

# Part III : Inherent And Exchanged Metals For Efficiency Calculation Of Metal Eliminators

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## ABSTRACT

*Metal control in the bleaching process is explained to improve the optical properties of pulp and paper in the mills. Distinction between metals inherent from wood with non-exchangeable behaviour and exchangeable from external source has been brought out. The amounts of metals fixed onto the pulp at the 3 stages of CEHH bleaching sequence after chlorination, have been calculated using an empirical eqn.:*

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

*Where  $M_{\text{fixed}}$  = Metals fixed from external source by exchange mechanism,  $T$  = Total metal content of pulp and  $I$  = Inherent metals of the pulp. Histograms showing  $M_{\text{fixed}}$  values for Fe, Cu, Mn, Ca, Mg, Na and K are presented. The method of calculating efficiency of metal elimination process has been shown, SEM pictures of fibre surfaces with metal exchange sites are presented.*

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## INTRODUCTION

Metal elimination processes are invariably being incorporated in modern pulp and paper manufacturing units (1-4) in abroad. As these mills are aiming for zero effluent discharge (5-7) of complete recycling (8,9) of water, the accumulation of trace metals in the process liquor becomes significant and thus elimination of excess metals becomes a necessity. Harmful effect of excess metals is attributed to undesirable decomposition of  $H_2O_2$  at the extraction stage of bleaching process (10,11) with traditional  $CE_pH$  (H) sequence or with chlorine dioxide and ozone (12).  $H_2O_2$  is, quite costly compared to traditional bleaching chemicals and low concentrations of 0.2 - 0.3% are normally employed. The trace metals such as Fe, Cu and Mn present in the liquor, cause undesirable decomposition of  $H_2O_2$  and thus, its oxygenation efficiency for the pulp is reduced. In case of mechanical pulp, as much as one third of  $H_2O_2$  is reported to be lost because of such decomposition. Metal management in the system is therefore considered vital in manufacturing of kraft pulp and subsequently the papers.

Apart from these catalytic elements, metals such as Ca, Mg, Na and K are also present in the liquor but these are not considered deleterious. However, though these metals will not effect the decomposition kinetics of  $H_2O_2$ , they can remain on the fibre surface and reduce the optical properties of pulp. Presence of these noncatalytic metals in substantial amount is common in other bleaching stages such as extraction and hypo treatments.

## EXPERIMENTAL

The details of metal analysis in the pulp samples are given in Part-I (13). The unbleached pulp samples were collected from nearby paper mill which is based on bamboo : hard wood (80:20) as raw material with kraft process. The bleached samples are partly brought from the mill and partly produced in laboratory.

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## RESULTS AND DISCUSSION

The metals in the bleach liquors can

- (i) originate from the raw materials, or
- (ii) from the process.

In the present paper (i) will be termed as I as these metals are inherent in wood and (ii) will be termed as E, as these are from external sources namely from :

Water (W),

Pulping chemical (P),

Bleaching chemicals (B),

Due to corrosion of metal surface (S)

From various contaminants (C), and

Metals eliminated from the wood itself (W).

Thus, the total metal content (T) in the system is expressed as:

$$T = I + E \quad \text{----- (1) or more precisely}$$

$$T = I + (P+B+S+C+W) \quad \text{----- (2).}$$

The problem here is analysis of T, because of pulp analysis which can be done after converting into ash, and if the liquor is straightaway analysed, only E will be estimated. However, in view of reactions taking place on the fibre surface during any bleaching process, analysis of pulp for metal content will be more preferable than analysis in the liquor though both can give idea on the total metal content. Secondly, 1 of pulp represents not only the metal present in the wood and structurally bonded metals (M) but also those exchanged (X) on to the fibre surface from the liquor.

