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Lignosulfonian – przyjazny dla środowiska i godny zaufania surowiec do produkcji domieszek

LIGNOSULFONATE – A GREEN AND RELIABLE RAW MATERIAL FOR CONCRETE ADMIXTURES

Streszczenie

Lignosulfoniany są „koniem roboczym” przemysłu domieszek do betonu, używanym we wszystkich zastosowaniach budowlanych, ale w ostatnich latach obserwowaliśmy spadek ich dostępności. W związku z tym podjęto inwestycje aby lignosulfoniany pozostały dostępnym surowcem do produkcji domieszek na długi czas. Ponadto usunięcie wąskich gardeł w istniejących zakładach zapewni dostępność lignosulfonianów. Gdyby jednak zamykanie celulozowni postępowało dalej, produkcja może być kontynuowana w opatentowanej i wypróbowanej technologii BALI™

Lignosulfoniany są stosowane jako plastyfikatory do betonu od lat 30. Efekt ten jest osiągany głównie przez elektrostatyczny mechanizm działania. Rozwój technologii betonu pokazał ograniczenia związane z używaniem lignosulfonianów. Jednak na rynku są już dostępne produkty o polepszonej kompatybilności, polepszonej zdolności zmniejszenia ilości wody zarobowej i mniejszych właściwościach opóźniających.

Nowoczesne mieszanki, takie jak beton samozagęszczalny (SCC) mogą być dyspergowane z użyciem lignosulfonianów. Pozwalają one uprościć produkcję przez nadanie spoistości w efekcie znacząco obniżając ryzyko wydzielenia wody i segregacji.

Ekstruzja betonu jest sprawdzona jako szybka i ekonomiczna technologia m.in. do stawiania barier rozdzielających pasy ruchu na drogach oraz krawężników. Tiksotropowe działanie lignosulfonianów pozwala tu na stawianie około 15 metrów w ciągu 1 minuty.

Niemniej jednak, większość (80%) betonu produkowanego na świecie ciągle należy do niskich i średnich klas wytrzymałości (<40 MPa po 28 dniach). W roku 2005 w Europie było to 91% < 35 MPa. Używanie lignosulfonianów w tym segmencie rynku jest bardzo

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opłacalne ze względu na korzystny stosunek ceny do wydajności, a także ze względu na stabilność jaką dają mieszance, pozwalającą na radzenie sobie ze zmiennością innych parametrów takich jak stosunek w/c, zawartość frakcji pylastych w piasku, jakość wody, zanieczyszczenie gliną i wiele innych.

Abstract

Lignosulfonates are the workhorse of the concrete admixture industry, catering to all construction applications, but in recent years a decline of availability was seen. In order to allow lignosulfonates to stay a sustainable precursor for admixture formulations, investments into long term sustainability have been decided. Additionally, debottlenecking of existing plants will secure the sustainability of lignosulfonate. In case closures of pulp mills will continue, the patented and verified BALITM technology can be pursued.

Lignosulfonates are utilized to plasticize concrete since the 1930's. This is mainly achieved via an electrostatic working mechanism. Recent concrete technology developments showed restrictions for the usage of lignosulfonates. Lignosulfonates with improved compatibility, water reduction capacity and reduced retardation have been developed.

Modern concrete mix designs such as Self Compacting Concrete (SCC) can be dispersed with a lignosulfonate, which reduces the complexity at the production level by providing cohesiveness hence significantly reducing the risk of bleeding and segregation.

Also, concrete extrusion proved to be a fast and cost efficient method to place for example high speed freeway separators or rim stones. The thixotropic effects of lignosulfonates allow a fast placing of up to 15 meter in 1 minute.

Nevertheless, the majority (70-80%) of the concrete volume produced worldwide still belongs to low to mid-range strength class (<40 MPa at 28 days). The use of lignosulfonates in this market segment is highly beneficial due to favorable cost to performance ratio and the robustness provided to the concrete, which allows dealing with variability of several parameters such as water to cement ratio, fine content of the sand, water quality, temperature, clay contamination, and many more.

1. Introduction

Lignosulfonates are mostly manufactured in biorefineries by chemical separation from the cellulose of wood. Thus lignosulfonates are produced from a green and renewable resource: trees. As trees use the carbon dioxide to build the lignin this leads to permanent CO_2 capture within the lignin molecule and thus CO_2 is withdrawn from the atmosphere.

