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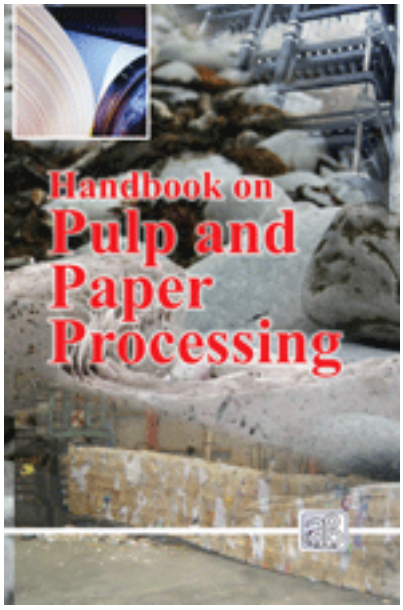
Handbook on Pulp and Paper Processing



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The pulp and paper industry comprises companies that use wood as raw material and produce pulp, paper, board and other cellulose based products. The pulp and paper sector presents one of the energy intensive and highly polluting sectors within the Indian economy and is therefore of particular interest in the context of both local and global environmental discussions. Increases in productivity through the adoption of more efficient and cleaner technologies in the manufacturing sector will be most effective in merging economic, environmental, and social development objectives. Papers are mostly used product starting from writing to packaging. It plays an important role in commercial field as well as in academic field also. Without paper nothing is expressible and reliable, so paper is part and parcel of our life. Adequate amount of raw materials for processing paper and pulp is available. Bamboo is the main raw material for Indian paper industry. New bamboo areas even at high cost are being trapped. Some of the examples of high yield pulping process are mechanical process, semi chemical process, alkaline chemical process, sulfite process, etc. Physical strength properties of paper depend on the quality of raw material, its pulping, bleaching and subsequent paper making processes. Technology has made it easy to process these raw materials in an economic and lucrative way to meet the global demand. Raw materials like, straw, bagasse, wood, bamboo is almost available in most of the places. So it is great opportunity for the entrepreneurs to start up such kind of industry. Paper Industry has tremendously increased in India in the last 20 to 30 yrs. The Paper industry is a priority sector for foreign collaboration and foreign equity participation up to 100% receives automatic approval by Reserve Bank of India. Several fiscal incentives have also been provided to the paper industry, particularly to those mills which are based on non conventional raw material.

Some of the fundamentals of the book are bleaching of bamboo cold, high yield semi chemical pulping of mixture of bamboo and mixed hardwoods, sulphate semi chemical process, kraft green liquor semi chemical process, neutral sulphite semi chemical process, thermo mechanical pulps for newsprint, zeta potential concept in paper sizing, sodium carbonate in alkali extraction during bleaching bamboo , maintenance engineering in pulp and paper industry, design and application of refiners in stock preparation, paper machine effluent etc.

This book explains about the various raw material, their processing and utilizations and also the possible waste treatment of such paper and pulp making industry. To draw attention for manufacturing quality product with all possible latest technologies is the main purpose of this book. The book is very resourceful for new entrepreneurs, technocrats, existing units and research scholars.

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Sample Chapter:

Bleaching of Bamboo

Cold Soda Pulps

Bleaching studies were carried out on bamboo cold soda pulp with a view to attain a brightness of about 50% ISO for use in making newsprint. The present investigations were undertaken at the instance of the National Newsprint and Paper Mills Limited Nepa Nagar. Results of the laboratory investigations are presented in this report.

As is the case with chemi mechanical pulps lignin content in the pulp is high i.e. most of the lignin is retained in the pulp.

Bleaching experiments were carried out with increasing dosages of hypochlorite. The bleaching conditions and results are given in Table 2.

Even with 25% hypochlorite the brightness attained was only 45% ISO. During the bleaching experiments it was observed that the brightness development in the initial stages was rapid and then brightness decreases with prolonging time. The effect of retention time on brightness in hypochlorite bleaching is given in Table 3.

It can be observed that pre extraction improves the brightness and extraction at 80ºC seems to be optimum.

Effect of Peroxide in Alkali Pretreatment

Use of 0.5% H2 O2 in alkali pre extraction improves the brightness of the subsequent two stage hypochlorite bleached pulp. The results are given in table 5. The sequence E3P0.5 provides the maximum brightness.

Pretreatment with Dye

The unbleached pulp has 53% yellowness which hinders in brightening of the pulp. With a view to reduce the yellowness of the pulp the pulp was treated with 0.05% to 0.75% victoria blue dye at 2% consistency in a disintegrator thoroughly mixed and dewatered prior to bleaching with two stage hypochlorite. Though addition of dye reduces the yellowness of the pulp considerably further bleaching does not improve the brightness more than that achieved in the absence of dye.

Addition of dye for the final bleached pulp to reduce the yellowness and then use of optical whitening agent (Ranipal) to improve the brightness further was also not effective significantly.

H2 O2 Treatment

The pulp was given pre edta treatment to complex the metal ions and then bleached with increasing dosages of H O2. Bleaching conditions and results are given in Table 6.

The bleaching conditions and results are given in Table 7. It can be observed that sequence with peroxide gives maximum brightness of 48% with 20% hypochlorite and 41.8 with 15% hypochlorite. With increasing brightness bleached pulp yield drops down. Bleached pulp yield for two stage hypochlorite is 97% whereas with pre extraction in presence of peroxide it is 91%. So for attaining 6 points gain in brightness about 5 6% yield has to be sacrifised. The unbleached and bleached pulp strength properties are given in tables 8 to 10 and strength properties are compared at 200 ml CSF in Table 11.

It can be observed that strength properties of pulps bleached by different sequence are similar though bleached pulps with pre extraction possess somewhat higher burst and tensile strength.

Minimum bleaching time just sufficient for complete exhaustion of hypochlorite has to be given coupled with efficient mixing. In two stage hypochlorite bleaching 15 minutes was found sufficient for first stage in the laboratory trials. Prolonging the bleaching time after exhaustion of hypochlorite reduces the brightness.

High Yield Semi Chemical Pulping of Mixture of Bamboo and Mixed Hardwoods

Paper industry has tremendously increased in India in the last 20 30 years. At present the total paper production capacity in India is about 12.35 lakhs tonnes as against the installed capacity of 18 16 lakhs tonnes which will be increased to 22 lakh tonnes by 1986 28 lakhs tonnes by 1991 and 42.5 lakhs tonnes at the end of this century. To fulfill this requirement lot of cellulosic raw material will be required whereas our forest (the main resources of raw material) is limited and it is decreasing day by day. The paper maker s are aware of this from longback and hence efforts have been made from time to time to develop some new sources of fibrous raw material as well as new methods of pulping so that more paper may be obtained from the same amount of raw material.

Bamboo is the main raw material for Indian Paper Industry. New Bamboo areas even at high cost are being trapped. Looking the future shortage of this valuable raw material more and more of hardwoods and many short rotation plants like agricultural residues some variety of grasses and Bagasse. Gunny bags Jute sticks etc. are being used these days to meet the growing demand.

The semi chemical process which was first developed by United States Forest Product Laboratory Madison in 1926 is now being gradually adopted in other countries in order to conserve the fibrous resources to bring down the cost of production and to make the paper product more competitive with other materials.

The primary objective in the development of semi chemical process was not only to utilize hardwoods to obtain higher yield of usable pulp than could be obtained by the conventional pulping process but also to counteract the steadily increasing raw material cost. Semi chemical pulping is a two stage process involving chemical treatment of wood chips to obtain a softening and partial removal of ligni cellulosic bonding material followed by mechanical treatment to complete the fiber separation.

This process is attractive economically because of the high yield attainable low chemical consumption and because the process lends itself to small units and a minimum of plant investment. In this case because the action of cooking liquor and bleaching agents is directly selectively on the lignin bleached hardwood pulp could be obtained in higher yields also. It also produces a stronger pulp than could be obtained by fully chemical cooking when the hardwoods species are used. Unbleached semi chemical pulps at present are used for making corrugating board speciality board. Newsprint and wrapping papers and may have possibilities of being used as liner and towelling. The bleached semi chemical pulps at present are being used for making Books Magazines (coated and uncoated) Bond Writing Glassine Grease proof paper Food board Speciality and may have possibilites of being used as waxing carbonizing and towelling tissue etc.

Literature survey revealed that some valuable work has been done on high yield pulping. Jauhri used sulphate Semi chemical process to produce high yield pulp from Dendrocalmus strict us. Nicolas used the cold soda pulping for Philippine Bamboo to obtain high yield pulp. Beckker used neutral sulphite semi chemical pulping for corrugating medium. A comparative study of neutral sulphite and green liquor semi chemical pulping for corrugating medium has been done by Raymond Michael conducted N.S.S.C. pulping of young European black alder Yuichiro and Yuiko prepared high yield pulp containing no fiber bundles. Worster and Mc Candless prepared semi chemical pulp using kraft green liquor. Agrawal and Singh prepared semi chemical pulp from a mixture of hardwoods using neutral sulphite semi chemical process and sulphate semi chemical process. Guha Singh and Grover used sulphate and neutral sulphite semi chemical process to produce high yield pulp from a mixture of Maharastra hardwoods.

With these ends in view and to increase the yield investigation were undertaken to find the suitability of mill

chips (comprising of 60.70% Bamboo and 30 40% mixed hardwoods) for the production of semi chemical pulp using sulphate semi chemical green liquor semi chemical and neutral sulphite semi chemical processes. The study also includes to find out the suitability of bleached semi chemical pulp for the production of bleached grade writing and printing paper after blending with bleached chemical mill pulp.

Raw Material

Chips were collected from the Silo conveyor belt of the chipper house section of our mill. Chips comprised of 60 70% bamboo and 30 40% mixed hardwoods like sal salai etc. These were air dried before starting the pulping experiments.

Experimental and Results

The chips were processed by sulphate semi chemical process Kraft green liquor process and neutral sulphite semi chemical process.

A. Sulphate Semi Chemical Process

Trials were carried out by the sulphate process in a stationary forced circulation type electrically heated autoclave of 30 liter capacity. 25kg O.D. chips were taken in each digestion. The material to liquor ratio was kept as 1 4. The chemical percentage was kept as 5 8 & 11% as Na2O. The time of the digestion was 3½ hrs. (Including 3 hrs. to rise to 170°C). The softered chips were washed and refined in the Sprout Waldren disc refiner using plate no. D2 A 501. The power consumption during refining was determined. The unbleached pulp yield and permanganate number of the pulp were also determined. The spent liquor was collected and analysed for R.A.A. Tweddle pH and calorific value of the liquor was also determined. The digestion and refining condition pulp yield permanganate number and black liquor analysis are recorded in Table 1A.

The pulp obtained (of cook No. 3) was beaten in laboratory valley beater to a freeness of 25 35 45 and 55°SR and standard sheets were made and tested for their strength properties according to Tappi standards. The results are recorded in Table 2A

The pulp of the cook no 3 was bleached by conventional multi stage bleaching under C/E/C/E H sequence. Bleached yield of the pulp brightness copper number viscosity post colour number of the pulp were determined. Bleaching condition bleached yield brightness copper number viscosity and post colour number are recorded in Table 3.

The fiber classification of bleached pulp was carried out in Bauer Mc Nett fiber classifier. Results are recorded in Table 4.

The bleached pulp was beaten in laboratory valley beater to a freeness of 25 35 45 and 55°SR and evaluated for strength properties. Results are recorded in Table 5.

Bleached semi chemical pulp (beaten to 45°SR) was blended in different proportions with mill bleached chemical pulp (beaten to 45°SR) and the blends were evaluated for strength properties. The strength values of the blends are given in Table 6.

Kraft Green Liquor Semi Chemical Process

Pulping trials were also carried out using Kraft green liquor in similar manner as in A. The total chemicals applied were as Na20% on total active alkali basis. As in sulphate semi chemicals process pulp obtained with 11% alkali was proceeded further. The results are recorded in Table 1B 2B 3 4 5 and 7.

Neutral Sulphite Semi Chemical Process

Pulping trials were also carried out by the N.S.S.C. process in a similar manner as in A. The ratio of sodium sulphite to sodium carbonate was kept as 7 1. The percentage of chemicals was calculated as Na2O. As in sulphate semi chemical process pulp obtained with 11% alkali was proceeded further. The results are recorded in Table 1C 2C 3 4 5 and 8.

Discussion

Sulphate Semi Chemical Process

It is observed in Table 1 A that power consumption decreases from 380 KWh/Tonne to 100 KWh/Tonne and the yield of the pulp decreases from 75.4 to 55.13 when the percentage of alkali is increased from 5 to 11%. With this increase in alkali the permanganate number decreases from 36.1 to 34.1 and R.A.A. increases from 6.20 to 9.30g/l. This indicates that the softening of the chips is more as the percentage of chemicals is increased as expected. The calorific value is satisfactory. Table 2 A indicates that unbleached pulp of cook no. 3 can be readily beaten upto 55°SR freeness in 59 mts. The physical strength properties of the unbleached pulp are encouraging. The tear factor of the pulp decreases with increase in °SR where as other strength properties increase in °SR freeness. Table 3 A shows that the total chlorine requirement is 26.6% and caustic demand is 6.6% to obtain a brightness of 73% PV. The total shrinkage of the pulp during bleaching is 20%. This pulp has a satisfactory viscosity post colour number and copper number indicating that it is not degraded and has a satisfactory keeping quality.

The fiber classification of bleached pulp recorded in Table 4A shows that the fiber percent retention on 70 mesh is maximum. From Table 5 A it is observed that on bleaching the beating time is reduced and the physical strength properties improved considerably this improvement in strength is due partly to the removal of lignin from the fibers and partly to the increase in specific surface which tends to increase inter fiber bonding.

The results recorded in Table 6 indicates that bleached sulphate semi chemical pulp is of superior quality in comparison to the mill bleached chemical pulp in respect of strength properties hence with the increase in proportions of semi chemical pulps the properties of blends are better than the mill pulp.

Green Liquor Semi Chemical Process

It is observed in Table 1 B that power consumption decreases from 240 KWh/Tonne to 120 KWh/Tonne and the yield of the pulp decreases from 70 percent to 58.8 percent when the percentage of alkali is increased from 5 to 11%. With this increase in alkali the permanganate number decreased from 36.48 to 34.78 and R.A.A. increases from 9.30 to 13.95 g/l. This again indicates that the softening of the chips is more as the percentage of chemical is increased. The calorific value is normal. In Table 2 A it can also be seen that unbleached pulp of cook no. 6 can be readily beaten upto 55°SR freeness in 28 mts. The strength properties increases with increase in °SR freeness except in case of tear factor.

From Table 3 B it is observed that total chlorine requirement is 23.5 percent and caustic demand is 6.65 percent to obtain a brightness of 72 percent PV. The total shrinkage of pulp during bleaching is 17.7 percent. This pulp has satisfactory viscosity copper number post colour number indicating that it is not degraded and has a satisfactory keeping quality. The fiber classification of bleached pulp recorded in Table 4 B indicates that maximum fibre percent retention is on 70 mesh. From Table 5 B it is observed that after bleaching the beating time is reduced and physical strength properties improve considerably.

