

An Approach to 'Inplant Colour Reduction' of Bleach Plant Effluent Using Calcium Hypochlorite

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SUMMARY

At Orient Paper Mills, Amlai, the effluents of Caustic extraction stage and washing stage are Combined and treated separately as they are darkish brown in colour and contain about 85% of the BOD load. The BOD load from this brown coloured effluent is 20-25 Kg. per tonne of pulp. The total quantity of the effluent is about 18000 M³/day after neutralisation with chlorine washer filtrate. 60-65% effluent is from caustic extraction stage.

The present study was undertaken to decolourise and reduce the pollution load of the caustic extraction stage effluent by inplant process. The bleaching sequences studied were HC/E/H and HC/EH/H and compared with C/EH/H.

It is found that the HC/EH/H and C/EH/H Sequences are excellent in removal of 76% colour and reducing pollution load by 45-50% with marginal increase in the bleach chemicals cost.

The bleached pulp obtained by HC/EH/H/Sequence is slightly inferior compared to C/E/H/Sequence. The pulp quality in case of C/EH/H is comparable with conventional sequence. The C/EH/H sequence is preferred over HC/EH/H Sequence in view of cost of chemicals and quality of pulp. The sequence can be incorporated in the Indian pulp mills without modification and calcium hypochlorite is easily available at cheaper prices.

The main advantages of this inplant colour removal process is saving of nutrients used in an anaerobic and aerobic treatment by 30% and possibility of reusing the water back in Chipper house and coal ash disposal after treatment. The excess effluent after treatment can be discharged or used for irrigation purpose as the effluent meets the tolerance limits specified by ISI.

INTRODUCTION

One of the most pressing problems faced by the paper industry is effluent colour.

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Effluent which is high in colour presents an aesthetic problem and impairs the process of photosynthesis which in turn retards biological activity and transmission of sunlight into water. Many external processes have been proposed for colour removal such as massive lime¹, alum c agulation², resin absorption^{3,4}, activated carbon⁵ and amine absorption⁶. All these processes require relatively high capital expenditure, and in some cases present a sludge disposal problem. These processes

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are effective in reducing colour and also to some extent BOD and toxicity but none is particularly attractive at present in India. A much better solution to the problem is the use of an inplant process which does not increase the cost of bleaching and does not affect the quality of pulp.

When hypo-chlorite is added early in the bleaching sequences, the pulp contains sufficient lignin to consume the added chemical in competition with carbohydrate component⁷. During chlorination only 20% residual lignin is dissolved of unbleached pulp and the rest is not fully accessible to chlorine due to hydro phobic nature of lignin. With the initial oxidation prior to chlorination the lignin is fairly exposed to chlorination and alkali extraction.

The sequential addition of hypo before chlorination might result in the lighter colour of caustic extraction stage of effluent.

Therefore, the present study was undertaken to reduce the colour of caustic stage effluent by HC/EH/H. The C/EH/H sequence studied in this laboratory⁸ and elsewhere^{9,10}, was also studied and compared with these two sequences.

EXPERIMENTAL

The mill sulphate unbleached pulp having Kappa No. 27.2 and containing about 70% bamboo and 30% mixed hardwoods was used for the study. The unbleached pulp was bleached by C/E/H, HC/E/H, HC/EH/H, and C/EH/H sequences in laboratory.

First the optimum dose of elemental chlorine was found out by adding different amounts of chlorine to pulp (Table - 1). The caustic extraction conditions were fixed and optimum amount of hypochlorite needed to get 78-80% brightness was found out.

The sequential addition of calcium hypochlorite (Hc) was studied by varying the quantity and effect on the caustic extraction stage effluent (Table 2). The optimum addition of sequential addition of hypo was arrived. The reaction of hypo was carried out at 6.5% consistency and retention time was only 10 mts. Without washing further chlorination was conducted.

The sequence HC/EH/ was studied keeping Calcium hypochlorite at 2% and varying the hypochlorite in the second stage (EH) Table 3. The effluent of second stage was studied for various characteristics.

The unbleached pulp was bleached by C/E/H, C/EH/H, HC/E/H and HC/EH/H sequences to 78-80% brightness employing optimum dose of chemical in each stage. The effluent characteristic of the second stage and final pulp quality results are recorded in Table-4.

