

## DESORPTION OF METAL IONS FROM KRAFT PULPS. PART 1. CHELATION OF HARDWOOD AND SOFTWOOD KRAFT PULP WITH EDTA

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Chelation of unbleached and oxygen bleached hardwood and softwood kraft pulps with EDTA was studied. The main focus was on the desorption of magnesium, manganese, and iron due to their impact in TCF-bleaching. Desorption of other metal ions present were also studied in order to get an over-all estimation of the metal ion concentrations and their desorption during chelation. By using the concept of side reaction coefficients, an estimation of the chelating strength of EDTA at different pH can be made. Metal ion concentrations were determined by DCP-AES and ICP-MS techniques. Mn, Zn, and Cd were the metal ions that could almost completely be chelated with EDTA. Most of the metal ions were found to be desorbed from the pulps at low pH values by ion exchange with hydrogen ions. With EDTA chelation 50 to 70% of the iron was desorbed. By EDTA chelation the highest Mg/Mn concentration ratios were obtained in the pH range 4 to 6. For oxygen-bleached softwood pulp the ratio was over 7000. Our study showed that both unbleached and bleached pulps can quite successfully be chelated by EDTA.

*Keywords: Desorption; EDTA; Hardwood kraft pulp; Softwood kraft pulp; Metal ions; Side reaction coefficients; Chelation*

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### INTRODUCTION

The oxygen-based bleaching chemicals that are used in elemental chlorine free (ECF) and totally chlorine free (TCF) bleaching processes of cellulose pulps are sensitive to catalytic decomposition caused by transition metal ions (Colodette et al. 1998; Yuan et al. 1997; Lachenal et al. 1997). Some ions such as  $Mg^{2+}$ ,  $Ca^{2+}$ , and  $SiO_3^{2-}$  have an adverse effect on this decomposition (Gilbert et al. 1970; Basta et al. 1994; Lapierre et al. 1995; Ali et al. 1986). Lapierre et al. (2000, 2003) have reported that magnesium is more effective during peroxide bleaching when it is complexed either with the pulp or a chelating agent. Lidén et al. (1998) have shown that also high concentrations of aluminium can be used to improve the tolerance to iron and manganese in hydrogen peroxide bleaching. Some metal ions may also give quality-impaired products. Iron ions, for example, can cause colorization of pulp and the final paper product (Gupta 1970; Forsskåhl 2000). The effluent systems in modern pulp mills are closed to a high degree, inducing accumulation of metal ions in the process liquors. Calcium can cause scale formation on the digester and black liquor evaporators. Therefore it is crucial to manage the metal ion flows in a pulp mill. Karhu et al. (2000a, b) have studied two-phase equilibria of metal ions in pulping process from impregnation to oxygen delignification.

Metal management prior to bleaching can be done by acid wash or by using chelating agents such as EDTA (ethylenediaminetetraacetic acid) and DTPA (diethylenetriaminepentaacetic acid) (Bouchard et al. 1995; Basta et al. 1991; Bryant et al. 1994). The acid wash removes most metal ions and requires an addition of stabilizing ions, such as magnesium, to the pulp. A prolonged acid treatment at elevated temperature has been shown to greatly improve the removal of metal ions, compared to a standard acid wash or chelation. A too harsh acid treatment, however, will decrease the pulp viscosity and strength (Lapierre et al. 1997). Strong synthetic chelating agents on the other hand can be used to remove only certain metal ions from the pulp. Brelid et al. (1996) have shown that treatment of pulp by ion exchange with calcium or magnesium in a pretreatment step can reduce the need of chelating agents in the chelation step. It is also possible to remove metal ions already from the chips before the kraft cooking by acidic leaching or chelation (Kangas et al. 2002; Saltberg et al. 2006; Moreira et al. 2008).

In this first part of our study we focus on chelation of both unbleached and oxygen delignified hardwood and softwood kraft pulps with EDTA. In part 2 we will focus on chelation of the same pulps with other chelating agents and by using reducing agents in the chelation process. There is only little information in the literature about the difference in the efficiency of metal ion removal between unbleached and oxygen-delignified pulps. There are also only few studies about desorption of the more uncommon metal ions like  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Al}^{3+}$ . DTPA and EDTA have similar chelating properties (Ringbom 1963), but EDTA was used in this study because it theoretically has a slightly stronger ability to complex iron(III) in acidic and alkaline environments (Fig. 2). In a recent paper Norkus et al. (2006) have studied the use of DCTA (1,2-diaminocyclohexane-tetraacetic acid) as a chelating agent in alkaline media. Hyvönen et al. (2006) have studied new environmentally friendly chelating ligands showing rather equal performances as obtained with EDTA and DTPA.

### EDTA and its Complexation Reactions with Metal Ions

EDTA, ethylenediaminetetraacetic acid, is a multidentate chelating agent with 6 coordinating sites (Fig. 1), and it forms 1:1 complexes with most metal ions (Ringbom 1963). EDTA contains both  $-\text{COOH}$  and  $-\text{NH}_2$  as the functional groups and forms a ring structured chelate around the metal ion.

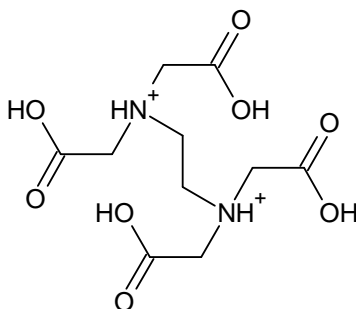


Fig. 1. Chemical structure of EDTA in the protonated form

The reaction between metal ions and chelating agents is strongly affected by pH of the solution, but also by other interfering ligands and cations in the system. Thus a

direct comparison between the thermodynamic stability constants does not give the right quantitative information how strongly metal ions are bound to different chelating agents. A comparison of the real chelating strength of different chelating agents at varying pH has to be based on the concepts of  $\alpha$ -coefficients and conditional constants developed by Ringbom (1963) and defined in the following sections.

Metal ions (M) mainly react with EDTA and other polyaminocarboxylic acids (L=ligand) in the ratio of 1:1 according to the following chelation reaction:



Concentrations of the species in a solution at equilibrium are defined by the law of mass action,

$$K_{ML}^{M,L} = \frac{[ML]}{[M][L]} \quad (2)$$

where  $K_{ML}^{M,L}$  is the stability constant of the chelation reaction. The notation used here for the constant indicates that the complex ML (subscript) is formed when M and L (superscript) react with each other. All charges are omitted for the sake of clarity.

The species M, L and ML in the reaction (1) may also participate in interfering side reactions with other existing ions and molecules in the system. The side reactions of these species can be considered by using  $\alpha$ -coefficients. The  $\alpha$ -coefficients or the side reaction coefficients are a measure of the extent of the side reactions and are defined by Ringbom (1963) as follows:

$$\alpha_M = \frac{[M']}{[M]}, \quad \alpha_L = \frac{[L']}{[L]}, \quad \alpha_{ML} = \frac{[(ML)']}{[ML]} \quad (3) \quad (4) \quad (5)$$

where  $[M']$  is the sum of the concentrations of all species containing M that has not reacted with L to form the 1:1 complex ML. Likewise  $[L']$  is the sum of the concentration of all the species containing L that has not reacted with M to form ML.  $[(ML)']$  is the sum of all complexes that contain M and L in the ratio 1:1. An  $\alpha_M$  value of e.g.  $10^3$  means that 0.1% of the total content of the ion M is in the form of free, uncomplexed ions.

