Hydrogen peroxide reinforced alkali extraction of bagasse chemical pulp

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INTRODUCTION :

According to the projections of National Commission On Agriculture (1976), the sugar requirement in 2000 A.D. in India at 18 million tonnes and that of cane at 300 million tonnes inclusive of Jaggery and Khandsari. However, present rate of consumption indicates that sugar cane need might be around 300 million tonnes by 1994-95 (1). It is assumed that during 1990-91 crushing season sugar production in India is 11 million tonnes. This indicates that sugar industry itself has generated 16 million tonnes of bagasse. This does not include bagasse from Jaggery and Khandsari industry. Even after fulfilling the requirement of fuel for boilers in sugar mills, it is expected that there is surplus bagasse still available for paper industry. In India, already there are many paper mills in production of paper by usage of bagasse. Bagasse will continue to play a key role in future as a potential raw material for paper in India. The literature (2-10) especially relevant to Indian conditions have been published on pulping of bagasse.

BLEACHING :

Chemical pulp of bagasse is considered to be easy to bleach. By and large chemical pulp of bagasse is bleached by either CEH or CHH bleaching sequence. This type of short bleaching sequence is useful for short and weak fibres (2, 5, 9) such as bagasse, rice straw etc. These short sequences render good brightness to the fully bleached pulp. However, to achieve this brightness, one has to use sufficient quantity of hypochlorite at H stage as pulp is not properly delignified or brighten at CE stage. Due to this uncontrolled usage of hypochlorite, there is a degradation of cellulose and thus, there is a loss in mechanical strength of pulp This affects productivity in paper industry. The strength of the pulp is, therefore, corrected by usage of expensive long fibred soft wood pulp. However, brightness of the pulp cannot be enhanced by usage of any foreign or external material. Naturally, there is quest to adopt suitable techniques to improve brightness of the pulp without jeopardising the strength of pulp. Many large mills are modernising their bleacheries by introducing chlorine dioxide, oxygen etc. in their bleaching sequences. This, of course, needs high investment which is out of reach of smaller paper mills.

Secondly, usage of chlorine compounds such as hypochlorite leads to the generation of chloroform and other organically bound chlorine compounds (11-15) which are toxic in nature. At bleacheries with hypochlorite stages between 44% and 94% of the chloroform and intermediates produced in the bleach plant were formed in the hypochlorite stage (13). This indicates that major source of chloroform is hypochlorite stage. The literature also states that chloroform generation in hypochlorite stage is a function of hypochlorite application rate and CEK number of the pulp entering hypochlorite stage. It also states that the gain in chloroform and intermediates in the sewer system increased when more residual hypochlorite was sent to sewer. Due to this reason, the usage of chlorine for pulp and paper industry is rapidly being phased out in advance countries. Canada has substituted 30-40% and U.S. has replaced 20-30% of pulp and paper chlorine (16). Naturally, if CEK number is low (brighter the CE pulp), the lower will be the consumption of hypochlorite and lesser will be the generation of chloroform and intermediates.

One of the ways to lower CEK number is to cook the pulp soft. Soft cooking of the pulp needs high dosages of chemicals. There is also danger of loss of yield as well as strength of the pulp. Hence, without

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disturbing the pulping conditions one tries to seek alternative method for bleaching of pulp to high degree brightness.

The usage of hydrogen peroxide at alkali extraction stage is an unique technique to lower CEK number (17-23). Literature also confirms that incorporation of small amount of hydrogen peroxide at alkaline extraction stage increases the efficiency of bleaching during subsequent stage. Recent years literature (24, 25) have been published the studies carried out on peroxide reinforced delignification of Indian Fibrous Raw Material viz., bamboo, tropical hardwood, bagasse etc. In this paper studies on chemical bagasse pulp with special reference to the usage hydrogen peroxide reinforced delignification have been discussed.

