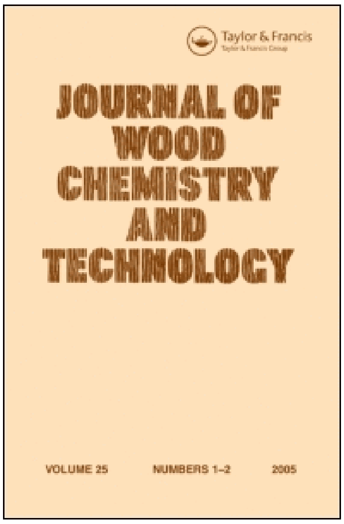

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Behavior Of Calcium, Magnesium and Manganese Compounds During Oxygen Bleaching of Kraft Pulps

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BEHAVIOR OF CALCIUM, MAGNESIUM AND MANGANESE COMPOUNDS DURING OXYGEN BLEACHING OF KRAFT PULPS

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ABSTRACT

During oxygen bleaching of kraft pulps manganese compounds can, depending on their amounts, the charges of sodium hydroxide and of magnesium protector, and on the presence of trace amounts of catalytically active transition metals retard or promote the depolymerization of the cellulose. The present report deals with pulps pretreated with 2 % nitrogen dioxide. As shown in forthcoming papers similar results were obtained with pulps without pretreatment with nitrogen compounds.

Pretreatment with nitrogen dioxide at 80°C followed by washing with water removed about 95 % of the magnesium and manganese from kraft pulps. Subsequent oxygen bleaching for 180 min removed 40-90 % of the calcium remaining in the pretreated pulps. Produced hydroxycarboxylate ions gave rise to low molecular complexes of calcium and of magnesium, added as protector. Competition for complexing ligands contributed to a decreased dissolution of calcium with increasing addition of magnesium. When magnesium was applied large amounts of colloids of polynuclear magnesium species were produced. These contained lignin fragments and less abundant metal compounds such as manganese and calcium.

Wet oxidation of both low molecular complexing agents and of organic fragments of larger size contributed to a decreased or unchanged concentration of low molecular metal complexes and metal compounds linked to the colloids with hydrated magnesium oxide as the main constituent. The conditions which favored the wet oxidation were similar to those which led to an increased attack on the lignin and carbohydrates in the fibers and thus promoted the dissolution of low molecular metal complexes and the formation of metal ions containing colloids. Under certain conditions precipitation of sparingly soluble manganese compounds of oxidation states higher than +2 had a predominant influence on the concentration of manganese in the liquor.

INTRODUCTION

After successful application for more than two decades it has now been generally recognized in most countries that oxygen has to be used as bleaching agent in at least one stage to achieve an economically feasible process for production of fully bleached pulp without unacceptable water pollution. An optimization of the bleaching process with recovery and burning of spent liquors from the oxygen bleaching together with the spent cooking liquor requires a better knowledge of the simultaneous presence in the liquor of varying amounts of metal compounds from wood and other sources. When spent liquors from the final bleaching are included in the recovery system, additional complications can be expected.

The main purpose of this report is to elucidate the recirculation of magnesium compounds applied to protect the cellulose and of liquors containing manganese compounds which have to be taken into consideration in attempts to approach a closed recovery. The experiments are restricted to oxygen bleaching of pulps pretreated with nitrogen oxides. The most prominent advantage gained by this process is a modification of the lignin which leads to an increased delignification rate and a retarded attack on the cellulose during the subsequent oxygen bleaching[1]. The nitric acid produced as an intermediate during the pretreatment can dissolve metal compounds from the pulp[2,3]. This can give rise to a gain in selectivity but also to negative effects which are known too little[4]. Similar effects can occur also in other bleaching sequences of current interest, e.g.in stages with peroxide or ozone.

EXPERIMENTAL

Two softwood pulps (mainly from Pinus sylvestris) produced in a Swedish kraft mill were impregnated with 11.1 g industrial black liquor[3] and 46 mmol sodium nitrate per 100 g pulp. After removal of air the pulp was brought in contact with 2 % NO_2 at 27 % consistency and 60°C. After 15 min a diluent simulating spent liquors from the pretreatment, heated to 60°C, was introduced so that the consistency decreased to 8 %. The diluent contained nitric acid corresponding to 10 or 20 mmol free nitric acid[5] and 184 mmol sodium nitrate per 100 g pulp. The pulp suspension was heated to 80°C in 20 min and ripened for 0-180 min at this temperature. The pulp was filtered off and liquor samples withdrawn for analyses before washing with deionized water and pressing to about 30 % consitency.

The oxygen bleaching was carried out in 1500-ml autoclaves rotated in a polyclycol bath preheated to the reaction temperature (106°C). The oxygen pressure was 0.6 MPa determined at 22°C. The reported additions were calculated on 100 g dry untreated pulp. The solutions of magnesium and manganese(II)sulfate were impregnated into the pulp before adding the solution of sodium hydroxide (pro analysi grade).

The liquors reported on in the present paper were produced in a previous investigation on the influence of metal compounds on the delignification and depolymerization of the cellulose during the oxygen bleaching[6].

After reaction periods from 20-240 min the oxygen bleaching was terminated by rapid cooling in tap water. Reproducible results were not obtained with a shorter duration than 20 min (including the heating period) in the oxygen bleaching. The pulp suspension in the autoclaves was transferred to a Buchner funnel. The filtrate was passed twice through the filter cake of pulp to remove undissolved material. The spent liquor was brown in color and weakly opalescent. A precipitation occurred when the spent liquors from bleaches with magnesium addition were kept at room temperature for a few days. To avoid errors due to the precipitation all liquors were analyzed shortly after the sampling.

