Optimized oxygen bleaching of kraft pulp treated with nitrogen dioxide

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ABSTRACT: Oxygen bleaching of kraft pulp pretreated with nitrogen dioxide causes a rapid delignification with high selectivity at low sodium hydroxide concentration and low oxygen pressure. The pulps contained magnesium and transition metal compounds dissolved during pretreatment. Without magnesium protector applied before the oxygen bleaching, addition of 300 ppm of manganese decreased the depolymerization rate of cellulose. With 60 ppm manganese, a net catalytic or retarded effect occurred depending on the bleaching conditions. In bleaches containing manganese, the depolymerization rate increased with a mall magnesium sulfate addition. An increased Mg/Mn ratio suppressed the depolymerization

KEYWORDS: Bibliographies, kraft pulps, lignins, magnesium, manganese, nitrogen dioxide, optimization, oxygen bleaching, pretreatment.

Earlier investigators described the influence of the conditions during oxygen bleaching of kraft pulp following pretreatment with nitrogen dioxide *(1–3)*. A new pretreatment technique provided markedly improved delignification *(4)*. This makes it possible to bleach the pulp to 91% ISO brightness without chlorination. The brightness stability is extremely high, and the strength properties compare to those of pulps bleached by conventional methods *(5, 6)*. This report describes the conditions during oxygen bleaching following such pretreatment indicated here as S.

Experimental conditions

The pulps in this investigation were from kraft cooks of softwood using mainly *Pinus sylvestris*. Table I shows the pulp designations and properties. Before pretreatment, the undried pulp had impregnation with 11.1 kg of industrial black liquor per 100 kg dry pulp *(7)*. A 3400-mL reactor contained an amount corresponding to 180 g of dry pulp. After removal of air, 2% NO_2 contacted the pulp at 27% consistency and 60°C. Introduction of a diluent into the reactor at 60°C after 15 min simulated recycled spent pretreatment. Consistency decreased to 8%. The diluent contained nitric acid corresponded to 20 mmole free nitric acid *(4)* and 184 mmole sodium nitrate per 100 g pulp. There was also addition of 46 mmole sodium nitrate per 100 g pulp into the black liquor before the pretreatment.

The pulp suspension underwent heating to a final temperature of 80°C in 20 min and ripened at this temperature. With pulp S (kappa no. 28.2, viscosity 1300 dm^3/kg), the ripening of the pulp suspension lasted for 180 min. With pulps U1 and U2 from another pulp mill (kappa nos. 28.5 and 24.3 and viscosities 1173 and 1149 dm^3/kg, respectively), the time decreased to 120 min.

After washing with deionized water, the pulps underwent pressing to approximately 30% consistency. Oxygen bleaching occurred at 8% consistency and 106°C in 1500-mL autoclaves which rotated in a polyglycol bath preheated to the reaction temperature *(8)*. The amount of undried pulp corresponded to 10 g pulp. In the experiments with additions of either magnesium sulfate or manganese (II) sulfate or both, the mixing of the sulfate solutions into the pulp was before the addition