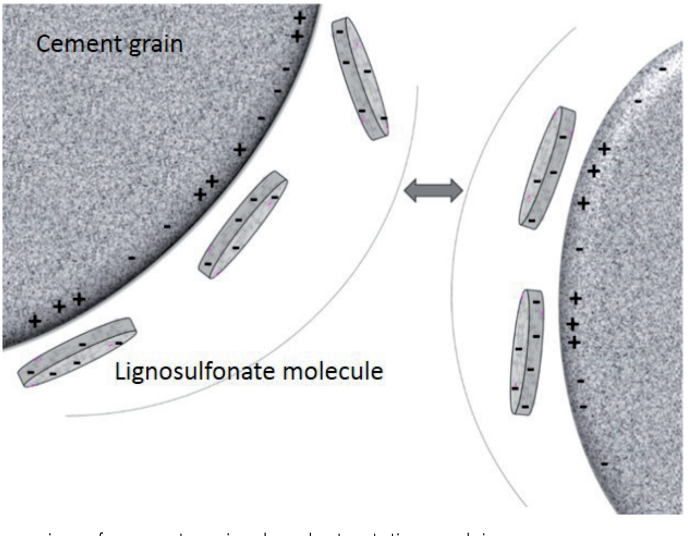
In order to allow lignosulfonates to stay a sustainable precursor for admixture formulations, investments into long term sustainability have been decided. Additionally, debottlenecking of existing plants will secure the sustainability of lignosulfonate. In case the closures of pulp mills will continue, the patented and verified BALI™ technology can be pursued to bring the required volume to market.

Concrete is the most utilized building material globally. Over the last decades the concrete technology has emerged to rather complex mix designs adjusted to a huge variety of applications within the field of construction. To deal with more and more challenging technical requirements and increasing complexity, a huge variety of concrete admixtures has been developed. The most commonly used concrete admixtures today belong to the dispersants family: use of these admixtures allows improving concrete workability and/or reducing the added water amount for improved mechanical strength and durability [2]. This is achieved through dispersion of the cement grains via electrostatic and/or steric mechanisms. Lignosulfonate (LS) is the most frequently used raw material for such formulations.

This paper will explain why lignosulfonate is and will remain a green and sustainable raw material to meet today's concrete challenges.

2. Working mechanism of dispersion of lignosulfonates

Lignosulfonates are used to plasticize concrete since many decades [1]. These natural polymers work as dispersants to de-agglomerate the cement and fine particles present in



Picture 1. Dispersion of cement grains by electrostatic repulsion

the concrete mix designs. Cement dispersion is mainly achieved thanks to an electrostatic working mechanism. As an initial step, the polymers adsorb onto the cement particle surfaces changing, as a consequence, the surface into a mainly negatively charged surface. Secondly, cement and fine particles are dispersed thanks to electrostatic repulsion effect. At a macroscopic level, this dispersing effect allows, either to use less water in concrete whilst keeping good workability, or to increase workability without increasing water content.

3. Recent product development based on lignin chemistry

Recent concrete technology developments increased the requirements for chemical admixtures even further and this resulted in some limitations to the use of standard lignosulfonates. A lignosulfonate with improved compatibility in formulation, stronger water reduction capacity and controlled retardation has therefore been developed by Borregaard LignoTech and is commercially available. The performances of this new product have been evaluated in different concrete mix designs and with various cement types, comparatively to a regular lignosulfonate on one hand, and to sulfonated naphthalene formaldehyde (SNF) on the other hand. Both the enhanced lignosulfonate and the regular lignosulfonate have been defoamed with triisobutylphosphate (TiBP) prior to testing, to prevent uncontrolled air to be formed in the concrete.

3.1. Concrete Mix Design

The concrete mix design used in this work is given in table 1. Water to cement ratio has been adjusted to achieve 140 mm of initial slump on concrete mix added with 0,40% solid by weight of cement (sbwc) of SNF. It has then be kept constant for all other mixes.

Table 1. Concrete mix design

Material	Amount (kg/m3)
Cement	350
Water to cement ratio w/c	0,47
Natural sand 0/4	378
Crushed sand 0/4	542
Crushed aggregates 4/10	396
Crushed aggregates 10/20	404

3.2. Measurements

All experiments have been performed in a concrete laboratory at 20°C or 27°C. Measurements have been conducted on 20 liter concrete batches according to the mix design given in table 1.

Collomatic XM 2-650 concrete mixer has been used. The following mixing procedure has been followed for all testing:

- Dry mixing during 30 sec
- Addition of water and admixture during 30 sec
- Mixing during 60 sec

– Stop mixing during 60 sec
– Mixing during 60 sec
- **Total: 240 seconds.**

For all concrete mixes, the following parameters have been measured:
– Initial slump at 10 minutes after contact of cement with water
– Slump retention during 90 minutes
– Fresh density and air content
– Compressive strength at 1, 7 and 28 days
– Initial set time by thermologger.

3.3. Results

Dosages are expressed in percentage of solid by weight of cement (% sbwc).

