# Chapter 16
# Eco-Friendly Concrete Admixture from Black Liquor Generated in Pulp and Paper Industry

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**Abstract** Black liquor, a lignin rich colloidal suspension, generated during pulping of lignocellulosic bio-resources in pulp and paper industry is often considered as a waste. Though a waste, it is a valuable resource for producing fuels, chemicals and several other value added products. Cement admixture is yet another value added product that can be developed from pulp and paper industry black liquor. Researchers around the world are concerned towards reducing the consumption of cement in construction due to the hazards of carbon emissions associated with it production process. Efforts are being made to develop admixtures which can reduce the quantity of cement clinker and at the same time preserve the quality of concrete. Use of admixtures in concrete is aimed towards resource conservation by reducing water requirement and energy consumption. In this series, black liquor has been found to be an effective admixture for concrete by researchers. Nevertheless, the performance of cement admixture depends on the physico-chemical properties of black liquor used. This paper aims to review the research carried out on utilization of black liquor as admixture in construction industry. It describes different types of admixture developed from black liquor such as set retarder admixture, viscosity modifying admixture etc. It discusses the effect of physico-chemical properties of different types of black liquor generated from variety of biomass based on different pulping processes. It reflects the performance of black liquor as admixture in terms of properties such workability, compaction, honeycombing, settling time, storage time, viscosity modification, shrinkage, compressive strength, tensile strength etc. Finally, this paper presents relevant conclusion drawn from different studies and advocates effective utilization of black liquor as admixture in construction industry.

**Keywords** Agro-waste · Lignin · Lignosulfonate · Pulp and paper · Waste management

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## 16.1 Introduction

Two major alkaline pulping processes to produce chemical pulps include Kraft (or sulphate) and soda. During chemical puling process, lignin is dissolved in cooking liquor and cellulose fibres are disassociated from lignin. The pulping process conducted in a pressurized digester at elevated temperatures. Typically, cooking liquor is made of Sodium Hydroxide (NaOH) or in Kraft process, Sodium Sulfide is also used. During the final pulping stages, significant amount of lignin condensation reactions take place resulting in a high molar mass lignin entity. Molar mass of lignin increases appreciably at the end of cooking, which results in a complex polymeric structure of lignin in comparison to cellulose, hemicelluloses and organic acids present in black liquor. This high molar mass lignin is difficult to biodegrade. In wood based mills where chemical recovery operations are successful, these lignin laden black liquor is combusted in boiler to recover energy. However, in majority of the small agro based mills, where chemical recovery is not feasible this lignin rich black liquor, till last decade, was discharged and caused several problem of pollution. As a consequence, the small agro based mills which once used to contribute nearly 30% of the total paper production in the country is now presently contributing merely 8.57%. In India where wood is deficient and the cost of recycled fibre import is exceeding; revival of agro based mills is very much anticipated. This revival is possible only when lignin rich black liquor produced in these mills can be managed through utilization in some value added applications. One such option is its use as concrete admixture.

A material other than water that is used as a component of concrete or mortar and is added to the batch immediately before or during mixing to modify one or more properties of Concrete is known as a concrete admixture. Depending on application, these can be accelerator additives, retarder additives, water reducing additives, air inlet additives, superplasticizer additives, and superplasticizer retarder additives. The use of these chemical additives in concrete is increasing rapidly in India. The number of industries producing additives has grown tremendously as awareness of the usefulness of these additives increases. There is no doubt that the use of admixtures has greatly influenced concrete pouring practice in India in recent years. Concrete is a range of graded aggregates (coarse and fine) that are connected together by a hardened cement paste. The concrete must be strong, free from excessive changes in volume and resistant to the ingress of water. The strength of the concrete results from the hydration of the cement by the water. The cement ingredients progressively crystallize to form a gel or paste that surrounds the graded aggregate and binds them together to create a conglomerate. In general, the strength and permeability of concrete are determined by its water and cement content. For high strength and low permeability, the ratio of cement to water should be low. Conversely, for ease of placing and compaction the easiest way of increasing workability is to increase the free water content. Nowadays chemical admixtures (plasticizers and water-reducing agents) are used for better strength and workability of cement.

