Interactions between metal compounds during oxygen bleaching of kraft pulp in virtually closed recovery systems

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ABSTRACT

Kraft pulps—freed from catalytically active transition metals and alkaline earth metals by soaking with SO_2–water and alkaline EDTA—were oxygen bleached in the presence of small additions of manganese (II) sulfate to simulate oxygen bleaching in systems designed to approach effluent-free production of bleached kraft pulps. Small additions of magnesium resulted in severe depolymerization of cellulose, while greater magnesium additions markedly suppressed this attack, giving rise to pulps of high selectivity. Chemical analysis of raw, ultrafiltered, and ultracentrifuged spent liquors from oxygen bleaching showed that manganese and the lignin fragments produced during bleaching were linked by stable bonds to polydisperse magnesium colloids consisting mainly of polymerized, hydrated magnesium oxides. Formation of the complex colloids relied on (a) covalent bonds, e.g., oxo bonds, (b) ionic bonds, e.g., ion exchange, and (c) coordinate (complexing) bonds of high stability. This permits complete removal of manganese from a "closed" system before final bleaching.

Application:

Laboratory results suggest strategies for eliminating manganese from closed bleach-plant recovery systems.

THE VIABILITY OF OXYGEN bleaching as a means of producing chemical pulps depends on the integrated recovery and incineration of spent liquors from both the oxygen bleaching stage and the cooking stage. The current practice is to use spent bleach liquors to displace the spent cooking liquors from the pulp entering the oxygen stage. This and other schemes *(1, 2)* transfer large amounts of organic and inorganic compounds from the bleach and cooking liquors to the oxygen stage. Recent laboratory bleaches *(3, 4)* show that a closed-mill system leads to complications and unforeseen improvements. The situation is complicated by the presence of transition-metal compounds, e.g., those of Mn, which can give rise to either catalytic effects on the oxygen reactions in alkaline media or retard these reactions. In bicarbonate media, Mn—under the proper conditions—can promote delignification of lignocellulose and retard the depolymerization of the cellulose *(5, 6)*, giving rise to an increased selectivity (defined as viscosity at a given kappa number).

The most favorable results with kraft softwood pulps during bleaching with sodium hydroxide as the added alkali were obtained with pulps pretreated with NO_2 before oxygen bleaching *(3)*. The pretreatment removed catalytically active transition metals and Mg almost quantitatively and modified the lignin so that it was removed rapidly. We here report on oxygen bleaching of kraft pulps that were pretreated by soaking in SO_2–water and EDTA (ethylenediamine tetraacetic acid) to remove Mg and transition metals. Attention is given to the recirculation of spent oxygen-bleach liquor, which has not been studied in previous publications with carefully controlled amounts of metal compounds in the bleach liquor *(3, 7)*.

EXPERIMENTAL CONDITIONS

Kraft pulp from softwood, mainly *Pinus sylvestris*, produced in a mill in southern Sweden was washed carefully with water. The pulp was soaked at 5% consistency in an aqueous solution of SO_2 for 30 min at 20°C and pH 2.5. This treatment removed most of the Mg, Ca, and Mn from the pulp. It then was soaked at 5% consistency in EDTA solution containing 6 g/L of the disodium salt. After addition of sodium hydroxide solution, the soaking continued at pH 9.2 for 22 h. After washing and an additional soaking with SO_2–water, the pulp was washed and centrifuged to 35% consistency. Deionized and subsequently distilled water was used in all washings. The soaked pulp had a kappa number of 32.1 and an intrinsic viscosity of 1182 dm^3/kg.

To prepare large amounts of spent bleach liquor containing very low quantities of Mg and catalytically active transition-metal compounds, 40-g batches of the soaked pulp underwent oxygen bleaching for 60 min in rotating 1500-mL autoclaves at 106°C, 8% consistency, and an addition of 3% NaOH (calculated on dry pulp). The initial oxygen pressure was 0.6 MPa. Analysis of this liquor, denoted spent liquor B, is given in **Table I** together with that of spent liquor C, which was prepared under more severe conditions (5% NaOH, 1.0 MPa O_2, 180 min).

Spent liquor	pH	Total solids, g/kg liquor	Ash, g/kg liquor	CONCENTRATION, mmole/kg liquor Na	Mg	Mn	CO_2
B	11.3	6.6	4.0	58	0.033	0.0018	6.7
C	10.8	8.1	5.0	92	0.033	0.0018	9.6

*Minor elements in the soaked pulp, mmole/100 g dry pulp: Mg 0.04, Mn 0.002, Fe 0.02. Iron was mainly present in inactive form in silicates (cf. *(4)*).

I. Analyses of the spent bleach liquors B and C prepared from soaked kraft pulp*

Oxygen bleaching

Samples of the soaked pulp (corresponding to 16 g dry pulp) were mixed in 1500-mL autoclaves with deaerated aqueous solutions of manganese (II) sulfate, magnesium sulfate, and, in some cases, complexing agents. Finally, NaOH solution (3% by weight on dry pulp) was added to the pulp, which was at 8% consistency. The initial oxygen pressure at 22°C was 0.6 MPa, and the temperature during bleaching was 106°C.

Solutions of two complexing agents (glycolate and galactarate) were prepared from pro analysis grade by mixing with deaerated NaOH solution to saponify the ester linkages at room temperature and obtain a pH that remained at 8.0 for at least one hour. The solution for the third complexing agent (EDTA) was prepared by dissolving the disodium salt of EDTA in water and mixing with NaOH so that the composition of the added complexing agent corresponded to the tetrasodium salt. If not otherwise stated, the additions of complexing agents corresponded to one mole per mole of added $MgSO_4$.

In many bleaches, a portion of the water was substituted for the same weight of spent liquors B or C, thus simulating recirculation of spent bleach liquor.

Cooling the autoclaves in tap water terminated the bleaches after 60, 120, or 180 min, including the heating period to 106°C. The pressure was released after shaking the autoclaves at room temperature so that the carbon dioxide transferred to the gas phase was in equilibrium with the spent liquor. Filtration through a Buchner funnel separated the pulp from the liquor. The opalescent filtrate was passed twice through the filter cake (height = 1.5 cm) to remove suspended particles. Aliquots of the spent liquor were passed through ultrafilters (UF) with separation limits of 100,000, 10,000, and 1000 (reported by the manufacturer Amicon Corp., Lexington, MA). Large amounts of brown material were retained.