The results recorded in Table 7 indicates that bleached green liquor semi chemical pulp is superior in comparison to the mill bleached chemical pulp in respect of strength properties hence with the increase in proportions of semi chemical pulps the properties of blends are better than the mill pulp and the brightness of the blends decreases from 78 to 68 percent PV with the increase amount of semi chemical Pulp in the blends however this brightness is sufficient for writing and printing grade paper where higher brightness is not needed.

Neutral Sulphite Semi Chemical Process

From Table 1 C it is observed that power consumption decreases from 180 KWh/Tonne to 120 KWh/Tonne and the yield of the pulp decreases from 77.60 to 68.60 when the percent of alkali is increased from 5 to 11% as Na_2O (10.16 to 22.33% as Na SO_3 respectively). With this increase in alkali the permanganate number decreases from 36.64 to 35.58 and R.A.A. increases from 4.65 to 10.85 g/l as Na_2O. This indicates

that the softening of the chips is more as the percentage of the chemicals is increased as expected. The pH of the spent liquor remains around 7.5 to 8.5 and calorific value is normal.

In Table 2 C it can also be seen that unbleached pulp of cook no. 9 can readily be beaten upto 55 SR freeness in 29 minutes only. The physical strength properties of the pulp decreases with increase in °SR freeness whereas other strength properties increases with increase in °SR. The pulp has very good bulk (1.7 to 1.68).

From Table 3 C it is evident that the total chlorine requirement is 24.71% and caustic demand is 6.35% to obtain a brightness of 70.5% PV. Total pulp shrinkage during bleaching is 20.8%. This pulp has satisfactory viscosity copper number and post colour number indicating that it is not degraded and has a satisfactory keeping quality.

The fiber classification of bleached pulp recorded in Table 4C shows that fiber percent retention on 20 mesh is maximum. From Table 5 C it is observed that on bleaching the beating time is reduced and the strength properties are improved considerably N.S.S.C bleached semi chemical pulp has very good bulk (2.12 to 1.61). From Table 8 it is observed that bleached neutral sulphite semi chemical pulp is superior in comparison to the mill bleached pulp as the bleached semi chemical pulp has better breaking length stretch and burst factor hence with the increase in proportions of bleached semi chemical pulps the properties of the blends are better than the mill pulp (Except when 20% and 40% bleached semi chemical pulp are mixed in the blends in this case strength properties of these blends are camparable with the mill pulp).

Brightness of these blends decreased from 78 to 67.5% PV with the increase amount of bleached semi chemical pulp in the blends however these brightness are satisfactory for printing and writing grade paper where too high brightness is not needed.

On the whole it can be observed that when the same amount of chemicals as Na2O are used the yield by the sulphate semi chemical process are lower than that of neutral sulphite semi chemical process but the strength properties are better. The pulps obtained by neutral sulphite semi chemical process are bulkier than the pulp obtained by the sulphate process. The physical strength properties of sulphate semi chemical unbleached pulp are also superior in comparison to the green liquor semi chemical unbleached pulp however the physical strength properties of green liquor semi chemical unbleached pulp are equivalent to neutral sulphite semi chemical unbleached pulp. Power consumption during refining is towards higher side in sulphate semi chemical in comparison to the neutral sulphite and green semi chemical process. Similar trends are observed during beating of unbleached pulp as beating time is more in sulphate semi chemical process comparatively. Sulphate semi chemical and green liquor semi chemical unbleached pulps are darker as compared to the neutral sulphite semi chemical unbleached Pulp. As recorded in Table 3 sulphate semi chemical green liquor semi chemical and neutral sulphite semi chemical pulp could be bleached upto a brightness of 70% in multi stage bleaching following C E/C/E/H sequence. In case of green liquor semi chemical process total chemical requirement for bleaching is 23.5% which is lower in comparison to the sulphate semi chemical process (26.6%) and neutral sulphite semi chemical process (24.71%). The bulk and strength properties of sulphate semi chemical bleached pulp are lower than that of neutral sulphite semi chemical and green liquor semi chemical bleached pulp. After bleaching beating time is reduced in all pulps. In case of sulphate semi chemical unbleached pulp beating time is higher as compared to other pulps.

It is also observed that green liquor semi chemical pulp are equivalent to neutral sulphite semi chemical pulp in strength characteristics however they may result in denser sheets.

The physical strength properties of all the blends of sulphate semi chemical green liquor semi chemical and neutral sulphite semi chemical pulps are satisfactory. However the exact quantity of the pulp to be blended depends upon the strength values and brightness of the finished sheet. The brightness can be

improved further by the addition of suitable fillers.

Development in High Yield Pulping Process

The scarcity of raw material is being felt a serious problem all over the world specially in developing countries. In our country the pulp and paper production is below the normal needs due to growing population and more demand of paper and its products. Our forest resources are limited. In this context high yield pulping offers one way to the solution of the problem of scarcity of raw material. This makes a way to minimize the gap between availability and requirement of raw material.

Mechanical Process

The main factors to this process are the absence of chemicals costs and the almost quantitative yield from wood the yield losses being only 2 5 percent. Mechanical pulping in grinders has several drawbacks resulting to the pulp of low purity and inferior strength.

To achieve acceptable grade of mechanical pulp from lower priced hardwood and softwood saw mill waste methods have been developed which start from chips and use of disc refiners of various types. Various types of chemical pre treatments have also been tried from simple addition of sulfite and bisulfite in the refiner to achieve somewhat brighter as well as stronger pulps. In order to reduce energy consumption with or without chemicals thermal softening of the inter fibre bonds can be utilized. Hence during last 10 years thermomechanical chemimechanical and chemithermomechanical pulping processes are being developed to overcome the drawbacks of mechanical pulp. Ultra high yield pulps are also attracting increasing commercial interest.

Semichemical Process

Semichemical process involves with chemical treatment followed by the treatment in advanced mechanical fiberizing equipment. By addition of chemicals to the grinder showers it is possible to achieve certain effect. These processes are representing a transitional stage to semichemical. As impregnation was found to be one of the main problems in semichemical pulping of bolts interest soon concentrated on the treatment of chips. Hydrolysis of wood has been studied from different angle and thermal softening has been considered the main purpose of this rocess. However the treatment in cold alkali lie at concentrations of 7 8 gpl NaOH followed by mechanical fiberizing gives cold caustic straw pulps in 75 85 percent yield suitable for Corrugating board.

To obtain acid sulfite pulp in high yield pulping conditions should be chosen to give somewhat slower reactions. Slower reaction is achieved by lower temperature or higher combined SO_2 (lower acidity). The semi chemical Kraft pulps are obtained in 55 70 percent yield corresponding to Roe number 17 31 for American softwoods. The yield of hardwoods pulps is somewhat higher than 55 percent.

Pulping in neutral or alkaline sulfite solutions was already suggested and then repeatedly investigated. A semi chemical process using the neutral sulfite process had been worked out by the U.S. Forest Products Laboratory. The most common yield range of 85 70 percent for well buffered neutral sulfite cooks. Neutral sulfite pulps from eucalyptus give very interesting paper characteristics. Hardwood pulps made from this process are frequently stronger than chemical hardwood pulp. Extremely mid neutral sulfite cooks giving pulp yield of 85 95 percent from both hardwood and softwoods are also of interest for newsprint.

Chemical Process

Mc Govern has reported that there are three general approaches to high yield chemical pulping process.

Improved uniformity of delignification adopting optimization of pulping conditions.

Stabilization of Carbohydrate fraction.

Resorption of polymeric carbohydrates in early stages of cooking.

The attack of chemicals on cellulose and hemicellulose depends on the type and concentration of

chemicals employed in cooking. The extent of attack on the particular fraction of carbohydrate may be dependent on its degree of polymerization manner of combination with other carbohydrates as well as lignin.

Alkaline Chemical Process

High yield kraft pulps in the yield range of 60 70 percent have been obtained by various worker by optimizing the pulping conditions. The increase in yields of practical interest attempt have been made with the use of inorganic chemicals. A systematic search for oxidents and reductantes have been tested. Sodium dithionite and Sodium tetrahydroborate are investigated. The increase in yield was found to originate entirely from an increase in gluco mannan yield 6 percent of wood and possibly some increase in cellulose yield 1 percent of wood.

Polysulfide pulping is one of the recent innovations in the field of high yield pulping. Data of Kleppe based on the experience of mill scale polysulfide pulping indicate that yield could be increased by 1.5 2.0 times the amount of added sulfur when 20 30 kgs. of sulfur per metric ton of pulp dissolved in white liquor charged to a dual vessel Kamyr digester although the sulfidity of cooking liquor was 4 5 percent. An increase of 63 percent in the pulp yield was observed with addition of 2 5 percent polysulfide sulfur to the cooking liquor.

Sulfite process

The removal of lignin was significantly more by sulfite cooking while the attack on extractive was considerably less. The carbohydrates of sulfite cook are subjected to several changes and the most important reaction of which is acid hydrolysis of the glycosidic bonds. The extent of carbohydrate decomposition is largely controlled by three factors time temperature and acidity. On the increasing of pH of the cooking liquor and thereby bysulfite ion concentration more favourable conditions for the preservation of acid sensitive carbohydrates are secured. Therefore only significant higher yields at certain degree of delignification are secured on increasing the combined SO2 charge from the normal level.

Organic Catalyst to High Yield Pulping

Recently trials have confirmed the benefits to be gained by employing the organic catalyst in digester. Various quinones and amines have been tried to accelerate the delignification with stabilization in carbohydrate fraction. The cost and availability of the catalyst could prove limiting factors. Acceptance of anthraquinone (AQ) as an attractive means of improving Pulping economics has been faster than is typical in the paper industry.

CIL Laboratory results showed that 0.05 percent AQ increased the yield of southern softwood pulp by 2 3 percent. At this time there are about 10 Companies in the world which are operating AQ pulp mills. In Japan AQ producer Kawasaki Kasei chemicals has patented and commercialized its technology concurrently with CIL.

What Holtan does predict is that one of the optimum ways of using AQ will be as a combination to reduce the H factor as well as the alkalinity in order to control its effects. A 10 15 percent reduction in the amount of active alkalinity or in H Factor is possible at standard AQ application rates. AQ can and will be used in many different way and as Holtan says The reasons chosen by actual mills will be as unique as the mill themselves .

AQ Pulping Technology

AQ is only effective in alkaline pulping where it accelerates delignification and also improves pulp yield of between 2.5 4 percent. Laboratory results indicate that larger reductions in alkali charge could be made and that use of yield gains of as much as 2 3 percent on wood at constant kappa number for southern pine chips. Ghosh et al. reported that addition of small amounts of AQ resulted in significant increases in the delignification and pulp yield and reduction of rejects without significant losses in strength for hard woods.

Virkola et al. presented the details of NS AQ pulping then its potential application. The alkaline liquor consists mostly of Na2So3 plus some Na2Co3 and NaOH the apparent optimum Na2So3 proportion being 80 85 percent of the total alkali. Light coloured unbleached softwood pulp is achieved with a big yield advantage over conventional kraft pulp (7 10 percent points higher than total yield at 410 kappa number). The yield gain is primarily due to better retention of hemicellulose NS AQ pulp at about 80 kappa is about 19 percent points higher yield than kraft. With maritine pine Alcaper provides 2 percent higher yield than kraft at 30 kappa adopting a new technique by combining the catalytic effect of anthraquinone and the delignifying capability of hydrogen peroxide into a single process.

Polysulfide AQ Process

Glen Brown of Head Corp. spoke about pilot scale trials of maxy polysulfide pulping with and without AQ and also about AQ s effect on the soda and kraft processes. Brown s Key piece of information about AQ in polysulfide pulping The yield increases of polysulfide and AQ the Kraft process are additive. First describing results on mixed hard woods Brown provided that 0.1 percent AQ on wood gave upto 3.5 percent greater yield in soda pulping and about 1.4 percent higher yield in the kraft and polysulfide processes. The observation with a pine spruce mixtures were similar upto 2 percent higher yield using 0.15 percent AQ in either kraft or polysulfide processes.

Alkaline Sulfite AQ Pulping

Paper units are facing a problem of high cost of production. This problem is due to ever increasing cost of raw material cooking bleaching and pollution treatment chemicals. One way to solve this problem is to investigate an alternate high yield pulping process which will result to high yield of semibleached pulp. In this direction an attempt has been made in our laboratory using wheat straw as a raw material.

The cooking liquor for alkaline sulfite pulping consists NaOH and Na2SO3. The cooks were conducted to achieve the optimum Na2SO3 proportion with and without AQ. The optimum Na2SO3 proportion was found to be having 65 70 percent of the total alkali for wheat straw. The effect of AQ charge was studied and optimum charge was found to be 0.05 percent on old straw. Soda and Kraft like alkali concentration and material to liquor ratio were used. It is observed that in the study of alkaline sulfite pulping the pH of cooking liquor drops quickly during the early part of the cook and most of the pulping is progressed at pH 9.5 10.2. The temperature was kept 150°C for two hours. The pulps so formed are 60 65 percent yield having Kappa number 20 25. In this study it is interesting to note that the pulps are light yellow in colour having the brightness 55 60º GE. The properties of the pulp are shown in Table No. 1.

Thermo Mechanical Pulps for Newsprint Manufacture from Tropical Pines

To meet the expanding demand of newsprint it will be essential to identify the suitability of pulps from alternative raw materials. Tropical pines in this regard cannot be overlooked. Considerable work done on plantations of tropical pines has revealed that these could be grown in several parts of the country. Pande has indicated that vast potential exists in the various states like Andhara Pradesh Madhya Pradesh Orissa Tamilnadu Uttar Pradesh West Bengal for growing tropical pines. Table 1 gives the area estimated under tropical pine plantations in India.

Besides above some plantations have also been raised in the states like Kerala Karnataka and Bihar but the details and potential are not yet available.

Conventionally newsprint is made from a blend of mechanical pulp and chemical pulp. High yield pulping processes like cold soda process is of particular interest for production of newsprint grade pulps from hardwood and cold soda pulps. The two new mills being set up viz. Mysore Paper Mills and Kerala

Newsprint will utilise eucalyptus bamboo and eta reed.
Thermo mechanical pulping process (TMP) is the most recent mechanical process yielding a strong pulp having all the essential requirement for newsprint production. The key feature of this process is reduction or complete elimination of chemical pulp in the furnish thus not only eliminating one pulping street but also pollution arising out of chemical pulp mill.
The reported study was undertaken to evaluate pulping characteristics of P. patula and P. caribaea by thermo mechanical pulping process. The results reported are very encouraging. On pilot plant newsprint grade paper was also made from 100% Thermo mechanical pulp from P. patula. The runnability on experimental pilot plant was good.

Raw Materials

P. patula logs were supplied from 1972 73 plantation of Kanasar 6 plantations by Silviculturist Sal region U.P. The logs were 10 15 cm in diameter and 2 2.5 m. in length. The specific gravity of wood as received was 0.343.
Pinus caribaea logs were supplied from experimental plantation of Forest Research Institute by Director Forestry Research Forest Research Institute Dehra Dun. The plantations were raised in 1963. The specific gravity of wood as received was 0.400. The chip density of P. patula and P. caribaea was 170 and 165 (o.d. kg/m3) respectively.

