Quality Lignosulfonate for Concrete

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Introduction

Cement is a much agglomerated powder that has to be dispersed to be fully utilised when making concrete. Lignosulfonate is a group of dispersing aids used in making concrete. It disperses the cement in the mixing water of the concrete and increases the utilisation of the cement. The workability of the concrete is also increased. Lignosulfonate belongs to the group of plasticizing admixtures, also called water reducing admixtures.

The use of lignosulfonate as water reducing admixture in concrete started in the 1930-ties and is documented in US patent 2,081,642 [2], Figure 1. The first use was of unmodified thick liquor from the sulphite pulp cooking. An impressive water reduction of 10-12 % was achieved in a 1:3 standard mortar by adding 0.15 % of lignosulfonate by weight of cement. The lignosulfonate used as water reducing admixture today are much more refined and modified than the ones used in the 1930-ties. Some aspects of refining lignosulfonate and parameters defining the quality of lignosulfonate will be discussed in this paper.

From Lignin to Lignosulfonate

The raw material for production of lignosulfonate is trees. Trees can be grouped as softwood and hardwood.

The wood in trees is composed of different cells, which give the mechanical strength to the trees. The wood cell consists mainly of cellulose, hemicellulose and lignin. A simplified picture describes a skeleton of cellulose surrounded by other substances functioning as a matrix (hemicellulose) and encrusting (lignin) materials. Wood can be separated into two categories of molecules: macromolecules and low molecular weight substances. Macromolecular substances:

- Cellulose (45 %)
- Hemicellulose (20–25 %)
- Lignin (softwood 27–37 %, hardwood 16–29 %)

The properties and chemical composition of lignin and hemicellulose differ in softwood and hardwood. The cellulose is a uniform component of all wood.

Low molecular weight substances

- Extractives (terpenes, alcohols, aliphatic acids, aromatic compounds, etc.)
- Mineral components (K, Ca, Mg, Si, etc.)

The word lignin is derived from the Latin word “lignum” meaning wood. Lignin forms an essential part of the wood stems. It does not only act as an “encrusting” material or as a binder of some secondary nature, as is often misleading stated, but performs multiple functions that are essential to the life of the plant: Transport of nutrition and durability of the wood. Lignin imparts rigidity to the cell walls and acts as a binder between wood cells, creating a composite material that is outstandingly resistant to impact, compression and bending. Lignin, a natural polymer made up of phenylpropane units, is a major component of vascular plants. After polysaccharides, lignin is the most abundant organic polymer in the plant world. Whereas the lignin content within a species is reasonably constant, there may be considerable variation among species.

In nature every plant uses carbon dioxide (CO2) from the atmosphere and converting it into plant material through the process of photosynthesis:

\[ \text{CO}_2 + \text{H}_2\text{O} + \text{energy} \rightarrow \text{Sugars} + \text{O}_2 \]

Photosynthetic processes using chlorophyll in green leaves to produce sugars:

![Photosynthesis Diagram](image)

Sugars condense with dehydration to polymers:

\[ \text{sugars} + \text{H}_2\text{O} \rightarrow \text{cellulose} + \text{hemicellulose} + \text{polysaccharides} \]

Figure 2: The photosynthesis consuming CO2, water and energy to produce plant material.
air in the photosynthesis to produce plant material. This is also the start of the production of lignin. The photosynthesis is transformation of CO2 to carbohydrates (sugars) using light as the energy. This is shown schematically in Figure 2.

The photosynthesis is consuming 1.5 kg CO2 from the air for every kg of lignosulfonate [4]. Taking the effect of ware reduction which is enabling the production of concrete with less cement for a given concrete quality, the emissions caused during the production of lignosulfonate and also the photosynthesis into account the total reduction in emission and saving in CO2 is 14 kg for every kg of lignosulfonate used as water reducing agent or superplasticizer in concrete. (Figure 3)

As a result of different enzymatic reactions in the plant, glucose (sugar) is through different complex steps transformed into other chemical components, which can be called the phenylpropane lignin precursors.

The precursors are
- p-Coumaryl alcohol,
- Coniferyl alcohol and
- Sinapyl alcohol.

Lignin in wood is mainly composed of combinations of coniferyl alcohol and sinapyl alcohol.

Because it is not possible to isolate native lignin from wood without degradation, the true molecular mass of lignin in wood is unknown. It is important to keep in mind, however, that the term “lignin” or “lignosulfonate” normally refers to a mixture of substances having similar chemical composition but structural differences.

Lignosulfonate can be classified as hydrophobic polyelectrolytes. This description refers to the fact that the polymer is dependent on its ionised groups for water solubility. Lignosulfonate is in that respect similar to sulfonated synthetic polymers used as water reducing admixtures, e.g. sulfonated naphthalene formaldehyde condensate (SNF) and sulfonated melamine formaldehyde condensate (SMF). Both are intrinsically hydrophobic polymers. Compared to common linear polymers there is a significant complexity inherent to the chemical structure of lignosulfonate. The lignin polymer is probably more complex than most polycarboxylates (PCE) used in concrete.

