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BLEACHING

The principal bleaching agents used are chlorine, $C10_2$ and hypochlorite, generally in stages with alkali wash in between two stages. Other agents used such as peroxide are in very small quantity.

Chlorination needs pH to be maintained between 1.0 and 2.0, and temp. less than 40° C to avoid loss of strength. 40-70% of av. Cl² demand may be added at this stage, but it is obstacled by resins present, which are not easily removed in caustic extraction when chlorinated. This, however, can be avoided by adding C10² with C1², particularly in case of Hardwoods having more resinous matter.

When $C10_2$ used alone in place of $C1_2$ in chlorination of Kraft pulp under the conditions of low temp. and consistency, normally used, lowers brightness and rate of delignification as sodium chlorite formed reacts very slowly.

Precisely the function of C10₂ in chlorination is not yet established. Rapson explains as C10₂ reacts with lignin to form chlorite, which reacts with C1₂ to form more C10₂ Repetition of this cycle decrease concentration of elemental chlorine, thus diminishing rate of attack on carbohydrates. Thus chlorination would behave as if most of the reaction has been carried out with C10₂.

Till development of R-2 process, C10² was costlier than chlorine, and replacement of chlorine with C10² in chlorination stage was uneconomical, since cost of C10²

A Study of Modern Methods in Bleaching Processes and Effluent Recovery

Bleach plant effluents from various stages are used to be disposed off in lakes or streams nearby. Because of enforcement of laws and regulations by Government to prohibit or limit the water pollution, the problem is becoming more acute. Some foreign mills have started Advanced Waste Treatment, some using less water for washing, to reduce effluent volume; resulting into carry over of costly chemicals with pulp which affected adversely. Deepwell burial disposals etc. were tried, but all those were found uneconomical

No one suggested for recovery of bleach plant effluents because of lcck of practical ways to handle and evaporate large volumes (90-150 M^3 per tonne of pulp.)

With recent advancement of practical ways to reduce volume by recycle, use of chlorine dioxide and chlorine mixture in place of chlorine in chlorination stage of multistage bleaching plant, cheap production of mixture of chlorine and chlorine dioxide by R-2 process, crystallizing out of Na $_2SO_4$ from NaCl bleach plant effluent recovery has become possible.

Use of $C1_2$ and $C10_2$ mixture, pH about 7.0 in a multistage bleaching system, permits the washing system to be countercurrent in a single line resulting into substantial voalume reduction. This liquor effluent used on final stage of washing of unbleached pulp as wash water introduce all the residual $C1_2$ NaOH, carbohydrate fraction and other organic compounds into B. L. recovery cycle and chlorine introduced are recovered into Electroprecipitators ash as NaCl. NaCl is recovered by crystallization and used as raw material for $C10_2$ and $C1_2$ manufacture by R-2 process and recycled.

by Mathiesson process is high. In U.S. and Canada, by thorough research in many laboratories and long continued full scale mill operation, use of Cl_2 and $Cl0_2$ mixture in chlorination stage has been established. This results in an increase in pulp viscosity, improvement in pulp strength and decrease in colour reversion.

In some places of southern U.S., cost of $Cl0_2$ is very close to that of published cost of equivalent element chlorine. Since quantity of $Cl0_2$ is very close to that of published cost of equivalent elemental chlorine. Since quantity of $Cl0_2$ required will be doubled, in chlorination as well as in latter dioxide stages, it will lower both capital and operating costs.

Those mills having rubber-lined equipments needs to be replaced and install the new enlarged units for $C10_2$ production and NaC1 recovery suggested in this system.

Capital cost and operating cost of effluent treatment plant and savings in NaOH in C. E. stage, heat and others, offset cost of new equipment. A typical study of effect of using $C10_2$ in place of $C1_2$ in chlorination stage is enumerated in Table I.

Use of 0.05% - 0.1% C10² lessens viscosity drop and improves brightness. There is a sharp improvement of colour reversion due to lowering of resin content. At temp. 50-60°C, a sharp increase in brightness has been found. Uniform temp. throughout the bleach plant simplifies operation and control. C1² and C10² mixtures can be easily prepared by a single process, R-2 process. C10² has relatively less effect on carbohydrates under normal bleaching conditions.