Experimental

The detailed description of the Thermo mechanical pulp pilot plant was reported in an earlier publication.

A Study on Replacement of Sodium Sulphate by AQ Large Scale Trial

The kraft pulping process has several well established advantages in providing good quality pulp high chemical and energy efficiency etc. Moreover it is capable of pulping any cellulosio raw material. But the deficiencies of the process in terms of inferior yield coupled with economic and environmental pressure provide strong incentive for further search of superior processes. The efforts have been aimed at alternative processes capable of eliminating the deficiencies of the Kraft process while retaining its advantages.
The importance of Soda process as a viable alternative was realized if however the basic drawbacks of the process viz. low pulp yield inferior quality longer cooking time high temperature and caustic charges could be overcome by the use of suitable additives.

Anthraquinone an Aid to Pulping

The suitability of a process incorporating very small amount of Anthraquinone 2 mono sulphonate sodium salt (AMS) into the system was indicated in the year 1972 by Bach and Fiehn. The additive was effective both in Kraft and soda processes and it resulted in improved yield a reduction in rejects and accelerated delignification without any adverse effect on physical strength properties of the pulp produced. Holton in 1977 found that Anthraquinone alone instead of its derivative was extraordinarily effective in pulping wood chips and was superior to (AMS).
Kraft liquor is already a moderately effective delignifying agent hence greater effectiveness of anthraquinone was expected in soda process and was established. Holton observed that the small amounts of Anthraquinone so dramatically accelerated the soda pulping process that it was thought that it could effectively compete with or surpass the sulphate process in some respect. Moreover its application does not require any special technique and equipments.
The concept of pulping by incorporating Anthraquinone into the system has drawn worldwide attention.
It has eliminated or reduced the pollution caused by sulphur and its compound.

Investigations have also shown that the addition of Anthraquinone did not enhance the toxicity of untreated bleached kraft effluents and that no difference in treatability or effluent characteristics were observed between the two effluents.

Research and investigations carried out in different parts of the world have corroborated the findings of Holton.

Investigations carried out in different laboratories and mills of our country have revealed following facts about anthraquinone usage.

Soda Anthraquinone process gives yield and pulp quality similar to Kraft level and better than soda level in case of pulping Eucalyptus and pine wood.

In case of pulping of Eucalypus hybrid it was observed that for identical pulping conditions addition of anthraquinone resulted in reducing the Kappa number of pulp by 10 15. It was also observed that anthraquinone is more effective in smaller dosages. There was improvement in physical strength properties of the resulting pulp.

Work done on bamboo (D. strictus) at the Research Centre of West Coast Paper Mills reveals that the benefits in the terms of increase in yield reduction in H factor and lowering of sulphidity can be obtained (either singly or in combination) by the addition of as small as 0.05% AQ on the basis of raw material during kraft pulping.

AQ is also effective on mixed tropical hardwoods. For 0.05% dosage there was reduction in active alkali charge by 2.0 to 2.4% producing pulp of kappa number 32 approx. Simultaneously there was increase in yield by 1.5%. If active alkali charge is not reduced there is 16% saving in H factor (cooking time reduced) for 31 32 kappa number. Simultaneously the gain in yield is by 1.2%. If active alkali charge or h factor are not reduced for a constant kappa no. of 34 there is scope for reducing the sulphidity from 25 to 5% by using AQ. No adverse effect has been observed in the bleachability beating characteristics and strength properties of the pulp obtained by AQ pulping. Black liquor properties are also not affected.

Anthraquinone is effective in reducing active alkali charge H factor and chlorine requirement in bleaching. At the same time it increases yield. But it was found economical only when active alkali charge was reduced for maintaining mill kappa number at the same level. (Raw material bamboo and mixed hardwoods).

Plant trial with AQ at Central Pulp mills has indicated that use of anthraquinone during cooking helps to reduce reject percentage which in turn gives rise to higher pulp yield. It is possible to maintain a higher kappa number in pulp with easy bleaching characteristics. Cost saving are possible as the sulphidity range as low as 12 15% can be maintained enabling replacement of costly salt cake by other less expensive sodium make up.

Laboratory Scale Investigations at Central Research Laboratory Dalmianagar

Investigations were carried out in the laboratory to see the effect of anthraquinone on pulp yield bleachability and strength properties of both Soda and Sulphate pulps of our normal commercial chips. Commercial chips consisting of 70% bamboo and 30% hardwoods were taken for laboratory trials. Soda and Sulphate cooks with and without anthraquinone were carried on chips from same lot and under identical cooking conditions (Table 1). The pulping was done in 15 litre capacity laboratory rotary digester. The cooked material was screened on a 7 mesh screen with water jet pressure. The material passing through the screen are termed screened pulp and that retained on the screen as the reject. Screened unbleached pulp yield and percentage rejects were evaluated. The unbleached pulp was bleached under conventional multistage bleaching system consisting of CEHH sequence. Total chlorine consumption and bleached pulp yield were also determined. The unbleached and bleached pulps were beaten in the laboratory valley beater to 45º S.R. freeness standard sheets were made on the British Standard Sheet

making machine and the sheets tested for various physical strength properties. The cooking data are presented in Table 1 and unbleached and bleached pulp characteristics in Table 2.

Following inferences are drawn from the experimental results

There is increase in yield of screened unbleached pulp and bleached pulp in case of AQ pulping.

Under identical conditions of cooking the reject percentage is reduced by the use of AQ. The reduction is 4.9 and 0.4 percent respectively in soda and sulphate process.

Anthraquinone is more effective in delignification in soda pulping than sulphate pulping. For 0.05% charge of AQ the drop in permanganate are 4.7 units in soda pulping as compared to 1.8 units in sulphate pulping under similar cooking condition.

The reduction in permanganate number by the use of AQ has resulted in lower consumption of bleaching chemicals. This reduction being 3.0 and 1.1 percent respectively in soda and sulphate process.

The strength properties of pulp are more or less uneffected by the use of AQ.

The soda anthraquinone pulping results are nearer to normal sulphate pulping.

Plant Trial with AQ

On the basis of investigational results large scale trial in the mill with a view to eliminate the use of sodium sulphate was undertaken. Accordingly two tonnes Anthraquinone was procured from M/s. Indian Dyestuff Industries. Nearly 4000 tonnes of bone dry chips were cooked during the trial. The anthraquinone corresponded to 0.05% on b.d. chips was charged. The furnish during the trial was 70% Bamboo and 30% hardwoods. Anthraquinone was added to the digester when half of the digester was loaded with the chips. Other operational conditions of cooking and bleaching were similar to those maintained during normal sulphate pulping (Table 3). The use of sodium sulphate in the soda recovery plant was completely stopped during the trial period. The sulphidity dropped to 3.0% during the trial.

Evaluation of Mill Pulp

The consumption of different chemicals on b.d. chips and pulp characteristics like permanganate number copper no. and brightness are given in Table 3 and 4. Samples of both unbleached and bleached pulp were collected in the factory round the clock. The composite samples were evaluated in the laboratory as per TAPPI. Standards for various characteristics. The pulp evaluation results along with those of similar pulp produced during the period preceeding the AQ trial are incorporated in Table 5. These comparative figures speak of the relevance of AQ addition. Summary of Paper and board characteristics produced with and without AQ pulp are given in Table 6.

Zeta Potential Concept in Paper Sizing

Internal sizing of paper with alum rosin size is one of the most important and yet one of the most complex process of paper making For a better understanding of this sizing it is important to have an exact mechanism whereby alum sets the rosin size on the fibre can precisely be defined. The chemistry of alum rosin size reaction the complex products therein formed and its subsequent adherence to the fibre surface deserves further study so as to put certain modification to the existing theories. Precipitation is a charge transfer phenomenon and adherence of precipitate on the surface is a surface phenomenon involving adsorption/ absorption. The application of the above said phenomenon fully to the water fibre rosin size alum system without some reservations has been restricted because of the polyphase nature of the system and also by the wide variation of acidity which effect many radical charges in the system. Based on the critical evaluation of the different theories it seems that the sizing of paper can satisfactorily be explained through Electro Kinetic Theory . Since the Electro Kinetic Theory deals with the surface phenomena it should be remembered that not only the surface chemistry of the fibre but also the surface of suspension containing viz. rosin aluminium rosinate and aluminium hydroxide are also important. An attempt has been

made in this review to highlight the role of Electro Kinetic Potential (Zeta Potential) as a means of evaluating the water fibre rosin size alum system and to delineate the individual roles of the variables so as to project a coherent theory.

Electro Kinetic (Zeta) Potential A Concept

A colloidal particle in a polar liquid can get the electrical charge by a number of mechanisms one of them is through ionization . The other mechanism being the adsorption of a cation or an anion from the bulk liquid having a specific affinity to the particle. The Dipole Dipole adsorption is yet another mechanism which results in the specific orientation of particular charge towards the outside of the particle giving the particle specific residual and surface charge. The particle once in possession of a particular charge the like charges are repelled away and the opposite charges are attracted towards it. So at any time with reference to a particular charge on the particle there will be on the average more ions of opposite than like sign in the vicinity of the charged particle. The excess opposite charge accumulates as a differential ionic layer called Guoy Chapmann layer.

The distribution of this diffuse ionic layer of Gegenions (the Guoy Chapmann Layer) in the liquid surrounding the ion species strictly follows Poisson Boltzmann s equation. The movement of diffuse layer in the liquid creates a potential difference between the charged mobile layer and the surrounding bulk liquid. The Zeta Potential is then defined as the integral of the work done to transport an unit charge from an infinite source to a chosen arbitary plane of shear. For simplicity it has been assumed that the infinite source is the interior of the liquid and the arbitary plane of shear is a point near the solid substance. Representing a pad of fibrous mass as equivalent to a mass of fine capillaries. Quinkie observed electric osmotic phenomenon. He further observed that if the liquid is allowed to flow through the pad by the application of a pressure gradient a flow of electrical charges occur.

The generated streaming current and its relationship with the streaming potential and the resistance of the pad is given by Von Helmoltz which is modified and generalized afterwards by Smoluchowski as follows. Indicating the stream potential to be independent of the dimensions and conditions of the packing pad. The origin of surface electrical conductance in addition to electrolytic conduction depend on the electro osmotic transfer of current. So the value z in equation (3) is always too high. By replacing the electrolyte with the one of high concentration Briggs found the value of (z) and Briggs value of z has taken as the source of most of the Zeta Potential data reported for fibres.

But Briggs failed to take account of the following complications. In the equation the dimensions of the pad is eliminated. Bikerman pointed out that the pads get swollen in the electrolyte and that the paths for the ionic transfer and fluid flow are unlikely to be identical as given in equation (2) So an appreciable amount of electricity can flow through as well as around the fibres. A second but less serious complication arises from the ultra low frequency dispersion of electrical resistance.

Where b is the effective volume of the swollen fibre m the density of the pad.

From the relation between the and m the Zeta Potential d is calculated at the n=O intercept point. The specific volume ß and the specific surface s are calculated from the slope and intercept of the rectilinear form of the Kozency Carman permeability equation.

In contrary to the belief of Helmoltz Guoy showed that due to the presence of excess counter ions near the charged colloidal particle the electrostatic attraction of the counter ions further away from the particle are screened and hence instead of a sharp potential gradient at the interface the potential drops rapidly at first and then slows down with the increasing distance coming to a Zero charge at distance infinite away from the particle surface. As to be expected the attraction of the central colloid is the greatest of course close to itself. Due to this fact the neutralizing counter ions are concentrated much more at these regions and becomes negligible as the distance further away. In addition to this the furtherance of the diffuse layer from

the central colloid depends upon the charge of the bulk liquid and also on the concentration of the simple salts which gives the charge to this electrical system. An interesting aspect of this phenomenon is that the increase in the valency of the counter ions significantly affect the diffusion layer because both the screening effect and the electrical attractions are magnified. This is an important point in dealing with the sizing of the paper as a whole electro kinetic system because the effect of polyvalent ion has as will be discussed later a profound effect on the sizing efficiency.

Stern s Modified Double Layer

Stern pointed out that Guoy Chapmann double layer theory contains certain omissions and the assumptions made are not consistent to the charge evaluated for the system. He pointed out that all the counter ions and solvent molecules are not mobile. The narrow layer of counter ions always fixed to the surface at a closer distance. He has applied a correction for the finite size of the ions in the first layer adjacent to the charged surface. Due to the electrostatic and Van der Wall s forces a specific ion adsorption is possible. This results in a compact layer of counter ions attached to the surface. According to him the double layer is in two parts One the layer which has approximately a single ion thickness and remains fixed to the solid surface. The potential drop in this layer is therefore very sharp. The second part of the layer extends some distance into the liquid phase in diffused state. The free movement of the ions in this regions are affected by the thermal agitation but the distribution of positive and negative ion is not uniform because of the preferential attraction of ions of opposite sign. The result is a gradual fall of potential into the bulk liquid where the charge distribution is uniform. The fixed layer to the surface is called Stern s rigid layer and the diffuse layer is called Guoy Chapmann (Fig. 2).

Economics of Bamboo and Hardwood Pulping by Anthraquinone Catalysed Kraft Process

While developing a certain pulping process the cost design has to be always kept in mind and the question Shall we realise profit from this venture? needs satisfactory solution. An effort has been made by the authors to answer this question particularly with reference to Kraft AQ pulping of bamboo and tropical mixed hardwoods (MHW) which are the major raw material source to paper industry in developing countries like India.

Holton found that even small quantities of Anthraquinone (AQ) in Kraft cooking liquor improve pulp yield reduce sulphidity demand and produce pulp of better quality. With various wood species use of AQ in pulping has been found to have a marked catalytic effect leading to lower chemical and energy demands. Besides enhancing the rate of delignification AQ is said to stabilise carbohydrates and at comparable kappa numbers unbleached yield is reported to be higher for Kraft AQ pulps with seemingly no adverse effect on bleachability beating characteristics and strength properties of bleached and unbleached pulps. With a view to study the economy of pulping using AQ the present work was undertaken. Following approaches of immediate interest have been made in the present work to study how far AQ would be useful in reducing the cost of pulp manufacturing

Results & Discussions

Approach 1

Active alkali reduction with simultaneous yield gain With 14% AA and 1330 H factor Bamboo was cooked to 31.8 kappa number with 46.5% yield (control cook B 1). Under the same conditions kappa number was found to be reduced by 5.2 units with 0.05% AQ (cook B 2). AA charge was then reduced in steps of 1% from 14% to 11% maintaining H factor the same. It was observed that kappa number gradually increased from 26.5 to 38.3. On figure 1 by drawing a 13 no. cooks were carried out in all under cooking conditions

mentioned below & detailed in Table 1. Dilution ratio was so maintained that all the chips remained submerged in liquor.

Horizontal line at control cook kappa number of 31.8 it was found that the line intersects the curve at 12.2% AA charge indicating a possible reduction of 1.8% in AA or 18Kg. AA/Ton bamboo using 0.5 Kg. of AQ/Ton OD Bamboo for maintaining kappa number at the same level.

Also at 12.2% AA & 0.05% AQ the yield was more by 2 3% as compared to control cook B 1 as seen by the intercept of vertical line OQ with yield versus alkali curve.