The bleach chemicals cost, reduction of colour, B.O.D. & C.O.D. of second stage effluent, final pulp brightness, pulp viscosity etc. are recorded in Table-5 for various sequences studied.

The physical strength properties of bleached pulp are recorded in Table-6 for C/E/H, HC/E/H and HC/EH/H sequences.

The light absorption of Caustic extracted effluent was measured on 'Systronics' Spectrophotometer Type 106 (MK-11) at 465 mm and converted to absorption values of chloroplatinate colour units and standard curve was prepared. Post colour no. of pulp was determined by keeping pulp at 105°C for 18 hours in an oven.

TABLE-I OPTIMIZATION OF CHLORINATION STAGE OF BLEACHING
(KAPPA NO. OF PULP 27.2)

S. No.	Particulars	Expt. 1	Expt. 2	Expt. 3
1.	Pulp taken (g)	50	50	50
2.	Chlorine added (%) (on O.D. Pulp basis)	6.5	7.0	7.5
3.	Consistency of Pulp (%)	3.0	3.0	3.0
4.	Chlorination time (Mts.)	60	60	60
5.	Net Chlorine consumed	6.43	6.70	6.79
6.	Chlorine consumed (%) (on Cl ₂ applied)	98.89	95.7	90.53

Note : In all the bleaching experiments of Table 2, 3, 4, 5 & 6, the Decker pulp of Kappa No. 27.2 was used.

TABLE-2. OPTIMUM CALCIUM HYPOCHLORITE DOSE IN HC/E/-SEQUENCE

Sl. No.	Particulars	HC/E/-Sequence				C/E/-
		Expt. 4	Expt. 5	Expt. 6	Expt. 7	Expt. 8
1.	Sequential Hypochlorite Stage*					
	(i) Hypochlorite added (%) as available chlorine	1.0	2.0	3.0	4.0	—
	(ii) Hypo consumed	—	—	99.27	99.0	—
2.	Chlorination Stage					
	(i) Chlorine added (%) (on O.D. pulp basis)	7.0	6.0	5.0	4.0	7.0
	(ii) Chlorine consumed (%)	6.55	5.50	4.93	3.95	6.70
3.	Alkali Extraction Stage					
	(i) Alkali applied (%)	2.5	2.5	2.5	2.5	2.5
	(ii) End pH	10.75	11.25	11.25	11.5	10.9
	(iii) Colour of Effluent	9640	8880	8240	8080	10000
	(iv) Colour reduction (%)	3.6	11.2	17.4	19.2	—
	(v) COD (Mg/L)	1459	1337	—	1276	1398
	(vi) Pulp Loss %	—	2.16	4.52	6.4	1.64
	(vii) K. No. (25 ml)	6.5	5.7	5.2	4.7	8.0
	(viii) Pulp brightness (%) P.V.	49	52	55	59	46

*Consistency of pulp in sequential hypochlorite stage was kept at 6.5% and retention time 10 mts.
Constant Conditions

Stage :	C	E
Consistency (%)	3	5
Temperature °C	27	55±1
Time (mts.)	60	60

TABLE-3. OPTIMUM CALCIUM HYPOCHLORITE DOSE FOR ABOUT 80% COLOUR REMOVAL IN - EH/- STAGE OF HC/EH/H SEQUENCE.

Sl. No.	Particulars	HC/EH - Stage			
		Expt. 9	Expt. 10	Expt. 11	Expt. 12
1.	Sequential Hypochlorite Stage				
	(i) Hypochlorite added % as available chlorine	2.0	2.0	2.0	2.0
	(ii) Consistency of pulp %	6.5	6.5	6.5	6.5
	(iii) Retention time mts.	10	10	10	10
2.	Chlorination Stage				
	(i) Chlorine added % (on O.D. Pulp basis)	6.0	6.0	6.0	6.0
	(ii) Chlorine consumed %	5.88	5.88	5.88	5.88
3.	Alkali Extraction Stage				
	(i) Alkali added %	2.5	2.5	2.5	2.5
	(ii) Hypochlorite added %	0.25	0.50	0.75	1.0
	(iii) Colour of Effluent Chloroplatinate units	5360	3100	2040	3180
	(iv) Colour reduction %	46.4	69.0	79.6	88.2
	(v) End pH	11.1	11.0	10.9	10.8
	(vi) COD, mg/L	1188	982	871	676
	(vii) BOD ₅ Mg/L	180	160	140	120
	(viii) Pulp loss, %	2.8	3.28	5.20	5.85
	(ix) K.No. (25 ml)	5.16	5.06	4.7	4.38
	(x) Pulp brightness % (PV)	54	55	56	56

