modulus water glass solution to obtain a lower modulus solution. In many cases, it is not appropriate to do so after production but only directly by mixing the final solution used for alkaline activation [13].

Sodium carbonate was originally used as a chemical additive to Portland cement. At low doses, sodium carbonate acts as an accelerator of cement hydration, but at high doses it acts as a retarder. It has also proven to be a good activator for many cement components. Sodium carbonate occurs in three hydrates: sodium carbonate monohydrate ($Na_2CO_3 \cdot H_2O$), sodium carbonate heptahydrate ($Na_2CO_3 \cdot 7H_2O$) and sodium carbonate decahydrate ($Na_2CO_3 \cdot 10H_2O$). The formation of the type of hydrated product depends on the concentration and temperature of the sodium carbonate solution [13].

The parameters of the alkaline activator have an observably strong influence on the properties of the final product. The most relevant parameters that affect the mechanical strength of alkali-activated blast furnace slag mortars are: nature of the alkaline activator, activator concentration, curing temperature. Many authors have also noted that the optimum concentration of alkaline activator is in the range of 3 wt.% to 5 wt.% Na_2O. Using Na_2O above these limits can lead to inefficient mixtures and flowering problems.

2.4 Alkaline activation of blast furnace slag

The process of alkaline activation of blast furnace slag is a hydration process. By hydration we mean a chemical reaction between slag and water with added activator. For alkali-activated slag, the activator can be added in three ways: (1) dissolved in mixed water, (2) mixed in the slag, (3) added to the slag before mixing with water. The ground slag particles are then dispersed in water mixed added activator, resulting in a paste. The use of an alkaline activator leads to an acceleration of hydration, while it is possible to observe an increase in the rate of hydration with increasing addition of activator. [13, 16]

When the slag particles encounter water, the bond between Si–O, Al–O, Ca–O breaks on their surface under the polarizing effect of OH-. These dissolved chemicals are found in water in the form of ions ($H_2SiO_4)^{2-}$ ($H_3SiO_4)^-$ ($H_4AlO_4)^-$ and Ca^{2+}. The bond between calcium and

oxygen in Ca–O is much weaker compared to the bonds in Si–O, Al–O leading to a much higher concentration Ca^{2+} in water, and on the surface of the particles a rapid formation of the Si–Al layer occurs. This layer can be absorbed H^+ ions in water, leading to an increase in OH^- or an increase in the pH of the solution. However, this concentration OH^- is still unable to break a sufficient amount of Si–O and Al–O bonds to form significant amounts of C–S–H, C–A–H or C–A–S–H. No significant hydration can be observed after 24 hours in water and only a small amount of C–S–H begins to form after 150 days. [13]
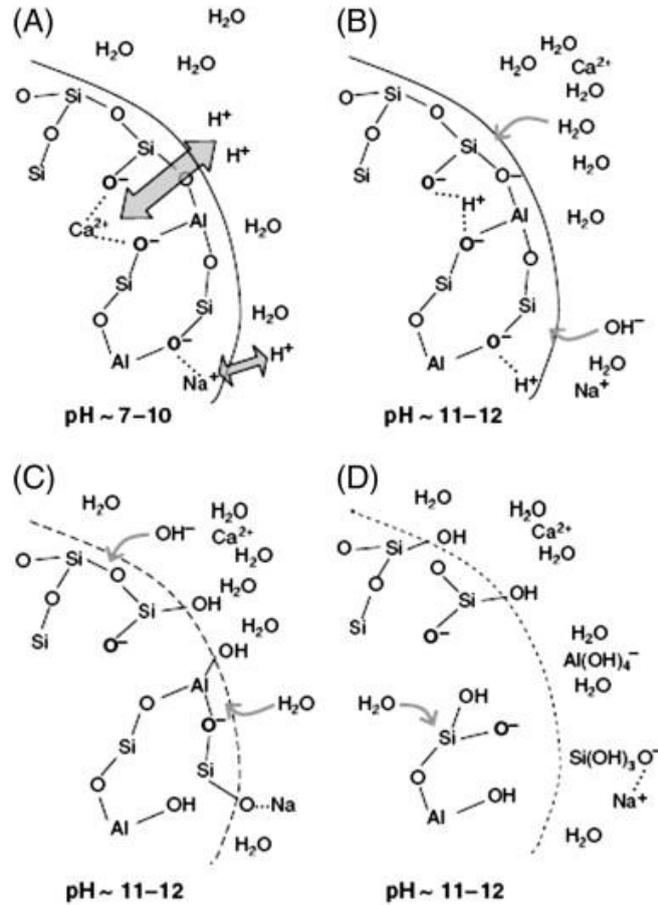

Fig. 5*. : Mechanism of dissolution of aluminosilicate glass during the early stage of the reaction: (A) exchange of H $^+$ ions for Ca $^{2+}$ and Na $^+$, (B) hydrolysis of Al–O–Si bonds, (C) depolymerization of the glass network and (D) release of Si and Al [17]*

The hydration products of the alkaline activation are primarily formed by the precipitation and dissolution mechanism, mainly in the early stages of the reaction, but even in the later stages, the reaction is able to continue in solid state. [17]

If we consider the glassy phase of the slag with a high calcium content and a low aluminium content, Fig. 5. shows the mechanism of dissolving the glass containing monovalent and divalent cations modifying the network. It is possible to observe a stark difference between the depicted Na $^+$ and Ca $^{2+}$ sites where there is a greater extent of "damage" caused by the removal of the divalent cation from the glass structure. [17]

2.5 Plasticizing admixtures: plasticizers and superplasticizers

Chemical admixtures are nowadays a very important part of the design of concrete mixtures and are an essential part of the preparation of concrete with a low impact on the environment. They can modify the properties of fresh or hard concrete or, in some cases, both. They act mainly on the rheological properties of fresh concrete and increase resistance. [19] Superplasticizers and plasticizers, also called high-range water-reducing admixtures, are natural or synthetic polymers. These are chemical admixtures whose primary task is to improve the workability of concrete, specifically to reduce the mixed water, which leads to an increase in the strength of the final product. The use of the first plasticizers can be traced back to 1930, when it was mainly the use of natural polymeric plasticizers. Today, superplasticizers of synthetic origin are mainly used in practice due to their higher dispersing ability, but even so, plasticizers of natural origin are still highly represented in the concrete industry, mainly due to low production costs. [19]

Plasticizers and superplasticizers can be used in concrete mixtures for a wide range of purposes(Fig. 6.). They can be used to: 1. increase workability without changing the composition of the mixture; 2. a reduction in the mixed water and the water-cement ratio, which leads to an increase in the strength and durability at a given workability; 3. reduction of mixed water together with cement at a given workability in order to reduce spillage, shrinkage and thermal stress caused by hydration heat.
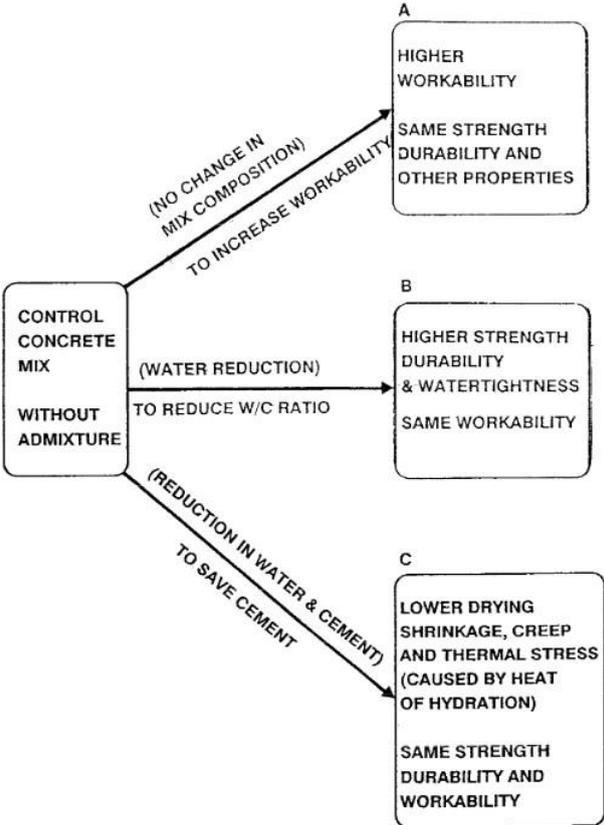

Fig. 6.: *Influence of superplasticizer on concrete mixtures [18,20]*

2.5.1 Main types of superplasticizer admixtures

In this section, superplasticizers are presented in terms of their increased ability to reduce water:
• Lignosulfonates (LS), with a limited ability to reduce mixed water of around 10%. They are mainly used today in formulations to increase workability retention in application mixtures.
• Sulfonated naphthalene formaldehyde condensates (PNS), also known as poly naphthalene sulfonates (PNS), with weak interaction with clay minerals. Their ability to reduce water is at 30%.
• Poly melamine sulphonate (PMS) and sulphated melamine formaldehyde condensate (PMS) which show a possible reduction of the water content in the concrete by more than 20-30%.
• Synthetic polymers such as polycarboxylates and acrylic copolymers (PCE). They are substances that have versatile chemical structures and can achieve up to 40% water reduction, but generally have a low tolerance to clay minerals.

