

**HYDROGEN PEROXIDE-  
METALS- CHELATING  
AGENTS;  
INTERACTIONS AND  
ANALYTICAL TECHNIQUES**

**JAAKKO  
RÄMÖ**

Department of Process and  
Environmental Engineering,  
University of Oulu

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## **Rämö, Jaakko, Hydrogen peroxide- metals- chelating agents; interactions and analytical techniques**

Department of Process and Environmental Engineering, University of Oulu, P.O.Box 4300, FIN-90014 University of Oulu, Finland  
Oulu, Finland  
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### ***Abstract***

Information about interactions among metals, hydrogen peroxide and chelating agents is needed to develop environmental technology and the operating efficiency of modern elemental chlorine free and total chlorine free bleaching processes. The work presented here focused on the properties of metal chelates and corrosion of titanium in an alkaline hydrogen peroxide solution. A comparative study between three rapid analysis methods, ICP-AES, XRF and ISE, was performed in pulp matrix and error sources of ISE were investigated in detail. Sensitive and selective GC methods for chelating agents ADA and NTA in water matrices were developed.

Decomposition of ADA (percentage of residual 71) was observed already at the hydrogen peroxide anion level of 400 mg/l in which DTPA was more persistent (percentage of residual 94). EDTA was stable even in the hydrogen peroxide anion level of 1200 mg/l, in which its percentage of residual was 94. DTPA, EDTA and ADA were more soluble in the presence of iron and manganese than in the absence of these metals. The chelation of iron appeared to be thermodynamically limited in hydrogen peroxide bleaching conditions.

Unalloyed (Grade 2) and alloyed (Grade 5) titanium corroded at the hydrogen peroxide anion level of 200 mg/l. The presence of calcium and silica inhibitors and further iron and manganese enhanced the critical hydrogen peroxide anion levels. Grade 5 was inferior to Grade 2. During rapid uniform corrosion, the potential of unalloyed titanium was under 200 mV (SHE) and lower than that of platinum.

Over 90% of manganese and many other metals could be leached into aqueous phase for ICP-AES analysis using chelation or acid hydrolysis. An XRF method for manganese, iron and copper in pulp including little or no sample treatment was developed. Measuring temperature differences and atmospheric carbon dioxide were observed to be notable error sources of the ISE technique.

***Keywords:*** bleaching, chelating agents, hydrogen peroxide, metals



## Preface

This dissertation has been performed in VTT, Helsinki University of Technology and in University of Oulu during the years 1994-2001.

Professor Mika Sillanpää, the supervisor of this thesis, is gratefully thanked for all his guidance and the long-term cooperation.

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Finally, I am deeply indebted to my family for the warm and supporting environment.

Oulu, 20.9.2002

Jaakko Rämö





## Glossary

AAS	atomic absorption spectrometry
ADA	$\beta$ -alaninediacetic acid
AES	atomic emission spectrometry
C	concentration
CE	capillary electrophoresis
$C_{in}$	concentration of incoming stream
$C_{out}$	concentration of outgoing stream
D	chlorine dioxide stage
DOC	dissolved organic carbon
DTPA	diethylenetriaminepentaacetic acid
DTPMP	diethylenetriaminepentakis (methylenephosphonic acid)
E	electrical potential
ECF	elemental chlorine free
ED	energy dispersive
EDTA	ethylenediaminetetraacetic acid
EP	alkaline peroxide stage
EU	European Union
$f_i$	activity coefficient of a univalent ion
FTIR	Fourier transform infrared
GC	gas chromatography
GLUDA	glutamate, N, N-bis(carboxymethyl)
HDAN	heptadecanoic acid nitrile
ICP-AES	inductively coupled plasma – atomic absorption spectrometry
IDS	iminodisuccinate
IUPAC	International Union of Pure and Applied Chemistry
ISE	ion selective electrode
IUPAC	International
$K_a$	acidity constant
$K_w$	ionic product of water
LC	liquid chromatography
MGDA	methyleneglycine diacetic acid