The delignification rate and the rate of depolymerization of the cellulose were estimated from decreases in kappa number (SCAN C1:77) and intrinsic viscosity (SCAN C15:62), respectively. Metal determinations were carried out by atomic absorption. The concentrations of Mg and Mn in spent liquors and ultrafiltrates differed by less than 2% from those found after acidification with sulfuric acid (H_2SO_4:H_2O 1:3 w/w). Carbon dioxide in the cooled spent liquors was determined by acidification, stripping at 50°C with a stream of nitrogen, absorption in barium hydroxide solution, and gravimetric determination as barium carbonate.

Ultracentrifugation

The separation of the colloids in the spent liquors from oxygen bleaching was investigated by ultracentrifugation (Sorvall RC-5B ultracentrifuge with rotor SS-34) at varying numbers of revolutions. The maximum RCF (relative centrifugal force) was 47,800 *g* obtained at 20,000 revolutions per minute (rpm). Mg and Mn were determined in samples of the clear solution. The absorbance at pH 6.6 was determined in the same solution after mixing 1.00 g of the solution with 49.0 g of a phosphate buffer *(8)*.

Wet oxidation of organic compounds in bleach liquors

The wet oxidation (wet combustion) of dissolved organic solutes in bleach liquors was studied in the absence of pulp. The autoclaves used in the oxygen bleaches were employed under conditions similar to those during the oxygen bleaches of pulp. After the oxygen treatment, the cooled liquor passed through a tight glass filter (Pyrex, por. 3) to remove suspended particles formed in small amounts during the wet oxidation. Portions of this opalescent liquor were analyzed and ultrafiltrated. A constant weight (180 g) of deaerated spent bleach liquor was mixed in the absence of air with a solution containing $MgSO_4$ and $MnSO_4$ and diluted with water to 200 g. In some experiments, the spent liquor was concentrated by evaporation at 50°C before introduction into the autoclave and bringing the mixture in contact with oxygen. Evaporation was carried out to solids contents within the range used in integrated recovery and burning of liquors from industrial oxygen bleaching and cooking. The formation of carbon dioxide was calculated as the difference between the determinations of CO_2 before and after the wet oxidation.

RESULTS AND DISCUSSION

Delignification and depolymerization of cellulose—effects of manganese and magnesium additions

Comparison of the first four bleaches in **Table II** shows that Mn addition gave rise to an appreciable loss in viscosity under the applied conditions, while the effect on delignification was small. In the bleaches with a constant amount of Mn (0.6 mmole/100 g pulp), the addition of Mg at 4.5 mmole/100 g pulp (molar ratio of Mg:Mn = 4.5:0.6 = 7.5) had no appreciable effect on pH or delignification while contributing strongly to a loss in viscosity. These

results agree with those in model experiments with cellobiitol *(4)* and oxygen bleaches of kraft pulps pretreated with NO_2 *(3)*. Evidently, the Mg compounds that are commonly applied to protect the cellulose in industrial bleach plants can give rise to an increased attack on the cellulose when Mn is present in the pulp.

Increasing the Mg addition by 100% to 9.0 mmole/100 g pulp (molar ratio of Mg:Mn = 9.0:0.6 = 15.0) retarded delignification somewhat while markedly suppressing cellulose depolymerization. The increase in Mg addition had no effect on final pH.

The soaked pulp responded dramatically to changes in the Mg:Mn ratio, similar to the pulps pretreated with NO_2 *(3)*. The rapid delignification of the pretreated pulps—depending both on the oxidative reactions in the presence of oxygen and on rapid alkaline cleavages of covalent lignin bonds in the absence of oxygen—contributed to observed differences *(9)*.

Recirculation of spent liquor B led to an increase in viscosity in comparable bleaches for 60 or 120 min. In the bleaches with additions of both Mn and Mg, the recirculation gave rise to greatly improved selectivity because of markedly slower depolymerization of the cellulose and increased delignification rates. Results for the addition of complexing agents also are reported in Table II. The largest effects occurred with EDTA. Both the delignification rate and the depolymerization rate of the cellulose increased with EDTA addition in the bleaches with recirculation of spent liquor. In the bleaches without recirculation, EDTA retarded delignification, while during an early period, the rate of depolymerization of the cellulose increased. Smaller effects were obtained with the hydroxycarboxylates (glycolate and galactarate).

The threefold addition of glycolate and galactarate in bleaches with recirculated bleach liquor C increased the viscosities after a given residence time, as seen in **Table III**. The influence on the delignification was small.

The influence of Mg and Mn dur-

Residence time, min	Final pH	ADDITIONS Mg	Mn	Complexing agent [a]	PULP PROPERTIES Kappa number	Viscosity, dm³/kg
		mmole/100 g pulp				
No recirculation of spent bleach liquor						
60	11.3	0	0	…	18.8	957
120	10.0	0	0	…	15.0	920
60	11.3	0	0.6	…	18.2	905
120	10.0	0	0.6	…	15.0	887
60	11.1	4.5	0.6	…	18.1	887
120	10.0	4.5	0.6	…	15.2	839
60	11.1	9.0	0.6	…	21.3	940
120	10.0	9.0	0.6	…	16.6	905
60	11.1	4.5	0.6	Glycolate	19.0	890
120	10.0	4.5	0.6	Glycolate	15.1	851
60	11.1	4.5	0.6	Galactarate	19.1	870
120	10.0	4.5	0.6	Galactarate	15.4	839
60	11.7	4.5	0.6	EDTA	21.3	848
120	10.3	4.5	0.6	EDTA	16.4	839
With recirculation of spent bleach liquor B [b]						
120	10.4	0	0	…	15.2	935
120	10.4	0	0.6	…	13.3	909
60	11.1	4.5	0.6	…	17.7	928
120	10.0	4.5	0.6	…	14.7	901
60	11.1	4.5	0.6	Glycolate	18.0	916
120	10.0	4.5	0.6	Glycolate	14.6	902
60	11.1	4.5	0.6	Galactarate	17.2	950
120	10.0	4.5	0.6	Galactarate	14.7	929
60	11.7	4.5	0.6	EDTA	14.2	909
120	10.3	4.5	0.6	EDTA	11.5	875

[a] Complexing agents added at 1 mole per mole of added $MgSO_4$
[b] Recirculated total solids from spent bleach liquor B = 2.2 g per kg mixed liquor before oxygen bleaching

II. Influence of additions of $MgSO_4$, $MnSO_4$, and complexing agents on kappa number and intrinsic viscosity after oxygen bleaching (60 or 120 min at 106°C). Bleaches were carried out with and without recirculation of spent bleach liquor B.