Fig. 2. Pulping Parameters of Tropical Mixed Hard Woods for AQ Catalyzed Kraft Process.

This reduction may require Rs. 35 × 5 × 300 × 50 = 26 25 000/ worth of AQ in one year which is even more than the total initial capital savings. Even the increased yield is not much to offset this price.

Reduction of bleaching chemical consumption Using a 0.05% dosage of AQ in pulping at the same AA charge kappa no was found to be reduced by about 5.2 units in both the raw materials. This reduction if observed in kappa no. & the mill Kappa no. is controlled at 26.5 the chlorine consumption is expected to be reduced by about 2.1% on unbleached pulp of 21 kg per ton unbleached pulp or approximately 10 kg on OD RM.

Effect of Bleached Pulp Viscosity on Strength Properties of Bamboo Sulfate Pulp

The physical strength properties of paper depend on the quality of raw material its pulping bleaching and subsequent paper making process. The bleached pulp viscosity gives a relative indication of the extent degradation of raw material during the various stages of processing and ultimately reflects on the strength properties of paper. This is because the viscosity of pulp is also a measure of the average degree of polymerization and has a direct bearing on the strength properties of pulp. However some anomalies exist in this relationship. For instance two pulps of the same raw material prepared by different processes of bleaching will not show the same viscosity strength relationship although the % lignin removed may be more or less same in these samples. On the other hand these pulp samples bleached with any given process will show a reproducible trend of viscosity strength relationship.

The viscosity test is less cumbersome and quick as compared to the laboratory evaluation of pulp for physical strength properties as a guide for further processing. However no Conclusion can be drawn about pulp strength properties from viscosity results unless previous investigations have identified the relationship. Khanna & Coworkers reported the relation of bleached pulp viscosity for a mixture of Bamboo and Eucalyptus with its strength properties. But the variation in bleaching pulp viscosity was one by varying the cooking conditions to get the unbleached pulp of varying Kappa nos. and viscosity and then bleaching under optimum conditions. Pai and Meshramkar reported the variation of pulp viscosity at every stage of bleaching (CEHH) for bamboo Eucalyptus and Mixed hardwoods. The lower mechanical properties of bleached sulphate pulps for low viscosity values were also reported by other authors.

This study has been undertaken to establish a correlationship between the various strength properties of Bamboo (Dendrocalamus strictus) and the pulp viscosity after bleaching. The variation of pulp viscosity is made by changing the bleaching conditions and chemicals for a pulp brightness of 75 80%.

Experimental

Sound bamboo (Dendrocalamus strictus) chips were collected and classified in Williams chips classifier. The chips classification data are recorded in Table 1.

Pulping

The pulping was carried out using a 15 lit. capacity electrically heated rotary digester. The chemical and conditions were adjusted to obtain a pulp of 35+2 Kappa No. The conditions of cooking and results are recorded in Table 2.

Bleaching

A CEH sequence was used for bleaching the pulps. In order to get the variation in the pulp viscosity several small scale (50 g OD) bleachings were carried out under different conditions in a laboratory set up and then large scale bleachings (500 g OD each) were carried out under the optimized conditions of bleaching. The bleaching conditions and results are recorded in Table 3.

Observations and discussion

For this study unbleached pulp of a high Kappa No. was selected because of its high initial viscosity so as to obtain a wide range of bleached pulp viscosities for subsequent studies.

The variation in pulp viscosity was obtained by varying chlorine charge during chlorination and hypo stage as well as by selectively adding NaOH in the hypo stage. But in the alkali extraction stage optimum alkali was added to get a final pH of 9.5

It can be observed from Fig. 1 and Table 4 that with increasing viscosity (4 10 cps) all the properties i.e. burst factor tear factor double fold and breaking length increase. However after a viscosity of 8 cps the increase in strength properties is not significant. It was not possible to obtain a pulp with viscosity < 11 cps in the given brightness range.

Fig. 2 shows that with increasing pulp viscosity the alpha cellulose content increases upto about 90% and then levels off.

Alkali/Oxygen Delignification and Bleaching of Soda Bamboo Pulp

Molecular oxygen is a unique oxidizing agent. In the normal form of oxygen the electronically stable form two of the electrons are unpaired. It has a strong tendency to react with organic substances and radial chain reactions are initiated. Several intermediate i.e. peroxides organic radical and hydroxy radicals are formed. These intermediates are non specific oxidative agents and in pulp bleaching it is necessary to control their formation if severe degradation of the cellulose is to be avoided.

In the middle of 1950 s the Soviet Researchers commenced investigations into the possibilities of using molecular oxygen together with alkali for the bleaching and refining of dissolving pulps. Further development on the oxygen bleaching was started in France at the beginning of 1960 s. The object was to improve the process in such a way that it would be applicable to the bleaching of paper pulps and the detrimental effect of oxygen alkali treatment on the strength would be eliminated. Robert and associates worked on several inorganic chemicals for inhibiting the formation of several intermediate compounds i.e. peroxide organic radicals and hydroxy radical which have higher degradation effect on cellulose. They observed that $MgCO_3$ was the best.

Other researchers also found that Magnesium salts addition as carbonhydrate degradation inhibitors is necessary in maintaining the strength properties of oxygen pulp at acceptable levels especially for unbleached grades. It was also pointed out by others that if $MgCo_3$ was mixed up with pulp prior to NaoH the viscosity and strength properties were improved quite substantially.

Environmental considerations are having a substantial influence on the development of technology for existing plants and new installations in the pulp and paper industry. At the same time raw material and processing cost are on the increase. These problems have promoted much interest in search for novel sulfur free pulping process which could offer the desired higher pulp yields and qualities and which are less

polluting then the conventional Kraft process. Among the various approaches investigated during the past two decades the two stage oxygen pulping system seem to offer the most promising alternative to the existing kraft process in terms of yield and pulp qualities. Most of the recent work consists of soda cook to high yield followed by defibrization prior to oxygen delignification in one or several stages. Preliminary work on oxygen bleaching has been carried out at Forest Research Institute on soda pulps from Eucalyptus Hybrid and Kinetics of oxygen alkali delignification of high yield pulps. In the present study the effect of oxygen bleaching on high Kappa no. soda cook and low kappa no. soda cook has been carried out and compared with conventional bleaching sequence.

Experimental

Caustic cooking of Bamboo chips (22+10 mm size) was carried out using 15.0% 16.0% 17.0% 19.0% and 21.0% alkali and bath ratio 1 4. Cooking conditions and results are recorded in Table 1. The resulting pulps were passed through sprout waldran disc refiner at a clearance of 254 microns using refiner plate D2A 501. The refined pulps were analysed for Kappa number and yield (%).

Bamboo pulp of cook no. 5 (Table 1 Kappa no. 45.4) was bleached with oxygen at 7% consistency using 2%. 3% 4% and 5% alkali respectively MgCo3 (0.5%) was added as inhibitor to check degradation of cellulose. Oxygen was injected at 120°C 9.0 Kg/ cm2 pressure) for 90 mts. through a non return valve connected with the side flange of the digester. Shrinkage of pulp (%) Kappa No. and brightness of the pulps are given in Table 2. These oxygen pulps (Expts. No. 2 5) were beaten at 25 35 45 and 55 SR freeness in a laboratory valley beater. Standard sheets were made as per Tappi standards. Physical strength properties of oxygen bleached pulps are represented in Fig. 10 12.

Oxygen delignified pulps of (expts. No. 2 5) were further bleached under C/E/H sequence. The alkali stage effluents were analysed for BOD5 and COD. The bleached pulps were analysed for copper no. viscosity P.C. no. and brightness. Bleaching conditions and results are recorded in Table 3.

Unbleached bamboo pulp (Cook no. 5) was also bleached under C/E/H sequence for comparison with O/C/E/H sequence bleached pulps. Bleached bamboo pulps were also beaten in laboratory valley beater at 25 35 45 and 55°SR freeness. Physical strength properties of oxygen bleached pulps O/C/E/H sequence bleached pulps and C/E/H Sequence bleached Pulp are represented in Figs. 13 15.

Bamboo pulp of expt. No. 2 having higher Kappa No. (Table 1 Kappa No. 71.5) was also bleached with oxygen (Oxygen pressure 9.0 Kg/cm2) using 7% alkali pulp consistency (7%) and reaction temperature 120°C. Oxygen was injected for a period of 90 minutes. Magnesium carbonate (0.5%) was added to avoid pulp loss. Shrinkage of pulp (%) Kappa No. and brightness of the pulp are recorded in Table 4. Oxygen bleached pulp was further bleached under C/E/H sequence using 9% chlorine in the first stage and 4% hypochlorite in the third stage bleaching BOD COD and pH of alkali extracted effluent was also analysed (Table 5). The number of double folds of alkali/oxygen delignified pulp O/C/E/H bleached pulps of lower & higher Kappa No. are recorded in Table 6 along with double folds of C/E/H bleached pulp of lower Kappa number. Bleached pulp was analysed for copper number viscosity P.C No. and brightness. Oxygen bleached Pulp and O/C/E/H bleached pulps were evaluated for physical strength properties. Physical strength properties of oxygen pulp and O/C/E/H pulps are represented in Figs. 16 18.

Two competing reactions delignification and carbohydrate degradation occur simultaneously during oxygen bleaching. Degradation of wood polysaccharide occurs due to oxidative hydrolysis which depends on both temperature and alkali concentration. Bamboo refined pulp (Kappa No. 45.4) was delignified with alkali/oxygen using 2.0% 3.0% 4.0% and 5.0% alkali to find out optimum alkali dose (Table 2). The effect of alkali addition in oxygen delignification on Kappa No. of pulp and brightness is shown in Fig. 3. Kappa No. of the pulp reduced sharply with 2% alkali and then steadily upto 5% alkali. The brightness of the pulp improved moderately which is caused by delignification and not by lignin bleaching. The effect of alkali/oxygen delignification on pulp shrinkage (%) is represented in Fig. 4.

Alkali/oxygen delignified pulps were evaluated for physical strength properties. The effect of beating these pulps at different freeness on tensile index depicted in Fig. 10 shows that tensile index decreased with increase in alkali percentage. Burst index of these pulps increased with increase in alkali percentage (Fig. 11). Tear index was much affected in alkali/oxygen delignification as depicted in Fig. 12. Lower tear index is being a property which is adversely affected by oxygen bleaching treatment. Double folds of alkali/oxygen delignified pulps increased with increase in alkali addition.

Oxygen stage bleaching is the only solution when the aim is for complete removal of colour lowering of BOD and toxic elements in effluent from fully bleached pulps. Application of chlorine chemicals results in higher brightness pulps. Therefore alkali oxygen delignified pulps were bleached with different chlorine and hypochlorite dosages in First and Third stage respectively. After alkali extraction the caustic extracted effluents of these pulps were analysed for BOD 5 and COD as per standard methods. The effect of chlorine addition on COD and BOD 5 of caustic extracted effluent is represented in Fig. 5 & 6 respectively. Blank experiment for bleaching the soda bamboo pulp under C/E/H sequence was also carried out. COD and BOD 5 of caustic extracted effluent of blank experiment are depicted by dotted lines in Fig. 5 & 6 respectively COD reduction in O/C/E/H sequence (Expt. No. 2 5) was 25.5% 44.3% 50.5% and 55.7% respectively whereas BOD 5 reduction was 31.9% 50.0% 63.6% and 72.7% respectively as comped to C/E/H sequence. The total chlorine consumption in Blank experiment under C/E/H sequence was higher as compared to O/C/E/H sequence bleached pulps (Table 3).

The effect of total chlorine addition on viscocity & copper no. of O/C/E/H sequence bleached pulp projected in Fig. 7 & 8 (Dotted lines of these figures indicated viscosity & copper no. of C/E/H sequence bleached pulp) show that viscosity of O/C/E/H pulps was higher than C/E/H pulp and reverse trend was observed with copper no. & P.C. No. Oxygen bleached pulps have better brightness stability than conventional bleached pulp. The total pulp shrinkage in O/C/E/H sequence was higher than C/E/H sequence.

This shown that the pulps degrade to a lesser degree when oxygen stage of bleaching is applied.

Sodium Carbonate in Alkali Extraction During Bleaching Bamboo (D. Strictus) Pulp

In recent years Pulp and Paper Industry in India is also facing the world wide inflation and escalation of cost of chemicals. This makes the Industry to look for alternative cheaper chemicals wherever possible. In this paper an attempt has been made to study the viability of using sodium carbonate as an extraction chemical to substitute sodium hydroxide.

Though the alkaline chemistry of sodium hydroxide and sodium carbonate is almost similar in several respects the weak basicity of sodium carbonate has limited its use.

Singh have reported that the extraction stage delignification follows two distinct phases (i) a rapid initial phase and (ii) a slower second phase. The change in the Kappa number or the rate of delignification during the second phase was found to have a linear relationship with the caustic soda consumption which is effected by the temperature of the system. They also observed that the caustic soda consumption is a zero order reaction for first twenty minutes and then becomes negligible. The drop in Kappa number in the rapid phase amounted to 65% of the total drop consuming only 13% of sodium hydroxide. The consumption of caustic soda in both phases is around one fifth of its addition indicating thereby that the amount of alkali utilized in delignification is quite less and the rest is utilized in maintaining the pH of the system so as to avoid lignin redeposition.

Peter Axegard observed the Kappa number to never reach a constant level but continue to decrease even after a long period. Thus in the slower reaction phase the very slow rate of delignification within a defined period of about two hours put the reaction as an independent function of the alkali consumption following a

zero order reaction in hydroxyl ion concentration. The initial rapid and the later slower phase reactions are two separate first order reactions with respect to the Kappa number of the pulp. He also opined that the chlorinated lignin upon extraction yields lignin of two types eliminated easily and with difficulty. It is likely that in the rapid phase a favoured topographical condition exposes a maximum amount of lignin to chemical attack accelerating the delignification upto a short period. After words the residual lignin is so difficult to reach that the reaction slows down considerably. He also believed the rapid phase delignification to be a function of hydroxyl ions following a reaction order between zero and one. Thus this mechanism though different from that of Singh et al indicates the initial rapid phase delignification to depend on the alkalinity temperature and chlorination of the pulp.

Coniferyl aldehyde the main constituent of soft wood lignin being quite resistant to alkaline hydrolysis a strong alkali may be necessary to extract it but bamboo lignin contains mostly syringyl groups which are not so resistant to alkaline hydrolysis. Further soft wood hemicelluloses contain 1 4 glucan which can undergo isomerisation to 1 4 mannan during alkaline hydrolysis to get stability whereas bamboo hemicelluloses which contain 1 4 xylan do not undergo this change. They get removed during sodium hydroxide extraction. Hence a milder alkali can possibly reduce the alkaline hydrolysis of bamboo hemicelluloses and preserve them.

Emll Heuser has believed that a certain amount of alkalinity is being maintained during extraction with the same delignification irrespective of the type of alkali used. Chang reports the isolated lignin from unbleached pulp equally soluble in sodium hydroxide as well as sodium carbonate. Arnold et al. have found sodium carbonate and ammonium hydroxide to be at par in efficiency when compared to sodium hydroxide. All this is of relevance to the present study. As the literature though limited is confined to temporal soft and hardwoods authors initiated this study on the possibility of sodium carbonate as a substitute for sodium hydroxide.

