Metal Control During Bleaching Process of Paper Manufacturing

Part II: Improvement in optical properties of bleached pulps by washing, leaching and chelating

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ABSTRACT:-- Bamboo-hard wood pulps of various stages, bleached with CEpHH sequence, have been subjected to washing with water, leaching with HCl and H_2SO_4 and chelating with EDTA. The brightness and P.C.No. of the washed, leached and chelated pulps have been determined and significant improvement on washing and leaching with HCl have been reported. Metal contents in the final pulps have been determined and the improvement in optical properties has been attributed to removal of exchanged metals from the pulp fibres. Applicability of these processes have been discussed from techno-economical points of view for Indian pulp and paper industries.

INTRODUCTION

Concentrations of Fe, Mn, Cu, Ca, Mg, Na and K in the unbleached bamboo-hard wood and their mixed pulp after each stage of CEpHH and final stage of OC/DEoD bleachings, have been reported in an earlier publication (1).

A rational classification of metals, namely catalysts and non-catalysts vis-a-vis H_2O_2 decomposition has been introduced (2) along with a mathematical equation for total metal in the pulp bleaching system:

$$T = K [R_I + F_E]$$

where T = Total metal content, K = Constant, R_I = Removal rate of Inherent metals and F_E = Fixation rate of metals from external source by exchange.

The levels of various metals exchanged in the pulp during E, H-I and H-II stages were calculated (2) using Eqn:

$$M_{fixed} = T - I$$

where M_{fixed} = Metals fixed, T = Total metal content and I = Inherent metal content.

M_{fixed} need not be the catalytic elements such as Fe, Cu and Mn; it includes noncatalytic metals also (Ca, Mg, Na, K etc.)

The present understanding of improving the optical properties (brightness and colour reversion) is essentially by bleaching of the residual lignin in the unbleached pulp by a multistage bleaching process including chlorine, Ca-hypochlorite, ClO_2, O_2, H_2O_2 and ozone. It is reported that the structure of residual lignin polymer and its reaction with these bleaching reagents are still not fully understood

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(3-5). The need for a clear understanding of the structure and reactions of lignin, has become very exigent because of environmental pressure of TOCl and AOX (6-10). The understanding may help arresting formation of chlorophenolic compounds including dioxan and furan. The whole bleaching technologies are changing gradually because of TOCl and AOX with complete and substantial substitution of Cl_2 with ClO_2.

While objective of this work is other than on TOCl, it may be mentioned that very little studies have been carried out on metals and their effects on pulp properties. It is possible that the metals are structurally bonded with the residual lignin (11) and removal of these metals may accompany removal of lignin and its chlorinated products forming TOCl or AOX. The present work will show that the brightness and P.C.No. can be improved significantly by washing with water, leaching with acid or treatment with EDTA. Such improvement in brightness and colour reversion properties is of interest for the mills but the results may also be examined with relevance to environment, namely on lignin and chloroorganic compounds.

EXPERIMENTAL

The metals have been analysed according to standard procedures (12-13) with some modification for preparation of the pulp sample. The pulp is dissolved in triacid mixtures ($HCl + H_2SO_4 + HNO_3$).

RESULTS AND DISCUSSION

One of the most economically viable processes of improving the surface properties of any solid is by washing with water. But the need was rarely felt as probably the cause of poor pulp properties was assumed to be only lignin and chromophoric groups. However, it was shown in Part-I (1) that, this could be due to metal ions, that too fixed through exchange mechanism. Consequently, it may not be difficult to wash away with water and obtain brighter pulp without undergoing drastic chemical treatments, normally required for delignification or for removal of chromophoric groups.

In Table 1 and 2, the optical properties (brightness and P.C.No.) of pulp before and after washing are given. It is interesting to see that there is substantial improvement in brightness on simple washing with water; 1-4% El. In the final stage (H-II), there is increase of ~1% El from 80.6 to 81.3% El with P.C.No. decrease from 6.93 to 5.73. It appears that more of washing may help further gain in optical properties.

Table-1

Optical properties of pulp on washing with water

	Brightness (% El)	
	Before washing	After washing
Unbleached pulp	27.9	31.2
C	30.4	35.0
E	41.5	42.6
H-I	71.2	75.2
H-II	80.6	81.3

Table-2

Optical properties of pulp on washing with water

	P.C. No.	
	Before washing	After washing
Unbleached pulp	8.1	8.4
C	6.7	6.8
E	6.2	6.8
H-I	6.4	6.3
H-II	6.9	5.7

The optical properties of pulp before and after washing with HCl, are given in Tables 3 and 4. The increase in brightness value to 79.3% El in H-I stage

Table-3

Optical properties of pulp on leaching with HCl

	Brightness (% El)	
	Before leaching	After leaching
Unbleached pulp	27.9	31.0
C	30.4	34.1
E	41.5	47.6
H-I	71.2	79.3
H-II	80.6	82.0

Table-4

Optical properties of pulp on leaching with HCl

	P.C. No.	
	Before leaching	After leaching
Unbleached pulp	8.1	8.5
C	6.7	7.1
E	6.2	7.0
H-I	6.4	3.7
H-II	6.9	3.1

from 71.2% El is remarkable. Corresponding decrease in P.C.No. by 2.7 should be considered quite significant. The reason for such improvement in brightness can be due to removal of chromophoric groups as well as metals with probably residual lime and its contaminants. The brightness improvement in the second hypo stage is also significant i.e. 1.4% El with P.C.No. decrease from 6.9 to 3.1 i.e. 3.8 no.