In general lignosulfonate samples tend to have a greater polydispersity than synthetic polymers produced by condensation reactions. The polydispersity make the lignosulfonate less well defined since, not only are there several functional lignosulfonate groups, the content of these groups is also depending on the lignosulfonate molecular mass (Mw).

The role of the relative content of different functional groups is more difficult to predict than configurational differences, and the effect of which may be expected to differ from system to system. An important phenomenon for the function of lignosulfonate in cementitious systems is that a low ratio of sulfonate to phenolic and carboxylic groups leads to a reduced stability of lignosulfonate in alkaline solutions rich in calcium ions. Because of this effect precipitation of Ca-lignosulfonate complexes in alkaline solution occur with several families of sulfonated lignins.

Pulp has mostly been produced from wood. Pulp has predominantly been used for papermaking but also processed to various cellulose derivatives. An important part of the pulping processes is to liberate the fibres, which can be accomplished either chemically or mechanically or by combining these two types of treatments.

The principal behind the chemical pulping process is to separate the cellulose by dissolving other macromolecules like hemicellulose and lignin into the lignosulfonate liquor.

The typical processing condition of acid sulfite pulping (140 °C, pH 1–2) results in effective delignification.

Two reactions during the sulfite cook are of importance in the formation of lignosulfonate: Fragmentation and sulfonation. These reactions are the main ones, but there will also be others such as condensation. The result of the reactions is water-soluble sulfonated lignin (lignosulfonate). The hemicellulose (sugar polymer) will under the acidic sulfite conditions be hydrolysed to monomeric components like D-mannose, D-glucose, D-xylene, L-arabinose, D-galactose and L-ramnose (reducing sugars) in the cooking liquor. This means that the lignosulfonate intermediate (the “liquor” after removal of the pulp) contains sulfonated lignin fragments of different molecular size (the lignosulfonates),
sugar monomers, inorganic salts and small amounts of extractives from wood. The lignosulfonate used in water reducing admixtures is further modified to give it the desired properties and to make it suitable for formulating and combining it with other raw materials.

Good quality lignosulfonate is consistent and have very small variations from batch to batch on these parameters. The same applies for pH, amount of insoluble and concentration (dry matter).

**Performance of Lignosulfonate**

The performance of admixtures in concrete is defined by a number of parameters: water reduction or initial workability, workability retention, set retardation, air entrainment, and early and final strength. Figure 5 shows a performance window defined by water reduction and workability retention. Traditional plasticizers with water reduction in the range of 8-12 % are typically used in lower grade – every day – concrete with strength in the range of 25-30 MPa. The workability retention needed is normally moderate. Lignosulfonate – Borresperse CA-SA, Norlig SA, Borresperse NA-SA – and/or gluconate is typically used in formulations of such admixtures. Traditional superplasticizers cover a wider range of workability retention, and are formulated based on SNF or PCE. The formulation typically contains lignosulfonate and/or gluconate to provide workability retention and to provide retardation when needed. Borregaard offers lignosulfonate that have similar performance to such superplasticizers: Ultrazine. The water reduction is in the range 15-20 % and workability retention is 60 minutes or more. Admixtures with higher water reduction and longer workability retention are formulated based on PCE. Lignosulfonate are in some cases included in these formulations to provide retardation and workability retention.

The hydration of cement is exothermic and the rate and amount of heat generated is depending on the chemistry of the cement, the particle size distribution of the cement, w/c and admixtures that are added to the cement paste. Figure 6 shows the heat development of three EN 197-1 CEM I (OPC) cements measured in the isothermal calorimeter in Borregaard’s cement and concrete laboratory in Mumbai, India. The blue curve shows a normal hardening 42.5 (MPa) grade cement. The green curve shows a rapid hardening 42.5 grade, and the red curve shows a rapid hardening 42.5 grade.
Figure 7. The heat development rate (dQ/dt) and the developed heat (Q) of an OPC cement; EN 191-1 CEM I 52.5 R in combination with three different lignosulfonate; Borresperse CA-SA, Borresperse NA-SA, and Norlig SA. The lignosulfonate samples were added at dosage: 0 % sbwc; 0.30 % sbwc; 0.40 % sbwc.

Figure 8. Summary of the heat development of three OPC cements, EN 197-1 CEM I in combination with three lignosulfonate from Borregaard. (dQ/dt @ 0.8 h) shows the heat development rate after 0.8 hours which is the first data point measured, and at the end of the initial heat development peak. Set time is determined as the time of \(\frac{1}{2} \times (\text{maximum } dQ/dt)\), and (maximum dQ/dt) is the peak value of the silicate hydration peak.
hardening 52.5 grade cement. The higher the cement strength (grade) is the more rapid is the heat development. The rapid hardening cement has of course a much faster heat development than the normal hardening cement. It is obvious that the early strength will be higher with a rapid hardening than a normal hardening cement. The higher the grade is the higher is also the early strength. The early strength correlates with the accumulated heat (Q) as shown in Figure 6.