On account of the fact that the admixture industry has emerged well with the time, use of lignin/lignosulfonate from agro based paper mills as concrete admixture can increase the profitability of agro based mills since these mills are struggling to survive. This will also help in resource conservation and at the same time will reduce import bill of the country. Hence, in order to understand the role of black liquor/lignin/lignosulfonate based admixture in cement this article is aimed to present an overview on utilization of black liquor as admixture in construction industry. The reminder of the article is sectionized as follows. Section two gives a brief account of black liquor, lignin and lignosulfonate. It describes the characteristics of black liquor obtained from pulping of different agro based raw materials, lignin and lignosulfonates. Section three presents an overview on different applications of black liquor and lignosulfonates as concrete admixture. In last, section four outlines relevant conclusion drawn from the study.

## 16.2 Black Liquor, Lignin and Lignosulphonate

### *16.2.1 Black Liquor*

The spent pulping liquor, known as black liquor, is a complex mixture of organic and inorganic compounds with organic to inorganic ratio of 70:30. Table 16.1 shows the typical analysis of black liquors obtained from bagasse, wheat straw and rice straw. The black liquor consists of dissolved lignin as well as other carbohydrate polymers and has different combustion and transport properties compared to cooking liquor. The amount of lignin present in black liquor varies from 30% to 40% and has an extremely high cost value. Typical pulp mill operation contains a chemical recovery system to recover as many as chemicals as possible as well as to use the

**Table 16.1** Characteristics of different black liquors

| Parameter | Unit | Bagasse | Wheat straw | Rice straw |
|---|---|---|---|---|
| pH | | 12.5 | 12.3 | 11.2 |
| Total solid | % w/w | 13–16 | 13–16 | 16–18 |
| Inorganics as NaOH | % w/w | 33–35 | 34–36 | 35–36 |
| Organics | % w/w | 65–67 | 64–66 | 65–64 |
| Chlorides as NaCl | % w/w | 0.7–0.9 | 1.3–1.7 | 1.0–1.2 |
| Silica as $SiO_2$% w/w | % w/w | 1.0–1.5 | 2.5–3.0 | 0.05–0.1 |
| Residual active alkali | g/l as $Na_2O$ | 5–7 | 5–7 | 5–6 |
| Swelling value ratio | ml/g | 13–15 | 9–13 | 20–25 |
| Calorific value as GCV | cal/g | 3100–3200 | 3050–3150 | 3000–3100 |
| Carbon as C | % w/w | 34–35 | 32–33 | 32–34 |
| Hydrogen as H | % w/w | 4.1 | 2.9 | 3.2 |
| Nitrogen as N | % w/w | 0.3 | 0.4 | 0.4 |
| Sulphur as S | % w/w | 0.5 | 0.5 | 2.0 |

**Table 16.2** Viscosity levels of different black liquors

| | Viscosity, mPa-s at 100° at total solids % w/w | | | | |
|---|---|---|---|---|---|
| Raw material | 45 | 50 | 55 | 60 | 65 |
| Pine | 9.1 | 18 | 40 | 160 | 215 |
| Eucalyptus | 2.3 | 83 | 380 | 490 | 640 |
| Eta reeds | 41 | 100 | 395 | 470 | 615 |
| Bamboo | 2 | 11 | 31 | 125 | 398 |
| Wheat straw | 40 | 89 | 299 | 450 | 1000 |
| Bagasse | 125 | 161 | 912 | 1100–1250 | 3100–3300 |
| Rice straw | 112 | 316 | | | |

lignin as energy source in recovery boiler to reduce the load on ETP plant. However, the efficiency of the chemical recovery system majorly depends on the raw material used, pulping method and the behaviour of the black liquor during evaporation and combustion. Since viscosity of agro-based liquor is higher compared to wood black liquor, agro-based black liquor is difficult to process. Table 16.2 shows the viscosity of black liquor obtained from different papermaking raw materials at different solids.

