"Lignosulfonate" is a Valuble By-Product From The Black Liquor

Chatterjee A.K.

K.R. Pulp & Papers Limited, Shahjahanpur - 242001 (U.P.)

ABSTRACT

"Alkaline Sulfite cooking of wood-chips/bamboo/wheat straw/bagasse/sarkanda etc can produce the most valuable Product called "LIGNOSULFONATE" from the black-liquor, which is used to make admixture for cement-concrete, used in oil-drilling, as coal-dust binder to make smokeless fuel and many other"

Introduction

The Indian paper industry, one of the oldest industrial sectors accounting for about 1.6% of the world's production of paper and paperboard, provides employment to more than 0.12 million people directly and 0.34 million people indirectly. The pulp and paper industry in India has a long history with the first mill being commissioned in 1812 in the eastern state of West Bengal. With less than 20 paper mills in 1950 (total capacity of 0.137 million tons), today there are around 550 paper mills with installed capacity of 8.5 million tons (65% of capacity utilized) and it is estimated to touch 14 million tons mark by 2015-16 (WRI, 1994, WRI, 2010; FAO, 1997).

The paper industry is divided into three categories viz. i) wood/ forest based, ii) agro-based and iii) waste paper based accounting for 40%, 32% and 28% respectively. The industry in future classified on the basis of capacity i.e. large scale mills (capacity of 24000 TPA & above), middle scale mills (capacity < 24000 TPA but > 5000 TPA) and small scale mills (< 5000 TPA). All large scale paper mills are based on wood/forest based raw materials with a few exceptions. The proportion of non-wood raw material based paper is increasing over the years and at present about 60.8% of total production is based on non-wood raw material and 39.2% on wood.

The agro-based paper mills generate much higher pollution load than the large integrated wood and bamboo based paper mill due to non-utilization of spent black liquor for recovery of chemicals. The absence of a dependable and economical technology always remains a limiting factor while addressing this problem. However, now the paper mills have started to look for other viable options in view of directions given by Central Pollution Control Board (CPCB), New Delhi in the "Charter on Corporate Responsibility for Environmental Protection" (CREB) issued in March, 2003.

Production of Lignosulphonates

The raw materials was cut, dedusted, washed and mixed with cooking chemical i.e. Sulphite in the Lye-Mixer and fed into the spherical rotary digester duly SS cladded. The direct steam was used for cooking. The cooked pulp is blown into a blow tank and subsequently washed in the counter current washing plant, enabling to achieve maximum percentage of total solids in the black liquor. This black liquor obtained in the previous step was clarified in a clarifier to remove sand, dust and suspended solids and filtered through a 40 mesh screen. The clarified black liquor was concentrated to 45% solids in multi-effect evaporators. The concentrated lignosulphonate, thus produced in 'the evaporator at about 45% total solid was treated chemically to adjust the pH to 7.5-8.0 and to reduce the sugars to 5-6%. The desugared lignosulphonate was stored in the storage tank after adding required dose of preserve.

i) Raw Material

Sarkanda (*saccharum munja*) was used as raw material for the studies. Botanically, Sarkanda commonly known as-Kana Grass is Saccharum munja and belongs to the family Grammineae (Poaceae). Sarkanda is a very large erect mass growing in clumps up to a height of 4-5 meters. It grows well on alluvial Sandy banks of the river streams all over and is abundandantly available in northern belt of India, Culms are biennial, pale, solid, pithy, and smooth with an inconspicuous growth ring and root zone. Some species of Sarkanda grow in very dry climate. Sarkanda grass is a promising cellulose raw material, which could easily supplement the growing need of agro-residue based paper mills for their raw materials. The Proximate analysis of Kanha Grass is given in Table-1.01:

Table- 1.01:
Proximate analysis of Saccharum munja.

