DESORPTION OF METAL IONS FROM KRAFT PULPS. PART 2. CHELATION OF KRAFT PULPS WITH DIFFERENT COMPLEXING AGENTS AND WITH EDTA IN A REDUCING ENVIRONMENT

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Desorption of metal ions from oxygen-bleached hardwood and softwood kraft pulps by different chelation treatments were studied. The main focus was on desorption of manganese, iron, and magnesium ions, but also on desorption of some other common metal ions. The metal ion concentrations were determined by the DCP-AES and ICP-MS techniques. Acid treatments with nitric and oxalic acids removed manganese and magnesium very effectively and partially iron as well. Some potential complexing agents such as triethanolamine (TEA), citric acid, oxalic acid, and formic acid were also tested. By using the concept of side reaction coefficients, a comparison of the chelating strengths between different chelating agents can be made. TEA is a strong chelant for iron and did remove part of iron at pH 10. The effect of chemical reduction simultaneously with EDTA was studied by using sodium borohydride, sodium dithionite, and sodium bisulfite as reducing agents. The reducing environment improved desorption of manganese but did not improve removal of iron. The measured redox potentials indicated that the reducing effect with the used agents was not enough to convert iron(III) to iron(II). The effect of the reducing agents was decreased by their decomposition during the chelation experiment.

Keywords: Desorption; Kraft pulp; Acid wash; EDTA; TEA; Citric acid; Oxalic acid; Redox potential

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INTRODUCTION

It is well known that transition metal ions, such as manganese and iron, have negative impacts during elemental chlorine free (ECF) and totally chlorine free (TCF) bleaching of kraft pulps. These metals catalyze the decomposition of oxygen–based bleaching chemicals (Colodette et al. 1998; Yuan et al. 1997). Magnesium ions induce an inhibiting effect on this decomposition (Lapierre et al. 1995, 2003; Gilbert et al. 1970). Therefore a metal management step is usually introduced prior to bleaching. The most common way is to use complexing agents such as EDTA (ethylenediaminetetraacetic acid) and DTPA (diethylenetriaminepentaacetic acid) for the metal ion removal. However, a successful chelation with these chelating agents requires that pH is decreased to 4-6 (Granholm et al. 2010; Basta et al. 1994; Bryant and Edwards 1994). Metal ions can also be removed by acid treatment. However, this requires an addition of stabilizing ions such as magnesium (Lapierre et al. 1997). The acid leaching can even be performed on wood chips before the kraft cook. (Kangas et al. 2002; Saltberg et al. 2006; Moreira et al. 2008). Removal of iron ions has been shown to be very difficult (Granholm et al.

2010; Kujala et al. 2002; Bryant and Edwards 1996). Due to the low biodegradability of EDTA and DTPA, some new, more environmentally friendly chelating agents have been introduced. Orama et al. (2002) and Hyvönen et al. (2003) have shown that ethylenedisuccinic acid (EDDS) and iminodisuccinic acid (ISE) have good complexing properties for metal ions. Recently the same group has presented additionally three new environmentally friendly chelating ligands (Hyvönen et al. 2006). Karhu et al. (1999) have studied the possibility to recirculate chelating agents by precipitating them in their electrically neutral acidic form. Ni et al. (1998, 1999) have shown that a reducing agent assisted the DTPA chelation by improving the removal of manganese and iron from mechanical pulps. An improvement of removal of copper, iron, and manganese from kraft pulp with EDTA, when using sodium dithionite as the reducing agent, has also been reported (Lachenal et al. 1997).

Metal ions are mainly bound to the pulp by acidic functional groups such as carboxylic and phenolic groups (Sjöstrom 1989). Trivalent iron may exist as precipitates on pulp fibers (Sundén et al. 2000; Södö et al. 2007). There is also a possibility that some metal ions like calcium, strontium, barium, and lead are precipitated as carbonates in the pulp phase at alkaline pH. A decrease in pH will increase the solubility of the eventual carbonate precipitates. The metal ions can also occur as salts of low solubility such as hydroxides, oxalates, sulfates, phosphates, etc. Our studies with a column chromatographic technique showed that the metal ions are bound to kraft pulps with different strengths (Södö et al. 2007; Su et al. 2008, 2009).

In Part 1 of these papers, we studied how different parameters like pH, time, ligand concentrations, etc. affect EDTA chelation (Granholm et al. 2010). This second part is focused on chelation of oxygen bleached hardwood and softwood kraft pulps with some other complexing agents and on chelation with EDTA in a reducing environment.

Complexation Reactions

The chelating or complexing properties of chelating agents or ligands in different media can be expressed with α_M-coefficients and conditional stability constants and were discussed in Part 1 (Granholm et al. 2010). The α_M-coefficient gives the degree of complexation between a metal ion (M) and a complexing ligand (L). Due to the strong influence of pH and other conditions on the complexation reactions it is important to compare these coefficients instead of only the thermodynamic stability constants. The α_M-coefficients presented in Figs. 1-3 are calculated by using critical collections of equilibrium constants given in the textbook by Ringbom (1963), according to the principles described in Part 1 (Granholm et al. 2010). The equilibrium constants are given at 20 ºC or 25 ºC. These α_M-coefficients give a good estimation of the strength of the metal complexes and can be used to predict their behavior in chelation of metal ions in cellulose pulps.

