# LigniOx lignins – A new type of high performance concrete plasticizer

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**Abstract**
Large quantities of lignin are available from chemical pulping and emerging bio refineries. Even if lignin is an important energy source for the pulp mills, there is great potential to use lignin also for the production of higher value applications. The main technical lignins, Kraft and soda lignins are especially rich in phenolic hydroxyl groups. Molecular oxygen, an environmentally friendly and low-cost oxidizing agent, is active towards phenolic lignin under alkaline conditions. VTT has recently developed a simple and cost-efficient alkali oxidation (LigniOx) process for conversion of technical lignins into concrete superplasticizers. The LigniOx process introduces acidic groups into the lignin polymer, while retaining its polymeric structure. Depending on the oxidation conditions, (especially pH), the negative charge and molar mass of lignin can be adjusted in a controlled way. The recent studies on mortar and concrete plasticization have demonstrated that the LigniOx lignins have great potential to compete with lignosulfonates in their traditional markets, and even with synthetic polycarboxylate ethers. This work includes the results of using kraft lignin based LigniOx solutions for mortar plasticization in comparison to several commercial lignosulfonates and synthetic superplasticizers. In addition, testing the performance of LigniOx solutions in mortars prepared using alternative cement qualities is presented, and the adsorption phenomena and interaction of the LigniOx lignins and commercial plasticizers on cement surface is discussed.

**Keywords:** Lignin; alkaline oxidation; concrete superplasticizer

## 1. Introduction

Dispersants are widely used for suspending colloidal particles in cosmetics, paints, pharmaceuticals, oil drilling mud, cement, and ceramic applications. Besides lignosulfonates, mainly synthetic polymers are used as dispersants in these applications. For substituting the current non-biodegradable polymers with bio-based and less expensive materials, technical lignins have been modified in several ways (e.g. by sulfomethylation, oxidation, carboxymethylation, grafting with PEG, hydroxymethylation/propylation and sulfonation, fractionation, enzyme utilization) to convert them into water soluble dispersants. Despite the encouraging results, the modification procedures seemed to be industrially unattractive and the property-performance relationships for lignin-based dispersants are case dependent [1].

LigniOx technology, recently developed by VTT, is a simple and cost-efficient alkali-$O_2$ oxidation process for conversion of technical lignins into ready-to-use products for concrete plasticization, i.e. cement dispersing, or versatile dispersants [2,3]. The LigniOx process can be integrated into biorefineries, or operated in stand-alone units e.g. by the chemical industry. The oxidation is active with respect to phenolic hydroxyls groups and introduces carboxylic acidic groups in the lignin polymer, while retaining its polymeric structure. Depending on the oxidation conditions, (especially pH), the negative charge and molar mass of lignin can be adjusted in a controlled way. The previous studies on mortar and concrete plasticization have demonstrated that the soda and kraft LigniOx lignins have great potential to compete with lignosulfonates in their traditional markets, and even with synthetic products. LigniOx lignins have also shown high dispersing performance of several inorganic pigments, such as $TiO_2$, colour pigment, and $CaCO_3$, used e.g. in paints [4,5]. Currently, the oxidation technology is optimized for several different lignin raw materials [6].
In this study the very recent results of applying kraft lignin based LigniOx lignins as plasticizers in mortar are presented. The adsorption tendency of the LigniOx lignins on cement surface is discussed. Additionally, we have tested the concrete plasticizing performance using several cement qualities.

**Table 1:** Structural characteristics of the LigniOx samples

| **Plasticizer** | **Mw** | **Mn** | **PD** | **Charge meq/g** |
|---|---|---|---|---|
| LigniOx KL 1 | 3000 | 1100 | 2.9 | -4.1 |
| LigniOx KL 2 | 6100 | 1600 | 3.9 | -5.5 |

## 2. Experimental Work and Raw Material

An initial benchmark study has been carried out using the concrete water reducers listed in the following table.