2.5.2 Lignosulfonate plasticizers

Lignosulfonates (LS) were the first dispersants used as water-reducing admixtures in concrete. LS have been used since the 1930s as plasticizers and mixed water reducing agents. The largest application is the use of ready-mix concretes. [21]

Lignosulfonates are obtained as by-products of wood processing. In particular, it is a process for the bisulphite pulping of wood pulp, which is used in the separation of pure cellulose fibres by dissolving hemicellulose and lignin. Lignin is a natural biopolymer present in wood and is the second most abundant organic molecule on earth after cellulose. The production of extracted lignin is around 70 million tons per year. Most of the lignin thus produced is burned for the purpose of regeneration of spinning substances and only 5% is used as a chemical product. Lignin itself is insoluble in water, forming a complex three-dimensional network composed of randomly crosslinked monolignols such as coumaryl, conyferil and synapyl alcohols. [21]

The delignification process involves the use of either sulphite (SO_3^{2-}) or bisulfite salts (HSO_3^-). During this process, a reduced molecular weight lignin is formed due to the breakdown of the ester bonds that connect the lignin units (fragmentation). Simultaneous introduction of sulfone groups on aliphatic chains makes water-soluble lignin (sulfonation). Lignosulfonates are further modified as plasticizers for specific applications to achieve the desired properties. [21]

The chemical process of sulphite pulp (delignification) involves the use of sulphite (SO_3^{2-}) or bisulphite (HSO^{3-}) salts (usually sodium, magnesium, ammonium, or calcium) at high temperatures (140 - 170 ° C). During this process, a reduced molecular weight lignin is formed due to the breakdown of ester bonds that connect the lignin units (fragmentation). Simultaneous introduction of sulfone groups on aliphatic chains makes water-soluble lignin (sulfonation). The insoluble cellulose fibers are separated from the LS by filtration. The resulting by-product, called "spent liqueur", contains weakly sulphonated lignins of various molecular sizes, inorganic salts, wood and pentose and hexose sugars derived from the acid hydrolysis of hemicellulose. The LS for specific applications are further modified to achieve the desired properties. Lignosulfonates as dispersants in concrete mixtures show a limited

ability to reduce water (8-10%) at an average dose of about 0.1-0.3% by weight of cement. In order to improve the water reduction effect, lignosulfonates and lignins have been the subject of many studies which, when examining lignosulfonates of different molecular weights, have resulted in discovery that fractions with higher molecular weight lead to better plastic effect, allowing water reduction of up to about 20% with mild retardation effect. [21]
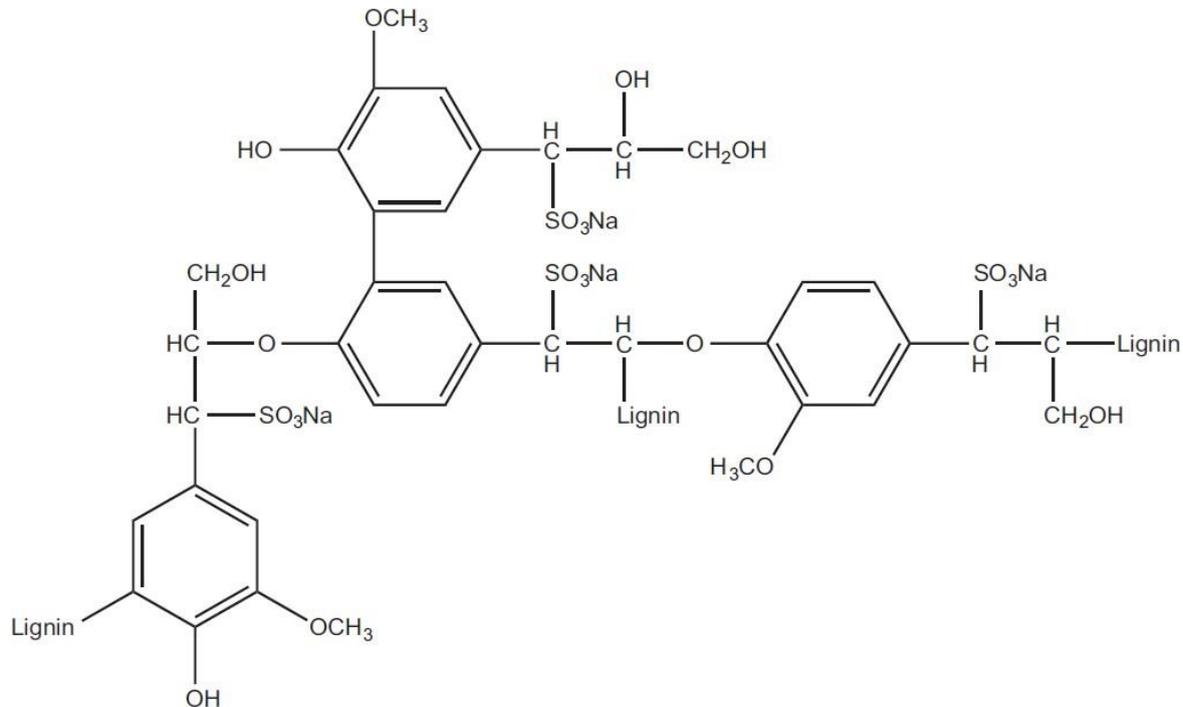

Fig. 7.: Chemical structure of lignosulfonate [21]

2.5.3 Use of Lignosulfonates in alkali-activated materials

LSs are among the cheapest concrete admixtures available on the market, costing about five times less than a commercial polycarboxylate-ether (PCE)-based polymer.

First use of LS based plasticizer was recorded in 1983. It was used in a so called "F-Concrete" developed and patented in Finland. [31, 32] It is consired as a first attemped use of water-reducing admixture in a alkaline binder. However, the behavior of these admixtures in activated systems was not explained. [3] In later studies conducted by Douglas and Brandstetr [33] it was reported that neither lignosulfate superplasticisers were found to be effective in their alkali-silicate activated BFS paste systems. In another study conducted by Wang et al. [34] they conluced that lignosulfonate-based admixtures were reducing compressive strength without improving workability.[3]

In more recent studies Bakharev et al. [22] concluded that lignosulfonate-based admixtures showed similar behavior in alkali-activated systems as in Portland cement concrete. Furthermore he reported positive effects that can be achieved with the use of LS where an increase in workability can be observed with the lignosulphonate admixture for all types of activators. He also observed a slight reduction in a shrinkage compared to mixtures where no admixture was used. However lignosulphonates may lead to a retarded strength development and reduced flexural strength of AAS concrete. [3,22]

3 Experimental

3.1 Used raw materials

- Granulated blast furnace slag SMŠ 400, KOTOUČ ŠTRAMBERK, spol s.r.o
- Na_2CO_3
- Distilled water
- Water glass with silicate module 2.0
- Sodium hydroxide PENTA s.r.o
- Plasticizing additive
  - CHRYSO®Plast 461 lignosulfonate plasticizer

3.2 Methods

3.2.1 Preparation of paste mixtures

The same procedure was used to mix all the paste mixtures. The mixture consisted of the basic components, namely finely ground blast furnace slag, appropriate alkaline activator, distilled water, and the addition of a plasticizer. During the activation with water glass, water glass with modulus of 2.0 was used. The required modulus was then achieved by the addition of NaOH. The contents of the individual components are listed in Table 1. The plasticizer was added to the mixture by mixing it into the mixing water. The individual additions of the plasticizer are listed in Table 2. The paste was mixed with an water/slag ratio of 0.32. The individual components were mixed using a KitchenAid mixer. The paste was homogenized for 3 minutes. The homogenized paste was then used for further measurements.

Table 1.: Composition of alkali-activated pastes

Activator	GBFS [g]	H_2O [g]	NaOH [g]	WG module 2.0 [g]	Na_2CO_3 [g]
NaOH	600	322	124	-	-
WG module 0.5	600	144	45.35	38.5	-
WG module 1.0	600	133.5	28.75	77	-
WG module 1.5	600	123.2	12.15	115.5	-
Na_2CO_3	600	192	-	-	41

Table 2.: Addition of lignosulfonate

Addition [hm.%]	Addition [g]
0.2	1.2
0.4	2.4
0.6	3.6
0.8	4.8
1.0	6.0

3.2.2 Determination of workability of paste

The mixture was used to measure the workability of the paste using the slump method. The measurement was performed according to the ČSN EN 1015-3 standard. An steel cone was placed in the middle of the shaker table, which was then filled with paste. The cone was

removed, and the mixture was left loose on the pad. The mixture was then slumped by 15 strokes and then its diameter was measured in two perpendicular directions.

3.2.3 Determination of setting time of paste

The Vicat apparatus according to the ČSN EN 196-3 standard was used to determine the setting time. The Vicat ring was filled with paste and the surface was levelled. The needle of the Vicat apparatus was placed in a position just above the surface of the paste and lowered into the paste at regular intervals. When the needle was stopped at the desired value, the initial time of solidification was recorded. After solidification began, the Vicat ring was inverted and a circular needle was attached. Again, it was placed just above the surface of the paste and lowered. The measurement was terminated when the circular tip did not leave a trace on the surface of the paste after the needle was lowered.

3.2.4 Measurement of flexural and compressive strength

Determination of mechanical properties took place after 1, 7, 28 days of curing process according to the ČSN EN 196-1 standard. Beams measuring $40 \times 40 \times 160$ mm were used to measure flexural and compressive strength. The homogenized mixture was left in the molds for 24 hours. After 24 hours, the beams were demolded and placed under water to prevent volume contraction. First, the measurement of flexural strength was performed on the DESTTEST 3310, and then the two halves of the beam were used to measure the compressive strength, the values of which were averaged.