3.3.1. Dispersing effect / Water reduction

Water content and initial workability are key parameters in concrete production. Lignosulfonate based plasticizers are recognized by the concrete industry to act as efficient dispersants for cement, allowing water reduction and/or initial workability improvement. The enhanced lignosulfonate allows going one step beyond what is achievable with regular lignosulfonate grades by reaching typical water reduction performances of superplasticizers like sulfonated naphthalene formaldehyde based formulations. Similar or higher initial slump as SNF can easily be achieved by using the enhanced lignosulfonate (Figure 1).

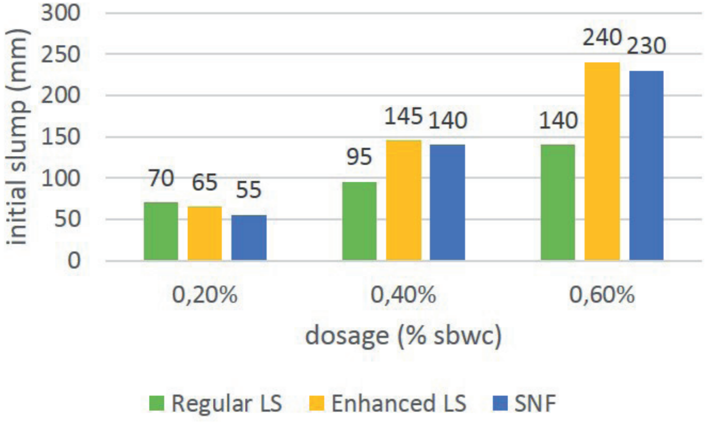


Figure 1. Initial slump plotted as a function of dosage for the enhanced lignosulfonate, a regular lignosulfonate grade and a commercially available sulfonated naphthalene formaldehyde grade at T = 27°C.

3.3.2. Workability retention

Workability retention is a critical parameter for concrete producers, especially in hot weather conditions where the hydration kinetics are accelerated. The enhanced lignosulfonate provides extended workability retention versus naphthalene based formulations, especially when high ambient temperatures are considered (T=27°C for the results plotted in figures 2 and 3). Longer workability retention (more than 90 minutes) can be achieved if higher dosage levels are used.

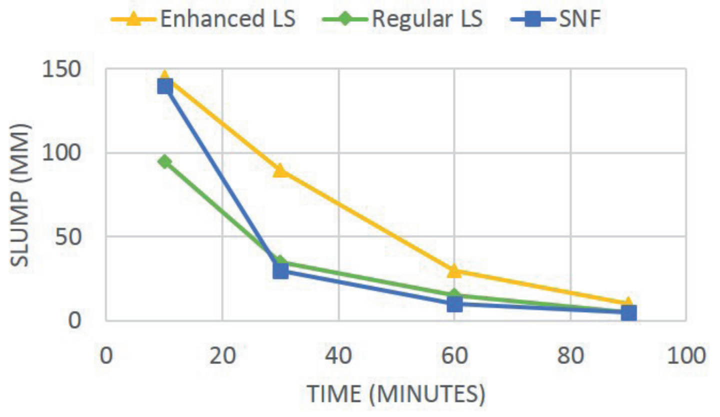


Figure 2. Slump as a function of time – Admixtures dosed at 0.40% sbwc at T = 27°C.

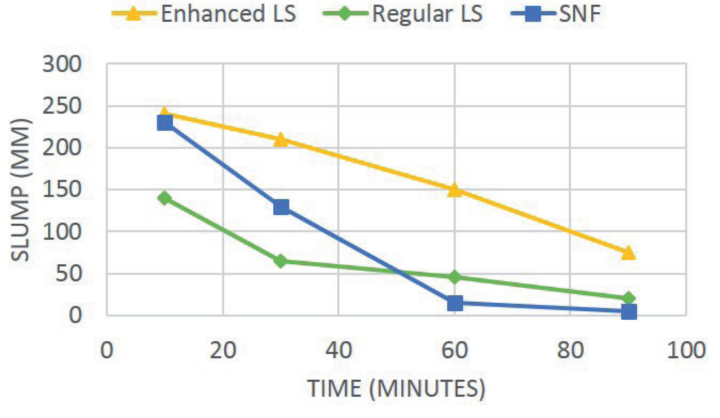


Figure 3. Slump as a function of time – Admixtures dosed at 0.60% sbwc at T = 27°C.

3.3.3. Set times and strength development

One of the limitations of lignosulfonate based plasticizers is their retarding effect. This is even more critical as secondary cementitious additions (SCM) are increasingly used in the construction industry and are known to increase set times due to slower hydration rates. In the case illustrated in figures 4 and 5, set times and 1 day compressive strength are measured at temperature of 27°C on concrete mixes produced with a blended cement containing 30% slag (GGBS). Thanks to the modification of specific functionalities the enhanced lignosulfonate offers significantly shorter set times than regular lignosulfonate grades and consequently ensures faster strength development. Additionally, a linear evolution of set times with dosage is observed with the enhanced lignosulfonate which leads to highly predictable performances. Also the early compressive strength development shows a positive trend with increased dosage.