Two aliquots were passed through ultrafilters with nominal separation limits corresponding to a molecular mass of 10000 and 1000 respectively (reported by the manufacturer, Amicon Corp. Lexington, Mass.). The ultrafiltrates were clear (to the naked eye). A large proportion of the brown-colored solutes was retained on the coarse ultrafilter. The ultrafiltrate from the tighter filter was yellow. A comparison with results obtained by gel permeation chromatography[7] shows that the colored organic material removed by ultrafiltration consisted mainly of lignin fragments.

The results of the ultrafiltrations are reported as the concentrations of calcium, magnesium and manganese in the ultrafiltrates (mmol per liter) or as a percentage of the total concentration found in the spent liquor separated from the pulp at ambient temperature. Small amounts of these metal ions were present already in the ultrafiltrates from the spent liquors obtained after bleaching for 20 min. The concentrations of magnesium and manganese were not reproducible and only results with ultrafiltrates from bleaching for 70, 120 and 240 min will therefore be reported.

All determinations of the metal ions were carried out by atomic absorption.

RESULTS AND DISCUSSION

Dissolution of Metal Ions during Pretreatment

The pretreatment with NO_2 gives rise to an extremely rapid formation of nitric and nitrous acids. These can dissolve various metal compounds present in the pulp and react with the

TABLE 1

Dissolution of Magnesium, Manganese, Calcium and Iron during Pretreatment of pulps[a] U1 and U2 including Ripening at 80°C. Addition of Nitric Acid corresponding to 20 mmol per 100 g Pulp.

	Metal compounds (total)				Dissolution %, calc. from analysis of			
	mg per kg pulp		mg per kg liquor		liquor[b]		pretr. pulp[b]	
	U1	U2	U1	U2	U1	U2	U1	U2
Mg before pretr.	261	276						
Mg after pretr.	15	16	21.8	23.8	95.5	98.6	94.3	94.2
Mn before pretr.	79	70						
Mn after pretr.	5.3	3.9	6.7	6.0	96.3	97.2	93.4	94.5
Ca before pretr.	1903	1360						
Ca after pretr.	136	87	154	111	92.9	93.6	93.0	93.7
Fe before pretr.	31	27						
Fe after pretr.	14	13					55	52

a. Kappa no. and intrinsic viscosity according to SCAN: Pulp U1 28.5 and 1173 dm^3/kg; Pulp U2 24.3 and 1149 dm^3/kg.

b. The trace amounts present in the black liquor were added to the amounts in the pulps before pretreatment.

lignin resulting in a regeneration[2] of NO$_2$ and other active nitrogen compounds.

As shown in Table 1 the proportions of dissolved metals calculated from the liquor analysis differed only slightly from those obtained from the analysis of the pretreated pulp.

As expected an almost complete removal of magnesium and manganese occurred during the pretreatment[2]. Both types of metal compounds are mainly derived from the wood. Calcium which is in part derived from the limestone applied in the recovery system was removed to more than 90 % while about 50 % of the total iron content in the untreated pulp remained after the pretreatment. A similar behavior of iron compounds in industrial wood pulps has

TABLE 2

Influence of the addition of free Nitric Acid and of the Ripening Time at 80°C on concentrations in the Liquor of Magnesium, Manganese, Calcium and Iron during Pretreatments with 2 % NO_2.

Free HNO_3 mmol per 100 g pulp	Ripening time min	pH in liquor	Liquor concentrations Mg	Mn	Ca	Fe
			milligram per liter			
10	0	1.9	21	7.0	133	0.3
10	30	2.0	20	6.6	139	0.35
10	90	2.2	20	7.0	111	0.75
10	180	2.3	20	7.1	123	0.9
20	0	1.9	19	7.0	119	0.35
20	30	2.0	19	6.5	113	0.55
20	90	2.1	20	7.0	113	0.9
20	180	2.2	21	7.1	120	1.0

been observed during other treatments in acid media and has been ascribed to silicate particles from the mill water. Fortunately, iron compounds of this type exert a negligible catalytic activity during oxygen/alkali treatments of wood pulp compared to that of the iron compounds which are easily dissolved in weakly acid media[8,9]. The investigated kraft pulps exhibited a very similar behavior during the pretreatment.

A kraft pulp of the same type was used in the pretreatments given in Table 2 which shows the effect of the added amount of nitric acid during pretreatments for varying lengths of time. It is noteworthy that an increased addition from 10 to 20 mmol free nitric acid per 100 g dry pulp had no significant influence on the concentration of magnesium and manganese compared at the same ripening time[3,5]. The effect on the dissolution of calcium was small while a modest increase in the dissolved proportion of iron was obtained.