### *16.2.2 Lignin*

Lignin is one of the natural polymers found in wood and accounts for around 30% of the weight. It is even the second most common organic substance in the world after cellulose. The chemical structure of lignin, like that of many other natural polymers, is very complex. As lignin is normally insoluble in non-polar and organic solvents, a frequent method used to separate cellulose from lignin is to treat wood chips with a chemical solution at high temperatures. Lignin is a complex colloidal molecule. During pulping part of the lignin gets dissolved and major portion is solubilized as large colloidal macro molecule. The nature of lignin in black liquor depends mainly on raw material; the pulping conditions employed like the cooking chemical charge, temp, time, steam pressure, etc. and the pulping process adopted viz. soda, sulphite or Kraft. Table 16.3 illustrates the physicochemical characteristics of the commercially available lignin isolated from agro residue black liquor. The chemical structure of lignin is shown in Fig. 16.1.

### *16.2.3 Lignosulfonate*

By virtue of their exceptional properties, lignosulfonates are widely used, among others in animal feed, pesticides, surfactants, oil well additives, stabilizers in colloidal suspensions and as plasticizers in concrete additives. Lignosulfonates can be polymerized, hydrolyzed, halogenated, nitrated, oxidized, dehydrogenated or

**Table 16.3** Characteristics of lignin from agro based black liquor

| Parameters (On dry wt. basis) | Values | |
|---|---|---|
| | Crude lignin | Washed lignin |
| Moisture on as such basis% | 78.9 | 80.0 |
| Ash% | 16.5 | 11.7 |
| Lignin purity% | 73.4 | 80.1 |
| Silica% | 8.0 | 8.2 |
| Sodium% | 1.03 | 0.4 |
| Sulphates% | 1.15 | 0.17 |
| Chloride% | 1.16 | 0.64 |
| Elemental analysis | Carbon – 47.5%<br>Hydrogen – 5.2%<br>Nitrogen – 1.5%<br>Sulphur – 3.1% | Carbon – 49.24%<br>Hydrogen – 5.03%<br>Nitrogen – 1.17%<br>Sulphur – 3.485 |
| Gross calorific value cal/gm | 5535 | 6381 |

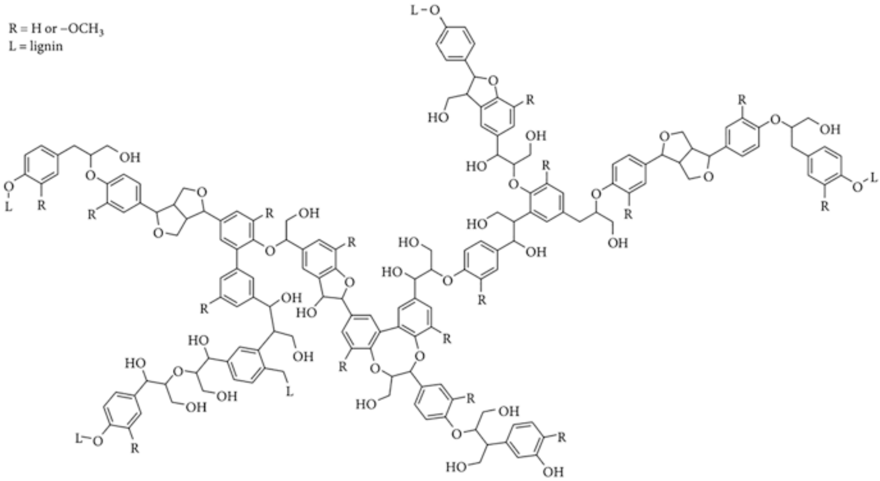


**Fig. 16.1** Chemical structure of lignin (Lu et al. 2017)

desulfonated. They can enter into mixed dimeric reactions with other functional groups, for which they are excellent fillers. Polysaccharide groups can be oxidized, inverted, or removed by molecular separation processes. Depending on the specific application lignosulfonates can be available in a number of different bases such as sodium lignosulfonates, magnesium lignosulfonates, calcium lignosulfonates, and ammonium lignosulfonates. Figure 16.2 shows the appearance of different types of Lignosulfonate available in the market. The general properties of lignosulfonate include Sulfur amount 3.5–8.0 wt %, Sulfonated content [mmol $g^{-1}$] 0.5–10, Charge density [meq $g^{-1}$] 0.9, *M*W [g $mol^{-1}$] 1000–150,000 (Aro and Fatehi 2017). The market volume for lignosulfonates was $700 million in 2015 and is forecast to grow


**Fig. 16.2** Appearance of Lignosulfonate available in the market (Source: https://www.greenagrochem.com)

by more than 3.5 GR by 2024, propelled by strong expansion in the construction segment. It is mainly employed as a water reducing chemical and gives cement the essential workability much at inflated temperatures. Conditions such as infrastructure expansion and population surge in the BRIC countries will stimulate the market for lignosulfonates in the residential and non-residential sectors. In addition, the low cost of the product causes them more appropriate for exploitation in those countries where the need for water reducing chemicals is substantially higher.

