Alkaline Chlorine Dioxide Bleaching Of Casuarina (CJ9) Wood and Its Environmental Impact

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ABSTRACT

The bleaching chemistry indicates that pH affects the effectiveness of chlorine dioxide treatment and the standard recommendations have been to maintain a final stage pH range for brightening with chlorine dioxide between 3.5 and 4.0. In Casuarina (CJ9) pulp bleaching sequence, without Oxygen delignification(ODL) stage ,we found that the optimum pH for initial Do and final D_1 chlorine dioxide bleaching is dependent on chlorine dioxide charge but this stage should be operated with a final pH close to alkaline, when a typical chlorine dioxide charge is applied. We have noticed that maintaining a pH close to alkaline side throughout the bleaching stage. Primary objective of the bleaching sequence is to improve pulp brightness in initial chlorine dioxide treatment, which could later promote more economic and efficient use of bleaching chemicals in the next stage of bleaching. The sulphate scale forming potential of sulphuric acid addition in acidic Do stage and sulphur dioxide addition to reduce residual chlorine could be eliminated and also reaction temperature is reduced by 15^0C when compared to ADhotEopD1 bleaching sequence. The alkaline pH bleaching methods can improve the pulp bleachability without affecting pulp strength properties, optical properties, physical properties and improved effluent characteristics. The target brightness can be effectively achieveded if the first treatment with alkaline pH followed by extracting alkali soluble compounds in a subsequent (Ep) stage, and by then continuing bleaching with final chlorine dioxide (D_1)stage. With the increasing cost of wood, the modified continuous cooking (MCC) to lower the pulp kappa number is questioned. A strategic shift in pulping and bleaching is discussed to decrease wood use per ton of pulp while decreasing the kappa number of pulp to bleach plant. Such a shift would allow the mills to lower bleaching cost, comply with the environmental requirements and, allow the closure of bleach plants effectively.

Introduction

Advances in pulping technology have continued nowadays in response to the environmental and market demands. The ability to lower the content of lignin in wood pulps prior to bleaching facilitates environmentally compatible bleaching practices, reduces operating costs, and may assist in the development of lesser effluent during pulp production. The fundamental principles involved in extending kraft delignification while retaining pulp strength properties were established in late 1970s and early1980s. (1,2,3). These principles include leveling out the alkali concentration, maintaining a high sulfidity particularly at the beginning of the cook, reducing the dissolved lignin concentration, employing lower cooking temperatures, and Isothermal cooking. Further improvements have been made in continuous modified wood chip cooking technology to enhance delignification while improving pulp strength and uniformity (4, 5). Despite these significant advances in pulping technology, very little is known about how pH changes in the wood pulping process which can influence Brightness in initial Chlorine dioxide bleaching stages. To address this issue, we have begun to characterize the bleaching efficiency of Casuarinas (CJ9) pulps at higher pH. One concern is the capital requirement for oxygen delignification and the rate of return (%ROI) on the investment. The other aspect is recirculation of oxygen stage(s) filtrate to recovery and the impact on solids and heat load to the recovery boiler. The oxygen stage filtrate has lower heat value (HHV), since the solids are oxidized (6).

The pulp bleachability of initial Chlorine dioxide treatment would be directly related to the amounts of phenoxy groups present in the lignin as per the literature. This result was significant since most bleaching text books (7) assert that the ClO_2 bleaching chemistry occurs primarily via phenoxy groups and that this unit in lignin controls pulp bleachability. To define the influence of pH on ClO_2 bleaching of Casuarinas pulps, a Laboratory cooked pulps of 16% and 17% white liquor (TAA) addition was prepared, analysed, and bleached without Oxygen Delignification (ODL) stage via $DoEpD_1$ sequence. The present bleaching study relates to a process for the delignification and bleaching of an aqueous lignocellulosic pulp under acidic and alkaline pH conditions in the initial

Chlorine dioxide bleaching sequence and its environmental impacts.The changes in pulp bleaching at acidic and alkaline pH bleached pulp were evaluated to determine the bleachability of Casuriana (CJ9).