The  $\alpha$ -coefficients defined above (equations (3) through (5)) can be used to calculate the conditional constant for a metal chelate system. In the conditional constant the side reactions, under particular experimental conditions, are taken into consideration and the stability constant is defined as:

$$K_{(ML)'}^{M',L'} = \frac{[(ML)']}{[M'][L']} \quad (6)$$

and can be calculated from the equation:

$$K_{(ML)'}^{M,L'} = K_{ML}^{M,L} \frac{\alpha_{ML}}{\alpha_M \alpha_L} \quad (7)$$

The primed subscript and superscripts in the expression of the conditional constant (equation (7)) indicates that the side reactions of the corresponding species are considered. When using an excess of a chelating agent, e.g. EDTA, the concept of  $\alpha_{M(L)}$ -coefficient can be used (Granholm et al. 2009). In this case the  $\alpha_{M(L)}$ -coefficient, which is the measure of complex formation of a metal ion by the ligand L, can be calculated by the following equation:

$$\alpha_{M(L)} = \frac{[M] + [(ML)']}{[M]} = 1 + \frac{[(ML)']}{[M]} = 1 + [L'] K_{(ML)'}^{M,L'} \quad (8)$$

where  $[L']$  is the excess of total concentration of the complexing agent (ligand concentration) and  $K_{(ML)'}^{M,L'}$  is the conditional constant, where the side reactions of the ligand (L) and the metal complex (ML) have been considered but not the side reactions of the metal ion with other ligands. The  $\alpha_{M(L)}$ -coefficient will therefore mainly be dependent on the ligand concentration (excess) and the value of the conditional constant which strongly depends on pH. The conditional constant,  $K_{(ML)'}^{M,L'}$ , in equation (8) can be calculated by using equation (7) in the following way:

$$K_{(ML)'}^{M,L'} = K_{(ML)}^{M,L} \frac{\alpha_{ML(H,OH)}}{\alpha_{L(H)}} \quad (9)$$

The  $\alpha_{ML(H,OH)}$  stands for the side reactions of the complex (ML) with hydrogen or hydroxide ions:

$$\alpha_{ML(H,OH)} = 1 + [H] K_{MHL}^{ML,H} + [OH] K_{M(OH)L}^{ML,OH} \quad (10)$$

and  $\alpha_{L(H)}$  stands for the side reactions of the ligand with hydrogen ions:

$$\alpha_{L(H)} = 1 + [H] K_{HL}^{H,L} + \dots + [H]^n K_{H_n L}^{nH,L} \quad (11)$$

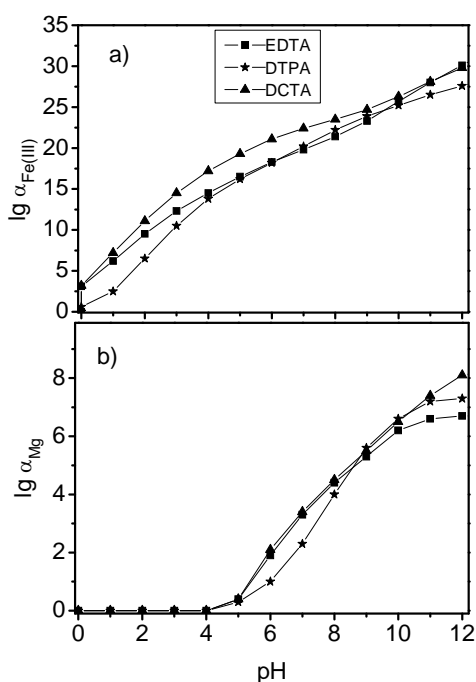
The side reaction of the metal ion with hydroxide ions ( $\alpha_{M(OH)}$ ) can be calculated with the following equation:

$$\alpha_{M(OH)} = 1 + [OH^-] K_{MOH}^{M,OH} + \dots + [OH^-]^n K_{M,(OH)_n}^{M,nOH} \quad (12)$$

In this paper the side reactions of the metal ions with hydroxide ions are included in the given  $\alpha_M$ -coefficients. At higher pH values the side reactions of the metal ion with hydroxide ions can dominate. Hence, the sum of the side reactions of the metal ion has to be considered:

$$\alpha_{M(\text{tot})} = \alpha_{M(\text{OH})} + \alpha_{M(\text{L})} - 1 \quad (13)$$

In Fig. 2 the  $\alpha_M$ -coefficients of iron (III) and magnesium(II) are plotted as function of pH for EDTA, DTPA, and DCTA, i.e. the chelating agents that are commonly used for desorption of metal ions in pulping processes. The  $\alpha_M$ -coefficients presented in Figs. 2 and 3 are based on the equilibrium constants given by Ringbom (1963) at 20 °C or 25 °C. The side reactions of the metal ions with hydroxide ions are included in the given  $\alpha_M$ -coefficients. The ligand concentrations are assumed to be 0.01 M. As the trivalent iron has harmful effects on the pulping process, the  $\alpha_{\text{Fe(III)}}$ -coefficient should be as high as possible in order to enable an effective desorption of iron(III).

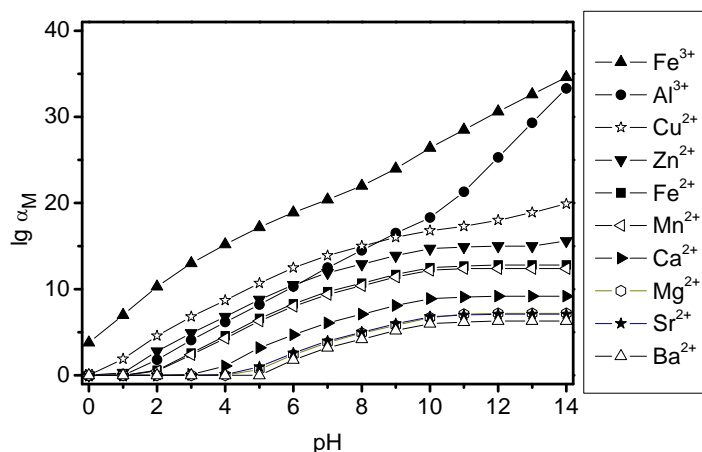


**Fig. 2.** The strength of complexation between the chelating agents and the metals: a) iron(III) and b) magnesium(II) expressed as  $\lg \alpha_M$  vs. pH. The ligand concentrations are 0.01 M

All the three chelating agents show quite similar curves (Fig. 2a) but DCTA has, compared with EDTA and DTPA, a slightly better ability to complex with iron(III) at pH below 9. Chelation of iron(III) is very effective with all three chelating agents in the alkaline and neutral pH regions. However, still at pH 1 the  $\alpha_{\text{Fe(III)}}$ -coefficients for DCTA and EDTA are as high as ca  $10^7$ . At pH values higher than 11 iron(III) starts to precipitate as  $\text{Fe}(\text{OH})_3$  even in presence of the chelating agent.

Magnesium ions have stabilizing effects during the bleaching process, and therefore the chelation effect of magnesium should be as low as possible. Comparison of the  $\alpha_{Mg}$ -coefficients of these chelating agents (Fig. 2b) shows that in the neutral pH range EDTA binds magnesium more strongly than DTPA. At pH>10 the order is reversed. The differences however, are marginal. At pH 4 and below there is no complexing effect for magnesium by any of the three chelating agents.

Calculated  $\alpha_M$ -values for some metal ions with 0.0027 M EDTA are shown in Fig. 3. Alkali metal ions, like Na, K, and Li that form very weak chelates with EDTA (Smith and Martell 1989) are not included in the figure, as their  $\alpha_M$  values are close to 1. It can clearly be seen that the metal ions are chelated by EDTA with varying strengths.  $Fe^{3+}$ ,  $Al^{3+}$ , and  $Cu^{2+}$  form the most stable chelates, but also  $Zn^{2+}$ ,  $Fe^{2+}$ , and  $Mn^{2+}$  form rather strong chelates with EDTA. It is important to note the large difference in the chelating strength of EDTA for iron(II) and iron(III) within the entire pH range. This means that the oxidation state of iron in the chelating step of the pulping process is of great importance. A clear pH effect on the chelating power of the EDTA can also be seen in Fig. 3. The lower the pH is the lower is the chelating effect of EDTA. This is due to protonation of EDTA.



