Technical Upgradation In Pulp Washing & Bleaching Stages To Improve The Final Pulp Quality And To Reduce The Pollution Load

Saibaba K., Venkateshwar Rao M., Gnanasekaran Arul, Hamsagar A.S. and Singh Amar

ABSTRACT

To meet the present day market demand in quality product, there was a high stress on pulp mills to deliver highest quality of pulp with low operating cost in production to maintain profitability apart from meeting the norms stipulated by CREP, Central and State pollution control boards. Keeping this in view, improved washing and bleaching methodologies were followed. Washing considerations for effective pulp bleaching in hardwood Kraft line and the application of suitable wash aid chemicals in the brown stock washing have proven to be the cost effective solution. By using wash aid, reduction in alkali (Soda) loss, uniformity and increase in black liquor solids are observed. Partial dosage of ClO_2 in Chlorination stage increased the brightness of pulp and reduced the pollution impact apart from getting improved pulp viscosity. Effective oxidation by the addition of hydrogen peroxide in E(o) stage increased the brightness of pulp and reduced the CE kappa of the pulp and filtrate color.

INTRODUCTION

BGPPL Unit: Kamalapuram is one of the best units in South India for manufacturing Dissolving Grade pulp with capacity of 98000 TPA, supplying to textile industries. This Unit is located in Kamalapuram of Warangal District in Andhra Pradesh. This Unit has latest equipments and entire plant is controlled through DCS (Distributed Control System). Unit was awarded "Three Green Leaves" by Centre for Science and Environment, New Delhi for Green rating project and has been placed in the 5^{th} position out of 29 Units participated. Unit has major customers include Grasim Nagda, who manufactures Viscose Staple and Viscose Filament yarns. Presently, usage of specialty chemicals in Pulp mill is slowly increased for the cost benefits. Hardwood (Eucalyptus, Casurina, Subabul) street is of conventional design with Disc Chippers, drum chipper, Stationery Digesters, brown stock washing (DD washer), followed by Screening and C/D, E(op), D-stage and E(p) bleaching sequence.

LITERATURE REVIEW

Pulp and paper industry is to develop technology that minimize impact on the environment, meets the high product quality standards of the marketplace and minimizing capital and operating cost. Since the replacement of existing equipment to meet these demands may not be viable for some mills, enhancing the existing system's performance by other means becomes increasingly important. The objective of pulp washing is to remove as much of the soluble impurities as possible with minimum levels of fresh water usage. Poor washing can lead to resin build up, which can manifest itself as pitch deposits, causing down time and production problems. While large amounts of resin are removed in brown stock washing, substantial amounts can still remain with the pulp. Increasing washing efficiency will reduce resin content as well as total solids in the pulp. Reducing carryover of total dissolved solids to subsequent processes will enhance recovery and bleaching operations. Resin and chemical carryover can negatively affect surface and strength properties of unbleached paper, as well as cause deposit problems on the sheet making equipment in bleached mills. Additionally, high carryover in brown stock and bleach plant areas can limit the functioning of bleach chemicals destroying their bleaching capabilities and increasing chemical demand.

Washing of pulp can be done accordingly to three different principals, i.e. 1) by dewatering, 2) by displacement or 3) by pressing. An industrial washer usually includes more than one of these principles. Bleach plant washing has become a factor of ever increasing importance as bleach plants are made more closed at the same time as more expensive chemicals are being utilized in the sequence. Washing efficiency with respect to COD and metals are influenced by temperature, pH, the type of washer used and the volume, and the quality of wash water. The concentration of scaling substances increases as the degree of bleach plant closure increases. Therefore it is essential to use a washer which establishes a barrier between stages and to open up the filtrate loop at the correct points. The market place prefers new chemical technology to be environmentally friendly. Example of this trend are oil-free defoamers and alkyl phenol ethoxylate-free (APE) surfactants. Trial with new wash-aid in actual mill conditions with a new APE-free surfactant technology have resulted in improved washing, lower organic and inorganic carryover, increased mat consistency, and lower shower flows. These benifits have been demonstrated in DD Washer and bleach plant vacuum drum washers and chemi-washers. Other mill objectives such as reduction of mill bottlenecks, decreased deposition, lower bleach chemical cost, increased production, and reduced environmental discharge can be realized using this technology. This paper will discuss the technology, its benefits and case histories.