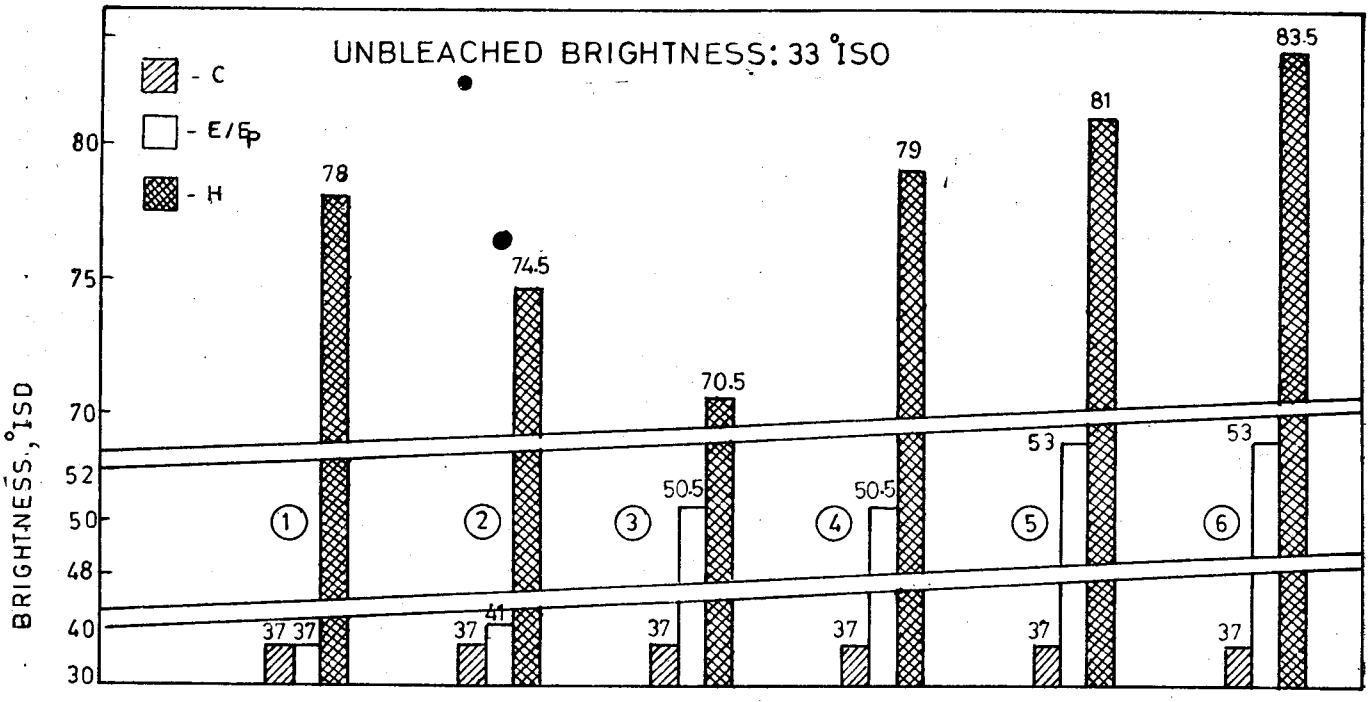
EXPERIMENTAL

Chemical bagasse pulp samples were collected from mills located in Maharashtra, Karnataka and Tamilnadu for these studies. The pulp samples were bleached at Research Centre of National Peroxide Limited by usage of either CEH or CHH sequences by simulating conditions in the respective mills. Stock solution of 5% hydrogen peroxide was prepared and 0.3 to 0.5% H_2O_2 (100%) on O.D. pulp was used at extraction stage based on our earlier experiences. The adjustment of temperature and pH was made as given in Tables enclosed. Initial pH was maintained around 11.0. Alkali extracted pulp was further bleached by usage of only necessary quantity of calcium hypochlorite. In one of the cases CHH sequence was modified to CEpH which is also discussed in detail in this text.

The brightness values at each of the stages were determined on Technibrite-TB-1C instrument. The mechanical properties were studied as per TAPPI procedure. The colour of extraction filtrate was determined on HAZEN scale using Lovibond Colour Comparator.