#### 16.2.3.1 Sodium Lignosulfonates

Sodium lignosulfonate is obtained from the digestion liquid by purification, evaporation, chemical treatment and drying. Sodium lignosulfonate is a natural anionic surfactant made from a high molecular weight polymer, abundant in sulfo and carboxyl groups, and has superior water solubility, surfactance, and dispersibility. It

**Table 16.4** Specification of Lignosulfonate available in the market

| Name | Grade one | Grade two | Grade three |
|---|---|---|---|
| Product code | GAC-NaLS-1 | GAC-NaLS-2 | GAC-NaLS-3 |
| Appearance | Brown powder | Brown powder | Brown powder |
| pH | 7.0–9.5 | 9.0–13.0 | 4–7 |
| Dry matters | 95% | 95% | 95% |
| Water-insoluble | 1.5% max | 2% max | 2% max |
| Water reducing capacity | 8% min | 5% min | 8% min |
| Sulphate | 2–5% | 0 | 1–2% |
| Calcium and magnesium | 0.5 max | 0.5 max | 5% around |
| Lignosulphonate | 55% min | 60% min | 50% min |
| Reducing sugar | 7% max | 7% max | 10% min |
| Moisture | 7% max | 7% max | 7% max |

Source: https://www.greenagrochem.com

can be utilized for several different industries. Sodium lignosulfonate (lignosulfonic acid, sodium salt) can be utilized in the food industry, as a defoamer for paper production and in adhesives for food contact. It has preservative characteristics and is employed as a constituent in animal feed. It is also implemented in construction, ceramics, mineral powder, chemical industry, textile industry (leather), metallurgy, petroleum industry, fire retardant materials, rubber vulcanization and organic polymerization. Typical applications of sodium lignosulfonates include dispersant for concrete additives; plastifying additive for bricks and ceramics; tanning agents; deflocculant; bonding agent for fibre boards; binding agent for moulding of pellets, carbon black, fertilizers, activated carbon, foundry moulds; and dust reduction agent during spraying for non-asphalted roads and dispersion in the agricultural domain. Table 16.4 displays the properties of typical Sodium Lignosulfonate manufactured from spent sulphite pulping liquor**.**

#### 16.2.3.2 Calcium Lignosulfonates

Calcium lignosulfonate additive has been utilized in the food industry for several years and is used, e.g., as an emulsifier in animal feed, as a raw material in the making of vanillin, etc. Other typical applications of Calcium Lignosulfonates include Concrete, Plaster Board, Activated carbon, Carbon Black, Agglomeration, Chip Board, Ceramics, Resins PF, Soil stabilization, Tanning, Pigments, Pellet Binder, Corrugated Flute, Chemicals, Fertilizers and Dyestuff.

#### 16.2.3.3 Magnesium Lignosulfonates

Typical applications of magnesium sulfonates include concrete, ceramics, paperboard, oil well drilling, ore flotation, fertilizers, wetting agent.

#### 16.2.3.4 Ammonium Lignosulfonates

Typical applications of ammonium lignosulfonates involve for concrete additives; plastifying additive for bricks and ceramics; tanning agents; deflocculant; bonding agent for fibreboards; binding agent for moulding of pellets, carbon black, fertilizer, activated carbon, foundry moulds; dust reduction agent during spraying for non-asphalted roads and dispersion in the agricultural domain.

