Influence of sulfur compounds, manganese, and magnesium on oxygen bleaching of kraft pulp

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ABSTRACT

Kraft pulp from softwood, freed almost completely from metals by soaking with SO_2-water and EDTA, was oxygen bleached in the presence of different alkali sources, e.g., white liquor and oxidized white liquor. Sodium sulfide was found to affect the pulp quality adversely, while the influence of sodium thiosulfate was slightly favorable. The total amount of sulfur present during the bleaching appeared almost quantitatively in the spent bleach liquor, mainly as thiosulfate and sulfate. However, a large proportion of the sulfate that was formed during the bleaching could not be derived from thiosulfate. The addition of a substantial amount of manganese suppressed the depolymerization of the cellulose markedly, giving rise to increased selectivity, defined as the viscosity at a given kappa number. When magnesium protector was added in the molar ratio Mg:Mn = 10, a further gain in selectivity was obtained, but the rate of delignification was somewhat retarded.

Application:

Manganese removal from the pulp can be done during the oxygen bleaching, yielding a pulp that is easier to further bleach.

OXIDIZED WHITE LIQUOR HAS been used in place of sodium hydroxide, as an alkali source, in the oxygen delignification stage for many years. The use of oxidized white liquor maintains the mill's sodium balance when the spent bleach liquor is recycled to the recovery system. The white liquor is oxidized to convert the sulfide, which otherwise could adversely affect the pulp during the bleaching. However, the necessity of oxidizing the white liquor is disputed, since a very rapid conversion of sulfide is expected during the oxygen bleaching stage. Contradictory results have previously been reported *(1, 2).* Moreover, interactions between catalytically active transition metals and sulfur compounds can take place during the bleaching. This paper details the influence of varying sulfur compounds, e.g., sulfide and thiosulfate, on medium-consistency oxygen delignification. The influence of manganese and magnesium protector is investigated as well. For this reason, the unbleached pulp is first carefully purified by soaking to avoid the influence of other metals during bleaching and then impregnated with salt solutions of manganese and magnesium.

EXPERIMENTAL

Preparation of soaked pulp

Kraft pulp from softwood, consisting of *Picea abies* (70%) and *Pinus sylvestris* (30%), was washed with deionized and distilled water. To remove most of the magnesium, calcium, and catalytically active transition metals, the pulp was soaked with a solution of sulfur dioxide for 30 min at pH 2.5. After washing, the pulp was soaked at 5% consistency and pH 8.5 for 24 h in an ethylenediaminetetraacetic acid (EDTA) solution containing 6 g/L of the complexing agent. The pulp was then washed again, soaked with SO_2- water, and finally washed and centrifuged to a consistency of 31.5%. This pulp was used in all experiments. Analysis of the soaked pulp is given in **Table I.**

Preparation of alkali sources

To investigate the influence of varying sulfur compounds during oxygen bleaching, five different alkali sources, denoted A–E, were used in these experiments. Analyses of these liquors are given in **Table II.** The first liquor (A) was prepared by dissolving NaOH (105 g), Na_2CO_3 (20 g), and $Na_2S \cdot 9 H_2O$ (138 g) in distilled water to form 1 L of solution. This liquor had a composition close to that of a mill white liquor. Liquors B and C were prepared from liquor A by oxidation in 1500-mL rotating autoclaves for 20 and 60 min, respectively. The temperature during these oxidations was 100°C, and the initial oxygen pressure was 0.5 MPa, determined at 20°C.

The liquors were oxidized in 200-g portions. The initial molar ratio of O_2:S^{2-} during these oxidations was above 2, thus theoretically permitting all of the sulfide to be converted to sulfate. As can be seen in Table II, the sodium sulfide in liquor A was almost completely converted to other sulfur compounds, mainly thiosulfate, following the longer oxidation time, while 18% of the sulfide remained unconverted after the shorter oxidation time. Liquor B, with a large content of polysulfide sulfur (PS = S_nS^{2-}, n>0), had a dark brown color. Liquor C had a pale yellow color.