Final pH	ADDITIONS Mg	Mn	Complexing agent [a]	PULP PROPERTIES Kappa number	Viscosity, dm³/kg
	mmole/100 g pulp				
With recirculation of spent bleach liquor C [b]					
10.4	0	0.6	…	13.1	901
10.2	4.5	0.6	…	14.0	879
10.2	4.5	0.6	Glycolate	13.9	885
10.1	4.5	0.6	Galactarate	13.5	901
10.4	4.5	0.6	EDTA	12.1	860
9.9	4.5	0.6	Glycolate *	14.5	900
9.9	4.5	0.6	Galactarate *	14.3	913

[a] Complexing agents added at 1 mole per mole of added $MgSO_4$ except for those marked with an asterisk, where the addition was increased to 3 moles per mole of added $MgSO_4$
[b] Recirculated total solids from spent bleach liquor C = 2.6 g per kg mixed liquor before oxygen bleaching

III. Influence of additions of $MgSO_4$, $MnSO_4$, and complexing agents on kappa number and intrinsic viscosity after oxygen bleaching (120 min at 106°C). Bleaches were carried out with recirculation of spent bleach liquor C.

Final pH	ADDITIONS Mg	Mn	Complexing agent [a]	PULP PROPERTIES Kappa number	Viscosity, dm^3/kg
	mmole/100 g pulp				
No recirculation of spent bleach liquor					
9.2	4.5	0.6	…	12.0	835
With recirculation of spent bleach liquor B [b]					
9.3	0	0	…	11.9	835
9.2	0	0.6	…	10.5	846
9.3	4.5	0.6	…	11.7	837
9.2	4.5	0.6	Galactarate	11.1	867

[a] Complexing agent added at 1 mole per mole of added $MgSO_4$
[b] Recirculated total solids from spent bleach liquor B = 2.2 g per kg mixed liquor before oxygen bleaching

IV. Influence of additions of $MgSO_4$, $MnSO_4$, and galactarate on kappa number and intrinsic viscosity after oxygen bleaching (180 min at 110°C). Bleaches were carried out with and without recirculation of spent bleach liquor B.

ing bleaching to lower kappa numbers was studied in bleaches at elevated temperature and residence time. These results are reported in **Table IV**. Mn addition increased the selectivity, as demonstrated by improved delignification and a slight increase in viscosity. When Mn was present, the addition of Mg (molar ratio = 7.5) decreased the selectivity, as indicated by the suppressed delignification and an increased attack on the cellulose. In contrast to the bleaching under milder conditions, the influence of the recirculated bleach liquor was small.

Analysis of spent liquors

Magnesium. **Tables V–VII** show the measurements of Mg and Mn in spent liquors and in ultrafiltrates from the oxygen bleaches with added $MgSO_4$ and $MnSO_4$. With regard to the beneficial effect of the recirculation on the selectivity, most metal determinations were carried out after bleaches with recirculation. With addition of 4.5 mmole Mg per 100 g pulp, the highest concentration amounted to 3.9 mmole of Mg per kg liquor, i.e., close to the value 4.5/1.15 = 3.91 estimated under the assumptions of (a) complete dissolution of Mg compounds in the liquor during bleaching and (b) equal concentrations in the liquor inside the fibers, on the fiber surface, and in the external liquor separated from the pulp *(10)*. As shown in Tables V–VII, a virtually complete dissolution of the added Mg occurred in most bleaches.

The lowest concentration of Mg in the spent liquor, corresponding to 64% of the added amount, was found after bleaching without complexing agents and recirculated liquor at a final pH of 11.1 (row 2 in Table V). Increasing the residence time from 60 to 120 min increased the dissolution to 85%. This increase can be mainly attributed to the decreased concentration of hydroxide ions (pH 10.0), resulting in a marked increase in the solubility of precipitated hydrated Mg oxides *(11, 12)*. The decrease in hydroxide concentration during bleaching is mainly due to the formation of various organic acids from the fiber constituents (cellulose, hemicellulose, and lignin). Glycolic acid is—at least under certain conditions—the most abundant carboxylic acid *(13)* and belongs to the acids known to give soluble complexes of high stability with both Mg and Mn. The produced complexing agents contribute to the dissolution of Mg during oxygen bleaching.

Compared at the same pH, the additions of the complexing agents glycolate and galactarate increased the dissolution of Mg (Table V). Galactarate contains two carboxylate ions and four hydroxyl groups. Its structure suggests that Mn of higher oxidation states than +II gives stable galactarate complexes, especially at high alkalinity during bleaching *(4, 14–16)*. Anions corresponding to several other dicarboxylic hydroxy acids are present in appreciable amounts in spent liquors from oxygen bleaching *(17)*.

In comparable bleaches at the same pH during the final part of the bleaching, the concentration of Mg increased markedly by the recirculation of spent bleach liquors (Table V). In the bleaches with recirculation of spent liquor B, the addition of glycolate or galactarate led to slightly increased concentrations of Mg in the liquor, while a complete dissolution occurred with EDTA despite a higher pH.

Addition of three moles of glycolate or galactarate per mole of Mg led to a complete dissolution, even during bleaching without recirculation of spent liquor (Table VI). With the recirculated spent liquor C, containing larger amounts of organic hydroxy acids, the dissolution was complete even in bleaches without other additions of complexing agents than those in the recirculated liquor.

Increasing the Mg addition by 100%, to 9.0 mmole per 100 g pulp, resulted in higher Mg concentrations in the liquor than in the other reported bleaches, as seen in Table V. An appreciable proportion was retained in the filter cake (about 37% after 60 min and 21% after 120 min). The retained Mg was present mainly as precipitated basic Mg compounds. The comparatively low proportions in the liquor are due to the absence of added complexing agents.

Colloids and aggregates. In the second bleach liquor in Table V (row 2, the liquor containing only 64% of the added Mg), the proportion in the ultrafiltrate from the coarse filter (UF 100,000) was only 5% of the added Mg. In the ultrafiltrate from the tighter filter (UF 10,000), the proportion was 3%. Increasing the bleaching time from 60 to 120 min