OBSERVATIONS AND DISCUSSIONS

a. Fig. 1 and TABLE 1 show that CE brightness for pulp is 37° ISO which is practically same as C



STAGE	CHEMICAL	GM/100GM ON OD PULP					
		1	2	3	4	5	6
C	AV. CHLORINE	6·0	6·0	6·0	6·0	6·0	6·0
OR E	NaOH	0·15	0·15	0·5	0·5	1·0	1·0
OR Ep	H_2O_2 (100%)	—	0·3	0·3	0·3	0·3	0·3
H	AV. CHLORINE	2·0	1·0	0·25	0·5	0·5	1·0

FIG·1 THE EFFECT OF CAUSTIC AND HYPOCHLORITE ON HYDROGEN PEROXIDE REINFORCED ALKALI EXTRACTION-BAGASSE CHEMICAL PULP

Table—1 The effect of Caustic and Hypochlorite on Hydrogen peroxide Reinforced Alkali Extraction of Bagasse Pulp.

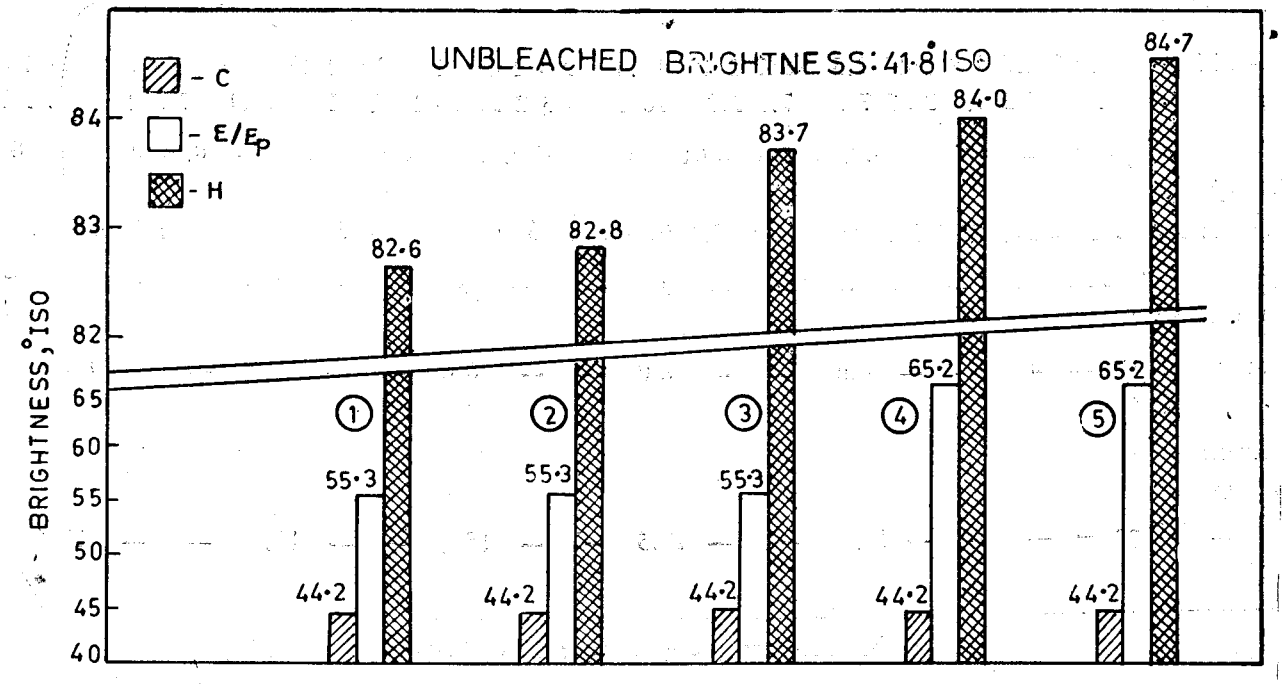
Sequence	CEH			CEpH			CEpH			CEpH			CEpH			CEpH		
Parameters	C	E	H	C	Ep	H	C	Ep	H	C	Ep	H	C	Ep	H	C	Ep	H
1. % Chlorine (A.C)on OD pulp	6	—	—	6	—	—	6	—	—	6	—	—	6	—	—	6	—	—
2. % Ca hypo „ „	—	—	2	—	—	1.0	—	—	0.25	—	—	0.5	—	—	0.5	—	—	1.0
3. % NaOH „	—	0.15	—	—	0.15	—	—	0.5	—	—	0.5	—	—	1.0	—	—	1.0	—
4. % H_2o_2 (100%) „	—	—	—	—	0.3	—	—	0.3	—	—	0.3	—	—	0.3	—	—	0.3	—
5. Temperature °C	Amb.	45	Amb,	Amb	45	Amb.	Amb.	45	Amb.	Amb.	45	Amb.	Amb.	45	Amb.	Amb	45	Amb
6. Consistency %	1.5	5	5	1.5	5	5	1.5	5	5	1.5	5	5	1.5	5	5	1.5	5	5
7. Retention time (min)	45	90	90	45	90	90	45	90	90	45	90	90	45	90	90	45	90	90
8. pH—Initial	2.45	8.6	9.8	2.45	8.5	9.7	2.45	11.0	9.6	2.45	11.0	9.8	2.45	11.21	9.5	2.45	11.18	9.6
Final	2.35	7.2	7.8	2.35	7.1	7.5	2.35	10.2	7.3	2.35	10.2	7.4	2.35	10.9	7.6	2 36	10.9	7.53
9. Residual Cl_2/Hypo/H_2O_2%w/v³	0.01	—	0.02	0.01	0.005	0.01	0.01	0.001	0.005	0.01	0.001	0.009	0.01	—	0.01	0 01	—	0.012
10. Brightness °ISO	37 0	37.0	78.0	37.0	41.0	74.5	37.0	50.5	70.5	37.0	50.5	79.0	37.0	53.0	81.0	37.0	53.0	83.5
11. Additional chemicals kg/tonne pulp — Caustic	—	—	—	—	—	—	—	3.5	—	—	3.5	—	—	8.5	—	—	8.5	
H_2O_2 (50%)	—	—	—	—	6.0	—	—	6.0	—	—	6.0	—	—	6.0	—	—	6 0	
12. Chemical Savings kg/tonne pulp — Hypo	—	—	—	—	10.0	—	—	17.5	—	—	15.0	—	—	15.0	—	—	10.0	

