Effect of Some Metal Ions on Degradation of Cellulose in Alkaline Media

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ABSTRACT

The alkali cellulose, a reaction product of cellulose and sodium hydroxide, was aged under atmospheric oxygen in presence of different metal ions. The aging rate of sulphite and kraft pulps have been studied and shown in the kinetic curves of average degree of polymerization. Ag (I) showed the retarding effect on cellulose depolymerization whereas Fe (II) in lower concentration showed catalytic effect. The effect of higher concentration of Fe (II) on aging characteristic of alkali cellulose has also been studied.

INTRODUCTION

The viscose process may be divided into number of different stages viz. the pulp is converted into alkali-cellulose by treatment with sodium hydroxide. The alkali-cellulose is then shredded and aged at a controlled temperature for a definite time. During aging, the cellulose degree of polymerization (D.P.) decreases by a complex oxidation reaction involving the pulp, sodium hydroxide, atmospheric oxygen and the trace of metal impurities present in the pulp or in the sodium hydroxide solution. The second important stage is the treatment of aged alkali-cellulose with carbon-di-sulphide to form cellulose xanthate, which is dissolved in dilute alkali. solution to get viscose. Viscose is further ripened, filtered and deaerated. The third stage is the regeneration of cellulose in the form of fibres of film by extruding the viscose in acidic bath. The regeneration is effected by viscose viscosity and ripening index. Both parameters are important for final product quality. The ripening index can be controlled by temperature and time adjustment of viscose. However, viscosity control is more difficult as the viscose viscosity depends on the degree of polymerization of cellulose in the viscose at the required cellulose and NaOH contents. Cellulose D.P. is adjusted only at aging stage and correction of D.P. is not possible, once the viscose is prepared.

The aging of alkali-cellulose is an oxidative reaction, which is complicated phenominon due to presence of three hydroxyl groups in each chain unit since they have different reactivities and accessibilities towards the chemicals. However, the net cause of the oxidation is the shortening of chain length associated with weight losses. Similar oxidative reactions are also observed in alkaline peroxide bleaching of textiles[1] and oxygen bleaching of wood pulp[2, 3]. Normally the rate of oxidative depolymerization of cellulose during the aging of alkali cellulose can be controlled with temperature and catalysts. The depolymerization of cellulose during aging of alkali cellulose and oxygen bleaching of wood pulp have been studied by Samuelson et al[4] and others[5-9]. In both these processes, peroxide and free radical intermediates seem to play an important role. The transition metal ions are known[10-12] to be the effective oxidative catalysts in

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aging of alkali cellulose as well as in bleaching of pulp with oxygen or peroxides[13, 14] . The catalytic effect is quite complex and contradictory results have been reported by different workers[15, 16]. J.A. Matter[16] had studied the aging reaction but could not get any evidence of alkali cellulose oxidation by free radical mechanism as explained by Samuelson[4]. He postulated that alkali-cellulose oxidation is based on ionic intermediate formation.

It is known from the work of Entwistle et al[5] that the intital rate of oxygen consumption during alkali-cellulose aging, is proportional to the amount of reducing groups present in cellulose, as measured by its copper number. The aldehyde groups present in the cellulose acts as Lewis acid in alkaline media and forms complexes. These complexes are able to react with oxygen to form per hydroxyl ions[17], (equation 1 and 2).

The per-hydroxyl ion, that is formed by the initiation reaction of oxygen (equation-2) would result with the cellulose causing depolymerization. Kleinert[18] has shown that there is one rupture of cellulose chain for every per hydroxyl ion in alkaline media.

In viscose process, aging of alkali-cellulose is carried out by atmospheric oxygen but the exposure of alkali-cellulose to excessive amount of air is avoided, since it causes the formation of carbonates due to presence of CO_2 in air, resulting filtration and spinning difficulties[19]. To avoid such excessive exposure of atmospheric oxygen, for prolonged time it is preferred to use heavy metal salts such as manganese or cobalt to accelerate aging. Although, some metal ions have definite accelerating or retarding effect on degradation of cellulose but their effects on different type of pulps has not been attempted extensively.