Bleach time, min	Final pH	ADDITIONS Mg mmole/100g pulp	Mn	Complexing agent [a]	FOUND, mmole/kg liquor or filtrate: Spent liquor Mg	Spent liquor Mn	UF 100,000 Mg	UF 100,000 Mn	UF 10,000 Mg	UF 10,000 Mn	UF 1,000 Mg	UF 1,000 Mn
No recirculation of spent bleach liquor												
120	10.1	0	0.6	…	…	0.086	…	0.057	…	0.040	…	…
60	11.1	4.5	0.6	…	2.5	0.22	0.20	0.013	0.12	0.011	…	…
120	10.0	4.5	0.6	…	3.3	0.26	0.65	0.045	0.53	0.036	…	…
60	11.1	9.0	0.6	…	4.9	0.34	2.0	0.057	1.52	0.040	…	…
120	10.0	9.0	0.6	…	6.2	0.38	3.0	0.076	2.0	0.057	…	…
120	8.0 [b]	4.5	0.6	…	3.6	0.24	2.0	0.11	1.83	0.092	0.22	0.013
With recirculation of spent bleach liquor B [c]												
60	11.1	4.5	0.6	…	3.5	0.45	0.40	0.038	0.34	0.023	…	…
120	10.0	4.5	0.6	…	3.6	0.45	1.72	0.10	1.37	0.083	…	…
120	10.4	0	0.6	…	…	0.10	…	0.058	…	0.044	…	…
60	11.1	4.5	0.6	Glycolate	3.6	0.45	0.45	0.040	0.37	0.020	…	…
120	10.0	4.5	0.6	Glycolate	3.6	0.46	1.65	0.092	1.23	0.072	…	…
60	11.1	4.5	0.6	Galactarate	3.6	0.46	1.00	0.081	0.64	0.041	0.25	0.004
120	10.0	4.5	0.6	Galactarate	3.6	0.46	2.2	0.13	1.27	0.090	…	…
60	11.7	4.5	0.6	EDTA	3.9	0.40	3.6	0.17	2.8	0.13	…	…
120	10.3	4.5	0.6	EDTA	3.9	0.46	3.9	0.31	3.6	0.25	…	…
120	8.7 [b]	4.5	0.6	…	3.7	0.46	2.9	0.19	2.0	0.057	…	…
120	8.7 [b]	4.5	0.6	Glycolate	3.7	0.46	2.9	0.21	2.4	0.11	…	…
120	8.7 [b]	4.5	0.6	Galactarate	3.7	0.46	3.1	0.25	2.7	0.13	0.49	0.013
120	8.7 [b]	4.5	0.6	EDTA	3.9	0.46	3.9	0.45	3.9	0.43	0.65	0.044

[a] Complexing agent added at 1 mole per mole of added $MgSO_4$
[b] NaOH addition decreased from 75 mmole (3 g) to 25 mmole (1 g) per 100 g dry pulp
[c] Recirculated total solids from spent bleach liquor B = 2.2 g per kg mixed liquor before oxygen bleaching

V. Influence of additions of $MgSO_4$, $MnSO_4$, and complexing agents on concentrations of Mg and Mn in spent liquor from oxygen bleaching (60 or 120 min at 106°C) and in ultrafiltrates (UF) with separation limits 100,000, 10,000, and 1,000. Bleaches were carried out with and without recirculation of spent bleach liquor B.

Final pH	ADDITIONS Mg mmole/100 g pulp	Mn	Complexing agent [a]	FOUND, mmole/kg liquor or ultrafiltrate: Spent liquor Mg	Spent liquor Mn	UF 100,000 Mg	UF 100,000 Mn	UF 10,000 Mg	UF 10,000 Mn
No recirculation of spent bleach liquor									
10.0	4.5	0.6	Glycolate *	3.9	0.48	1.8	0.11	1.52	0.093
10.0	4.5	0.6	Galactarate *	3.9	0.48	2.8	0.27	1.81	0.19
With recirculation of spent bleach liquor C [b]									
10.4	0	0.6	…	…	0.10	…	0.052	…	0.040
10.2	4.5	0.6	…	3.9	0.46	2.0	0.10	1.22	0.062
10.2	4.5	0.6	Glycolate	3.9	0.46	2.0	0.10	1.30	0.067
10.1	4.5	0.6	Galactarate	3.9	0.46	2.2	0.12	1.41	0.077
10.4	4.5	0.6	EDTA	3.9	0.46	3.9	0.29	3.5	0.22
9.9	4.5	0.6	Glycolate *	3.9	0.48	2.2	0.13	1.71	0.10
9.9	4.5	0.6	Galactarate *	3.9	0.48	2.5	0.34	2.3	0.23

[a] Complexing agents added at 1 mole per mole of added $MgSO_4$ except for those marked with an asterisk, where the addition was increased to 3 moles per mole of added $MgSO_4$
[b] Recirculated total solids from spent bleach liquor C = 2.6 g per kg mixed liquor before the oxygen bleaching

VI. Influence of additions of $MgSO_4$, $MnSO_4$, and complexing agents on concentrations of Mg and Mn in spent liquor from oxygen bleaching (120 min at 106°C) and in ultrafiltrates (UF) with separation limits 100,000 and 10,000. Bleaches were carried out with and without recirculation of spent bleach liquor C.

Final pH	ADDITIONS Mg	Mn	Complexing agent [a]	FOUND, mmole/kg liquor or ultrafiltrate: Spent liquor Mg	Spent liquor Mn	UF 100,000 Mg	UF 100,000 Mn	UF 10,000 Mg	UF 10,000 Mn
	mmole/100 g pulp								
No recirculation of spent bleach liquor									
9.2	4.5	0.6	…	3.9	0.38	3.2	0.19	2.9	0.11
With recirculation of spent bleach liquor B [b]									
9.2	0	0.6	…	…	0.13	…	0.11	…	0.073
9.3	4.5	0.6	…	3.9	0.50	3.2	0.24	2.8	0.15
9.2	4.5	0.6	Galactarate	3.9	0.50	3.3	0.29	2.9	0.21

[a] Complexing agent added at 1 mole per mole of added $MgSO_4$
[b] Recirculated total solids from spent bleach liquor B = 2.2 g per kg mixed liquor before oxygen bleaching

VII. Influence of additions of $MgSO_4$, $MnSO_4$, and galactarate on concentrations of Mg and Mn in spent liquor from oxygen bleaching (120 min at 110°C) and in ultrafiltrates (UF) with separation limits 100,000 and 10,000. Bleaches were carried out with and without recirculation of spent bleach liquor B.

increased the total proportion of Mg in the liquor to 85% and led to markedly increased concentrations in the ultrafiltrates. Evidently, the increased duration of the oxygen–alkali treatment transferred Mg from the fibers into the liquor phase and decreased the size of the colloids in the liquor. This fragmentation of the colloids and aggregates is reflected by the very large increases in the concentrations in (a) the ultrafiltrates from the bleaches with recirculation of spent liquor and (b) ultrafiltrates with glycolate, galactarate, and above all, EDTA. In the experiments carried out with lower additions of NaOH, 100% of the added Mg was present in the liquor containing both recycled liquor and EDTA. Likewise, 100% was present even in the ultrafiltrates UF 100,000 and UF 10,000, indicating fragmentation of colloids and aggregates in the solution with a final pH of 8.7. Even the liquor from oxygen bleaching for 120 min with the larger addition of NaOH (final pH 10.3) contained 100% of the added Mg in the spent liquor and in UF 100,000, while in the test with the tighter ultrafilter (UF 10,000), 92% passed through the filter. A complete dissolution of the added magnesium in the spent liquor occurred even after 60 min, despite the higher pH. The ultrafiltrates contained 92% and 72%, respectively, of the amount of Mg before the ultrafiltrations. Evidently, increasing the bleaching time increased the fragmentation into smaller units.