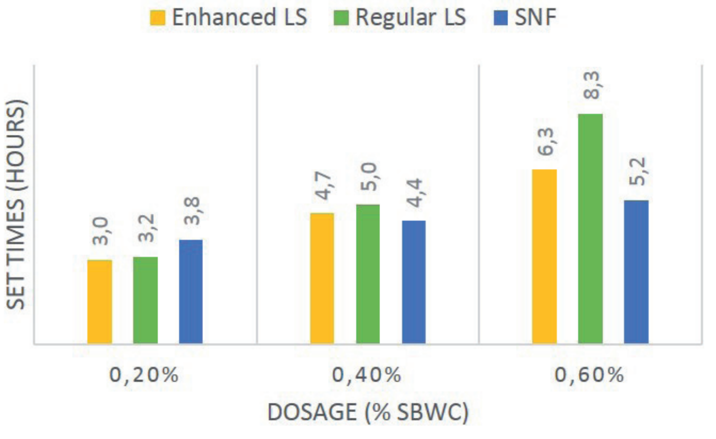


Figure 4. Set times as a function of dosage – Slag cement (Heidelberg) at T=27°C.

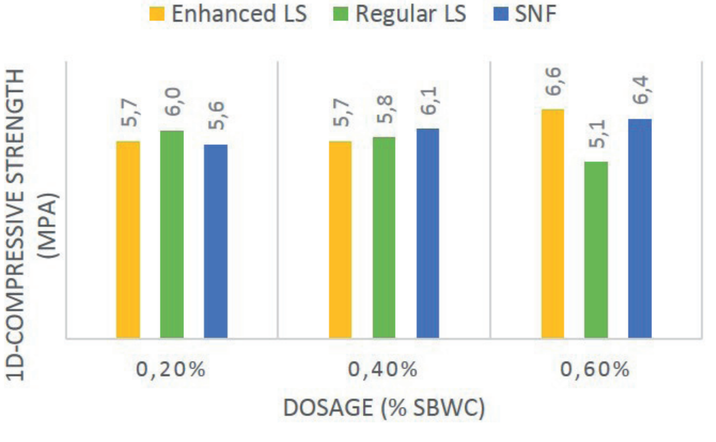


Figure 5. Compressive strength at 1 day as a function of dosage – Slag cement (Heidelberg) at T=27°C.

4. Main value elements of lignosulfonates used as dispersants in concrete

The majority (80%) of ready mix concrete volume placed worldwide still belongs to low to mid-range when it comes to strength requirements (below 40 MPa). In 2005 this value was 91% < 35 MPa for Europe [6]. Here the use of lignosulfonates is beneficial due to a favorable cost to performance ratio. Furthermore, lignosulfonate brings robustness to the concrete mixes hence facilitates the everyday production.

Additionally, lignosulfonate is generally compatible with most of the raw materials used in plasticizer and superplasticizer formulations. Last but not least, lignosulfonate is a renewable and green raw material with favorable environmental and carbon footprints meeting today's challenges regarding CO_2 emissions reduction.

4.1. Cost effectiveness

It is not always clear if polycarboxylates could be more cost effective solutions to lignosulfonates in the plasticizer market segment (C25 – C40). Work has been conducted in the Construction Materials Laboratory of Borregaard to compare several lignosulfonates from Borregaard's product range to commercially available grades of polycarboxylates sold to the ready mix concrete industry. Different concrete mix designs and cement types have been used. The methodology consists in adjusting polycarboxylate dosage to reach same initial flow as with 0.30% sbwc (solid by weight of cement) of lignosulfonate at a fixed water to cement ratio. The parameters slump/flow and retention over time (up to 90 minutes) have been measured, as well as density, air content, set times and compressive strength at 1, 7 and 28 days. The results given in next figures have been obtained on concrete mix design given in table 2. Temperature for these trials was 20°C.

Table 2. Concrete mix design.

Material	Amount (kg/m3)
Cement CEM II B-M 42,5N	320
Sand 0/4	736
Aggregates 4/16	828
Aggregates 16/32	276
Water	180
w/c	0,563

Cost analysis has been conducted based on obtained results, comparing the products on the same initial slump basis. Very similar flow retention for both tested products (Figure 6) were observed, with slightly higher 1 day-strength for the polycarboxylate and similar strength values for both tested products at 7 and 28 days (Figure 7).