Therefore :

$$I = M + X \quad \text{----- (3) and}$$

$$T = (M+X) + (P+B+S+C) \quad \text{----- (4).}$$

The improvement in optical properties on washing with water and leaching with acid (HCl)

are shown in Table-1 and 2 respectively. Both these processes induce elimination of metals from the pulp and it may easily be inferred that metal removal brings an improvement in optical properties of pulp. In Table-1, the improvement in brightness by 4% EI in H-I stage and 4.6% EI at C-stage on washing is reported; the maximum P.C. No. (Post colour no.) reduction of 1.2 is found with H-II pulps. Results in Table-2 are, however extremely interesting with increase in brightness by 8.1% EI in H-I and P.C. No. reduction by 3.8 on leaching with HCl. Analysis carried out and reported in Part-I correspond decrease in not only catalytic but noncatalytic elements also.

| Sample                  | Increase in brightness<br>(% EI) | Decrease in P.C. No.<br>(No.) |
|-------------------------|----------------------------------|-------------------------------|
| Unbleached Pulp         | 3.3                              | -0.3                          |
| Chlorinated Pulp (C)    | 4.6                              | -0.1                          |
| Extracted Pulp (E)      | 1.1                              | -0.6                          |
| Hypotreated Pulp (H-I)  | 4.0                              | 0.1                           |
| Hypotreated Pulp (H-II) | 0.7                              | 1.2                           |

| Sample                  | Increase in brightness<br>(% EI) | Decrease in P.C. No.<br>(No.) |
|-------------------------|----------------------------------|-------------------------------|
| Unbleached Pulp         | 3.1                              | -0.4                          |
| Chlorinated Pulp (C)    | 3.7                              | -0.4                          |
| Extracted Pulp (E)      | 6.1                              | -0.8                          |
| Hypotreated Pulp (H-I)  | 8.1                              | 2.7                           |
| Hypotreated Pulp (H-II) | 1.4                              | 3.8                           |

Perusal of literature shows that any enhancement in optical properties of pulp has been accounted due to bleaching involving chlorination or oxidation of lignin, residual lignins of their converted organic compounds and nowhere the role of metals has been recognised.

The metal eliminators can work efficiently if required understanding and control can be made on these six different categories of metals and that too at all stages of a bleaching sequence.

It was observed previously in some plant materials that the structurally bonded metals cannot be eliminated without total decomposition of the fibrous cellulosic networks (14, 15). As the primary objective in paper manufacturing is to preserve the strength properties, very drastic chemical treatments to remove these structurally bonded metals can never be recommended. In fact, the most severe treatment stages in the bleaching sequence normally adopted in India (CE<sub>p</sub>HH) are the chlorination (C) and then hypo (H). In the chlorination stage, the pH can be as low as 2.5 and therefore, the metallic elements which can reside at such pH cannot be other than the structurally bonded. It may therefore be quite logical to take the metal contents of the bleached pulp to be only due to "M" and thus eqn. 4 becomes simply

$$T = K R_1 \quad \text{----- (6)}$$

As the pH in extraction as well as hypo treatment stages is alkaline, metal elimination from the fibre structure can not take place but this alkaline condition will be favourable for fixation of metals from the liquor to the fibres following to an exchange mechanism. The exchangeable metal ions remain in equilibrium between the fibre surface and the liquor. Based on the fibre surface characteristics, the metal ions are adsorbed or exchanged on to the fibres which finally become part of the pulp. During E, H-I and H-II stages thus eqn. (6) can be represented as:

$$T = K F_E \quad \text{----- (7)}$$

The amount of metals exchanged during these stages can be calculated from the difference of total metal contents of the pulp (T) and inherent metal content (I) i.e.;

$$M_{\text{exchanged}} = T - I \quad \text{----- (8)}$$

In a metal eliminator, M<sub>exchanged</sub> should be calculated at each stage and actions can be taken so as to minimize it. I being essentially not

exchangeable, only M<sub>exchanged</sub> can be controlled and the overall efficiency of a metal elimination process can be calculated. Estimation of metal contents in the liquor for deciding the efficiency may not be justified as the metals in the pulps during peroxide treatment as well as other stages are really important for the pulp optical properties.