NPD	nitrogen phosphorus detector
NPE	non process element
NTA	nitrilotriacetic acid
P	peroxide stage
Q	complexing stage, flowing stream
SHE	standard hydrogen electrode
SIMS	secondary ion mass spectrometry
S,S'-EDDS	S,S'-ethylenediaminedisuccinate
TCF	total chlorine free
V	volume
WD	wave length dispersive
WWTP	waste water treatment plant
XPS	X-ray photoelectronic spectrometry
XRF	X-ray fluorescence
Z	ozone stage

## List of original papers

The thesis consists of a summarizing review, the following articles and some unpublished data.

- I Rämö J & Sillanpää M (2001) Degradation of EDTA by hydrogen peroxide in alkaline conditions. *J. Cleaner Prod.* 9: 191-195.
- II Sillanpää M & Rämö J (2001) Decomposition of  $\beta$ -alaninediacetic acid and diethylenetriaminepentaacetic acid by hydrogen peroxide in alkaline conditions. *Environ. Sci. Technol.* 35: 1379-1384.
- III Rämö J, Sillanpää M, Orama M, Vickackaite V & Niinistö L (2000) Chelating ability and solubility of DTPA, EDTA and  $\beta$ -ADA in alkaline hydrogen peroxide environment. *J. Pulp Paper Sci.* 26(4): 125-131.
- IV Saarinen K, Korvela T & Rämö J (1995) Corrosion performance of titanium in alkaline hydrogen peroxide environments. 8th World Conference on Titanium, Birmingham, UK, 22-26 October 1995, London, Institute of Materials, 9 p.
- V Rämö J, Saarinen K & Sillanpää M (2002) Uniform corrosion of titanium in alkaline hydrogen peroxide conditions; influence of transition metals and inhibitors. *Mater. Corr.* 53: 898-901.
- VI Sillanpää M, Rämö J, Piepponen S & Rahikkala A (2002) Metal analysis in pulps by ICP-AES: Practical aspects of on-line determination. *Pap. Timber* 84: 116-119.
- VII Rämö J, Sillanpää M, Klasila T & Piepponen S (2001) Determination of Mn, Fe, and Cu in chemically-treated wood pulps by the XRF addition method. *Fresenius J. Anal. Chem.* 370: 1105-1108.
- VIII Rämö J & Sillanpää M (2003) Impact of temperature, atmospheric carbon dioxide and ion strength adjustor on ion selective analysis of pH, calcium and sodium. *Appita J.*, in press.
- IX Vazquez M, Mikhelsson K, Piepponen S, Rämö J, Sillanpää M, Ivaska A, Lewenstam A & Bobacka J (2001) Determination of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Cl}^-$  ions in wood pulp suspensions using ion-selective electrodes. *Electroanalysis* 13: 1119-1124.
- X Sillanpää M, Vickackaite V, Rämö J & Niinistö L (1998) Determination of  $\beta$ -alaninediacetic acid in waste waters and aquatic environment using GC-NPD. *Analyst* 123: 2161-2165.

XI Tuulos-Tikka S, Sillanpää M & Rämö J (2000) Determination of nitrilotriacetic acid in waste and natural waters. *Intern. J. Environ. Anal. Chem.* 77(3): 221-232.

The research work described in these articles has been performed in VTT, Helsinki University of Technology and in University of Oulu during the years 1994-2002. Author's role was to plan and carry out the research as well as to prepare the manuscripts. Articles I and II describe decomposition and article III solubility properties of synthetic chemicals already during an industrial process. Articles IV and V deal with corrosion of common construction material at the same circumstances. Further, articles VI, XII, XIII and XI report analytical methods for controlling the process and reduce emissions. Analytical methods reported in articles X and XI can be utilized in environmental analytics, too.