Unbleached pulp brightness : 33.0 °ISO

brightness. This is because alkali extraction is carried out at low pH. i.e. at 8.6. Even by introducing 0.3% H_2O_2 (100%) on O.D. pulp CE brightness does not go beyond 41° ISO. This is because mild alkali extraction (at low pH) is not effecctive at all. This causes the waste of chemicals, time, energy and naturally money. When peroxide delignification pH was increased from 8.6 to 11.2, there was a significant increase in CE brightness to 50.5 °ISO. This high CE brightness was utilised in subsequent H stage to raise brightness to 81 ° ISO and 83.5° ISO by usage of 0.5% and 1.0% hypochlorite (on A.C.) in respective cases. The pulp with higher CEH brightness can be obtained even by reducing consumption of hypochlorite by almost 75%. It is interesting to note that extraction temperature here was 45°C.

b. Fig. 2 and TABLE 2 show that CEH brightness values of pulp do not increase remarkably even after 2% and 3% hypochlorite from 1% on O.D. pulp. This indicates that there is a limitation for hypochlorite to bleach pulp further at H stage from same CE brightness level Here 0.3% H_2O_2 on O.D. pulp was introduced at E stage and pH was adjusted to around 11.0. This has resulted in savings in caustic of 6 kgs/tonne on O.D. pulp at E stage and CE brightness went up from 55 to 65°ISO. CEpH brightness was matched to that of CEH brightness even after reduction of 66% hypochlorite (A.C.) at H stage.

c. FIG. 3 is an excellent example reproduced here from our earlier publication (24). It is well known that hydrogen peroxide is effective at elevated temperature i. e around 60°C. However it is also observed that even at ambient temperature, hydrogen peroxide was effective for bagasse pulp at alkali extraction stage. In our earlier studies, sodium silicate was used as stabilizer along with caustic at extrattion stage. However, it has been avoided in our further studies as it has no specific role to play during peroxide reinforced delignification.