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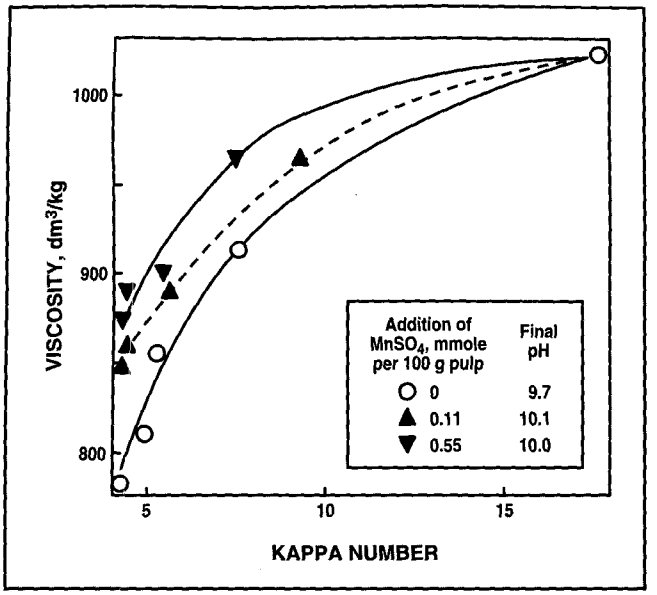
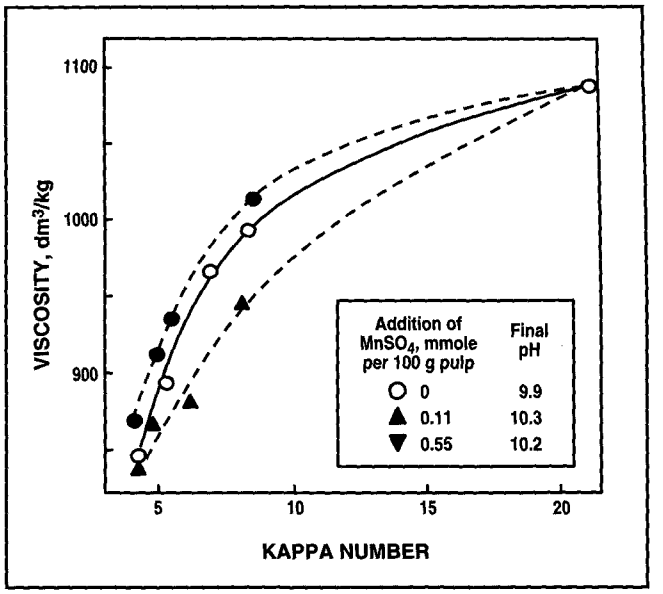
1. Influence of the addition of manganese sulfate during oxygen bleaching of pulp U2



2. Influence of the addition of manganese sulfate during oxygen bleaching of pulp U1



of sodium hydroxide solution. The oxygen pressure was 0.6 mPa determined at 22°C. The chemicals were analytical grade. The water was deionized with subsequent distillation. Calculations of the reported additions were on dry untreated pulp. They refer to 100 g pulp unless stated otherwise. Analyses were as previously described *(7)*. The pretreated pulp U1 contained 5.3 mg Mn, 15 mg Mg, and 136 mg Ca per kg pulp. For pulp U2, the values were 3.9 mg Mn, 16 mg Mg, and 87 mg Ca.

I. Analyses of unbleached pulps

Pulp designation	*Kappa number* [1]	*Viscosity* [2], *dm³/kg*	*Remaining alkali* [3], *mmole/100 kg*
S (industrial)	28.2	1300	2.0
U1 (industrial)	28.5	1173	8.7
U2 (industrial)	24.3	1149	15.0