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# 1 Introduction

Use of chlorine gas in pulp bleaching applications has almost been abandoned because of the organic chlorine compounds it generates, many of which are detrimental to the environment and human health. Modern bleaching consists of several stages, a typical sequence being, for example,  $O_2 - ClO_2 - NaOH - O_2 - H_2O_2 - ClO_2 - ClO_2$ . This kind of process is called an elemental chlorine-free (ECF) process, because of the absence of chlorine gas. If the generation of organic chlorine compounds will be entirely eliminated, totally chlorine free (TCF) processes containing no chlorine dioxide or any other chlorine compound are to be applied.

The alkaline stage is an important part of bleaching in both ECF and TCF, lines and also in the case of mechanical pulping. This stage is strongly intensified by hydrogen peroxide due to the formation of hydrogen peroxide anion ( $HOO^-$ ) which reacts nucleophilically with chromophores of lignin [1]. The alkalinity itself holds a key role because many degradation compounds generated in the chlorine dioxide stages are dissolved in alkaline solution.

Transition metals, mainly manganese, iron and copper, are a serious problem involved in the alkaline hydrogen peroxide stages. They catalyze degradation of hydrogen peroxide [2-5], diminishing the concentration of the  $HOO^-$  ion, and thus the bleaching efficiency. In the presence of copper [2, 6] and also iron in certain bleaching conditions [6], decomposition occurs with a free radical mechanism, and generated hydroxyl and superoxide anion radicals may react with carbohydrates causing worsening of strength properties and yield losses. In addition, metals accelerate darkening of the final product [7]. Fortunately, acidic conditions in the chlorine dioxide stages diminish concentrations of the transition metals. Metals can also be effectively removed from pulp before the introduction of hydrogen peroxide by using complexing agents (DTPA, EDTA) [8, 9] or acidic wash [10]. In addition to the alkaline hydrogen peroxide stages, transition metals perturb the oxygen stages, and magnesium sulphate is added to diminish this effect. Magnesium has beneficial properties also in the hydrogen peroxide stages [11]. Corrosion of titanium in alkaline hydrogen peroxide conditions has been a practical problem in many plants [12]. Sodium, as the main component of the non-process element (NPE) load, and calcium as a disturber of the targeted chelation of transition metals [13], but a protector of the titanium constructions [14], are also of importance.

The matters above have launched a need to increase precise information about metals in bleaching lines. The purpose of this study was to increase knowledge of the behaviour of metals in alkaline hydrogen peroxide conditions. Complexing agents are extensively used in metal management, in Finland thousands of tons a year, and their properties were an essential part of the present work. These properties included chelating ability, solubility and decomposition. Interactions between titanium and hydrogen peroxide were investigated, and critical conditions were charted, including influences of other metals on corrosion rates. In general, metal analytics are closely connected with research and process control purposes, and a comparative study between three rapid analytical methods, namely inductively coupled plasma atomic emission spectrometry (ICP-AES), X-ray fluorescence (XRF) and the ion selective electrode (ISE) method was implemented in this study. In addition, hydrogen peroxide and pH measurements were studied, concentrating on error sources of determinations of the pH with glass electrodes. These error sources were the effect of different measuring temperature and the formation of a carbonate buffer. Gas chromatographic (GC) methods for alternative chelating agents,  $\beta$ -alaninediacetic acid (ADA) and nitrilotriacetic acid (NTA), in water matrices were developed.



## 2 Hydrogen peroxide in alkaline solutions

### 2.1 Dissociation

Hydrogen peroxide is an acid and dissociates to hydrogen peroxide anion ( $\text{HOO}^-$ ), which is a strong nucleophil, with a nucleophilic constant 7.8 [15]. Knowledge of the  $\text{HOO}^-$  anion concentration is of high technical importance. In the alkaline hydrogen peroxide bleaching stages of chemical and mechanical pulp bleaching, for instance, this anion attacks nucleophilly to double bonds and carbonyl carbons of residual lignin [1]. It also has high importance in the chemical decomposition of different organic compounds, including metal chelates [I, II]. Moreover, it holds a crucial role in the corrosion of titanium [IV, V, 16]. Dissociation constants as a function of temperature have been tabulated as a function of temperature in references [17] and [18], for instance.