STAGE	CHEMICAL	GM/100 GM ON OD PULP				
		1	2	3	4	5
C	AV CHLORINE	5·0	5·0	5·0	5·0	5·0
OR E	NaOH	2·0	2·0	2·0	1·4	1·4
OR Ep	H_2O_2 (100%)	—	—	—	0·3	0·3
H	AV CHLORINE	1·0	2·0	3·0	1·0	2·0

FIG·2 THE EFFECT OF HYPO ON CEH AND CEpH BRIGHTNESS

TABLE—2

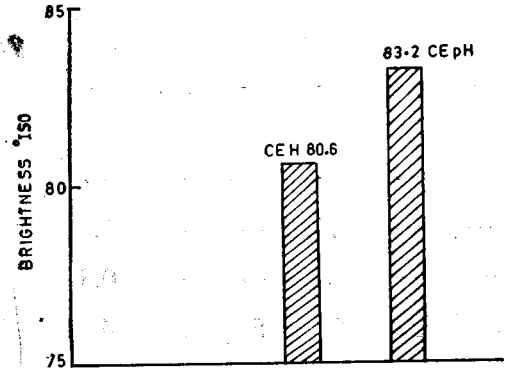
THE EFFECT OF HYPO ON CEH AND CEpH BRIGHTNESS

Sequence	CEH			CEH			CEH			CEpH			CEpH		
Parameters	C	E	H	C	E	H	C	E	H	C	Ep	H	C	Ep	H
1. % Chlorine(A.C.) on OD pulp	5.0	—	—	5.0	—	—	5.0	—	—	5.0	—	—	5.0	—	—
2. % Ca Hypo(A.C) on OD pulp	—	—	1.0	—	—	2.0	—	—	3.0	—	—	1.0	—	—	2.0
3. % NaOH " "	—	2.0	—	—	2.0	—	—	2.0	—	—	1.4	—	—	1.4	—
4. %H_2O_2(100%)"	—	—	—	—	—	—	—	—	—	—	0.3	—	—	0.3	—
5. Consistency %	2	5	5	2	5	5	2	5	5	2	5	5	2	5	5
6. Temperature °C	Amb.	60	35	Amb.	60	35	Amb.	60	35	Amb.	60	35	Amb.	60	35
7. Retention time (min)	45	60	120	45	60	120	45	60	120	45	60	120	45	60	120
8. pH - Initial	2.25	11.6	10.05	2.25	11.6	10.4	2.25	11.6	10.5	2.25	11.25	10.4	2.25	11.25	10.59
Final	2.10	11.45	8.7	2.10	11.45	8.6	2.10	11.45	8.51	2.10	10.8	8.49	2.10	10.8	8.69
9. Colour of extraction liquor(Hazen units)	—	3750	—	—	3750	—	—	3750	—	—	2500	—	—	2500	—
10. K. No.	4.0	1.63	—	4.0	1.63	—	4.0	1.63	—	4.0	1.0	—	4.0	1.0	—
11 Freeness °SR			26			26			27			26			26
12. Brightness °ISO	44.2	55.3	82.6	44.2	55.3	82.8	44.2	55.3	83.7	44.2	65.2	84.0	44.2	65.2	84.7
13. Post Colour no.			0.5			0.55			0.55			0.42			0.38
14. Tear factor mN/g/m^2			45.3			45.3			44.0			46.6			44.0
15 Burst factor kpa/g/m^2			27.76			28.26			27.43			29.30			28.40
16. Breaking length mtrs.			3811			3960			3800			4013			3981
17. Chemical savings) Caustic kg/ton pulp) Hypo											6.0	20.0		6.0	10.0
18. Additional chemical H_2O_2 (50%) kg/ton pulp											6 0			6.0	

Unbleached pulp brightness : 41.8 °ISO

BAGASSE SODA PULP-UNBLEACHED BRIGHTNESS: 37.7 °ISO

STAGE	CONSISTENCY %	RETENTION TIME MINUTES	TEMP. °C	pH	
				INITIAL	FINAL
C	2	60	AMBIENT	2·2	2·2
OR E	10	60	AMBIENT	11·9	11·8
OR Ep				11·0	10·5
H	5	120	AMBIENT	10·1	8·7