Ippta, July, Aug., Sept. 1969, Vol. VI No. 3

36

TABLE I

		CEDED	DEDED
1.	Brightness	92.8	92.3
2.	Aged brightness	87.9	89.4
3.	P.C. No.	0.55	0.30
4.	Viscosity	28.9	39.3
5.	Kappa No. after E,	4.1	3.9
6.	Brightness after D	81.9	83.4
7.	Aged brightness after D	75.2	79.1
8.	P.C. No. after D ₁	2.2	1.1

Conditions: Kappa No. of unbleached pulp = 18.6

 $C = 6\% C1_2$ at 3% consistency, temp. 25°C for 45 min.

D = 1.9% $C10_{\circ}$ (5% Av. Cl₂) at 3% consist temp. 50°C for 45 min. E₁ = 3.0% NaOH at 15% consistency, temp. 60°C for 2 hours.

 $D_1 = 0.96\%$ C10₂ at 6% consistency, temp. 70°C for 3 hours. + 0.1% C1₂

 $\rm E_2=1.0\%$ NaOH at 15% consistency, temp. 60°C for 2 hours. $\rm D_2=0.36\%$ C10 $_2$ at 6% consistency, temp. 70°C for 3 hours. + 0.04% C1 $_2$

P.S. Av. $C1_2/C10_2$ percentage on B.D. pulp basis.

Better results are obtained when pH, immediately after mixing $C10_2$ is 7.0, but since there is a rapid drop in pH, often NaOH is added to keep pH in right range. This promotes use of counter current system, alkaline wash of caustic extraction stage.

WASHING & ALKALI EXTRACTION

Little of Kraft lignin dissolves during chlorination, but enters into solution in alkali wash. Washing with water alone remove 50% of chlorinated lignin and remainder is made soluble in NaOH to be extracted out. In addition alkali wash removes natural dye stuff, water insoluble organic acids and resins, resulting into less hypothlorite or C10² consumption in subsequent stages.

In a multiple stage bleaching system, thorough washing needs about 45 M^3 /stage, because of limitations only a total quantity of 90-150 M^3 of water is used.

Fresh water is added in the last stage of bleaching operation and wash from this stage is partly recirculated and partly used in preceeding stage. In this way only outcoming stream is from chlorination stage, using Cl₂ and Cl0₂ mixture, which contains 60-70% of impurities removed (1% carbohydrate lost in bleaching, 9.5% lignin during chlorination and 4% in alkali extraction).

Reuse of "white water" is even better than fresh water, because pulp mat will remove many im-

Ippta, July, Aug. Sept. 1969, Vol. VI No. 3

purities such as heavy metal cations, suspended coloring matter and will decrease fiber content in the effluent. This system of washing, however, can be used in Kamyr continuous diffuser washer, which will work at constant capacity.

Evaporator condensate can be used in place of fresh water in final stage atfer oxidising evil smelling S compounds with small quantity of $C10_2$, and thus final wash will be slightly acidic free from cations. If it becomes acidic, hydrogen sulphide will be released. So NaOH is added to keep it alkaline. This will eliminate problem of disposal of evaporate condensate and reintroduce some sulphur in B. L. recovery system, reducing losses.

USE OF WHITE LIQUOR IN PLACE OF ALKALI IN CAUSTIC EXTRACTION

The new system of chemical cycle and introduction of R-2 process results into excess quantity of white liquor from R-2, Na2SO4. However, this white-liquor can be used in place of NaOH in alkali extraction with certain reservations.

If W.L. is used in place of NaOH, only 72% of soda in W.L. is effective as alkali since $\frac{1}{2}$ Na2SO4 and Na2CO3 are inert from caustic extraction. 1 Kg NaOH will 142

quire
$$\frac{1}{80 \times 0.72} = 2.46$$
 Kg.

Na2SO4. However, this excess quantity can be supplied by R-2 process itself. But carry over of Na2S alongwith pulp creates problem in bleaching in subsequent stages. It consumes CI_2 and H₂S is released at lower pH. It may thus need extra washing to trap Na2S out of pulp. Sulphur or sulphides going along with pulp will result in staining the paper which is not at all desirable.