The α-coefficients of manganese complexes with EDTA, oxalate, and citrate are shown in Fig. 1. The strength of the Mn-EDTA complex clearly increases rapidly with pH, and the value reaches its maximum at pH 10. Values of the α-coefficients of the manganese complexes with oxalate and citrate are much lower than with EDTA indicating lower complexing strength of these ligands. The strength of the manganese complexes with oxalate and citrate reaches the maximum value at pH>6.

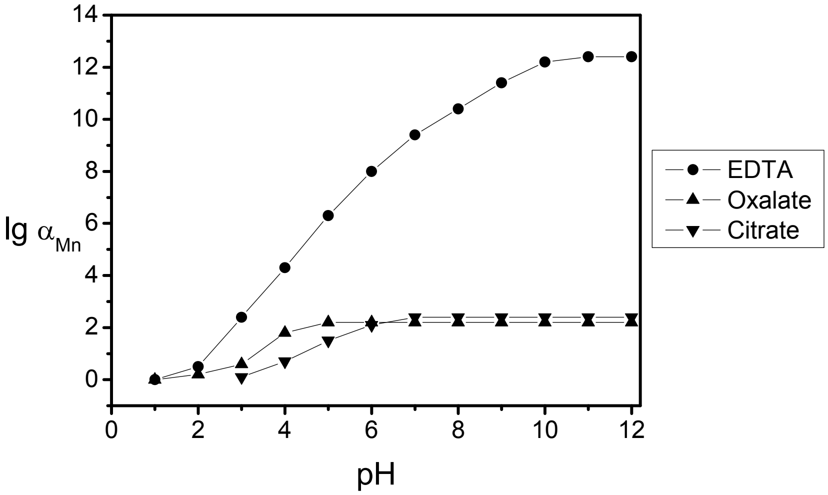

Fig. 1. The strength of complexation between manganese and the complexing agents: EDTA, oxalate and citrate expressed as lg α_{Mn} vs. pH. The ligand concentrations are 0.01 M.

The side reaction coefficients of iron(III) complexes with TEA, EDTA, oxalate, and citrate are presented in Fig. 2. Fe(III) forms very strong complexes, especially at neutral and high pH values, with these ligands. Fe(III)-TEA complexes are exceptionally strong at high pH and are even stronger than the Fe(III)-EDTA complexes at pH > 11. The Fe(III)-oxalate complexes are of equal strengths as the Fe(III)-EDTA complexes at pH<4. However, the strength of the Fe(III)-oxalate complex remains rather constant at pH>5. The α-value of the Fe(III)-citrate complex increases with pH monotonously but is still several orders of magnitudes less than the α-value of the Fe(III)-EDTA complex.

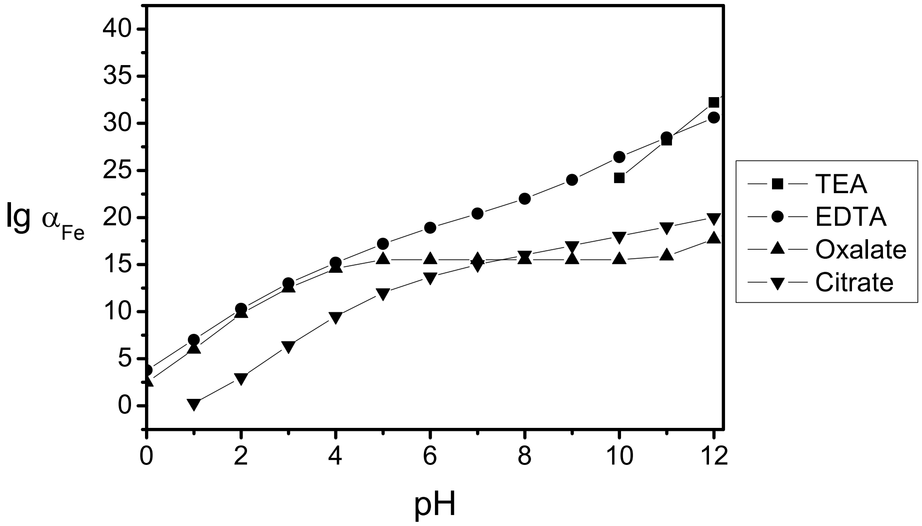

Fig. 2. The strength of complexation between trivalent iron and the chelants: TEA, EDTA, oxalate and citrate expressed as lg α_{Fe} vs. pH. The ligand concentrations are 0.01 M.

The α-coefficients of magnesium complexes with EDTA and citrate are presented in Fig. 3. At pH values below 5 the formation of Mg-EDTA complexes are negligible. The α-values of Mg-citrate are low over the whole pH range.

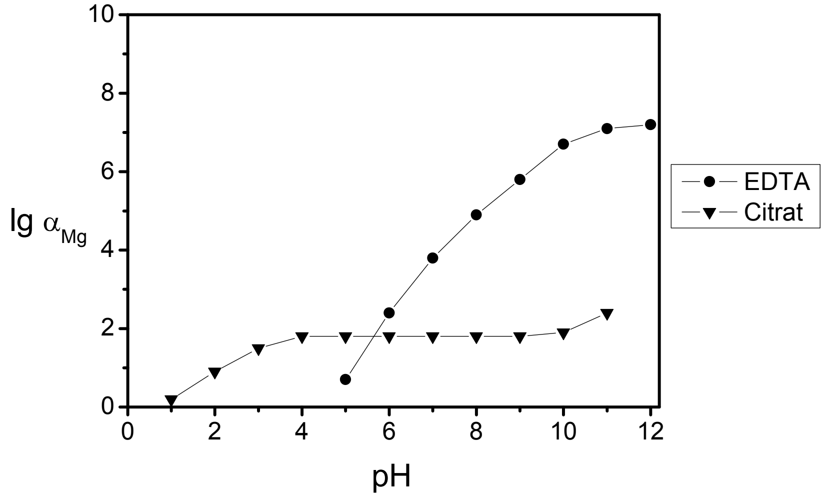

Fig. 3. The strength of complexation between magnesium and the chelants: EDTA and citrate expressed as lg α_{Mg} vs. pH. The ligand concentrations are 0.01 M.