The hydrogen peroxide anion concentration can be evaluated with equation (2.1), if the total hydrogen peroxide concentration, pH and temperature are known. Analyses of these are discussed in section 5.2. Here it is only pointed out that due to rapid decomposition (section 2.2) hydrogen peroxide analysis must be performed immediately after sampling. The pH must be measured in real operating temperature, either on line or rapidly before the cooling of a sample.

$$c(\text{HOO}^-) = \frac{10^{pH - pK_a} c(\text{HOO}^- + \text{HOOH})}{f_1 + 10^{pH - pK_a}} \quad (2.1)$$

$c(\text{HOO}^-)$	hydrogen peroxide anion concentration
$pH$	pH at real operation temperature
$pK_a$	$pK_a$ value of hydrogen peroxide [17, 18]
$c(\text{HOO}^- + \text{HOOH})$	total hydrogen peroxide concentration (result of the titration)
$f_1$	activity coefficient of univalent ion (typically about 0.8 in ionic strengths of hydrogen peroxide bleaching)

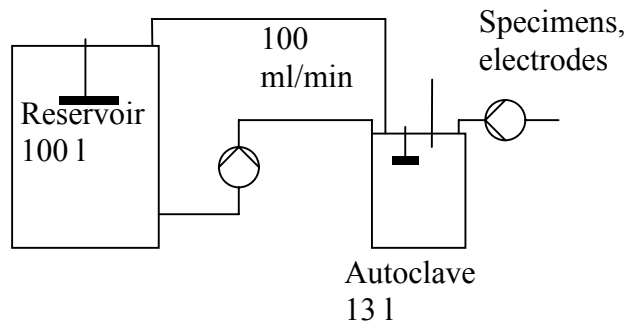
## 2.2 Decomposition

It is well-known that hydrogen peroxide is vulnerable to decomposition. Many mechanisms for this have been proposed such as the base catalytical ion mechanism (1), the base catalytical free radical mechanism (2), the transition metal involved free radical mechanism (3), the emerging of unstable metal peroxides or metal complexes (4) and heterogenic surface catalytic reaction formed by transition metal oxide or hydroxide (5) [2]. It is important to recognise the possibility of the existence of free radicals, due to their tendency to degrade carbohydrates in addition to lignin. There is evidence, however, that free radical formation in bleaching stages occurs to a small extent, because only slight degradation of lignin can be observed [19] and alkaline hydrogen peroxide bleaching is generally considered to be lignin retaining [1]. Base catalytical mechanisms (1) and (2) may be unimportant because the decomposition has been completely eliminated by DTPA during exposure of 120 min at pH 10.8 and 50 °C [2]. It has also been suggested that peroxide decomposition induced by manganese(II) does not involve radicals and occurs by a two-electron transfer [20]. In alkaline hydrogen peroxide bleaching conditions, manganese has been even observed to decrease the radical formation [2, 6], and manganese(II) has been shown to be catalytically inactive [21]. Magnesium inhibits radical formation in alkaline hydrogen peroxide bleaching, where it precipitates as hydroxide, which interrupts free radical chain reactions by catching the superoxide anion radicals [11]. In hydrogen peroxide bleaching conditions, there is a controversy over whether the presence of iron increases [6] or decreases [2] free radical formation. Copper has been shown to generate free radicals with hydrogen peroxide, which also has been observed in hydrogen peroxide bleaching conditions [2, 6]. Fortunately, concentrations of copper in fibre lines are generally lower than those of manganese and iron.

## 2.3 Experimental investigation of alkaline hydrogen peroxide solutions

Due to the decomposition of hydrogen peroxide, laboratory simulation of the alkaline hydrogen peroxide environment for investigation is difficult, and special large scale instrumentation is needed. An appropriate research system is presented in Fig. 1. The desired chemical environment is simulated to the autoclave to which hydrogen peroxide itself is fed with a pipe pump from a separated vessel. Controlling the concentration of hydrogen peroxide is carried out by regulating revolutions of the pipe pump. Electrodes and wires can practically be fed through the lid by using natural rubber o-ring gaskets or screws through which a hole has been drilled.