[1]Scandinavian Standard Method (SCAN) 1:77
[2]SCAN 15:88
[3]Titration to pH 4.5

Results and discussion

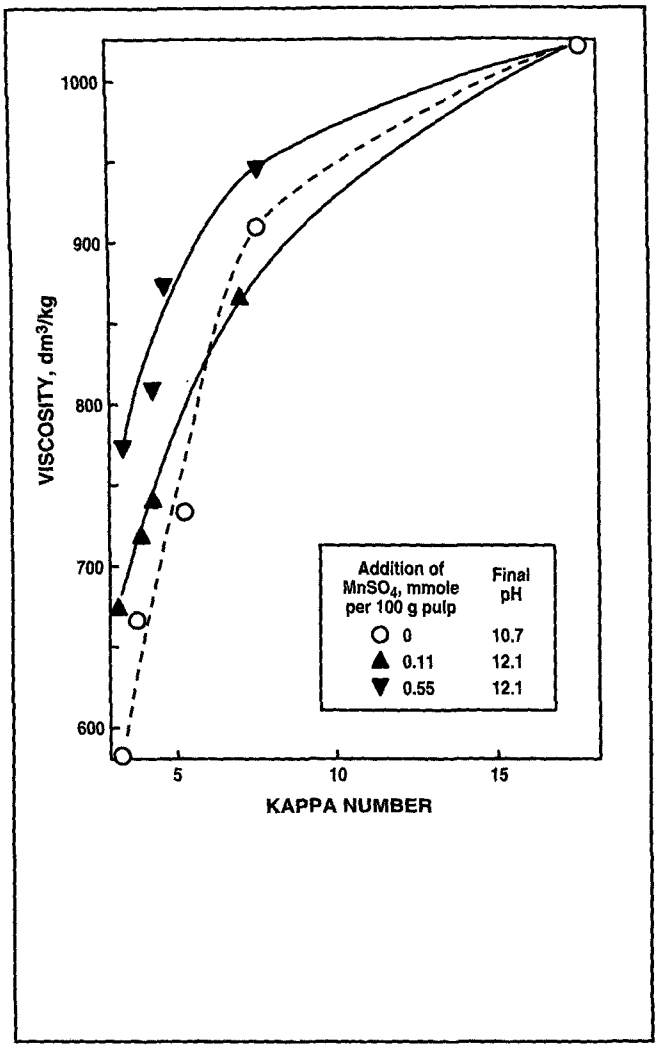
Plots of viscosity vs. kappa number illustrate the delignification and the depolymerization of the cellulose during the pretreatment and during the subsequent oxygen bleaching. The pulp with the highest kappa number on each curve is the pretreated pulp. The pulps with decreasing kappa numbers are those subjected to oxygen bleaching for 20, 70, 120, and 240 min. The time is from the moment of insertion of the autoclaves into a preheated polyglycol bath to the moment of cooling the autoclaves in a stream of tap water. Although the selectivity curves show excellent reproducibility, the reaction rates during the early period of the bleaching are only roughly estimated. The reported conclusions regarding the influence of the process conditions are only for those instances with large effects.

Charge of NaOH and oxygen pressure

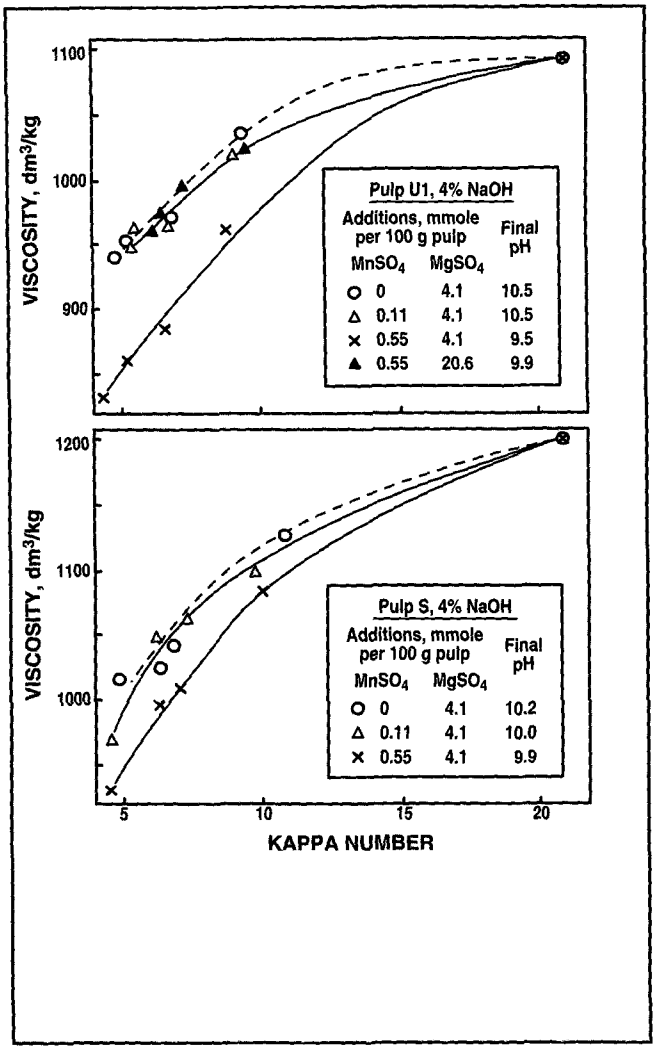
Varying additions of magnesium sulfate in oxygen bleaches provided a study of the influence of the charge of NaOH and of the initial oxygen pressure. The pretreated pulps contained virtually no manganese compounds. As one example, oxygen bleaching of pretreated pulp S for 240 min at 0.6 mPa with addition of 8.2 mmole of $MgSO_4$ gave an oxygen bleached pulp of kappa no. 6 and viscosity 1050 dm³/kg with 4% NaOH application. With 6% NaOH, the kappa number decreased to 4.5 while the viscosity decreased to 970 dm³/kg. This is over the limit of 950 dm³/kg commonly considered acceptable for oxygen bleached softwood pulps with high strength properties.