Although the chorine dioxide speciation into chlorite, chlorate, chloride and organically bound chlorine, etc. is quite well investigated for "normal (60-70°C)" chlorine dioxide delignification/bleaching and brightening (Chang et al. 2001; Ni 1992; Rapson, Strumila 1979; Strumila, Rapson 1976).

The oxidized lignin compounds remains in the pulp fiber after the Do stage, and can only be removed by a subsequent alkaline extraction stage. As expected, the charge of sodium hydroxide necessary to extract the oxidized, water-soluble material quantitatively is related to the kappa number of the pulp entering the D_0 stage .The pH profile has a major effect in determining the efficiency of chlorine dioxide bleaching. During acidic or alkaline pH bleaching, the pH is decreased considerably during the first reaction phase due to the formation of organic and hydrochloric acids. Hence, sodium hydroxide must be added to maintain the optimal end pH in the range between 3.7 and 3.8 (D_0). According to Reeve and Rapson, approximately 0.6 kg NaOH should be added for each kg ClO_2 charged to the air dried ton of pulp to ensure an optimal end pH but in this alkaline pH Do stage followed by extraction stage has consumed 0.45 kg NaOH instead of 0.9kg consumed by acidic pH Do stage.

Experimental

Raw material preparation: Clone Casuarina (CJ9) wood log were chipped in a mill Disc chipper and screened in a standard laboratory Chip screen and the accepted chips were air dried at room temperature. After getting constant moisture, the chips are packed in a polythene bag and stored for a day to get homogeneous moisture of the chip for cooking.

Table: 1. Unbleached pulp Casuarina (CJ9) Properties

S.No .	Particular	16%TAA	17%TAA
1	Screened pulp yield ,%	50.55	50.62
2	Reject, %	1.37	1.04
3	Kappa number	22.8	20.2
4	Pulp brightness, %ISO	27.7	28.7

Pulping: The chips were pulped (alkali charge 16 % and 17% as Na_2O, bath ratio 1:2.8, cooking temperature: 165^{0}C, time: 65 minutes) in a Laboratory bomb digester. At the end of cooking, the contents of the bomb were discharged into a bowl followed by sequential washing with DM water, disintegrated in a rod mill for 20 minutes, screened on a flat - slotted laboratory screen (slot width 0.15mm), centrifuged, and then granulated. Total pulp yield, amount of screen reject, kappa number and black liquor properties were determined using TAPPI standard methods (Table: 2). after dewatering and fluffing, kappa number, percentage rejects, and total yield were determined. The unbleached pulp properties were listed in Table:3.

Bleaching

During wood pulp bleaching, large amounts of dissolved organic compounds and spent chemicals may be released to aquatic ecosystems. As a result, mills must treat their effluents and are under increasing pressure to modify their processes to comply with environmental regulations. The major processes occurring in a bleached Kraft pulp mill are pulping (alkaline cooking of wood chips) and bleaching (oxidative degradation of colour causing compounds) (Dence and Reeve, 1996). Pulp bleaching is a process whereby wood pulp is whitened by sequential bleaching and extraction. Under acid or alkaline conditions, chlorine dioxide reacts oxidatively with colour causing organic compounds, degrading them and increasing the brightness of the pulp. Alkaline stages, with or without chemicals such as oxygen and hydrogen peroxide, are used between the acidic oxidizing stages to solubilise and remove the reacted material from the pulp. Bleach filtrate from each step of pulp bleaching are usually analyzed to identifying organic compounds that are toxic or that could cause oxygen depletion.

Unbleached Casuarina (CJ9) pulps were prepared from laboratory cooking process was used without Oxygen Delignification. The two pulps were bleached in the laboratory to achieve a brightness of 87% ISO according to the following stage bleaching sequence: $D_0E_PD_1$.