The objective of present study is to investigate the effect of some metal ions on the process of aging of alkali-cellulose for different pulps and selection of most suitable metal catalyst to accelarate aging reaction for commercial process to save time and energy.

EXPERIMENTAL

Materials - Eucalyptus hardwood pulp made by sulphite pulping process (S-pulp) and kraft pulping process (K-pulp) were taken for this study. The S-pulp was in the form of sheets whereas the K-pulp was in the form of powder i.e. flash dried pulp. Sodium hydroxide solution of rayon grade quality was used for converting pulp into alkali cellulose.

Metal ions chosen for this study are:

(i)	Fe (II)	$(FeSO_4 . 7H_2O)$
(ii)	Co (II)	$(CoCl_2 . 6H_2O)$
(iii)	Mn (II)	$(MnSO_4 . 4H_2O)$
(iv)	Ag (I)	$(AgNO_3)$
(v)	Mg (II)	$(MgSO_4 . 7H_2O)$

The most of the chemicals used were of Analar (AR) grade from Qualigen or E-Merck chemicals.

Preparation of Alkali-Cellulose

The alkali-cellulose was made by treating the pulp with sodium hydroxide solution in the following way:

The steeping of pulp was carried out by slurry method. The slurry of pulp with 4% consistency was made in 18.3% sodium hydroxide solution at 45°C. The slurry was then pumped to a SUNDS' pilot plant press to make the cake of alkali cellulose by removing the excess of alkali-solution and pressing the cake to get desired composition of alkali-cellulose. The aqueous solutions of metal salts, under study were sprayed uniformly over the pressed alkali-cellulose cake.

Shredding

The pressed alkali-cellulose cakes were then shredded into a fluffy mass in a sigma blade shredder for atleast 3 hrs. During this period the temperature of mass was maintained to 40°C. The shredding efficiency was analysed by determining the bulk density of the shredded mass.

Aging

Oxidative depolymerization of cellulose takes place during the aging of alkali-cellulose in presence of atmospheric oxygen. The oxygen available from the air within the fluffy mass is sufficient to degrade the cellulose. The aging study of alkali-cellulose prepared from the above pulps was carried out in a container with provision of inter-mixing. The temperature was maintained by circulating hot water through the jacket of aging vessel. The exposure of alkali-cellulose to excessive amount of air was avoided to minimise the carbonate formation by carrying out the aging in a

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Parameters		S. Pulp	K. Pulp
Alpha cellulose	%	93.1	94.6
Solubility in 10% NaOH solution	%	8.8	6.3
Solubility in 18% NaOH solution	%	4.9	3.6
Copper Number	No.	1.00	0.70
Pentosans	%	2.70	2.80
Resin	%	0.22	0.40
Iron	ppm	12	34
Calcium	ppm	76	100
Silica	ppm	84	165
Manganese	ppm	0.2	0.25
Copper	ppm	0.15	0.2
Degree of polymerization	DP	885	740

closed container. The aging was carried out at 40°C with and without metal ions.

Viscosity measurements

The shredded alkali-cellulose was with hot distilled water to remove alkali. It was then treated with 1% acetic acid solution to neutralize the remaining alkali and washed throughly with distilled water. The thin sheets of approximately 0.70 gm of cellulose was prepared and dried in an oven at 105°C for 45 minutes. The control measurement showed that these treatments had no significant influence on viscosity data. The viscosity was then determined by making 1% cellulose in cuprammonium solution by TAPPI standard T-206 method, using a viscosity tube of 10-15 sec. efflux time with distilled water at 20°C. The degree of polymerization (D.P.) of the sample was calculated using following formula:

D.P. = (1000 log n - 400)

where n = viscosity of cellulose solution in centipoise (Cp).

The other constituents of pulp like alphacellulose, pentosans, resins, metal ions etc. are determined using Tappi standard methods.