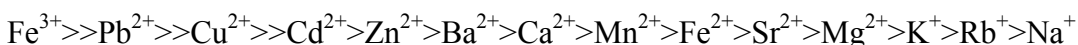
**Fig. 3.** The strength of chelation between EDTA and different metal ions expressed as  $\lg \alpha_M$  vs. pH. The ligand concentration is 0.0027 M

### Binding of metal ions by pulp

The effect of the removal of metal ions from pulp by chelation depends also on how strongly these metal ions are bound to the pulp. It has been shown, by using ESR spectroscopy, that the metal ions form complexes with kraft pulp components (Cardona-Barrau et al. 2001). It was also concluded in that paper that the affinity of metal ions to lignin is much higher than to carbohydrates. Adsorption of metal ions, such as Pb, Cu, Zn, Cd, and Fe, by lignin has also been reported by other authors (Perat et al. 2001; Carrot et al. 2007). The obvious metal binding groups in kraft pulps are phenol groups and carboxyl groups (Sjöström 1989). The phenolic groups originate from the residual lignin.

Most carboxyl groups in kraft pulp are in hexenuronic acids that are formed during the kraft cooking, and they have been shown to bind the transition metal ions very strongly (Teleman et al. 1995; Buchert et al. 1995; Denevyns and Chauveheid 1997). These carboxyl groups give to the pulp the properties that are close to a weakly acidic cation exchanger. Karhu et al. (2002c) have demonstrated that the stoichiometry of the ion exchange reaction between monovalent and divalent metal ions on kraft pulp varies within the range 1:1.9 to 1:2.0. This supports the theory that divalent metal ions are bound to two functional groups in the pulp. Tokareva et al. (2008, 2009) have studied the distribution of metal ions and acidic groups in wood samples and found that both metal ions and acidic groups are located in pit membranes and parenchyma cells.

According to our studies about the affinities of metal ions to kraft pulps, the different metal ions are bound to pulp with various strengths (Södö et al. 2007; Su et al. 2008, 2009). In other words, the metal ion sorption to pulp is rather specific. The following series with decreasing affinities to oxygen delignified hardwood kraft pulp was obtained by a column chromatographic technique (Södö et al. 2007):



From this series it can be seen that the metal ions that form strong complexes with synthetic chelating agents are also bound more strongly to the kraft pulps. This will create a competition of the metal ions between the binding groups in pulp and the chelation agents used in metal ion removal. Our studies on metal ion affinities to pulps also confirmed that during sorption of metal ions to protonated metal ion free pulp, at neutral pH, an equivalent amount of hydrogen ions is released (Su et al. 2009). The only exception from all the studied metal ions was trivalent iron, which probably forms oxide/hydroxide precipitates of very low solubilities on the pulp (Sundén et al. 2000; Södö et al. 2007). Södö et al. found by the column chromatographic technique that the number of equivalents of iron(III) sorbed to the column exceeded 8 times the total binding capacity (ca 90 µeq/g) of the pulp. Other authors have also found that iron is very difficult to remove from the pulp (Ant-Wuorinen et al. 1965; Basta et al. 1991; Bryant et al. 1994). Norkus et al. (2004) have shown that copper forms weak complexes with cellulose pulp and that during this formation the pH decreases due to a replacement of hydrogen ions from carboxylic acids. There is also a possibility that the metal ions can occur as salts of low solubility such as hydroxides, oxalates, sulfates, and phosphates at alkaline pH (Ringbom 1963).

## EXPERIMENTAL

### Pulps and Chemicals

Unbleached and oxygen-bleached hardwood and softwood kraft pulps obtained from two different Finnish pulp mills were used in this work. The unbleached and oxygen bleached pulp samples were taken approximately at the same time from the pulping line. The unbleached pulp samples were taken just before the oxygen delignification step, and the oxygen-bleached pulp samples were taken immediately after the oxygen delignifica-

tion step. The pulps were washed separately by the mill personnel and sent to our laboratory, where the pulps were stored in a freezer until used in the experiments. EDTA (Fluka) in the protonated form ( $H_4L$ ) was used as the chelating agent in this work. All the chemicals used were of pro analysi grade. Deionized water was used and was prepared with an ELGA Maxima Ultra Pure Water apparatus having the resistivity over 18.2  $M\Omega\text{cm}$ .

### Chelation and Sample Preparation

All chelation experiments were done with a 2% pulp consistency at 70 °C with constant stirring (400 rpm) for 1 h. Mainly 0.4% and 0.2% EDTA (calculated per dry pulp) was used in the experiments. This corresponds to a  $0.27 \cdot 10^{-3}$  M and  $0.14 \cdot 10^{-3}$  M EDTA concentration in the aqueous phase, respectively. Adjustment of pH of the pulp slurry was done either with NaOH or  $H_2SO_4$ . After the chelation step the pulp samples were washed thoroughly with deionised water and filtered (Schleicher and Schuell, Black ribbon 589<sup>1</sup> filter paper). The samples were then dried at 105 °C in order to get the metal ion concentration on dry pulp basis. The dry pulp samples were then digested in a mixture of  $HNO_3$  (5 ml) and  $H_2O_2$  (1 ml) by the microwave oven technique and diluted to 50 ml with deionized water before the analytical determinations. In the first survey experiments (Tables 1 and 2) 0.4 - 0.5 g of pulp was used in the digestion and only one sample was taken from each chelation. To reduce the influence of heterogeneity in the rest of the experiments, 15 to 20 g of pulp were dry ashed before the digestion. Additionally, two samples were taken from each chelation to calculate the mean value for each experiment.

### Analytical Methods

The pH measurements were made with a combined glass and calomel electrode, and the electrode system was calibrated with KH-phthalate (pH = 4.01) and phosphate (pH = 7.00) buffers.

Concentrations of the elements in the first survey experiments (Tables 1 and 2) were determined with inductively coupled plasma mass spectrometry (ICP-MS) using a semiquantitative mode. This method enables a simultaneous determination of a great number of elements except O, C, N, F, and Cl. The ICP-MS instrument used was a Perkin Elmer Elan 6000 (PE Sciex, Toronto, Canada). The more accurate concentrations of magnesium, manganese, and iron in the samples were determined by using DCP-AES (direct current plasma atomic emission spectroscopy). It should be pointed out that the semiquantitatively obtained results cannot directly be compared with the quantitative results obtained by DCP-AES. The instrument was a Spectraspan 7 DCP (ARL, California, USA). The used wavelengths were 280.270 nm for magnesium, 257.610 nm for manganese, and 259.940 nm for iron. Each concentration was calculated as a mean value of three replicate measurements. The linear range of the calibration line for the analytical determinations was tested by using several standard solutions of respective metal ions.

## RESULTS AND DISCUSSION

### Study on Chelation Effects using Semiquantitative Analysis

The over-all estimation of the metal ion concentrations in the hardwood and softwood kraft pulp samples, before and after the chelations, was done by using ICP-MS technique in a semiquantitative mode (Tables 1 and 2). In these assays ca. 0.5 g of the pulp samples were digested. This amount was later found to be too small due to the heterogeneity of the pulp samples. Metal ions with concentrations close to the detection limits of the analytical method are not included in the tables.

This first desorption study was made by chelation with 0.2% EDTA (calculated per o.d. (oven dried) pulp) at three different pH values: 5, 7, and 10. The chelation experiments were done with both unbleached and oxygen bleached kraft pulps in order to study the possible differences in metal ion desorption from these pulps.