The three bleaches with Mg at 110°C (Table VII) gave rise to a complete dissolution not only in the experiments with recirculation but also in the experiment without recirculation and without complexing agents. In this experiment, UF 100,000 contained 82% of the added Mg, while 74% was present in UF 10,000. The relatively large proportions in the ultrafiltrates can be ascribed to the combined effects of a large consumption of hydroxide ions and a rapid formation of complexing agents from the fiber constituents.

In the bleaches with recirculation of bleach liquor C (Table VI), which contained larger amounts of complexing hydroxy acids than liquor B, the added Mg was dissolved completely. The largest proportions in the ultrafiltrates—100% in UF 100,000 and 90% in UF 10,000—were again present after bleaching with EDTA as the complexing agent.

Manganese. In all bleaches with Mn, the added amount of $MnSO_4$ was 0.60 mmole per 100 g pulp, which corresponds to 0.60/1.15 = 0.52 mmole Mn per kg liquor if a complete dissolution occurs. In the bleaches with recirculation but without added Mg, only 19% of the added Mn (Tables V and VI) and 25% of the added Mn (Table VII) were present in the spent liquor.

A striking effect shown in Tables V–VII is the markedly enhanced concentrations of Mn both in the spent liquors and in comparable ultrafiltrates as a result of the addition of $MgSO_4$ before the oxygen bleaching. In the bleaches at 106°C with Mg addition (Table V), the largest proportion of Mn in the spent liquor was 88% of the added amount both under standard conditions and with the charge of NaOH decreased to 25 mmole per 100 g dry pulp. The smallest proportion, 42%, was found after bleaching for 60 min without recirculation or introduction of complexing agents. Increasing the time to 120 min increased the proportion in the liquor to 50%. The proportion in UF 100,000 increased from 2.5% to 9% and that in UF 10,000 from 2.1% to 7%. In general, the prolonged bleaching time increased the Mn concentration in the ultrafiltrates. This shows that colloids containing Mn were subjected to fragmentation during bleaching. The molar ratio Mg:Mn in the ultrafiltrates was affected only slightly by the increased time, indicating that Mn was linked by stable bonds to the hydrated MgO colloids containing lignin.

The severe conditions during the oxygen bleaching in Table VII were reflected in enhanced Mn concentrations in the liquor and in the ultrafiltrates. The highest concentration in the liquor corresponded to 96% of the Mn added to the liquor. In most bleach liquors, the concentrations of

ADDED IN BLEACHING			Centrifuge time	CONCENTRATION, mmole/kg liquor						
Mg	Mn			In bleach liquor			In diluted liquor			Absorbance
mmole/kg liquor		Mg:Mn [a]	(10,000 rpm), min	Mg	Mn	Mg:Mn [a]	Mg	Mn	Mg:Mn [a]	(at 280 nm)
Low Mg addition [b]										
3.9	0.52	7.5	0	3.3	0.26	12.7	1.11	0.087	12.8	1.139
3.9	0.52	7.5	15	3.0	0.23	13.0	0.92	0.072	12.8	1.110
3.9	0.52	7.5	30	2.8	0.21	13.3	0.85	0.068	12.5	1.072
3.9	0.52	7.5	45	2.5	0.19	13.2	0.83	0.060	13.8	1.053
3.9	0.52	7.5	90	2.5	0.19	13.2	0.83	0.060	13.8	1.051
High Mg addition [c]										
7.8	0.52	15.0	0	6.2	0.38	16.3	2.1	0.13	16.2	1.062
7.8	0.52	15.0	15	5.5	0.32	17.2	1.75	0.098	17.9	1.026
7.8	0.52	15.0	30	4.9	0.26	18.8	1.60	0.086	18.6	1.002
7.8	0.52	15.0	45	4.5	0.21	21.4	1.51	0.071	21.1	0.955
7.8	0.52	15.0	90	4.5	0.21	21.4	1.52	0.072	21.1	0.953

[a] Molar ratio
[b] Corresponding to 4.5 mmole Mg and 0.60 mmole Mn per 100 g pulp
[c] Corresponding to 9.0 mmole Mg and 0.60 mmole Mn per 100 g pulp

VIII. Influence of duration of centrifuging (at 10,000 rpm) on Mg and Mn concentrations and on absorbance (at 280 nm) in clear centrifuged liquors from oxygen bleaching (120 min at 106°C). The bleach liquors were the same as in Fig. 1.

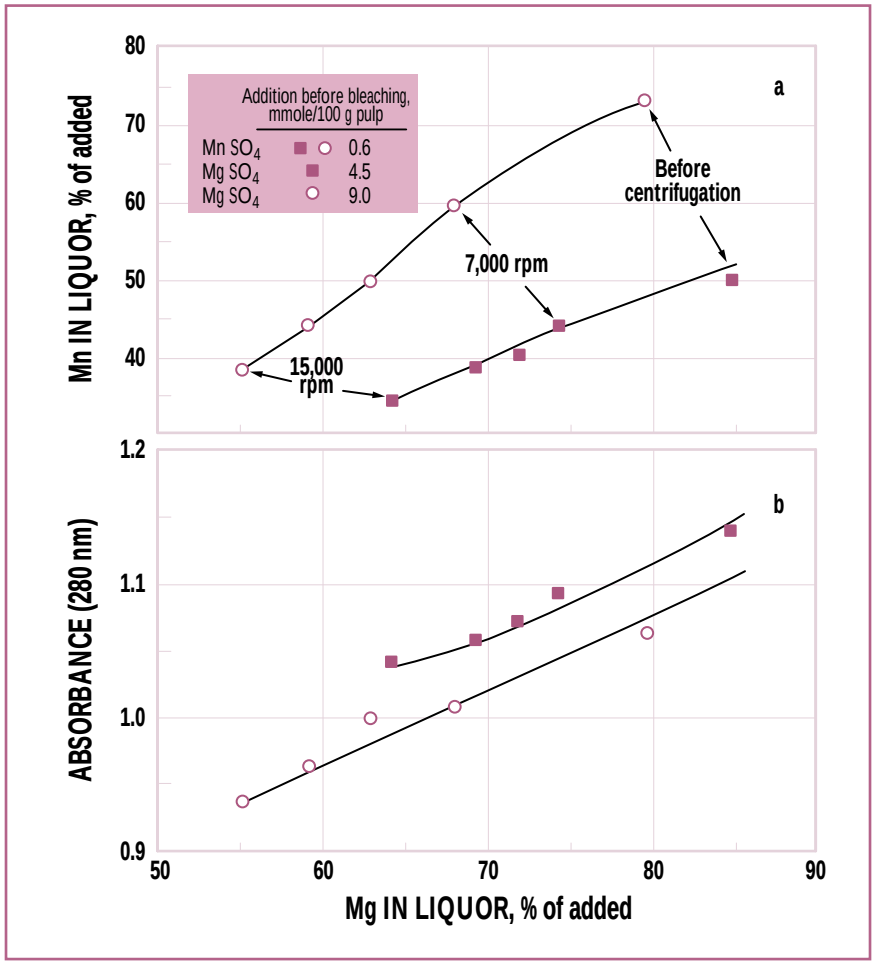
Mn parallelled those of Mg. This result, together with the analyses of the ultrafiltrates, supports the conclusion that the Mn in the liquors was linked to the Mg colloids by bonds of high stability. D'Ans and Mattner *(18)* found that manganese (II) ions can be removed effectively from NaOH solutions by coprecipitation with magnesium hydroxide and that the Mn is not deprived of its catalytic activity. Indeed, Mn precipitated together with hydrated magnesium oxides exerts strong catalytic effects *(19)*.