Consultant Conditions

Stage :	C	E
Consistency %	3	5
Temperature °C	27*	55±1
Time (mts)	60	60

TABLE—4 BLEACHING OF DECKER PULP UNDER C/E/H, C/EH/H, HC/E/H, AND HC/EH/H SEQUENCES

Sl. No.	Particulars	C/E/H Sequence	C/EH/H Sequence	HC/E/H Sequence	HC/EH/H Sequence
1.	<i>Sequential Hypochlorite Stage</i>				
	(i) Hypochlorite added (%)	—	—	2.0	2.0
	(ii) Retention time (mts)	—	—	10	10
	(iii) Consistency of pulp (%)	—	—	6.5	6.5
2.	<i>Chlorination Stage</i>				
	(i) Chlorine added (%) (on OD pulp basis)	7.0	7.0	6.0	6.0
	(ii) Chlorine consumed (%) on added basis	6.814	6.844	5.544	5.52
3.	<i>Alkali Extraction Stage</i>				
	(i) Caustic added (%)	2.5	2.5	2.5	2.5
	(ii) Hypochlorite added (%) as available chlorine	—	1.0	—	0.75
	(iii) End pH	11.3	10.9	11.0	10.8
	(iv) Colour of Effluent, Chloroplatinate units.	8150	2000	7100	1900
	(v) Colour reduction (%)	—	75.4	12.8	76.8
	(vi) BOD (mg/L)	340	180	320	140
	(vii) COD (mg/L)	1447	796	1208	776
4.	<i>Hypochlorite Stage</i>				
	(i) Hypochlorite added (%) as available chlorine	4.0	3.5	3.0	3.0
	(ii) Hypo consumed (%)	2.83	2.71	2.23	1.89
	(iii) End PH	8.4	8.1	7.9	8.2
	(iv) Pulp Brightness (%) P.V.	79.5	79.5	81.0	79.5
	(v) P. C. No.	2.35	1.93	1.94	1.99
	(vi) Pulp loss (%)	9.11	9.15	8.96	9.36
	(vii) Viscosity of pulp (CED) cps	6.28	6.37	6.63	5.87
	(viii) Copper No.	1.15	1.11	1.10	1.26
	(ix) Total Chlorine Consumed (%)	9.674	10.554	9.770	10.156
	(x) Total Hypochlorite as available chlorine consumed (%)	2.83	3.71	4.226	4.636
Constant Conditions					
	Bleaching Stage	C	E	H	
	Consistency of pulp %	3	5	5	
	Temp °C.	27	55±1	40 ± 1	
	Time (Mts)	60	60	—	

TABLE—5 COMPARATIVE DATA OF DIFFERENT BLEACHING SEQUENCES

Sl. No.	Particulars	C/E/H Sequence	C/EH/H Sequence	HC/E/H Sequence	HC/EH/H Sequence
1.	<i>(a) Caustic Extraction Stage Effluent</i>				
	(i) Colour of effluent Chloroplatinate units.	8150	2000	7100	1900
	(ii) BOD ₅ (Mg/L)	340	180	320	140
	(iii) COD (Mg/L)	1447	796	1208	776
1.	<i>(b) Reduction % during Causticizing extraction stage.</i>				
	(i) Colour	—	75.4	12.8	76.8
	(ii) BOD ₅	—	47.06	5.88	58.82
	(iii) COD	—	44.99	16.53	46.37
2.	Total Elemental Chlorine consumed (%)	6.844	6.844	5.544	5.520
3.	Total hypochlorite consumed (%) (as available chlorine)	2.830	3.710	4.226	4.632
4.	Total Caustic consumed (%)	2.5	2.5	2.5	2.5
5.	Viscosity of bleached pulp (Ced) cps	6.28	6.97	6.63	5.866
6.	Copper No. of bleached pulp	1.15	1.11	1.10	1.26
7.	P.C. No. " "	2.35	1.93	1.94	1.99
8.	Total chemical cost in rupees/Tonne of unbleached Decker pulp.	215.54	228.96	225.45	231.50