The results of chapters 3 and 4 of this study, dealing with the properties of metal chelates and the corrosion of titanium, are based on simulation experiments using the recirculation system described in Fig. 1. The detailed experimental procedures are documented in articles [I-V].



**Fig. 1. The pilot plant scale system used in investigation of alkaline hydrogen peroxide solutions.**

### 3 Properties of chelating agents

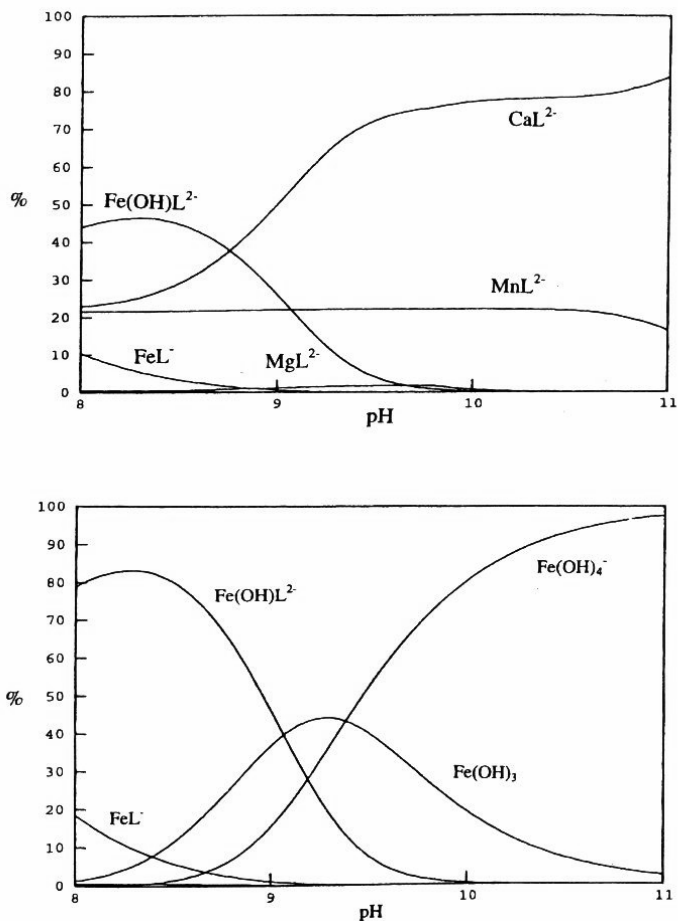
Complexing agents are extensively used in many applications, the major use being in the detergent component. In the pulp industry, they are utilized to form stable water soluble chelates with transition metal ions, and so remove these metals before hydrogen peroxide bleaching [8, 9]. In addition to assisting the removal of metals, chelating agents may prevent their contact with hydrogen peroxide and so reduce the catalytic decomposition of the bleach [9, 22]. The use of chelators can be expected to increase further if closure of water cycles and TCF bleaching processes will be applied more widely. Chelating agents may also find use in ECF-processes that incorporate hydrogen peroxide stages.

The behaviour of DTPA and EDTA in waste water effluents [23] and a natural aquatic environment [24-27] has received attention. In addition to increasing the total nitrogen contents, DTPA and EDTA remobilize the most toxic heavy metals from solid matter into water solution and thus extend their biological life cycles [28-31]. Moreover, when iron is removed by these ligands from precipitated phosphates, the phosphate is converted to a soluble form [32]. Although successful biodegradation in certain industrial wastewater treatment conditions has been observed [33], and elevated pH has been observed to increase decomposition rates in activated sludge plants [34, 35], biochemical [36, 37] and photochemical [38, 39] degradations are not totally adequate to eliminate the environmental threat. The influence of metal speciation is of the utmost importance to understand the environmental behaviour of these compounds [40].