Lignosulfonate is known to retard setting and strength development. The extent of the retardation is depending on the lignosulfonate. In Figure 7 an example with three lignosulfonate used with the EN 197-1 CEM I 52.5 R cement also used in Figure 6 is shown. The dosage of the lignosulfonate was: 0; 0.30 % sbwc ; 0.40 % sbwc. The three lignosulfonate are:
- Borresperse CA-SA – calcium lignosulfonate with 2.0 % reducing sugars
- Norlig SA – calcium/sodium lignosulfonate with 2.4 % reducing sugar
- Borresperse NA-SA – sodium lignosulfonate

The retardation increases with increasing dosage of all three lignosulfonate. The retardation can be seen as the delay in the main heat development peak (maximum of dQ/dt), known as the silicate hydration peak. The maximum value of the rate of heat development (dQ/dt) is also reduced slightly by increasing dosage of the lignosulfonate samples. The retardation is the same with Borresperse CA-SA and with Norlig SA in this case. Borresperse NA-SA is causing slightly more retardation. This is also shown in Figure 8. The effect on retardation of Borresperse CA-SA, Norlig SA, and Borresperse NA-SA with the three cements shown in Figure 6 is summarised in Figure 8. Generally the retardation is stronger the lower the cement grade is.

Increased retardation has significant positive effect on the
Admixtures Lignosulfonate

Microstructure of the cement paste. In [1] it is demonstrated that the increased retardation caused by lignosulfonate caused decreasing porosity of the matrix (cement paste of the concrete). Lignosulfonate cause the volume of pores smaller than 275 nm to be reduced. The volume of larger pores is the same as that produced with superplasticizer addition. The study included one polycarboxylate, one sulfonated naphthalene formaldehyde condensate and four lignosulfonate samples. The admixture dosage was selected to produce the same concrete slump with all the samples. In accelerated chloride penetration experiments it was shown that retardation produce concrete with higher resistance to chloride ion penetration. This is due to the reduction in porosity and permeability of the concrete matrix. Further it is demonstrated that the addition of lignosulfonate results in lower early strength by higher later age strength than with the addition of the superplasticizers.

The effect of plasticizing admixture on the workability of concrete is measured by slump or slump flow. These methods are single point methods, i.e. they provide some information on the workability but they do not provide a fundamental description and it can be difficult to compare different plasticizing or superplasticizing admixtures. Measuring the rheology provides basic information and different admixtures can easily be compared. Yield value correlates with 1/(slump) for concrete.

In Borregaard’s cement and concrete laboratory in Mumbai, India the rheology of cement paste, mortar and concrete is measured. An example of the effect of five Borregaard lignosulfonate on the rheology of cement paste with three different cements is shown in Figure 9. The yield value and the plastic viscosity are plotted in rheographs as described in [3]. The dosage of the lignosulfonate was 0; 0.10 % sbwc; 0.30 % sbwc; 0.40 % sbwc. All the samples produced similar effect. Increasing dosage of lignosulfonate reduced both the yield value and the plastic viscosity in the EN 197-1 CEM I 42.5 N cement. The lowest dosage of lignosulfonate caused a small increase in plastic viscosity with the fly ash cement. Increasing the dosage caused reduction in both yield value and plastic viscosity. The combination of slag cement and low dosage of lignosulfonate caused reduction in plastic viscosity and no effect on yield value. Increasing the lignosulfonate dosage caused reduction in both yield value and plastic viscosity. In concrete the effect of admixture on rheology and trends seen in cement paste will be slightly different. Similar effect on the yield value is normally observed, but the effect on reducing the plastic viscosity is often less: In Figure 9 the effect of increasing lignosulfonate dosage is causing “movement” towards origo. In concrete the trend would probably be more towards the abscissa axis.

The performance of an admixture in concrete is as shown in Figure 5 defined by a number of parameters. An example of a required performance of a water reducing admixture is shown in Figure 10. The concrete has to have a specific workability – slump – when it arrives at the construction site. To reach this workability the concrete normally has to be produced with a higher workability at the ready mixed concrete plant to accommodate the workability loss during the transport of the concrete to the construction site. Different water reducing admixtures have different workability retention and the initial workability has to be different. The different admixtures are thus added at different dosage as shown in Figure 10. Although the dosage-set time response curve of the different admixtures might be very different, there might be only minor difference in set time taking the dosage into account. Different admixtures and raw materials for formulating admixtures have to be compared based on the performance profile and dosage-response performance. The cost-in-use of the admixture or the raw material in the formulation is depending on the dosage.

Conclusion

Lignosulfonate are made from renewable materials and 14 kg of CO2 is saved for every kg of lignosulfonate used in concrete.

The quality of lignosulfonate is not only defined by its performance in concrete, but also by its compatibility with other raw materials. Good quality lignosulfonate should be easy to handle, and change in temperature should not cause formation of crystals or sludge and insoluble material.

Lignosulfonate are robust admixtures and variations in the cement chemistry and quality has limited effect on the performance of lignosulfonate based water reducing admixtures. However, some differences are observed between different cements.

The performance profile of the lignosulfonate should be taken into account when evaluating it and doing cost-in-use calculations.

Reference