The above assumptions that metal elimination becomes dominant at low pH and exchange of metals to fibres becomes favourable at higher pH have been shown experimentally to hold true in

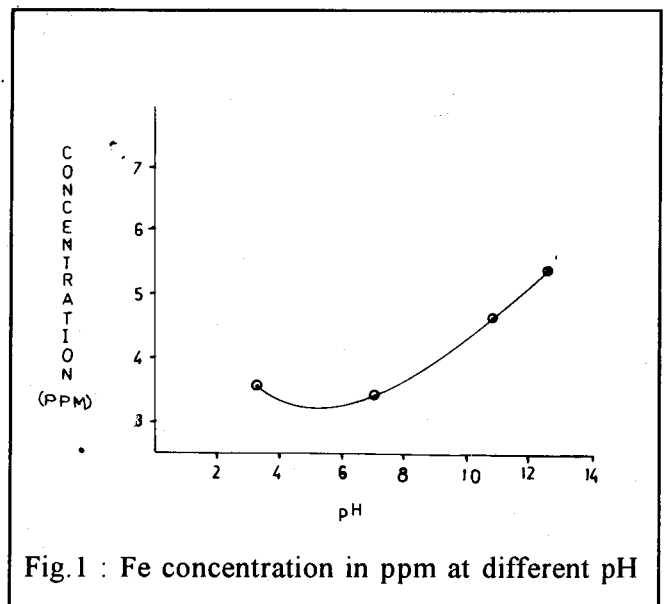


Fig. 1 : Fe concentration in ppm at different pH

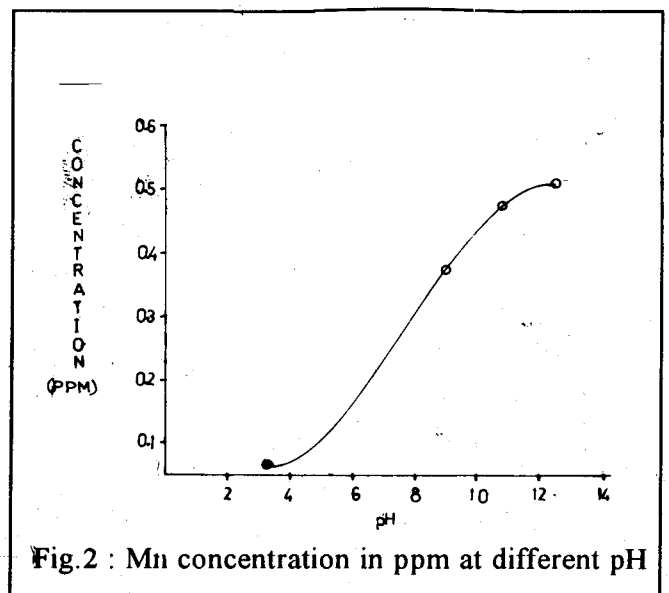


Fig. 2 : Mn concentration in ppm at different pH

and Fig.2. In Fig.1, Fe and in Fig. 2. Mn concentrations in the pulp have been plotted against pH from ~3 to ~13. According to the smoothed curves the fixation of metals takes place above pH of 7 and it increases with rise in pH. The range of pH <6, specially at pH of lower than 5, metal elimination becomes prevalent, more so at pH of 2.5 - 3 as in chlorination stage of paper manufacturing. Similar observation is made for Mn (Fig.2).

A corollary constant K can be fixed to denote T as

$$T = K (R_i + F_e) \quad \text{----- (5)}$$

Where R = Removal rate and F= Fixation rate.

On examination of the SEM micrographs in Figs. 3-5. on the nature of fibres, the release of trace metals from the fibres as well as fixation of metals from external source to the fibres can easily be conceived. The wood fibres are essentially made up of cellulose ( $\alpha$ ,  $\beta$  and  $\gamma$ ) and hemicellulose with lignin, pectin, carbohydrates, fatty acids, resins etc. (16, 17) and trace metals. Each fibre is constituted of primary, secondary and tertiary cell walls with lumen in the middle and lignin as cementing material in the middle lamella portion. It is presumed that the metals in the plant material (15) are bonded with varying bonding energy in the cellulosic structure, may be with lignins and therefore, release of metals from the surface will take place as the chlorine concentration will rise or pH will decrease.