After preparation, these liquors were stored at 4°C in completely filled bottles and used in the oxygen bleaching experiments within 24 h. The results of the oxidations in Table II agree well with those obtained under alternative conditions *(3, 4).* As can be seen in Table II, the effective alkali (EA = NaOH + 0.5 Na_2S) in liquors A–C is approximately constant (slightly decreasing with increasing time of oxidation). For this reason, the addition of sodium hydroxide to the following

Kappa no.	Int. viscosity, dm^3/kg	Mg	Ca	Mn	Fe
17.8	965	0.044	0.027	0.0027	0.022
-	-	10.7	10.8	1.5	12.3

*Iron was mainly present in an inactive form in silicates *(10)*.

I. Analysis of the soaked kraft pulp. Metal concentrations are given in mmol per 100 g pulp (upper values) as well as in ppm wt./wt.*

Alkali source	NaOH, g NaOH/L	Na_2CO_3, g Na_2CO_3/L	Na_2S, g S/L	Na_2S_2O g S/L	PS[a], g S/L	Na_2SO_3, g S/L	Na_2SO_4, g S/L	EA[b], g NaOH/L
A	105.0	20.0	18.5	-	-	-	-	116.5
B	111.0	20.0	3.3	9.7	4.1	0.2	0.8	115.1
C	113.6	20.0	0.2	14.1	0.5	1.8	1.6	113.9
D	116.0	20.0	-	18.5	-	-	-	116.0
E	116.0	20.0	-	-	-	-	-	116.0

[a]PS = Polysulfide sulfur = $S_n S^{2-}$, n >0
[b]EA = Effective alkali = NaOH + 0.5 Na_2S

II. Analyses of alkali sources A–E

two solutions was increased. Liquor D, in which all of the sulfide in liquor A was replaced by one half the molar amount of thiosulfate, was prepared by dissolving NaOH (116 g), Na_2CO_3 (20 g), and $Na_2S_2O_3$ (46 g) in 1 L of distilled water. Finally, liquor E was prepared as a reference by dissolving NaOH (116 g) and Na_2CO_3 (20 g) to form a 1-L solution. Hence, liquor E is lacking in sulfur compounds. The concentrations of PS and sulfate in liquors B and C were determined gravimetrically [*(5)* and TAPPI T 624 cm-85, respectively], while the concentrations of other sulfur compounds, i.e., sulfide, sulfite, and thiosulfate, were determined iodometrically *(6)*. More than 98% of the sulfur present in liquors B and C appeared as PS, sulfide, sulfite, thiosulfate, or sulfate (Table II). The concentrations of NaOH, Na_2CO_3, and EA were determined by acidic titration (SCAN-N 2:63).

Oxygen bleaching

Samples corresponding to 20 g dry pulp were mixed with solutions of aqueous manganese (II) sulfate (when applied), aqueous magnesium sulfate (when applied), and distilled water. Finally, 5.0 g of one of the solutions (A–E) was added to obtain a pulp consistency of 10%. The oxygen bleaching was executed in three series, denoted 1–3. Series 1 is characterized by no additions of metal compounds to the pulp before the bleaching. Series 2 is characterized by the addition of 0.5 mmol manganese(II)sulfate per 100 g pulp (275 ppm wt./wt.) and series 3 by the addition of 0.5 mmol manganese(II)sulfate and 5.0 mmol magnesium sulfate per 100 g pulp (275 and 1215 ppm wt./wt., respectively) before the bleaching.

The oxygen bleaching was carried out in 1500-mL autoclaves at 100°C and an initial oxygen pressure of 0.5 MPa, determined at 20°C. The bleaches were terminated after 15, 30, 60, and 120 min (including the heating period to 100°C) by cooling the autoclaves in tap water. After releasing the pressure, the pulp was separated from the spent liquor by filtration through a 10 cm diameter Buchner funnel. The spent liquor was passed once through the filtercake to remove suspended particles. An aliquot of the spent liquor was passed through a coarse ultrafilter with a separation limit corresponding to a molecular mass of 100,000 (reported by the manufacturer, Amicon Inc., Beverly, MA). This separation limit also corresponds to an approximate effective diameter cutoff of 5 nm.