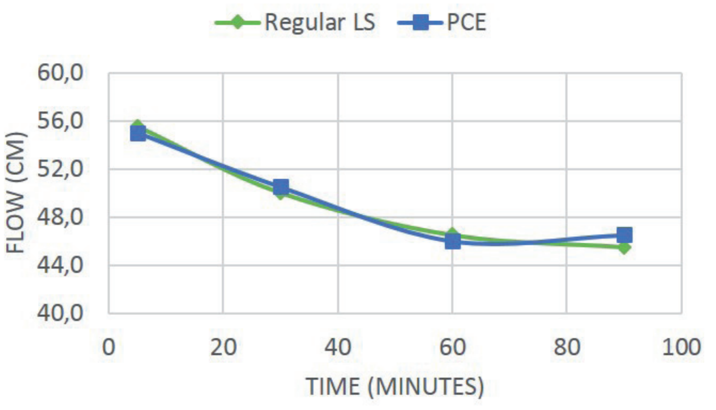


Figure 6. Flow as a function of time – Lignosulfonate vs. polycarboxylate.

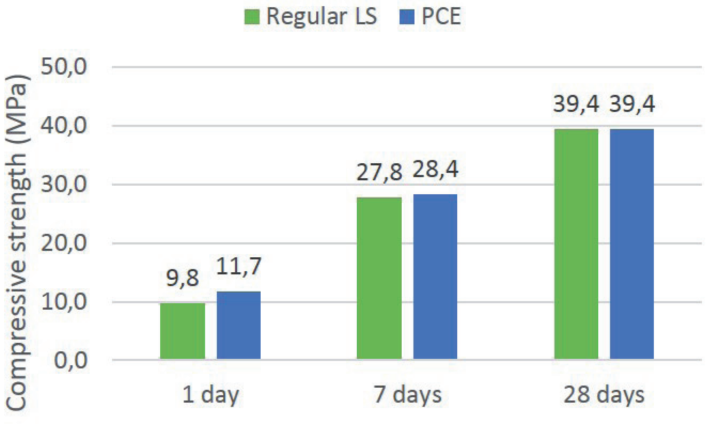


Figure 7. Compressive strength at 1, 7 and 28 days – Lignosulfonate vs. polycarboxylate (comparison at same initial flow).

Even if the dosage of lignosulfonate required to achieve similar initial flow as polycarboxylate was three times higher (in solid), the cost analysis showed a far better cost effectiveness for the lignosulfonate (Figure 8).

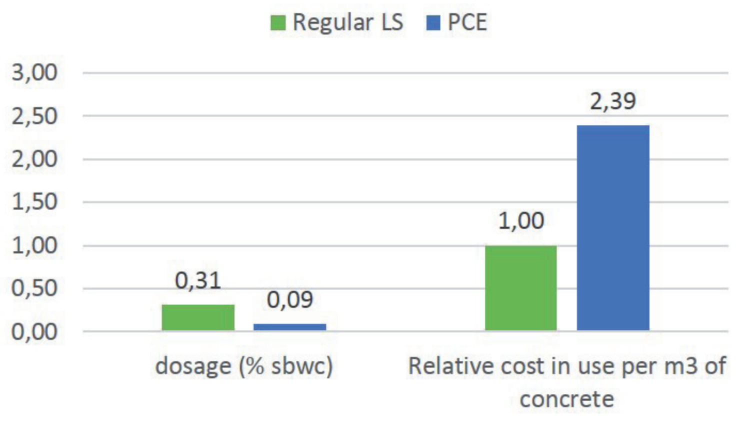


Figure 8. Dosage to reach similar initial flow and relative cost in use - Lignosulfonate vs. polycarboxylate.

For the plasticizer market segment, it was therefore demonstrated that lignosulfonate is a much more cost effective solution compared to polycarboxylate.

4.2. Robustness

Robustness means that the admixture performances in concrete do not vary too much with:

- cement and additions (batch to batch variations, type, source)
- water content (inaccuracy of production process, humidity of the aggregates)
- sand and aggregate quality (clay, fine content)
- temperature
- mixing time
- …

One way to illustrate the robustness of an admixture is to plot initial slump as a function of dosage or water content (Figure 9). A small change in water content or dosage will have a drastic impact on initial slump in case polycarboxylate is used, since the slope of the "fluidification curve" is much steeper. The impact will be much less when lignosulfonate is used, which facilitates the everyday concrete production. Using lignosulfonate in combination with polycarboxylate also improves the robustness of the concrete mix.

Studies are currently in progress at Borregaard`s Construction Materials Laboratory to quantify the ability of lignosulfonate to deal with the most important variables in concrete production, e.g. cement and additions variations in quality, varying fine content of the sands, clay contamination of sands, etc.