3.2.5 Determination of zeta potential

Zeta potential is a key variable in determining the strength of an electric bilayer between particles. This force is important in determining flocculation and dispersion in suspension. A Zetasizer Nano ZS instrument was used to determine the zeta potential (ζ) of blast furnace slag particles dispersed in solution. The ELS (electrophoretic light scattering) method was used. A reference sample was prepared by dispersing 1 g of blast furnace slag in 100 ml of distilled water. For the other samples, an activator was added to the solution, namely NaOH, water glass with modulus 1.5; 1.0; 0.5 and Na_2CO_3. The activator was added in a quantity so that the mixture contained 2, 4, 6, 8, 10 wt.% of Na_2O calculated on the amount of slag. For a mixture containing 4 wt.% of Na_2O, lignosulfonate was added by titration in 0 to 1 wt.% quantity.

4 Results and discussion

In the following section, the measured data will be taken into consideration and the impact of the lignosulfonate-based plasticizer on the workability, strength, zeta potential and hydration process of alkali-activated blast furnace slag will be commented on. The results will be presented in the same order.

4.1 Influence of lignosulfonate plasticizer on workability of paste

In Figure 10 we can observe a significant effect of lignosulfonate plasticizer on GBFS activated by NaOH. With each addition of plasticizer, an increase in the diameter of the paste cake compared to the reference sample is clearly observable. There was also observed an increase in the time during which the mixture could be processed. At maximum addition up to a 4.5-fold increase in setting time was observed.
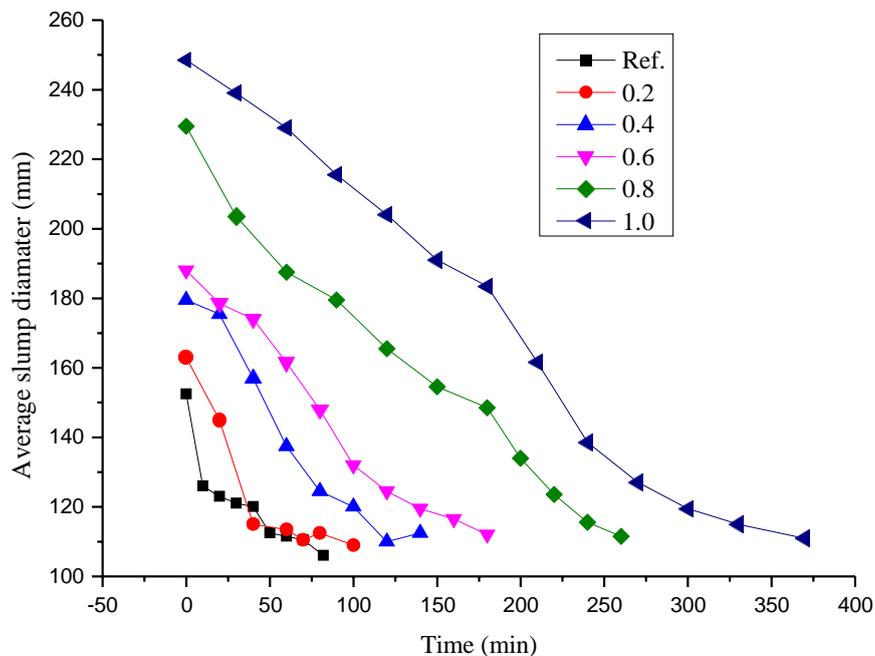

Fig. 10.*: Influence of lignosulfonate plasticizer on workability of GBFS activated by NaOH*

The effect of the lignosulfonate plasticizer on water glass-activated GBFS was significantly less observable than that of the NaOH-activated mixture. In Figures 11-13, the initial values of the paste cake diameter were very similar regardless of the addition of plasticizer. A similar trend could also be observed with the loss of workability, when, independent of the addition of a plasticizer, the mixture lost workability at similar times. However, with each addition of plasticizer, the blends achieved a higher setting time than the reference sample. For mixtures in which water glasses with a silicate modulus of 1.0 and 0.5 were used, the addition of 0.6 wt.% and 0.4 wt.% of lignosulfonate, respectively, reached the highest workability times. In a mixture with a modulus of 1.0, we can also observe that with the addition of 0.4 wt.% of lignosulfonate, the diameter of the paste cake increased after the first 15 minutes and only

then began to decrease. A similar trend could be observed with the 1.5 modulus mixture at the addition of 0.6 wt.% of lignosulfonate.

An interesting change in workability can be observed when changing the water glass (WG) modulus. The paste cake activated by WG mixture with a modulus of 0.5 reached a diameter between 130-140 mm and the paste cake of the activated WG mixture with a modulus of 1.5 reached a diameter between 260-280 mm. As the modulus increases, i.e. the SiO_2 molar content increases, the workability of the paste itself increases.
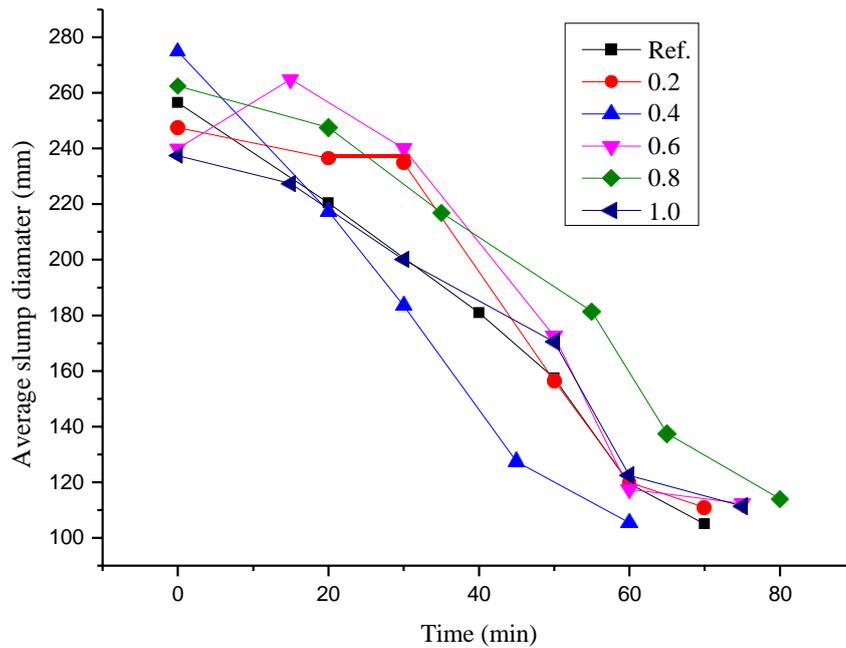

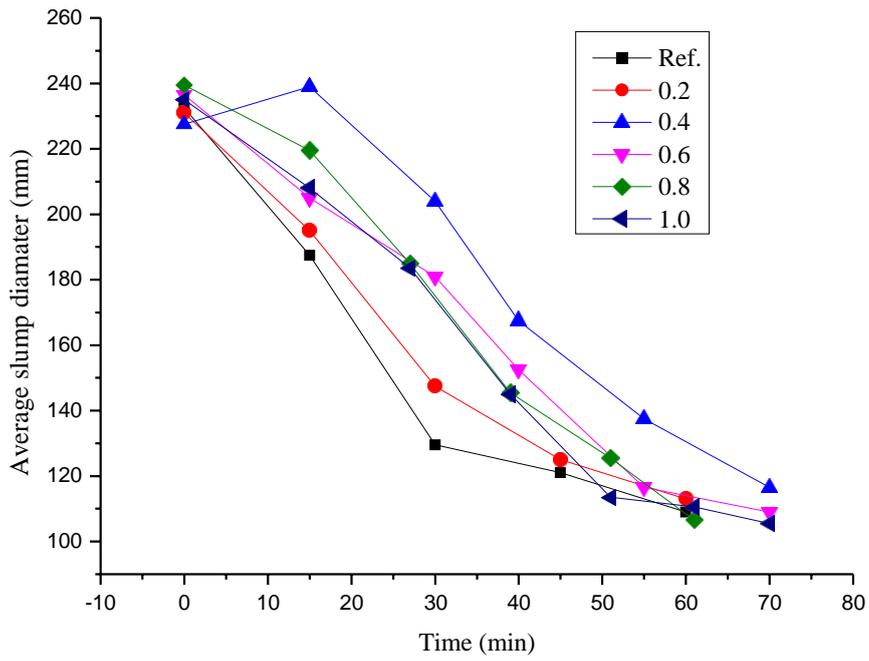***Fig. 11.****: Influence of lignosulfonate plasticizer on workability of water glass activated GBFS with silicate modulus of 1.5*