Experimental

After encouraging results were obtained from preliminary studies on the use of sodium carbonate as a substitute for sodium hydroxide in alkali extraction detailed studies were carried out.

Study on Sequentially Chlorinated (H/C) Pulp

Extraction of sequentially chlorinated pulp (H/C) was done at 55°C using sodium carbonate and sodium hydroxide alone as well as in a 50 50 mixture both expressed as NaOH. Hypo stage bleaching was then carried out substracting 1.0% chlorine on the weight of unbleached pulp in form of hypochlorite added during sequential bleaching from the total demand of chlorine for achieving 80+1° Elrepho brightness. The pulps were tested for their chemical and physical properties. The conditions maintained and results obtained are tabulated in Table 1.

Study on Chlorinated Pulp

Extraction of chlorinated pulp was carried out at 55°C with sodium carbonate and sodium hydroxide as above. The pulps were subsequently bleached with hypochlorite to get a brightness of 80+1° Elrepho and tested for their chemical and physical properties. The conditions maintained and the results obtained are in Table 1. Effluent characteristics of the filtrate from alkali extraction stage were studied and are in Table 1. For all tests Standard Procedures were followed. The pulp was beaten in valley beater to a freeness of 40° SR. A plant trial was taken to confirm the results of bench scale studies. Results are tabulated in Table 2.

Results and Discussion

From Table 1 it is obvious that the pulp extracted with sodium hydroxide has shown a slightly lower permanganate number than the carbonate extracted pulp probably for the following reasons.

The carbonate extracted pulp contains more of hemicelluloses which consume permanganate and show a higher number

After the removal of rapid phase lignin the residual lignin content in the pulp is higher in the case of carbonate extracted pulp.
The sequentially chlorinated as well as chlorinated pulps when extracted with sodium carbonate (or a 50 50 Na_2CO_3 & NaOH mixture) show a tendency for less shrinkage as compared to the NaOH extracted pulp. This can probably be attributed to less degradation of hemicelluloses owing to the milder action of sodium carbonate. The extracted pulp on subsequent hypochlorite bleaching gave practically same brightness physical and chemical properties as that of NaOH extracted pulps.
The pH of the pulp during the carbonate extraction has a comparatively lower value than during hydroxide extraction (Table 1 & 2). This can be explained since the alkalinity provided by sodium carbonate is weaker than that of NaOH at equivalent concentrations. In the case of carbonate extracted pulp the addition of buffer during the hypochlorite bleaching is also reduced indicating a better pH stabilization in the system.
From the effluent characteristics (Table 1) it is observed that the effluent generated from carbonate extracted pulp at the extraction stage is less polluted in terms of total solids and COD.
Results of the plant scale trials conducted in an integrated pulp and paper mill using bamboo and following sequential chlorination confirmed the findings of the bench scale studies (Table 2).
The advantage of using sodium carbonate in terms of cost benefit is two fold viz. (a) it is substantially cheaper than sodium hydroxide and (b) it is more readily available.

Effect of Hemicelluloses on Unbleached Softwood Kraft Pulp

Pretreating unbleached kraft pulp with polysaccharides minimizes or eliminates formation of undesirable chloro organic by products during chlorination. Exactly how these enzymes break down lignin during bleaching however is not understood.
If residual lignin is covalently bonded to hemicellulose and chemical evidence indicates that it is enzymatic cleavage of hemicellulose glycosidic bonds could solubilize lignin with fewer lignin bonds cleaved by the bleaching agents. Physical association of hemicelluloses with cell wall lignin may pose a barrier to delignification by hindering the accessibility of bleaching reagents to lignin or restricting diffusion of degraded lignin from the cell wall. Enzymatic hydrolysis could remove this barrier. One hypothesis considers the reprecipitated xylan to be a physical barrier. In softwood kraft pulps the main hemicelluloses are xylan and mannan thus xylanase and mannanase are used to degrade xylan and mannan.
To determine the effect of xylanase and mannanase on kraft pulp the study reported here used classical microscopy stain methods combined with chemical composition analyses and other physical techniques. The chemical and physical interpretation of the stain results was investigated.

Materials and Methods

Enzyme Treatments

Enzymes used for the treatment of unbleached kraft pulp samples included CARTAZYME HS xylanase (Sandoz Chemicals Corporation Lexington MA) and a mannanase enzyme solution (Sandoz Chemicals Biotech Research Corporation Lexington MA). The starting unbleached kraft pulp was obtained from mill in the northeastern United States and consisted primarily of spruce fir larch and pine with about 1% hardwood. The kappa number of the pulp was 24.3 mL/g. The pulp was treated with xylanase at three levels (1.6 and 10 units/g) mannanase at two levels (5 and 10 units/g) and a mixture of the two enzymes (1 xylanase plus 5 mannanase units/g) (Table 1). The pulp samples were incubated at 50°C pH 4.8 for 2 to 18 h. The samples were then either washed with water or extracted with a 2.0% sodium hydroxide solution for 1 h at 70°C. Control pulp samples were prepared the same as enzyme treated samples except

that the enzyme solution was replaced with water. The wet pulps were refrigerated until analyzed.

Bleaching Experiments

Control and enzyme treated pulps were subjected to a standard CDED1 ED2 bleaching sequence with 10% chlorine dioxide substitution in the chlorination stage.

The CD stage was carried out at 3.5% consistency for 1 h at 25°C with active chlorine charge of 4.8% (% on pulp =0.22 × kappa number). Chlorine and chlorine dioxide were premixed before addition to the pulp samples. Extraction stages were carried out at 10% consistency and 70°C for 1 h with a caustic loading of 0.6 times the active chlorine used in the CD or D stages. During the first chlorine dioxide stage (D1) pulp samples were bleached with 0.8% C102 and 0.35% NaOH at 10% consistency for 3 h at 70°C. The chlorine dioxide charge for the second stage (D2) was 0.4% under the previously stated conditions.

At three stages during the enzyme/chemical bleaching sequence ISO brightness values were determined.

Chemical Composition and Kappa Number Analyses

Freeze dried samples were ground in a Wiley mill hydrolyzed and analyzed for the five major wood sugars. The high performance liquid chromatography (HPLC) was performed with a Dionex model chromatograph using a CARBO PAC PA I column. Kappa numbers were determined by the TAPPI microkappa number analysis method (UM246). The microkappa number was used because the available sample size was limited.

Microscopic Analysis

Slides were prepared according to the TAPPI T401 om 88 procedure. Graff C stain was purchased from Integrated Paper Service. Three drops of the stain were applied to the fiber field on a microscope slide. The wet fibres were covered with a cover glass and allowed to stand 1.5 min. The surplus stain solution was drained off and the fibers were examined immediately.

Direct blue 1 and direct orange 15 dyes for Simons stain were provided by Pylam Products Inc. under the commercial names Pontamine Sky Blue 6BX and Pontamine Fast Orange 6RN. Separate solutions one consisting of 1% direct blue 1 dye and the other of 0.2% high molecular weight (25 000) direct orange 15 dye were prepared. The solutions were mixed in a ratio of 1 1 Eight drops of the mixed dye solution were applied to the fibers on a slide. The slide was dried at 75°C washed with water and examined.

The quantitative microscopic analyses were performed following the TAPPI T401 om 88 procedure using an Olympus research microscope model AH 2.

Numerical Measurement of Colour

Photomicrographs of Graff C stained fibers were taken at preset locations on the slide for randomization. The L a b system color values were measured from the photographs with a Minolta Chroma Meter CR 200 at preselected points to provide further randomization. About 300 400 data were obtained from each sample for analysis. (The b values were not absolute but relative. Because of the large head size on the Chroma Meter we modified the procedure by measuring the colored fiber through a 3 by 6 mm hole in white paperboard.)

Results and Discussion

Chemical Changes After Enzyme Treatment

The enzyme treatment did not result in a large hemicellulose loss. After xylanase treatment the xylan content decreased from 6.8% of the total polysaccharides to 6.2%. After mannanase treatment the mannan content decreased from 7.9% to a low of 6.8%. Xylanase and mannanase treatments each resulted in losses of their respective hemicelluloses on the order of 10%. The mannanase effected somewhat more of a loss of mannan than xylanase did of xylan. For both xylanase and mannanase a high dosage of enzyme resulted in more xylan or mannan loss and 18 h of treatment resulted in more xylan and mannan loss than 2 h. The alkali extraction removed somewhat more xylan after xylanase treatment but

the mannan content was unaffected by alkali extraction after mannanase treatment.

Most of the lignin loss occurred with the alkali extraction with or without enzyme treatment. The treatment with both xylanase and mannanase released slightly more lignin especially at the higher enzyme dosages and 18 h treatment time. It appeared that the mixture of xylanase and mannanase resulted in more lignin loss than the additive effects of the individual treatments. The magnitude of the difference however was about that of the experimental error.

Bleaching Experiments

The results of bleaching experiments with various enzyme treatments are shown in Table 2. In terms of brightness gain the improvement brought about by enzyme pretreatment was apparent after the CDE stage and carried through to the fully bleached pulp. This implied that the improved bleaching was related to an easier delignification in the first stage.

Graff C Stain

Graff C stain an iodine stain consisting of potassium iodide iodine aluminium chloride calcium chloride and zinc chloride is used extensively in microscopic fiber analysis. This stain is sensitive to the chemical composition of fiber. For unbleached kraft pulp the stained fiber colour ranges from yellow through green to blue depending on the degree of cooking. Raw or slightly cooked fibers with high lignin content stain yellow medium cooked fibers with medium lignin content stain green to brown and well cooked fibers with little or no lignin content stain gray to blue. This stain was used to analyze the enzyme treated pulp by counting the number of fibers in each colour category (Table 3).

After enzyme treatment the percentage of yellow fibers decreased from 20.3% to 17.2% for xylanase and to 13.2% for mannanase while the percentage of green fibers increased from 15.4% to 17.6% for xylanase and to 222% for mannanase. The relative number of brown fibers and gray blue fibers remained unchanged after either xylanase or mannanase treatment. For both xylanase and mannanase treatment changes occurred between the yellow and green fibers. These changes indicated that lignin was lost primarily from high lignin content fibers.

Numerical Measurement of Colour

Instead of sorting the fibers by color subjectively color can be expressed numerically according to a system adopted by the International Commission on Illumination. In their L a b system color is expressed in three dimensions as L a and b values. The numerical scales for a and b are shown in Fig. 1.

The b value decreases from positive values to negative as the color changes from yellow to blue. This is similar to the fiber color stained with Graff C stain which is yellow when the lignin content is high and blue when the lignin content is low. Therefore the b value of a Graff C stained fiber indicates lignin content the higher positive b values represent high lignin content and the negative b values represent low lignin content.

The exact color of fibers stained Graff C stain depends on the structure and conformation of the polysaccharides as well as the lignin content (Yu in preparation). Nevertheless for a given pulp the influence of lignin on the colour appeared to dominate and we used the b value to describe the lignin content change in kraft pulp after enzyme treatment (Table 4 Fig. 2).

After enzyme treatment the average b values decreased from 3.3 to 2.9 for xylanase and to 2.4 for mannanase. The b distribution showed that for both xylanase and mannanase b distribution narrowed at the expense of fibers with higher b values. These results corroborated those of the more subjected visual examination of Table 3. The b value analysis also suggested that upon enzyme treatment the lignin content distribution narrowed at the expense of fibers with the highest lignin content.

Accessibility Changes and Simons Stain

Deuterium Oxide Exchange

Deuterium oxide exchange measures fiber accessibility. It is generally believed that hydroxyl hydrogens in the less crystalline regions and on the surface of the crystalline regions of cellulose are accessible deuterium oxide while the hydroxyl hydrogens in the highly crystalline regions are not (12). After treatment with deuterium oxide the accessible hydroxyl hydrogen s exchanged with deuterium and the hydroxyl absorption peak in the infrared moved from 3300 cm 1 to 2500 cm 1. The inaccessible unexchanged hydroxyl absorption remained the same. Therefore the ratio of absorbance at 2500 cm 1 (A2500) to absorbance at 3300 cm 1 (A3300) indicated the fiber s accessibility (Table 5).
Enzyme treatment did not increase the A2500/A3300 ratio but rather decreased it slightly. Thus neither xylanase nor mannanase opened the crystal lattice in the fiber. The slight decrease of A2500/A3300 after enzyme treatment was probably due to the loss of some xylan and mannan that was accessible to deuterium oxide in the control pulp.

Simons Stain

Simons stain (9 13 14) consists of two direct dyes direct blue 1 which has a well defined structure with a molecular weight of 992.82 and direct orange 15 a polymeric mixture containing a high molecular weight fraction. This stain is relatively independent of the chemical composition of the fiber but is sensitive to its physical structure. The Simons stain is used to measure the size of the fiber cell wall micropores the same way that the solute exclusion technique does. The accessibility measured is not the same as that measured by deuterium oxide exchange. Fibers with pores accessible to the high molecular weight fraction of the orange dye stain orange or yellow. Fibers with pores accessible to the blue dye but not accessible to the high molecular weight fraction of the orange dye stain blue [14]. In a given fiber there may be some areas that are accessible to the high molecular weight orange fraction while some areas are inaccessible. Such fibers will stain a mixture of orange and blue and will appear green Table 6.

Thermodynamic Functions of the Reaction between Lignin and Hydrogen Peroxide during Bleaching

Kinetic investigations provide valuable information regarding the mechanism of the reactions. Thus from time to time the kinetic studies of the several types of reactions involving organic substrates have been made to provide the necessary data for deciding the mechanism of a reaction. The advancements in this Branch of chemistry are associated with the advances in separation procedures new analytical techniques physical measuring devices and in chemical theories. The governing notion of Arrhenius that the activation of some kind is essential for chemical change is of universal validity and has dominated the subject of chemical kinetics since the days of Arrhenius.
An important aspect of kinetic study is to show how the reaction rates vary with temperature. The role of solvent in reaction kinetics has been explained by Eyring s theory of absolute reaction rates Kinetic is regarded as the science of motion. It will not be out of place to contrast thermodynamics with its static view point with that of chemical kinetics representing the dynamic view point. Thermodynamics is interested in the initial and final states of a system and an important fundamental postulate of thermodynamics is the state principle which leads directly to the concept of an equation of state. Because of the greater rigour of thermodynamic methods there has been considerable effort in the last thirty five years to approach kinetics from the thermodynamic viewpoint particularly combined with the methods of statistical mechanics. The important feature of this effort is to treat reaction rates as involving an equilibrium between average molecules and high energy molecules which are aligned and activated ready for reaction or between molecules in the initial state and in the so called transition state or activated complex . Even in such a treatment a fundamental problem remains calculating for rate of decomposition of the activated complex.

Only quantum mechanics seem to offer a complete answer.

Thermodynamics is a fundamental subject of great importance and it helps to laydown the criteria for predicting feasibility or spontaneity of a process including a chemical reaction under a given set of conditions. In other words it helps to predict whether a given process or a chemical reaction is feasible under given conditions of temperature pressure and concentration. It also helps us to determine the extent to which a process including a chemical reaction can proceed before attainment of equilibrium.