To simulate the carry-over of black liquor all pretreatments were started with pulp impregnated with diluted black liquor. Within 2 min after the introduction of the nitrogen dioxide at 60°C the pulp became acid due to produced nitric and nitrous acids. In addition organic acids were formed in lignin and carbohydrate reactions[10]. After the dilution to 8 % consistency, with a solution of sodium nitrate in dilute nitric acid simulating spent liquor from the pretreatment, the suspension was heated to 80°C and ripened at this temperature. As a result of the generation reactions[11] which convert nitric acid to nitrogen dioxide and other active nitrogen compounds the pH increased markedly already before the final ripening temperature was reached[3]. The generation reactions are favored by high concentrations of both nitrate and hydrogen ions. This explains the observation that, after a given duration of the ripening at 80°C, the pH in the pretreatments with the larger addition of nitric acid was about the same as found with the smaller addition. The pH-values in Table 2, potentiometric titration and kappa numbers found after similar pretreatments permit the conclusion that generation reactions continued at an appreciable rate when the residence time was increased from 90 to 180 min. The small effect of the continued regeneration on pH is explained by the formation of organic acids[3].

Table 2 shows that no appreciable change in the concentrations of magnesium and manganese occurred by the increased duration of the ripening. The dissolution of these compounds was virtually complete already during the heating period. In both series of pretreatments the calcium concentration was somewhat higher at the beginning of the ripening at 80°C than after 90 min. The concentrations increased during the period 90-180 min. It should be emphasized that the calcium concentrations were so high that precipitation of various sparingly soluble calcium salts can be anticipated. The formation of the corresponding acids and their destruction on prolonged treatment as well as formation and destruction of complexing ligands during the pretreatment can explain the observed changes in the calcium concentrations. It can be mentioned that oxalic acid is among the produced organic acids.

As already mentioned the proportion of dissolved iron was much lower than that of the other metal compounds. Table 2 shows that the rate of dissolution of iron compounds was low compared to the dissolution rates of the other metals. This supports our conclusion that a large proportion of the iron was present in silicates.

Dissolution during the Oxygen Bleaching

Unless special precautions are taken, metal compounds dissolved during the pretreatment will in a virtually closed system be recycled and transferred to the other stages in the bleaching sequence and into the digestion. Oxygen/alkali treatments of cellobiitol[9], and kraft pulp soaked with SO_2-water and complexing agents[12] show that the rate of attack on the carbohydrates and the delignification can be affected dramatically by the simultaneous presence of manganese and magnesium. This has been confirmed in our recent paper which includes a detailed study on the behaviour of calcium ions. As mentioned above the metal analyses and studies of the properties of the spent liquors, reported on in the present paper, were carried out with the spent liquors from this investigation[6].

The values in Fig.1 and in other diagrams refer to pH in the spent liquors determined at 22°C.

Calcium in Bleach Liquors

Determinations of calcium in the spent liquors from the oxygen bleaching showed that a large proportion of the calcium which remained in the pulps after the pretreatment was dissolved during the bleaching. With pulp U1 (Figs.1 and 2) which had the largest initial calcium content the dissolved proportion after bleaching for 180 min amounted to 40 - 90 %. For pulp U2 (Fig.3 and Table 3) the corresponding values were 60 and 80 %.

Oxygen bleaching gives rise to various organic acids with the ability to give calcium complexes soluble in alkaline media. Examples are glycolic, dihydroxybutanoic and carboxylic acids containing three or more hydroxyl groups[13-15]. Our results indicate that formation of calcium complexes is a main reason of the dissolution of calcium from the pretreated pulps.

As shown in Figs.2 and 3 the dissolution of calcium during an early period decreased markedly when increasing amounts of magnesium sulfate were added. This is a combined result of at least three effects: (a) competition between calcium and magnesium (present in large amounts) for the produced complexing ligands in the solution, (b) decreased concentration of hydroxide ions in the solution due to precipitation of hydrated magnesium oxides and (c) retarded autooxidation of lignin and carbohydrates in the pulp. The two last effects suppress the formation of complexing agents[14,15]. Compared to the retarding effects of magnesium sulfate on the dissolution of calcium from the pretreated kraft pulps the amounts of manganese of current interest exerted only small effects (Fig.1).

The highest rate of dissolution was found during the first 20-min period in the experiments without magnesium addition. In most bleaches the concentration of calcium in the liquor increased continuously with increasing bleaching time. Exceptions with a decrease in concentration during the period from 20 to 70 min are the bleaches without magnesium protector with either 0.28 or

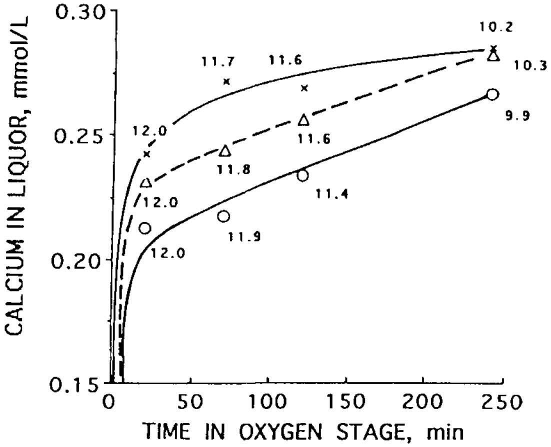

FIGURE 1. Calcium in liquors from oxygen bleaching with 100 mmol (4 g) NaOH per 100 g pulp U1 without magnesium addition. Additions of $MnSO_4$ per 100 g pulp:

○ 0 mmol; △ 0.11 mmol; X 0.55 mmol

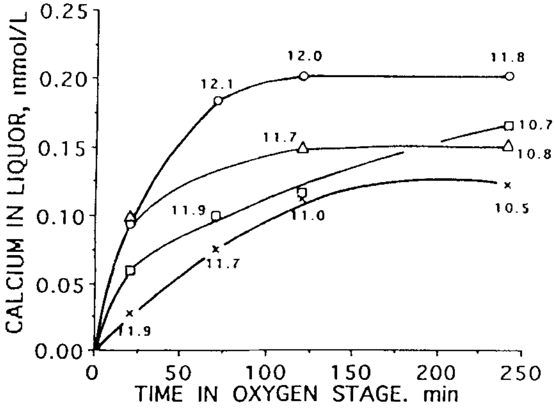

FIGURE 2. Calcium in liquors from oxygen bleaching with 150 mmol (6 g) NaOH and 0.55 mmol $MnSO_4$ per 100 g pulp U1. Additions of $MgSO_4$ per 100 g pulp:

○ 0 mmol; △ 4.1 mmol; □ 8.2 mmol; X 20.6 mmol

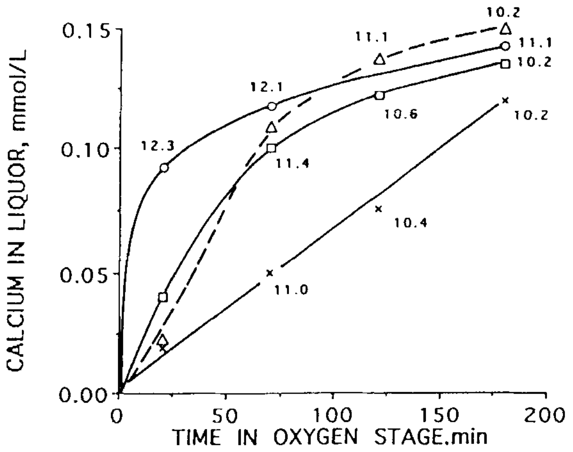

FIGURE 3. Calcium in liquors from oxygen bleaching with 100 mmol (4 g) NaOH and 0.55 mmol $MnSO_4$ per 100 g pulp U2. Additions of $MgSO_4$ per 100 g pulp:
○ 0 mmol; △ 4.1 mmol; □ 8.2 mmol; × 20.6 mmol

TABLE 3

Influence of the Duration of the Bleaching with 0.75 millimol NaOH (3 g) per 100 g of Pulp U2 on the Concentration of Calcium Compounds (micromol Ca per liter) in Bleaches with additions of 0, 4.1 and 20.6 millimol Magnesium per 100 g Pulp.

Time	Spent	Liquor		Low molecular complexes			Colloids 1000-10000			Colloids >10000		
min	0	4.1	20.6	0	4.1	20.6	0	4.1	20.6	0	4.1	20.6
20[a]	115	60	45	16	4	22	36	30	20	63	26	3
70[a]	90	100	85	12	10	25	45	52	49	33	38	11
120[a]	110	125	100	16	15	32	49	55	58	45	55	10
240[a]	125	130	140	16	17	50	56	65	42	53	48	48
20[b]	106	50	42	14	12	25	24	22	17	68	16	0
70[b]	95	87	75	14	10	32	28	47	43	53	30	0
120[b]	106	112	102	18	13	41	29	49	43	59	50	18
240[b]	117	120	131	15	15	55	50	67	37	52	38	39

a.0.28 mmol $MnSO_4$ per 100 g pulp. b.0.55 mmol $MnSO_4$ per 100 g pulp.

0.55 mmol manganese per 100 g pulp (Table 3). We conclude that destruction of ligands in the dissolved organic material by wet combustion contributed to this decrease in calcium concentration.

This destruction competes with the formation of complexing compounds which continues during the whole bleaching process. During the first 20-min period their formation was favored dramatically by the rapid delignification and attack on the carbohydrates. Both reactions give rise to water soluble products of varying molecular size[7].

Ultrafiltration of the bleach liquors (Table 3) showed that the added amount of magnesium sulfate exerted much larger effects on the calcium concentration in the ultrafiltrates than the change of the manganese addition. Already after oxygen bleaching for 20 min an appreciable proportion (10-60 %) of the calcium in the spent liquors passed through the tightest ultrafilter (separation limit 1000) as low molecular complexes. In the liquors from bleaching with the largest addition of magnesium the concentration of these low molecular calcium compounds increased markedly even during the bleaching period 120-240 min while in the bleaches without magnesium and with the small magnesium addition the amount of calcium in this fraction was only slightly affected. This does not mean that the reactions which gave rise to low molecular calcium compounds had ceased. Large additions of magnesium sulfate protect not only the lignin and carbohydrates in the fibers against degradation but also the dissolved fragmentation products present in the bleach liquors[7,16]. Hence, it can be concluded that the wet oxidation of the complexing ligands in the soluble low molecular calcium complexes was retarded so strongly by the magnesium protector that the concentration of these complexes increased during the whole bleaching period.

In most ultrafiltrates from the coarse filter the calcium concentration was more than twice that observed in the low molecular fraction. The difference corresponds to calcium in colloids with the separation limits 1000-10000. Calcium linked to these colloids was in all bleaches found already after 20 min (Table 3). An increased residence time to 120 min gave rise to increased concentrations. During the period 120-240 min an increased or decreased proportion was obtained depending on the bleaching conditions.