Freshly prepared solutions of chlorine dioxide solution and other bleaching and extracting chemicals sodium hydroxide and hydrogen peroxide were prepared in the lab.

Table: 2. Do Ep D_1 SEQUENCE CASUARINA (CJ9) WOOD BLEACHING CONDITIONS

S.No.	Parameters	16 % ACIDIC			16 % ALAKLI			17% ACIDIC			17% ALAKLI		
		Do	Ep	D_1	Do	Ep	D_1	D_0	Ep	D_1	D_0	Ep	D_1
1	Initial pH	7.8	4.5	7.6	**7.8**	**4.7**	**7.6**	7.8	4.6	7.6	**7.8**	**5.3**	**7.2**
2	Acid /alkali addition,%	0.20	0.90	0.00	**0.03**	**0.45**	**0.00**	0.20	0.90	0.00	**0.03**	**0.45**	**0.00**
3	pH	2.8	10.1	7.6	**9.8**	**10.3**	**7.6**	3.2	10.2	7.6	**9.9**	**10.5**	**7.2**
4	ClO_2/H_2O_2addition,%	1.80	1.00	0.80	**1.80**	**1.00**	**0.80**	1.80	1.00	0.80	**1.80**	**1.00**	**0.80**
5	pH	2.2	9.7	5.0	**3.7**	**9.7**	**5.0**	2.5	9.5	5.0	**3.8**	**9.7**	**5.2**
6	Brightness,%ISO	56.5	74.0	85.4	**56.7**	**73.8**	**85.8**	56.6	74.5	85.8	**56.9**	**74.3**	**86.6**
7	Kappa number	4.7	2.1	1.0	**4.9**	**2.4**	**1.2**	4.6	2.0	1.2	**4.7**	**2.2**	**1.1**

Water and bleaching or extracting chemicals were added to 200 g of Oven dried pulp in polyethylene bags. The bags were kneaded by hand and placed in a temperature controlled water bath. After each of the bleaching stages, pulp was filtered with Buckner funnel to collect the spent bleaching liquor. The pH of the spent liquors was measured, and the liquors stored in plastic containers. Between bleaching stages, the pulp was washed with clean water, which was filtered from the pulp and discarded. The brightness of a sub sample of bleached pulp was measured according to the standard TAPPI Test Method (T 452) to ensure that Laboratory scale bleaching produced pulps at a final brightness of 87% ISO.

Although the chemistry of bleaching might not be as obscure as some of the earlier reviews have indicated; the complexity of the partial reactions makes it extremely difficult to understand the overall effect. Obviously there is need for a full computational simulation package that can bind together the kinetics and equilibria of chemical reactions and mass transfer (Kuitunen et al. 2005).

D_0 Stage

Screened Casuarina (CJ3) pulp of 10% consistency was used and pH adjusted to both acidic or alkaline ClO_2 bleaching experiments. Then freshly collected ClO_2 was added into the poythene bags and the pulp was mixed well and put the pulp contained polythene bags in a preheated water bath at 75^{0}C for 90 minutes with intermittent mixing of the pulp content. Then the pulp was filtered, washed with hot water and thickened for preparing next stage. Kappa number and optical properties of the washed pulp were determined. The D_O bleaching conditions were as in table: 2.

Ep Stage

The pulp from the D_0 stage pulp was adjusted to 10% consistency with demineralised water and NaOH addition was chosen to yield a terminal pH of 10.5-11.0. After that, 1.0 % Hydrogen peroxide was added and measured the pH. Then (Ep) bleaching stage was performed in a preheated water bath at 75^{o}C for 120 min. At the end of the (Ep) stage, the pulp was filtered and the effluents were collected, and the pulp was thoroughly washed and prepared for final chlorine dioxide (D_1) bleaching sequence. The Ep bleaching conditions were as in table: 2.