Redox Potential

The strength of a reducing or an oxidizing environment can conveniently be determined by measuring the redox potential. The concentration ratio of a redox couple can be calculated from this potential by using the Nernst equation. As iron(III) forms very stable precipitates in pulps, the Fe^{3+}/Fe^{2+} concentration ratio is of special interest.

For a redox couple like Fe^{3+}/Fe^{2+} at 70º C, the Nernst equation can be written in the following way,

$$E_{Cell} = E^{o}_{Cell} + 68.0 mV \cdot lg \frac{[Fe(III)]}{[Fe(II)]} \tag{1}$$

where E_{Cell} is the measured potential. The standard potential of the electrode system (E^{o}_{Cell}) can be calculated from the standard potentials of the Fe^{3+}/Fe^{2+} redox couple (Tagirov et al. 2000) and of the used reference electrode (in our case: saturated calomel electrode):

$$E^{o}_{Cell} = E^{o}_{(Fe^{3+}/Fe^{2+})} - E_{ref} = 845 mV - 208 mV = 637 mV \quad (\text{at } 70^{o}\text{ C}) \tag{2}$$

The ratio of the total concentrations of trivalent iron ([Fe(III)′]) to divalent iron ([Fe(II)′]) in aqueous solutions can be calculated from the following general equation (Södö et al. 2007),

$$\frac{\left[\mathrm{Fe(III)'}\right]}{\left[\mathrm{Fe(II)'}\right]}=\frac{\alpha_{\mathrm{Fe(III)}}\left[\mathrm{Fe}^{3+}\right]}{\alpha_{\mathrm{Fe(II)}}\left[\mathrm{Fe}^{2+}\right]} \tag{3}$$

where $\alpha_{\mathrm{Fe(III)}}$ and $\alpha_{\mathrm{Fe(II)}}$ stands for the sum of the side reaction coefficients of the respective oxidation state of iron. The theory of α-coefficients and conditional constants is discussed in Part 1 (Granholm et al. 2010). The equilibrium constants used in the calculations are valid at 20 ºC or 25 ºC.

EXPERIMENTAL

Pulps and Chemicals

The pulps used were oxygen bleached hardwood and softwood pulps obtained from two Finnish pulp mills. The pulp samples were taken directly after the oxygen delignification step and were washed separately by the mill personnel. The pulp samples were stored in a freezer until used in the experiments.

All of the chemicals used in this study were of pro analysi grade. The deionized water used in all the experiments was prepared with an ELGA Maxima Ultra Pure Water apparatus and had a resistivity over 18.2 MΩcm.

Chelation and Sample Preparation

The chelation experiments were done with a 2% pulp consistency at 70 °C for 60 minutes with constant stirring of the suspension (400 rpm). The acid washes were done with a 1% pulp consistency at 60 °C for 15 min. The concentrations of the chelating agents, acids, and reducing agents in the experiments are expressed as weight-% of oven dried pulp. For example 0.2% EDTA corresponds to $0.27\cdot10^{-3}$ M EDTA in the aqueous phase. NaOH and H_2SO_4 were used to adjust pH in the chelation experiments. All pulp samples were thoroughly washed and filtered immediately after the treatments. Two pulp samples from each treatment were taken for analysis and a mean value of the metal ion concentrations was determined. The samples (15-20 g) were dry ashed, digested by a microwave oven technique in a mixture of 5 ml HNO_3 and 1 ml H_2O_2 (Mileston mls 1200 mega) and diluted with deionized water to 50 ml prior to the analytical determinations.

Analytical Methods

The redox potentials were measured using a platinum electrode and a saturated calomel electrode. The pH was measured 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 manganese, iron, and magnesium were determined with direct current plasma atomic emission spectroscopy (DCP-AES). The DCP-AES instrument was a Spectraspan 7 DCP (ARL, California, USA) and the used wavelengths were for manganese 257.610 nm, for iron 259.940 nm and for magnesium 280.270 nm. Each concentration was determined as a mean value of three replicate measurements. The semiquantitative analyses of the other metal ions studied in this work were performed with inductively coupled plasma mass spectrometry (ICP-MS). The ICP-MS instrument used was a Perkin Elmer Elan 6000 (PE Sciex, Toronto, Canada).

RESULTS AND DISCUSSION

Desorption of Mn, Fe and Mg

Manganese, iron, and magnesium were studied in more detail due to their special impact on the bleaching process. Different treatments were used on oxygen bleached hardwood and softwood kraft pulps for removal of these metals. For comparison, chelations with EDTA at pH 5 were also made. The results from the treatments studied are shown in Table 1 and Table 2 for hardwood and softwood pulp, respectively.