The main elements in the studied pulp samples were Na, Ca, and Mg, their concentrations exceeding 100 ppm (ppm = mg/kg o.d). In the oxygen bleached hardwood pulp the concentration of Mn and K also exceeded 100 ppm. Concentrations of Mn, K, Si, Zn, Al, and Ba were in the range 10 to 100 ppm in most samples.

**Table 1.** Concentrations of Different Ions in *Hardwood* Kraft Pulps Before and After Chelation with 0.2% EDTA at pH 5, 7, and 10 Determined by the Semiquantitative ICP-MS Technique

Element	Unbleached hardwood kraft pulp				Oxygen bleached hardwood kraft pulp			
	Original concentration (ppm)	Concentration after chelation (ppm)			Original concentration (ppm)	Concentration after chelation (ppm)		
		pH 5	pH 7	pH 10		pH 5	pH 7	pH 10
Na	750	250	790	630	1100	310	560	840
Ca	640	560	490	540	710	570	610	570
Mg	400	330	350	390	380	300	340	360
Mn	60	10	19	36	120	13	28	86
K	48	47	110	51	180	72	100	66
Si	22	20	6.4	26	29	19	6.4	21
Zn	15	3.9	4.9	6.0	49	3.5	170	44
Ba	14	13	11	4.8	15	12	14	14
Al	10	12	6.6	13	14	12	12	13
Sr	8.4	7.4	6.8	4.7	7.8	7.0	7.5	7.0
B	4.9	10	7.2	8.4	1.7	14	1.3	1.3
Fe	4.4	6.2	4.2	3.7	7.9	12	4.3	5.7
Cu	0.37	2.8	0.40	0.44	0.56	0.74	0.66	0.90
Pb	0.16	0.43	0.08	0.13	0.42	0.35	0.46	0.32
Cd	0.11	0.05	0.05	0.09	0.15	0.03	0.05	0.03
Ni	0.13	0.05	0.20	0.12	0.14	0.07	2.6	0.63
As	0.11	0.09	0.01	0.04	0.14	0.00	0.00	0.21
Rb	0.26	0.27	0.75	0.18	1.3	0.33	0.83	0.38
Zr	0.06	0.19	0.02	0.05	0.16	0.13	0.13	0.43
Sn	0.04	0.08	0.06	0.09	0.04	0.01	0.05	0.06

**Table 2.** Concentrations of Different Ions in *Softwood Kraft Pulp* Before and After Chelation with 0.2% EDTA at pH 5, 7, and 10 Determined by the Semiquantitative ICP-MS Technique

Element	Unbleached softwood kraft pulp				Oxygen bleached softwood kraft pulp			
	Original concentration (ppm)	Concentration after chelation (ppm)			Original concentration (ppm)	Concentration after chelation (ppm)		
		pH 5	pH 7	pH 10		pH 5	pH 7	pH 10
Na	380	29	160	38	400	99	29	660
Ca	570	280	430	430	500	360	430	310
Mg	230	120	210	210	220	170	200	200
Mn	39	0.3	2.8	19	35	0.8	1.9	30
K	18	16	13	14	22	9.5	13	8.9
Si	23	9.8	6.5	14	22	12	14	14
Zn	8.5	2.0	2.0	5.4	5.0	44	32	10
Ba	5.2	3.1	5.1	5.0	4.6	4.3	5.0	4.2
Al	10	3.9	7.4	8.3	11	6.2	8.7	7.3
Sr	4.9	2.8	4.8	4.5	4.2	3.9	4.5	3.8
B	6.6	2.6	2.9	3.1	2.0	1.0	1.7	2.3
Fe	5.2	3.4	4.5	5.6	6.1	4.0	4.6	6.3
Cu	0.44	0.36	0.44	0.35	0.26	0.12	0.17	0.28
Pb	0.12	0.10	0.13	0.27	0.08	0.01	0.05	0.13
Cd	0.07	0.00	0.00	0.01	0.07	0.01	0.00	0.01
Ni	0.20	0.12	0.13	0.16	0.10	0.04	0.00	0.22
As	0.02	0.02	0.01	0.01	0.08	0.10	0.21	0.00
Rb	0.06	0.00	0.00	0.01	0.07	0.00	0.00	0.00
Zr	0.04	0.09	0.04	0.09	0.10	0.03	0.06	0.16
Sn	0.00	0.02	0.01	0.00	0.07	0.04	0.07	0.06

As can be seen in Table 1, the concentrations of several metal ions, especially sodium, potassium, and manganese, were much higher in the oxygen bleached hardwood kraft pulp than in the unbleached hardwood kraft pulp. One reason for this may be that the oxygen bleaching step increases the concentration of metal binding anionic groups in the pulp. Su et al. (2004) showed by potentiometric acid-base titrations that the concentration of carboxylic groups increased during oxygen delignification of kraft pulps. Table 2, however, indicates that in the softwood kraft pulp the concentration of the metal ions both in unbleached and oxygen bleached pulps were rather similar. Although there were big differences in the original metal ion concentrations between unbleached and oxygen bleached hardwood pulps, the concentrations of magnesium, manganese and iron in the unbleached and oxygen bleached pulps were rather similar after the chelations, indicating a rather effective chelation power of EDTA under the used experimental conditions. Hence, the chelation can successfully be done either before or after the oxygen delignification.

From the ICP-MS results presented in Tables 1 and 2 a clear desorption can be seen for most metal ions, especially at pH 5 and 7. As can be expected from the very low side reaction coefficients, the remaining concentrations of sodium, potassium, magnesium, calcium, strontium, and barium were still rather high in the pulps even after chelation. Nevertheless, the concentrations of the metal ions in general decreased at lower pH during the chelation, due to the ion exchange of the metal ions with hydrogen ions.

The relatively small degree of removal of calcium from the hardwood pulp (Table 2) can be due to the fact that some of the calcium may be present as precipitates (e.g. oxalate) of low solubility in the pulp and therefore can not effectively be removed (Lundqvist et al. 2006; Duong et al. 2006).

In the chelation experiments at pH 10 high sodium concentrations were obtained for the pulp samples because a NaOH solution was used in the pH adjustment.

For manganese ions, which form quite strong complexes with EDTA (Fig. 3), the concentrations were considerably decreased at lower pH values. Manganese was actually the only metal ion that could be removed to a large extent. Iron, especially trivalent iron, which forms very strong complexes with EDTA, was not removed to the same extent. Several authors have also reported that iron is very strongly bound to the pulp and is difficult to be removed (Södö et al. 2007; Bryant and Edwards 1996). One reason may be that trivalent iron forms hydroxides and/or oxides of low solubility and is to a greater extent in the form of a precipitate rather than bound by an ion exchange mechanism, as most of the other metals. LA-ICP-MS studies on single pulp fibers, done by our group (Su et al. 2004), showed an apparent heterogeneous distribution of iron in single fibers. This heterogeneous distribution of iron can also be explained by iron precipitates. Studies on metal ion affinities to hardwood kraft pulps have also shown that especially trivalent iron is very strongly bound to the pulp (Södö et al. 2007).

It is important to remove copper ions as well as iron and manganese ions from the pulp before the ECF/TCF bleaching. The original copper concentrations in the studied pulps were rather low, below 0.6 ppm. Nevertheless, it seems that the major part of the original copper ions is not removed during the chelation. Difficulties in copper removal have also been reported by other authors (Devenyns et al. 1994; Kangas et al. 2002; Kujala et al. 2004). The very toxic metal ion cadmium is present at very low concentrations (0.07 to 0.15 ppm) in the unchelated pulp samples. The EDTA chelations clearly decrease the concentration of cadmium. The quite large variation in the silicon concentration is probably due to the poor dissolution of silicon during sample digestion and due to heterogeneity of distribution of silicon in the sample.