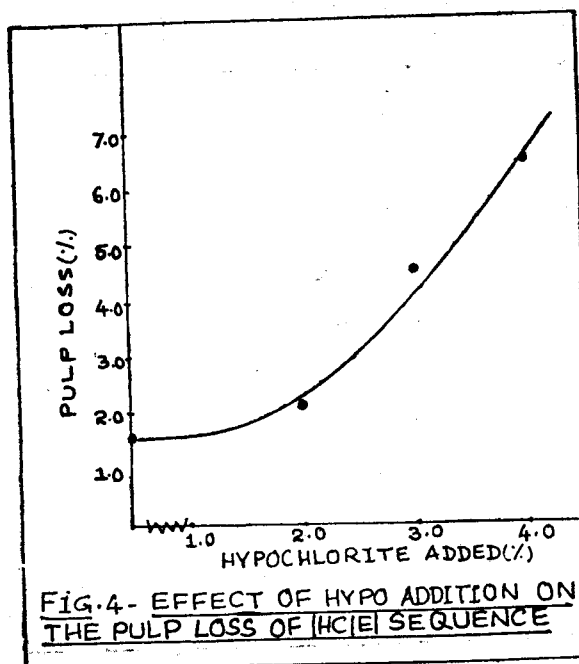
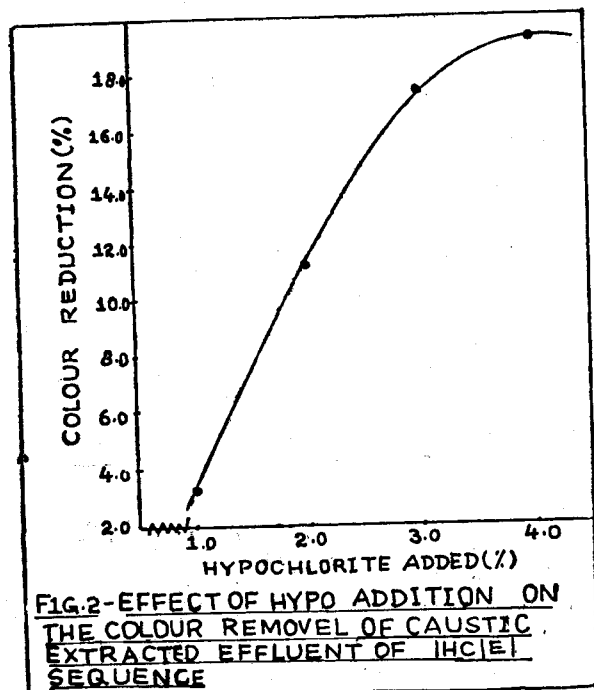
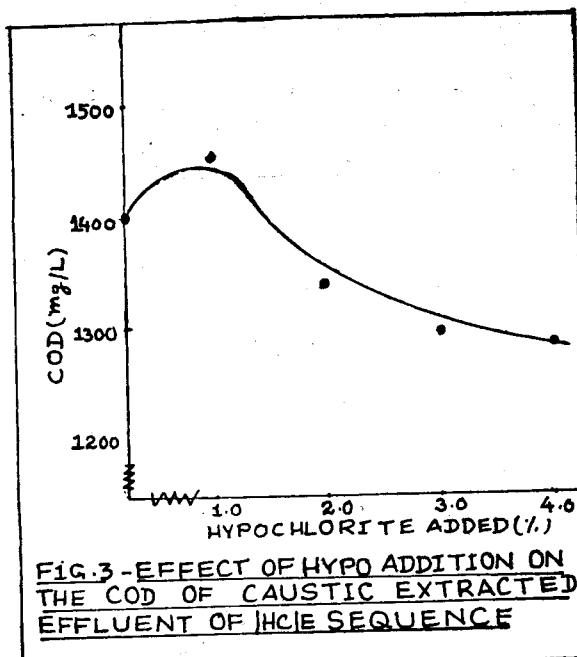
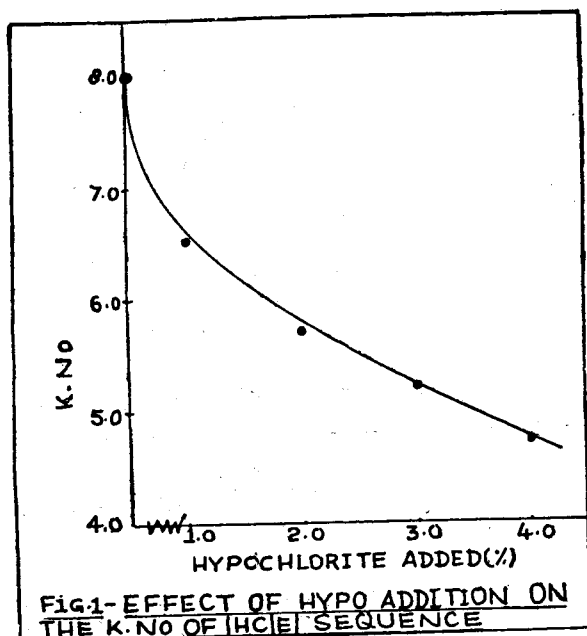
TABLE-6 PHYSICAL STRENGTH PROPERTIES OF BLEACHED PULPS OF C/E/H, HC/E/H AND HC/EH/H SEQUENCES