Acid washes

The oxygen bleached hardwood and softwood kraft pulps were washed with 0.2 M nitric acid solution and with 0.1 M oxalic acid solution. The results are given in Tables 1 and 2. The nitric acid wash removed rather effectively the studied metal ions from both pulps, although still almost half of the iron was left in the pulps. In general, the nitric acid wash removed manganese and iron ions better than the chelation with EDTA at pH 5, but it removed also most of the magnesium ions. The removal of metal ions with nitric acid is based on ion exchange reaction of hydrogen ions with metal ions on pulp. A decrease in pH will also increase solubility of the sparely soluble metal salts.

Table 1. Metal Ion Concentrations in Oxygen-Bleached *Hardwood* Kraft Pulp Before and After Chelation or Acid Treatment

	pH	Mn (ppm)	Fe (ppm)	Mg (ppm)
Original concentration		150	6.6	450
EDTA (0.2%)	5	14	6.4	300
Nitric acid (0.2 M)	<1	1.1	2.8	5.7
Oxalic acid (0.1 M)	~1	30	6.3	9.3
TEA (0.2%)	5	72	6.4	230
TEA (0.2%)	10	110	5.6	370

The use of oxalic acid (pH~1) was studied due to the ability of oxalate to complex manganese and iron, which can be seen from the side reaction coefficients in Figs. 1 and 2. The oxalic acid wash, which had a higher pH than the nitric acid wash, did remove all three metals very effectively from the softwood pulp, as can be seen in Table 2. In fact oxalic acid wash left only 0.8 ppm (mg/kg) iron in the softwood pulp, which is much less than the value obtained with the nitric acid wash or with the EDTA chelation at pH 5. The effective removal of iron can be explained by the complexing ability of oxalate with iron(III) even at very low pH, as can be predicted from the lg α_{Fe} value in Fig. 2. For the hardwood pulp, however, the oxalic acid wash was not as effective in removing manganese and iron ions from the pulp (Table 1). Nitric acid wash (pH<1) removed the metal ions rather well from the hardwood kraft pulp. These treatments show that especially manganese is more strongly bound to hardwood pulp than to softwood pulp.

Table 2. Metal Ion Concentrations in Oxygen-Bleached *Softwood* Kraft Pulp Before and After Chelation or Acid Treatment

	pH	Mn (ppm)	Fe (ppm)	Mg (ppm)
Original concentration		38	4.4	250
EDTA (0.2%)	5	1.2	2.3	180
Nitric acid (0.2 M)	<1	0.6	2.2	3.6
Oxalic acid (0.1 M)	~1	1.4	0.8	2.5
TEA (0.2%)	5	30	4.4	180
TEA (0.2%)	10	33	2.6	220

Triethanolamine (TEA) as the chelating agent

The stability constants of the TEA-Fe(III) complex (lg K = 41.2) (Ringbom 1963) and the α_M-values for the complex, shown in Fig. 2, indicate that TEA would be a potential chelant for iron. Oxygen bleached hardwood and softwood kraft pulps were chelated with TEA at pH 5 and 10 in order to study the effect of TEA in removing transition metal ions from kraft pulps. As can be seen from the results presented in Tables 1 and 2, TEA removes iron from the pulps at pH 10, but not at pH 5. This is more apparent for the softwood pulp (Table 2), where almost half of the iron was removed at pH 10. The degree of desorption of iron with TEA at pH 10 was about the same as desorption with EDTA at pH 5. Hence, TEA at pH 10 forms iron-complexes that are strong enough to remove a part of iron from pulps. Manganese was on the other hand not removed by TEA at either pH values, indicating that manganese forms only very weak complexes with TEA. These experiments show that TEA can only be used to remove iron from kraft pulps at high pH values.

Citric, oxalic and formic acid as complexing agents at pH 5 and 10

The α_M-values of citrate- and oxalate-complexes with manganese, iron(III), and magnesium ions are presented in Figs. 1, 2, and 3. These side reaction coefficients show that both citric and oxalic acids have quite good complexing abilities. As for the most ligands the values of α_M increase with increasing pH. Also formic acid can be expected to have some ability to bind metal ions due to its carboxylic group. In order to study complexing abilities of these organic acids, oxygen bleached hardwood and softwood kraft pulps were chelated with them at pH 5 and 10 (Table 3 and 4).

The manganese, iron, and magnesium concentrations before and after the chelation experiments are presented in Table 3 for the hardwood kraft pulp and in Table 4 for the softwood kraft pulp. For comparison, chelation experiments with EDTA at pH 5 and 10 are also included in the tables. The variations between the original concentrations given in Table 1 and 2 and in Table 3 and 4 are probably due to the heterogeneity of the iron and manganese concentrations in the same pulp batch.

Table 3. Metal Ion Concentrations in Oxygen-Bleached *Hardwood* Kraft Pulp Before and After various Treatments. Each treatment was done both at pH 5 and 10. The redox potentials are measured in the beginning and in the end of each treatment.