## 16.3 Black Liquor/Lignosulfonateas Cement Admixture

Lignosulfonate from alkaline sulphate pulping could be used as a source of retardant in concrete admixtures. Literature on evaluation of lignosulphonate indicated good possibility of utilizing these sodium based lignosulphonate as retardant in concrete admixture. Application of Lignosulfonate from black liquor has been utilized as concrete admixture since 1930s. By virtue of its special morphology, with particular functional groups like -$SO_3^{2-}$, -$OH^-$, and -$O^-$, lignosulfonates possess a considerable degree of reactivity and find a wide utilization in manufacturing water-reducing admixtures (Lou et al. 2013; Yu et al. 2013; Zhang et al. 2015). In order to maintain both workability and strength, water to cement ratio has to be optimized. When more water is added, workability of the cement is increased, but strength decreases (Nikhil and Jayasree 2018). Admixtures are specifically used for increasing the workability with minimum water cement ratio. However, admixtures should not decrease the strength of the cement.

The major benefit of water reducers is to diminish the water quantity by 5–10% to enhance the strength of the concrete by adequate to 25% for a provided fluidity (Yu et al. 2013). In general, the water reduction rate of typical plasticizers is less than 12%, however, it can be reduced over 12% by using superplasticisers. Commonly used admixtures or super plasticizers are lingo-sulphonates and hydrocarbolic acid salts. They are usually based on lignosulphonates, which are derived from wood pulping liquor (Nikhil and Jayasree 2018).

To obtain finished solid material as lignosulfonate, black liquor is treated by filtration, evaporation, sulphonation and drying in spray drier (El-Mekkawi et al. 2011). However, this process can be high-priced due to the cost of the sulfonation process, since the separation of the lignin from the black liquor is a very complicated operation. Bagasse pulp liquor, which is a by-product of the digestion process, may too be employed like a chemical mixture in building materials (Ananthkumar et al. 2018). The replenishment of 1% of water by black liquor from the digestion of bagasse enhances the freshness of the concrete and the substitution of 2% of water by black liquor improves the mechanical features of the concrete and functions as a setting retarder (Ananthkumar et al. 2018).

Lignosulfonates obtained from acidic pulping process can also be utilized like a workability boost for cement. Alkali lignin can be recovered form black liquor and after sulfonation may be employed like a cement admixture (El-Mekkawi et al.

2011). Sodium Lignosulfonate can be modified via combined oxidation-sulfomethylation to increase the fluidity of cement by 15% (Lu et al. 2017). Various dosage of black liquor generated by Rakta Pulp and Paper Mill form soda pulping process of rice straw with 10% total solids content was used as a cheaper cement admixture to enhance workability and impede setting of concrete (El-Mekkawi et al. 2011). The results showed that the when the black liquor is mixed directly with cement as admixture, it increased compressive strength of cement by 85% when 15% water was replaced by black liquor.

El-Mekkawi et al. (2011) explored different possibilities of using black liquor from rice straw pulping from different mills in Egypt to explore the possibility of using black liquor directly as cement admixtures. Black liquor from soda pulping of rice straw was examined at 10% total solids and added to the cement as admixtures in different proportion to evaluate its effect on strength and water reducing capacity. It was found that black rice straw liquor can be used as an inexpensive additive to enhance workability and delay the setting time of concrete. Black liquor made from rice straw improved the compressive strength of concrete by 85% with a 15% substitution of water by black liquor. Based on the results of the chemical analysis of the hardened concrete, it was also determined that the black liquor is safe for reinforced concrete, and it was determined that the admixture meets the pertinent Egyptian standards (El-Mekkawi et al. 2011).

Takahashi et al. (2014) explored a process of developing a water-reducing admixture in concrete from soda-AQ lignin in black liquor. The wheat straw lignin obtained from soda pulping black liquor was sulphonated and used as an additive for concrete, which demonstrated the reducing impact of water on concrete. Soda-AQ lignin precipitated from black liquor by lowering its pH from 10.5 to 2.0 using 20% sulphuric acid. The precipitated soda-AQ lignin was recovered by centrifugation. Soda-AQ lignin extracted below pH 8.5 was found to perform better as a water reducing admixture than extracted at pH 10.5. The assessment of Soda-AQ-Lignin also made it clear that Soda-AQ-Lignin with a relatively lower molecular weight and a higher content of phenolic hydroxyl groups might be more suitable like a water reducing admixture (Takahashi et al. 2014).