After washing the pulp with distilled water, the kappa number (SCAN-C 1:77) and the intrinsic viscosity (SCAN-C 15:62) were determined. The metal determinations in the spent liquors were carried out by atomic absorption, and the concentrations of total sulfur were measured on a sulfur determinator [SC 132 (Leco)]. Values for sulfate and thiosulfate in the spent liquors were determined gravimetrically and by potentiometric titration with mercuric chloride, respectively (TAPPI T 625 cm-85).

RESULTS AND DISCUSSION

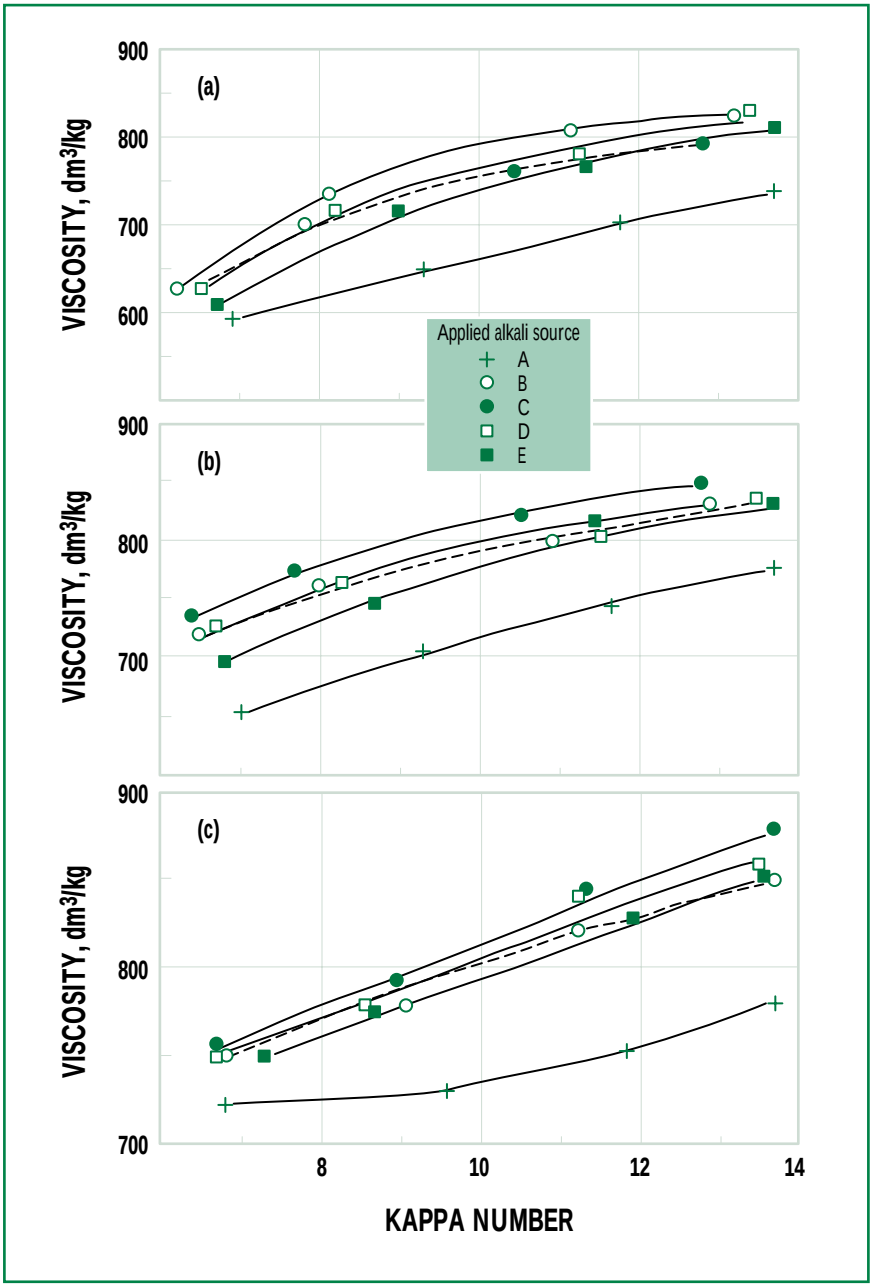
Selectivity

Figure 1(a) shows a plot of viscosity vs. kappa number after bleaching for 15, 30, 60, and 120 min, according to series 1 (no addition of metals). As can be seen in the figure, the lowest selectivity, defined as the viscosity at a given kappa number, was found after bleaches in which alkali source A was used. The loss in selectivity, as compared to the other bleaches in the series, resulted from increased depolymerization of the cellulose and a decreased rate of delignification. Hence, the sulfide initially present in liquor A adversely affected the selectivity. The differences between the other bleaches in the series were minor, although a slight loss in selectivity was observed when liquor E was applied, primarily due to a decreased rate of delignification.

Evidently, the presence of a large amount of thiosulfate during the bleaching (alkali source D) does not reduce the selectivity. The influence of PS is much more difficult to study, since these compounds are already quite unstable at room temperature and exist in a complicated equilibrium involving sulfides of varying chain lengths. However, the presence of small amounts of sodium sulfide and PS at the start of the bleaching do not seem to affect the selectivity (alkali source B). This is certainly due to a very rapid oxidation of these compounds in the initial stage of the bleaching. The pulp, e.g., the phenolic lignin, probably acts as a catalyst *(7–9),* and the initial molar ratio, O_2:S^{2-}, is about 500 when liquor B is used as the added alkali. The pulp viscosities in this series are markedly decreased in all bleaches after 60 and 120 min. This may be due to the catalytic effects of transition metals still remaining in the pulp after the soaking. Extremely small amounts of transition metals such as iron could also be present in the alkali sources *(10).*