Fig. 12.*: Influence of lignosulfonate plasticizer on workability of water glass activated GBFS with silicate modulus of 1.0*
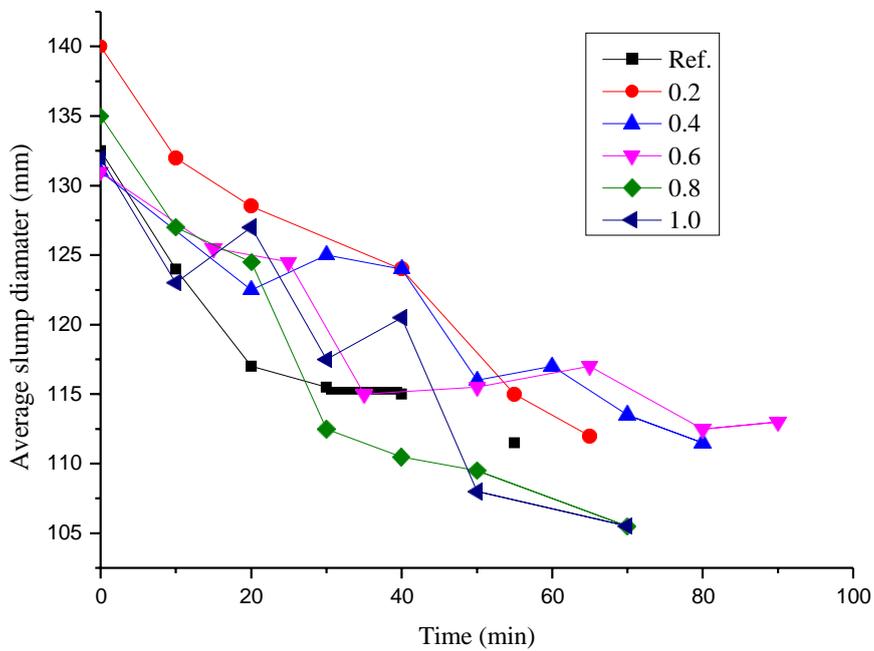

Fig. 13.*: Influence of lignosulfonate plasticizer on workability of water glass activated GBFS with silicate modulus of 0.5*

With a mixture activated by Na_2CO_3, a minimal improvement can be observed with the addition of a plasticizer. The differences in the diameter of the paste cakes with the addition of lignosulfonate and the reference sample were in the range of 10 mm, which is in the range of the measurement error bars. It can be said that lignosulfonate does not affect the workability of Na_2CO_3-activated GBFS. However, when observing the time for which the mixture could be treated with the addition of lignosulfonate, it increased significantly. The addition of 0.2 wt.% lignosulfonate lost workability at a similar time as the reference mixture. A significant increase in workability time begins to manifest itself from the addition of 0.6 wt.% of lignosulfonate when the addition of 1.0 wt.% extended the workability of the mixture by 75 minutes.
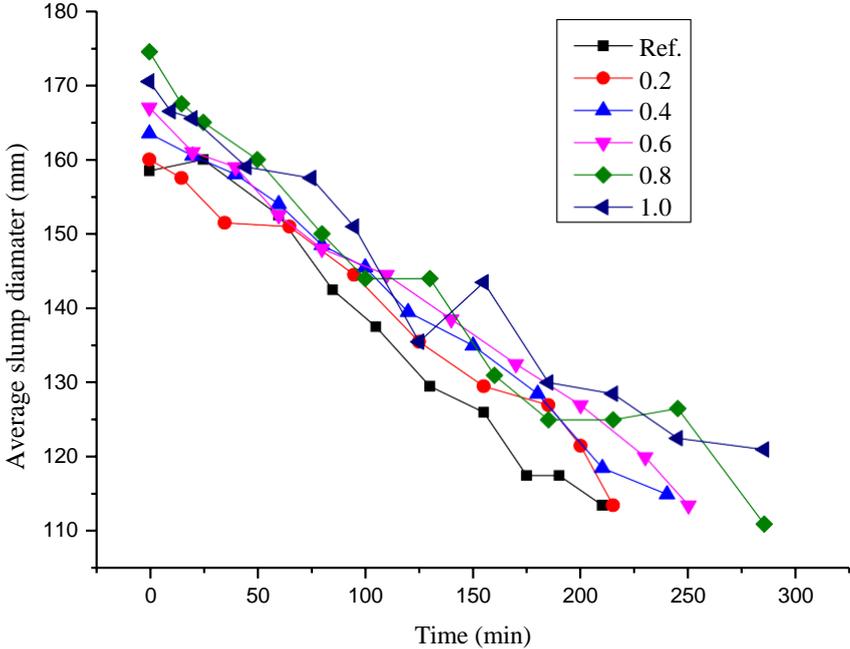

Fig. 14.*: Influence of lignosulfonate plasticizer on workability of GBFS activated by Na₂CO₃*

4.2 Determination of the initial and final setting times of paste

In the following section, the initial and final setting times of the concrete paste with the addition of lignosulfonate are discussed. All measured values are summarized in Table 3.

Table 3.: Initial and final setting time of the paste mixture with the addition of lignosulfonate

Paste	Addition of plastisizer	Initial setting time	Final setting time	Δt
GBFS + NaOH	0%	144 min	204 min	60 min
	0.2%	280 min	338 min	58 min
	0.4%	358 min	406 min	48 min
	0.6%	414 min	469 min	55 min
	0.8%	550 min	600 min	50 min
	1.0%	630 min	685 min	55 min
GBFS + VS 1.5	0%	66 min	81 min	15 min
	0.2%	68 min	87 min	19 min
	0.4%	73 min	93 min	20 min
	0.6%	73 min	97 min	24 min
	0.8%	75 min	99 min	32 min
	1.0%	77 min	115 min	38 min
GBFS + VS 1.0	0%	70 min	85 min	15 min
	0.2%	76 min	93 min	17 min
	0.4%	77 min	97 min	20 min
	0.6%	77 min	96 min	19 min
	0.8%	82 min	105 min	23 min
	1.0%	79 min	99 min	20 min
GBFS + VS 0.5	0%	375 min	430 min	55 min
	0.2%	415 min	475 min	60 min
	0.4%	460 min	517 min	57 min
	0.6%	510 min	576 min	66 min
	0.8%	540 min	620 min	80 min
	1.0%	580 min	650 min	70 min
GBFS + Na_2CO_3	0%	480 min	1216 min	736 min
	0.2%	510 min	1262 min	752 min
	0.4%	536 min	1296 min	760 min
	0.6%	550 min	1362 min	812 min
	0.8%	574 min	1374 min	800 min
	1.0%	610 min	1430 min	820 min

As we can see in Table 3., the GBFS + NaOH mixture interacted with the addition of lignosulfonate resulting in significantly prolonging the initial setting time. Already with the addition of 0.2 wt.% lignosulfonate, the initial setting time was prolonged by 2 hours and 15 minutes, while the addition of 1.0 wt.% caused an increase of up to 8 hours and 20 minutes. For mixtures activated with water glass with modules of 1.5 and 1.0, we can observe that the initial setting time occurred much earlier than the mixture activated with NaOH. Likewise, the addition of lignosulfonate to these mixtures did not have a significant effect on the change of the initial or final values of the setting time, but it is still possible to observe a slight prolongation of the observed values with increasing addition. With a water glass-activated mixture with a modulus of 0.5, there is a significant change when the final setting time of the mixture is closer to GBFS-activated by NaOH than to those activated with water glass. However, compared to the GBFS + NaOH mixture, the GBFS + WG mixture reached a high initial setting time already at the reference sample, and this time did not increase so radically

with each addition. The results of this mixture are close to the results of the GBFS + NaOH mixture. This behaviour could be explained by the large amount of NaOH that was used in the mixture to achieve the desired modulus of 0.5. This addition brought the properties of the mixture closer to the GBFS + NaOH mixture then mixtures activated by WG, thus bigger effect of admixture could be observed.

With the GBFS + Na_2CO_3 mixture, both the initial setting and the final setting times were prolonged. Overall, however, even without the addition of lignosulfonate, the mixture reached very high times when the reference sample showed the final solidification after 20 h. With the addition of 1.0 % by weight of slag, this time increased to 24 hours and 50 minutes. During the measurement, there was also the so-called "bleeding effect" when after leaving the mixture in the Vicat rings, the mixed liquid began to rise strongly on its surface together with the plasticizer. This is an undesirable phenomenon.

4.3 Determination of compressive and flexural strength

This subchapter deals with the determination of compressive and flexural strength of individual hardened mixtures.

Figures 15-16 show strength data obtained using a mixture of GBFS + NaOH with the addition of lignosulfonate. Compared to the results obtained from the other blends, the GBFS + NaOH blend showed the highest flexural strength with all wt.% plasticizer additions. In contrast, the compressive strength of this mixture was the lowest compared to other mixtures. The results show that almost all additions increased the overall strength of the cured mixture compared to the reference sample. The reference mixture showed better results only for the samples cured for 1 day, where its value of compressive and flexural strength exceeded the sample with the addition of 0.2 wt.% of lignosulfonate. The highest strengths in both cases were achieved by the sample with the addition of 1.0 wt.%, Namely 12.69 MPa of flexural strength and 46.77 MPa of compressive strength, respectively.
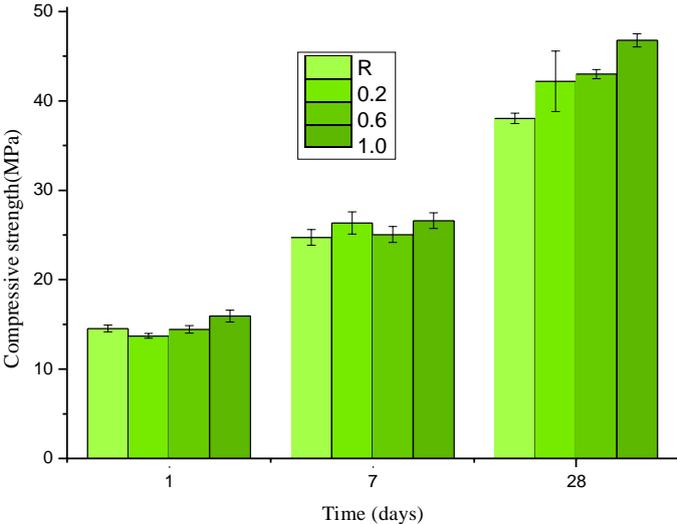