Zhang et al. (2015) examined how water-reducing rate, setting time and compressive strength of concrete get influenced with black liquor ratio in concrete. The black liquor graft polymerization process with sulfonated acetone-formaldehyde was investigated. The black liquor was acquired by sulfate cooking of wheat stalks having 69.3% lignin and 19.5% ash. To synthesize the BSAF (black liquor sulfonated acetone formaldehyde) copolymer, a solution of black liquor, hydrogen peroxide, and ferrous sulfate was heated to 60 °C with stirring. After the post-sedimentation time of 60 min, formaldehyde was added to initiate polymerization, which was carried out at 95 °C for 2 h. A BSAF copolymer was obtained with a solids content of 32% and a pH in the range 12–13. It was found that increasing BSAF gradually enhanced the water reduction rate of the concrete and significantly increased the setting time of the concrete. BSAF also improved the long-term compressive strength of concrete (Zhang et al. 2015).

Ananthkumar et al. (2018) investigated the use of bagasse black liquor as a cement admixture. Black liquor was added to the fresh concrete mix in various doses of 1–5% substitute of water by black liquor to investigate the effect on workability, compressive strength, flexibility, tensile strength and setting duration. It was found that the maximum processability was detected with a 2% substitute of water with black liquor. The utmost compressive strength was noted for a 1% substitution of water for black liquor. With a 2% substitution of water for black liquor, the maximum setting time was seen. The substitution of 2% water by black liquor boosts the mechanical characteristics of concrete and functions as a setting retarder. Experiments and results also showed that black liquor had a lower accomplishment with respect to lignosulfonate additives found in market for producing self-compacting concrete (Ananthkumar et al. 2018).

Yu et al. (2013) investigated a way to modify sodium lignosulfonate by combined oxidative sulfomethylation to make concrete superplasticizers. The black liquor was produced from the alkaline sulphite cooking of a raw material furnish having 80% reed and 20% wheat straw. The chemical characteristics of black liquor demonstrated pH: 8.16, Solids: 16.48%, Organics: 10.88%, Inorganics: 5.6%, Hemicellulose: 0.59% and Sodium Lignosulfonate: 12.69%.Sodium lignosulfonate superplasticizer was synthesized by mixing black liquor, PAA solution and $FeSO_4$ and heating the mixture to 60–100 °C with agitation of 800 rpm. After oxidation time of 0.5–3 h, formaldehyde and sodium sulphite were added and sulfomethylation reaction was conducted at 80–100 °C for reaction time of 1–4 h. Once the solution temperature became ambient it was processed in a spray drier. It was established that the fluidity and water reducing capability of sodium lignosulfonate improved significantly when the sodium lignosulfonate was prepared by oxidation at 80 °C for 2 h with 30% PAA and 0.5% $FeSO_4$ and sulfomethylation at 95 °C for 3 h with 20% formaldehyde and 30% $Na_2SO_3$ (Yu et al. 2013) .

Lou et al. (2013) used wheat straw kraft pulp black liquor and synthesized lignin-based superplasticizers applying $H_2SO_4$ acid precipitated lignin. Sulfonated graft lignin of medium molecular weight and content of sulfonic groups has been found to exhibit excellent dispersion in the cementite system. It was also noticed that the molecular weight of the sulfonated graft lignin intensified with the concentration of reactant and the dose of acetone and formaldehyde, while the opposite was noted with the rise in the dose of the sulfonating agent. The content of sulfonic acid groups of the sulfonated graft lignin boosted with the dose of the sulfonating agent. The sulfonated graft lignin produced had high water-reducing ability, low slump loss, and intense compressive strength. Higher molecular weight grafted sulfonated lignin had a higher dispersion performance (Lou et al. 2013).

Nikhil and Jayasree (2018) examined a possibility of using black liquor sludge as super plasticizer. The black liquor sludge that was used possessed the following properties – pH: 8, BOD: 16000 mg/l, Chlorides: 375 mg/l, Sulphides: 300 mg/l, Total solids: 9105 mg/l, TDS: 2115 mg/l and TSS: 6990 mg/l. Water was replaced by black liquor for 5%, 10%, 15% and 20% of water. It was established that the black liquor encourages concrete workability, enhances compaction and decreases honeycombing when 15% of water was replaced by black liquor. All the mechanical properties of the cement were found to be within acceptable limits and satisfied IS (Indian Standards) specifications. It was observed that black liquor sludge can be effectively used as admixture in concrete for increasing workability for both strength and high strength mixes. It could also be used for structural applications (Nikhil and Jayasree 2018).