Treatment	pH	Mn (ppm)	Fe (ppm)	Mg (ppm)	Redox potential 0 min (mV)	Redox potential 60 min (mV)
Original concentration	10.2	230	3.6	470		
EDTA (0.4%)	5	14	1.0	210	160	170
	10	130	3.2	320	-28	-25
Citric acid (0.01 M)	5	20	0.7	26	150	160
	10	150	2.4	270	-74	-71
Oxalic acid (0.01M)	5	56	1.0	55	140	140
	10	180	3.5	300	-59	-54
Formic acid (0.01 M)	5	100	1.5	170	53	48
	10	200	3.7	200	-71	-76
Sodium borohydride (0.2%) + EDTA (0.4%)	5	11	0.9	190	-270	100
	10	115	3.6	280	-550	-140
Sodium ditihonite (0.5%) + EDTA (0.4%)	5	8.5	0.8	170	-510	27
	10	95	3.3	280	-630	-100
Sodium bisulfite (1.0%) + EDTA (0.4%)	5	8.9	1.1	200	10	30
	10	120	3.3	290	-130	-97

It can be seen from these results that citric acid removed manganese, from both pulps both at pH 5 and 10, almost as effectively as EDTA. However, most of the magnesium was also removed from both pulps at pH 5, which makes citric acid less attractive as a chelating agent for kraft pulps. The α_M-values of Mn-citrate and Mg-citrate complexes are quite low at pH 5 and 10 (Figs. 1 and 3). Therefore the effective manganese and magnesium removal cannot be explained only by strong complex formation with citric acid, but some other physical and chemical changes in the sample may take place as well. Citric acid also removed iron better than EDTA even though the iron(III)-complexes with citrate are theoretically not as strong as the iron(III)-EDTA complexes (Fig. 2).

According to the α_M-values, in Figs. 1 and 2, oxalate should form as strong complexes with manganese and iron(III) as citrate. Hence, oxalic acid should be as effective a chelant as citric acid. However, the manganese concentrations in the pulps after the chelations with oxalic acid were still rather high compared to the concentrations in the pulps chelated with EDTA and citric acid. The iron removal, on the other hand, was as effective with oxalic acid as with EDTA, but nevertheless not as effective as it was with citric acid. Chelation with formic acid at pH 5 removed a part of the studied metal ions. The reason, however, is obviously not only interaction with formic acid, but rather the ion exchange with hydrogen ions.

Table 4. Metal Ion Concentrations in Oxygen-Bleached *Softwood* Kraft Pulp Before and After various Treatments. Each treatment was done both at pH 5 and 10. The redox potentials are measured in the beginning and in the end of each treatment.

Treatment	pH	Mn (ppm)	Fe (ppm)	Mg (ppm)	Redox potential 0 min (mV)	Redox potential 60 min (mV)
Original concentration	9	48	6.9	310	70	
EDTA (0.4%)	5	0.5	2.4	220	120	160
	10	17	6.1	320	16	33
Citric acid (0.01 M)	5	2.8	2.3	18	60	130
	10	19	3.6	120	-85	-62
Oxalic acid (0.01M)	5	6.9	3.5	27	140	150
	10	47	3.5	210	-8	1
Formic acid (0.01 M)	5	29	7.0	150	55	38
	10	53	5.4	350	-71	-76
Sodium borohydride (0.2%) + EDTA (0.4%)	5	0.1	1.2	190	-150	-35
	10	7.2	5.4	280	-360	-60
Sodium ditihonite (0.5%) + EDTA (0.4%)	5	0.1	0.9	190	-450	55
	10	11	5.6	280	-680	-140
Sodium bisulfite (1.0%) + EDTA (0.4%)	5	0.1	2.5	200	72	60
	10	20	5.5	250	-57	-61

Also in these experiments the original content of manganese was lower in softwood pulp than in hardwood pulp. However, manganese was more effectively chelated from the softwood pulp, which again indicates that manganese is more weakly bound to functional groups in softwood pulp than in hardwood pulp

Chelation with EDTA in a reducing environment

Iron, especially iron(III), is very difficult to be removed from kraft pulps. One possible reason to this may be the formation of iron(III) precipitates of low solubility (Sundén et al. 2000). In this study we tried to solve the problem by reducing trivalent iron to divalent iron by using reducing agents in order to increase the solubility of iron(III) precipitates by reduction. The affinity of divalent iron ions to the pulp is, according to our previous studies (Södö et al. 2004), about the same or even less than the affinity of manganese ions. Additionally, EDTA forms stronger complexes with divalent iron than with manganese (Granholm et al. 2010). Also citric, oxalic and formic acid show some reducing properties as can be seen from the redox potentials in Tables 3 and 4.

In Table 5 the [Fe(III)´]/[Fe(II)´] ratios are calculated according to equations (1) and (3), for some redox potentials at pH 5 and 10 in the aqueous phase. Side reactions of iron ions with hydroxide ions and EDTA are considered in these calculations. Therefore, the concentration ratios shown in Table 1, give a good estimation of the behavior of the iron redox couple in the chelation experiments. The calculations show that at pH 5, divalent iron is dominant (>99%) at potentials lower than -230 mV and trivalent iron is dominant (>99%) at potentials above 40 mV. If the redox potential is between these values both redox species will exist in relevant concentrations. At the redox potential -100 mV and at pH 5 [Fe(II)´] and [Fe(III)´] would be equal in the aqueous phase. At pH 10, Fe(II)´ dominates (>99%) at potentials lower than -450 mV and Fe(III)´ dominates (>99%) at potentials above -180 mV. Equal concentrations of Fe(II)´ and Fe(III)´ can be obtained at the potential -310 mV when pH is 10. These potentials are slightly lower than at pH 5.

