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

Kim Granholm, a* Leo Harju, a and Ari Ivaska a*

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 Mg²⁺, Ca²⁺, and SiO₃²⁻ have an adverse effect on this decomposition (Gilbert et al. 1970; Basta et al. 1994; Lapierre et al. 1995; Ali et al. 1986). Lapière 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; Forsskål 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 Cd\(^{2+}\), Pb\(^{2+}\), and 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 -COOH and –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](image)

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 α-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:

$$M + L \leftrightarrow ML$$  \hspace{1cm} (1)

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

$$K_{ML}^{M,L} = \frac{[ML]}{[M][L]}$$  \hspace{1cm} (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 α-coefficients. The α-coefficients or the side reaction coefficients are a measure of the extent of the side reactions and are defined by Ringbom (1963) as follows:

$$\alpha_M = \frac{[M']}{{[M]}}$$ \hspace{1cm} (3)
$$\alpha_L = \frac{[L']}{{[L]}}$$ \hspace{1cm} (4)
$$\alpha_{ML} = \frac{[(ML)']}{{[ML]}}$$ \hspace{1cm} (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 α-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:

$$K_{ML}^{M',L'}^{(ML)} = \frac{[(ML)']}{{[M'][L']}}$$  \hspace{1cm} (6)

and can be calculated from the equation:
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:

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

(8)

where $[L']$ is the excess of total concentration of the complexing agent (ligand concentration) and $K_{(ML')}^\prime$ 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, $K_{(ML')}^\prime$, in equation (8) can be calculated by using equation (7) in the following way:

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

(9)

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

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

(10)

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

$$
\alpha_{L(H)} = 1 + [H]K_{H,L}^{H,L} + ... + [H]^nK_{H^n,L}^{nH,L}
$$

(11)

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

$$
\alpha_{M(OH)} = 1 + [OH]K_{MOH}^{M,OH} + ... + [OH]^nK_{M(OH)^n}^{M,nOH}
$$

(12)
In this paper the side reactions of the metal ions with hydroxide ions are included in the given α_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:

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

In Fig. 2 the α_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 α_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 α_M-coefficients. The ligand concentrations are assumed to be 0.01 M. As the trivalent iron has harmful effects on the pulping process, the α_{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 α_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 α_{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 Fe(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 $\alpha_{M_{E}}$-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):

$$\text{Fe}^{3+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Ba}^{2+} > \text{Ca}^{2+} > \text{Mn}^{2+} > \text{Fe}^{2+} > \text{Sr}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Rb}^+ > \text{Na}^+$$

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 (H₄L) 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 MΩcm.

**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 0.27·10⁻³ M and 0.14·10⁻³ M EDTA concentration in the aqueous phase, respectively. Adjustment of pH of the pulp slurry was done either with NaOH or H₂SO₄. After the chelation step the pulp samples were washed thoroughly with deionised water and filtered (Schleicher and Schuell, Black ribbon 589¹ 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 HNO₃ (5 ml) and H₂O₂ (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

<table>
<thead>
<tr>
<th>Element</th>
<th>Original concentration (ppm)</th>
<th>Concentration after chelation (ppm)</th>
<th>Original concentration (ppm)</th>
<th>Concentration after chelation (ppm)</th>
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<td>pH 10</td>
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Table 2. Concentrations of Different Ions in Softwood Kraft Pulps Before and After Chelation with 0.2% EDTA at pH 5, 7, and 10 Determined by the Semiquantitative ICP-MS Technique

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<td>0.00</td>
<td>0.01</td>
</tr>
<tr>
<td>Zr</td>
<td>0.04</td>
<td>0.09</td>
<td>0.04</td>
<td>0.09</td>
</tr>
<tr>
<td>Sn</td>
<td>0.00</td>
<td>0.02</td>
<td>0.01</td>
<td>0.00</td>
</tr>
</tbody>
</table>

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.

![Graph showing the remaining manganese concentrations in oxygen bleached hardwood and softwood kraft pulps after chelations with EDTA of different concentrations](image)

**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 5th 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.

![Graph](image-url)

**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 pH < 5 the main reaction is the ion exchange between magnesium and hydrogen ions.

![Graph showing remaining concentrations of manganese, iron, and magnesium vs. pH](image)

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 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 α-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 α-Mn(EDTA) at pH 1 and α-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

<table>
<thead>
<tr>
<th>pH</th>
<th>EDTA Mg/Mn</th>
<th>Without EDTA Mg/Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>15</td>
<td>3.0</td>
</tr>
<tr>
<td>4.0</td>
<td>38</td>
<td>4.1</td>
</tr>
<tr>
<td>5.1</td>
<td>26</td>
<td>5.3</td>
</tr>
<tr>
<td>6.7</td>
<td>7.9</td>
<td>6.1</td>
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<td>2.8</td>
<td>9.2</td>
</tr>
<tr>
<td>10.0</td>
<td>2.4</td>
<td>10.0</td>
</tr>
<tr>
<td>11.0</td>
<td>2.4</td>
<td>11.0</td>
</tr>
<tr>
<td>12.0</td>
<td>2.2</td>
<td>12.0</td>
</tr>
</tbody>
</table>
Table 4. Mg/Mn Ratios in Softwood Kraft Pulps Chelated with 0.4% EDTA at Different pH Values

<table>
<thead>
<tr>
<th>EDTA</th>
<th>Without EDTA</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>Mg/Mn</td>
</tr>
<tr>
<td>3.3</td>
<td>340</td>
</tr>
<tr>
<td>4.1</td>
<td>910</td>
</tr>
<tr>
<td>5.0</td>
<td>73000</td>
</tr>
<tr>
<td>5.8</td>
<td>650</td>
</tr>
<tr>
<td>7.2</td>
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<tr>
<td>8.3</td>
<td>38</td>
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<tr>
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<td>25</td>
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<td>10.0</td>
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<tr>
<td>11.0</td>
<td>12</td>
</tr>
<tr>
<td>12.1</td>
<td>8.3</td>
</tr>
</tbody>
</table>

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 α-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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