Metal Control During Bleaching Process of Paper Manufacturing

Part I : Metal Contents in Raw Materials and Bleached Pulps

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ABSTRACT:-- The metal contents (Fe, Mn, Cu, Ca, Mg, Na and K) in bamboo, casuarina, cassia siamea, mixed hard wood and rice straw are reported. The complete methods of metal analysis are described.

Bamboo-hard wood unbleached pulp and samples after bleaching at various stages in CEHH sequence have been studied on their metal levels. Metals in bleached pulp following to OC/DEoD sequence have also been reported.

INTRODUCTION

Importance of metal contents during bleaching with H_2O_2 is slowly being realized by many paper mills (1.2) which is known since more than a decade (3,4). Attempts are still going on for better understanding on the metals and the process of elimination. Extensive works involving metals having catalytic effect on H_2O_2 decomposition, namely Mn, Cu and Fe have been carried out (4-16). It is reported recently that Fe and Cu cations effect the selectivity of ozone treatment and play important role in TCF pulping also. Control of transition metals is considered as the key to successful use of H_2O_2 in the bleaching of kraft pulp (4).

The metals in raw materials and the liquors can be divided into 2 categories (17-22):

(I) Inherent: The metallic cations present in the process originating from the raw materials (23-25).

(II) External: Metals from external sources, namely from water, pulping and bleaching chemicals, contamination and from the metallic surfaces in the process (5).

The metals can again be subdivided based on their effect on H_2O_2 decomposition:

(Ia) Catalysts - such as Fe^{3+}, Mn^{2+}, Cu^{2+} and Ni^{2+}

(Ib) Noncatalysts - such as Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Al^{3+}, SiO_2 etc.

Nickel is normally present in very small amount and it is harmless (13). In the second category, $MgCO_3$ and $MgSO_4$ have often been added with sodium silicate acting as stabilizer in the buffer action (3).

The H_2O_2 decomposition reaction takes place through evolution of perhydroxyl ion in the reaction (3):

$$H_2O_2 + H_2O \xrightarrow{pH > 9\text{-}13} H_3O^+ + OOH^- \quad ....(1)$$

(perhydroxyl ion)

In presence of catalysts, the reaction steps are presented as follows (7):

$$M + H_2O_2 \longrightarrow M^+ + HO + OH^- \quad ....(2)$$

$$M^+ + HO_2^- + HO^- \longrightarrow M + O_2^- + H_2O \quad ....(3)$$

$$M^+ + O_2^- \longrightarrow M + O_2 \quad ....(4)$$

$$O_2^- + HO \longrightarrow O_2 + HO^- \quad ....(5)$$

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where M represents metal ions such as Fe^{3+}, Mn^{2+} and Cu^{2+}

Excess of catalysts (M) cause undesirable decomposition of H_2O_2 and thus it becomes subject of economical significance specially as the cost of H_2O_2 is comparatively quite high. In case of mechanical pulp, it is reported that as much as 1/3rd of H_2O_2 is lost because of such undesirable decomposition (1).

The present paper is intended to establish presence of these metals in bamboo-hard wood pulp in CEHH bleaching (1, 2) which is still the common practice in the country. Attempts have also been made for eliminating these ions by leaching with water, HCl and chelating with EDTA (4, 19-22). The results obtained on optical properties of the acid leached pulp may be quite interesting where metals of Ib category namely Ca, Mg, Na and K are shown to be involved.

EXPERIMENTAL

Materials

The botanical names and sources of various raw materials used are given below:

	Raw material		
	Common name	Botanical name	Source of collection
1	Bamboo	Dendurocalamus Strictus	Chips from mill
2	Casuarina	Casuarina Equisetifolia	Chips from mill
3	Chakunda	Cassia Siamea	Chips from mill
4	Mixed hardwood (Eucalyptus+Casuarina)	--	Chips from mill
5	Rice straw	--	Local area

The pulp samples had also been procured from mill. Water sample is the tap water which is used normally for the process. Pulp bleached with OC/ DEoD sequence was from laboratory experiment.

HCl is of E-Merck (GR) and H_2SO_4 is of BDH (AR). EDTA is of E-Merck (AR) and NaOH is GPR-grade of BDH.

The analytical equipments used are: UV/Visible spectrophotometer, Flame photometer and Elrepho brightness tester.

The chips from hard wood, bamboo and cuttings from rice straw were ground separately in the Wieley mill for having the dust.

Chemical analysis methods

As analysis of metals is rarely carried out in the pulp and paper mills, it may be useful to describe the details of analysis methods for ready reference. These methods have been developed inhouse for adaptation of trace metal analysis in plant and pulp samples.