Colloids and aggregates of larger size were retained on the coarse ultrafilter. The concentration of calcium belonging to this group (denoted colloids >10000) was calculated as the difference between the calcium concentration in the spent bleach liquor and that in the ultrafiltrate from the coarse filter. As shown in the table the amounts of calcium in colloids >10000 were less affected when the manganese addition was changed from 0.28 to 0.55 mmol per 100 g pulp than by the applied changes in the addition of magnesium sulfate. The concentration of calcium linked to colloids >10000 retained on the coarse ultrafilter was much higher in the bleaching without magnesium protector than in the bleaches with the largest addition of magnesium (corresponding to 0.5 % on pulp). Furthermore, the concentration of calcium in the colloids which passed through this ultrafilter was, after bleaching for 70 and 120 min, much larger in the bleaches with this magnesium addition than in those without magnesium addition. As shown in the next section, very large proportions of the added magnesium sulfate were during the oxygen bleaching converted to colloids belonging to the group denoted colloids 1000-10000. From these and other results it can be concluded that in bleaches with magnesium protector an appreciable proportion of the calcium ions was linked to the magnesium colloids consisting of polymerized hydrated

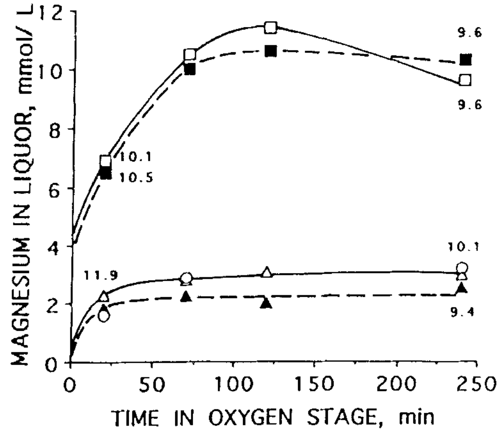

FIGURE 4. Magnesium in liquors from oxygen bleaching with 75 mmol (3 g) NaOH per 100 g pulp U2. Additions mmol per 100 g pulp:

Symbol	○	△	▲	□	■
$MnSO_4$	0	0.28	0.55	0.28	0.55
$MgSO_4$	4.1	4.1	4.1	20.6	20.6

oxides and polymerized basic magnesium salts which passed through the coarse ultrafilter.

In most bleaches without magnesium addition the largest proportion of the calcium ions present in the spent liquor belonged to the group colloids >10000.

Magnesium in bleach liquors.

Figs.4,5 and 6 show that, independent of the additions of sodium hydroxide and manganese the concentration of magnesium in the liquor after a given duration of the bleaching increased markedly with increasing magnesium addition. On the other hand the dissolved proportion calculated as a percentage of the added magnesium was affected much less. As an example it

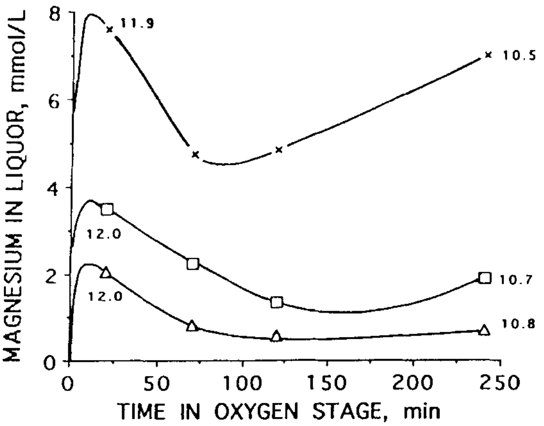

FIGURE 5. Magnesium in liquors from oxygen bleaching with 150 mmol (6 g) NaOH and 0.55 mmol $MnSO_4$ per 100 g pulp U1. Additions of $MgSO_4$ per 100 g pulp:

△ 4.1 mmol; ☐ 8.2 mmol; × 20.6 mmol

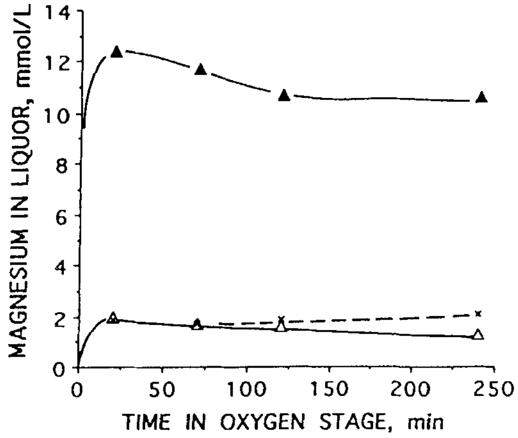

FIGURE 6. Magnesium in liquors from oxygen bleaching with 100 mmol (4 g) NaOH per 100 g pulp U1. Additions mmol per 100 g pulp:

Symbol	△	×	▲
$MnSO_4$	0.11	0.55	0.55
$MgSO_4$	4.1	4.1	20.6

can be mentioned that in the bleaches referred to in Fig.4 the largest proportion of magnesium in the solution was 85 % in the bleaching with the smallest addition. With the fivefold addition the corresponding proportion was 60 %. Furthermore, the observed magnesium concentrations were higher than those corresponding to the solubility of magnesium hydroxide in water and alkali hydroxide solutions of the same pH as the bleach liquors.These observations indicate that the liquor phase contained polymerized (polynuclear) magnesium complexes[17].

A common feature of all bleaches referred to in Figs. 4,5 and 6 was that under otherwise unchanged conditions,variations in the added amount of manganese within the range 0-0.55 mmol per 100 g dry pulp exerted a modest effect on the concentration of dissolved magnesium. Under applied conditions the added manganese catalyzed the depolymerization of the cellulose which indirectly promotes the formation of complexing anions[13]. Manganese addition exerts effects also on the destruction of produced complexing agents during the oxygen treatment. Other effects of the manganese may also have an influence on the dissolution. The modest net effect can be ascribed to competition between catalytic and retarding effects.