Table: 3. STRENGTH PROPERTIES OF UNBLEACHED AND BLEACHED PULP- Casuarina (CJ9)

S. No.	Parameters	unit	16 % TAA BLEACHED PULP			17 % TAA BLEACHED PULP		
			Unbleached	Acidic bld	Alkaline bld	Unbleached	Acidic Bld	Alkaline bld
1	CSF	ml	530	450	**440**	530	440	**430**
2	Bulk	cc g^{-1}	2.33	2.12	**2.10**	2.30	2.10	**2.08**
3	Tensile Index	N m g^{-1}	36.2	43.5	**48.7**	37.6	43.2	**44.7**
4	Tear Index	M N m^2 g^{-1}	6.00	6.02	**5.96**	6.04	6.15	**6.13**
5	Burst Index	K pa m^2 g^{-1}	1.74	2.27	**2.69**	2.03	2.44	**2.58**
6	Sc.Coefficient	m^2 kg^{-1}	38.5	55.3	**52.6**	37.5	52.6	**53.4**

Alkaline pH bleaching

During bleaching process, light scattering is retained and light absorption is reduced. The illusion of whiteness in bleaching is created by eliminating light absorption from pulp by the reduction of chromophore group present in the fiber. Chlorine dioxide is commonly used as bleaching agent today in majority of pulp mills throughout the world (8 & 9). It is a general practice to maintain the pulp pH at 2-2.5 in the D_{HT} stage (10) and it is maintained by the addition of sulphuric acid. However, addition of sulphuric acid has negative effects on environment and pipe line scale properties for example increasing calcium sulphate scale. The solubility of calcium sulphate scale is a temperature dependent. The solubility of calcium sulphate scale in water decreases with increase temperature. In other words, calcium sulphate scale is soluble in cold water but almost completely insoluble in super heated water. Consequently, calcium sulphate gets precipitated and form hard scale on the surfaces of the pipe lines. Acid stage bleach plant effluent, which is let out from the pulp mill, will also have high TDS, sulphate and temperature and needs special attention during downstream effluent treatment.

The following (DoEpD_1) bleaching sequences were carried out for Casuarina (CJ9) wood pulps:

D_1 stage

The pulp from the Ep stage was adjusted to 10% consistency with demineralised water and added chlorine dioxide charge was chosen to achieve a target Brightness (86.0 %ISO) for quality paper making. Then (D_1) stage was performed in a preheated water bath at 75^{o}C for 120 min. After that, the pulp was filtered and the effluents were collected, and the pulp was thoroughly washed and thickened and stored in a polythene bag for determination of strength and optical properties. The D_1 bleaching conditions were as in table: 2.

Pulp characterization:

At all stages brightness, kappa number and strength properties of the pulps were carried out as per TAPPI standard methods. Pulp brightness was measured with an optical Spectrometer by using white tiles as standard. For calculating tear, tensile and burst indices, the hand sheets were made as per ISO DP 5269 and dried on plates in standard conditions and conditioned at 27±1^{0}C and 65±5% relative humidity and tested according to TAPPI standards. Hand sheet properties are reported on an oven dry basis. The unbleached and bleached pulp properties were shown in table: 3.

Effluent analysis:

At all stages, the filtrate were collected and tested as per standard testing methods. Effluent characteristics like Colour, Total Dissolved solids (TDS) inorganic and Chemical Oxygen Demand (COD) were measured and the tested values listed in table: 4.