It may be reasonable and even necessary to find alternative, more biodegradable chelating agents of the future such as phosphonic acids, methylglycine diacetic acid (MGDA), iminodisuccinate (IDS), Glutamate, N, N-bis(carboxymethyl)(GLUDA) or S, S'-ethylenediamine disuccinic acid (EDDS) [24]. According to a recent investigation, especially S, S'-EDDS is a viable replacement ligand in bleaching applications, and also IDS is comparable to EDTA [25].  $\beta$ -alaninediacetic acid (ADA) is a potential alternative, too, because it has been shown to improve the whiteness gain [41]. Exceptionally low toxicity and 98% biodegradation have been observed in laboratory scale activated sludge simulation [42]. Hence, ADA was investigated together with DTPA and EDTA in the present study. Chelating of the pulp can also be carried out using a mixture of a nitrogen-containing agent and one or more non-nitrogen containing chelator like lactic, citric, tartaric, gluconic or glucoheptonic acid [43, 44].

In the work for this dissertation, decomposition (I, II) and solubility (III) of DTPA, EDTA and ADA were investigated under simulated bleaching conditions. Since these properties significantly may be dependent on chemical speciation, distribution of the different metal chelates was calculated from the assumed prevailing thermodynamic equilibrium, which is realistic since ligands were added to the experimental system as uncomplexed forms, reactions of which are rapid (except those with trivalent cations). The calculations were based on equilibrium constants of ligand protonation, metal complex formation, metal hydrolysis and solubility of metal hydroxides as well as the ionic product of water [45-47]. The complexation of metals in a known solution may be visualized by drawing curves of their percentage distribution among different complex species, e.g. as a function of pH. As an example, the percent EDTA and Fe(III) distributions in typical concentrations of the alkaline hydrogen peroxide bleaching stage are presented in Fig. 2 [48]. As can be seen, chelation of iron(III) is restricted due to its strong self hydrolysis.

In real bleaching lines, the results of speciation calculations should be considered critically. If the chelating agent is added before the alkaline hydrogen peroxide bleaching stages at pH 4-5, iron(III)chelate, if formed, might play an important role later at the higher pH due to the slow kinetics of trivalent cations. The initial speciation has an outstanding impact on properties of chelating agents also in waste- and receiving waters as well as in natural aquatic environment. While evaluating these properties, it must be noted, too, that the agents can hardly exist in their free or protonated forms in any practical circumstances [49].



**Fig. 2. Percentage distributions of (a) EDTA and (b) Fe(III) in concentrations typical of the alkaline hydrogen peroxide bleaching stage: EDTA 0.026 mmol/l; Ca 0.40 mmol/l; Mg 0.67 mmol/l; Fe 0.014 mmol/l and Mn 0.0058 mmol/l [48].**

### 3.1 Decomposition

As noted above, biochemical [36, 37] and photochemical [38, 39] degradations do not eliminate the possible environmental impacts of DTPA and EDTA. Therefore, chemical decomposition of the chelating agents already in industrial processes is of interest. The chemical degradation of EDTA in real bleaching lines has been evaluated earlier. According to mass balance calculations, EDTA did not degrade chemically in mechanical pulping when hydrogen peroxide was the bleach. Instead, ozone in combination with



Table 1. Conditions and results of the decomposition experiments [I, II].

	Experiments with EDTA	Experiments with DTPA	Experiments with ADA
<i>pH</i>	10.5	10.6	10.7
<i>Concentrations (mg/l)</i>			
HOOH+HOO <sup>-</sup>	5000	1100	1000
HOO <sup>-</sup>	1200	400	400
Mn	0.4	0.4	0.4
Fe	0.8	1	1
Ca	16	11	11
Mg	16	16	16
Ligand	10	11	3
<i>Ligand speciation (%)</i>			
Ligand as Mn(II) complex	20	25	15
Ligand as Fe(III) complex	0	0	0
Ligand as Ca(II) complex	80	70	80
Ligand as Mg(II) complex	0	5	5
<i>Results (%)</i>			
Residual of ligand	94	94	71
Residual of hydrogen peroxide	74	40	40

The results in Table 1 reveal that EDTA is a persistent compound in a solution of high total hydrogen peroxide and hydrogen peroxide anion concentrations, 5000 and 1200 mg/l, respectively. This is in accordance with the documented reaction of undissociated hydrogen peroxide with tertiary amine [2].