However it must be clearly understood that the laws of thermodynamics apply only to matter in bulk and not to individual atoms or molecules. Thus the laws of thermo dynamics apply to the behaviour of assemblages of vast number of molecules and not to individual molecules. Thermodynamics concerns itself only with the initial and final states of the system.

Thus the entropy of the system and its surroundings taken together increases in a thermodynamically irreversible or spontaneous process at constant temperature but remains unchanged in a thermodynamically reversible process.

In the present study lignin has been selected as a substrate for the reaction with hydrogen peroxide. Lignin is a major constituent of wood and grasses and in the pulps the colouring matter is predominantly lignin. Bleaching of pulps is an important step for the preparation of paper. Hydrogen peroxide is a very promising bleaching agent which causes the bleaching of pulp without delignification and with the least oxidation potential (0.3 volt) an essential for bleaching without cellulose degradation. The peroxide hiolignin reaction involves the action of DOH^{-} ions which cause the oxidation of chromophors and the degradation of aromatic units with free phenolic hydroxyl groups.

Present work mainly deals with the utilization of kinetic data for the estimation of various thermodynamic functions for peroxide thiolignin reaction in alkaline medium.

Experimental

Isolation of Thiolignin

The spent black liquor of sulphate process was utilized for the isolation of thiolignin. Purification of crude thiolignin was done by Ahlm s method.

Preparation of Hydrogen Peroxide Solution

Standard solution of hydrogen peroxide was prepared according to the Kingzett s method. The solution was stored in dark polyethylene bottle in refrigerator. Solutions for the reaction were prepared from it by suitable dilutions.

Reaction of Thiolignin with Hydrogen Peroxide

The preliminary experiments were conducted to estimate the quantities of sodium silicate and magnesium sulphate which were necessary to keep the solution of hydrogen peroxide quite stable under experimental conditions. Three necked Pyrex glass round bottom flask fitted with stoppers were used for carrying out the reaction. During the reaction the pH was maintained constant by adding suitable quantity of N NaOH from time to time.

Results and discussion

Analysis of Kinetic Data

The kinetic data was analysed by the differential method. According to this method the rate of reaction (dc/dt) is related to the concentration (C) of a reactant by the equation.

It is evident from equation (2) that a plot of the logarithm of the velocity against the logarithm of the concentration should give a straight line. If so the slope represents the order of reaction with respect to the substance whose concentration is being varied and the intercept on log (dc/dt) axis represents log k.

Based on this method the order of the reaction was found to be first (n=1) with respect to hydrogen peroxide concentration. The data was also analysed by following the method of integration where the

reaction was found to obey the first order integrated rate equation.

Sequential Bleaching

In India bamboo is and shall continue to remain the main raw material for the Pulp Industry and for its bleaching conventional multistage bleaching of CEH or CEHH sequence with or without an intermediate wash is commonly used. Super bleaching with Peroxide or Chlorine Dioxide has yet to be commercialized for reasons of high capital as well as recurring expenses. Small size of the Indian Pulp Mills is another restrain in this direction.

Sequential bleaching or Sequential Chlorination may be defined as the first stage treatment of unbleached pulp with an oxidizing agent namely hypochlorite chlorine Dioxide Oxygen or Ozone prior to chlorination. The residual lignin in unbleached pulp though low but being less hydrophilic in nature is less soluble when reacted upon by chlorine. Only about 20% dissolves during chlorination and the rest is not fully accessible to chlorine. Hence a further chlorination or oxidation by a suitable oxidant prior to chlorination is preferred. There is a thinking in recent times that due to poor accessibility of the kraft lignin the dominating reaction is oxidation by HOCI instead of substitution by chlorine as commonly believed. Recent developments reveal that the initial chlorination reaction covering the first few minutes is so rapid that any further substitution is hardly measurable. Oxidation reaction is also quite rapid. During the first few minutes it is almost half to that of substitution and continues to go fast in the first half an hour though the reaction continues for long but at a slower rate. With the initial oxidation prior to chlorination the lignin is fairly exposed to chlorination thus helping its better dissolution by chlorination and alkali extraction. The unbleached pulp being alkaline in nature is less susceptible to degradation by the oxidants. It appears to be a purely surface reaction making the pulp softer.

Chlorination of the resinous substances increases the tackiness especially is case of hard wood pulps making its removal very difficult during alkali extraction and results in the obvious disadvantages. In contrast Sequential Chlorination yields a harder and brittle resin facilating its removal.

Apart from the case of removal of lignin and other impurities Sequential Chlorination is supposed to reduce the colour of the effluents discharged. The bleaching process contributes largely to the pollution load of the mill s combined effluent and as such with the increasing stress on environmental pollution control the Sequential Chlorination is gaining popularity in advanced countries. Chlorine Dioxide to chlorine in the ratio of 50 50 reduces the colour by 30% acidity as HCI by 38%. Chlorie as HCI by 42% COD by 13% and BOD by 8%.

To examine the possibility of adopting this technique in Indian conditions extensive trials at the mills using calcium hypochlorite were undertaken.

Experimental Procedure

During the trials a strict control on the process conditions was maintained to ensure the uniform supply of unbleached pulp at a Permanganate No. of 17 to 18. The studies were made by comparing the results of normal bleaching sequence of CEHH and Sequential Bleaching of HCEHH for a period of about four months.

The first dose of calcium hypochlorite at 10% of the total chlorine demand was given at the collecting chest and the active chlorine for chlorination was adjusted accordingly. No change was made at the Alkali Extraction stage. The total hypochlorite usually required at the hypo stages was reduced proportionately by the quantity of hypo given prior to chlorination and about 80% of this quantity was given at the first stage of hypo. At the second stage the hypo was adjusted to obtain the standard brightness of 80+1% EL. The details are given in Table 1.

The pulp samples were drawn at regular intervals from different stages of bleaching to check pH K. No.

and viscosity etc. The final bleached pulp was tested for brightness post colour value alfa Cellulose content copper No. 1% caustic solubility and viscosity. The average comparative test results are compiled in Table 2.

The pulp samples from each stage were beaten in the laboratory valley beater and 60 gsm hand sheets made to evaluate their strength properties. The average comparative results are compiled in Table 3.

The filtrate from each stage was collected at regular intervals and a composite sample made and tested for pH colour and acidity/alkalinity. Results are given in Table-4.

For all tests carried out TAPPI or ISI Standard methods or standard methods for the examination of water and waste water were followed.

Discussions of the Results

Bleach Consumption

The data (Table 1) show a 16/17% reduction of chlorine demand at the chlorination stage. The total hypo requirement remains practically the same but it has been re distributed.

Physical and Chemical Properties

The comparative study (Table-3) indicates practically no difference in the strength properties of the pulp following the two different methods and thus it can be concluded that Sequential Bleaching has neither upgraded nor degraded the same at any stage of processing.

There is practically no change in the chemical characteristics of the final bleached pulp. Post colour value also remains unchanged.

Pollution Load of the Filtrate

About 30 to 33% reduction in colour of the filtrate from chlorination and extraction stages has been observed. The acidity as HCI of filtrate from chlorination reduces by about 35%. This is probably because of the fact that the preoxidation exposes comparatively higher lignin to chlorine leading to higher substitution reactions.

Manufacture of Corrugating Medium Paper Utilizing 100% Bagasse Furnish

Paper used for corrugating medium is defined as a paper (but generally classified as paper board) of 0.225 mm (0.009 inches) in thickness often known as 9 point but sometimes thicker to form the corrugated cushioning layer(s) in corrugated board and single faced corrugated wrapping.

To perform properly fluting medium must be able to accept the stresses and strains imposed on it during its passage into the corrugating laybrinth and be capable of quickly moulding to the flute contour of the corrugator rolls a major requirement in this respect is ready ability of the fluting to accept heat and moisture. A high moisture content in the web facilitates forming of the flutes and also helps in evenly distributing fibre net work throughout the sheet. Certain pulps have potential capability to produce a more regular sheet formation and profile than others.

Common fibrous raw materials used in fluting manufacture in decreasing order of purity are hardwoods softwoods bamboo straw (agricultural residues) bagasse (sugar cane) box shop waste (corrugated board trim etc.) and mixed waste paper. Whether it is made from wood furnish straw or from secondary fibre the singularly important property of fluting medium is does it run well on the corrugated board machine? .

The corrugated medium paper is usually made on a Fourdrinier machine but not necessarily and from a variety of fibre furnishes. The majority of fluting is made from semi chemical wood pulp. (But straw bagasse reeds and waste paper grades are very common raw materials in a number of countries).

Fluting medium when made from straw pulp is termed Schrenz and when made from waste paper is

termed Bogus .

Typical strength properties of corrugating medium paper are given in Annexure 1

Process Suggested for making Corrugating Medium from 100% Bagasse

Fibre Preparation

50% moist bagasse is screened in rotary drums or vibrating screens in sugar mills itself to remove as much pith as possible. The separated pith can be mixed with bagasse and burnt in boilers or otherwise disposed off. The partially depithed bagasse can be baled and stored in sugar mills yard till moisture comes down to at least 35% (to reduce transport cost). If the paper mill is located nearby it can be transported to (Paper) mills storage yard and stacked.

Depithing at Paper Mills

Wet depithing using a hydrapulper is the best method of depithing bagasse from the point of view of minimum dust nuisance and fibre damage. Necessary quantity of pith also gets removed without much fibre loss. The bales are fed to the hydrapulper and with addition of water to maintain a consistency of 3% the pith gets loosened almost instantaneously. A retention time of 4 5 minutes should suffice. It will be ideal if the depithed fibre contains 12 15% pith only and pith does not contain more than 10 15% fibre. Any further attempt to depith damages the fibre and results in more fibre loss.

Digestion Cycle

Theoretically for agricultural residues only rapid continuous digesters are most suitable in view of the low bulk density 3 kg/cft. However by adopting mechanization and controlling digestion cycle capacity of pulping can be maximized even from spherical digesters. Loading should be done by belt conveyors as fast as possible cooking time should not exceed 90 minutes for corrugating medium in a 12 dia rotary spherical digester.

Thus from one spherical digester 7 charges should be had and under slack conditions minimum 6 charges should be done. Per charge at least 2 tonnes of pulp at 55% yield is obtained. (5 tonnes of actual weight of bagasse at 20% moisture amounting to a charging of 4 tonnes of B.D. material). 12 tonnes of good pulp for corrugating medium can be obtained from each spherical digester.

Though neutral sulphite semi chemical pulping is most ideally suited for manufacture of corrugating medium paper there is no harm in using caustic for cooking (Soda Process).

Washing of pulp

(i) The pulp can be washed on a washing drum in a potcher having a breaker and washing drum below the rotary digester

(ii) The pulp can be blown to a blow tank

(iii) After blow tank it is important that the fibre bundles are defibrated in a conical or disc refiner of breaker at 4 5% consistency and washed well by passing the pulp through a screw press.

Effective Use and Recovery of Chemicals in Cold Soda Pulping

The cold soda process produces high yield pulp suitable for cheaper grade papers from many hardwood species. With the variation of the treatment it is possible to obtain pulp that can be substituted for softwood mechanical pulp1. The extremely high pollution loads which is generated by this CMP process will be one of limiting factor as it involves the environmental problems. In addition to dissolved organic the CMP spent liquor usually carried 50% of residual caustic. Baird et al. have studied extensively the effect of reuse and recycling of spent liquors in cold soda pulping.

The recycling of spent liquor will provide a solution for effective reuse of residual caustic in spent liquor and

reduction in pollution load. Further recycling of spent liquor will help in the build up of organic matters which will be desirable for chemical recovery.

The present investigation has been directed towards effect of counter current system involving reuse recycling of spent liquor in cold soda pulping of Eucalyptus tereticornis species on pulp properties pollution load and chemical recovery of spent liquor. The number cycles required amount of total solids (10 15%) and organic matter in spent liquor has been optimized. The effect of addition of cold soda spent liquor to eta reed black liquor on evaporation and burning properties of black liquors mixtures has been studied in detail. The paper also gives pollution load at various points in cold soda pulping.

Experimental

Chemical Treatment of E. Tereticornis

Eucalyptus tereticornis chips were impregnated in sodium hydroxide solution keeping chips to liquor ratio of 1 4 at room temperature for over night. The concentration of NaOH applied was 35 g/l.

After the first chemical treatment around 1200 ml of spent liquor was collected. This spent liquor was subsequently used for the next treatment. The alkali level of 35 gpl was maintained by supplimenting with additional sodium hydroxide.

The treated chips were refined in the laboratory Sprout Waldron 12 Disc. Refiner keeping the plate pattern same throughout the experiments. The refining was carried out in two stages at 10% consistency with plate clearances 0.25 mm and 0.07 mm respectively. The final volume of fiberizing liquor obtained after the two stage refining was 7000 ml. The refined pulp was washed finally with 8 litres of fresh water and the washed liquor was collected. Details are given in Fig. (1).

After refining the pulp was collected and screened in laboratory flat screen of 0.25 mm slit width. Yield and brightness of unbleached pulps were determined. The results are recorded in Table (2).

The spent liquors fiberizing liquors and washings obtained in each cycle were analysed for pollutional parameters and chemical composition as per standard method given in.

All the unbleached pulps were evaluated for strength properties at 100+10 ml CSF according to ISO Standard given in (4).

Eta Reed Sulphate Pulping

Kraft black liquors were prepared by pulping Eta reed chips (Ochlardra travencorica) with 14% active alkali at 170°C keeping H factor 943. Different diluents during the eta reed pulping were (a) water (b) fiberizing liquor of cold soda pulping (c) spent liquor and fiberizing liquor from cold soda pulping in 1 2 ratio.

Evaporation and Burning Properties of Kraft and Cold Soda Spent liquors

The evaporation and burning properties of eta reed and cold soda spent liquors were studied as per the procedures given. The results are given in Table (5).

Results and Discussions

The flow diagram for counter current closed system is illustrated in Fig. 1. The system involves complete recycling of spent liquor and fiberizing liquors. About 20% volume of the washings were recycled. The effect of recycling on chemical consumption pulp properties and pollution loads is discussed below

Flow diagram for closed cold soda pulping (lab. Scale)

The distribution of residual alkali in different liquor system is given in Table 1. Perusal of the results indicate that the concentration of residual alkali has not changed significantly in subsequent cycles. Sodium hydroxide balance in liquor system shows that alkali in the spent liquor is about (0% and 25% is going into fiberizing liquor and about 15% alkali is going to fibers washings. Thus 85% of residual alkali is carried by spent liquor and fiberizing liquor. The recycling helps in utilizing about 85% of residual sodium hydroxide. The results indicate that chemical consumption during in pregnation decreases slowly from 1st to 5th cycle and then increases continuously in subsequentl cycles. This increased consumption of alkali might be

attributed to liberation of more organic acids in subsequent cycles.

The volumes of recycled spent liquor and fiberizing liquors during impregnation is about 65% and 30% of the total dilution respectively. During impregnation in subsequent cycles only about 70% of fresh sodium hydroxide is added while 30% sodium hydroxide is being reused from the recycled spent liquor and fiberizing liquor. Thus the recycling with help in saving about 30% of the total chemical required in each cycle.