DD washer washing has a substantial impact on pulp mill and bleach plant operations. Poor DD Washer washing results in carryover of solids, particularly lignin, resin, and inorganic materials that directly influence bleaching chemical use, the formation

BILT Graphic Paper Products Ltd,
Unit: Kamalapuram,
Warangal.

of chlorinated organic and pulp brightness (1). The requirements for pulp washing equipment used in a modern bleach plant are continuously increasing. One reason is that new more expensive bleaching chemicals are being used, which means that losses of bleaching chemicals due to poor washing between the stages can no longer be accepted. A second reason is that TCF bleaching has become popular in many mills. The bleaching chemicals used, like hydrogen peroxide and ozone, are very sensitive to the presence of even low concentrations of transition metals, as these lead to decomposition of the bleaching chemicals. A powerful metal chelating stage and a good pulp wash should therefore be used in TCF sequences prior to peroxide and ozone stages. A third reason to improve the washing efficiency is the result of the trend in the industry to close up the bleach plant to reduce the environmental impact. If good washing can be combined with reduced consumption of wash water this becomes a primary alternative. Reduced effluent generation can also be important as a way to reduce the size, and indirectly the cost, of the external effluent treatment systems (2).

Another result of carryover in the generation of Adsorbable Organic Halides (AOX), research has shown that 10 to 20 % of the total AOX generated results from solids carryover during good washing and 25- 40 % during poor washing. Experts have stated that these solids consume 10- 25 % of the active chlorine charged to the first bleaching stage (3). Poor washing also results in the formation of more dioxin type compounds. The use of surfactants in broken stock washing can reduce dioxin formation by as much as 25 % (4). Removal of black liquor solid (Na, Mg, Ca ions and lignin derivatives) present in the stagnant areas between the pulp by the action of water / weak wash liquor is known as pulp washing. Some advantages associated with pulp washing are as follows: Costly Na-salts used in cooking the pulp are recovered, lignin based solutes are recovered for their heating value, clean pulp is obtained which reduce the consumption of bleaching chemicals & thereby environmental load is decreased. Mechanism of pulp washing is a combination of dilution, diffusion, displacement and extraction. This is further complicated by sorption, channeling, foaming, and incomplete mixing. Time allowed for diffusion of washable substance out of fibres is also an important factor. In absence of dispersion and diffusion phenomenon, it is possible to replace one volume of black liquor from pulp with one volume of wash water by displacement (5).

The study on the effect of phosphonates on DD Washer washing show that DTPMPA (Diethylene Triamine Penta Methylene Phosphonic Acid) is effective in reducing metal ions when applied in DD Washer. Another phosphonate known as HEDP (1-Hydroxy Ethylene diamine 1, 1-Diphosphonic Acid), EDTA (Ethylene Diamine TetraAcetic acid), and strong acid washing were compared with DTPMPA and SPAP (Sodium salt solution of Poly Amino Phosphonic acids). DTPMPA and SPAP addition did not produce significant differences in Mg, Cu, and Fe content in pulps, but Mn was reduced to very low levels. HEDP did not produce any difference in metal ions compared with as untreated pulp. In both cases, Mn levels after 0.1 % DTPMPA or SPAP addition in DD washer washing were reduced to below 2ppm without the use of a separate Q stage. Even though an acid washing at pH = 2 produced a beneficial reduction in ions, concomitant lignin precipitation onto fibres would make this operation un-viable. Washing efficiency would be reduced, revealed by an increase in kappa no. and reduction in COD, which would adversely affect the following oxygen stage (6).

Bowater Incorporated's Coated Paper and Pulp Division in Catawba, SC has four stages, kraft brown stock washing system. Installed in 1959 to wash 360 tons per day of 30 kappa kraft pulp, modifications have allowed mill personnel to operate the original equipment in the washing line at rates of 330 tons per day. A controlling point to operating the DD washer is the defoamer usage and type. The defoamer is silicone-based with a specific gravity higher than water, approximately 1.05. The silicone and water based defoamer replaced an oil-based, EBS containing defoamer about 2 years ago. Defoamer is applied to the shower headers in the first DD washer. A small amount of defoamer is applied to the #4 filtrate chest. A critical value when evaluating the DD washer defoamer at our mill is its ability to produce high black liquor solids in the filtrate from the #1 DDwasher. Defoamer usage averages approximately 0.9 kilograms per ton of pulp. A measured variable of washer operation is soda loss. The soda loss has been maintained at 10.3-18.5 kilograms per tonne. This range has been kept the same since 1959 even though the throughput has increased. With every increase of throughput, the equivalent increase of wash water was applied to minimize the soda loss (7).