S.No.	Particulars	C/E/H Sequence				HC/E/H Sequence				HC/EH/H Sequence			
1.	Initial freeness °SR			17				16				20	
2.	Pulp beaten at freeness (°SR)	25	35	45	55	55	45	35	25	55	45	35	55
3.	Beating time (mts)	10	16	20	24	24	17	12	6	23	20	15	25
4.	Basis weight (g.s.m.)	60.39	59.71	57.15	61.56	61.56	59.09	58.19	59.61	61.55	62.55	58.0	59.87
5.	Breaking length (km)	3.919	5.269	5.878	6.175	6.175	4.061	5.270	5.927	6.173	3.349	4.501	5.698
6.	Burst Factor	23.5	30.8	35.5	38.5	38.5	25.22	26.47	35.4	36.39	19.4	23.27	32.84
7.	Tear Factor	79.48	78.71	62.99	61.96	61.96	81.23	68.74	63.74	53.61	89.60	82.76	73.49
8.	Double fold	40	82	104	185	185	40	44	52	60	26	36	74
9.	Culper (microns)	94	84	82	82	82	9	90	87	85	98	90	86
10.	Bulk (g/c.c)	1.56	1.41	1.43	1.30	1.30	1.59	1.55	1.46	1.38	1.57	1.55	1.50

DISCUSSION

The addition of hypochlorite before chlorination did not reduce the colour of caustic stage effluent significantly (Fig.2). The colour reduction was only 19.2% with 4% hypo. The K. No. of HC/E/pulp decreased with increased amount of hypochlorite. (Fig. 1). The C.O.D. reduction of caustic

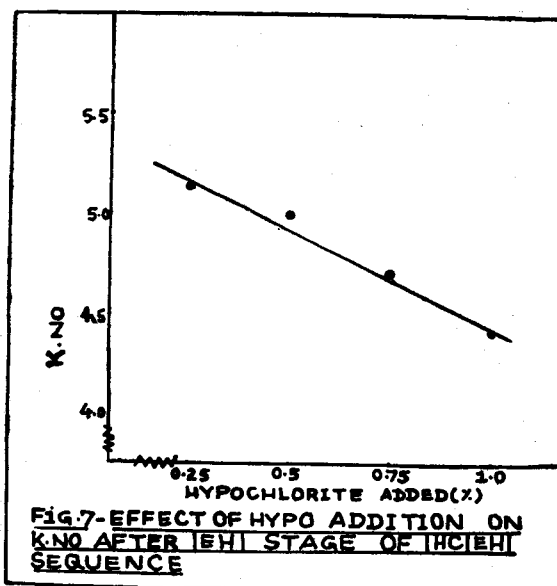
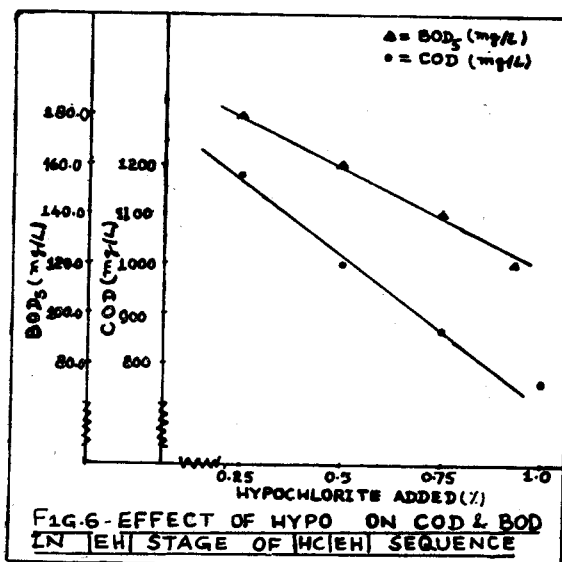
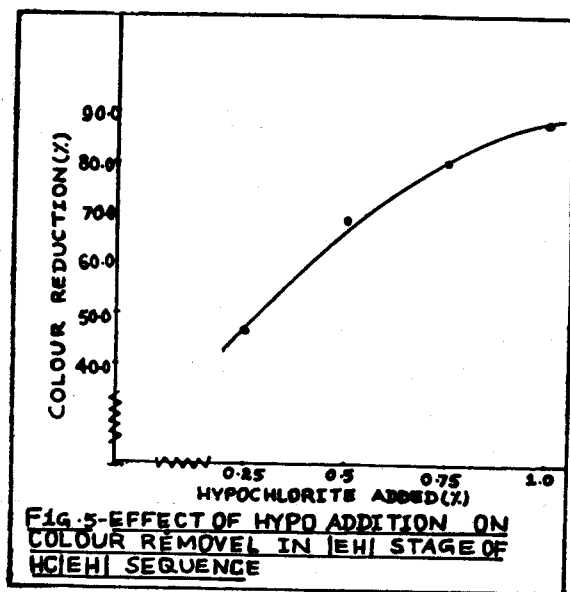
extraction (HC/E) was slightly more with 1% hypo and then gradually reduces with more use of calcium hypochlorite (Fig.3). The pulp loss of HC/E stage increases with the increased amount of hypochlorite in first stage (Fig. 4). The sequential addition of hypo before chlorination helps in reducing the colour of caustic extraction stage very little but it helps in better chlorination and reducing the