In order to obtain a reducing environment during chelation with 0.4% EDTA, the following three reducing agents were used: sodium borohydride, sodium dithionite, and sodium bisulfite. Both oxygen bleached hardwood and softwood pulps were chelated. The remaining manganese, iron, and magnesium concentrations and the redox potentials in the beginning and at the end of the chelations are shown in Tables 3 and 4.

From the redox potentials measured during the chelation experiments, it can be seen that the lowest potentials were obtained with 0.5% dithionite (ca. -400 mV to -600 mV), i.e. these chelations were done in the most reducing environment. Also borohydride and bisulfite decreased the redox potential. An increase in the concentration of the reducing agents would probably further decrease the redox potential. Without addition of any reducing agent to the pulp slurry the redox potentials were quite constant during the whole chelation experiment. However, with addition of borohydride and dithionite a clear increase in the redox potential from the start of the chelation (0 min) to the end of chelation (60 min) can be observed. This indicates that the reducing agents are consumed also by other reactions than reduction of the metal ions therefore decreasing the reducing power during chelation.

Table 5. [Fe(III)`]/[Fe(II)´] Ratios in the Aqueous Phase for some Redox Potentials and pH Values. The following α-coefficents have been used: $\alpha_{Fe(III)}=10^{14.9}$ and $\alpha_{Fe(II)}=10^{4.1}$ at pH 5 and $\alpha_{Fe(III)}=10^{24.2}$ and $\alpha_{Fe(II)}=10^{10.2}$ at pH 10 ([EDTA] = 0.0027 M).

pH 5				pH 10			
Redox Potential (mV)	$\lg\frac{[Fe(III)']}{[Fe(II)']}$	Fe(III)´ (%)	Fe(II)´ (%)	Redox Potential (mV)	$\lg\frac{[Fe(III)']}{[Fe(II)']}$	Fe(III)´ (%)	Fe(II)´ (%)
-500	-5.9	0	100	-600	-4.9	0	100
-230	-2.0	1	99	-450	-2.0	1	99
-100	0.0	50	50	-310	0.0	50	50
40	2.0	99	1	-180	2.0	99	1
250	5.1	100	0	20	4.9	100	0

The redox potentials, during the chelations without any reducing agents (ca. 0 mV to 200 mV), show, according to Table 5, that the trivalent iron was dominant. On the other hand, when using borohydride or dithionite as a reducing agent in the chelations, the divalent iron was dominant at the start of the chelation (0 min). However, the increase in the redox potentials during the chelation experiments oxidized the iron back to the trivalent state. Therefore, the strongest reducing effects were only temporary at the beginning of chelations. The redox potentials at the end of the chelations (60 min) were about 100 mV lower when using reducing agents than without any reducing agents at all, but these potentials (ca. 0 mV at pH 5 and ca. -100 mV at pH 10) are not low enough to reduce iron ions to the divalent form.

A clear improvement in the removal of manganese from both pulps can be seen when the chelations were done in reducing environment (Tables 3 and 4). Generally it can be stated that a lower redox potential gave also a lower manganese concentration in pulp after chelation. When the chelation was done at pH 5 and only with EDTA the remaining manganese concentration was 14 ppm and when using also dithionite in the EDTA chelation, the manganese concentration was reduced to 8.5 ppm for the hardwood kraft pulp. At pH 10 the manganese concentration was 130 ppm when using only EDTA and 95 ppm when using also dithionite. For the softwood pulp the remaining manganese concentration at pH 5 was decreased from 0.5 ppm to 0.1 ppm and at pH 10 from 17 ppm to 11, when using dithionite in the EDTA chelation.

The removal of iron from the pulps was, however, not improved, when using a reducing agent, as much as it did in removal of manganese. In the hardwood pulps the remaining iron concentrations, after chelation in a reducing environment, were almost the same as after chelation with only EDTA (Table 3). However, a small improvement of the iron removal from the softwood pulp can be seen (Table 4).

The magnesium concentrations after the chelations were also somewhat affected by the reducing agents. The magnesium concentrations in the chelated pulps were slightly decreased when using these reducing agents.

The effect of reduction at alkaline pH

Generally, the removal of manganese during chelation with EDTA at slightly acidic pH values is acceptable from the bleaching point of view (Granholm et al. 2010). It would, however, be desirable to do the chelation in a more alkaline media. In order to study the chelation at the more alkaline pH, series of chelation experiments with EDTA where done in the pH range 5-11, both with and without reducing agents.

In Figs. 4 and 5 we can observe that it was not possible to remove manganese quantitatively at higher pH from the pulps. Nevertheless, it was possible with 0.4% EDTA at pH 8 to remove more than 70% of the manganese from the hardwood pulp and almost 90% from the softwood pulp. Especially for the hardwood pulp the effect of reducing environment in removal of manganese with EDTA is better when the pH increases. This may be due to the lower redox potentials when pH increases. At pH 10, it was possible to improve the removal of manganese from the hardwood kraft pulp with ca. 15% and from the softwood pulp with ca. 10% by using dithionite during the chelation. However, the residual concentrations of manganese increased with increasing pH (Fig 4).