Results And Discussion

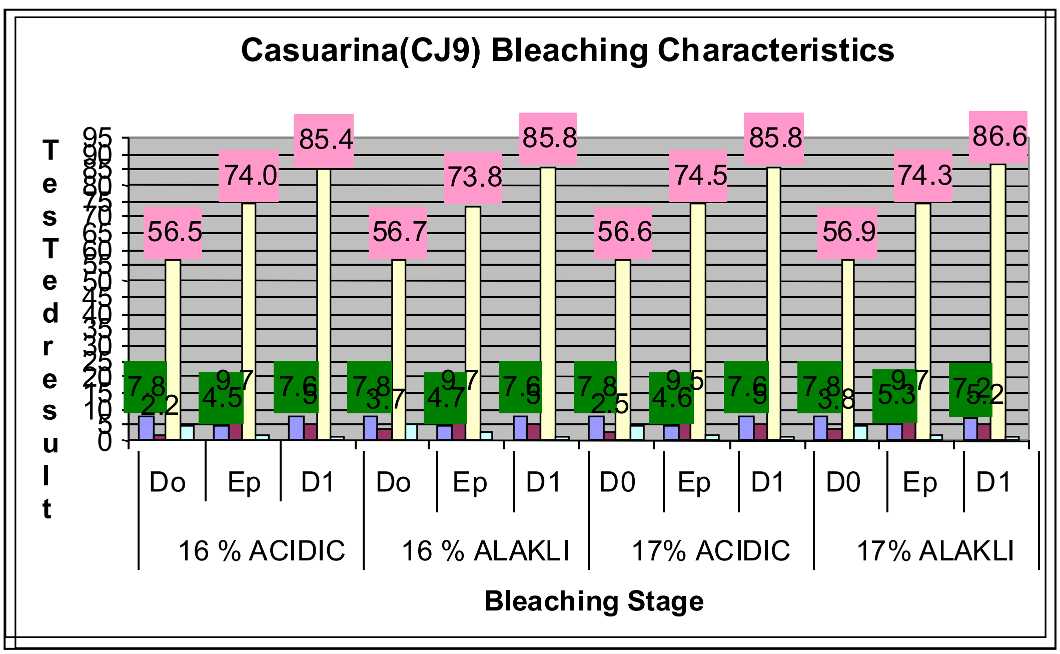
Reducing the bleaching chemical consumption, yet reaching the target brightness has important cost and environmental consequences. Bleach chemical consumption at the first stage is a function of pulp kappa number; the extracted kappa number that decides the bleach chemical consumption in the following stages depends on first-stage delignification. The changes made in pulping could influence the bleaching response of pulps. Therefore, it is important to determine whether the use of digester additives or oxygen delignification stage would impact the bleachability of pulps.

Results indicative of D_0 delignification efficiency of acidic and alkaline pH are in Table: 2 for the CJ9 pulps. As shown in Table: 2, no change in bleaching efficiency was noticed between acidic and alkaline pH delignification of the CJ9 pulps. In spite of the fact that same (1.80%) ClO_2 was consumed in both experiments; the kappa number after extraction was more or less identical. Previous works have shown that Lignin reduces ClO_2 to Chlorous acid or Chlorite ion depends on pH and hypochlorous acid in parallel reaction. In the present case, CJ9 pulp delignification efficiency in the D_0 stage, expressed as kappa number reduction per percent of active chlorine consumed, was 4.7 &4.6 for the Acidic D_0 stage, as compared with 4.9 &4.7 for the alkaline pH.

Table: 4. Effluent Characteristics of bleaching filtrate Casuarina (CJ9)