Pulp Properties

The results of effect of recycling on pulp properties are given in Table 2. The results indicate that the pulp yield increases with number of recycling. About 5% increase in pulp yield was observed at 10th cycle. However the yield increased after 6th cycle is not significant. No regular trend was observed in the brightness values of unbleached pulps. The brightness varied between 26 to 21.2%. Inspite of gain in the pulp yield the strength properties of unbleached pulps were not affected by recycling. The washed pulps with recycling system did not show any substantial alkalinity or carry over of sodium.

Composition of Liquors

Table 3 shows the variation in composition of spent liquor fiberizing liquor and washings with number of cycles. The total solids content of spent liquor was increased from 5.57% to 15% in ten cycles. The solids increase was also substantial in fiberizing liquor. In all the cases the colour load and COD values showed a sharp rise with recycling. Inorganic content of spent liquor showed a decreasing trend indicating. Inorganic content of fiberizing liquor and washings did not show any trend. The suspended solids in spent liquor showed an increasing trend Figure 2 shows variation in the concentration of total solids organic and COD in spent liquor with number of cycles. It is clear from the figure that the rise in these properties is sharp between 1st to 6th cycle and rather slow in subsequent cycles. Thus the organics and solids build up had reached a saturation point at 6th cycle.

Fig. 2.

Pollution Loads

The load due to various pollutional parameters is spent liquor fiberizing liquor and washings were calculated and are given in Table 4. The results indicate that in all the cases the COD and colour loads have increased significantly with recycling. In washings the COD and colour loads have increased by nearly as high as 14 and 9 times respectively from 1st to 10th cycle. The suspended solids load was considerable in spent liquor and fiberizing liquor. The total COD load from spent liquor fiberizing liquor and washings had increased from 205 Kg/t to 882 kg/t in the 10th cycle. At 10th cycle the COD loads contributed by spent liquor and fiberizing liquors were nearly 42% and 44% respectively. Washings at 6th cycle contribute nearly 15% of the COD load while at 10th cycle nearly 34%. Thus 6th cycle will be taken as optimum cycle where 85% of COD load was due to spent liquor and fiberizing liquor. In any event as the recycling enhances the build up of Pollution load it is necessary that the spent liquor fiberizing. should not be discharged after repeated recycling.

Properties of Spent Liquors

Spent liquor from 1st cycle will be having low total solids and high amount of inorganic content which is not desirable for recovery of chemicals. By recycling the solids content and organic contents were raised. The spent liquor from 10th cycle was mixed with eta reed kraft black liquor in varying proportions and the evaporation and burning properties of these mixtures were studied. The results are given in Table 5. The results indicate that with increasing the proportion of cold soda spent liquor the viscosity increases substantially. The swelling volume ratio also falls indicating the poor burning quality of cold soda spent liquor which might be attributed to high inorganic content as compared to eta reed kraft black liquor. Eta reed kraft black liquor prepared by using spent liquor as diluent during cooking also showed higher viscosity

and low swelling volume ratio. From extrapolation it was observed that about 10 20% spent liquor when mixed with eta reed kraft black liquor on dry solids basis will have reasonable viscosity level and swelling volume. When fiberizing liquor was used as a diluent during eta reed pulping did not affect the properties of resulting eta reed black liquor. It appears that combined recovery of chemicals from eta reed kraft black liquor and cold soda spent liquor is feasible.

Material Balances

The mass balances for production 30 tonnes of eta reed chemical pulp and 70 tonnes of cold soda pulps is illustrated in Fig. 3. Mass balance for cold soda pulping is essentially based on the process followed in laboratory. From the mass balance it is clear that when spent liquor and fiberizing liquor were recycled completely only 33 M3/tonne of pulp fresh water is required in washing stage. Without recycling of spent liquor and fiberizing liquor the quantity of fresh water required in the system would be about 56 M3/kg. Thus by recycling we can restrict the quantity of fresh water leading to conservation of water of about 41%. From the chemical pulping flow diagram it appears that about 5.5 M3 black liquor per tonne of pulp will be available for chemical recovery. When the recycling will be terminated at 6th cycle the quantity of eta reed kraft black liquor and cold soda spent liquor going to recovery will be 980 M3 and 205 M3 respectively. On dry solid basis the ration of eta read black liquor and cold soda spent liquor comes to 87 13. When the recycling is terminated at 10th cycle the quantities of eta reed and cold soda spent liquors available will be 1635 M3 and 205 M3 respectively. On dry solid basis the ratio comes to about 89 11. However these figures are subject to alterations depending on the nature of treatment in cold soda process and quantity of weak black liquor available in chemical pulping. In any case the proportion of cold soda spent liquor available will not be more than 20%.

Effective Use and Recovery of Chemicals in Cold Soda Pulping with Partially Closed System

The cold soda process produces high yield pulp suitable for cheaper grade papers from many hardwood species. With the variation of the treatment it is possible to obtain pulp that can be substituted for softwood mechanical pulp the extremely high pollution loads which is generated by this CMP process will be one of limiting factor as it involves the environmental problems. In addition to dissolved organic the CPM spent liquor usually carried 50% of residual caustic. Baird have studied extensively the effect of reuse and recycling of spent liquors in cold soda pulping.

The recycling of spent liquor will provide a solution for effective reuse of residual caustic in spent liquor and reduction in pollution load. Further recycling of spent liquor will help in the build up of organic matters which will be desirable for chemical recovery.

The present investigation has been directed towards effect of counter current system involving reuses and recycling of spent liquor in cold soda pulp of Eucalyptus tereticornis species on pulp properties pollution load and chemical recovery of spent liquor.

Chemical treatment of E. Tereticornis

Eucalyptus tereticornis chips were impregnated in sodium hydroxide solution keeping to liquor ratio of 1 4 at room temperature for over night. The concentration of NaOH applied was 35 gpl.

Fig. 1 shows the partial closed cold soda pulping. After the first treatment spent liquor was subsequently used in next cycle along with 610 ml of fiberizing liquor after the two stage refining. Treated chips were refined in two stages. The final volume obtained after two stage of refining was 16 litres and refined pulp was washed with 23.5 litres.

After refining the pulp was collected and screened in laboratory flat screen of 0.25 ml slit width. Yield and

brightness of unbleached pulps were determined. The results are recorded in Table (2).
The spent liquors fiberizing liquors and washings obtained in each cycle were analysed for pollutional parameters and chemical composition as per standard methods given in.
All the unbleached pulps were evaluated for strength properties at 100+10 CSF according to 150 Standard given in.
The evaporation and burning properties of cold spent liquors were studied as per the procedures given in. The results are given in Table (5).

Results and discussions

Residual alkali distribution in various liquors has been shown in Table 1. It is evident that concentration of residual alkali was not much changed in subsequent cycle. The residual alkali distribution was observed 56% in spent liquor 36% in fiberizing liquor and 8% in washing. This shows that 90% of residual alkali has been carried out by spent and fiberizing liquor. There was no trend in alkali consumption. The effect of reuse and recycling on pulp properties is given in Table 2. It is evident that pulp yield has not much changed at 6th cycle. The brightness of pulp have little variation. Strength properties of pulps did not change by recycling. Yield increased from original 8.44 to 85.7 and brightness dropped from 25.4 to 23.6.
From Table 3 it can be seen that the amount of total solid content present in spent liquor increase gradually with each cycle. The total solids content in spent liquor had build up to over 7.9%. The composition of fiberizing liquor coming from refiner is also given. The values show small gradual increase. In all cases the maximum usable volume for make up of the next impregnating liquor (or 23% of fiberizing liquor) was combined with the spent liquor.
From Table 4 it can be observed that pollution load (COD) varies from 142 kg/t to 284 t from 1st to 5th cycle. Colour load was considerably lower due to addition of fresh water in the system during processing. It is further evident from Fig. 1 that water consumption was as high as 83.7 m3/t pulp.
From Table 5 results indicate that the cold soda spent liquor had low viscosity. However it showed very poor swelling volume ratio which might be due to higher amounts of inorganic portion. This spent liquor which will be about 20M3 from each cycle for 70 t/d. production could be processed along with chemical spent liquor.

Maintenance Engineering in Pulp and Paper Industry

As the cost of production of pulp and paper is rising every day it is essential to study the ways and means to stabilize this cost. One of the easiest way of stabilizing this is by increasing the life cycle and productivity of the equipment used for the purpose. For achieving this aim it is essential to give the same careful consideration to the maintenance of pulp and paper equipment as given to labour relations and marketing. The maintenance engineer should be actively associated is planning layout and ordering of the equipment. The most important factor in low cost preventive and protective maintenance are
Selection of quality equipment
Intelligent planning and layout of the factory
Maintenance department
The maintenance department comprises of personnels maintenance programmes and available spare parts. The personnel s should be trained willing and disciplined mechanics.
A good plant maintenance requires full cooperation of both operating and maintenance personnels. Proper instructions to the operating staff for efficient running from maintenance point of view are essential. In the same way whatever maintenance programmes are chalked out should be in consultation with the operating difficulties in the process.
The maintenance work would include (1) Inspection (2) Lubrication of equipment (3) Servicing of

equipment at scheduled intervals.

Inspection

The inspection is very important for preventive maintenance. The schedule of inspection may vary from mill to mill but it should be frequent enough to catch any trouble in the initial stages. The checkpoints for the inspector are

Extremely hot or noisy bearings

Loose bolts

Oil leaks or stock leaks

Maul functioning of hydraulic and pneumatic systems

Unusual noise or vibrations

Motor temperature

Other unusual signs

A good maintenance engineer always makes a routine inspection of the plant observing factors enumerated above and makes a note of it. The maintenance job should be taken up at immediate opportunity.

Inspection of machine chests and agitators will have to be done only at down time when the chests are made empty.

Keeping proper records of inspection and maintenance can help in plant preventive maintenance which could result in increased equipment life and efficiency with less equipment down time. These records could be indicators of future action pertaining to the change of parts.

Lubrication

The successful operation of pulp and paper machinery depends to a large extent on correct and regular application of lubricants to the various bearings and friction points. It is a significant item in securing higher efficiency. A sound lubrication programme is based on

A thorough knowledge of each machine s oiling requirement.

Lubricant of the proper quality and correct application.

A system of standard schedule to assure regularity of attention.

The benefits derived from this lubrication could be

It assures continuity of operation.

The maintenance cost is reduced by elimination of bearing journals gears or other lubrication systems failures.

Improved life of bearings etc.

Lubricant material consumption decreases.

Higher operating speeds and temperatures can be safely maintained.

Reduction in power consumption

Production of higher quality.

The application of lubricants can be carried out by (a) bath or flooded method (b) forced lubrication (c) vick up or pan method (d) side feed oil cups (e) forced lubrication rings (f) gravity oiling system etc.

Lubrication should be the responsibility of master mechanic. All equipment should be properly lubricated after each repair before the start up.

Servicing

This will include not only overhauling the equipment efficient running but will also include replacement of the unserviceable parts of the equipment. For quick replacement it is essential to keep a minimum amount of the inventory of the spares. The amount of the spares could be determined from the type of the equipment work performance as well as from the old records of maintenance. The storage of the spares often required for changing may be done as near the equipment as possible to avoid more down time.

Proper cataloguing of the stores should be done to avoid more down time.
The proper knowledge of the equipment for installation should include not only the installation instructions but should also include practical difficulties in maintenance and productivity of the equipment.
The main operating departments and the equipment handled generally in a pulp and paper mill are as under
Raw material handling (conveyors clippers rechippers. Screens and pneumatic blowers etc.)
Pulping (digester heat exchangers blow tanks pipes pumps and agitators etc.)
Washing and screening (vacuum washers pumps centrifugal screens centricleaners rotatory and flat screens knotters etc.)
Recovery (evaporators boiler tubes furnace induced and forced draft fans precipitators etc.)
Bleaching (chests agitators vacuum washers pumps screw conveyors etc.)
Beating (beaters refiners pumps chests agitators etc.)
Paper making (machine drive wire parts press parts driers calendars reel drum etc.)
Paper finishing (sitters rewinders cross cutters etc.)
Instrumentation.

Maintenance problems

In the ensuring paragraph the maintenance problems of some of these equipment are detailed in brief
Chipper The main function of the chipper is to get chipper chips of uniform size with minimum amount of slivers end sawdust. To achieve these objects the following adjustments is the chippers should be made
The disc knife and bed knives should be sharp. Chipper knives should be sharpened every 8 hours.
The clearance between the disc knife and bed knife should not be more than 1/32 and preferably may be 1/64 .
Care should be taken to avoid any foreign matter going in the chipper by soaking the logs in water before chipping to avoid wear to the disc.
The thrust bearing clearance should be adjusted within prescribed limits.
Lubrication should be done according to schedule prescribed.
Digesters Digesters should not be allowed to deteriorate due to corrosion and erosion by the chemicals below the minimum wall thickness required for particular cooking pressure. To preserve the wall thickness overlay work well in advance must be taken up. Lining with stainless steel welded overlay has proved to be more economical and durable than lining the digesters with carbon brick or sheets.
Evaporators The maintenance procedure of black liquor evaporators could be divided into following
(1) Tube cleaning. (2) Tube replacement (3) Body inspection (4) Piping (5) Condensers (6) Air ejectors (7) Pumps and (8) Mixed liquor operation.
The most economical way of maintaining evaporator capacity is to boil out the equipment on the predetermined schedule. The hardness of the water used in boiling the tubes should be within the acceptable hardness. One acid cleaning of the black liquor system is recommended in a year. Acid strength and temperature are critical and must be watched closely to prevent severe corrosion damage to the evaporators. This treatment should be followed by thorough water flushing. Cleaning agents like sulphamic acid phosphoric acid citric acid and gluconic acid are now being used instead of hydrochloric acid used earlier as stainless steel tubes are being used.
A regular cleaning programme is essential in maintaining evaporator capacity. White liquor or a 10 to 15 per cent solution of sodium hydroxide is an effective scale removal agent for vapor side fouling. One of the methods of scale removal is as follows
The body should be isolated from the evaporator vent system by closing the vent valve. Remove the vent plug in the top tube sheet. Fill the steam chest of the body with undiluted white liquor or caustic. Maintain

the temperature of the liquor at about 160°F for at least 24 hours. Drain the white liquor to the black liquor feed tank. Water flushing and loose scale removal constitute the next step. And an effective method is quick water flushing. When the manhole cover is opened the body empties rapidly and the loose scale is flushed out. It may be necessary to flush the body several times to clean it thoroughly. The condensation should be checked to make sure that it is free of scale. A hydrostatic test for leaking tubes can be conducted while the steam chest is filled with water. Inspection openings in the lower liquor chamber can be opened and tubes checked for leaks. The top tube sheet should also be inspected for tube leaks. Extreme care should be taken in entering an evaporator body after cleaning as toxic fumes may be present. While replacing tubes care should be taken to avoid damage to the tube sheets.
Replacement tubes should be installed with care. The tube holes and tube ends both inside and out should be cleaned thoroughly. Foreign matter rolled into the joint can cause leaking. It is extremely desirable to roll all of the replacement tubes to a uniform tightness both over and under rolling is to avoided. The modern technique is to use tube expanders with automatic torque controls. These expanders presence tightness and stop automatically when the preset torque is reached.
Maintenance records containing information on tube cleaning frequency cleaning costs tube service life and replacement labour costs are most valuable. It is this type of data that makes it possible to anticipate tube failure and the need for cleaning. It is far easier and less costly to plan for this type of work than to be faced with an unscheduled shut down.
Periodic hydrostatic testing of piping is suggested as piping leaks can be trouble some especially in the high vacuum effects because erratic operation and foaming can result.
The required maintenance procedure on black liquor evaporators pumps is similar to that for the many other types of centrifugal pumps used in kraft pulp mills.
Due to the broad range of operating conditions liquor properties and varied evaporator designs used in kraft mills experience with a particular installation is required to establish an effective preventive maintenance programme. Maintenance records should be used as indicators for cleaning or repairs to avoid costly unscheduled shutdown.
Pressure screens The following points must be considered
Periodic check up for lubrication of bearings drive units should be done. It is preferred to use water proof lubricants.
Seals eccentric shaft bearing and straps should be checked and replaced periodically.
Proper alignment of drive belts and gears should be done.
Pressure more than recommended should not be used.
For cleaning the holes bypass line should be used.