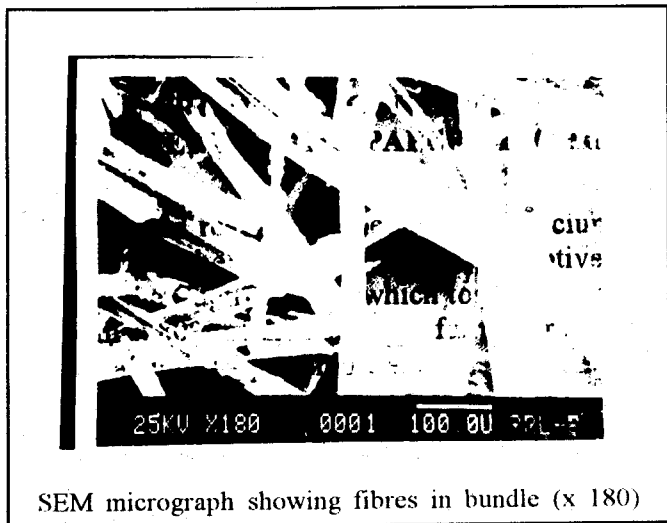


Fig.3

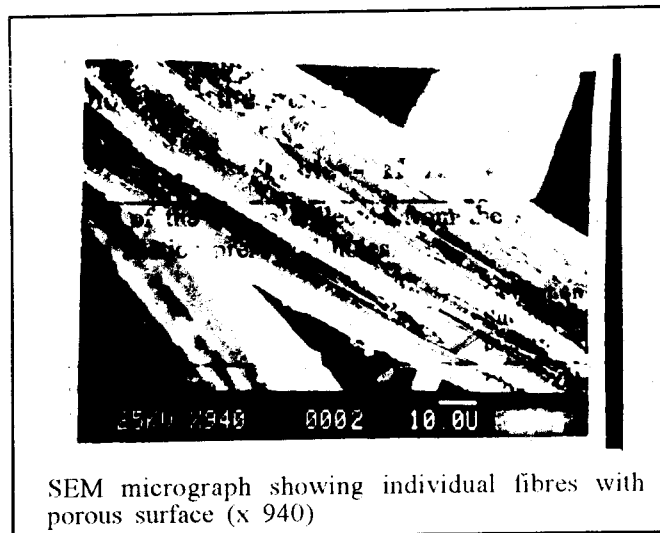


Fig.4

However, the metals which are bonded strongly will not be released from where the term "M" (structural metal) has been employed.

Fig. 3 is at low magnification of 180 X while Fig. 4 is at 940 X and Fig. 5 at 1500 X. Out of the many fibre bundles in Fig. 1, one is viewed in Fig. 2 showing the porous surface of fibres. Defibrillation takes place as delignification process advances during the bleaching stages. On further enlargement (Fig. 5), the cell structures are well evident over which exchange of metals is quite evident.

Now, using eqn. 8 and data in Part-I the  $M_{\text{fixed}}$  can be calculated at the three stages of

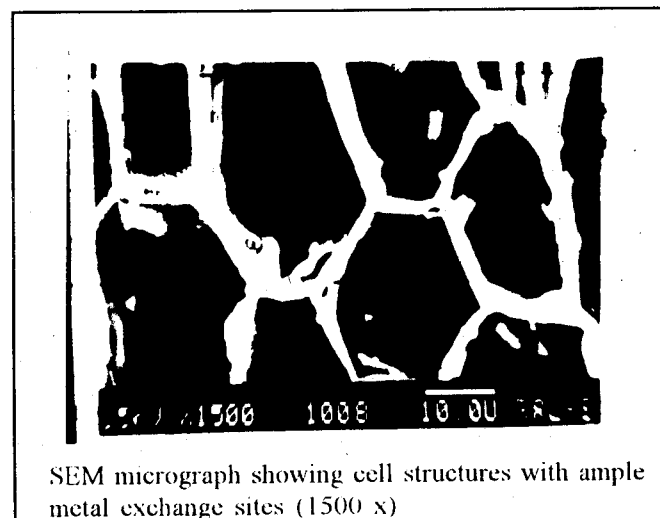


Fig.5

bleaching after chlorination stage in CEHH bleaching sequence. The calculated values for

increase (upto 0.55 ppm) compared to its low concentration at the initial stage. Amount of Cu is