About 5 gm of OD sample was taken in a silica crucible for ignition in electrical muffle furnace at 600°C to convert into ash. The soaking period was 3 hours at 600°C. The crucible is taken out when the furnace is cooled to room temperature. 0.5 gm of ash was digested with triacid mixtures of HCl, HNO_3 and H_2SO_4 (5 ml of 6N HCl+ 3ml of concentrated HNO_3 + 6.6 ml, 1:1 H_2SO_4). As some insoluble particles were present, it was evaporated to dryness and again treated with 1 Ml of HF It was further evaporated to dryness and the residue was dissolved in distilled water and made upto 100ml. It was taken as stock solution. This procedure was followed for all the pulp samples.

For the experiments on leaching with acids, 25 gm of pulp was taken to which 2 l of 1% HCl or 1% H_2SO_4 was added, followed by 2 l of distilled water.

Washing of 100 gm of pulp with water was made with 10 l of process water.

Analysis of Fe

10 ml of the stock solution was pipetted into 50 ml volumetric flask to which 1 ml of hydroxylamine hydrochloride, 15 ml of sodium acetate and 1 ml of 1, 10 - phenanthroline hydrochloride were added. After waiting for 15 minutes for colour development, it was made upto the mark with distilled water. The absorbance was measured in a UV/vis spectrophotometer at 510 nm. Iron is obtained by comparison of absorbance with standard iron solution.

Manganese

10 ml of stock solution was pipetted into a silica crucible. It was evaporated to dryness and then drops of sodium sulfite solution and 5ml 1.5N HNO_3 were added. It was further evaporated to dryness. The residue was dissolved in distilled water and transferred to a 50 ml volumetric flask.

The solution was heated to which 2 ml of periodate-phosphoric reagent was added and again heated for 5 min. It was cooled and then diluted with 30 ml of conc. H_2SO_4 in 970 ml of water. The absorbance at 525 nm was measured in Visible spectrophotometer. From the standard graph, Mn concentration was determined.

Copper

10 ml of stock solution was pipetted into a separating funnel to which 10 ml of EDTA solution and 5 drops of phenolphthalein were added. The solution was neutralized with NH_4OH, cooled to room temperature and then 5 ml of diethylene dithiocarbamate solution was added along with 20 ml of CCl_4 and then shaken vigorously for 3 minutes. The lower phase was separated and then filtered using a cotton plug on the outlet of the separating funnel into a photometric cell. The absorbance at 440 nm was measured with the extract of reagent blank as reference in the Spectrophotometer.

Calcium

10 ml of stock solution was pipetted into a conical flask where pH was adjusted to 12-13. The solution was then titrated with EDTA using murexide as indicator.

Magnesium

10 ml of stock solution was pipetted into a conical flask to which 10 ml of ammonia buffer and Eriochrome black-T indicator were added. The solution was titrated with EDTA. This gives the total calcium and magnesium present. From this magnesium concentration was obtained by difference.

Sodium and Potassium

Na and K were determined in the Flame photometer using standard Na and K solutions.

RESULTS AND DISCUSSION

Bamboo with mixed hard wood (80 : 20) is the raw material which has been taken for digestion, washing and then bleaching through CEpHH sequence. Metal contents of bamboo and mixed hard wood are given in Table 1, for Fe, Mn and Cu (Cat Ia) and in Table 2, for Ca, Mg, Na and K (Cat Ib). Results of two other local hard woods, namely casuarina and cassia siamea along with that of rice straw are also given for comparison in Table 1. It can be seen that all the 5 raw materials studied contain the 7 metallic elements in ample quantity. Fe, Ca, Mg and K are in macro amount while Mn and Cu are in very small level. Based on the soil conditions in particular, the concentration of each metal is found to be varying.

Analysis results of relevant metals in process water used in the present study are given in Table 3. In category I, Fe and in Category II Ca, Mg, Na and K are reported which are bound to add to the metal value of the pulp samples.

Table-1

Catalyst contents in raw materials (in ppm)

Raw material	Fe	Mn	Cu
Bamboo	124.60	3.04	1.53
Casuarina	144.92	1.76	--
Cassia siamea	295.82	--	--
Mixed hardwood	45.50	3.25	2.21
Rice straw	245.15	0.292	--

Table-2

Metal contents in raw materials (in ppm)

Raw material	Ca	Mg	Na	K
Bamboo	88.47	110.80	291.09	1374.60
Casuarina	572.79	145.61	158.79	477.36
Cassia siamea	491.89	80.38	843.75	3758.53
Mixed hardwood	322.50	59.10	751.46	856.67
Rice straw	499.54	201.68	451.26	4194.09

Table-3

Metal contents in process water (in ppm)

Metals	Concentration
Fe	1.25
Ca	23.55
Mg	21.58
Na	24.00
K	4.00
SiO_2	4.00

In the present study, following pulp samples of bamboo-mixed hard wood have been taken:

Unbleached pulp (U)
Chlorinated pulp (C)

Extracted pulp (E), and Ca-hypochlorite bleached pulp in 2 stages (H-I and H-II).