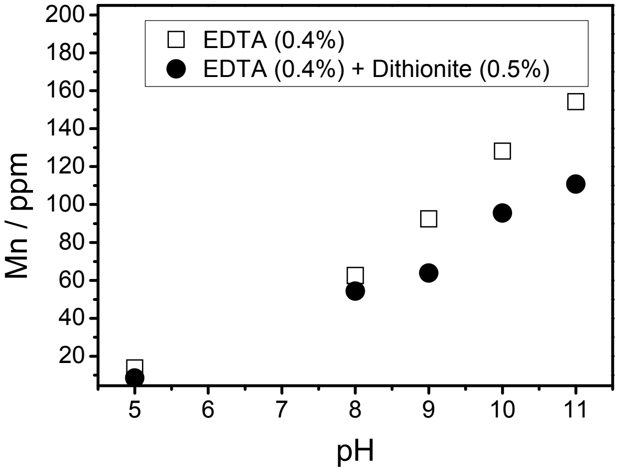

Fig. 4. Concentrations of manganese vs. pH in oxygen bleached *hardwood* kraft pulp after EDTA chelations with and without sodium dithionite. The manganese concentration before the chelation was 232.8 ppm.

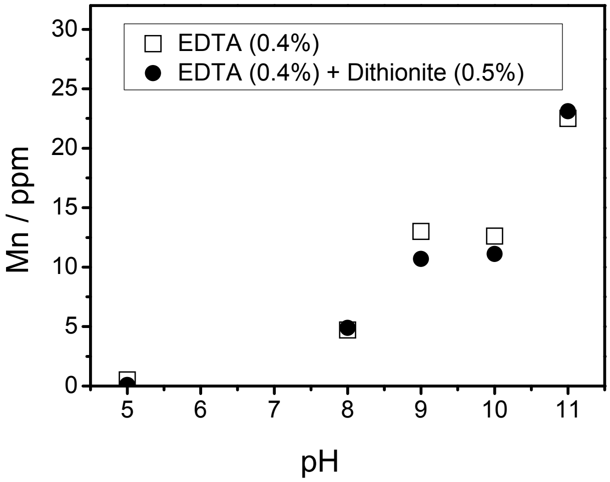

Fig. 5. Concentrations of manganese vs. pH in oxygen bleached *softwood* kraft pulp after EDTA chelations with and without sodium dithionite. The manganese concentration before the chelation was 48.1 ppm.

Most of iron still remained in the pulps after the chelations which were done at pH values over 8. For hardwood pulp only ca. 1 ppm of iron was removed at pH 8, and at the higher pH values the iron removal was negligible (Fig. 6). For softwood pulp the removal of iron at high pH values was also very small (Fig. 7). At pH 8 only about 3 ppm iron was removed, and at higher pH values even less. It should be pointed out that iron is rather heterogeneously distributed in pulp and may even considerably vary within samples of the same batch.

The reducing environment, obtained with 0.5% dithionite, did not improve the EDTA chelation of iron. This indicates that the reducing environment was incapable to reduce the bound trivalent iron ions. Another reason is obviously that stable iron precipitates, such as iron hydroxides or oxides are not affected by the reducing environment.

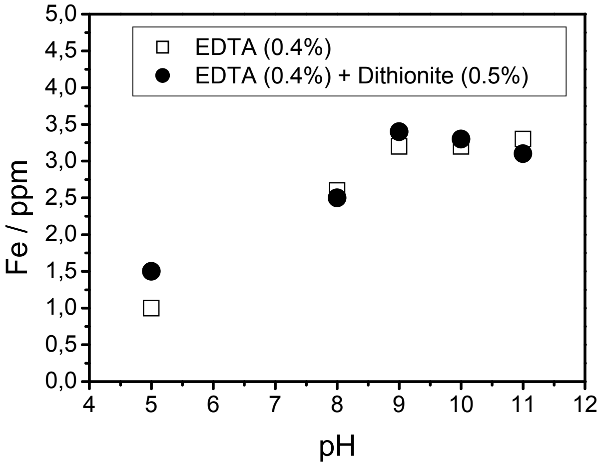

Fig. 6. Concentrations of iron vs. pH in oxygen bleached *hardwood* kraft pulp after EDTA chelations with and without sodium dithionite. The iron concentration before the chelation was 3.6 ppm.

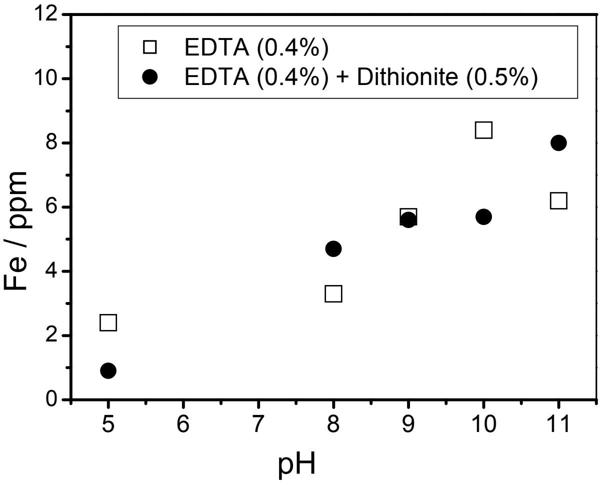

Fig. 7. Concentrations of iron vs. pH in oxygen bleached *softwood* kraft pulp after EDTA chelations with and without sodium dithionite. The iron concentration before the chelation was 6.9 ppm.

Study on Removal of some Other Metals Ions

In order to study desorption behavior of some other metals than manganese, iron, and magnesium, the samples were also analyzed by the ICP-MS method in a semiquantitative mode on a selection of differently treated pulps. The results given in this chapter are from the same experiments as the results given in Tables 3 and 4.