Fig. 15.: Compressive strength of GBFS activated with NaOH with the addition of lignosulfonate
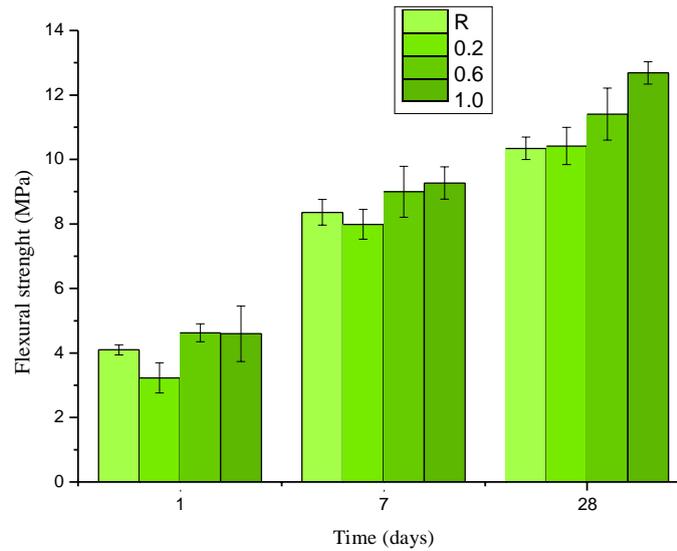
Fig. 16.*: Flexural strength of GBFS activated with NaOH with the addition of lignosulfonate*

In Figures 17-18 we can see the plotted values of the strengths of the mixture activated by WG with a module of 1.5. The mixture reached the high compressive strengths after only one day of curing, when almost all samples showed strengths of about 30 MPa. The exception was a mixture with the addition of 1.0 wt.% lignosulfonate, when this mixture reached a strength of only 5.43 MPa. This behaviour is probably due to overdose of the mixture with lignosulfonate, the high concentration of which caused a poor strength development after 24 hours. However, this trend was no longer as was demonstrated at 7- and 28-day strengths when the mixture showed similar and after 28 days even higher strengths than the other mixtures. At flexural strength, the LS addition of 0.2 % by weight of slag showed the highest 7- and 28-day strengths, and no further addition was able to exceed the strength of the reference sample.
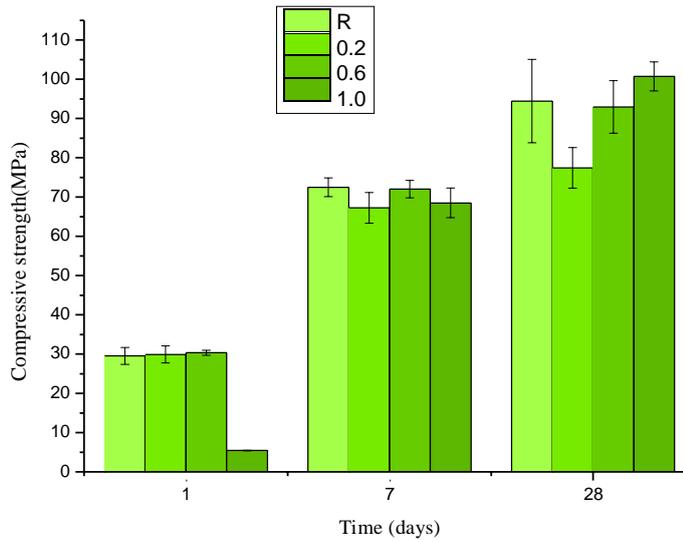
Fig. 17.: *Compressive strength of GBFS activated by WG with a modulus of 1.5 with the addition of lignosulfonate*
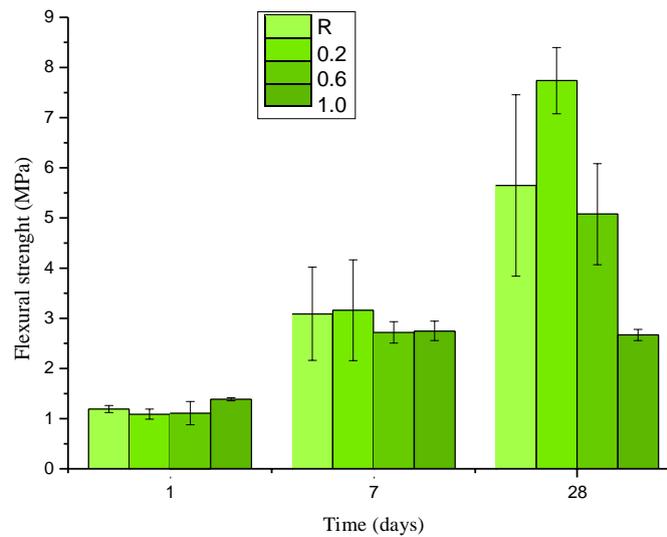

Fig. 18.: *Flexural strength of GBFS activated by WG with a modulus of 1.5 with the addition of lignosulfonate*

For mixtures activated by WG with module of 1.0, which are shown in Figures 19-20, there was no clear trend in the effect of lignosulfonate addition on their strength. At 1-day strengths, a similar behaviour was observed for samples activated by WG with a modulus of 1.5. We can also assume that there was an overdose of the admixture, which caused significantly lower final compressive strength. However, the difference is not as significant as with a mixture activated by WG with a modulus of 1.5, which could indicate the importance of the interaction between SiO_4 and lignosulfonate and the effect of this interaction on the early development of strength. When observing the flexural strength, no effect of lignosulfonate is apparent when the reference sample reached the highest 28-day strengths. At

1- and 7-day strengths, only a minimal difference among the samples is visible. It is worth noting that the flexural strength increased only minimally with time and in some samples, it even showed a higher 7-day strength than the 28-day strength.
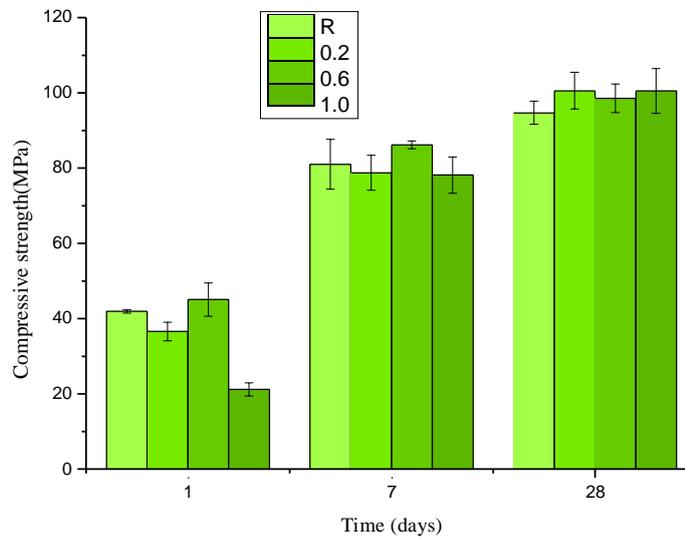

Fig. 19.: *Compressive strength of GBFS activated by WG with a modulus of 1.0 with the addition of lignosulfonate*
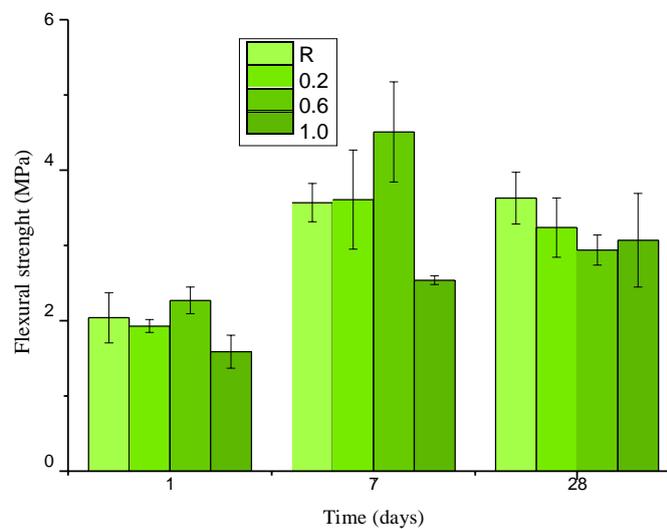

Fig. 20.: *Flexural strength of GBFS activated WG with a modulus of 1.0 with the addition of lignosulfonate*