In the bleaches with the lowest addition of sodium hydroxide (75 mmol) and 20.6 mmol magnesium sulfate per 100 g dry pulp a large proportion of the hydroxide ions in the solution was during an initial period of the bleaching precipitated as hydrated magnesium oxide. This was reflected in a much lower pH after 20 min in these treatments than in those with a magnesium addition decreased by 80 % (Fig.4). In all bleaches a rapid dissolution occurred already during the first 20-min period. The magnesium concentration increased rapidly with increasing time in the bleaches with the larger addition and passed through a maximum after about 120 min. The ascending part of the curves is mainly ascribed to an increased formation of complexes including colloidal species consisting mainly of hydrated polynuclear magnesium species. The descending part reflects the wet combustion of produced complexing agents. Curves similar to those in Fig.4 have been reported for oxygen bleaches at 1 and 2 % consistency[18] of kraft pulps which had not been pretreated with NO_2.

The doubled alkali addition (Fig.5) compared to the bleaches in Fig.4 led to markedly increased rates of delignification and degradation of the carbohydrates[6]. Both reactions consumed hydroxide ions. This explains the observation that after bleaching for 20 min with the smallest magnesium addition the pH was only slightly affected by the doubled alkali addition. With the fivefold magnesium addition a large difference in pH was obtained. This is ascribed to the rapid precipitation and slow dissolution of hydrated magnesium oxide[19]. Despite the increase in pH from 10.5 to 11.9 the concentration of magnesium in the liquor was approximately the same independent of the increased concentration of hydroxide ions in the solution. This was not unexpected since the composition of the produced organic solutes depends on the alkali concentration.

In contrast to the plots of the magnesium concentration in the liquor versus the bleaching time during bleaching with 3 % NaOH the highest magnesium concentration was with the doubled alkali charge found already after the shortest time studied by the applied technique (20 min). An increased duration resulted in concentrations which passed through a minimum after about 100-130 min.

During the period when the magnesium concentration in the liquor decreased a destruction of the complexes in the liquor was more prominent than the formation of soluble magnesium species. It can be concluded that the wet combustion of organic complexing agents contributed to this decrease. The observed maximum concentration after less than 20 min indicates that besides the wet combustion, aging of the polynuclear magnesium species in the liquor and of sparingly soluble magnesium compounds in the solid phase contributed to the decrease in the magnesium concentration in the liquor. The ascending part of the curves after the minimum is ascribed to the decreased pH in the bleach liquor which leads to a suppressed wet combustion[16] of complexing ligands and increases the solubility of the sparingly soluble magnesium compounds.

From the shape of the curves in Figs.4 and 5 it can be predicted that the bleaching time should have less effect on the concentration of magnesium when an intermediate amount of sodium hydroxide was applied. The bleaches in Fig.6 which were carried out with an addition of 100 mmol NaOH per 100 g pulp confirm this prediction. In the bleaches with the largest magnesium addition the highest magnesium concentration was found after a residence time of 20 min.

Another factor which can affect the concentration of dissolved magnesium is that the other cations from the pulp such as calcium and manganese compete with magnesium for the complexing ligands in the liquor. Analysis of the pretreatment liquors showed that magnesium and manganese were dissolved effectively during the pretreatment and that a large proportion of calcium was also removed. Since the addition of manganese was small compared to that of magnesium the effect of this competition must be of little importance under applied conditions. This does

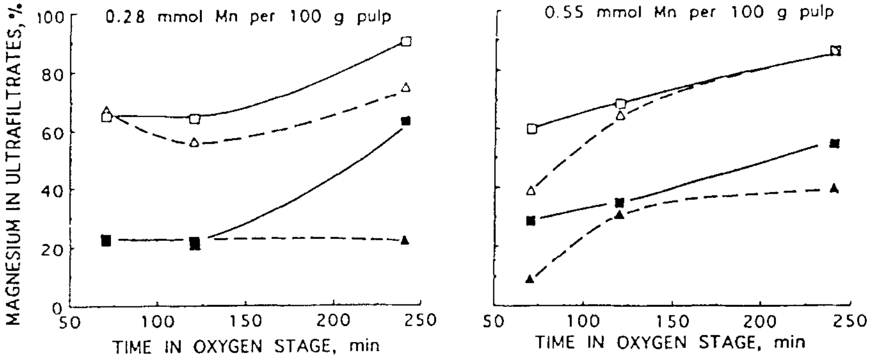

FIGURE 7. Magnesium concentration in ultrafiltrates, calculated as a percentage of that in the liquor after the oxygen bleaches referred to in Fig.4. Open symbols: coarse ultrafilter. Filled symbols: tight ultrafilter. Additions of $MgSO_4$ per 100 g pulp:

△ ▲ 4.1 mmol □ ■ 20.6 mmol

not necessarily mean that the same holds true for a closed system with recirculation of the liquors.

The concentration of magnesium was also determined in the liquors from oxygen bleaching under the same conditions without any addition of magnesium sulfate. The values were within the range 0.031-0.037 mmol per liter of the spent liquor. This means that of the small amount present after the pretreatment approximately 50% was dissolved during the oxygen bleaching.