Wet Felt Designing Techniques

Eversince the advent of continuous sheet manufacture paper machines have undergone radical changes in the areas of water removal in wire part press section and dryer Section. Although basic principle of sheet formation of continuous web has remained the same but machine speeds have increased tremendously as a consequence to effective removal of water at wire part press part and efficient drying. The object of this paper is to present in layman s language about the fundamentals of various pressing concept for better understanding of operation of press Section. The efficient operation of press section is an effective tool in the hands of paper makers leading to improved production and thereby cost reduction.

Pressing

It is essential that optimum operating conditions are established & most effective felt design is applied. The single most easily changed variable in press section is the press felt and in order to select a suitable felt it is

must that there should be proper understanding of fundamentals of pressing and techniques of felt designing. The press works as continuous system with paper sheet entering and leaving with different moisture content with net removal of water as net result. The way water is extracted from the system is important for the efficiency of pressing operation. The analysis of the nip conditions confirm basic mechanisms as being the compression of paper in the ingoing part of the nip resisted by pressure in the structure and the fluid flow through paper and felt also rewetting in expanding outgoing nip thereby transferring water from felt to paper. In the plain press nips the water flows by gravity from the nip. For all transversal flow nips special arrangements are needed to remove water from the system. Machinery manufacturers have designed various types of presses to create water receptacles under the felt suction roll grooved rolls Blind drilled rolls whereas felt designers have provided various structures and compression properties in felt so that water handling is enhanced. The fluid flow component is the only major dynamic mechanism in pressing and is dependent on pressure basis weight speed nip width and drainage resistance. The uniformity of pressure application is dependent on characteristics of the felt. Mid nip dryness will be determined by specific pressure applied in the nip compressional characteristics of the mat and flow resistance in the system. For optimizing mid nip dryness the felt designer has minimized the flow distance through the felt by needling technique and water receptacles are provided in the felt structure itself. The progress had been from ordinary 10% woollen woven felts to 20 25% synthetic component in the felt to 50 100% synthetic needled felts. The felt structure has been changed from batt on base to batt on mesh. The choice of base in the batt on mesh felt is single double or tripple layer is very much based on the amount of void space and compressibility required in the felt. The void space the actual or space inside the felt which will hold water depends on the wt. of sheet machine speed & if type of conditioning is poor e.g. there is no felt vacuum box or very little vacuum capacity in it void space in the felt should be lower so that felt carries less water as most of the water should be expressed at the press nip. The degree of compressibility needed in the felt i.e. resistance to compassion is determined partly by press nip pressure. If nip pressure is high the felt must be able to withstand it without compacting and therefore more incompressibility is needed in the felt. Generally the higher the nip pressure the less compressible the felt. Single layer base will have more compressibility and being thinner will have less void space than a double layer base or tripple layer base.

When considering single layer double layer or even tripple layer design. Various factors have to be taken under consideration i.e. type of press type of paper grade furnish press loading speed of machine and very important factor is conditioning equipment full width suction box and showers. In general paper maker is looking for either improved felt life improved machine efficiency or solution to certain problems like shadow marking press picking or crushing. Moving from Batt on base felt to single layer batt on mesh felt should yield improved felt like and increase in the amount of water removed from the sheet provided there is full width suction box. But at this stage some other problems may be prevalent like shadow marking on suction press or there may be some need to increase the loading on the press. In order to achieve this we will need to move to a bigger void volume felt i.e. double layer. Having got to this stage we would expect again provided good conditioning equipment a felt giving excellent life and improved runnability.

Once again to final move up to tripple layer is usually decided by customer who is basically looking for improved performance i.e. further increase in press loading better water removal of still find himself having a particular on M/c problems which could only be solved by a new felt style. It does not necessarily follow that felt life will increase when moving from double layer to tripple layer felt.

Tripple layer base is very incompressible and therefore needs very high nip pressure both to press water into it and out of it. Unless nip pressure is very high i.e. say 75 kg/cm plus the triplex will not dewater very much but it will simply run round acting more as a transporter and not adding to efficiency of press dewatering. Lifetime of such a felt will be very long because it is hot compressed. However its water

removal will be very poor.
The secret therefore of a good wet felt selection is to select a good compromise between good water removal and long life. This means carefully considering how much void space and compressibility to build into the felt partly be the choice of base apart from other factors.
In general the principle behind Batt on mesh felt is incompressibility combined with new terms called void volume the bigger the mesh structure the greater the void volume the greater its water handling capacity. If we look a little more closely at this term void volume it would highlight the dewatering capabilities of each quality
These figures are not absolute but are related to one particular supplier design.
The void volume loosely described as saturated wt. shows the huge potential of felt structures available in today s market.

Case Study

Medium size mill producing 25 t day writing/ptg. grades on single machine. Batt on mesh felts in comparison to needled felts are expensive but this extra cost is amply offset by long life attainable on batt on mesh felts and other gains. Life of batt on mesh felt is at least 2.5/three times that of batt on base felts. Other advantages are saving in downtime as less felt changing would be required. Another major advantage would be saving in steam posts. Following is the nett gain

Paper Machine Effluent

In our country effluent from an integrated Pulp and Paper Mill on an average comes to 240 360 M3 per tonne of paper (1) which when compared to the advanced countries is very high mainly because of low reuse of back waters. When the modern trend is towards Zero effluent discharge our water consumption as well as effluent discharge is quite high which besides polluting the stream to a high degree affects the economics of the paper mills as well as poses a problem for the treatment of high quantity of effluent to make it suitable for discharge to the stream/river.
The paper machine effluent which forms a sizable quantity of the mills combined effluent consists of fibers fines fillers dyes sizing chemicals and grits etc. can be treated easily and economically to remove the pollutants from it leaving behind the classified effluent suitable for rouse in the process.
If this effluent could be segregated from the mills combined effluent and treated it would reduce the pollution load as well as the volume of the combined effluent and also the requirement of mill water. This would also facilitate and make it economical to treat the remaining effluent which would be comparatively lesser in quantity by adopting extensive methods of treatment.
Keeping the above in mind a detailed study was undertaken at the Institute. To confirm the observations and results obtained an integrated Pulp and Paper Mill of repute was requested to try it out on plant scale at their mills.

Experimental

For carrying out various chemical as well as physical tests during the course of our study standard testing procedures as per Tappi/I.S.I. were followed. Measurement of flow was made with the help of v notch/rectangular weir.
Two hourly samples were collected from various effluent drains along with their flow measurement and composite samples made for the day by mixing quantities proportionate to the flows at the time of respective sample collections. The samples were analysed for total suspended and total as well as suspended volatile solids C.O.D. B.O.D5 pH colour and odour etc. (Table 1).
Settling studies were carried out on Paper Machine effluent in a standard one litre measuring cylinder. 1000 ml. of effluent was taken and the rate of settling was studied without and with the coagulant Alum in

varying doses. The classified effluent after settling was analysed for suspended solids (Table 2) alkalinity and total hardness in terms of CaCo3 and compared with normal mill water (Table 3).
Classified effluent during coloured paper runs were bleached with Calcium Hypochlorite.
The figures reported in the tables are based on the average of series of experiments carried out covering a wide period.

Discussions

Table 1 indicates that paper machine effluent forms approx. 25% of the total volume 20% of total solids 30% of suspended solids 25% of C.O.D. and 30% of B.O.D5 of the mills combined effluent. The pH is generally in the vicinity of 7.0 whereas the combined effluent is always on alkaline side. Colour of the Paper Machine effluent depends upon the colour of papers running on machines and it is more or less odourless. The combined effluent has a yellowish brown colour having an unpleasant odour.
Table 2 indicates that paper machine effluent has got good settling characteristics and requires about 15 minutes to settle down about 95% of its total suspended solid content. Any retention beyond has no appreciable effect on the clarity of the classified effluent. The alum addition does not appear to be effective.
Table 3 indicates that though alkalinity of clarified effluent has a wide variation (35 150 ppm) but it is not very different from that of mill water which too fluctuates in wide range depending upon the season of the year (30 105 ppm). The hardness is on higher side (110 150 ppm) but cannot be considered unacceptable to the process for obvious reasons.
The bleaching results indicate that excepting the yellow coloured effluents all other can be bleached well with a very small dose of chlorine.
To conclude the studies indicate that if Paper Machine effluent can be segregated it can be easily treated separately resulting in reduction by approx. 25% in the mills combined effluent volume which in turn will reduce mills total pollution load by about 85/30%. The clarified effluent being more or less equivalent to normal mill water in all respects can safely be reused in the process at convenient points.

Mode of Treatment for Paper Machine Effluent

Based on the above a simple primary clarification device was thought sufficient enough to treat the paper machine effluent with three objectives namely appreciable reduction of volume and pollutants of the combined effluent less demand of mill water in the mill to conserve the same and allow less draw from the river and finally making it convenient for the remaining mills combined effluent to get extensive and economical treatment.
This thinking is also supported by Hanumanulu and Subrahmanyan (1). Mohan Das Rao and Chhabria (2) Saxena et al (3) and Singhal and Tapadar (4).
Based on the parameters obtained from the laboratory studies a suitable clarifier for primary clarification of Paper Machine effluent was designed. (Details of designing are not covered in this paper). The process in brief is (Fig. 1) collection of each paper machine s effluent in individual sumps their diversion to a common sump either by gravity flow or pump where there is a provision for regulation of flow as well as a set of strainers to prevent foreign materials going to the next stage for obvious reasons Pumping this combined paper machine effluent to a set of hopper type grit removal chambers in series followed by a set of screens of desired mesh to trap lighter foreign materials a circular clarifier having a feed device in the centre for horizontal flow and peripherical overflow for the collection of the clarified effluent a reservoir for clarified effluent collection and then pumping it to the consuming points a sludge pit for collection of the sludge coming out from the clarifier which can be disposed off in a befitting manner.

Results

The above treatment plant installed at a Paper Mill has given quite satisfactory results based on the working of about two years. The salient observations are as under

The reduction in total suspended solids. C.O.D. and B.O.D5 content of paper machine effluent has been approximately 92 93 and 82% respectively (Table 4).
The clarified effluent has got the alkalinity similar to that of mill water about it possesses higher hardness. pH is almost the same (Table 5).
There has been a reduction in the volume suspended solids C.O.D. and B.O.D5 of the mills combined effluent by about 26 32 25 and 28% respectively (Table 6).
The disposal of sludge coming out from the clarifier which is in sizable quantity has been studied in detail. Though the details are beyond the scope of this paper it could be said that the sludge has a good potential for the use for making cheaper grades of papers or boards.

Conical Refiners and Wide Angle Refiners in Continuous and Batch Refining Systems for Bamboo and Hardwood Furnish

Introduction

The types of papers made in Seshasayee Paper and Boards cover both cultural types such as writing printing laids woves industrial papers such as kraft posters duplex boards and speciality papers like dye line base paper and safety cheque paper. The stock preparation in the mill has been designed to offer versatility in preparing the stock simultaneously for making various types of papers on the four machines. The versatility and flexibility has been achieved by interconnection of the different refining streets in such a way that availability of enough number of refiners is not a constraint for the type of stock needed for a particular variety of paper. Separate refiners are available for deflaking and dispersing wastepaper furnish for the backliner of duplex board.
Over the years due to shortage of conventional raw materials like bamboo the mill has stepped up use of hardwoods in paper making and during the last 2 years the mill is using around 60% hardwood in the furnish the remaining 40% bamboo. The main varieties of hardwoods at present used by the mill are
The use of this high percentage of hardwoods has posed some problems with regard to the strength and thus the runnability of the machines. But by proper adjustment of ash and refining it has been possible for the mill to make paper of acceptable quality in all varieties mentioned above. Wood fibre being shorter in length (average fibre 0.9 to 1.00 mm for hardwood against 1.8 mm for Bamboo) has more of fines passing through 100 mesh. A fibre classification analysis of unbleached pulp from a mixture of 90% bamboo and 10% hard wood and a mixture of 40% bamboo and 60% hardwood is given in Table 1.
It can be seen that hardwoods contribute to more fines. These fines which are mostly vessel elements peculiar to hardwoods escape the refining treatment and come out as fines in dryers causing fluff problem. A study of power consumption with 10% hardwood in the furnish and 60% hardwood in the furnish showed an interesting revelation. While the refining power was 400 450 KWh per tonne in the earlier days with 10% hard wood in the furnish the same is now 350 KWh per tonne clearly indicating a much lower power consumption with increased percentage of hardwood in the furnish for the same ºSR development and quality of the paper.

Types of Refining Systems in the Mill

SPB has both continuous and batch systems of refining the pulp as per attached.
Three old machines have the continuous systems whereas the new MF machine has been provided with the batch system of refining. The idea of providing batch system of refining for the new MF machine stock preparation arose due to the following reasons

To get closer control of operations influencing fibre treatment. Recycling could be done in batch refining whereas the pulp makes only one pass in continuous series refining.

Better attention could be given for matching specifications.

Greater flexibility as various operations and addition of ingredients could be carried out independently.

Easier grade changes due to larger time available during the stock run out.

Easier blending of stocks particularly rags chemical pulp and wastepaper each requiring different types of treatment.

Added to this batch system could take care of fluctuations in pulp brightness and enable sufficient time to be given for matching the shade.

No doubt the batch system is labour intensive. But now with the availability of better instruments such as magnetic flow meters ratio relays and stock proportioners it should be possible to get the same advantage in continuous system as in batch system which suffers from the disadvantage of filling in for each batch causing variation in consistency and therefore in the basis weight. Continuous system is less power intensive as recycling is avoided.

A typical example of MF kraft made on successive days on No. IV machine by continuous stock preparation and by batch process shows the power consumed/tonne of pulp was 223 KWh by the continuous system and 250 KWh by batch system. The power consumed for 1º SR/ton was 14 KWh by continuous system and 15.5 KWh by batch system. Obviously when energy conservation has become a necessity this should be taken note of. In making papers where rise of 15º SR is required a 50 tpd stock preparation by batch system will consume 1125 KWh more/day than the continuous system.

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