When a large amount of manganese (0.5 mmol per 100 g pulp) was added before the oxygen bleaching (according to series 2), the depolymerization of the cellulose was greatly retarded in all bleaches after 60 and 120 min [see **Fig. 1(b)**]. The effect on the delignification rate was small. Similar results have been achieved under other conditions *(11–13).* Hence, the added manganese suppressed the catalytic effects of other transition metals, probably by favoring reaction paths that gave rise to reduced depolymerization of the cellulose.

The trend in this series is approximately the same as that obtained during bleaching without the addition of manganese [Fig. 1(a)]. Even in series 3, when both manganese (0.5 mmol per 100 g pulp) and magnesium (5.0 mmol per 100 g pulp) were added before the bleaching, the trend was, on the whole, unchanged [see **Fig. 1(c)**].



1. Influence of alkali sources A–E during oxygen bleaching of the soaked pulp. Original pulp kappa no: 17.8; original viscosity: 965 dm³/kg. (a) No additions of metals before the bleaching. (b) Addition of 0.5 mmol Mn per 100 g pulp (275 ppm wt./wt.) before the bleaching. (c) Additions of 0.5 mmol Mn and 5.0 mmol Mg per 100 g pulp (275 and 1215 ppm wt./wt., respectively) before the bleaching.

However, in this series, the depolymerization of the cellulose, as well as the delignification rate, was slightly retarded. It should be emphasized that all bleachings were carried out at a high alkalinity. The final pH values in the spent liquors, after bleaching for 15, 30, 60, and 120 min, were 12.7, 12.6, 12.4, and 12.0, respectively, for series 1 and 2, and 12.6, 12.5, 12.3, and 11.7, respectively, for series 3.

The results from series 1–3 clearly demonstrate that the selectivity is greatly impaired by the initial presence of a large amount of sulfide during the bleaching. Hence, it is necessary to at least partially oxidize the white liquor. The presence of a large amount of thiosulfate results in a slight gain in selectivity.