The solutes in the ultrafiltrate from the filter with the separation limit 1000 (UF 1000), denoted as low-molecular-weight solutes, contained complexes including oligomers of small size (Table V). The total Mg concentration was extremely low in UF 1000. Evidently, Mg colloids of fairly large dimensions constituted the predominant proportion of the Mg in the spent liquors. The lowest concentrations of the low-molecular-weight complexes were present in the liquors with an incomplete transfer of the added Mg into the liquor phase. The highest concentration of Mg in UF 1000 was found in the experiment with recirculated spent liquor and EDTA. The Mn concentration in UF 1000 was higher after this bleaching than in the bleaches that gave rise to lower concentrations of Mg in the ultrafiltrates. The results suggest that Mg and Mn were linked together also in soluble complexes of low relative molecular mass, e.g., in polynuclear compounds linked by covalent bonds *(15)*.

Ultracentrifugation of spent bleach liquors

Spent liquors from the oxygen bleaching were subjected to ultracentrifugation at varying revolutions per minute to study the possible separation of lignin fragments dissolved during bleaching and of Mn from the colloid, mainly consisting of polymerized hydrated MgO. After centrifugation for 30 min, a sediment adhered to the bottom of the centrifuge tubes. Its color was brown to dark brown, indicating varying contents of lignin fragments and manganese. Samples of the clear solutions were withdrawn and analyzed, and the results are presented in **Fig.1**.

The marked decrease in Mg concentration with increasing speed of the ultracentrifuge confirms the results from ultrafiltration, i.e., that the colloid containing hydrated magnesium oxide as the main constituent was polydisperse. Figure 1a shows the relationship between the proportion of Mn in the clear liquors and the proportion of Mg in the same liquors. Fig.1b shows a plot of the absorbance at 280 nm vs. the proportion of Mg in the same liquors. The highest value in each curve refers to the liquor before centrifugation. The decreasing values refer to the same liquor centrifuged at increasing number of revolutions per minute. Both the proportion of Mn in the liquor (Fig. 1a) and the absorbance (Fig. 1b) decreased continuously with decreasing proportion of Mg in the centrifuged liquor (calculated as a percent of the amount added during bleaching). The results confirm our conclusion from analyses of spent bleach liquors and ultrafiltrates that both Mn and lignin fragments in the spent liquors from the oxygen bleaching were linked by stable bonds to the Mg colloid. In fact, no appreciable separation of these species from each other occurred during the centrifugation. For example, the molar ratio Mg:Mn



1. (a) Percent manganese remaining in centrifuged spent liquor from oxygen bleaching and (b) absorbance of centrifuged liquor vs. percent magnesium remaining in liquor at two levels of Mg addition. (Spent liquor obtained after bleaching for 120 min at 106° C; no recirculation of spent liquor or addition of complexing agents; liquor ultracentrifuged for 30 min at 7000, 10,000, 12,000, and 15,000 rpm.)

in the bleaches with the lower addition of Mg increased from 12.6 to 13.3 to 13.9 when the centrifuge speed was increased from 7000 rpm to 10,000 rpm to 15,000 rpm. With the double Mg addition during bleaching, the corresponding ratios were 17.1, 18.8, and 20.0. Similarly, the influence of centrifugation speed on the ratio Mg: absorbance at 280 nm was negligible.

In their pioneering work with gold sols, Svedberg and Rinde *(20, 21)* studied the sedimentation during varying periods of time in ultracentrifuges run at constant speed. **Table VIII** shows some results obtained with our bleach liquors after centrifugation at 10,000 rpm for 15–90 min. Zero time denotes spent liquor before centrifugation. The spent bleach liquors were the same as in Fig 1. In all centrifugations, the concentration of Mg in the clear bleach liquor decreased markedly with increasing centrifugation time from 0 to 45 min, while extending the time to 90 min exerted no effect detectable by the technique used in the commercial ultracentrifuge. The results confirm that the Mg colloids in the bleach liquors were polydisperse.

In the first bleach liquor, the added Mg before O_2 bleaching was 3.9 mmole per kg liquor. The concentration in the spent liquor decreased to 3.3 mmole, which shows that 0.6 mmole, i.e., 15% of the added Mg, was retained in the filter cake of pulp. The retained amount of Mn was 50% of the added Mn. During the bleaching with the double addition of Mg, the percentage remaining in the pulp cake increased to 20%, while the retained Mn calculated in percent of the added Mn decreased to 27%. It is well known that Mn can be coprecipitated *(18)* effectively with hydrated Mg oxides, including $Mg(OH)_2$. Under the applied conditions, this effect was less important than the interactions responsible for the bonding of Mn to the dissolved Mg compounds. With addition of 4.5 mmole Mg per 100 g pulp, the molar ratio Mg:Mn in the clear solution increased during the time interval 0–45 min. The ratio was unaffected when the centrifugation time was increased to 90 min. With the double addition, the ratio increased somewhat more during the interval 0–45 min but was again unaffected by increasing the time to 90 min. The increased addition of Mg during the bleaching resulted in an increased molar ratio. Dilution before centrifugation of the spent liquors with water in the proportion 1:2 (w/w; liquor:water) had a slight effect on the ratio.