The water activated GBFS mixture with a modulus of 0.5 showed relatively high compressive strengths after only one day of curing, but the reference mixture recorded the highest strength. For mixtures left to cure for 7 and 28 days, an increase in the strength of the mixture with the addition of a plasticizer can be observed. The highest strength was achieved by the mixture with the addition of 0.2 wt.% lignosulfonate, namely 79.67 MPa at 28 days. Additions of 0.6 wt.% and 1.0 wt.% also reached a higher 28-day compressive strength. In the case of flexural strengths, we can observe that the samples cured for one day exceeded with their flexural

strength samples cured 7 and 28 days. Assuming that the strength of the mixture increases with the time it is let to cure, we can consider this behaviour an anomaly. Such behaviour could be due to the autogenous shrinkage of 7- and 28-day mixtures, resulting in a uniform reduction in internal moisture due to GBFS hydration and subsequent cracking. The resulting cracks subsequently significantly reduce the resulting flexural strength. The highest one-day flexural strength was achieved by the mixture with the addition of 0.2 wt.% lignosulfonate. Higher additions did not increased the strength of the reference mixture. For 7- and 28-day mixtures, the addition of 1.0 wt.% Lignosulfonate showed the highest flexural strength. [28,29]
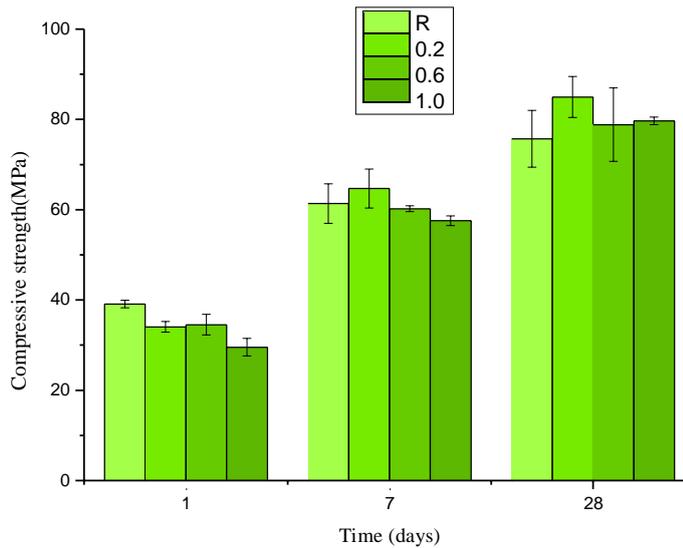

Fig. 21.*: Compressive strength of GBFS activated by WG with a modulus of 0.5 with the addition of lignosulfonate*
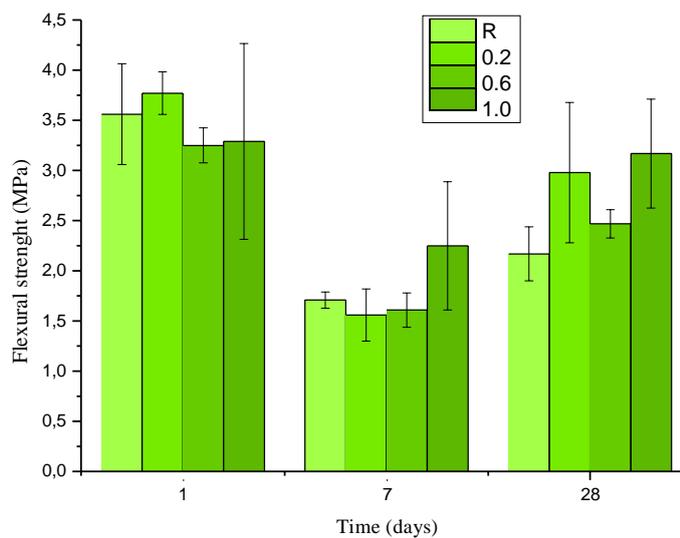

Fig. 22.*: Flexural strength of GBFS activated by WG with a modulus of 0.5 with the addition of lignosulfonate*

In the experimental determination of the strengths of the GBFS activated with Na_2CO_3, the strength after one day of curing process was omitted, due to insufficient cohesion of the mixture, which could not be subjected to mechanical properties measurements according to ČSN EN 196-1. The highest 7- and 28-day compressive strength was reached by the mixture with the addition of 0.2 wt.% lignosulfonate. With higher addition of lignosulfonate, the compressive strength did not exceed the strength of the reference sample.

The 7-day flexural strength was again highest with the addition of 0.2 wt.% and further additions did not reach a higher strength than the reference mixture. At 28 days of flexural strength, it can be observed to increase with each addition of plasticizer when the highest strength was reached by the mixture with 1.0 wt.% addition.
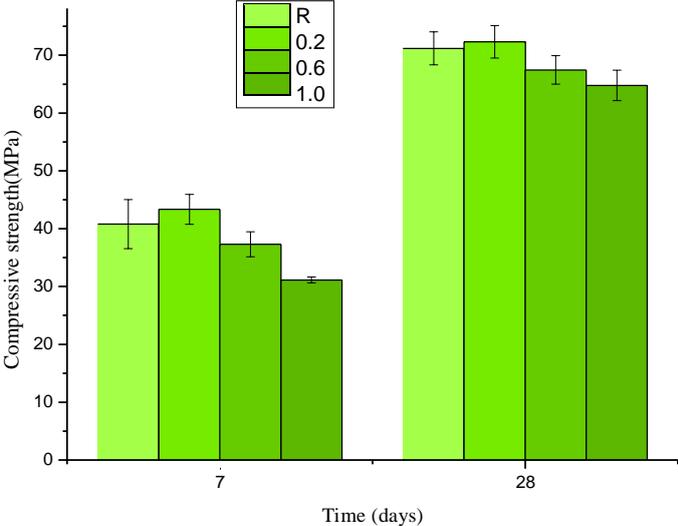

Fig. 23.*: Compressive strength of GBFS activated with Na₂CO₃ with the addition of lignosulfonate*
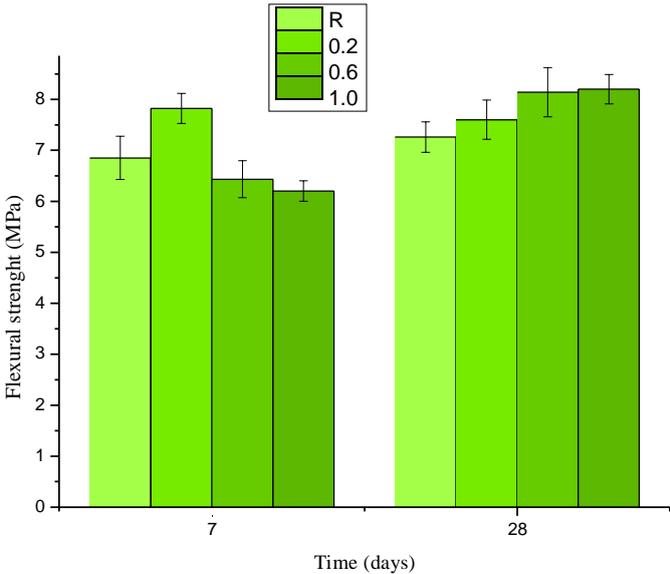

Fig. 24*: Flexural strength of GBFS activated with Na₂CO₃ with the addition of lignosulfonate*

4.4 Zeta potential of dispersed blast furnace slag particles

In the following subchapter, the zeta potential, and its dependence on the wt.% of Na_2O using various activators will be monitored. At the same time, the effect of the addition of lignosulfonate on the zeta potential of the activated mixture would be obtained.

In Figure 25. we can observe the change in zeta potential with increasing amount of Na_2O in the sample. In the reference sample, the dispersed GBFS particles showed negative zeta potential values. This phenomenon occurs due to the high pH value that a suspension of GBFS in water acquires. The high pH subsequently causes deprotonation of the silanol groups on the surface of the particle, leading to the formation of a negative surface charge. Subsequently, cations such as Ca^{2+}, Na^+ begin to adsorb to the deprotonated silanol groups, which form positively charged sites on the surface in the bilayer structure. [24] As shown in Figure 25, the addition of NaOH to the suspension results in an increase in the zeta potential and its subsequent transition to positive values. [25] This observation contradicts the assumption that from rising pH caused by the addition of NaOH, the zeta potential will become negative. This indicates the release of Ca^{2+} cations from the slag that enters the suspension upon its partial dissolution, caused by the increased pH. Their interaction with M^+ cations has a great influence on the surface properties of the particle. [24]

Fig. 25*: Dependence of the zeta potential (ζ) on the wt.% of Na_2O in NaOH activator*

Subsequently, the zeta potential was measured by adding lignosulfonate to a mixture of NaOH-activated slag with 4 wt.% of Na_2O. Already at the first addition, the zeta potential began to decline and take on more negative values. With each new addition, the zeta potential decreased almost in a linear trend. This behavior can be explained by coating of the blast furnace slag grain with a negatively charged lignosulfonate, leading to a change in the positive charge of the slag to a negative one.