STAGE	CHEMICALS	GM/100 GM ON O.D. PULP	
C	AVAILABLE CHLORINE	4·5	4·5
OR E	NaOH	1·2	0.65
Ep	H_2O_2 (100%)	–	0·25
	SOD SILICATE (38°Be)	–	0·5
H	AVAILABLE CHLORINE	2·0	2·0

16·3 LABORATORY STUDIES ON USAGE OF HYDROGEN PEROXIDE AT ALKALI EXTRACTION STAGE OF BLEACHING OF BAGASSE CHEMICAL PULP UNDER AMBIENT CONDITIONS

d. FIG. 4 and TABLE 4 is an another example where CE brightness is 57.8° ISO with 2% caustic on O. D. pulp at extraction stage. This CE brightness value was increased to 67°ISO by usage of 0.3% H_2O_2 (100%) on O. D. pulp at extraction stage, even by reducing caustic from 2% to 1% on O. D. pulp. CEpH brightness of 86 0° ISO was achieved by reducing hypochlorite (A. C.) by 70% at H stage.

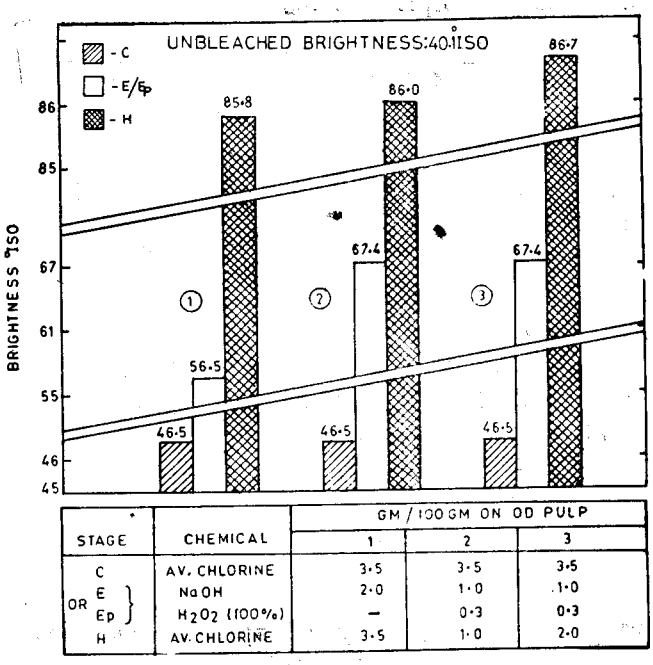
e. FIG. 5 and TABLE 5 give a classic example where CHH sequence was used for bleaching. CHH brightness achieved was 83.9° ISO. It was observed that amount of caustic used at first H stage was sufficient to raise the pH to 11 0 and temperature was 50°C. This sequence was, therefore, modified to CEpH by utilising the conditions available at first hypo stage of bleaching sequence. 0.5% H_2O_2 (100%) on O D. pulp was used instead of 4% hypochlorite (A. C) on O. D. pulp. Even after this modification in bleaching, CEpH brightness achieved was 84 3° ISO. This has resulted in reduction of 40 kg hypochlorite (A. C.) per tonne of pulp.

TABLE — 3

Laboratory Studies on Usage of Hydrogen Peroxide at Alkali Extraction Stage of Bagasse Chemical Pulp Under Ambient Conditions.