By proper choice and additions of chemicals for bleaching, with counter current washing the water leaving first stage of bleaching will be slightly alkaline, rather than acid. This slightly alkaline liquor is proposed to be used in washing of unbleached pulp.

NaCl BUILD UP AND PURGING OUT FROM KRAFT RECOVERY SYSTEM

When chlorination stage extraction liquor is introduced into B. L. cycle, all chlorine in the form of elemental C1₂, hypochlorite or C10² will build up as NaCl in white liquor. However, this will be reduced from 1.3% to 0.1% if C10³ alone is used in chlorination stage, since C10³ has oxidising power 5 and introduce only one atom of chlorine.

A typical analysis of precipitator dust is given in Table II.

TABLE II

A typical analysis of precipitator ash using no such effluent rec. system.

		%
1.	Moisture	0.55
2.	Insoluble matter	0.15
3.	Chlorides	1.55
	(as NaCl)	
4.	Carbonates	0.10
	(as Na ₂ CO ₃)	
5.	Sulphates	96. 50
	$(as Na_2SO_4)$	

If the precipitator dust is thrown away, NaCl would be purged out, but Na2S04 lost is 3 times that of NaCl, which will be uneconomical. Another procedure suggested by Dr. Richard L. Hummel, Associate Professor of Chemical Engg. University of Toronto, to leach the dust with insufficient water at 90° C and the saturated solution is drained off. This will reduce proportion to 1 Kg. Na2S04 per 5.8 Kg. of NaCl. (losses being 9 Kg. Na2S04 and 52 Kg. NaCl/tonne pulp). Part of this leached solution can be used in R-2 feed solution.

NaCl introduced by this recovery system may be 5%. This should

37

present no difficulty as some coastal mills having NaCl in precipitator ash as high as 37% are operating quite successfully.

A typical analysis of W.L. of coastal mill has been shown in Table III.

TABLE III A Typical analysis of

W.L. of a coastal mill.

NaOH	93 gpl
Na2S	41
Na ₂ CO ₃	22
Na_2SO_3	0.24
NaCl	26
Na_2SO_4	3.5

ERCO-Rapson-Installation of Generator-Crystalizer-Evaporator unit can recover 23-27 Kg. of NaCl and 4.5 Kg. of Na2S04 per tonne of pulp and can be effect-ively used for C102 generation and as make up chemicals.

R-2 PROCESS FOR MANUFACTURE OF CI02.

R-2 process use NaC10s and NaC1 SOIn to generate C102 H2SO4 is used to maintain solutions acidic. NaC103 can be economically manufactured from NaCl electrolytically.

Recations taking place are:

 $\begin{array}{l} NaClO_{3} + NaCl + H_{2}SO_{4} = ClO_{2} \\ + \frac{1}{2} Cl_{2} + Na_{2} SO_{4} + H_{2}O_I \\ NaClO_{3} + 5NaCl + 3H_{2} SO_{4} = \\ 3Cl_{2} + 3Na_{2} SO_{4} + 3H_{2}O_II \end{array}$

Proportion of products formed are controlled by proportion of feed constituents. H2S04 required is twice weight of C10, to purge out extra sodium ions, which was problem to accomodate.

Development by Elec. Reduction Co. of Canada, utilising crystal-liser unit and evaporator, produce anhydrous Na2S04 (used as make up chemicals) and H2S04 concentrated and recycled, has been successfully installed and operated in some U.S. Mills.

Because of simplicity of operation, no controls are needed and only flows are to be adjusted, no operator, is needed. This R-2 process is of particular help where electricity is cheap.

CHEMICALS CYCLE

Say chlorine required is 10% on pulp. Since NaCl0^s equivalent weight is 17.7, approximately half of chlorine; only 5% (50 Kg/ tonne) will be required.

50 Kg. of NaC10^s will produce 66.5 Kg. Na2S04 and make up

Na2S0, required is only 45 Kg/ Additional Na2S0, protonne. duced by reaction I is 21.5 Kg. White Liquor produced by this quantity of Na2S0. is sufficient to be used in place of NaOH in alkali extraction stages.