Washing in the oxygen delignification stage in aspen kraft pulping has been shown to have a positive effect on the reduction of extractives in pulp. Bouchard et al have previously shown that this positive impact can be enhanced by the addition to oxygen delignification of certain generic types of surfactants. Based on these results, further work has been carried out to investigate the effect of a selection of commercially available surfactant blends on providing an even greater efficacy in extractive reduction. One of the formulations was particularly effective in enhancing extractive removal in an oxygen stage environment (8). Addition of carbon dioxide (CO_2) to the washing system of an alkaline pulp significantly improves the washing performance. The improvement can be seen as improved washing efficiency, improved runnability of the wash plant, including reduced maintenance and higher production capacity. The application of carbon dioxide in washing is now in permanent operation in several European mills. In those mills the CO_2 applied with different objectives to reduce maintenance cost, increase production, reduce carryover, reduce effluent load, or to decrease wash water consumption (9). The introduction of oxygen delignification in the modified kraft pulping process has been driven by environmental, economic and energy related considerations. The reduction of kappa number in the pulp going to chlorination affects linearly the effluent COD and AOX. The total active chlorine consumption depends linearly on kappa number (10).

RESULTS AND DISCUSSION

1. Improved drainage using Wash Aid in brown stock washer (DD washer)

Results from the table 1 indicated that using of 0.6 kg of wash aid per ton of pulp in the DD washer reduced 5.0 kg/t of Alkali loss, 1.5 % increase in mat consistency, increase in vacuum of 100 mmHg in DD washer, reduction in hot water spray of around 25m^3/hr and increase in WBL quantity around 10m^3/hr were observed in comparison with the blank result. Drainage can refer to drainage rate and/or drainage volume. Both are important to the efficient operation of a brown stock or bleach plant washer. Defoamer's impact drainage rate by minimizing the air bubbles in the stocks that tend to block liquor flow through the channels between the fibres. The new wash aid technology works with the defoamer to incrementally increase drainage volume.

Drainage volume is impacted by decreasing the surface tension of the liquid in the mat resulting in an increase in the volume of liquid drained from the mat. Based on the Laplace equation, which relates surface tension to capillary pressure, if surface tension is reduced so is capillary pressure, which results in a decrease in the quantity of liquid held in the capillary. The pores or channels in the pulp mat function similarly to capillaries, therefore if the surface tension of the liquid is reduced; mat consistency is expected to increase. The following problems can occur as a consequence of these carryover problems: Cooking chemical makeup demands increase, Foam due to the combination of resins and alkaline pH, Potential scale problems such as Barium Sulphate, Calcium Oxalate and Calcium Carbonate, High dirt due to pitch and scale, Carry-over of resinous materials can deposit on sensing equipment-causing loss of bleach pulp control. The reduced carryover or dissolved solids will enhance pulp mill and bleach plant runnability. Pulp washing has a substantial impact on pulp mill and bleach plant operations. Due to environmental and market pressures, more mills are closing up or being required to change their bleaching strategies. The wash aid discussed in this paper enhances overall washing efficiency. In addition to reducing lignin carryover to the bleach plant, this technology offers additional benefits of deresination, pitch deposition control and enhanced overall DD washer drainage to reduce system bottlenecks. The wash aid enhances washing by compensating for the changing behaviour of the stock characteristics through the washers. These benefits allow the mill to use less shower water, reduce their evaporator load, or maintain their shower flows resulting in cleaner pulp. In the current era heightened environmental concern, bleach plants are striving to improve effluent quality while maintaining pulp quality and low bleaching cost. As the trend towards closure or totally non chlorine bleached chemical pulp continues, combination of newer technologies is going to be required. Wash aid allows the mill to purge the impurities from the system resulting in reduced bleach plant chemical usage, reduced pitch deposition or dirt in the sheet and reduced salt cake loss. The wash aid enhances DD washer drainage and compensates for liquor component behaviour. Additionally, increased drainage might allow the mill to reduce fresh water shower usage or increase production at equal shower flow.

2. Partial usage of Chlorine Dioxide in Chlorination stage

ClO_2 addition started in Chlorination stage in addition to Chlorine (Cl) which increases the brightness of pulp and reduces the pollution load in terms of COD apart from getting improved viscosity (Strength) in reinforced oxidative extraction stage. The details are given in table - 2. By using 3.0 kg/t of ClO_2 in chlorination stage which in-turn reduces 15.0 kg/t of Chlorine. Increase in pulp brightness of 4.0 points was observed which will decrease the consumption of chemicals in the further stages. Reduction in COD of 10% on filtrate was also observed.