It can be summarized from the survey experiments, by the semiquantitative ICP-MS measurements, that the only metals studied in this work and that were chelated to a large extent, at neutral and slightly acidic environments, from kraft pulps were manganese, zinc, and cadmium. Sodium was also removed quite effectively at pH 5, however, not by the chelation reaction with EDTA, but probably due to the low affinity of sodium to pulp. Metal ions that were not removed to any significant degree with EDTA at pH>5 were calcium, potassium, magnesium, barium, aluminum, strontium, lead, and copper. Södö et al. (2007) and Su et al. (2008, 2009) have shown that lead and copper are sorbed with higher affinity in a much larger extent to kraft pulps than other metal ions.

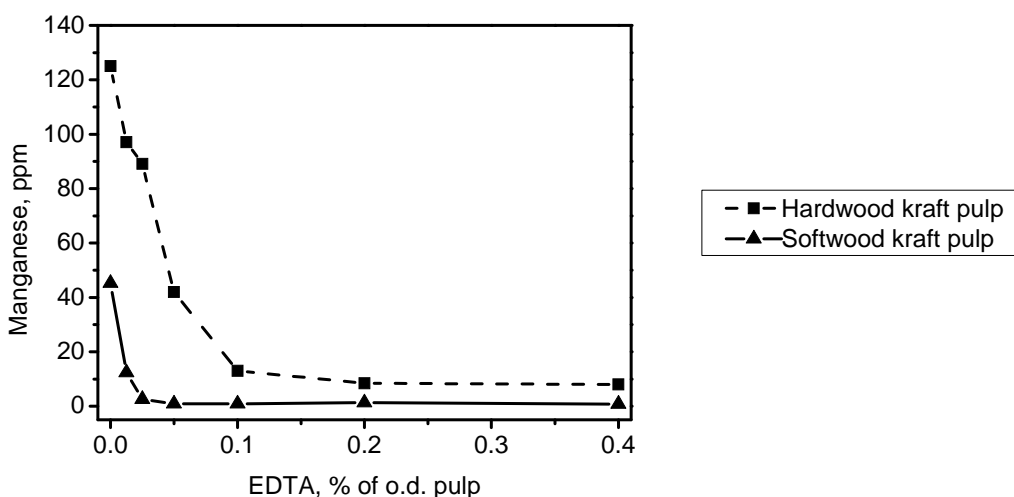
In the next sections, accurate chelation experiments based on strict quantitative determinations of metal concentrations in the pulp samples are presented for Mg, Mn, and Fe, which are the metal ions having particular impact on the bleaching process.

### Effect of the EDTA Concentration

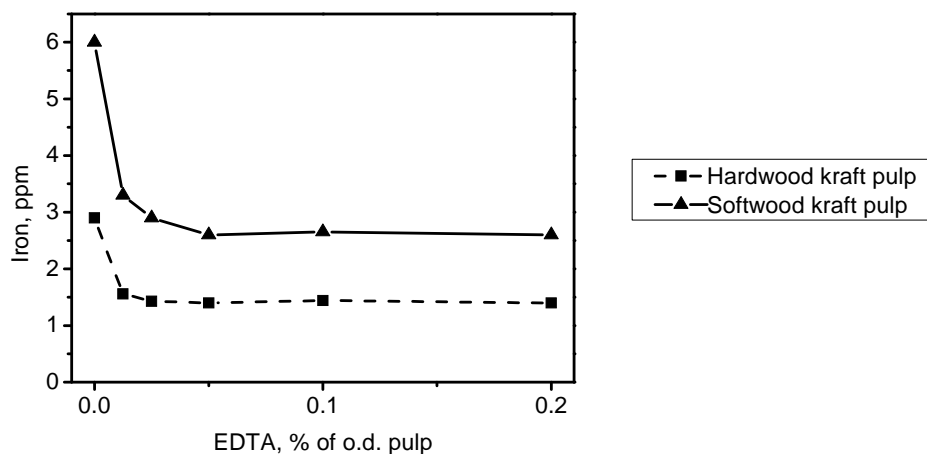
The influence of the EDTA concentration in the chelation step was studied by using different EDTA concentrations in the chelation experiment. Most metal ions are bound in 1:1 stoichiometry with EDTA. This means that for optimal chelating agent usage the number of moles of EDTA should theoretically be at least as high as the sum of the number of moles of the metal ions in the pulp. In pulping processes chelation of manganese and iron is of most importance. The remaining manganese and iron concentrations in the pulp after chelation of oxygen bleached hardwood and softwood kraft pulps, using different concentration of EDTA, are shown in Figs. 4 and 5. The chelation experiments were done at pH 5 due to the good chelation in this slightly acidic environment. In order to obtain the maximal chelation of manganese (Fig. 4) the EDTA concentrations had to be over 0.025% of o.d. pulp for the softwood kraft pulp. For the hardwood kraft pulp the concentration had to be over 0.1% of o.d. pulp. The number of moles of EDTA at these concentrations was approximately equal to the sum of number of moles of manganese and iron.

The EDTA concentration for the best removal of iron did not have to be as high as for the best removal of manganese (Fig. 5). This is probably due to a higher complexing stability of the iron(III) chelate and the lower original content of iron. On the other hand, only slightly over 50% of the total iron in the pulps could be removed, which would indicate that iron is in such a form in pulp that only a part of it can react with EDTA. Especially iron(III) is more difficult to remove from the pulps than iron(II) (Södö et al. 2007).

In order to ensure the best chelation effect, the concentration of EDTA should be 0.2% or higher. EDTA concentrations above 0.4% are, however, not required according to our results. An EDTA concentration below 0.2% can be used if the metal ion concentrations are low and known. Kujala et al. (2004) have developed an on-line method to monitor the metal profile in the pulp before chelation.



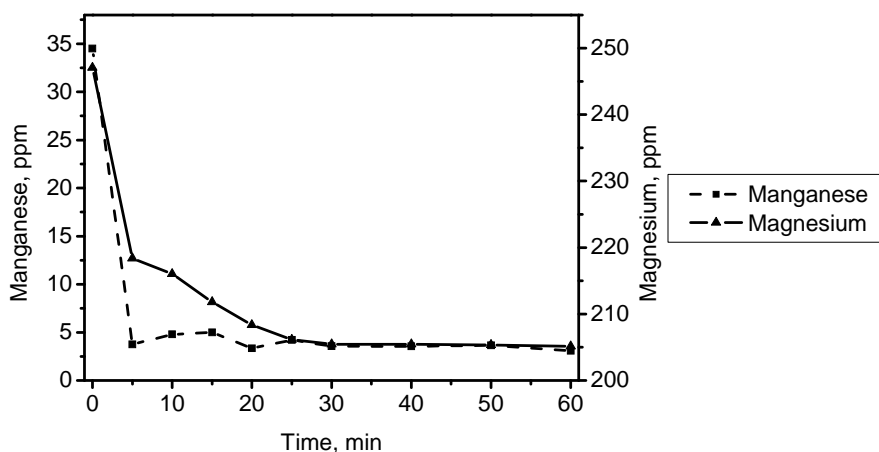
**Fig. 4.** The remaining manganese concentrations in oxygen bleached *hardwood* and *softwood* kraft pulps after chelations with EDTA of different concentrations



**Fig. 5.** The remaining iron concentrations in oxygen bleached *hardwood* and *softwood* kraft pulps after chelations with EDTA of different concentrations

### Chelation Kinetics

In order to study the time required for the chelation reaction, pulp samples were taken from the pulp slurry every 5<sup>th</sup> minute during the chelation experiment, followed by an immediate thorough washing. The chelation was done with 0.2% EDTA at pH 5 on oxygen-bleached softwood pulp. The manganese and magnesium concentrations during this chelation experiment are shown in Fig. 6.