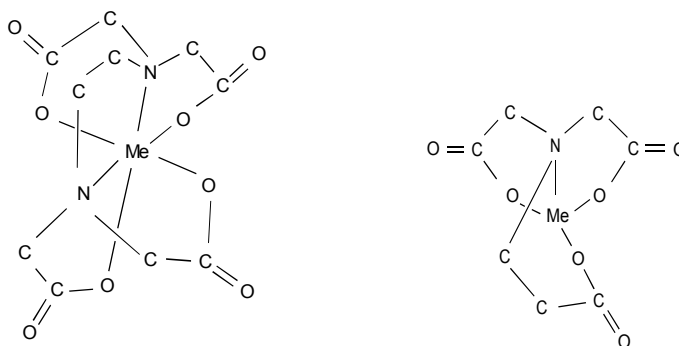
According to the mechanisms of equations (3.2) and (3.3), chelating agents are not directly degraded through the reaction with undissociated hydrogen peroxide, which partly explains the high percentages of EDTA residual observed in this work and suggests that the undissociated form is not responsible for the decomposition. It has also been observed earlier that evidently no reaction occurs between the Cu(II)-EDTA complex and hydrogen peroxide in the absence of biological reductants [55].

Table 1 reveals that ADA decomposed clearly already at the HOO<sup>-</sup> level of 400 mg/l, in which DTPA was persistent. In conclusion, ADA is more degradable than the other two agents.

As mentioned earlier, hydrogen peroxide anion is often considered to be an outstanding bleaching [1] as well as corroding [14] species. It may break organic bonds other than chromophores of lignin including those of the chelates, in which the chemical bonds are C-C, C=O, C-O, C-H, O-H, and C-N with bond energies of 339, 724, 331, 410, 456, and 276 kJ/mol, respectively, for hemolytic bond dissociation [15]. In all likelihood, nucleophilic bond breaking by HOO<sup>-</sup> occurs at the weakest bond, C-N. Figure 3 reveals



that ADA should be a better substrate than EDTA. In ADA, three carboxylic groups cause the single nitrogen to be more positive charged and consequently more favorable for the attack of the  $\text{HOO}^-$  anion. In EDTA, only two carboxylic groups are attracting the electron density of the nitrogen atom making it less vulnerable to the nucleophilic attack. Also in DTPA, two carboxylic groups are attracting the electron density of nitrogen atoms, or even one in the nitrogen in the center of the molecule. In an earlier investigation, it has been stated that the degradation of DTPA and EDTA indeed results from cleavage of the C-N bond. In this mechanism, one acetic acid is substituted by hydrogen. The main product of this breakdown has been identified as glyoxylic acid, which further oxidizes to oxalic acid [56].



J.R, P.V.

**Fig. 3. Molecular structures of  $\text{MeEDTA}^{2-}$  and  $\text{MeADA}^-$  complexes.**

It can be concluded from the species distribution calculations that under 10% of manganese remained unchelated in the experiments with DTPA and EDTA. In the case of ADA, 70% existed in unchelated form, due to the observed decomposition and due to the lower stability constant of  $\text{Mn(II)-ADA}$  chelate as compared to DTPA and EDTA. This gives rise to the formation of manganese (III, IV) oxides, which are facile oxidants for organic compounds, for example EDTA [57]. This may also explain the better decomposition of ADA as compared to the other two agents.