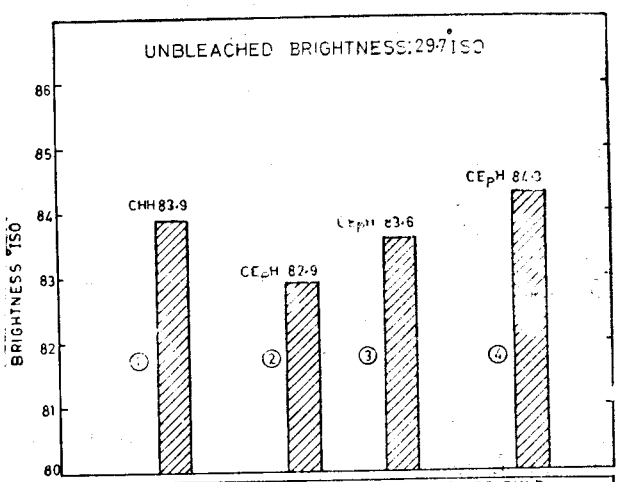
Parameters	Sequence	CEH			CEpH		
		C	E	H	C	Ep	H
1.	% Chlorine (A. C.) on O. D. pulp	4.5	—	—	4 5	—	—
2.	% Ca. Hypo (A. C.) " "	—	—	2.0	—	—	2.0
3.	% H_2O_2 (100%) " "	—	—	—	—	0.25	—
4.	% NaOH " "	—	1.5	—	—	0.65	—
5.	% Na. Silicate (38° Be) "	—	—	—	—	0.5	—
6.	Consistency %	2	10	5	2	10	5
7.	Temperature °C	Amb.	Amb.	Amb.	Amb.	Amb.	Amb.
8.	Retention time (min.)						
9.	pH — Initial	2.2	11·9	10.1	2.20	11.0	10.1
	Final	2.2	11.8	8.7	2.20	10.5	8.6
10.	Residual Cl_2/hypo/H_2O_2 % on O. D. pulp	0.3	—	0.31	0.3	0.05	0.4
11.	Brightness °ISO	—	—	80.6	—	—	83.2
12.	Caustic saving kg/ton pulp	—	—	—	—	8.5	—
13.	Additional chemicals kg/ton pulp : 1) H_2O_2 (50%)	—	—	—	—	5.0	
	2) Na. silicate (38°Be)	—	—	—	—	5.0	

Unbleached pulp brightness : 37.7 °ISO.



STAGE	CHEMICAL	GM / 100GM ON OD PULP		
		1	2	3
C	AV. CHLORINE	3·5	3·5	3·5
OR E / Ep	NaOH	2·0	1·0	1·0
	H_2O_2 (100%)	—	0·3	0·3
H	AV. CHLORINE	3·5	1·0	2·0

FIG·4 IMPROVEMENT OF CE BRIGHTNESS BY USAGE OF HYDROGEN PEROXIDE AND ITS EFFECT ON HYPO CHARGE AT H STAGE



STAGE	CHEMICAL	GM / 100GM ON OD PULP			
		1	2	3	4
C	AV. CHLORINE	8·0	8·0	8·0	8·0
OR H / P	NaOH	1·5	1·5	1·5	1·5
	AV. CHLORINE	4·0	—	—	—
	H_2O_2 (100%)	—	0·5	0·5	0·5
H	AV. CHLORINE	4·0	2·0	3·0	4·0
	HYPO. SAVING KG/TON PULP		60	50	40

FIG 5 ALTERATION OF CHH BLEACHING TO CEpH LEADING TO SAVINGS IN HYPO CONSUMPTION AT SAME BRIGHTNESS LEVEL

TABLE—4 Improvement of CE Brightness by Usage of Hydrogen Peroxide And Its Effect on Hypo charge at H Stage.

Sequence	CEH			CEpH			CEpH		
Parameters	C	E	H	C	Ep	H	C	Ep	H
1. % Chlorine (A.C.) on OD pulp	3.5	—	—	3.5	—	—	3.5	—	—
2. % Ca-hypo ,, ,, ,,	—	—	3.5	—	—	1.0	—	—	2.0
3. % H_2O_2 (100%) ,, ,,	—	—	—	—	0.3	—	—	0.3	—
4. % NaOH ,, ,,	—	2.0	—	—	1.0	—	—	1.0	—
5. Consistency %	3	8	10	3	8	10	3	8	10
6. Temperature °C	Amb.	70	Amb.	Amb.	70	Amb.	Amb.	70	Amb.
7. Retention time (min.)	45	60	150	45	60	150	45	60	150
8. pH—Initial	2.48	11.51	10.41	2.48	11.0	10.31	2.48	11.0	10.35
Final	2.31	11.10	8.20	2.31	10.41	7.90	2.31	10.41	8,10
9. Colour of extraction		4500	—	—	3000	—	—	3000	—
10. Brightness ISO	45.2	57.8	85.2	45.2	67.2	84.8	45.2	67.2	86.0
11. Chemical savings) Caustic					10.0			10.0	
kg/ton pulp) Hypo					25.0			25.0	
					6.0			6.0	
12. H_2O_2 (50%) kg/ton pulp									
13. Burst factor kpa/g/m²			26.9			30.0			
14. Tear factor mN/g/m²			27.0			29.8			
15. Breaking length (metres)			3444			3777			

Uunbleached pulp brightness : 40.1 °ISO

Table – 5 Modification of CHH Bleaching Sequence to CEpH Leading To Savings in Hypo Consumption at Same Brightness Level.