In the centrifugations at constant rate and varying centrifugation time (Table VIII), the lignin fragments recorded at 280 nm, like those depicted in Fig. 1b, sedimented together with the colloid containing hydrated magnesium oxides.

All regularities during the ultracentrifugation and chemical analyses of spent liquors and ultrafiltrates from oxygen bleaches of kraft pulps in the presence of both Mg and Mn show that dissolved Mn ions and lignin fragments were linked by stable bonds to a polydisperse Mg colloid consisting mainly of hydrated, polymerized magnesium oxides. It can be concluded that under the applied conditions (a) covalent bonds such as oxo bonds, (b) ionic bonds, e.g., ion exchange, and (c)

Time, min	Final pH	ADDITIONS, per kg liquor [a] Total solids, g from liquor C	Mg, mmole	Mn, mmole	FOUND, mmole/kg liquor or ultrafiltrate Treated liquor Mg	Treated liquor Mn	UF 100,000 Mg	UF 100,000 Mn	UF 10,000 Mg	UF 10,000 Mn	CO_2 formation, mmole/kg liquor	COD, [b] g/kg liquor
30	9.9	3.3	3.6	0.48	3.6	0.48	2.6	0.027	2.1	0.018	0.6	…
60	9.8	3.3	3.6	0.48	3.6	0.48	2.7	0.027	2.1	0.018	0.6	3.4
120	9.6	3.3	3.6	0.48	3.6	0.48	2.9	0.027	2.2	0.018	0.8	…
60	10.3	12.1	0	0	…	…	…	…	…	…	1.2	13.2
60	10.3	12.1	0	0.48	…	0.30	…	0.016	…	0.012	4.0	12.8
60	10.4	12.1	0	0.96	…	0.20	…	0.027	…	0.018	3.1	13.0
60	10.1	12.1	3.6	0	3.6	0	2.7	…	2.1	…	1.6	…
60	10.1	12.1	3.6	0.48	3.6	0.48	2.6	0.082	2.2	0.050	2.4	13.2
60	10.1	12.1	7.2	0.48	7.2	0.48	4.5	0.103	3.0	0.062	1.6	…
60	10.5	24.0	0	0.48	…	0.30	…	0.027	…	0.018	6.2	24.1
60	10.5	24.0	0	0.96	…	0.18	…	0.035	…	0.022	5.1	25.0
60	10.3	24.0	3.6	0.48	3.6	0.48	1.6	0.098	1.2	0.056	5.1	25.0
60	10.3	24.0	7.2	0.96	7.2	0.96	3.1	0.18	2.4	0.10	5.0	25.1

[a] Mixed liquor before O_2–NaOH treatment
[b] Chemical oxygen demand of the oxygen-treated liquor determined according to German standard method DIN 38409-H41

IX. O_2–NaOH treatment of recirculated spent bleach liquor in the absence of pulp

coordinate (complexing) bonds of high stability were of great importance for the formation of the complex colloid. The ultraviolet (UV) absorbance in the centrifuged solutions shows that the lignin fragments that sedimented together with the hydrolyzed magnesium ions belong to the group denoted basic salts *(22)*.

Wet oxidation of liquors from oxygen bleaching

During oxygen bleaching of wood pulp, dissolved compounds derived from lignin, extractives, and carbohydrates in the fibers are degraded further by oxygen in the alkaline liquor. Among the reaction products are numerous carboxylic acids, with lower molecular mass than most hydroxycarboxylic acids, and other products dissolved during an early period of bleaching *(13, 23)*. Oxygen treatment of alkaline spent liquors from oxygen bleaching led to a decrease in the relative molecular size, as determined by gel-permeation chromatography (GPC) of the dissolved lignin fragments *(9)*. Carbon dioxide is among the final reaction products *(23, 24)*.

Increased oxygen pressure *(25)*, temperature *(25)*, and sodium hydroxide concentration *(25, 26)* promote wet oxidation. In previous oxygen treatments of bleach liquors, addition of Mg acetate gave rise to slightly retarded wet oxidation. Hardly significant effects on oxygen consumption were found with additions of either 3 or 30 mmole of manganese (II) hydroxide per liter of the spent liquor *(25)*. Those laboratory experiments were carried out with industrial bleach liquors containing Mg, Ca, Fe, and Mn.

With regard to the complex effects of the metal composition on the oxygen bleaching, e.g., in the presence of both Mg and Mn in various compounds and in different amounts, we have used well-defined additions of Mg and Mn to spent liquors virtually free from alkaline earth metals and catalytically active transition-metal compounds.

Wet oxidation during oxygen treatments of bleach liquors in the absence of pulps is shown in **Table IX**. Even with the lowest concentration of total solids containing the lowest concentration of complexing compounds, an addition of 3.6 mmole of Mg per kg liquor was recovered quantitatively in the treated liquor passed through the glass filter. The twofold amount of added Mg also was recovered quantitatively in the oxygen-treated spent liquors containing either 12.1 g or 24.0 g total solids per kg liquor. The added amount of Mn also was recovered quantitatively in the treatments with Mg addition. No precipitate could be seen on the glass filter in any of these experiments, while a black precipitate, mainly consisting of hydrated manganese oxides, was filtered off after the oxygen treatments when the addition of Mg was omitted. In the oxygen treatments with no added Mg and the lower addition of Mn (0.48 mmol/kg liquor), 63% of the added Mn was in the liquor that passed through the glass filter. In the treatments with no added Mg and the double amount of Mn (0.96 mmol/kg liquor), only 20% of the added Mn was dissolved in the liquor after passage through the same filter. Likewise, the concentrations of Mn in the ultrafiltrates UF 100,000 and UF 10,000 were

Bleach time, min	Final pH	Recirculated solids, g/kg liquor	PULP PROPERTIES Kappa number	Viscosity, dm³/kg	FOUND, mmole/kg liquor or ultrafiltrate Spent liquor Mg	Spent liquor Mn	UF 100,000 Mg	UF 100,000 Mn	UF 10,000 Mg	UF 10,000 Mn
120	9.5	7.9	13.9	906	3.9	0.48	3.5	0.36	3.0	0.24
120	9.5	19.8	15.9	892	3.9	0.48	3.5	0.38	2.5	0.26
180	9.0	19.8	12.6	848	3.9	0.50	3.6	0.40	3.0	0.28
120	9.5	37.1	15.7	907	3.9	0.50	3.6	0.38	2.5	0.24
180	9.0	37.1	12.7	870	3.9	0.50	3.6	0.40	2.8	0.28

* Mixed liquor before oxygen bleaching with addition of 3.9 mmole Mg and 0.52 mmole Mn per kg liquor

X. Influence of total recirculated solids during oxygen bleaching (120 or 180 min at 106°C) in the presence of solids from recirculated spent bleach liquor C *

decreased markedly by omitting the addition of Mg.