With a magnesium addition decreased by 50% and a charge of 4% NaOH, a pulp with kappa number 5.0 and a viscosity of 1040 dm³/kg resulted after bleaching for 240 min. Higher kappa numbers and higher viscosities ensued when the NaOH addition decreased by 25%. An increased addition to 8% NaOH led to increased reaction rates and to a

3. Influence of the addition of manganese sulfate during oxygen bleaching of pulp U2



4. Influence of the addition of manganese sulfate during oxygen bleaching of pulp U1 and pulp S



large loss in selectivity (viscosity at a given kappa number) during the oxygen bleaching.

The delignification and the depolymerization occurred more slowly at an oxygen pressure of 0.15 mPa than at 0.6 and 1.0 mPa. Similar effects resulted in a previous study of oxygen bleaching at 5–30% consistency of well-washed kraft pulp pretreated with 4% nitrogen dioxide at 30% consistency at approximately 50°C *(2)*. Large additions of sodium hydroxide give extensive delignification. With such additions of sodium hydroxide, the selectivity was significantly higher after bleaching at 0.15 mPa than at higher oxygen pressures. This was true whatever the amount of magnesium protector. The results indicate that bleaching conditions that cause a rapid delignification suppressed the selectivity.

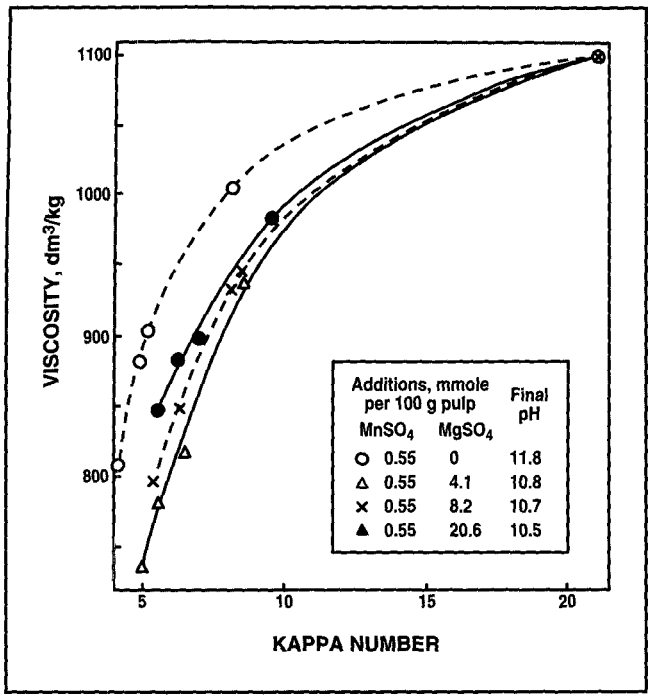
Influence of manganese compounds

Various transition metal compounds affect the delignification and can cause a serious depolymerization of cellulose and other polysaccharides during oxygen bleaching. Manganese compounds, which belong to the most abundant transition metal compounds in kraft pulps, dissolve to approximately 97% during pretreatment with nitrogen dioxide under conditions of current interest. Similarly, magnesium ions present in pulp are dissolved almost completely in the acid spent liquor. It is therefore possible to recirculate both types of compounds and carry them to the oxygen bleaching in a virtually closed recovery system. Optimization of the process therefore requires a better knowledge of the effects of manganese and magnesium compounds during subsequent oxygen bleaching *(9)*.