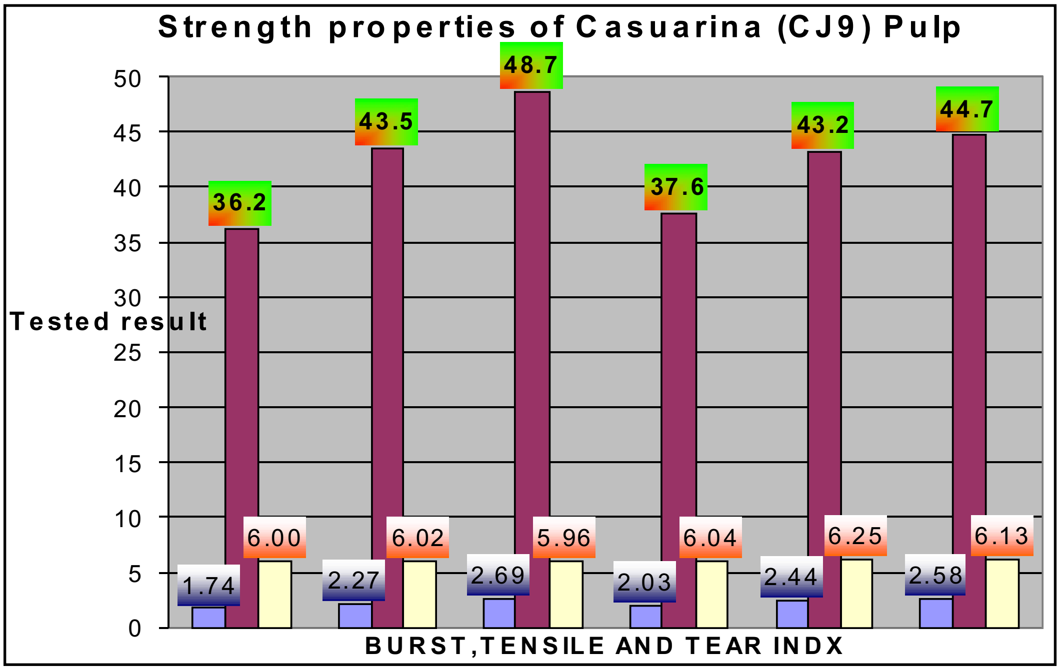
S.No	Parameters	Unit	16% TAA Acidic filtrate			17 % TAA Acidic Filtrate			16%TAA Alkaline Filtrate			17%TAA Alkaline Filtrate		
			D_0	Ep	D_1	D_0	Ep	D_1	D_0	Ep	D_1	D_0	Ep	D_1
1	Colour	Pt. Co.,	1125	1070	300	900	850	270	1000	750	300	850	700	260
2	Total dissolved solids	mg/l	2432	2262	1758	1976	1152	1302	2370	1092	902	1306	904	662
3	Suspended solids	mg/l	514	316	306	314	216	94	242	122	86	282	80	66
4	TDS Inorganic	mg/l	1700	1452	1222	1430	778	961	1469	730	604	902	648	470
5	TDS Inorganic	%	69.90	64.19	69.52	72.37	67.53	73.81	61.98	66.84	66.96	69.06	71.68	71.00
6	Total COD	mg/l	1935	1804	1752	1878	1660	1680	1699	985	894	1149	673	649
7	Toatal Hardness	mg/l	860	440	650	760	400	620	630	550	400	440	410	370
8	Calcium Hradness	mg/l	600	300	500	480	250	460	400	400	190	200	360	200
9	Magnesium Hardness	mg/l	260	140	150	280	150	160	230	150	210	240	150	170
10	Chlorides as Cl	mg/l	1030	1250	1070	1110	980	920	1270	730	600	810	560	550

Figure: 1. Bleaching Charecteristics of Casuarina (CJ9).



In the case of the acidic or alkaline pH pulps, as shown in Table: 2, there was no Brightness variation with respect to delignification efficiency

Figure: 2.Strength properties of Casuarina (CJ9)