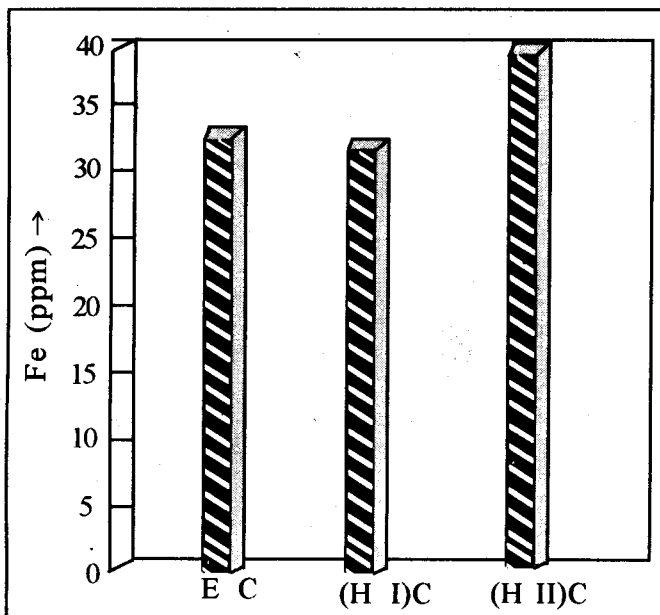


Fig.6

various metals are drawn in Fig. 6 to 12 for Fe, Mn, Cu, Ca, Mg, Na and K respectively. E represents extraction stage while H-I and H-II represent hypo-I and II stages. Fig.6 shows that Fe gets fixed to as high as 40 ppm in H-II stage which was ~33 ppm in E and H-I stages. The histogram in Fig.7 for Mn shows also significant

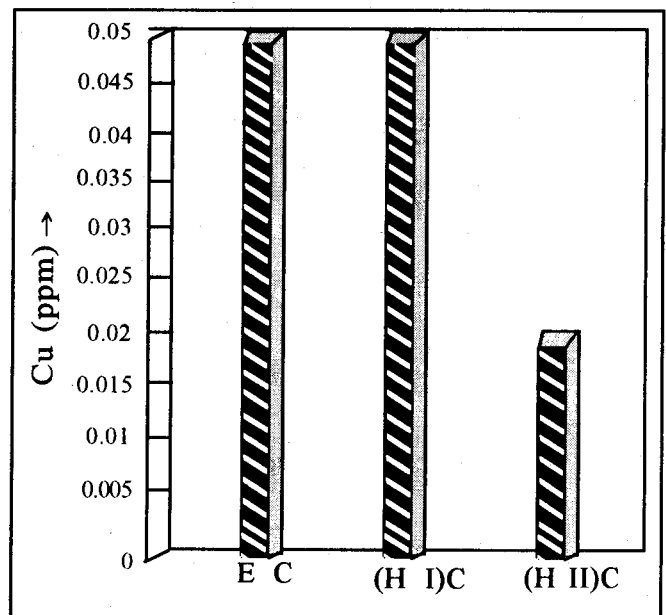


Fig.8

quite less but nevertheless the increase is significant at E and H-I stages (Fig.8). Calcium can be considered as macro element in the pulp (Fig. 9). During the extraction stage, little change is observed but in H-I and H-II stages, the amount of Ca ions exchanged is very significant (350 ppm). These are obviously due to carry over of Ca ions from Ca-