The catalyst metal contents (Fe, Mn and Cu) in unbleached pulp, chlorinated, extracted and Hypo-I and II samples are given in Table 4, while Table 5 contains Cat-Ib metal concentrations (Ca, Mg, Na, K). The unbleached pulp contains 26.8 ppm of Fe, 3.5 ppm of Mn and 0.76 ppm of Cu. This pulp was collected after washing stage. Compared to ~125 ppm of Fe in bamboo and 45.5 ppm in mixed hard wood, Fe content is reduced due to digestion in white liquor at 165°C and then washing. Mn has marginally increased (3.04 ppm in bamboo and 3.25 ppm in mixed hard wood) while Cu is reduced by more than half the quantity of bamboo + hard wood. Levels of Ca, Mg, Na as well as K have also decreased in the unbleached pulp compared to that in the raw materials.

The concentration of various metals in the chlorinated pulp is of interest; Fe, Mn and Cu are reduced to 5.01 ppm, 0.018 ppm and 0.39 ppm respectively (Table 4). Ca is reduced from 103.8 ppm in unbleached pulp to 10.5 ppm; Mg from ~92 to 3.3 ppm; Na from ~338 to 62 ppm and K from ~195 to ~25 ppm. Thus chlorination is the most important stage in the bleaching process governing the metal elimination rate. Probably no metal exchange takes place during chlorination.

In Tables 4 and 5, the increase of matel contents from that in C-stage, can be observed distinctly with Fe, Mn and Cu to ~38, 0.24 and 0.44 ppm respectively. The increase of Fe from 5 ppm to 38 ppm is substantial, same is the case with Mn but Cu has increased only marginally. Ca has increased to 34.8 ppm in E-stage while Mg remains practically unchanged from 3.3 to 3.6 ppm. Because of NaOH, the Na-content has increased to extremely high level i.e. to 1172 ppm from 62 ppm in chlorination stage; K has also increased (25 to 138 ppm). Because of alkalinity, the metals present in water get precipitated and consequently account for increase in metal concentrations in the pulp, unlike in the C-stage.

In case of Ca it increases from 35 ppm in E-stage to 368 ppm in H-I stage (Table 5) because of Ca in hypochlorite. Na and K are eliminated by about half due to Cl_2 in hypochlorite as chloride while Mg, Fe and Cu remain practically uneffected. In H-II stage, Mg is, found to increase from 3.6 ppm (in H-I) to 17 ppm which remains as contaminant in hypochlorite. Ca, Na and K decrease substantially because of their forming chlorite salt solutions.

The metal contents in the same bamboo-hard wood in the pulp bleached with OC/DEoD sequence (Table 6) show higher values than the final pulp produced with CEpHH sequence excepting Mn.

Table-4

Catalyst contents in the pulp at different bleaching stages (in ppm)

Sample	Fe	Mn	Cu
Unbleached pulp	26.79	3.50	0.76
C	5.01	0.0177	0.39
E	37.89	0.24	0.44
H-I	36.91	0.48	0.44
H-II	44.84	0.57	0.41

Table-5

Metal contents in bleached pulp at different bleaching stages (in ppm)

Sample	Ca	Mg	Na	K
Unbleached pulp	103.84	91.97	337.65	194.79
C	10.46	3.26	62.16	24.89
E	34.83	3.62	1172.37	137.93
H-I	368.20	3.64	638.89	69.45
H-II	329.80	17.13	195.90	49.28

Table-6

Metal contents in OC/DEoD bleached pulp (in ppm)

Metals	Concentration
Fe	48.32
Mn	0.186
Ca	94.57
Mg	30.94
Na	202.46
K	50.62

It is also possible that because of increase in pH due to ClO_2 in place of 100% Cl_2, the suppression in metal level is less effective in the present case. However it requires further study to ascertain reason for this difference in metal contents of pulp bleached with CEpHH and OC/DEoD bleaching.

CONCLUSIONS

The metals involved in the raw materials for paper manufacturing vis-a-vis H_2O_2 decomposition and during bleaching stages can be classified as (a) Catalysts, and (b) Non catalysts.

Out of the C, E, H-I and H-II bleaching stages, C-stage pulp contains least amount of catalyst metals (Fe=5.01 ppm, Mn=0.0177 ppm, Cu=0.39 ppm) as well as noncatalyst elements (Ca=10.46 ppm, Mg=3.26 ppm, Na=62.16 ppm and K=24.89 ppm). These metals are considered as inherent or structural metals as they originate from raw materials. The total metal contents in the pulp after E, H-I and H-II stages increase because of exchange of additional amount of metals from external source. The amounts of exchanged metals in the final pulp of CEpHH pulping are: Fe=39.8 ppm, Mn=0.55 ppm, Cu=0.02 ppm, Ca=319.3 ppm, Mg=13.9 ppm, Na=133.7 ppm and K=24.4 ppm. The rate of exchange of metals to the pulp increases with increase in pH.

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