Series no.	Alkali source	TS	15 min $S_2O_3^{2-}$	15 min SO_4^{2-}	TS	30 min $S_2O_3^{2-}$	30 min SO_4^{2-}	TS	60 min $S_2O_3^{2-}$	60 min SO_4^{2-}	TS	120 min $S_2O_3^{2-}$	120 min SO_4^{2-}
1	A	0.44	0.21	0.09	0.46	0.17	0.20	0.45	0.13	0.22	0.45	0.10	0.26
1	B	0.49	0.26	0.10	0.47	0.23	0.22	0.48	0.15	0.25	0.49	0.11	0.28
1	C	0.48	0.28	0.11	0.46	0.20	0.19	0.45	0.17	0.22	0.48	0.15	0.26
1	D	0.49	0.31	0.03	0.48	0.26	0.05	0.47	0.21	0.08	0.49	0.18	0.10
2	A	0.45	0.21	0.10	0.47	0.18	0.19	0.48	0.15	0.23	0.45	0.13	0.27
2	B	0.45	0.26	0.10	0.49	0.23	0.16	0.47	0.20	0.19	0.45	0.18	0.22
2	C	0.44	0.31	0.10	0.46	0.28	0.14	0.44	0.25	0.17	0.46	0.23	0.20
2	D	0.44	0.39	0.03	0.49	0.37	0.06	0.47	0.33	0.08	0.44	0.31	0.11
3	A	0.49	0.26	0.08	0.48	0.24	0.11	0.47	0.23	0.26	0.49	0.21	0.28
3	B	0.44	0.25	0.10	0.45	0.22	0.15	0.46	0.20	0.21	0.44	0.19	0.22
3	C	0.44	0.26	0.10	0.44	0.23	0.17	0.45	0.22	0.21	0.44	0.21	0.22
3	D	0.46	0.39	0.02	0.49	0.36	0.03	0.47	0.34	0.08	0.44	0.28	0.10

*The amounts of sulfate added as $Mn(II)SO^4$ and $MgSO^4$ in series 2 and 3 are deducted.

III. Total sulfur (TS), thiosulfate, and sulfate in spent liquors* after bleaching for 15, 30, 60, and 120 min. Concentrations are given in g S/L

Total sulfur, thiosulfate, and sulfate in spent liquors

Assuming complete dissolution during bleaching of the sulfur compounds derived from each of the alkali sources (A–D), the concentration of total sulfur in the spent liquor would be 0.514 g S/L. As shown in **Table III,** most of the sulfur (86–95% of the added amount in all bleaches) was found in the spent liquors. The differences are all within the limits of experimental error. Thus, as expected, most of the sulfur could be recovered in the spent liquor. Most of this sulfur appeared as thiosulfate and sulfate. Thiosulfate was the dominating species after bleaching for 15 min, while sulfate already predominated in several spent liquors after 60 min. Other sulfur compounds, e.g., polythionates, might be present as well. Conspicuous in this respect is trithionate, since higher polythionates readily decompose under many conditions to yield trithionate *(14).* As previously mentioned, it is likely that the oxidation rate of sulfide is increased in the presence of organic matter, e.g., phenolic lignin. When alkali source D was used, however, the formation of sulfate was markedly lower than in the bleaches in which other sulfur-containing alkali sources were applied (Table III).