In comparable treatments at constant time (60 min), the formation of CO_2 increased with increasing solids content. The influence of Mg depended on the working conditions and was hardly significant in some treatments. In the treatments with 0.48 mmole Mn per kg liquor, addition of 3.6 mmole Mg suppressed the formation of CO_2. An additional decrease occurred with a double amount of Mg.

The treatments without added Mg showed that, under comparable conditions, the effects on the formation of CO_2 and on the decrease in chemical oxygen demand (COD) were enhanced by adding 0.48 mmole Mn per kg liquor, while doubling the amount of Mn (to 0.96 mmole/kg liquor) had less effect. Evidently, these effects of Mn parallelled those on the depolymerization of the cellulose during the oxygen bleaching in the absence of Mg.

Influence of the amount of recirculated solids

In the bleaches in Tables II–VII with recirculation of liquors B or C, the amounts of solids in the mixed liquors introduced in the bleaches were lower than in recovery systems of current interest. The effect of larger amounts of solids—virtually free from Mg, Ca, and transition-metal compounds known to affect the reaction rates during bleaching—was studied by concentrating the liquor under vacuum in a film evaporator. As expected from the results in Tables VI–VIII, the increased recirculation of the solids from the bleach liquors promoted the conversion of sparingly soluble Mg and Mn compounds into complexes soluble in the bleach liquor. **Table X** shows that both the Mg and Mn added as sulfates were recovered quantitatively in the spent bleach liquors. No precipitated compounds containing Mg or Mn were present.

The concentrations of Mg and Mn in the ultrafiltrates increased when the bleaching time was increased from 120 min to 180 min and were higher than in bleaches with lower amounts of recirculated solids. The quantitative removal of the Mn with the spent liquor is of great importance for the production of, for instance, viscose pulps and paper pulps of high quality that must be fully bleached to high brightness without chlorination.

With 37.1 g of total solids per kg liquor introduced into the bleaching, the selectivity was virtually the same as that with 7.9 g solids per kg liquor. A slightly lower selectivity was found with the intermediate amount of solids (Table X). Oxygen consumption by wet oxidation was small.

CONCLUDING REMARKS

The interactions between various metal compounds are more intricate than described in available publications. The complexity of these interactions will require further study as the industry continues its efforts to develop effluent-free bleached pulp mills.

Like NO_2-pretreated pulp, containing a small amount of manganese (II) ions, soaked pulp suffered an increase in depolymerization when small amounts of Mg compounds were added before bleaching in the presence of Mn. Increasing the addition of Mg to a molar ratio (Mg:Mn) of 7.5:1 and recirculation of bleach liquors suppressed this depolymerization dramatically.

The total amount of Mg present during oxygen bleaching can be recovered in the spent bleach liquor. Under proper conditions, Mn is present completely in the same liquor and can be released from the pulp mill by known methods (e.g., in sludge and grits from clarification of green and white liquors). Effective dissolution of manganese during oxygen bleaching can provide great benefits in final bleaching sequences that do not use chlorination. Process conditions can be chosen to achieve both high selectivity and effective removal of manganese compounds. **TJ**

KEYWORDS
Bibliographies, bleaching effluents, closed systems, kraft pulps, lignins, magnesium, manganese, oxygen bleaching, processing, recovering, soaking, spent liquors, ultracentrifuges.

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LITERATURE CITED

1. Samuelson, H. O. and Noréus, S. E. O., Swedish pat. 314,581 (1968).
2. SSVL, *Environmental Care Project, 1970–1973*, Ängpanneföreningen, Stockholm, 1974, p. 74.
3. Samuelson, O. and Öjteg, U., *Tappi J.* 77(11): 127(1994); *J. Wood Chem. Technol.* 15(3): 303(1995); *Holzforschung* 50(4): 329(1996).
4. Järrehult, B. and Samuelson, O., *Nordic Pulp Paper Res. J.* 7(3): 307(1993).
5. Abrahamsson, K. and Samuelson, O., *Svensk Papperstid.* 78(4): 135(1975).
6. Manouchehri, M. and Samuelson, O., *Svensk Papperstid.* 80(12): 381(1977).
7. Samuelson, O. and Öjteg, U., *Cellulose Chem. Technol.* 29(1): 55(1995).
8. Larsson, P. and Samuelson, O., *J. Wood Chem. Technol.* 10(3): 311(1990).
9. Larsson, P. and Samuelson, O., *J. Wood Chem Technol.* 13(2): 237(1993).
10. Andersson, B. and Samuelson, O., *Svensk Papperstid.* 61(23): 1001(1958); 62(21): 775(1959).
11. Baes, C. F. and Mesmer, R. E., *The Hydrolysis of Cations*, Wiley, New York, 1976.
12. Einaga, H., *JCS Dalton* 6: 912(1977); *J. Inorg. Nucl. Chem.* 43: 229(1981).
13. Kolmodin, H. and Samuelson, O., *Svensk Papperstid.* 75(5): 369(1972); 76(2): 71(1973).
14. Sawyer, D. T., *Chem. Rev.* 64: 633(1964).
15. Bodini, M. E., Willis, L. A., Riechel, T. L., *et al.*, *Inorg. Chem.* 15(7): 1538(1976).
16. Magers, K. D., Smith, C. G., and Sawyer, D. T., *Inorg. Chem.* 17(3): 515(1978).
17. Löwendahl, L., Petersson, G., and Samuelson, O., *Cellulose Chem. Technol.* 10(4): 471(1976); *Acta Chem. Scand.* B29(4): 526(1975).
18. D'Ans, J. and Mattner, J., *Angew. Chem.* 65(14): 368(1953); 63(16): 368(1951).
19. Krause, A. and Plura, I., *Naturwiss.* 48(22): 693(1961).
20. Svedberg, T. and Rinde, H., *J. ACS* 45: 943(1923); 46: 2677(1924).
21. Svedberg, T., *Colloid Chemistry*, ACS monograph series 16, 2nd edn., ACS, New York, 1928.
22. Samuelson, O., *Transactions of the Royal Institute of Technology*, No. 5, Royal Institute of Technology, Stockholm, 1947, pp. 1–15.
23. Malinen, R., Sjöström, E., and Ylijoki, J., *Paperi Puu* 55(1): 5(1973).
24. Järrehult, B. and Samuelson, O., *Tappi* 63(11): 131(1980).
25. Abrahamsson, K., Löwendahl, L., and Samuelson, O., *Tappi* 62(3): 73(1979).
26. Samuelson, O. and Sjöberg, L. A., *Tappi* 62(12): 47(1979).