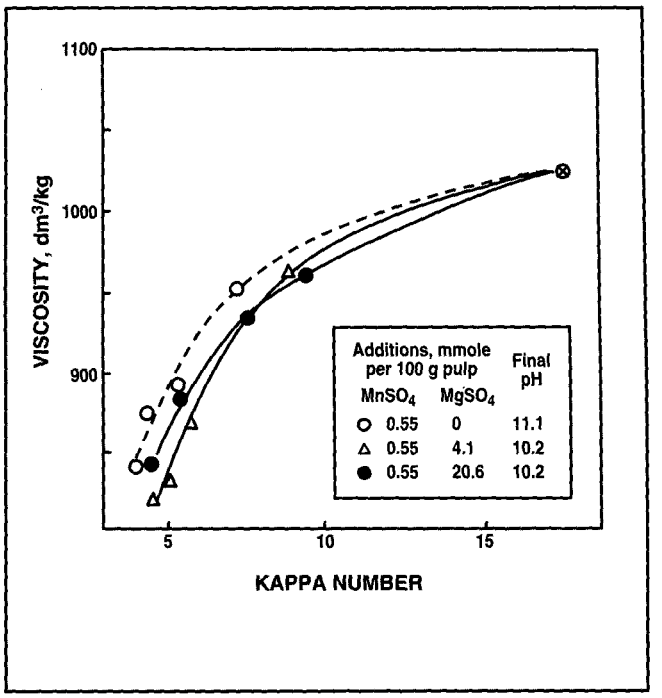
Bleaching without magnesium addition.

Oxygen bleaching of pretreated kraft pulps used either a large addition of manganese sulfate corresponding to 0.55 mmole per 100 g pulp (0.48 mmole per kg water) or with an addi-

5. Influence of the addition of magnesium sulfate during oxygen bleaching of pulp U1



6. Influence of the addition of magnesium sulfate during oxygen bleaching of pulp U2



tion decreased by 80%. These additions corresponded to 300 and 60 ppm Mn in the dry pulp, respectively. **Figure 1** shows that, during oxygen bleaching with 3% sodium hydroxide, there was retardation of the depolymerization of the cellulose both during early and late periods of the bleaching. This bleaching used 75 mmole NaOH per 100 g pulp without addition of magnesium compounds. In these oxygen bleaches, the longest residence time was 180 min rather than 240 min.

The largest protection resulted with the largest addition. The influence of the manganese on the delignification rate was small. This means that, under applied conditions, the manganese addition gave improved selectivity. Earlier work has shown a retarded depolymerization and a promoted delignification for oxygen cooking of acid soaked wood in sodium bicarbonate solutions *(10)*. During oxygen bleaching at 1% consistency of acid-soaked kraft pulp in 0.05*M* $NaHCO_3$ or NaOH, a retarded attack on the cellulose occurred. The effect of manganese (II) salts on the delignification was very small *(11)*.

Figures 2 and 3 show retardation by large addition of manganese and catalysis by smaller addition during an early period of the bleaching of pretreated pulps with 4% and 6% NaOH. In Fig. 2, the oxygen bleaching used 100 mmole NaOH per 100 g pulp without addition of magnesium compounds. For Fig. 3, the bleaching used 150 mmole of NaOH per 100 g pulp without addition of magnesium compounds. Earlier work has established the same influence of large and small additions of manganese on the aging of alkali cellulose *(12)*. During a later period of the oxygen bleaching, there was retardation with the smaller amount. The effect on the depolymerization rate of the larger addition was not significant. Our results confirm that the carbohydrate reactions during oxygen bleaching relate to those during the aging of alkali cellulose *(13)* and show that the hydroxide concentration has a large influence on the effect of the manganese.

Since these experiments had no magnesium protector, traces of active metal compounds such as iron would exert a large catalytic effect on the depolymerization of cellulose. The results indicate that the intermediates produced during the autoxidation, when manganese compounds were involved, were less aggressive on the cellulose than those produced by iron compounds. Model experiments with cellobiitol in sodium hydroxide solutions of extremely high purity showed that manganese caused either a catalytic or retarding effect depending on the amount of manganese and trace quantities of other metal compounds. These experiments used a small addition of glucose as initiator *(14)*.

In earlier experiments with purified cotton linters *(15)*, addition of 0.009 mmole of manganese (II) sulfate per L did not affect the depolymerization of the cellulose. With the same molar amount of iron (III) chloride, the viscosity decreased by 300 dm^3/kg. These experiments used 0.125*M* NaOH at 1.25% consistency. The same authors found that oxygen treatment in 0.5*M* NaOH containing sulfate lignin did not affect methyl β-D-glucopyranoside, even

when 0.36 mmole of Mn was present per L. With iron instead of manganese, approximately 40% of the glucoside degraded.