Nadif et al. (2002) utilized soda black liquor to obtain sulphur-free lignin by virtue of acid precipitation. The performance of sulfur-free lignin was also compared to existing additives available in the market like naphthalene sulfonates and lignosulfonates. The nature of lignocellulosic source plant form which the lignin got extracted, and the pulping process that was adopted by the pulp mill mainly dictated the performance of the lignin. Many of the flax lignins have been found to behave superior to lignosulfonates, which implies that this sulfur-free material can also be used as a replacement for sulfur-comprising admixtures. It was also observed that hemp lignin admixture performed better in terms of flow of mortar compared to wheat straw lignin admixture and flax lignin admixture performed better than both the hemp lignin admixture and wheat straw admixture. With every lignin investigated, from flax, hemp and what straw, mortar flow improved and some sulfur-free lignins obtained from the acid precipitation digestion process of soda exceeded market requirements (Nadif et al. 2002).

Kamoun et al. (1999) mixed black liquor with minor quantities of sulfonated naphthalene-formaldehyde polymer to make a useful cement dispersant with long-lasting effects. The mixture was prepared using 87% active matter of sulfonated naphthalene and formaldehyde condensate in brown powder form mixed with residual black pulping liquor containing lignin, reducing sugars, organic salts, mineral salts and free soda. It was observed that the admixture prepared by mixing black liquor with sulfonated naphthalene formaldehyde polymer ensured high plasticity and durable action. It has also been observed that the qualities of cement mortar, particularly plasticity, can be monitored by altering the proportion of sulfonated naphthalene-formaldehyde polymer and black liquor. It was found that the degree of plasticity is determined mainly by the proportion of sulfonated naphthalene-formaldehyde polymer, but then again, its durability is determined by the proportion of black liquor (Kamoun et al. 1999).

Darweesh (2016) studied high molecular weight lignosulfonates acquired as a consequence of the acid sulfate wood pulp process. The main function of retarding water-reducing admixtures has been found to be to retard the setting duration of concrete, which has a detrimental impact on successive strength improvement, while allowing a subsequent reduction in the water-cement ratio. . To estimate the effect of adding cellulose black liquor to the cement, the black liquor was dispersed in the mixed water in a dose of 0–3% and then added to ordinary and limestone Portland cement. Black liquor was detected to drop the setting duration of both the ordinary and limestone Portland cement. The compressive strength of hardened cement pastes has been increased. It was also noted that the water consistency of both types of cement increased gradually with the concentration of black liquor i.e. up to 31.67% from 28% for ordinary Portland cement and up to 32.45% from 28.5% for limestone Portland cement (Darweesh 2016).

Dixit et al. (2009) prepared lignin based chemical admixtures to be used in OPC (ordinary Portland cement) and investigated its hydration behaviour. They performed experiments for 3 days, 7 days and 28 days respectively to evaluate the water consistency, setting duration and compressive strength of cement mortar prepared using this chemical admixture. The overall mechanism of the working of lignin as plasticizers during the hydration of OPC was presented. It was found that the initial and final settling time of OPC increased tremendously by mixing 1–2% lignin by weight of cement. By mixing 1% lignin the initial and final settling time increased by 120 and 115 minutes respectively and by mixing 2% lignin the initial and final settling time increased by 150 and 170 minutes, respectively. Also, the compressive strength of OPC mortar one part cement and three parts sand in the presence of 0.3% lignin on cement basis increased by 3.5, 0.8 and 1.4 MPa respectively after 3, 7, and 28 days.

## 16.4 Conclusion

Lignosulphonates obtained as waste by-products from pulp and paper mills was established to function suitably like retardant in mortar/concrete admixture by various researchers. The compressive strength of admixtures may be improved significantly with the use of pulp and paper mill based lignosulphonates. Employing the processes discussed above the waste lignosulphonates thus obtained as waste by product could probably be efficiently used as an industrial product meeting the standards or any other specification. Saleable by-product thus developed could improve the economics of the paper mills employing lignin removal process which may assist paper mills in obtaining zero liquid discharge.

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