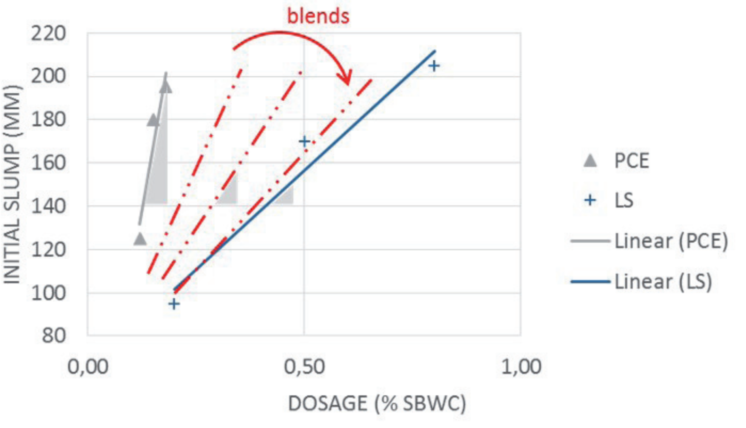


Figure 9. Illustration of robustness.

4.3. Compatibility of lignosulfonates in formulation with diverse raw materials

Lignosulfonates are often used in combination with other raw materials to formulate low to mid-range water reducers (LRWR/MRWR). Therefore the compatibility of different products of the Borregaard range in formulation was studied together with some of the most commonly used raw materials in admixture formulations:

- triethanolamine (TEA)
- sodium naphthalene sulfonate (SNF)
- polycarboxylate (PCE)
- sodium gluconate.

Lignosulfonate qualities included:

- softwood based, magnesium lignosulfonate
- softwood based, calcium lignosulfonate
- hardwood based, calcium lignosulfonate.

4.3.1. Formulation with triethanolamine

The following formulation has been studied: 30% LS (active) + 6% TEA (active) + 64% water.

No compatibility issues were observed with the softwood magnesium and calcium lignosulfonate. A thin insoluble / sludge layer was observed with the hardwood based calcium lignosulfonate. To prevent any incompatibility to occur with hardwood based calcium lignosulfonate, it is recommended to keep the dry matter at minimum 30% if possible.

4.3.2. Formulation with sodium naphthalene sulfonates (SNF)

The following formulations have been studied: ratio 75/25 and 25/75 LS/SNF (ratio expressed on % dry matter, blends formulated at 40% total dry matter). Three SNF qualities have been tested (Table 3): low, medium and high sulfate content.

Table 3. SNF qualities used in the testing program.

Name	DM (%)	SO_4 content (%)	Na_2SO_4 (%)
SNF-1	94,6	10,7	15,8
SNF-2	93,5	5,9	8,7
SNF-3	94,2	1,9	2,8

No compatibility issues were observed with the softwood magnesium lignosulfonates. Precipitation of $CaSO_4$ were observed in formulations with calcium lignosulfonates. The level of precipitation increased, as expected, with increasing amount of sulphates in the SNF. Based on these results, when formulating calcium lignosulfonates with sodium naphthalene, sodium naphthalene with low sulphate content should be used if possible. Another option is to formulate with magnesium or sodium lignosulfonates.

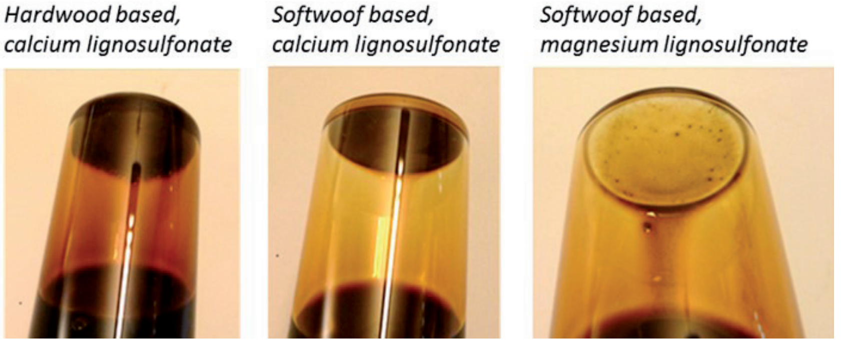


Figure 10. Three different types of lignosulfonates formulated with high sulphate content SNF.

4.3.3. Formulation with polycarboxylates (PCE)

There is a huge variety of PCEs based on various chemical natures, architectures, etc. available.

As it is not possible to test all of them, three representative types of the most frequently used PCEs were selected as follows (SC = side chain, AA = acrylic acid):

- PCE 1: SCL 1000g/mol, acrylic acid based, AA:SC = 3:1
- PCE 2: SCL 1500g/mol, acrylic acid based, AA:SC = 2:1
- PCE 3: SCL 5000g/mol, acrylic acid based, AA:SC = 7,5:1.