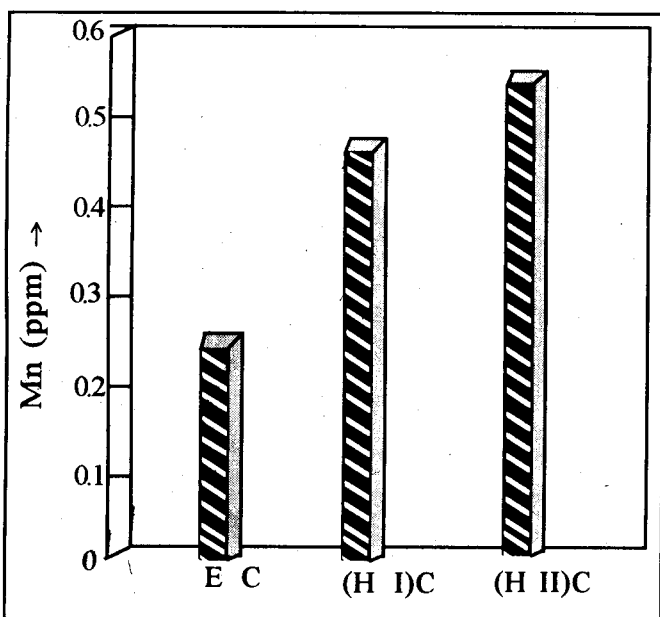


Fig.7

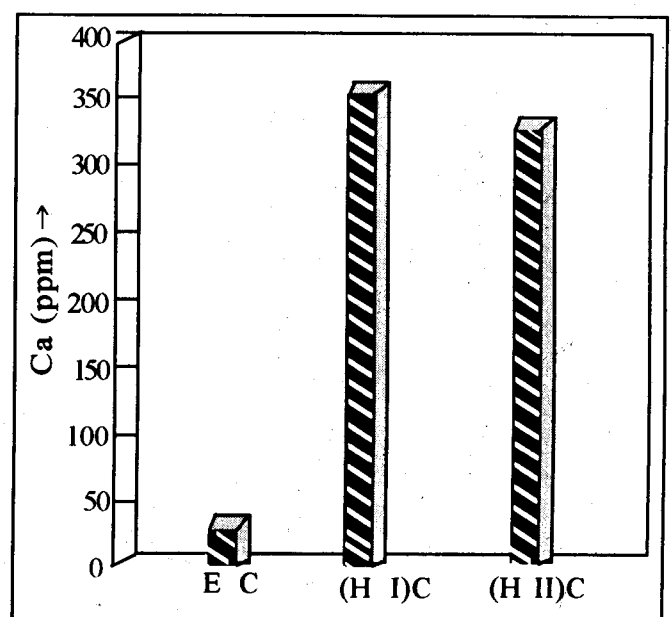


Fig.9

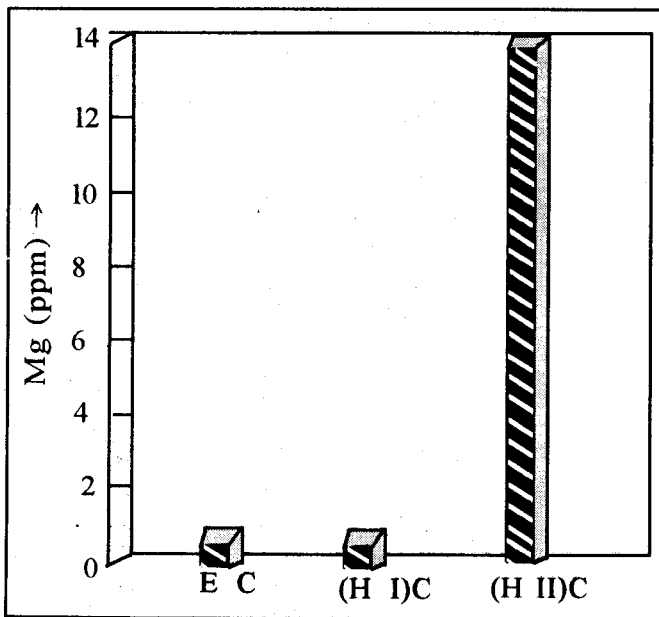


Fig.10

hypochlorite. Fixation of Mg ions is significant (14 ppm) surprisingly in H-II stages only (Fig. 10). Because of NaOH, in the extraction stage naturally Na-fixation (Fig. 11) can be maximum (1150 ppm) at this stage. In fact, the exchange capacity of extracted pulp can be indirectly known from this value. However, H-I and H-II cause removal of Na and  $M^{fixed}$  in H-II stage comes down to ~100 ppm. Similar trend as Na is observed for K