RESULTS AND DISCUSSIONS:

The major constituents of pulp samples have been shown in Table-1. It shows that S-pulp has lower amount of resin and metal ions than K-pulp. The resin content in K-pulp is although high but it is within acceptable range (i.e. below 0.5%). The iron, calcium and silica content in K-pulp is higher than the S-pulp. The other metal ions in both the pulps are quite close to each other. The copper number, which is indicative to some functional groups like aldehyde or carboxyl caused due to degraded cellulose/ oxycellulose present in S-pulp is higher than that of the K-pulp. The composition of alkali cellulose prepared from these pulps are shown in Table-2. The cellulose and alkali in both the samples were kept nearly same so as to avoid the effect of alkali on depolymerization rate of cellulose. The influence of various metal ions on aging of alkali-cellulose has

TABLE 2: Composition of alkali - cellulose

Parameters		S. Pulp	K. Pulp
Cellulose	%	33.8 - 34.0	33.7 - 34.0
NaOH	%	15.7 - 15.8	15.7 - 15.8
Bulk - density	g/l	128 - 130	135 - 137

TABLE 3: Aging time required to get 300 D.P. of cellulose in alkali-cellulose with different metal ions.

(aging temperature = 40°C)

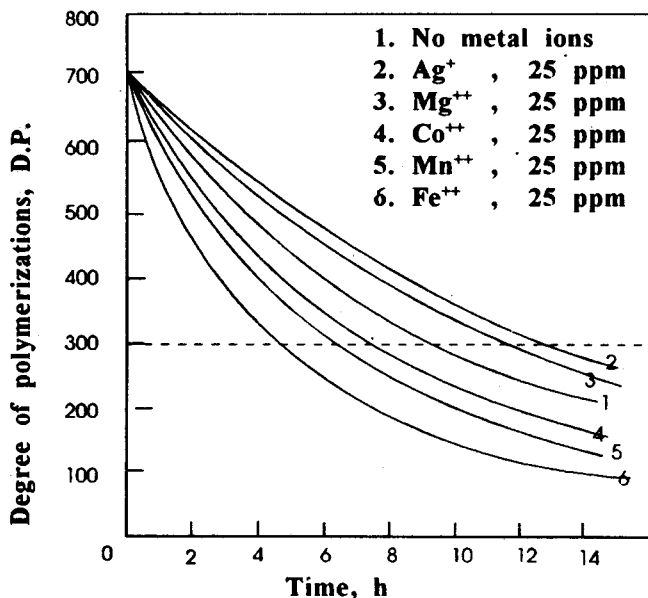| Metal ions	Aging time - h	
	S. Pulp	K. Pulp
Nil	8.0	10.0
Ag (I)	12.5	16.0
Mg (II)	11.0	13.0
Co (II)	7.0	8.0
Mn (II)	6.0	7.0
Fe (II)	5.0	5.5

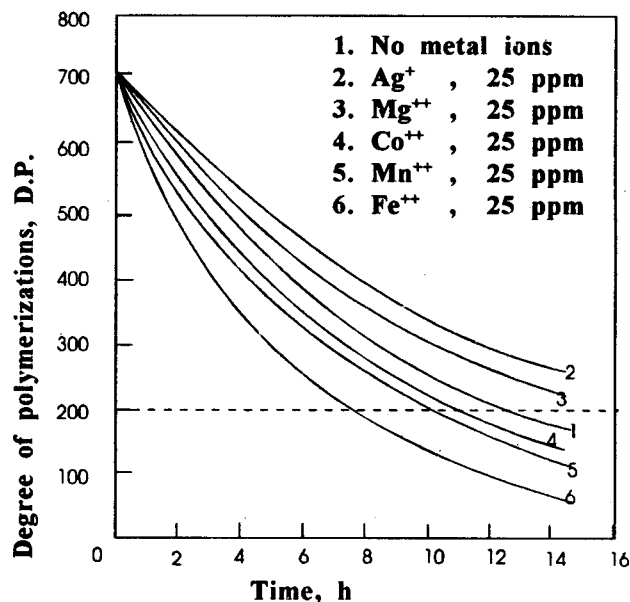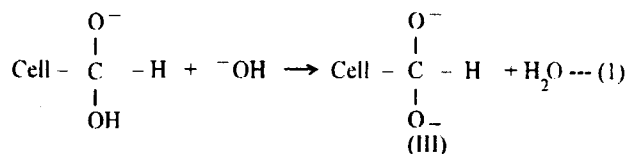Fig. 1: Effect of metal ions on aging of alkali-cellulose Aging temperature = 40°C, S - pulp.