**Table 2:** Water reducers used in a benchmark study

| Water reducer | Chemisty | Dry Matter [%] |
|---|---|---|
| PCE 1 | Acrylic PCE | 38 |
| PCE 2 | Acrylic PCE | 21.9 |
| PCE 3 | Acrylic PCE | 30.5 |
| SNF | Naphthalene sulfonate | 40 |
| LS | Lignin sulfonate | 30 |
| LigniOx KL 1 | Oxidized Lignin | 27.2 |
| LigniOx KL 2 | Oxidized Lignin | 27.0 |

Commercial polycarboxylate ether (PCE), sulfonated naphthalene formaldehyde condensate (SNF) based superplasticizers and lignosulfonate (LS) based plasticizers were used as references. The commercial products were dosed based on dry matter reported by the supplier. LigniOx solutions were dosed also based on the dry matter content in the solution.

The mortars are all based on a standard mortar formulation using CEM I 42.5R of Heidelberger Cement (Ennigerloh) and a typical blend of well-defined sands.

**Table 3:** Cement Mortar Formulation

| Component | (g) |
|---|---|
| Cement OPC CEM I 42.5 R | 500 |
| Quarzsand H 32 | 600 |
| Sand particle size 0.2 - 1 mm | 500 |
| Sand particle size 1 - 2 mm | 400 |
| Water Reducers (as solid); 0.38% on cement | 1.9 |
| Water/Cement Ratio 0.5 | 250 |

A constant water/cement ratio of 0.5 has been used in all formulations. The water introduced by some of the superplasticizers has been considered in the overall addition levels. In some formulations we have added a defoamer (0.2% Foammaster SI 2210, BTC) in order to obtain comparable fresh mortar densities in the range of 2.10 to 2.20 kg/l. The water reducers which required the addition of defoamers included lignin sulfonate and LigniOx samples. The dosage of the superplasticizers has been fixed at 0.38% based on cement in all cases.

Mixing of the mortar
While mixing on level one, the drymix was added to the mixing bowl which contained the required amount of water and the plasticizer and the resulting paste was mixed for 30 seconds on level one and then for 30 seconds on level two. The mixture was allowed to rest for 90 seconds to dissolve the additives, and then was mixed again for 60 seconds on level two.

Slump Test
A measure of how much a mortar is able to flow under its own weight and 15 strokes is described in DIN EN 1015-3:2007-05. In this test, the user places a cone funnel (slump cone) having a bottom opening diameter of 100 mm, a top opening diameter of 70 mm and a height of 60 mm onto a wetted glass plate with the bottom opening on the plate (wetted 10 seconds before testing). Then, one fills the cone with mortar and then quickly pulls the cone vertically off from the plate to fully release the mortar onto the plate followed by applying 15 strokes to the mortar. Once the mortar ceases to spread, the user measures the diameter of the resulting mortar cake in four locations spaced equally around the mortar cake. The average of the four diameters gives the slump value for the mortar.
The fresh mortar density has been measured by simply determining the net weight of a filled plastic beaker divided by the known volume.

## 3. Flow Performance

The following graphic illustrates the various flow properties of mortars using the different water reducers as listed in Table 2.