Magnesium was determined in the ultrafiltrates used for the calcium analyses reported in Table 3. Fig.7 shows that 40-90% of the magnesium present in the spent liquor passed through the coarse ultrafilter. The proportion of magnesium which passed through the tighter ultrafilter amounted to 10-65% of the total amount in the liquor. It is noteworthy that a larger or about equal proportion of magnesium passed through the ultrafilters in the bleaches with addition of 20.6 mmol magnesium sulfate per 100 g pulp compared to the parallel experiments with a magnesium addition lowered by 80%. The curves show that already after 70 min magnesium was present in large amounts both as low molecular complexes and as colloids, 1000-10000. In contrast the amount of magnesium in the fraction of colloids, > 10000, decreased significantly when the duration of the bleaching was increased from 70 to 240 min.

Manganese in bleach liquors

The added manganese ions of oxidation state +II are in the alkaline medium oxidized rapidly in the presence of oxygen. Sparingly soluble compounds of higher oxidation states are produced. In addition soluble complexes of oxidation states +III and +IV can be formed with soluble degradation products from the organic pulp constituents. Compounds containing only hydroxyl groups as ligands such as alditols can give multidentate complexes with manganese at high pH. During oxygen/alkali treatments of cellobiitol, complexes of this type exert a large influence on the autoxidation of the cellobiitol[9]. The formation of manganese compounds of different oxidation states and organic complexes with other ligands than those which bind calcium and magnesium in stable complexes complicate the interpretation of the effects of manganese.

The bleaches in Fig.8 were carried out without magnesium addition. The proportion of manganese in the liquor varied between 20 and 65 % of the added amount. The largest manganese concentration was in most series found after 20 min indicating a maximum after less than 20 min. The manganese concentration during bleaching with

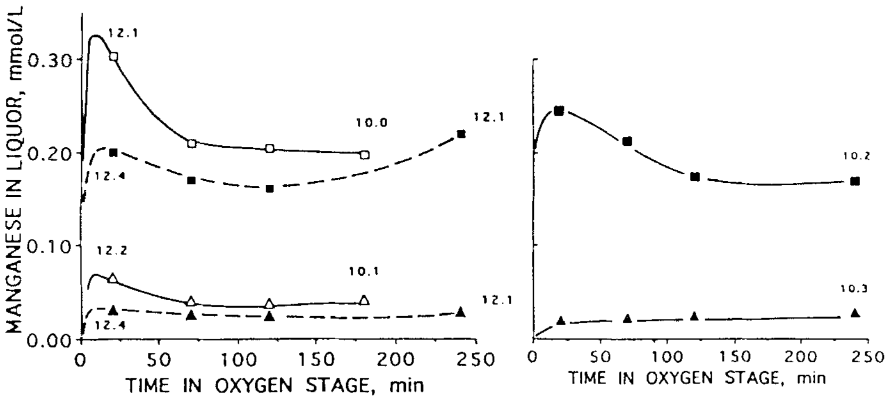

FIGURE 8. Manganese in liquors from oxygen bleaching without magnesium addition. Additions of 0.11 mmol (triangles) or 0.55 mmol (squares) of $MnSO_4$ per 100 g pulp. Left diagram: 75 mmol (open symbols) and 150 mmol (filled symbols) NaOH per 100 g pulp U2. Right diagram: 100 mmol NaOH per 100 g pulp U1.

the largest charge of sodium hydroxide exhibited a minimum on prolonged bleaching. The similarities in shape of these curves and those representing dissolved magnesium, (Fig.5) indicate that the formation and wet combustion of organic complexing agents affected the dissolution and precipitation of manganese compounds during the oxygen bleaching. It is noteworthy that in some comparable experiments a more than fivefold concentration of manganese was obtained in the liquor by a fivefold addition.

Fig.9 shows the determinations of manganese in the liquors from bleaches with a constant addition of manganese and increasing amounts of magnesium. The addition of sodium hydroxide was very high (6 % NaOH on pulp). Also in these experiments the plots of manganese concentration against time exhibited maxima after less than 20 min.

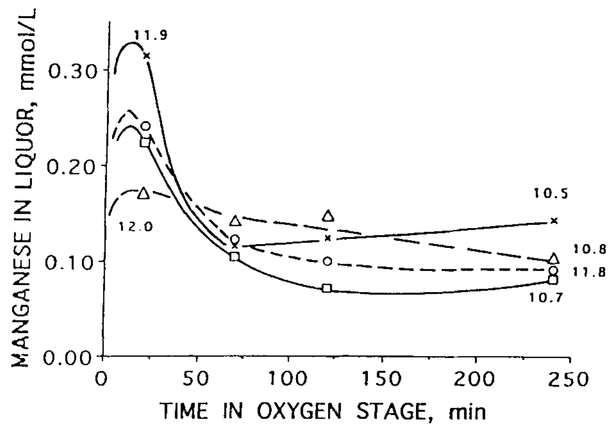

FIGURE 9. Manganese in liquors from oxygen bleaching with 150 mmol (6 g) NaOH and 0.55 mmol $MnSO_4$ calculated per 100 g dry pulp U1. Additional pH-values in Fig.2. $MgSO_4$, mmol per 100 g pulp:

○ 0 △ 4.1 □ 8.2 × 20.6

To visualize the relationship between the attack on the fibers and the concentrations of manganese and magnesium after an initial 20-min period of the oxygen bleaching the concentrations are in Table 4 compared with analyses of the corresponding pulps. As shown in the table the increased magnesium addition gave rise to a decreased attack on both lignin and cellulose. This should lead to a decreased formation of soluble complexing agents. In the absence of reactions which suppress the dissolution a decreased concentration of the dissolved manganese should therefore be anticipated. As shown in the table a reversed order was , however, observed. This observation is in agreement with our conclusions drawn from the determinations of magnesium that the formation of complexing agents was extremely rapid during a short initial period and that, already

TABLE 4

Influence of the Magnesium addition on Kappa number, Viscosity and Metal concentrations in Liquors from Oxygen Bleaching for 20 min with additions of 0.55 mmol $MnSO_4$ and 150 mmol NaOH per 100 g Pulp U1.