Chemistry & Kinetics: Chlorine dioxide is an oxidant which accepts 5 electrons per molecule in being reduced to chloride ion. The molecular weight of Chlorine dioxide is 67.5 and so its equivalent weight is 13.5 (67.5/5). Chlorine accepts two electrons when reduced to chloride ion, has a molecular weight of 71 and so has an equivalent weight of 35.5 (71/2)

$$ClO_2 + 4H^+ + 5e^- \quad Cl^- + 2H_2O$$

$$Cl_2 + 2e^- \quad 2Cl^-$$

Therefore in substituting Chlorine dioxide for chlorine to provide equivalent electron transfer, one weight unit of Chlorine dioxide can replace for 2.63 weight units (35.5/13.5) of chlorine. "Equivalent chlorine," also known as active chlorine, is a common unit if oxidant in bleaching technology; one weight unit of Chlorine dioxide is equal to 2.63 weight units of "Equivalent chlorine." The replacement of chlorine with Chlorine dioxide in the first bleaching stage changes the amount of sodium salts of organic acids, sodium chloride and sodium carbonate formed in the extraction stage. The amount of NaOH required in extraction is decreased by Chlorine dioxide substitution. This is achieved through the decrease in the amount of NaCl produced in the extraction stage. However, with the increased oxidation caused by chlorine dioxide substitution, greater lignin removal occurs in the washing step before extraction.

3. Addition of H_2O_2 in E(o) stage

Addition of H_2O_2 in the stage of E(o) along with oxygen increases the brightness of pulp and reduces the CE kappa of the pulp. Significant reduction in consumption of Hydrogen peroxide in the last stage E(p) was observed. The effect of peroxide charge on the CE kappa number and pulp brightness after extraction is given in table 3. Decrease in Oxygen dosage of around 3.0kg/t, 33% reduction in CE kappa and improvement in pulp brightness of around 10% was observed. COD reduction of around 15% and 35% of filtrate color reduction were also observed. The introduction of oxygen and hydrogen peroxide in to the extraction stage increases the amount of carbonate that is produced and also decreases the amount of residual NaOH. This increase in carbonate is caused by an increase in the degree of lignin oxidation and an increase in the concurrent formation of carboxylic acids. Oxidation, before and during extraction, stabilizes the carbohydrates against yield loss by the peeling reaction. Oxygen-reinforced alkaline extraction decreases the kappa number of the pulp compared with a non-oxidative extraction without affecting pulp viscosity to any significant degree. Even when E(o) technology was available, hydrogen peroxide was used additionally in the E(o) stage. Peroxide addition was used to decrease the amount of Chlorine-containing oxidant in the first bleaching stage. In oxygen-reinforced alkaline extraction, both peroxide and oxygen, is superimposed on the effect of alkali on the pulp.

CONCLUSIONS

By keeping in view of Pulp quality, Cost effectiveness & Environmental benefits, using of effective wash aid in DD washer enhanced overall washing efficiency and reduced the alkali loss significantly. In addition to reducing lignin carryover to the bleach plant, this offers additional benefits of deresination, pitch deposition control and enhanced overall DD washer drainage to reduce system bottlenecks. Other potential benefits are reduced salt cake makeup demands, increased mat consistency, increase in black liquor solids resulting in steam savings, decreased COD in effluent and decreased defoamer requirements in ETP decreased process variability.

By partial substitution of ClO_2 in chlorination stage, substantial amount of chlorine dosage was reduced and increased the pulp brightness and protected pulp strength (viscosity) from degradation by effective and selective delignification process. The effectiveness in brightness improvement will reflect in reduction of chemical consumption in further bleaching stages which reflected in cost reduction. Also adsorbable organic halides (AOX) levels will come down significantly. Pollutant load in terms of COD is reduced in ETP.

Effective Oxidative extraction (reinforced extraction) by utilizing hydrogen peroxide improved the brightness of the pulp, reduced the CE kappa level and protected the strength (viscosity). Dosage level of oxygen was reduced significantly. Reduction of chemical consumption in further bleaching stages will be reduced due to lower level of CE kappa and higher brightness. Filtrate color and COD were reduced substantially which reduced the effluent load in ETP. Overall Improvement in the intermittent & final pulp quality and reduction in pollution load was observed.