**Fig. 6.** The remaining manganese and magnesium concentrations vs. time during chelation of oxygen bleached *softwood* kraft pulp (0.2% EDTA, pH 5)

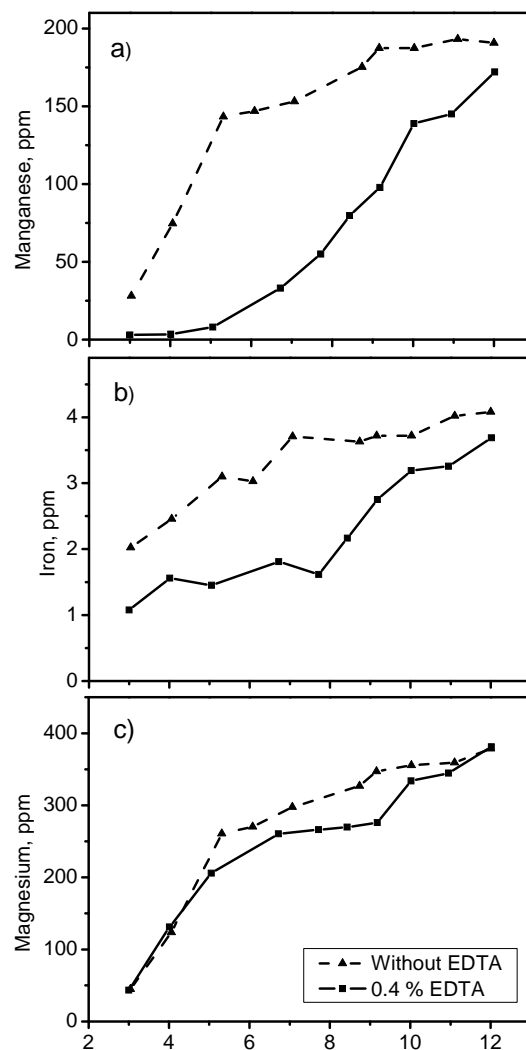
Desorption of magnesium ions is mainly due to ion exchange with hydrogen ions, and the reaction is therefore dependent on the pH as will be shown later in this work. Manganese, however, is mainly removed by the complexing reaction with EDTA. It can be seen that removal of manganese was rather fast and the chelation reactions had

reached equilibrium already within the first 5 minutes. Removal of magnesium, however, is a slower process and reached equilibrium first after 30 minutes. It can be seen in Fig. 6 that the highest Mg/Mn concentration ratio was obtained at five minutes of chelation.

## Influence of pH

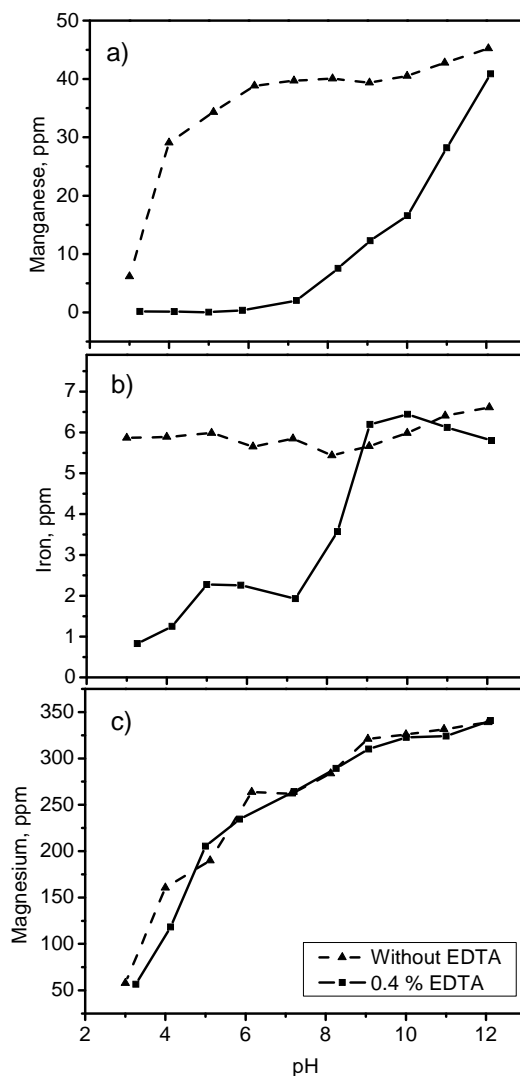
### *Desorption of manganese, iron and magnesium*

In order to study the influence of pH on the metal ion removal, the oxygen bleached hardwood and softwood kraft pulps were treated both with and without EDTA in the pH range 3-12. The remaining concentrations of manganese, iron, and magnesium in the pulp after these experiments are shown in Figs. 7 and 8.



**Fig. 7.** The remaining concentrations of a) manganese b) iron and c) magnesium vs. pH in oxygen bleached *hardwood* kraft pulp after the desorption experiments. The original concentrations were: Mn, 230 ppm; Fe, 3.6 ppm; Mg, 470 ppm.

As can be seen in Fig. 7a the chelation of manganese from oxygen bleached *hardwood* pulp showed very clear differences in the desorption curves with and without EDTA. Without EDTA the removal is due to ion exchange with hydrogen ions. With EDTA a clear chelation effect can be observed in the whole pH range studied. Removal of iron is more problematic. Even with 0.4% EDTA only slightly more than 50% of iron was chelated (Fig. 7b). In removal of magnesium from oxygen bleached *hardwood* pulp only a slight chelating effect with EDTA was obtained in the pH region 5 to 10 (Fig. 7c). At  $\text{pH} < 5$  the main reaction is the ion exchange between magnesium and hydrogen ions.



**Fig. 8.** The remaining concentrations of a) manganese b) iron and c) magnesium vs. pH in oxygen bleached *softwood* kraft pulp after the desorption experiments. The original concentrations were: Mn, 48 ppm; Fe, 6.9 ppm; Mg, 310 ppm.

In chelation of manganese from oxygen bleached *softwood* pulps 0.4% EDTA was very effective (Fig. 8a). At  $\text{pH} < 7$  the removal of manganese with EDTA was almost quantitative and more effective than from *hardwood* pulp. On the other hand, it was more

difficult to remove manganese from oxygen bleached softwood pulp (Fig. 8a) than from oxygen bleached hardwood pulp (Fig. 7a) only by the pH effect without EDTA. Ca. 70% of iron was removed by EDTA chelation at pH < 7 (Fig. 8b). As can be seen in Fig. 8b, the chelation process is effective when pH is less than ca 8. Only very small differences, however, can be seen in the desorption curves of magnesium obtained with and without EDTA in the pH range 3 – 12 (Fig. 8c).

Chelation had only a very weak effect on the removal of magnesium from oxygen bleached hardwood pulp (Fig. 7c). Magnesium ions are also only weakly bound to oxygen bleached softwood pulps and are removed mainly by ion exchange with hydrogen ions. The small differences between the curves in Fig. 8c are obviously due to experimental errors and have no practical relevance. The  $\alpha$ -coefficients given in Fig. 2b, calculated on theoretical basis, show that magnesium ions form a weak complex with EDTA at pH below ca 8, and in this pH range no chelation effect can hardly be obtained as was experimentally approved in Figs 7c and 8c. Lapierre et al. (1997) have shown that an acid wash (pH=1.5) removed efficiently manganese and magnesium. As we already have shown in Fig. 3, the  $\alpha$ -Mn(EDTA) at pH 1 and  $\alpha$ -Mg(EDTA) at pH 4 are ca. 1 and there is no chelation of these ions and the removal of manganese and magnesium at pH-values below 1 and 4, respectively, are entirely due to ion exchange with hydrogen ions.

#### *Mg/Mn concentration ratios*

In order to obtain the best TCF-bleaching results, the Mg/Mn concentration ratio has to be as high as possible. In Tables 3 and 4 the Mg/Mn ratios are given for oxygen bleached hardwood and softwood pulps at different pH values.