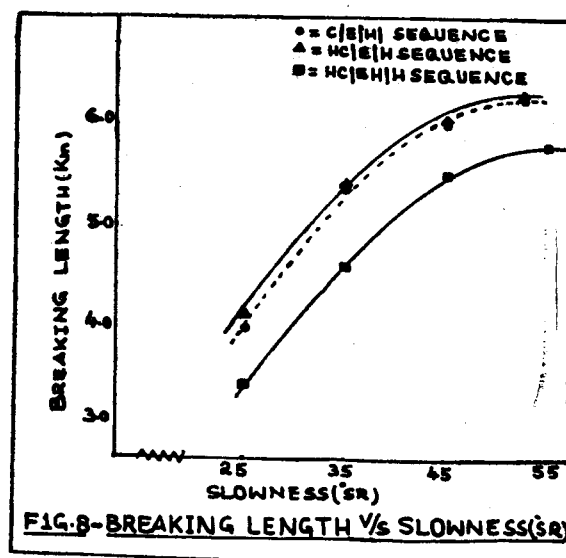
residual lignin content of HC/E/ Pulp. The optimum hypo was about 2% considering the total chlorine consumption and cost of chemicals, quality of pulp, pulp loss and pollution load compared to C/E/H sequence.

As we did not get significant reduction in colour and pollution load in the second stage, we thought of HC/EH/H sequence. The HC/EH sequence was studied in detail to find out the optimum dosage of hypochlorite in the second stage. It was found that more hypo addition results in more colour reduction, more reduction in pollution load and lesser residual lignin in HC/EH/Pulp (Fig. 5, 6 & 7). The optimum hypo condition was arrived