Added Magnesium mmol/100 g pulp	Kappa number	Viscosity dm^3/kg	Spent Bleach mmol/liter		Liquor pH
			Mn	Mg	
4.1	8.3	935	0.16	2.0	10.8
8.2	8.5	945	0.22	3.5	10.7
20.6	9.5	980	0.32	7.6	10.5

after less than 20 min, the reactions which led to a destruction of the complexing agents had a prominent effect on the net formation of complexes.

The reactions which have an influence on the formation of soluble manganese compounds and on the removal of manganese e.g by precipitation as sparingly soluble compounds are influenced by the hydroxide concentration. Accordingly, the concentration of manganese in the spent liquor depended on the added amount of sodium hydroxide. A comparison between Fig.9 and 10 shows that in the bleaches with 0.55 mmol $MnSO_4$ and either 4.1 or 20.6 mmol $MgSO_4$ per 100 g pulp an increased concentration of sodium hydroxide resulted in lowered manganese concentrations. Similarly, Fig.8 shows that during bleaching without magnesium addition an increased sodium hydroxide addition from 75 to 150 mmol per 100 g pulp led to a decreased manganese concentration in the spent liquors.

Under certain conditions competitive reaction paths are favored or retarded by the same change in the process conditions. An example is the formation of soluble complexing agents and their destruction by wet combustion. Both reaction paths are favored by an

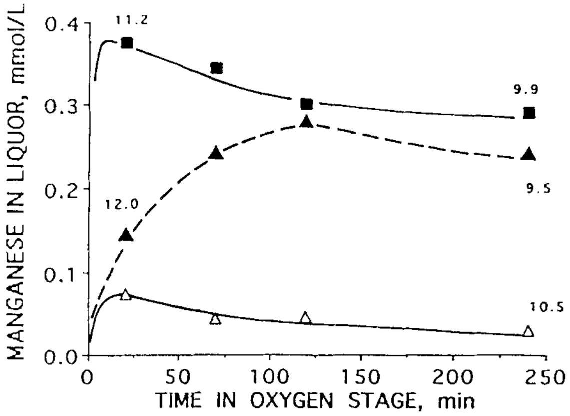

FIGURE 10. Manganese in liquor from oxygen bleaching with 100 mmol (4 g) NaOH per 100 g dry pulp U1. Additions, mmol per 100 g pulp:

Symbol	△	▲	■
$MnSO_4$	0.11	0.55	0.55
$MgSO_4$	4.1	4.1	20.6

increased charge of sodium hydroxide[16]. Competitive effects on the reactions of importance for the manganese concentration explain why the observed effects are rather small under conditions of current interest.

Another example (Fig.10) is that the increase in the magnesium addition by a factor five exerted a small effect on the manganese concentration after oxygen bleaching for 120 and 240 min while this change gave rise to a large effect after 20 min. This can be ascribed to the minor importance of the destruction of complexing agents during an early period of the oxygen bleaching without recirculation of bleach liquors containing complexing agents.

Manganese was determined in the ultrafiltrates of the liquors from bleaches with manganese addition, referred to in Fig.4 and in experiments without magnesium addition under otherwise unchanged conditions. The proportion in the ultrafiltrates was calculated as a percentage of the concentration in the corresponding spent liquor. For the liquors from bleaches for 70 min the proportion which passed through the tight filter was 2-8 %. This confirms that low molecular manganese complexes were present. The observed proportion increased by 100-300 % when the time was increased to 240 min.

Much larger proportions of the manganese passed through the coarse ultrafilter. The largest proportion (70 %) was found after bleaching for 240 min without magnesium addition and with an amount of 0.28 mmol $MnSO_4$ per 100 g pulp. This means that the fraction, colloids > 10000, contained only 30 % of the manganese in this liquor while after 70 min this colloid fraction accounted for 88 % of the total manganese concentration in the liquor. The decreased proportion of manganese in this colloid fraction with the increased duration of the oxygen bleaching was reflected in markedly increased proportions of both low-molecular mass manganese compounds and of colloids (1000-10000).

In the bleaches with addition of 4.1 mmol $MgSO_4$ and an unchanged amount of $MnSO_4$ (0.28 mmol per 100 g pulp) 35 % of the manganese in the liquor passed through the coarse filter already after bleaching for 70 min. This proportion decreased to 25 % after bleaching for 240 min. In parallel bleaches with the largest magnesium addition (20.6 mmol $MgSO_4$ per 100 g pulp) only 5 % of the manganese passed through the coarse ultrafilter after bleaching for 70 min. The proportion increased to 10 % after 240 min. The low proportions of manganese in the ultrafiltrates from the coarse filter compared to those in the experiments without magnesium addition support our conclusion that the magnesium colloids have the ability to bind manganese ions.

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