4 wt. % Na$_2$O

zeta potential (mV) vs. concentration of lignosulfonate (wt. % GBFS)
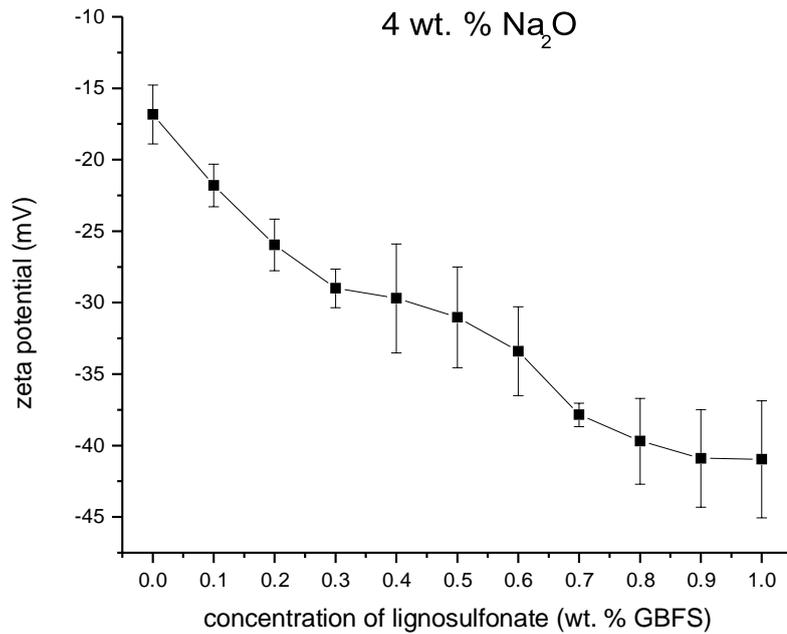
Fig. 26*.: Dependence of the zeta potential (ζ) on the addition of lignosulfonate in the GBFS mixture activated by NaOH*

In Figure 27 we can see the change in zeta potential depending on the use of water glass with different modules. In order to observe and confirm the trend, a water glass sample with a modulus of 0.25 was added. It is clear that with increasing water glass modulus, zeta potential acquires higher negative values. This trend appears to be directly proportional to the increasing wt.% of Na$_2$O in the suspension. The largest increase in the negative value of the zeta potential can be observed in most samples at 2 wt.% Na$_2$O. At this point adsorption of negatively charged SiO$_2$ which is rising in the sample together with Na$_2$O can be observed. Adsorped SiO$_2$ then changes the zeta potential to a negative value to the point where the surface of particles get saturated. With further addition, it was possible to observe only a very small increase in the negative value of the zeta potential, when after 4 wt.% Na$_2$O all WG models showed practically constant values.

The water glass solution reaches a high pH but not as high as the NaOH solution. The pH is high enough that upon contact of GBFS with the solution, OH-ions begin to break down the bonds between Ca–O, Si–O and Al–O. Subsequently, due to the high concentration of $[SiO_4]^{4-}$ and Ca^{2+}, a "primary C–S–H" gel is formed. [26, 27] The increase in the negative zeta potential when adding silicate particles to the GBFS suspension was caused by adsorption or precipitation of silica on the surface of the slag particles. Such behaviour was observed at high silicate concentrations compared to Ca $^{2+}$ concentrations. [24, 26]
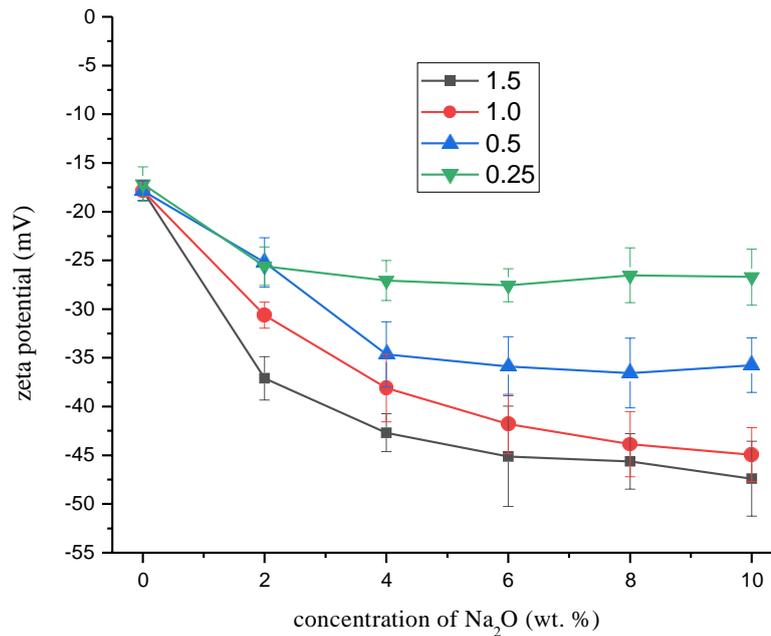
Fig. 27*: Dependence of the zeta potential (ζ) on the wt.% of Na₂O of WG activator with different modules*

Figure 28. shows the zeta potential values as a function of lignosulfonate addition. Lignosulfonate was titrated at 0.1 wt.%. As in the previous measurement, a water glass sample with a modulus of 0.25 was added to observe and confirm the trend. We can observe that with the addition of lignosulfonate, the zeta potential changes to positive values. Mixtures activated with modules of 0.25, 0.5, 1.0 show a minimal change, however, a sample with WG of module 1.5 showed a significant effect of lignosulfonate. The change in zeta potential manifested itself in this sample from the beginning as in the other modules, but with the addition of 0.7 wt.% lignosulfonate there is a sharp change, when its value rises significantly to zero. Such behaviour is non-standard, therefore, in order to confirm the monitored values, the measurement was performed 2 more times with freshly mixed samples. At the same time, the lignosulfonate addition was increased to 1.6 wt.%.

As we can see in Figure 29, similar behaviour was observed in all samples, which would confirm the observed trend. However, the zeta potential of the individual samples took different values when the greatest zeta potential was reached by sample No. 1 with the addition of 1.0 wt.% lignosulfonate and sample No. 2 did not reach this value even with an increased addition of 1.6 wt.% lignosulfonate. For this reason, the trend and not the absolute values of the zeta potential will be further monitored and discussed.

A possible explanation for this behaviour may be the aggregation of GBFS particles in solution and their sedimentation, where subsequently the Zetasizer Nano ZS performed measurements with a solution with insufficiently dispersed particles. This statement is supported by the performed measurement in which the intensity of particle scattering was monitored together with the zeta potential depending on the addition of lignosulfonate. In this measurement, it can be observed that with a sharp increase in the zeta potential, the intensity of scattering also decreases, when with the addition of 1.0 wt.% lignosulfonate the value of

the scattering intensity was almost zero. The results of this measurement are shown in Figure 29.
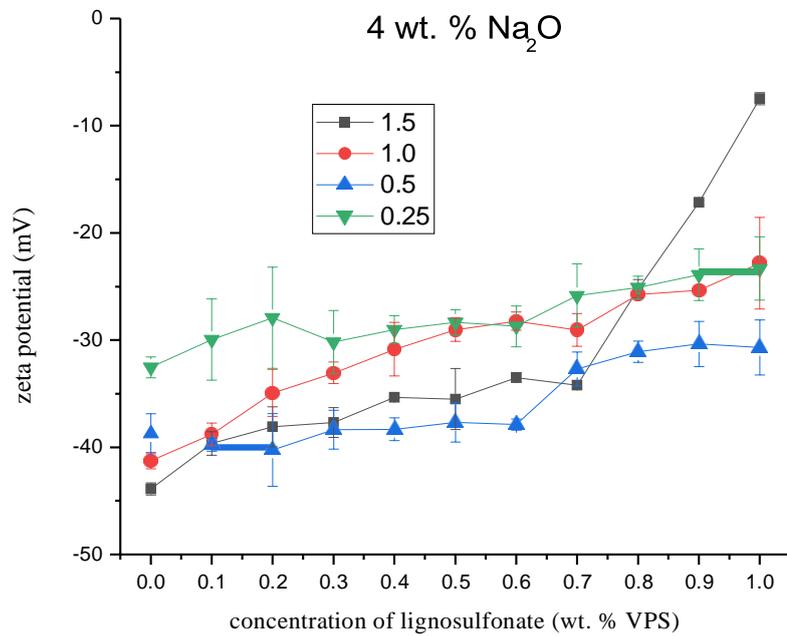

Fig. 28: *Dependence of the zeta potential (ζ) on the wt.% of the addition of lignosulfonate in the GBFS mixture activated by WG with different modules*
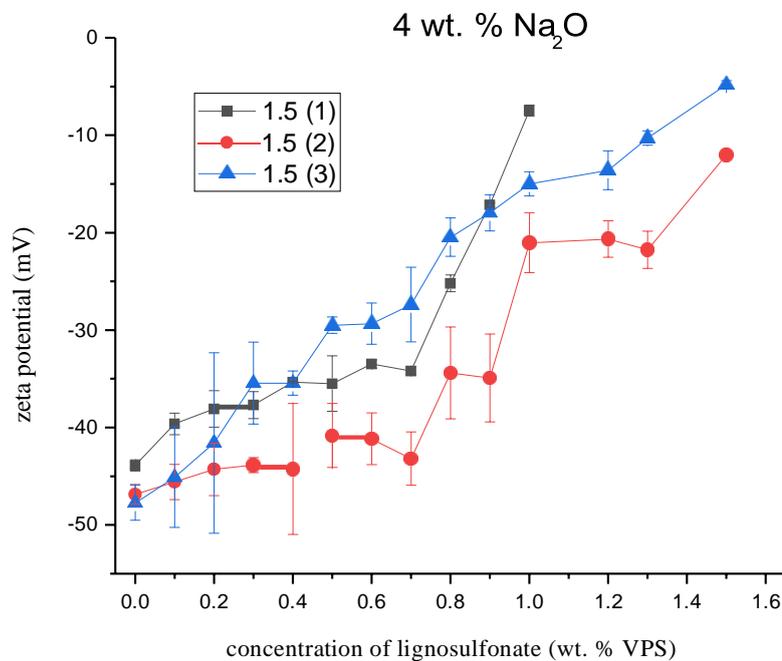

Fig. 29: *Dependence of the zeta potential (ζ) on the wt.% of the addition of lignosulfonate of the GBFS mixture activated by WG with a modulus of 1.5*

In Figure 30. we can observe the change of zeta potential depending on the wt.% of Na_2O using the activator Na_2CO_3. From the plotted values we can see that with increasing concentration the zeta potential decreases. Steep decrease in zeta potential manifested even at a small dose of Na_2O wt.%. As the wt.% of Na_2O increased, there were no further changes in the zeta potential, which leads us to the conclusion that the increasing addition of Na_2CO_3 does not affect the zeta potential of the dispersed GBFS particles. The measurement was performed twice to confirm the trend.