Sequence	CHH			CEpH			CEpH			CEpH		
Parameters	C	H	H	C	Ep	H	C	Ep	H	C	Ep	H
1. % Chlorine (A.C) on O.D. pulp	8.0	—	—	8.0	—	—	8.0	—	—	8.0	—	—
2. % Ca-Hypo (A.C.) „ „	—	4.0	4.0	—	—	2.0	—	—	3.0	—	—	4.0
3. % NaOH „ „	—	4 5	—	—	1.5	—	—	1.5	—	—	1.5	—
4 % H_2O_2 (100%) „ „	—	—	—	—	0.5	—	—	0.5	—	—	0.5	—
5. Consistency %	2.5	10	10	2.5	10	10	2.5	10	10	2.5	10	10
6. Temperature °C	Amb.	50	40	Amb.	50	40	Amb.	50	40	Amb.	50	40
7. Retention time (min)	45	60	60	45	60	60	45	60	60	45	60	60
8. pH — Initial	2.15	11.48	10.6	2.15	11.2	10.51	2.15	11.2	10.50	2.15	11.2	10 48
Final	1.95	8.31	8.21	1.95	9.95	8.19	1.95	9.95	8.15	1.95	9.95	8.20
9. Brightness °ISO			83.9			82.9			83.6			84.3
10. Ca-hypo savings kg/ton pulp						60.0			50 0			40.0
11. H_2O_2 (50%) required kg/ton pulp					10.0			10.0			10.0	

Unbleached pulp brightness : 29.7 °ISO

Brightness Stability

In most of above cases, there is reduction in usage of hypochlorite at H stage of CEH sequence. This would result the improvement in brightness stability. This has been shown in TABLE – 2.

Colour of Extraction Liquor

The usaga of small quantity of H_2O_2 (0.3 to 0.5%) on O. D. pulp at alkali extraction stage has resulted in reduction of colour of extraction liquor. This is given below :

3750 to 2500 (HAZEN UNITS) (TABLE — 2)
4500 to 3000 (HAZEN UNITS) (TABLE — 4)

Mechanical Properties

Strength properties were not studied in case of all the samples. Some of the important parameters studied are given in TABLE 2 and 4 for two pulp samples. It can be noted that there is an improvement in bursting strength as well as breaking length of the pulp. Tearing strength is practically same in one case (TABLE2) whereas it is improved in another case (TABLE 4). This improvement in strength is due to the improvement in degree of polymerisation of cellulosic chain. This improvement in D.P. is again due to reduction in consumption of harsh non-selective bleaching agent like hypochlorite for bagasse chemical pulp.

CONCLUSIONS

1. Alkaline extraction stage in CEH bleaching sequence can be utilised for brightening of pulp by usage of small quantity of hydrogen peroxide This can be very easily adopted by a mill withouth any major modification/alteration in bleachery.
2. As CEK number is reduced or CE brightness is improved during hydrogen peroxide reinforced alkali extraction the requirement of bleach (hypochlorite)in subsequent stage is substantially reduced even for improved final brightness.
3. The reduction in consumption of final hypo leads to stronger pulp with improved stability of brightness. It is, therefore, possible to minimise/eliminate the usage of expensive long fibred soft wood pulp blended at stock chest for making paper.
4. Due to improved strength of fully bleached pulp in above cases, it is expected that runnability of the paper on machine should improve.
5. The usage of hydrogen peroxide at alkali extraction stage reduces the colour of extraction liquor by 25 to 30%. Similarly, as there is reduction in usage of hypechlorite at subsuequent stage, there is reduction in generation of chloroform and other chloro organic compounds on paper as well as in the sewer. Thus effluent load in above respect could be kept low.

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