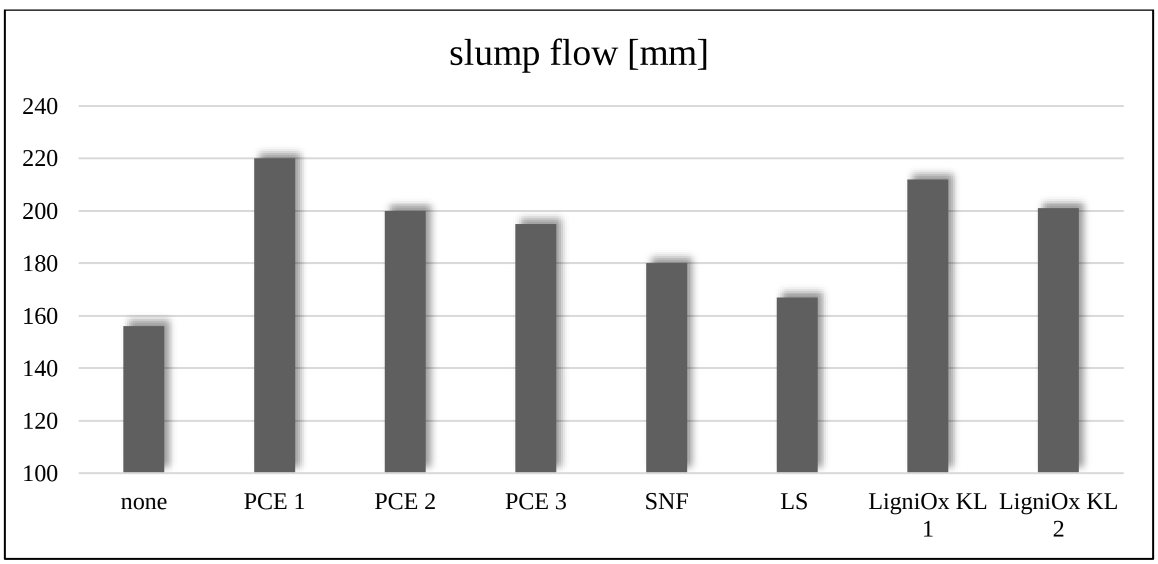


**Figure 1:** Slump flow of a cementitious mortar using different water reducers

The reference mortar without any dispersant shows only very little flow (from 100 mm to 150 mm). When adding PCE 1, a commercial polycarboxylate ether, the flow of the mortar increases to 220 mm as can be seen in figure 3. The two other acrylic PCE 2 and PCE 3 are less effective and allow the mortar to flow only for 200 mm and 195 mm, respectively. After the addition of PCE 1 the mortar showed some sign of segregation and water bleeding. All other formulations were stable. The sulfonated naphthalene based superplasticizer (SNF) is even less effective and increases the spread of the mortar only to 180 mm. Lignin sulfonate (LS) was only slightly better than the reference mortar. The two oxidized lignin dispersants demonstrated a strong dispersion effect almost reaching the value of the PCE 1 formulation.

When we changed the cement from CEM I 42.5 R to CEM II 42.5N or CEM I 52.5R, leaving the LigniOx KL1 superplasticizer constant at 0.28% (dry matter) on cement, all mortars performed equally well (Table 4). This indicates their effectiveness in different concrete formulations.

**Table 4:** slump flow data using different cement qualities

| **Cement** | CEM I 42,5 R<br>Heidelberger Cement Enningerloh | CEM II 42,5 N<br>Plussementti by Finnsementti | CEM I 52,5 N<br>Megasementti by Finnsementti |
|---|---|---|---|
| **Slump [mm]** | 208 | 205 | 213 |

## 4. Adsorption on Cement Particles

Concrete superplasticizers are reported to work either by electrostatic or steric repulsion between individual cement particles to achieve a full dispersion. The negatively charged functional groups of the superplasticizer, sulfonic and carboxylic groups, adsorb on the active sites (calcium aluminate, calcium silicate) of the cement particles giving them a negative charge, which leads to the electrostatic repulsion between the particles. The branched structure of the PCE superplasticizer achieves steric repulsion by forcing the cement particles apart [7]. Steric repulsion is known to be more effective in dispersion compared to electrostatic repulsion. In the case of lignosulfonates, it is postulated that the dispersing effect is mainly due to the electrostatic repulsion between the cement particles [8].

In previous studies, it has been shown that alkali-O2 oxidation (LigniOx) of lignin yields highly carboxylated lignin [9]. To gain understanding of the working mechanism of LigniOx lignins, their adsorption on ordinary Portland cement as a function of dosing was quantified and compared to selected commercial plasticizers (Figure 1). Adsorption of sulfonated naphthalene based product (SNF) and lignosulfonate (LS), showed rather similar behaviour as a function of the plasticizer dosing: the adsorbed amount increased steadily as increasing the dosing up to 0.5%, where after it was still increasing in lesser extent as increasing the dosing up to 1.0%. In the case of the LigniOx plasticizers, the maximum adsorption was reached already with the dosing of 0.5% on cement. The adsorption behaviour of the studied plasticizers could be interpreted using Langmuir isotherm equation with rather high correlation [10]. Based on this initial study, it can be postulated that the working mechanism of LigniOx lignins is somewhat similar to that of the commercial plasticizers.