To investigate the influence of pulp during the oxidation of sulfide and thiosulfate, two further experiments were carried out in the absence of pulp. Five grams of alkali source A and D, respectively, were each diluted with distilled water to 200 g and were oxidized separately for 60 min under the same conditions described previously. Hence, the molar ratio O_2:S^{2-} was the same as during the bleachings, i.e., approximately 100. After these oxidations, 47% of the total amount of sulfur in the liquor appeared as sulfate when alkali source A was applied, while only 4.8% was found as sulfate when alkali source D was applied. Thus, the formation of sulfate was nearly ten times as high in the former case. These results should be compared to the values in Table III, where 42–51% of the total sulfur in alkali source A appeared as sulfate in the spent bleach liquors after bleaching for 60 min. The corresponding value was 16% when liquor D was applied. Evidently, a great deal of the sulfate formed during the bleaching could not be derived from thiosulfate, although an increase in the formation of sulfate from thiosulfate occurred in the presence of pulp. Moreover, the thiosulfate seems to be better preserved in the presence of manganese and magnesium during bleaching (series 2 and 3). Thiosulfate is known to react with peroxides (which are formed initially and throughout an oxygen bleaching stage), according to the following reaction:

$$2\ S_2O_3^{2-} + 4\ H_2O_2 \rightarrow S_3O_6^{2-} + SO_4^{2-} + 4\ H_2O \qquad (1)$$

Also, magnesium compounds are well known to retard the decomposition of peroxides in alkaline media. The presence of magnesium compounds during the bleaching therefore could result in enhanced concentrations of thiosulfate. The in-

Series and alkali source	15 min		30 min		60 min		120 min	
	Mg	Mn	Mg	Mn	Mg	Mn	Mg	Mn
2A	-	0.055	-	0.062	-	0.065	-	0.073
2B	-	0.058	-	0.069	-	0.076	-	0.073
2C	-	0.055	-	0.060	-	0.060	-	0.069
2D	-	0.047	-	0.056	-	0.055	-	0.065
2E	-	0.055	-	0.069	-	0.078	-	0.078
3A	0.86	0.084	1.11	0.144	1.23	0.182	1.40	0.218
3B	0.91	0.084	1.22	0.126	1.58	0.171	2.00	0.212
3C	0.95	0.045	1.44	0.118	1.56	0.155	1.85	0.182
3D	0.91	0.085	0.99	0.109	1.07	0.146	1.40	0.158
3E	0.91	0.095	1.07	0.122	1.77	0.182	2.06	0.222

IV. Magnesium and manganese compounds in spent liquors after bleaching for 15, 30, 60, and 120 min. Metal concentrations are given in mmol/L.

Series and alkali source	15 min		30 min		60 min		120 min	
	Mg	Mn	Mg	Mn	Mg	Mn	Mg	Mn
2A	-	0.055	-	0.062	-	0.065	-	0.073
2A	-	0.011	-	0.011	-	0.015	-	0.018
2B	-	0.011	-	0.024	-	0.018	-	0.018
2C	-	0.015	-	0.015	-	0.015	-	0.018
2D	-	0.015	-	0.018	-	0.018	-	0.018
2E	-	0.005	-	0.016	-	0.016	-	0.020
3A	0.025	0.002	0.029	0.002	0.058	0.004	0.082	0.013
3B	0.016	0.002	0.025	0.002	0.060	0.004	0.196	0.011
3C	0.016	0.002	0.021	0.002	0.053	0.004	0.210	0.011
3D	0.037	0.002	0.045	0.005	0.062	0.005	0.210	0.016
3E	0.016	0.002	0.016	0.002	0.049	0.004	0.122	0.011

V. Magnesium and manganese compounds in the ultrafiltrates of the spent liquors after bleaching for 15, 30, 60, and 120 min. Separation limit of the ultrafilter corresponding to a molecular mass of 100,000. Metal concentrations are given in mmol/L.

creased concentrations of thiosulfate in the spent liquors, found in the presence of manganese only (series 2), are more puzzling. More exhaustive investigations are required to explain these observations. The trithionate formed in Eq. 1, which also could be formed in other reactions, is probably negligible in the oxidized white liquor, since it is much less stable at higher hydroxide ion concentrations, according to the following reaction:

$$2\ S_3O_6^{2-} + 6\ OH^- \rightarrow S_2O_3^{2-} + 4\ SO_3^{2-} + 3\ H_2O \qquad (2)$$

This reaction could also explain in part the slight loss in EA during the oxidations of white liquor (Table II) *(3).*