In Figure 31. we can see the change in zeta potential with the addition of lignosulfonate. The value of the zeta potential changes very slightly with the addition of lignosulfonate,. However, these values are burdened by a high standard deviation which, after consideration, indicates a minimal/no effect of lignosulfonate on the zeta potential of GBFS.

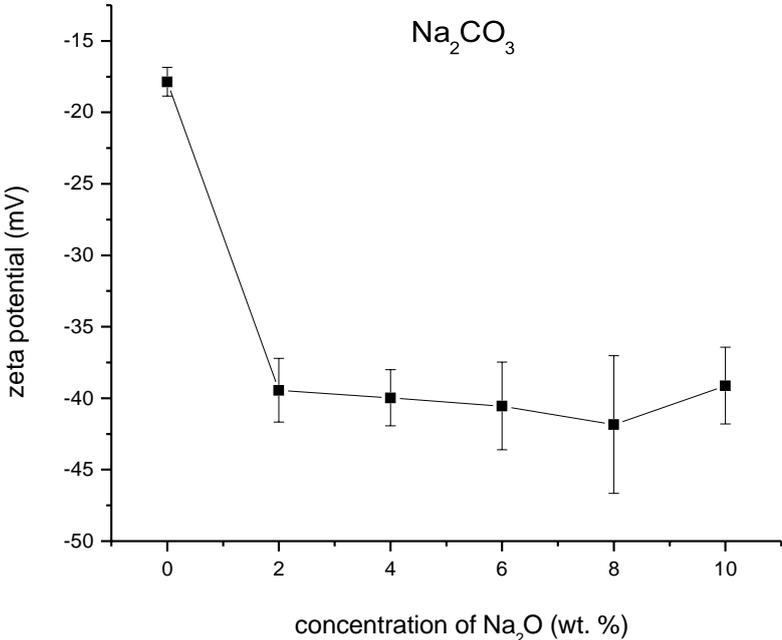

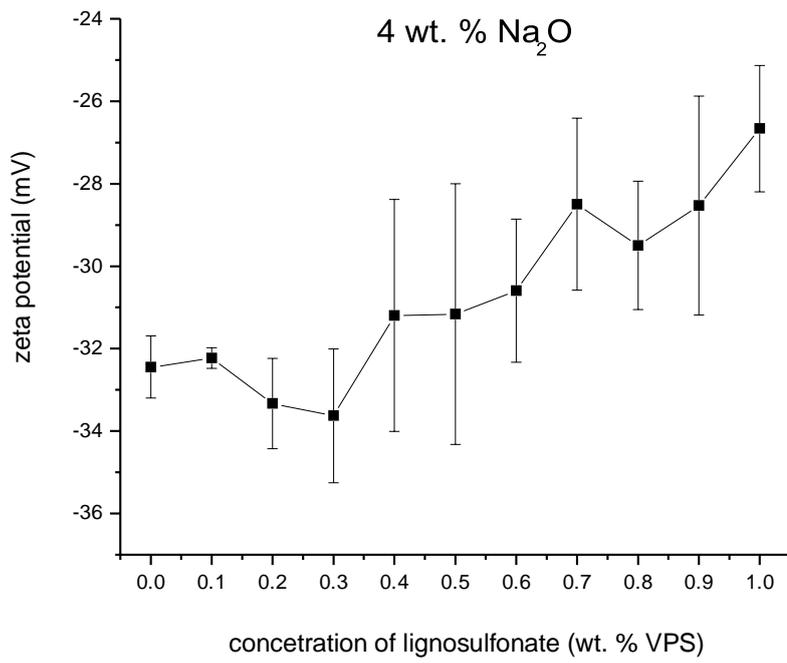*Fig. 30: Dependence of the zeta potential (ζ) on the wt.% of Na_2O activated by Na_2CO_3*

_Fig. 31.__.: Dependence of the size of the zeta potential (ζ) on the addition of wt.% of lignosulfonate in the GBFS mixture activated by Na₂CO₃_

5 CONCLUSION

This bachelor thesis dealt with the study of the use of a plasticizer based on lignosulfonate in alkali-activated materials. The aim was to determine the real impact and commercial viability of this plasticizer.

First, the workability, setting time and mechanical properties of the mixtures with the addition of lignosulfonate were monitored in the experimental part. Subsequently, the zeta potential of the particles was observed and its influence on the rheology of the mixture and its significance on all the above-mentioned properties was discussed.

In general, we can conclude that the workability of GBFS differed significantly based on the activator used. The effect of lignosulfonate on workability was also strongly related to the activator used. The most significant effect of lignosulfonate on workability could be observed with the mixture activated with NaOH. In this case, there was a significant improvement in workability with each addition of lignosulfonate, when the addition of 1.0 wt.% LS increased the workability time of the mixture up to 4.5 times. There was also a significant increase in the diameter of the paste cake. In contrast, with WG-activated mixtures, minimal or almost no effect of lignosulfonate on the mixture was observed. This statement applies mainly to mixtures in which WG with modules of 1.5; 1.0 was used. Such blends achieved high paste cake diameters even without the use of a plasticizer, but quickly lost workability and hardened. This behaviour is due to the presence of silica tetrahedra, which are involved in the formation of the C–S–H gel, thus resulting in its rapid formation. In contrast, the NaOH-activated mixture does not provide such tetrahedra and therefore a slower formation of the C–S–H gel from dissolved GBFS occurs. This behaviour is well observable with an activated WG mixture of module 0.5 when a high amount of NaOH was used to achieve the desired modulus. Behaviour similar to GBFS + NaOH was observed with this mixture. The limited effect of plasticizer on workability could be observed with the GBFS + Na_2CO_3 mixture. The diameter of the paste cake was kept constant in this case, independent of the addition of LS, but a consistent increase in time that the mixture was workable can be observed.

These results are also supported by monitoring the initial and final times of setting on Vicat device. Again, the activator used has a significant effect on the behavior of the mixture. The NaOH-activated mixture achieved higher values of the beginning and end of settings with the addition of LS. Conversely for mixtures with WG of 1.5; 1.0 silicate module there was a negligible impact. The mixture with WG of 0.5 silicate module again approached the results of mixture activated by NaOH. At the maximum addition of LS, they reached almost identical values. This is again due to the different content of silicate tetrahedra in the mixture and their formation of C–S–H gel. Almost no effect can be observed using Na_2CO_3. The initial setting time was prolonged, but due to the problematic nature of the mixture and the strong "bleeding" of mixing water with LS from the mixture, it is difficult to assess the effect of LS on this mixture. When observing the mechanical properties, the NaOH-activated mixture reached the highest 28-day strengths in both cases with the maximum addition of LS. However, if we take into account the error bars, it was a minimal difference compared to other samples. The most significant effect of LS on mechanical properties could be observed in mixtures with WG 1.5; 1.0, when with maximum addition there was a significant decrease in one-day strengths. In this case, it was an overdose of the mixture which subsequently

caused a slowing of hydration and the formation of a C–S–H gel. This behavior no longer occurred at 7- and 28-day cured samples.

The results of the zeta potential measurement again showed the influence of the activator on the behavior and properties of the mixture. When monitored, the zeta potential reference value was always negative due to the alkaline nature of GBFS in water. Upon addition of NaOH as an activator, the zeta potential reached positive values after adsorption of cations on the slag surface. After the addition of lignosulfonate, the zeta potential begins to decrease again to negative values. This indicates its adsorption on the particle surface and, due to the negative charge of the LS, a consequent change in the zeta potential. Such a change causes electrostatic repulsion of the particles, which could result in the observed strong effect of LS on the properties of the NaOH-activated mixture.

Interesting trends could be observed with water glass activated mixtures. In this case, the zeta potential reached constant negative values. Following the addition of LS, the zeta potential value began to rise slightly to positive values in most of the monitored water glass modules. Exception was the sample with WG of module 1.5 when there was a sharp increase in zeta potential to positive values. This behavior is abnormal. By monitoring the dispersion of the particles in the suspension, an possible explanation is given as to when the particles agglomerated in this sample which affects the zeta potential measurement. However, this phenomenon was also demonstrated in repeated measurements, which could indicate another reason for this behavior. Therefore, there is the potential for a closer examination of this phenomenon, which can have a high impact on the properties and rheology of the used mixture. The zeta potential of the Na_2CO_3-activated mixture decreased to negative values even at low activator concentrations and subsequently did not change. This was also the case with the addition of LS when he had almost no effect on the zeta potential.

Finally, we can conclude that the lignosulfonate-based plasticizer is one of the chemical additives that have their place in current as well as future material chemistry. Their positive effect has been demonstrated especially in the workability of alkali-activated mixtures and suggests a possible potential for further study of its influence on rheological properties which have a strong impact on the usability of such mixtures.

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7 SHORTCUTS

LS	Lignosulfonate
WG	Water glass
GBFS	Granulated blast furnace slag
AAS	Alkali-activated slag
BFS	Blast furnace slag
C–S–H	Calcium-silicate-hydrate
C–A–S–H	Calcium-aluminate-silicate-hydrate
C–A–H	Calcium-aluminate-hydrate
NMR	Nuclear magnetic resonance
OPC	Ordinary Portland cement
ELS	Electrophoretic light scattering