The blends were formulated with a ratio LS/PCE of 75/25 (ratio expressed on % dry matter, blends formulated at 40% total dry matter). PCE 1 and PCE 3 were compatible with all three lignosulfonate qualities tested, while PCE 2 gave a two phases system. At a later stage it was found that PCE 2 leads to phase separation by itself. The solution to potential incompatibility issues has to be found on case to case basis. Borregaard Ligno-Tech offers technical support to help their customers finding the best lignosulfonate to be used in combination with selected polycarboxylates.

4.3.4. Formulation with gluconic acid sodium salt

The following formulations have been studied: 75/25, 50/50 and 25/75 of LS/sodium gluconate (ratio expressed on % dry matter, blends formulated at 40% total dry matter). No incompatibility issue has been observed with magnesium based lignosulfonates, but some incompatibilities have been observed with calcium lignosulfonates, depending on the ratio of the blend. Therefore extensive work was conducted to establish phase maps for different Borregaard LignoTech products with varying calcium content (Figure 11). The fraction of lignosulfonate contained in the blend is plotted along the x-axis. Total dry solids (calcium lignosulfonate and sodium gluconate combined) is plotted along the y-axis. Incompatibility will occur for combinations of lignosulfonate and sodium gluconate above the different lines in the phase map.

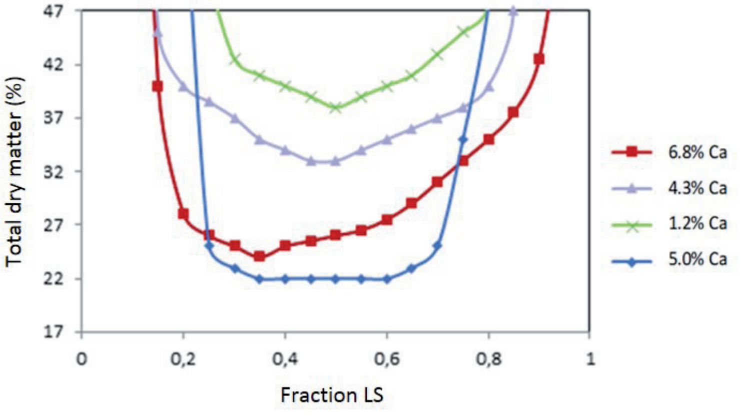


Figure 11. Phase maps - Total dry matter of the final product expressed as a function of the respective fraction of lignosulfonates containing varying calcium content.

Based on these maps and depending on formulations specificities and requirements, it might be needed to switch from calcium to magnesium (or sodium) lignosulfonates to solve incompatibility issues when using lignosulfonates in combination with gluconic acid sodium salts.

5. Examples of lignosulfonate uses in modern concrete technologies

5.1. Self-compacting concrete

Modern concrete mix designs such as Self Compacting Concrete (SCC) can effectively be dispersed with regular lignosulfonates [3-5]. Self-consolidating concrete or self-compacting concrete is characterized by a low yield stress, high deformability, and moderate viscosity necessary to ensure uniform suspension of solid particles during transportation, placement (without external compaction), and thereafter until the concrete sets. Here, in addition to their dispersing effect, lignosulfonate act as rheology improver by enhancing concrete cohesiveness and consequently reducing the risk of bleeding and segregation without leading to a sticky mix.

Four different SCC mix designs plasticized with a regular sodium lignosulfonate have been evaluated (table 4).

- Mix 1 is the reference mix containing micro-silica; Water to binder ratio (w/b) =0.57
- In mix 2, we have replaced micro-silica by cement; w/b = 0.57
- w/b ratio has been increased up to 0.59 in mix 3, and up to 0.63 in mix 4.

Lignosulfonate has been dosed at 0.40% sbwc in each mix.

Table 4. Tested self-compacting concrete mix designs.

Material	Mix-1	Mix-2	Mix-3	Mix-4
aggregates 10/20	105	105	105	105
aggregates 4/10	703	703	703	703
crush rock fine 0/4	289	289	289	289
natural sand 0/2	604	604	604	604
standard FA cement ACC PPC	352	376	376	376
micro silica	24	0	0	0
Water	213	213	223	235
water to binder	0,57	0,57	0,59	0,63
LS dosage % sbwc	0,40%	0,40%	0,40%	0,40%
aggr/sand ratio	0,90	0,90	0,90	0,90

A stable and homogeneous self-compacting concrete belonging to C40 strength class is obtained by using 0.40% sbwc of lignosulfonate as a dispersant. When micro-silica is removed from the mix design and replaced by equivalent amount of cement, the concrete mix remains stable and homogeneous (figure 12). Use of stabilizers are in this case not required.

Figure 12. Fresh concrete appearance – Mix 2.

Micro-silica tends to be detrimental to workability retention (figure 13) and there is no evidence in these trials of any positive effect of micro-silica on strength development (figure 14) despite the reduction of set times observed (figure 15).