**Table 3.** Mg/Mn Ratios in *Hardwood* Kraft Pulps Chelated with 0.4% EDTA at Different pH Values

EDTA		Without EDTA	
pH	Mg/Mn	pH	Mg/Mn
3.0	15	3.0	1.6
4.0	38	4.1	1.6
5.1	26	5.3	1.8
6.7	7.9	6.1	1.8
7.7	4.8	7.1	1.9
8.4	4.4	8.7	1.9
9.2	2.8	9.2	1.9
10.0	2.4	10	1.9
11.0	2.4	11	1.9
12.0	2.2	12	2.0

**Table 4.** Mg/Mn Ratios in *Softwood Kraft Pulp*s Chelated with 0.4% EDTA at Different pH Values

EDTA		Without EDTA	
pH	Mg/Mn	pH	Mg/Mn
3.3	340	3.0	9.4
4.1	910	4.0	5.5
5.0	73000	5.1	5.5
5.8	650	6.2	6.8
7.2	130	7.2	6.6
8.3	38	8.1	7.1
9.1	25	9.0	8.2
10.0	20	10.0	8.0
11.0	12	11.0	7.8
12.1	8.3	12.0	7.5

The Mg/Mn ratio for the hardwood pulp, when no EDTA was used, was about 2, and for the softwood pulp 6-9 within the whole pH range, i.e. the pH has only a very small effect on the Mg/Mn concentration ratio in these cases. By using EDTA, manganese was removed, but EDTA had only a weak or even no effect on the removal of magnesium. EDTA improved the removal of manganese at all the tested pH values, but the best improvement was obtained at the neutral pH values (pH 5-8). The highest Mg/Mn ratio, after chelation with EDTA was 38, obtained at pH ca. 4 for the oxygen bleached hardwood kraft pulp (Table 3), and for the oxygen bleached softwood kraft pulp the highest Mg/Mn ratio was as high as 7300 at pH ca. 5 (Table 4). An obvious explanation for the much lower Mg/Mn concentration ratio obtained for the hardwood pulp is that manganese is much more strongly bound to the functional groups in this pulp than to the softwood pulp.

## CONCLUSIONS

Desorption of metal ions from pulps by chelation with EDTA is chemically a complex process and is still not fully understood. The effect of the removal process mainly depends on the strength of the formed metal ion EDTA chelates, but also on how strongly the metal ions are bound to functional groups in pulps. Moreover, these reactions are strongly pH dependent due to the protonation of EDTA and the binding groups in pulp. Many of the metal ions studied in this work could be removed at low pH values even without using any chelating agent. The ICP-MS analyses of pulp samples for determination of several metal ions before and after chelation showed clear desorption effects for most metal ions, especially at pH 5 and 7. Based on the theoretical calculations using  $\alpha$ -coefficients it was possible to show that concentrations of alkali and alkaline

earth metal ions in pulps are not affected to any greater extent by EDTA chelation, explaining the experimental results.

Chelation of manganese, magnesium, and iron were studied in more detail in this work due to their impact on TCF-bleaching. In order to achieve maximum removal of manganese and iron, the EDTA concentration has to be at least 0.025% for softwood pulps and ca 0.1% for hardwood pulps, calculated per dry matter. Manganese can effectively be removed by chelation with EDTA, and favorable Mg/Mn concentration ratios are obtained at pH 4 to 5 for hardwood pulp and at pH 4 to 6 for softwood pulp. For oxygen bleached softwood pulp the Mg/Mn ratio were as high as 7300. With EDTA chelation only 50 to 70% of iron could be removed. The heterogeneity of distribution of iron in pulp and the difficulties to remove it are most likely due to the presence of iron(III) precipitates in pulp and their encapsulation in the pulp structures. As the main conclusion of our study we may state that both unbleached and oxygen bleached pulps can quite successfully be chelated with EDTA.

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## REFERENCES CITED

- Ali, T., McArthur, D., Fairbank, M., and Whiting, P. (1986). "The role of silicate in peroxide brightening of mechanical pulp. 1. The effects of alkalinity, pH, pre-treatment with chelating agent and consistency," *J. Pulp Pap. Sci.* 12(6), J166-J171.
- Ant-Wuorinen, O., and Visapää, A. (1965). "The retention of iron by cellulose," *Papper och Trä* 9, 477-487.
- Basta, J., Holtinger, L., and Hook, J. (1991). "Controlling the profile of metals in the pulp before hydrogen peroxide treatment," *Proc. 6<sup>th</sup> Int. Symp. Wood Pulp. Chem., Appita* Vol. 1, Melbourne, 237-244.
- Basta, J., Holtinger, L., Hermansson, W., Lundgren, P. (1994). "Metal management in TCF/ECF bleaching," *Proc. Int. Pulp Bleaching Conf., Paper Presentations*, Vancouver, Canada, 29-32.
- Bouchard, J., Nugent, H.M., and Berry, R.M. (1995). "A comparison between acid treatment and chelation prior to hydrogen peroxide bleaching of kraft pulps," *J. Pulp Pap. Sci.* 21(6), J203-J208.
- Brelid, H., Friberg, T., and Simonson, R. (1996). "TCF bleaching of softwood kraft pulp.

- Part 2. Reducing the need for chelating agent in hydroxide peroxide bleaching of softwood kraft pulp,” *Nord. Pulp Paper Res. J.* 11(2), 105-108.
- Bryant, P. S., and Edwards, L. L. (1994). “Manganese removal in closed kraft mill bleached plants,” *Tappi J.* 77(2), 137-148.
- Bryant, P. S., and Edwards, L. L. (1996). “Cation exchange of metals on kraft pulp,” *J. Pulp Pap. Sci.* 22(1), J37-J42.
- Buchert, J., Teleman, A., Harjunpää, V., Tenkanen, M., Viikari, L., and Vuorinen, T. (1995). “Effect of cooking and bleaching on the structure of xylan in conventional pine kraft pulp,” *Tappi J.* 78(11), 125-130.
- Cardona-Barrau, D., Lachenal, D., and Chirat, C. (2001). “Affinity of metal ions for kraft pulps studied by ESR. Inhibition of their catalytic action in oxygen bleaching,” *J. Wood Chem. Tech.* 21(3), 247-261.
- Carrot, P. J. M., and Carrot, M. M. L. (2007). “Lignin - from natural adsorbent to activated carbon: A review,” *Bioreces. Technol.* 98(15), 2301-2312.
- Colodette, J. L., Rothenberg, S., and Dence, C. W. (1998). “Factors affecting hydrogen peroxide stability in the brightening of mechanical and chemimechanical pulps. Part 1: Hydrogen peroxide stability in the absence of stabilizing systems,” *J. Pulp Pap. Sci.* 14(6), J126-J.132.
- Devenyns, J., Desprez, F., Troughton, N., and Plumet, L. (1994). “Metals control in TCF bleaching. Implications for kraft bleaching sequence design,” *Proceedings of TAPPI Pulping Conference*, TAPPI Press, Atlanta, pp. 381-385.
- Denevyns, J., and Chauveheid, E. (1997). “Uronic acids and metals control.” *Proc. 9<sup>th</sup> Int. Symp. Wood Pulp. Chem.*, Montreal, M5-1-M5-4.
- Duong, T. D., Nguyen, K. L., and Hoang, M. (2006). “Comparative sorption of Na<sup>+</sup> and Ca<sup>+</sup> ions on unbleached kraft fibres – A kinetics and equilibrium study.” *J. Colloid Interface. Sci.* 301(2), 446-451.
- Forsskåhl, I. (2000). “Papermaking Science and Technology,” *Book 3, Forest Products Chemistry*, Edited by Stenius, P., Fapet Oy, 279-332.
- Gilbert, A. F., Pavlovova, E., and Rapson, W. H. (1970). “Mechanism of magnesium retardation of cellulose degradation during oxygen bleaching,” *Tappi* 56(6), 95-99.
- Granhölm, K., Su, P., Harju, L., and Ivaska, A. (2009). “Study on desorption of Mn, Fe and Mg from TMP and evaluation of the complexing strength of different chelation agents using side reaction coefficients,” *Holzforschung* 63(6), 785-790.
- Gupta, V. N. (1970). “Effect of metal ions on brightness, bleachability and colour reversion of groundwood,” *Pulp Pap. Can.* 71(16), 69-77.
- Hyvönen, H., Orama, M., Arvelac, R., Henriksson, K., Saarinen, H., Aksela, R., Parene, A., Jäkärä, and Renvall, I. (2006). “Studies on three new environmentally friendly chelating ligands,” *Appita J.* 59(2), 142-149.
- Kangas, H., Robersten, L., and Vuorinen, T. (2002) “The effect of transition metal ions on the kraft pulping process,” *Paperi ja Puu.* 84(7), 473-477.
- Karhu, J., Snickars, P., Harju, L., and Ivaska, A. (2002a). “Two-phase equilibria of metal ions in pulping process from impregnation to oxygen delignification. Part I. Metal ion concentrations,” *Paperi ja Puu* 84(8), 519-525.
- Karhu, J., Snickars, P., Harju, L., and Ivaska, A. (2002b). “Two-phase equilibria of metal ions in pulping process from impregnation to oxygen delignification. Part II. Metal