Other workers performed an oxygen-NaOH treatment using high consistency for cotton linters purified by extraction with ethyelenediaminetetraacetic acid (EDTA) and 40% aqueous ethanol. Addition of 0.11 mmole manganese per 100 g pulp resulted in a slower decrease in viscosity than in a blank without addition of transition metals. A decreased addition of 0.018 mmole of manganese resulted in a loss in viscosity compared to this blank.

In contrast to the other carbohydrates mentioned above, the pretreated pulp contained nitrated lignin. It had delignification in subsequent oxygen bleaching more rapidly than the untreated pulp *(1)*. Intermediates produced in the lignin reactions can act as catalysts during the degradation of carbohydrates *(13)*. A common feature of the bleaching of pretreated pulp and oxygen and alkali treatments of other carbohydrates is that extremely small amounts of catalytically active transition metals other than manganese are present. There is chemical modification of the organic constituents during the pretreatment. One can conclude that the removal of active metal compounds from pulp has a decisive influence on the carbohydrate reactions during subsequent oxygen bleaching.

Bleaching with magnesium addition

Since recirculated and added magnesium compounds can cause unexpected effects in bleach plants with a closed system, our work examined the influence of manganese by experimenting with added magnesium sulfate. **Figure 4** shows in the upper part the results obtained by oxygen bleaching. Other conditions were the same as the pretreated pulp U1 referenced in Fig. 2.

Addition of 0.55 mmole of manganese gave improved selectivity after bleaching without magnesium protector. There was a serious loss in selectivity, however, with a modest amount of magnesium sulfate (4.1 mmole corresponding to 0.1 g Mg per 100 g pulp) added before the oxygen bleaching. The lower part of Fig. 4 shows similar results with pulp S.

A comparison of the upper diagram in Fig. 4 with Fig. 2 shows that in bleaches with 0.55 mmole of manganese the addition of 4.1 mmole magnesium sulfate led to an increased rate of cellulose depolymerization. The bleaching in Fig. 4 used 100 mmole NaOH per 100 g pulp and additions of magnesium sulfate. The depolymerization explains the large loss in selectivity. A comparison at kappa no. 5 shows the loss was 70 dm^3/kg.

The upper diagram of Fig. 4 shows that the addition of 4.1 mmole magnesium sulfate effectively suppressed the catalytic effect of a small amount of manganese (0.11 mmole) on the depolymerization shown in Fig. 2. A comparison between these diagrams shows that the magnesium protector eliminated the detrimental effect of 0.11 mmole of manganese on the selectivity.

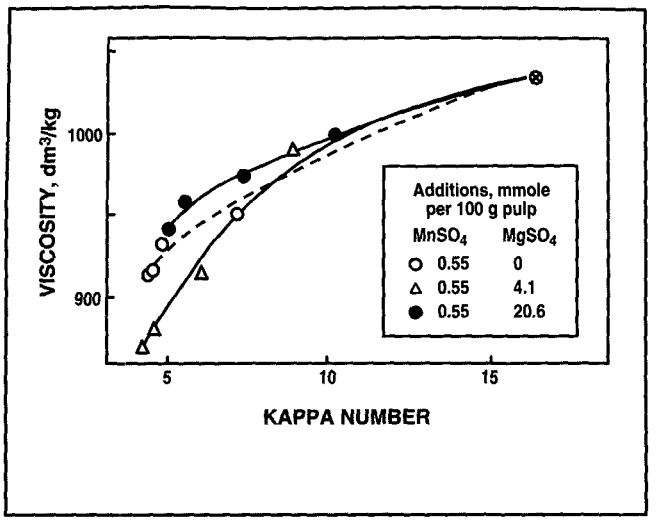
The bleaching with the fivefold addition of magnesium sulfate and 0.55 mmole manganese sulfate shown in the upper diagram in Fig. 4 led to a slow delignification and a slow depolymerization of the cellulose. This is partly due to the decreased concentration of hydroxide ions in the solution *(16)*. In the range where a comparison is possible, the selectivity was near that with the same amount of manganese sulfate without magnesium addition, as Fig. 2 indicates.