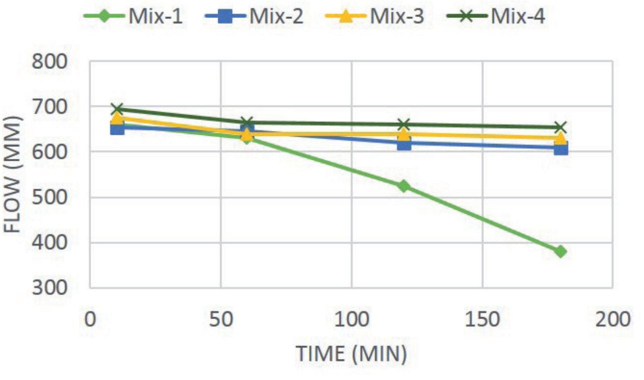


Figure 13. Flow plotted as a function of time for SCC mixes 1 to 4.

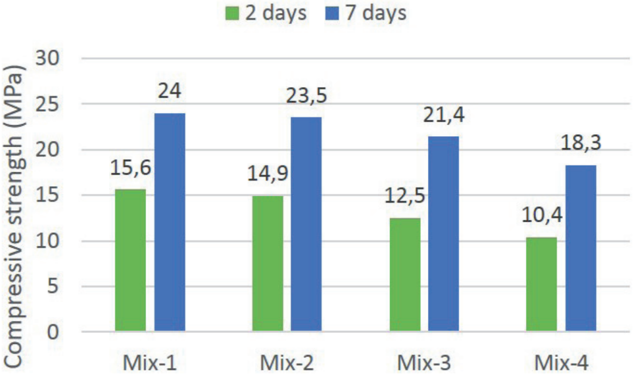


Figure 14. Compressive strength measured at 2 and 7 days on SCC mixes 1 to 4.

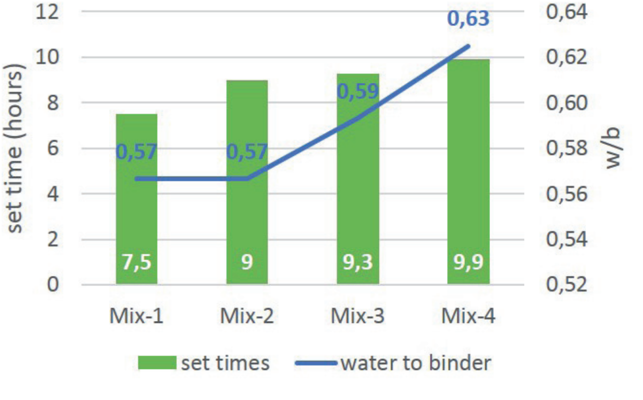


Figure 15. Set times measured on SCC mixes 1 to 4.

The concrete mixes made without micro-silica with 0.40% sbwc of lignosulfonate remain stable when water to binder ratio is increased from 0.57 up to 0.59 (which corresponds to 10 liters water addition per cubic meter of concrete). When w/b is further increased up to 0.63, segregation and bleeding start to be observed.

5.2. Concrete extrusion

Concrete extrusion (Picture 2) has been proven to be a fast and cost efficient method to produce high speed freeway separators or rim stones.

To be extrudable, the concrete has to:

- be soft enough to flow through the die
- be stiff enough to maintain its shape upon exit of the die
- not undergo phase migration
- require a reasonably low extrusion pressure
- show minimal surface defects.

The use of lignosulfonates in this case allows fast production rate of up to 15 meter per 1 minute with very smooth surface finish [7].

Figure 16. Concrete extrusion.

5.3. Roller compacted concrete

Another application is Roller Compacted Concrete (RCC) which is mainly used for massive concrete structures such as dams. Here, lignosulfonates again are a robust and easy to work with chemical admixture ensuring reliable concrete performance.

6. Conclusion

In this paper, it was shown that newly developed lignosulfonate grades allow reaching similar or better dispersing performances than naphthalene based polymers with improved workability retention.

Lignosulfonates are compatible with most commonly used raw materials for plasticizer and superplasticizer formulations. Using lignosulfonate, as is or in formulation with other components, allows to benefit from its intrinsic properties, like (amongst others):

– cost effectiveness
– robustness
– improvement of fresh concrete appearance (creaminess, non-sticky mixes, improved pumpability, good cohesiveness…)
– better behavior under compaction and/or vibration
– stability of very fluid mixes

…

These properties facilitate the everyday life of the concrete producers. They are key in explaining the reasons for longevity and popularity of lignosulfonate use as dispersant for concrete.

Lignosulfonates can be used in modern concrete technologies such as SCC, RCC and concrete extrusion.

Borregaard Lignotech has built considerable knowledge for efficiently supporting their customers to develop cost effective, innovative and environmentally-friendly solutions based on lignosulfonate to meet today's concrete challenges.

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