- ion balances,” *Paperi ja Puu* 85(1), 37-42.
- Karhu, J., Snickars, P., Harju, L., and Ivaska, A. (2002C). “Cation exchange of alkali and alkaline earth metal ions on hardwood kraft pulp,” *Appita J.* 55(5), 392-397.
- Kujala, M., Sillanpää, M., and Rämö, J. (2004). “A method to leach manganese and some other metal cations from pulp matrix to aqueous phase for the subsequent ICP-AES analysis: A potential tool for controlling the metal profile in a pulp bleaching process,” *J. Clean. Prod.* 12(7), 707-712.
- Lachenal, D., Nguyen Thi, N. B., Chirat, C., and Soria, L. (1997). “Optimum use of H<sub>2</sub>O<sub>2</sub> in kraft pulp delignification,” *Paperi ja Puu* 79(4), 252-256.
- Lapierre, L., Bouchard, J., Berry, R. M., and Van Lierop, B. (1995). “Chelation prior to hydrogen peroxide bleaching of kraft pulps: An overview,” *J. Pulp Pap. Sci.* 21(8), J268-J273.
- Lapierre, L., Paleologou, M., Berry, R. M., and Bouchard, J. (1997). “The limits of metal removal from kraft pulp by acid treatment,” *J. Pulp Pap. Sci.* 23(11), J539-J542.
- Lapierre, L., Berry, R., and Bouchard, J. (2000). “The effects of the order of chemical addition on the peroxide bleaching of an oxygen-delignified softwood kraft pulp.” *Holzforschung* 54(3), 279-286.
- Lapierre, L., Berry, R., and Bouchard, J. (2003). “The effect of magnesium ions and chelants on peroxide bleaching.” *Holzforschung* 57(6), 627-633.
- Lidén, J., and Öhman, L.-O. (1998). “On the prevention of Fe- and Mn-catalyzed H<sub>2</sub>O<sub>2</sub> decomposition under bleaching conditions,” *J. Pulp Pap. Sci.* 24(9), 269-276.
- Lundqvist, F., Brelid, H., Saltberg, A., Gellerstedt, G., and Tomani, P. (2006). “Removal of non-process elements from hardwood chips prior to kraft cooking,” *Appita J.* 59(6), 493-499.
- Moreira, E., Colodette, J., Gomide J., Oliviera, R., Regazzi, A., and Sacon, V. (2008). “Effect of acid leaching of eucalyptus wood on kraft pulping and pulp bleachability,” *J. Wood Chem. Tech.* 28(2), 137-152.
- Norkus, E., Vaičiūnienė, J., Vuorinen, T., and Macalady, D.L. (2004). “Equilibria of Cu(II) in alkaline suspensions of cellulose pulp,” *Carbohydr. Polym.* 55(1), 47-55.
- Norkus, E., Vaičiūnienė, J., and Vuorinen, T. (2006). “Removal of transition metals from alkaline suspensions of pulp using CDTA as a chelating agent,” *Carbohydr. Polym.* 66(3), 316-320.
- Perat, C., Ni, Y. (2001). “UV-VIS Spectra of lignin model compounds in the presence of metal ions and chelants,” *J. Wood Chem. Tech.* 21(2), 113-125.
- Ringbom, A. (1963). *Complexation in Analytical Chemistry*, Wiley, New York.
- Saltberg, A., Brelid, H., and Theliander, H. (2006). “Removal of metal ions from wood chips during acidic leaching. 1: Comparison between Scandinavian softwood, birch and eucalyptus,” *Nord. Pulp Paper Res. J.* 21(4), 507-512.
- Sjöström, E. (1989). “The origin of charge on cellulosic fibers,” *Nord. Pulp Paper Res. J.* 4(2), 90-93.
- Smith, R. M., and Martell, A. E. (1989). *Critical stability constants. Volume 6: Second supplement*, Plenum Press, New York.
- Su, P. (2004). *The determination of acid groups in pulp samples by potentiometric*

- titration and the analysis of metal ions in single fibres by laser ablation coupled plasma mass spectrometry*, Master of Science Thesis, Faculty of Technology, Åbo Akademi University, Finland, Turku.
- Su, P., Granholm, K., Harju, L., and Ivaska, A. (2008) "Use of column chromatography for the study of metal ion binding to oxygen bleached softwood pulp. *Proc.*" 2<sup>nd</sup> *International Papermaking & Environment Conf., Tianjin, China*, Book A. 242-245.
- Su, P., Granholm, K., Harju, L., and Ivaska, A. (2009). "Study of metal ion binding to unbleached softwood kraft pulp by column chromatography," *Appita J.* Accepted for publication.
- Sundén, A., Breliid, H., Rindby, A., and Engström, P. (2000). "Spatial distribution and modes of chemical attachment of metal ions in spruce wood," *J. Pulp Pap. Sci* 22(1), J37-J42.
- Södö, M., Su, P., Granholm, K., Harju, L., and Ivaska, I. (2007). "Study on metal ion affinities to oxygen delignified hardwood kraft pulp by a column chromatographic method," *Nord. Pulp Paper Res. J.* 22(4), 462-467.
- Teleman, A., Harjunpää, V., Tenkanen, M., Buchert, J., Hausalo, T., Drakenberg, T., and Vuorinen, T. (1995). "Characterisation of 4-deoxy- $\beta$ -L-threo-hex-4-enopyranosyluronic acid attached to xylan in pine kraft pulp and pulping liquor by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy," *Carbohydrate Research* 272(1), 55-71.
- Tokareva, E., Pranovich, A., Ek, P., and Holmbom, B. (2008). "Spatial distribution of anionic groups on wood and TMP surfaces after alkaline treatment and peroxide bleaching," *10<sup>th</sup> European Workshop on Lignocellulosics and Pulp, Stockholm, Sweden*, Proceedings, p. 336.
- Tokareva, E. N., Pranovich, A. V., Ek, P., and Holmbom, B. (2009). "Determination of anionic groups in wood by time-of-flight secondary ion mass spectrometry and laser ablation-inductively coupled plasma-mass spectrometry," *Holzforschung* 63. In Press.
- Yuan, M., d'Entremont, M. D., Ni, Y., and van Heiningen, A. R. P. (1997). "The role of transition metal ions during peracetic acid bleaching of chemical pulps," *Pulp Paper Canada* 98(11), T408-T413.

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