ICP-MS analysis of pulps treated with citric and oxalic acids

ICP-MS analytical data for hardwood and softwood kraft pulps treated with citric and oxalic acids are shown in Tables 6 and 7. For comparison also data for the pulps chelated with EDTA at pH 5 are shown in the tables.

From the results in Tables 6 and 7 it can be stated that the treatment with citric acid removed all the studied metal ions rather well. Aluminum and strontium were removed almost completely from both pulps. In fact, citric acid removed most of the metal ions determined better than chelation with EDTA. The only exceptions, in addition to sodium, were copper and lead, which were not removed as well as with EDTA. Also manganese was removed slightly better with EDTA, which was observed earlier (Tables 3 and 4).

The over-all removal of metal ions with oxalic acid was not as effective as it was with citric acid, although oxalic acid removed also most of the studied metal ions better than EDTA. Oxalic acid removed potassium from the pulps very effectively, especially from the softwood pulp in which the potassium concentration was only 3 ppm after the treatment. Calcium was not either removed with oxalic acid. The reason for this is that calcium oxalate has low solubility in water and therefore remains in the fiber phase. In addition to the good removal of potassium with oxalic acid at pH 5, also aluminum was removed exceptionally well from both pulps. Lead was removed to lesser extent with oxalic acid than with EDTA. The high remaining concentrations of sodium after citric and oxalic acid chelations are due to addition of NaOH in adjusting the pH.

ICP-MS analysis of pulps chelated with EDTA in reducing environment

ICP-MS analysis was also made for the pulps that were chelated with 0.4% EDTA in reducing environment at pH 5. From these results, given in Tables 6 and 7, one can see that the reducing environment during chelation with EDTA did only slightly improve the removal of the 10 metal ions determined semiquantitatively from pulp.

Table 6. ICP-MS Analyses of Oxygen-Bleached *Hardwood* Kraft Pulps After various Treatments at pH 5

Treatment	Na	Ca	K	Ba	Al	Sr	Cu	Rb	Pb	Cd
						(ppm)				
Before chelation	2700	740	81	30	10	6.9	1.0	0.5	0.3	0.1
EDTA (0.4 %)	710	260	79	23	2.7	4.6	0.7	0.1	0.05	0.05
Citric acid (0.01M)	1100	120	20	5.0	0.5	1.1	0.9	0.05	0.1	0.02
Oxalic acid (0.01M)	960	890	29	17	0.8	5.0	0.6	0.05	0.3	0.08
Sodium borohydride (0.2 %) + EDTA (0.4%)	780	440	50	20	2.6	4.2	0.3	0.1	0.02	<0.01
Sodium dithionite (0.5 %) + EDTA (0.4%)	840	460	70	22	3.3	4.6	0.3	0.1	0.02	0.01

Table 7. ICP-MS Analyses of Oxygen-Bleached *Softwood* Kraft Pulps After various Treatments at pH 5

Treatment	Na	Ca	K	Ba	Al	Sr	Cu	Rb	Pb	Cd
	(ppm)									
Before chelation	600	590	28	8.3	11	4.4	0.6	0.1	0.3	0.06
EDTA (0.4 %)	150	370	80	5.0	7.3	3.9	0.4	0.03	0.02	<0.01
Citric acid (0.01M)	580	79	28	1.5	1.4	0.7	0.6	0.03	0.1	0.01
Oxalic acid (0.01M)	270	520	3	2.8	1.0	2.9	0.3	0.01	0.2	0.03
Sodium borohydride (0.2%) + EDTA (0.4%)	230	360	61	4.9	5.7	3.5	0.3	0.03	0.02	<0.01
Sodium dithionite (0.5%) + EDTA (0.4%)	290	290	48	4.3	6.9	3.5	0.3	0.03	0.05	<0.01

The sodium concentrations were ca 100 ppm higher in both pulps when reducing agents were used. The reason for this is that sodium salts of the reducing agents were used. Potassium removal was slightly improved. The main improvement obtained was better removal of both copper and cadmium from both pulps.

CONCLUSIONS

The concept of α-coefficients was used to theoretically compare the complexing strengths of different ligands at different pH. The results from the desorption experiments were in satisfactory agreement with the theoretical calculations. There are, however, still many unknown parameters involved e.g. precipitates that cannot be taken into account in the calculations.

Manganese, iron, and magnesium can effectively be removed from the pulps by acid wash, due to the ion exchange reactions between the metal ions and hydrogen ions in the solution. A small part of metals, especially iron, could not be removed from the pulp, obviously due to the fact that they exist as precipitates of low solubility. The results of the acid washes and different chelations showed that manganese and iron are much more strongly bound to hardwood pulp than to softwood pulp.

Chelations with TEA removed a part of iron, but only at pH 10. Manganese, however, was not chelated at pH 10. Complexation with citric acid removed manganese ions better than with formic and oxalic acids. Citric acid also removed most of the other metals ions studied, including magnesium.

A combination of EDTA chelations with reducing agents improved the removal of manganese and copper ions. However, the better removal of manganese was more obvious at high pH values. Iron removal was on the other hand not enhanced by the reducing environment. One of the reasons may be that iron(III) was not effectively reduced to iron(II) due to the decomposition of the reducing agents during the chelation experiments as the theoretical calculations on measured redox potentials showed. Iron exists in the pulp as very stable salts and the used redox potentials were not low enough to enable dissolution of iron(III) from the stable salts.

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