EXPERIMENTAL

1. Wash aid Plant trial

Wash aid (supplied by standard specialized chemicals manufacturer) was used in unbleached pulp washer (DD washer). The trial duration maintained 7 days. Pulp through put was 12.5 tons per hour. The spray water temperature was 80°C and the spray water flow was 120/110 m^3 per hour. DD washer Mat consistency, Vaccum, flows of circulation pumps, DD washer torque, Alkali loss and WBL (Weak Black liquor) total solids were measured and the results are given in Table 1.

TABLE-1

EFFECT OF WASH AID IN BROWN STOCK WASHING (DD WASHER)

S.No	Parameter	Units	Blank	With wash aid	Remarks
1	Pulp through put	t/hr	12.5	12.5	
2	Wash aid dosage	Kg/t	-	0.60	
3	Washer inlet consistency	%	3.5	3.5	
4	Mat consistency	%	12.0	13.5	1.5 % increases
5	Alkali loss as Na_2SO_4	Kg/t	20	15	5 kg reduction
6	Load of washer (Torque)	KNm	250	180	70KNm reduced
7	WBL total solids	%	14.0	17.0	3% increases
8	WBL quantity generation	M^3/hr	150	160	10m3 increases
9	Hot water spray	M^3/hr	120	110	10m3 reduction
10	Hot water temperature	°C	80	80	
11	Drainage		Normal	High	
12	Foam generation		Very high	Control	
13	Washer vacuum	mmHg	200	250	
14	Chlorine requirement	Kg/t	50	45	5 kg reduction

2. Partial substitution of ClO2 in Chlorination stage

Plant trial was carried out for partial substitution of ClO2 in chlorination stage. Accordingly chlorine dosage was reduced. Reaction pH was maintained around 2.0 at ambient temperature. Pulp rate of 12.5 t/hr with inlet consistency of 3.0 % with retention time of 45 minutes. Chlorine dosage of 45.0/30.0 kg/t and ClO2 of 3.0kg/t was used. Brightness, viscosity of the pulp, residual chlorine & COD of filtrate was measured and given in table 2.

TABLE-2

EFFECT OF PARTIAL SUBSTITUTION OF ClO_2 IN CHLORINATION

S.No	Parameter	Units	Only Chlorine	ClO_2 + Chlorine	Remarks
1	Pulp through put	t/hr	12.5	12.5	
2	Chlorine dosage	Kg/t	45	30	15 kg reduction
3	ClO_2 dosage	Kg/t	-	3.0	
4	Washer inlet consistency	%	3.0	3.0	
5	Reaction pH		2.0	2.0	
6	Reaction temperature	°C	Ambient	Ambient	
7	Reaction time	Min	45	45	
8	Pulp brightness-PV	%	42	46	4 points increase
9	Viscosity (CAM)	Cp	23-25	25-27	Cp protected
10	Filtrate COD	‘ppm	2450	2205	10% reduction

TABLE-3

EFFECT OF H_2O_2 DOSAGE IN E(o) STAGE

S.No	Parameter	Units	E(o)	E(op)	Remarks
1	Pulp through put	t/hr	12.5	12.5	
2	Oxygen dosage	Kg/t	9.0	6.0	33% reduction
3	H_2O_2 dosage	Kg/t	-	4.0	
4	Reaction pH		>10.5	>10.5	
5	Reaction temperature	°C	70	70	
6	Reaction time	Min	120	120	
7	CE kappa		3.0	2.0	33% reduction
8	Pulp brightness-PV	%	55 to 60	65 to 70	10 points increase
9	Residual H_2O_2	mg/l	-	100	
10	Filtrate COD	‘ppm	2580	2190	15% reduction
11	Filtrate Colour	Pt.Co	4550	2950	35% reduction

3. Peroxide addition in E(o) stage

In the bleach plant, hydrogen peroxide addition was started in E(o) stage and the flow was regulated. Reaction pH was maintained above 10.5 at temperature 70°C with the retention time of oxygen reactor for 45 minutes with the oxygen dosage of 9.0/6.0 kg/t. pulp rate of 12.5 t/hr with the reaction time of 120 minutes. H_2O_2 dosage of 4.0 kg/t was given in E(o) stage. CE Kappa number, brightness of the pulp, residual H_2O_2 & filtrate COD were measured and given in table 3.

ACKNOLODGEMENTS

The authors would like to thank the BGPPL management for their kind permission for publishing the results of the study.

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