MAGNESIUM AND MANGANESE IN SPENT LIQUORS

Manganese in spent liquors from series 2

In the spent liquors from series 2, the concentrations of manganese were low, without exception (**Table IV**). If a complete dissolution of the added manganese (0.5 mmol per 100 g pulp) is assumed, then the concentration in the spent liquor would be 0.56 mmol/L. As shown in Table IV, the largest proportion of manganese in the spent liquor was 14.1% of the added amount. The amounts of manganese in the spent liquors increased slightly with increasing bleaching time, due to the formation of organic complexing agents, e.g., hydroxy acids.

The proportions of manganese in the filtrates from ultrafilter 100,000, present as colloids and low-molecular complexes, were very low (**Table V**). Thus, most of the manganese in the spent liquors was found in large colloids. The missing proportion of manganese in the spent liquor, calculated as the difference between the added amount and the amount found in the spent liquor, is either bound to the pulp, which is itself a good chelating agent for manganese at high pH values *(15),* or is present in colloids and aggregates of such large dimensions that they are retained by the filtercake when the spent liquor is passed through. As expected, the sulfur compounds present in most bleaches do not seem to form any soluble complexes with manganese, since the proportion of manganese in the spent liquor is not increased in the presence of soluble sulfur compounds.

Magnesium and manganese in spent liquors from series 3

When both magnesium and manganese were added in a molar ratio of 10:1, the amounts of manganese in the spent liquors were markedly increased (Table IV) due to coprecipitation of manganese with magnesium compounds, e.g., magnesium hydroxide, which later will be partially transferred into the liquor phase during the

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bleaching. In most spent liquors, the proportion of dissolved manganese paralleled the proportion of dissolved magnesium. Still, the largest dissolved proportion of manganese was only 40.0% of the added amount.

It should be emphasized that the concentrations of manganese in the ultrafiltrates (Table V) were lower when magnesium was added, compared to the ultrafiltrates from series 2. Hence, nearly all of the manganese in the spent liquors from series 3 appeared in colloids of large dimensions. The concentration of magnesium was enhanced with increasing bleaching time, mainly due to an increased solubility of precipitated hydrated magnesium oxides when the concentration of hydroxide ions was decreased *(16, 17)*. Yet, even after bleaching for 120 min (pH = 11.7), only a minor portion of the added magnesium was present in the spent liquor. An increased dissolution of magnesium and manganese during the bleaching could be obtained by a reduction in the added alkali (the final pH should be about 10.0 for a complete dissolution) or by the addition of complexing agents, e.g., hydroxy acids or EDTA *(18)*.

CONCLUDING REMARKS

The initial presence of a large amount of sodium sulfide during oxygen bleaching resulted in a dramatically impaired selectivity. It therefore is necessary to oxidize the white liquor, at least partially, before entering the oxygen bleaching stage. In fact, a conversion of 82% of the initial amount of sodium sulfide in the white liquor was found to be sufficient to produce a satisfactory selectivity after bleaching. The sodium thiosulfate formed during the oxidation had a slightly favorable influence on the selectivity. After bleaching for only 15 min, the total amount of sulfur present in the bleaches appeared almost quantitatively in the spent liquor, mainly as thiosulfate and sulfate. Only a minor portion of the sulfate formed during the bleaching could be derived from thiosulfate. Thus, other reaction paths must be primarily responsible for the formation of sulfate under these conditions.

A substantial addition of manganese improved the selectivity due to a decreased depolymerization of the cellulose. The concentrations of manganese in the spent liquors from these bleaches were low. When magnesium protector was added in a molar ratio Mg:Mn = 10, the depolymerization, as well as the delignification, was slightly retarded. The proportion of manganese in the spent liquors was markedly enhanced in the presence of magnesium. This manganese appeared almost completely in colloids of large dimensions. Apart from the increased amounts of thiosulfate in the spent liquors, interactions between metals and sulfur compounds produced no observable effects. **TJ**

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