Another batch of pulp U1 pretreated under the same conditions had oxygen bleaching with an increased alkali addition of 6% NaOH. **Figure 5** shows the addition of a large amount of manganese sulfate (0.55 mmole) and varying amounts of magnesium sulfate in the bleaches. The bleaching here used 150 mmole NaOH after addition of manganese sulfate. In comparable experiments, the increased NaOH addition from 4% to 6% provided a greatly increased depolymerization rate of the cellulose. A severe loss in selectivity reflected this. The smallest addition of magnesium gave a greatly increased rate of depolymerization of the cellulose. These results agree with those of Fig. 4. An increased addition suppressed the attack on the cellulose. The larger additions of magnesium sulfate led to a strongly retarded delignification. The large loss in selectivity with the large magnesium addition also reflected this.

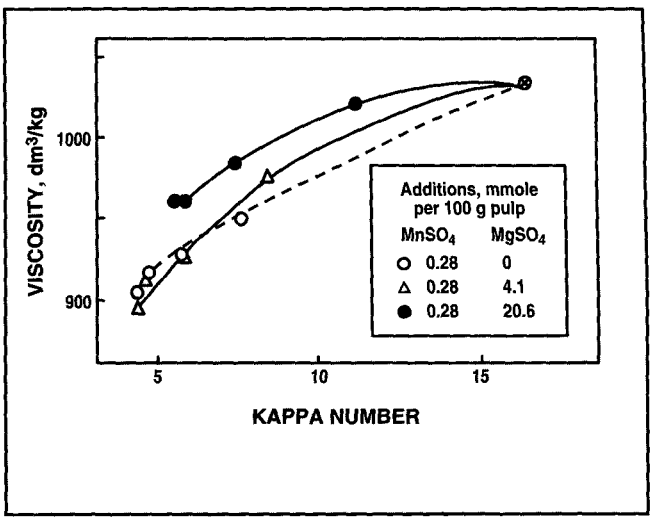
Experiments with kraft pulp with a much lower kappa number than those of Figs. 4 and 5 confirmed the loss in selectivity resulting from a small addition of magnesium sulfate to a pulp containing manganese (II). In the bleaches with 4% NaOH of **Fig. 6**, the loss in selectivity was larger with 4.1 than with 20.6 mmole magnesium per 100 g pulp. The bleaching here used 100 mmole NaOH per 100 g pulp after addition of manganese sulfate. In these oxygen bleaches, the longest time was 180 min instead of 240 min. With the 3% NaOH used in **Fig. 7**, the selectivity was higher with the largest addition compared to the blank without magnesium addition. The bleaching used 75 mmole NaOH per 100 g pulp after addition of manganese sulfate. The gain in selectivity was due to a retarded depolymerization of the cellulose. Note that the gain came despite the strongly suppressed delignification rate. As **Fig. 8** shows, similar results resulted with bleaches with 0.28 instead of 0.55 mmole manganese per 100 g pulp. The decreased manganese addition resulted in a large protection effect with the largest magnesium addition.

A comparison between Figs. 5–8 shows that the effects of magnesium sulfate addition to pulps containing

7. Influence of the addition of magnesium sulfate during oxygen bleaching of pulp U2



8. Influence of a decreased addition of manganese sulfate during oxygen bleaching of pulp U2 with different additions of magnesium sulfate



manganese sulfate depended strongly on the sodium hydroxide concentration. To visualize the effect of magnesium on the selectivity in these bleaches, **Fig. 9** plots the change in viscosity at kappa no. 5 resulting from the magnesium addition vs. the addition of NaOH. The change is the viscosity after bleaching with addition of both Mn and Mg minus the viscosity obtained with the same amount of Mn without $MgSO_4$ addition. The results show that a gain in viscosity resulted only during the bleaches with 3% NaOH and only with the largest magnesium addition. There was also an appreciable loss in selectivity with 4.1 mmole magnesium when 0.55 mmole $MnSO_4$ was present. The effect of 4.1 mmole magnesium was barely significant when the manganese addition decreased by 50%.

