An Experience With 'Sequential Bleaching'

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SUMMARY

Sequential Bleaching or Sequential Chlorination, gaining popularity in the advanced countries, has so far not found its due place in the Indian Pulp and Paper Industry. In this process, mild oxidative treatment in the form of Hypo, Oxygen, Chlorine Dioxide or Ozone is given to the unbleached pulp just before the usual chlorination starts.

Extensive plant trials conducted with 10% active chlorine as Hypo of the total chlorine demand prior to chlorination resulted in reduction of chlorine consumption at the chlorination stage and the colour of the effluent being discharged from the chlorination and extraction stages. The pulp strength, viscosity, brightness stability and tendency for colour reversion remains practically unchanged.

INTRODUCTION

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 commercialised 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 HOCl 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 suseptible 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 in case of hard wood pulps making its removal very difficult during alkali extrac tion 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

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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 HCl by 38%. Chloride as HCl 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—I.

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—II.

TABLE—I CHEMICAL DOSING DURING BLEACHING

Sl. No.	Particulars		CEHH	HCEHH
1.	Hypo addition prior to chlorination		—	1.0
2.	Chlorination	Chlorine	6.2–6.5	5.2/5.5
		Temperature	35	35
3.	Alkali Extraction	Alkali	2.4–2.6	2.4–2.6
		Temperature	55	55
4.	Hypochlorite at	Ist stage	3.0–3.5	2.5–2.6
		2nd stage	0.80–1.0	0 30/0.40
		Total	3.80/4.0	2.80/3.0
		Temperature	45	45
5.	Total chlorine consumption		10.0–10.5	9.0–9.5

NB : All figures given in form of available chlorine on the basis of OD unbleached pulp.

TABLE—II CHEMICAL CHARACTERISTICS OF THE FINAL BLEACHED PULP

Sl. No.	Particulars	Unit	CEHH	HCEHH
1.	Brightness	% El	79—80	79.5—80.5
2.	P. C. value	—	13—14	12—14
3.	Alfa cellulose content	%	81—82	81—82
4.	1% Caustic solubility	%	13—15	13—15
5.	Viscosity (0.5% CED Soln.)	Cps.	7.0 - 7.5	7 0—7.6
6.	Copper No.	—	1.6—2.0	1.5—1.9

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—III.

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– IV.

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

1) Bleach consumption

The data (Table–I) 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.

2) Physical and Chemical Properties :

The comparative study (Table-III) 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.

3) 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 HCl of filtrate from

TABLE—III COMPARATIVE STATEMENT OF STRENGTH PROPERTIES AT DIFFERENT STAGES OF BLEACHING

Particulars	Unit	Unbleached pulp		Chlorinated pulp		Extracted Pulp		After Ist stage Hypo		Finalbleached Pulp	
		CEHH	HCEHH	CEHH	HCEHH	CEHH	HCEHH	CEHH	HCEHH	CEHH	HCEHH
Initial Freeness	°SR	9	9	10	10	10	10	10	12	11	12
Final Freeness	,,	44	46	46	45	45	46	46	45	45	45
Beating time	Mts.	75	65	60	90	65	75	55	58	50	48
Consistency in) Lab Valley beater)	%	1.52	1.55	1.50	1.55	1.50	1.50	1.50	1.50	1.50	1
Burst factor	—	38	38	33	37	33	32	32	30	33	32
Breaking length.	Mts.	5680	5630	5190	5370	5390	5280	5110	5010	5000	4920
Double folds	Nos.	232	298	176	212	168	184	91	87	77	69
Tear factor	—	130	135	133	129	120	117	107	109	107	102

TABLE—IV COMPARATIVE STATEMENT OF FILTRATE CHARACTERISTICS

Sl. No.	Particulars	Unit	Chlorine Filtrate		Alkali Filtrate	
			CEHH	HCEHH	CEHH	HCEHH
1.	pH	—	2.6	3 0	9.1	9.3
2.	Colour	Pt—Co	170	120	1200	800
3.	Reduction in colour	%	—	30	—	33
4.	Acidity as HCl	ppm	200	130	—	—
5.	Reduction in acidity	%	—	35	—	—
6.	Alkalinity (as NaOH)	ppm	—	—	44	50
7.	Increase in alkalinity	%	—	—	—	13

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.

The alkalinity of alkali back water increases by about 10 to 12% in case of Sequential Bleaching which, probably, may help in reducing the alkali added at the extraction stage. However, this needs further studies.

CONCLUSION

In view of the above, it can be safely concluded that the Sequential Chlorination reduces the pollution load on the bleach plant effluent besides saving in total chlorine demand by about 10% of the total chlorine needed for bleaching without changing the characteristics of the final pulp.

Our country is now going in for more and more use of hardwoods, which contain comparatively higher quantity of resinous substances. Sequential Bleaching may probably play a significant role at the mills using appreciable quantity of hardwoods.

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