1st alkali extraction sage: NaOH consumption is 3%= 30 Kg/tonne (say) Required NaOH $= 30 \times 0.15$ = 4.5 Kg. (assuming 85% recoverý) Required Na2S04 = 4.5 x 2.5

= 11.25 Kg. II alkali extration sctage: NaOH consumption is 0.5% = 5 Kg/tonne (say)

Na2S04 required $= 5 \times 2.5$

= 12.5 kg. (assuming no recove-ry) Total Na2S04 required 23.75 Kg/tonne.

It can be supplied by R-2 process if 98.3% reaction go according to equation 1.

HEAT SAVING

In counter current washing heat saving is substantial. If evaporator condensate is utilised, heat re-quirement will be very small, if not totally eliminated. Since C10, and caustic extraction stages are carried out at 70°C, if same water is used in chlorination stage, high temperature may show

degrading effect. But use of mixture of $C10_2$ and C1 in chlonina tion stage wil definitely improve the properties and cold water solution of C10² mixture will drop the bleaching temperature to 60°C. Part of heat produced in electrolytic Sodium chlorate unit can be utilised to heat fresh water added.

ECONOMIC CONSEQUENCES

In normal Kraft mill about 8-10 Kg. water/Kg. of pulp is evapo-rated in black liquor evaporation system. It is expected that an additional quantity of 5 Kg. of water/kg. of pulp will be intro-duced with this proposed system of counter current washing. However, there is a net saving in capital cost \$28,00,000 and operating cost \$5.30 per tonne of pulp as shown in Tables IV and V.

Cost of water is further reduced by using evaporator condensate. Use of "white water" from paper machine wet end, where loading materials and other additives are used, is not desirable as it will introduce some alumina (from alum), resins, Ca, Mg and other impurities from additives. Two mills in U.S. has reduced the amount of water to 13.5 M³/tonne of pulp by means of counter current system and have resulted in large saving of heat.

TABLE IV

Possible costs and saving over Present Practice

Capital	Costs in U.S. \$	Savings
Evaporators Va°SO4 crystallizing Salt recovery 2umping piping for washer	$ \begin{array}{c} \$ 1,000,000 \\ 1,000,000 \\ 200,000 \\ 500,000 \end{array} $	
Water treatment Primary effluent treatment Secondary effluent treatment	300,000	1,500,000 1,500,000 2,500,000
Net capital saving	\$ 2,700,000 \$ 2,800,000	5,500,000

TABLE V

Operating cost per ton of pulp	Costs	Savings
1. C10 ₂ at $(26 i \text{ per Kg. for chlorination})$	1.50	
2. Decreased costs of C1026c per Kg.		0.85
3. NaCl separation	0.25	
4. NaCl recovered		0.40
5. Na ² SO ⁴ lost	0.15	
6. Water treatment		0.80
7. Primary effluent treatment		1.20
8. Secondary effluent treatment		1.60
9. Heat		1.00
10. C10, Cl, for evaporator condensate	0.25	
11. Interest, depreciation & maintenance $(20\% \text{ of capital})$	·	1.60
Net saving	\$ 2.15 \$ 5.30 per	\$ 7.45

Ippta, July, Aug., Sept. 1969, Vol. VI No. 3

It is obvious that the proposed system in modern methods of effluent recovery will eliminate effluent problem, reduce water requirement, improve pulp quality (brightness, viscosity, and colour stability); Simpler units and other savings.

This wil be of particular advantage to new mills location, units and capital investment.

Though it has not yet been practicised fully in any mill, parts where practcised have shown satisfactory results. Full utilization can only judge the suitability of the process, but it definitely opens the doors to new trends in effluent elimination and use of new type of equipments such as diffuser washer and subsequent economic and quality development.

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for the conception of modern multistage bleaching sequence

B. Biswas, Harcourt Butler Technological Institute, Kanpur. rine dioxide, peroxides and chlorites have been used extensively for improving the brightness of the chemical pulps. Though more costly than the hypochlorites, their uses as final bleaching The main purpose of breating is to remove lignin present in the pulp, and, in a way, bleaching can be regarded as a continuation of the chemical pulping process. The prime object of chemical

Ippta, July, Aug. Sept. 1969, Vol. VI No. 3

39