Parameters	%
Ash	4.67
Solubility- 1% NaOh	41.8
Alcohal	3.9
Cold Water	7.6
Hot Water	10.4
Pentogen	26.5
Lignin	22.0
Cellulose	58.0
Holo-cellulose	79.0

Sarkanda Grass (Saccharum Munja) In Wild

First Ligno-sulphonate Recovery Plant

Sarkanda Storage In The Stock Yard

Modified Ligno-sulphonate Recovery Plant

ii) Analysis and Evaluation of Lignosulphonates

The lignosulphonates were analyzed and evaluated in accordance with IS: 9103/6925-1999. the lignosulphonates thus developed were tested for various parameters as listed in table 1.02: a certain amount of sugars is always necessary in lignosulphonates to impart retarding effect to the concrete to avoid cracks during mass construction. The past reports also confirm the suitability of lignosulphonates with 5-7% sugar as set retarding admixture.

iii) Compliance of Lignosulphonate as water reducing and plasticizing admixture:

To evaluate lignosulphonates for compliance as water reducing ad-mixture as per IS:9103, the major parameters such as water content required, compressive strength & flexural strength after 3,7 and 28 days were determined. Percent-age length change and bleeding over control were also determined the result of the evaluation of agro-based lignosulphonates as water reducing and plasticizing admixture has been summarized in Table 1.03. At a dosage of 0,3% by v/w of cement, the water

Table 1.02:
Specification of agro based sodium lignosulphonates.

Parameters	Limit
Total Solids %	45
pH	7.5-8.0
Lignin %	48-50
Sugar %	5-6
Sp. Gravity gm/cc	1.30
Sodium%	3.0
Calcium %	1.3

Table- 1.03:
Sodium Lignosulphonate as Water Reducing Concrete Admixture.

Parameters	Test Results	Requirement of Is:9103-1999
Water Content % control Sample Max	90	95
Compressive Strength, % of Control Sample, Min. 3 Days 7 Days 28 Days	 120 116 115	 110 110 110
Flexural Strength, % of Control Sample, Min. 3 Days 7 Days 28 Days	 106 105 113	 100 100 100
Length Change, %Increase Over Control Max. 28 Days	0.008	5
Bleeding % Increase over Control, Max	3	5

content was reduced by 10% in comparison to control. The compressive strength and flexural strength tested after 3, 7 and 28 days with agro based lignosulphonates showed much improvement over control. The test results confirm that the agro based lignosulphonate can be used as a water reducing and plasticizing admixture.

iv) Comparison of agro-based sodium lignosulphonate with commercially available chemical admixture.

To compare the effect of agro-based lignosulphonate with of existing commercial admixture, M20 concrete WCLS subjected to both the product-along with a control run and the results are tabulated (Table 1.04). Although the compressive strength has been found to be slightly lower than control after one day but has been found to be higher and comparable to control and commercial chemical admixture respectively after 3, 7 and 28 days.

v) Effect of agro-based lingo-sulphonate on different brand of cement:

The result of cube test carried out with different brand of cement to see effect on compressive load taken summarized in Table 1.05 indicate that agro-based lignosulphonates have a positive effect on all brands of cement. The results of the tests carried out in Brick and Tiles Research Institute Essen Regd., Germany, to evaluate the effect of lignosulphonates in the brick and pipe clay formation process have been shown in Table 1.06. In both the cases the forming pressure could be reduced and the dry bending strength increased.

Table- 1.04:
Agro-based Sodium Lignosulphonates vs Commercial Chemical Admixture on Portland pozzolona Cement M 20.

Description	Slump Range (MN)	Compressive Strength (Mpa)				Flexural Strength (Mpa)	
		1 Day	3 Day	7 Day	28 Day	7 Day	28 Day
Control (W/c=0.6)	12-17	7.9	15.5	22.7	34.0	4.6	5.8
Lignosulphonate (W/c=0.6%)	50-52	6.8	15.8	23.0	35.3	4.4	5.6
0.6% Chemical Admixture 37% (W/c=0.6)	54-58	7.0	16.5	23.3	36.0	4.5	5.5

Table- 1.05:
Effect of agro-based Lignosulphonates on various brands of cement.

Cement	Curing Period	Cube Size	Compressive Load Taken (Control)	Compressive Load Taken (Agro-Based L S 0.6%)
Shree Ultra	7 days	15x15x15 cm.	17.5 T	19.1 T
Ambuja Silcate	7 Days	15x15x15 cm.	21.0 T	32.0 T
Birla Plus	7 days	15x15x15x15 cm.	17.5 T	29.5 T
ACC	7 Days	15x15x15 cm.	15.0 T	28.2 T
Vikram-Birla	7 days	15x15x15 cm.	18.0 T	31.0 T

Table- 1.06:
Results of adding Lignosulphonates and poly-phosphate to brick-clay sample: Stick, Diameter 25mm, And Mixing Water Content: 20% refer to dry.