Results of brightness and P.C.No. variations in unbleached pulp and in pulp samples bleached in C and E stages on washing with 1% H_2SO_4 given in Tables 5 and 6 show that there is practically no improvement on treatment with H_2SO_4.

Table-5

Optical properties of pulp on leaching with H_2SO_4

	Brightness (% El)	
	Before leaching	After leaching
Unbleached pulp	27.9	28.8
C	30.4	31.0
E	41.5	42.7

Table-6

Optical properties of pulp on leaching with H_2SO_4

	P.C. No.	
	Before leaching	After leaching
Unbleached pulp	8.1	8.4
C	6.7	6.8
E	6.2	7.0

In view of the improvement in optical properties by washing with simple water of pulp after H-I and H-II stages, it was considered worth-while analysing the colour causing metals such as Fe and Ca. The results are shown in Table 7. It can be seen that at H-I stage, the Fe content remains practically unaltered on washing with water i.e. from 36.91 ppm to 36.26 ppm but there is significant decrease in Ca content i.e. from 368.2 to 266.4 ppm. In H-II stage, there is elimination of Fe by 13.37 ppm while it is about ~102 ppm for Ca. Thus, the brightness increase can be probably accounted to removal of these metals. While the lignin and other colour causing organic compounds need to be determined, at this stage, it cannot be ascertained as it was not studied.

Table-7

Fe and Ca in pulp after washing with water (in ppm)

Sample	Fe		Ca	
	Before washing	After washing	Before washing	After washing
H-I	36.91	36.26	368.20	266.41
H-II	44.84	31.47	329.80	227.59

The results of Fe and Ca analysis of pulp samples treated with 1% H_2SO_4 are given in Table 8. It is observed that excepting in case of Ca in unbleached pulp and Fe in extracted pulp, the Fe and Ca contents remain either same or increase.

Table-8

Fe and Ca in pulp after leaching with H_2SO_4 (in ppm)

Sample	Fe		Ca	
	Before leaching	After leaching	Before leaching	After leaching
Unbleached pulp	26.79	27.67	103.84	70.65
C	5.01	10.91	---	---
E	37.88	33.98	---	---

Apart from acid leaching, EDTA has also been used for chelating the metals responsible for undesirable decomposition of H_2O_2 namely Mn and Fe. In order to find out the optimum EDTA concentration for removal of Mn and fe, the chlorinated pulp sample has been treated with 20, 50, 100 and 150 ppm of EDTA (Table 9). The washed pulp has been analysed for Mn and Fe. For Mn, it is observed that the elimination does not practically improve upon increasing the concentration of EDTA. Surprisingly, the concentration of Fe increases with increase in EDTA concentration. This is because of refixation of Fe-EDTA complex on the pulp. In case of Mn,

Table-9

Fe and Mn in pulp on chelating with EDTA (in ppm)

Concentration of EDTA	Fe	Mn
20	1.776	0.0126
50	1.946	0.0109
100	4.691	0.0106
150	4.170	0.0106

this complex apparently can be washed away unlike in case of Fe.

The optimum dose for EDTA can therefore be only 20 ppm. The solution obtained after treatment with 20 ppm of EDTA, was analysed for other metals such as Ca, Mg, Na and K also. The results are presented in Table 10 along with that of Mn and Fe. The metals before washing in Inherent metals in chlorinated pulp, are also tabulated for easy comparison. It can be seen that Ca and Mg have also got reduced while Na and K have increased significantly because of similar reason as in case of Fe but as EDTA is of Na-salt, the level is still very high in case of Na, In sum, the refixing of metals other than Mn over the pulp on EDTA treatment, is established from the results in Table 9 and 10.

Table-10

Metal contents in C stage pulp on chelating with 20 ppm EDTA (in ppm)

Metals	Before chelating	After chelating
Fe	5.01	1.77
Mn	0.0177	0.0126
Ca	10.46	4.66
Mg	3.26	0.0187
Na	62.16	2038.66
K	24.89	343.59

CONCLUSIONS

Brightness of pulps after C, E, H-I and H-II can be improved by washing with water as well as leaching with acid. Colour reversion property of the bleached pulp is enhanced significantly only by acid treatment. In the washing process, the optimum brightness obtained is in H-I pulp (4% El) and P.C.No. of 1.2 in H-II bleached pulp. Acid treatment of H-I pulp can improve brightness by 8% El and P.C.No. by 3.8 in H-II pulp. The results are correlated with metal contents of pulp samples.

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