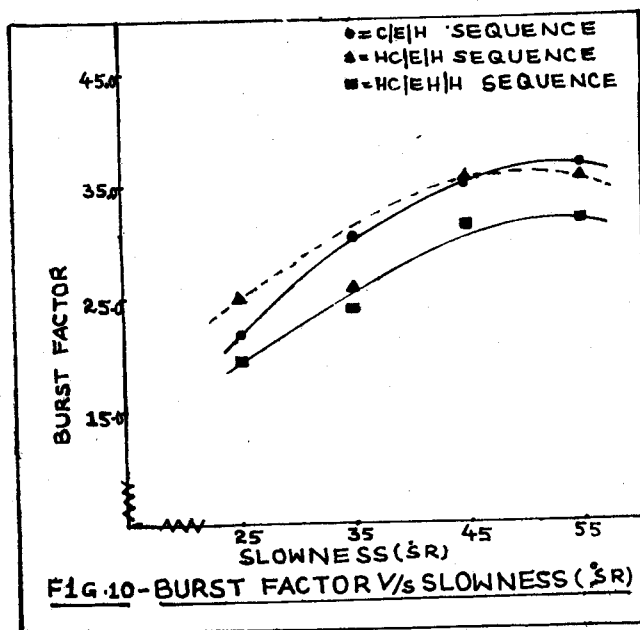
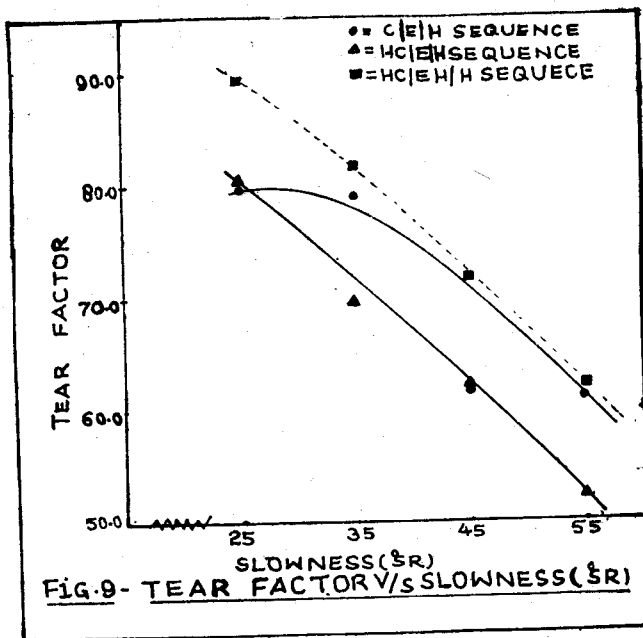
based on 76-80% colour removal of second stage effluent. The colour of effluent was light yellowish.



The physical strength properties of HC/EH/H are slightly lower compared to C/E/H and HC/EH/H sequences (Fig. 8, 9, 10).

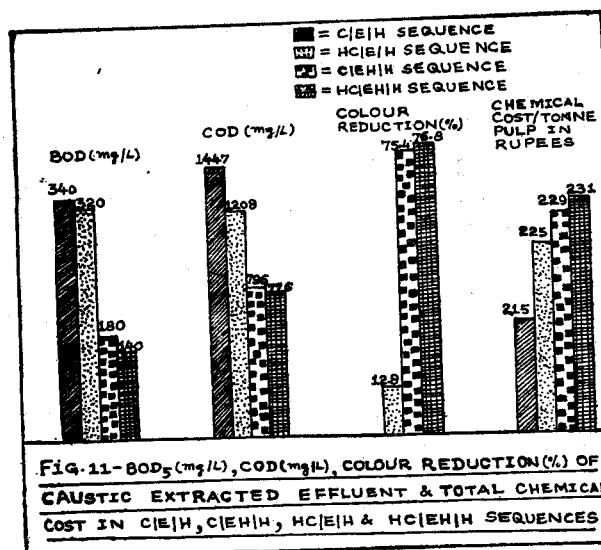


The bleaching chemicals cost of each sequence studied are compared with C/EH/H sequence. The C/EH/H sequence was earlier studied in same laboratory (8) and found that the physical properties were not effected of final bleached pulp. The cost of chemicals for sequences HC/EH/H and C/EH/H are higher by Rs 14-16 tonne of pulp



compared to C/E/H sequence. But the advantages regarding colour removal and pollution load of second stage is quite significant. 76-80% colour, 45-50% BOD, 40% COD can be removed. (Fig 11). The treatment of second stage effluent is done at present by anaerobic and aerobic methods. It involves the addition of nutrients in the anaerobic lagoon. The expenditure on nutrients is about Rs. 900/ per day.

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30% BOD load of coloured effluent can be reduced by adopting the inplant colour removal by using hypochlorite. Therefore the saving on nutrients addition works out to Rs. 300/- per day. The treatment effluent becomes easy and effluent can be reused in chipper house and coal ash disposal after treatment. It is quite suitable for land irrigation and discharge to river stream.

The hardness and chlorite content of effluent increase considerably, but it is possible to meet the tolerance limits of ISI for discharging to river and irrigation purpose by diluting with other pulp and paper mill effluent.

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