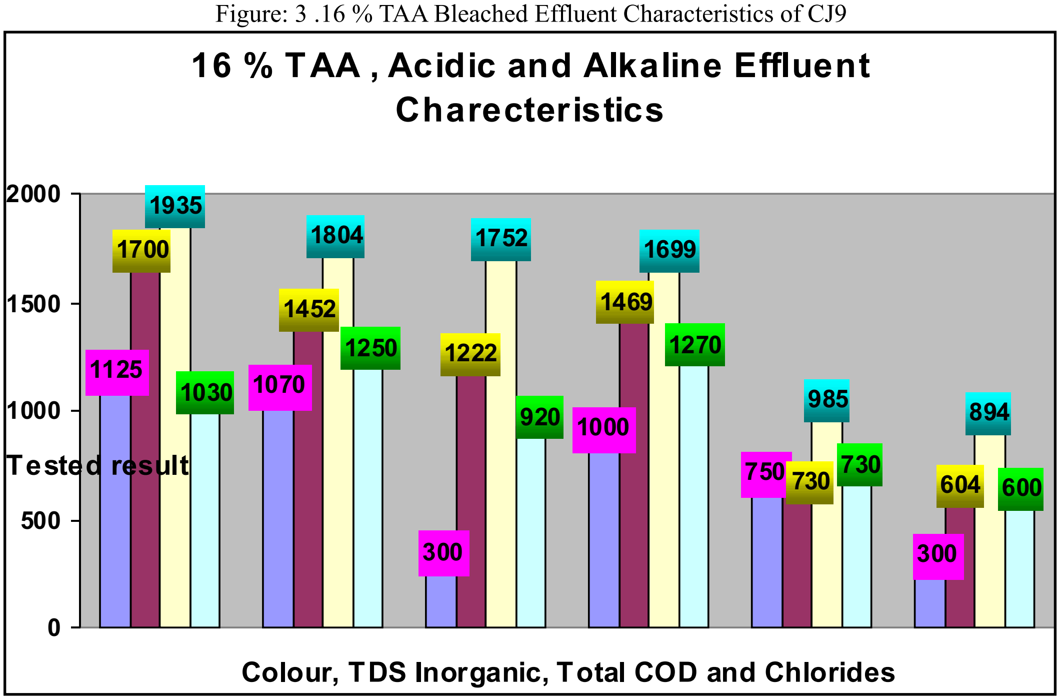
is sensitive to operating conditions and perhaps also to unbleached pulp characteristics. In this regard, it is worth noting that alkaline pH bleaching method was made an attempt to optimize the ClO_2 addition, for bleaching performance of Casuarin (CJ9) and its effluent quality and or filtrate recycling within the system.

It is apparent that there is no difference in D_0 (Ep) delignification efficiency between acidic and alkaline pH bleached pulps, or between the two kappa numbers investigated in this study. This suggests that the relative ease of bleaching of CJ9 pulps has ease of lignin removal of both unbleached kappa numbers.

The bleaching stage, chemical consumption was same during the acidic Do bleaching when compared to alkaline bleaching except sodium hydroxide and sulphuric consumption. The maximum saving was contributed by sodium hydroxide followed by sulphuric acid. The temperature in the Do stage is reduced by 10-15°C when compared to the conventional ECF method. This has resulted in the steam saving of around 10 kg/ton of pulp leading to considerable cost saving in pulp mill operations. The total saving in terms of chemical saving and steam saving is found to be encouraging to commercilise the alkaline pH ClO_2 in bleaching.