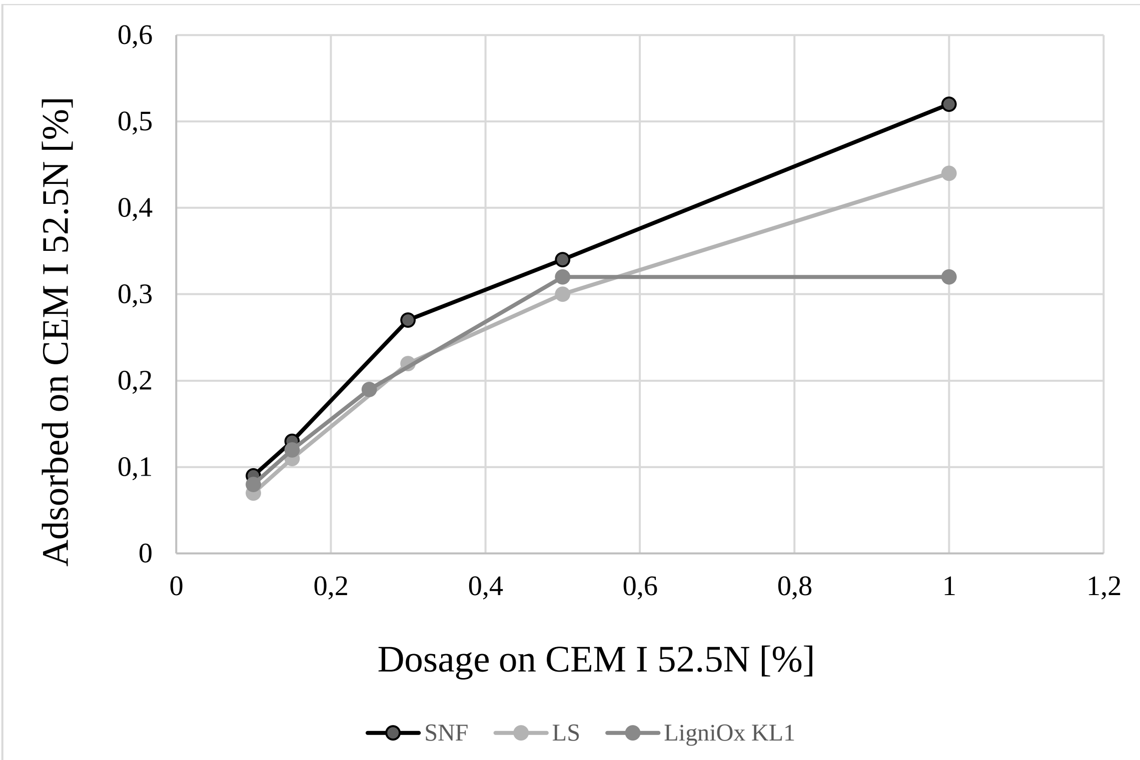


**Figure 2:** Adsorption of commercial plasticizers (SNF, LS) and kraft lignin based LigniOx KL1 on cement surface as a function of dosing.

## 5. Conclusions

LigniOx oxidation technology converts various industrial lignin raw materials to high-performing plasticizers and versatile dispersant. It was shown that kraft lignin based LigniOx solutions have high dispersing performance in cementitious material similar to polycarboxylate based concrete superplasticizers. We could demonstrate that this class of concrete water reducers works with various cement qualities, providing high dispersion effects. The dispersion effect is most likely based on adsorption on cement particles and the resulting electrostatic repulsion. A definite proof for this hypothesis does not yet exist.

Our test have shown that adsorption maxima are reached earlier compared to other cement plasticizers such as lignosulfonates or sulfonated naphthalene condensates.
More work needs to be done to better understand the interaction of the LigniOx dispersant with the cement components. Their impact on cement setting kinetics is still not fully understood.

## 6. Acknowledgements

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