1. No metal ions
2. Ag⁺ , 25 ppm
3. Mg⁺⁺ , 25 ppm
4. Co⁺⁺ , 25 ppm
5. Mn⁺⁺ , 25 ppm
6. Fe⁺⁺ , 25 ppm

Fig. 2: Effect of metal ions on aging of alkali-cellulose Aging temperature = 40°C, K - pulp.

1. No metal ions
2. Ag⁺ , 25 ppm
3. Mg⁺⁺ , 25 ppm
4. Co⁺⁺ , 25 ppm
5. Mn⁺⁺ , 25 ppm
6. Fe⁺⁺ , 25 ppm

been studied. The viscosity of regenerated cellulose after fixed interval of time was termined in each case under identical conditions of aging. Out of these metal ions, Fe (II) was found most drastic to reduce the cellulose viscosity in low concentration, whereas Ag (I) showed aging retardation effect. Co (II) and Mn (II) have more or less same degree of catalytic effect with both pulps. The effect of these metal ions on rate of depolymerization of cellulose are shown by kinetic curves of average degree of polymerization, in figs. 1 and 2. The different aging curves indicate that the intitial rate of depolymerization is much faster in S-pulp than K-pulp. Although, the iron content in original S-pulp is quite less than K-pulp but S-pulp showed higher rate of degradation. This can be co-related with higher values of copper number, which shows the amount of Oxycellulose and Carbonyl content present in that pulp. It can also be concluded that the rate of degradation of cellulose in alkali-cellulose during aging is higher with the pulp prepared by sulphite pulping method than the kraft pulping method, indicating that sulphite pulp contains more functional groups which are sensitive for chain scission reaction during aging under alkaline condition. Table-3 shows the aging times required to get desirable D.P of cellulose (i.e 300 DP) for normal viscose process at 40°C aging temperature with various metal ions. The data indicate that the time required to obtain 300 DP of cellulose in craft pulp is higher than the sulphite pulp. The aging time with Mn (II) is only 6 hours against 8 hours without Mn for S. Pulp. Similar effect was also observed with K-Pulp. Thus

by the use of suitable metal catalyst, substantial saving in aging time can be obtained:

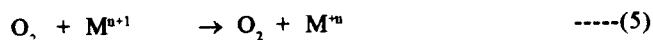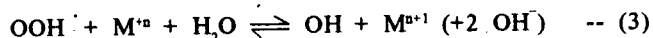The following mechanism of alkali-cellulose aging has been summerised by Matter[14] and Hermann[15].

1. The aldehyde groups of cellulose acts as a Lewis acid in alkaline media and form complexes II & III

$$Cell - C\underset{H}{\overset{O}{\lessgtr}} + {}^-OH \rightleftharpoons Cell - \underset{\underset{(II)}{OH}}{\overset{\overset{O^-}{|}}{C}} - H$$

$$(I)$$

$$Cell - \underset{\underset{OH}{|}}{\overset{\overset{O^-}{|}}{C}} - H + {}^-OH \rightarrow Cell - \underset{\underset{(III)}{O-}}{\overset{\overset{O^-}{|}}{C}} - H + H_2O \text{ --- (1)}$$