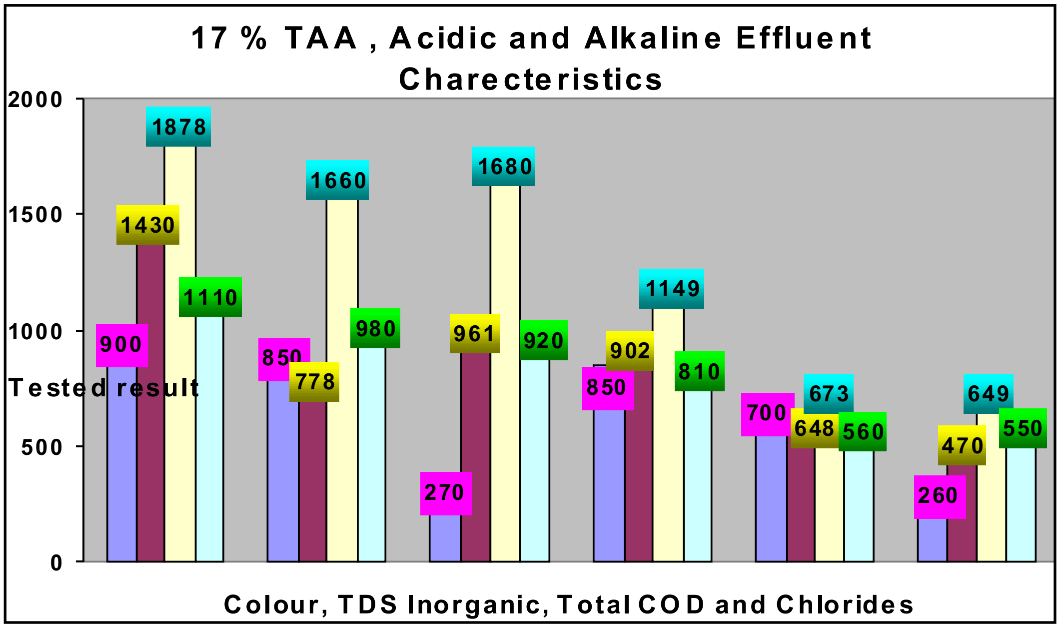
The strength properties like tensile, tear and burst indices are given in table: 2. The Acidic and alkaline pH chlorine dioxide bleached Casuarina (CJ9) pulp does not show any variation in two kappa number of bleached pulp. This shows that, the bleachability of casuarina pulp at alkaline pH bleaching has not showed any variation than acidic pH bleaching. The target brightness can be achieved easily, if the first treatment is done effectively by proper washing of reaction products and extracting alkali soluble compounds in a subsequent extraction stage and followed by second stage (D_1) chlorine dioxide bleaching.

Figure: 3 .16 % TAA Bleached Effluent Characteristics of CJ9



Information on the mechanisms of delignification at alkaline & acidic pH, and potential environmental effects was obtained by collecting and analyzing filtrates from each of the bleaching stages. The resulting data are presented in Table: 3, the result shows that, the alkaline pH chlorine dioxide bleached effluent has lower colour, total dissolved solids and COD than the acidic pH chlorine dioxide effluent. The initial Chlorine dioxide bleaching with alkaline pH followed by alkali reinforced hydrogen peroxide extraction has slown a positive impact of the filtrate recycle as closed loop in mill scale without any difficulty due

Figure: 4. 17 % TAA Bleached Filtrate Characteristics of CJ9



lower TDS inorganic content, this can be recycled back in to washing stages and taken to recovery cycle.

Do stage filtrate let into wastewater stream, contains less TDS inorganic, sulphate and chlorides (Figure-3&4) than acidic pH stage. High sulphate and low pH are the major contributes to filaments bulking, forming which affects the sludge settling leading to higher suspended solids carryover in secondary clarifier and performance of biological treatment (8, 9, 10, and 11). The lower TDS inorganic in wastewater is major environmental benefit, because there is no commercially viable technology available to reduce TDS inorganic for large scale integrated pulp and paper mills.

Conclusion

Alkaline chlorine dioxide bleaching of debarked Casuarina (CJ9) wood using D_o-Ep-D_1 bleaching sequence can produce pulp with acceptable brightness levels (85-87% ISO) and strength properties with reduced pollution load, chemical consumption and cost. Over all chemical consumption was low during the alkaline bleaching when compared to acid bleaching. The maximum chemical and cost saving was contributed by sodium hydroxide consumption followed by sulphuric acid and steam. Rapid Do bleaching of CJ9 pulp delignifies effectively and is beneficial in reducing the amount of AOX formed in the Do stage of the bleaching sequence. At high pH ClO_2 bleaching may possibly maximize extractives removal without brightness loss which decreases the deposit potential in paper machine.

Acknowledgment

Authors are thankful to TNPL management for giving permission to do this project in their Research and Development Department.

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