The loss in selectivity from the addition of magnesium sulfate increased dramatically with increasing additions of sodium hydroxide. Compared at the same amount of added sodium hydroxide, a lower selectivity resulted with 4.1 mmole (0.1%) Mg than with the fivefold addition. Whatever the alkali addition, an increased molar ratio of Mg to Mn led to an improved selectivity under the conditions for these bleaches.

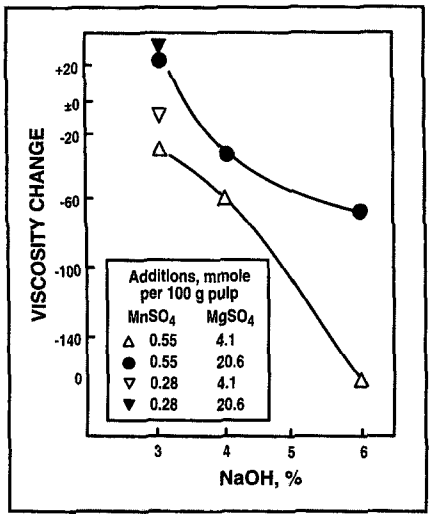
In the experiments with addition of both magnesium sulfate and manganese (II) sulfate described above, aqueous solutions of the salts underwent mixing with the pretreated and water-washed pulp before sodium hydroxide addition. In separate experiments, mixing the solutions of magnesium sulfate and sodium hydroxide at room temperature gave precipitation of magnesium oxide. The suspensions were impregnated into the pulp before addition of the manganese solution with stirring.

In another experiment, the suspension containing the hydrated magnesium oxide aged for 60 min at 95°C and, after cooling, impregnated into pulp. The other conditions were the same as in the bleaching in Fig. 8 with additions of 0.28 mmole Mn and 20.6 mmole Mg per 100 g pulp. The precipitation and the aging had no significant influence on the selectivity. The differences in viscosity at a given kappa number amounted to 15 dm^3/kg or less.

Effects similar to those shown above resulted in a study of oxygen and hydrogen carbonate bleaching of kraft pulp pretreated with nitrogen dioxide *(17)*. A large gain in selectivity came with addition of a small amount of manganese (II) sulfate. In the presence of the same amount of manganese, the addition of magnesium sulfate led to a loss in selectivity.

Pretreatment with nitrogen dioxide effectively removes the manganese compounds from kraft pulps. It is possible, however, to dissolve them by soaking under conditions that do not affect the lignin compared to that during the nitrogen dioxide treatment. Soaking a kraft pulp with SO_2-water for 30 min at room temperature followed by an aqueous solution of diethylenetriaminepentamethylene phosphoric acid (DTPMP) for 6 h led to a decrease in the manganese content from 137 ppm to 2.6 ppm. Oxygen bleaching at 30% consistency with NaOH as the added alkali and 4.1 mmole $MgSO_4$ (0.1 g Mg) per 100 g pulp resulted in a viscosity of 1020 at kappa no. 11. For the unsoaked pulp, the viscosity was 910 after bleaching to the same kappa number. Adding 0.24 mmole $MnSO_4$ per 100 g pulp (corresponding to 130 ppm Mn) to the soaked pulp gave a viscosity of 890 after the bleaching. Another sample of the SO_2-soaked pulp underwent treatment for 60 min with

9. Influence of the addition of NaOH on the change in viscosity (dm^3/kg) at kappa no. 5 by addition of magnesium sulfate to pulps impregnated with manganese sulfate



an amount of DTPMP decreased by 50%. Under otherwise unchanged conditions, the viscosity at kappa no. 11 was 990. In both series of bleaches, the improved selectivity was due to a slower depolymerization of the cellulose because of the soaking *(18)*.

With the unsoaked pulp, the same addition had a very small effect. The addition of manganese sulfate to a pulp with low contents of transition metal compounds led to a severe loss in viscosity during oxygen bleaching with magnesium addition. Evidently the combined effects observed with addition of manganese plus magnesium are not unique for pulps containing nitrated lignin. Instead the large effects relate to the extremely low contents of catalytically active metal compounds both in the pretreated and in the soaked pulps. Current investigations with soaked pulps confirm these results. TJ

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