Sr. No.	Additive Used	Amount of Additive	Stiffness (mm) (before extrusion)	Penetrometer Value (after extrusion)	Forming Pressure (bar)	Vacuum (bar)	Drying Shrinkage (%)	Water content % refer to Dry	Dry bending strength N/nm^2
1	Without	Without NIL	26.0	1.5	9.5	0.9	6.6	18.54	9.06
2	Lingnosulph-onate	0.5% refer to dry	26.8	1.5	8.2	0.9	6.3	18.41	10.65
3	FABUTIT 734	0.5% refer to dry	25.0	1.3	7.8	0.9	7.1	19.15	9.60

Table- 1.07:
Types, Price and Application of Lignosulphonates.

Sr. No.	Types of Lignosulphonates/ production Process	Value/ Metric Ton	Application
1.	No. Chemical Treatment, only Liquor Collection and Concentration to Approx. 50% Solids, Occasionally Spray drying	1. Spray Dried LS: 150-250 US $ ton (Depending on the type of cation and raw material) 2. Concentrated Liquid LS: 70-120 US $/ Liquid Ton	• Agricultural Chemicals • Binder for Pelletinzing • Binder for Briquetting • Extender in PF, UF & MF Resins • Ore Floatation Aid • Tanning Applications • Road Treatment
2.	Chemical Desugarization, No Fraction Ultra Filtration	Approx. 300 US $/Ton	• Concrete Additive • Gypsum board additive • Agricultural board • Additive
3.	Chemical Treatment with Slight or No Fractionation	Over 500 US $/Ton	• Oil Well Drilling • Secondary Dye Dispersants • Flocculants, Flotation and Chelating agents • Water Treatments
4.	Extensive Fractionation and Chemical Processing	Over 900 US $/Ton	• Asphalt Emulsion • Battery Additive • Dye Dispersants • Flocculants, Slurry • Explosives, Superpiastiezers

Economics:
Basis: A 100 TPD Agro-based Kraft Paper Mills.

Sr.No.	45 - 50% TS Ls Lye		Spray Dried Power
1	Production / Day MT	200	100
2	Cost Of Production, *Rs./Ton*	2000	8000
3	Selling Price, *Rs./Ton*	6000	20,000
4	Cost a additional Plants & Machinery *Price Rs. Cr.*	2	3
5	Savings, *Rs., Cr.*	24	36

vi) Various types of Lignosulphonates, its price & applications given in Table- 1.07:

Out of all varieties lignosulphonates emulsion or powder having maximum application in cement-concrete ad-mixture and in oil drilling in India.

Reference:

Thesis by- A.K. Chatterjee, HNB Central University Uttarakhand (2011)
Biotechnological UP- Gradation of Agro-Residue Based Pulping With By- Product Recovery Using Microbial Strains.

-- *Chatterjee, AK (2000). Lignosulphonates The Potential by-product from Black Liquor. In paper International (July-Sept, 2000): 16-17.*

-- *Chatterjee, AK; Sharma, N and Bhatt, AK (2004). Development of lingo-sulphonates from spent black liquor generated from optimized bisulphate pulping of Saccharum munja. Journal of Indian Pulp and Paper Technical Association (IPPTA) 16:35-39.*

-- *Chatterjee, AK; Sharma, Narendra; Bhatt, AK and Azmi, W (2001). Lignosulphonates A Viable Eco-Friendly Approach for Paper Industry. In: Brain-Storming-Workshop on "Biobusiness for Entrepreneurship and Employment Generation" (August 19-20, 2001). DBT, Govt of Himachal Pradesh, Shimla, pp. 89-91.*

-- *Chatterjee, AK; Sharma, Narendra; Bhatt, AK; Bihani, BL and Bhalla, TC (2002). High Yield alkaline-sulphite pulping and subsequent enzyme treatment of agro-residues with utilization of spent black liquor. Journal of Indian Pulp & paper Technical Association (IPPTA), Convention Issue: 81-86.*