2. These complexes are able to react with oxygen to form perhydroxyl ions:

$$Cell - \underset{\underset{O-}{|}}{\overset{\overset{O^-}{|}}{C}} - H + O_2 \rightarrow Cell - C\overset{O}{\lessgtr}_O + OOH^- \text{ ---- (2)}$$
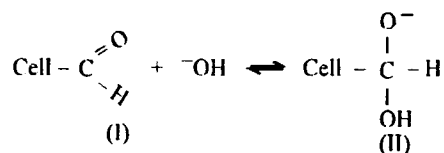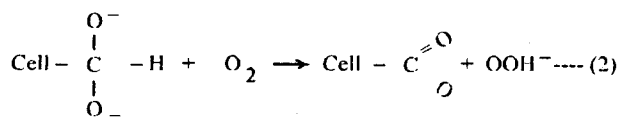
3. The perhydroxyl ions are complexed with metal ions to further catalyse the oxidation:

$$OOH^- + M^{+n} + H_2O \rightleftharpoons OH^- + M^{n+1} \ (+2 \ OH^-) \quad -- (3)$$

$$OOH^- + M^{n+1} \rightarrow O_2^- + M^{+n} \ (+H^+) \quad -----(4)$$

$$O_2 + M^{+1} \rightarrow O_2 + M^{+n} \quad -----(5)$$

The O_2 and M^{+n} are recycled in equation (2) and (3) respectively.

From the above discussions, it appears that the transition metal ion which has unpaired 'd' electrons in strong alkali solutions such as Fe (II), Co (II) etc. are more prone to react with perhydroxyl ions whereas metal ions like Ag (I) serve as an inhabitors since it has no unpaired 'd' electron in strong alkali solution.

The effect of iron on aging reaction of alkali cellulose was studied thoroughly and deploymerization nature has shown in Fig. 3. It can be seen that the viscosity of cellulose solution at different iron concentration on alkali-cellulose is different. An interesting nature of cellulose depolymerization in presence of iron was observed i.e at lower concentration of iron, the catalytic effect of depolymerization was increased but at higher concentration, this acted as an inhabitor and worked similar to Ag (I) or Mg (II) to retard the rate of depolymerization. However, the excessive use of iron produces the objectionable colour of alkali-cellulose as well as the fibre which is a serious drawback of final product of viscose process. Cobalt and manganese showed moderate catalytic effect
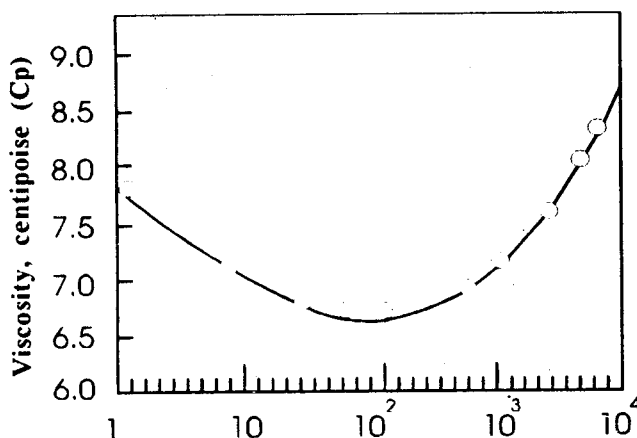
on degradation, (fig. 1 & 2) however, cobalt compound produces undesirable colouring effects on end products.

CONCLUSIONS:

From the afforesaid discussions, it can be concluded that different metal ions have different catalytic effect on depolymerization of cellulose during aging of alkali-cellulose. Iron being the most drastic at lower concentration. Silver and magnesium work as retardants to depolymerization whereas manganese and coblat have similar effect on catalytic depolymerization. Since cobalt produces some colouring effect, therefore, manganese (Mn) cab be used in the industrial viscose process to fasten the aging reaction under control condition.

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Fig. 1 Effect of Fe (II) on cellulose viscosity, during aging of alkali-cellulose.
Aging temperature = 40°C. time = 3 h, S - pulp.

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