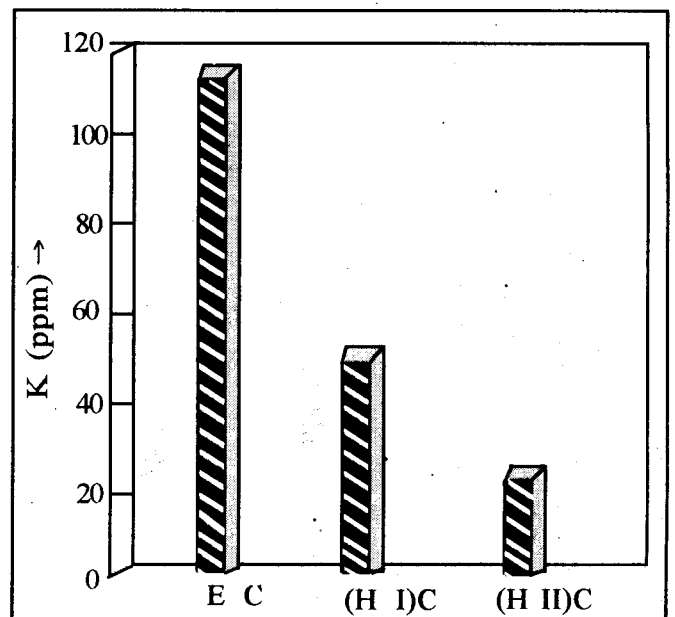


Fig.12

(Fig. 12);  $M^{fixed}$  is ~120 ppm in E stage which comes down to ~20 ppm at H-II stage.

Thus the  $M^{fixed}$  can be calculated with fairly good accuracy at all stages of bleaching and the overall metal elimination efficiency can be calculated. In the next part, it will be shown that on washing or leaching, the  $M^{fixed}$  can be removed and pulp with higher brightness can be obtained.

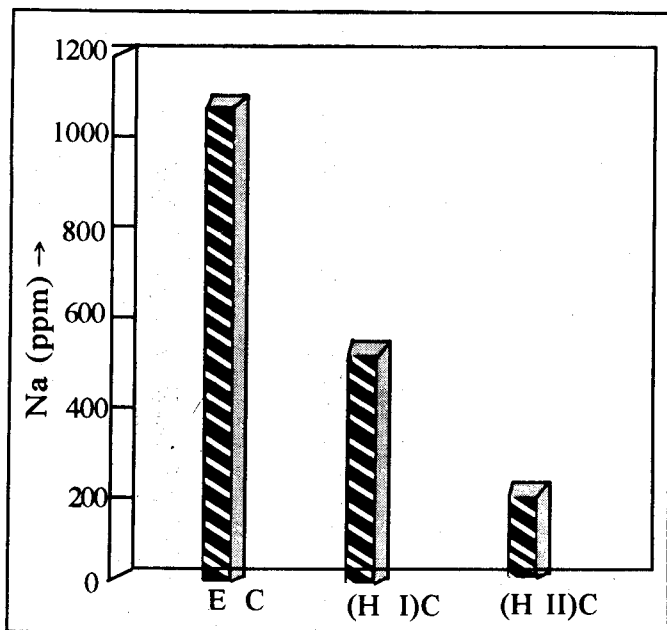
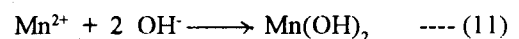
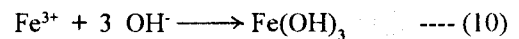


Fig.11

With increase in pH, the metal contents in the pulp increase because of precipitation of metals from external source. At low pH,  $Fe^{3+}$  and  $Mn^{2+}$  get eliminated as soluble chlorides from inherent metal source as follows:



At higher pH, the metals get precipitated as:



and remain fixed to the pulp. The Mn content increases more abruptly than Fe.

## CONCLUSIONS

The concepts of inherent (I) and exchanged (E) metals with reference to bleaching of pulp at different stages in CE<sub>p</sub>HH sequence has been explained using the eqn.:

$$T = K (R_I + F_E)$$

where T= Total metal content, K = Constant, R<sub>I</sub> = Rate of removal of I and F<sub>E</sub> = Rate of exchange of E.

M<sub>fixed</sub> has been calculated using eqn. M<sub>fixed</sub>=T-I.

Chlorination is the stage for metal elimination while extraction and hypo treatment stages are for metal fixation.

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