To summarize, EDTA appears to be a durable compound in alkaline hydrogen peroxide bleaching conditions [I]. The poor biodegradation has been reported earlier [23, 24, 36, 37]. It is recommended, therefore, to minimize the use of EDTA, until an effective means, such as chemical oxidation with an effective catalyst [58, 59], or improved biodegradation conditions [33-35] for its removal have been developed. An approach worth considering would also be the use of less recalcitrant ligands. ADA degrades chemically better than DTPA and EDTA [I, II], is biodegradable [42], has good technical performance in bleaching [41] and is thus a potential replacement ligand. The technical performance of biodegradable S, S'-EDDS [25] and mixtures of chelating agents [43, 44] should also be kept in mind.

### 3.2 Solubility

Metal complexes are generally hydrophilic compounds, but this does not exclude adsorption and different adsorption properties between chelate species. In natural aquatic conditions, adsorption is considered to be an important pathway of removal. EDTA has been found in lake sediments [60] and differences of the extent of adsorption between metal complexes of EDTA have been observed [61]. Adsorption mechanisms of EDTA on iron and aluminium oxides have been investigated in detail [62, 63].

In addition to natural conditions, adsorption of metal complexes may have a role during the bleaching process itself. An earlier investigation carried out in real bleaching lines nevertheless suggests that pulp has no significant ability to bind DTPA and EDTA [64]. In this study, solubility of DTPA, EDTA and ADA under alkaline conditions was investigated [III]. The purpose was to compare the solubility of the different complex species. Chelating agents in the aqueous phase were analysed by GC from simulated hydrogen peroxide bleaching solutions. The conditions in all systems were as follows: pH 10-12, hydrogen peroxide concentration during simulation 3000-5000 mg/l, concentration of Mg 0.5-0.8 mmol/l. Otherwise, the samples could be divided into two groups; those with 0.015 – 0.025 mmol/l of iron and manganese, and those with absence of these metals. An exact experimental description is presented in article III.

In the absence of the transition metals, soluble chelates were detected by GC to a limited extent. It could be shown by the species distribution calculations that ligands were totally present as magnesium complexes. Over 90% of magnesium existed as hydroxide,  $\text{Mg}(\text{OH})_2$ , the rest being complexed by ligand. It is quite possible that the magnesium complex adsorbed onto the magnesium hydroxide and hence was not found in the solution.

When the iron and manganese were introduced to the systems, solubilities were observed to be enhanced considerably. Soluble ligand content increased up to 20-25%, 80% and 30% of the added amount for DTPA, EDTA and ADA, respectively. This supports the conclusion on high chemical durability of EDTA presented in section 3.1. With regards to the species distribution calculation, for DTPA 45-60% of the added manganese was in the form of Mn-DTPA. The corresponding percentages for EDTA and ADA were 100 and 40, respectively. Evidently, manganese formed a stable complex transporting ligands into solution. Iron was calculated to exist totally as hydroxy species  $\text{Fe}(\text{OH})_4^-$ .

In the experiments described above, EDTA was more soluble than the other two agents. To confirm this conclusion, and to achieve better comparison between the three complexing agents, an experiment in which all the ligands were added was performed. The results of this experiment are presented in Fig. 4. in which chemical environment and the soluble chelating agent concentrations are presented as a function of experimental time. At first, when the transition metals were present, no DTPA, but almost all the EDTA, was in the solution. This may indicate that complexation of Mn(II) was more rapid with EDTA than with DTPA. In the course of time, part of the DTPA was transported into the solution, probably as a manganese complex. During the whole experiment, however, more EDTA was found in the aqueous phase as compared to the other two agents.

In summary, the solubility of the three chelating agents in an alkaline hydrogen peroxide bleaching environment is limited, but increases in the presence of iron and manganese. A possible explanation for the limited solubility is that the complexes, particularly the magnesium complex, are adsorbed onto magnesium hydroxide precipitate. Under the conditions investigated, manganese is well chelated especially by EDTA. Chelation of iron is thermodynamically difficult due to its strong self-hydrolysis. These experiments also support the conclusion of high chemical durability of EDTA presented in section 3.1.

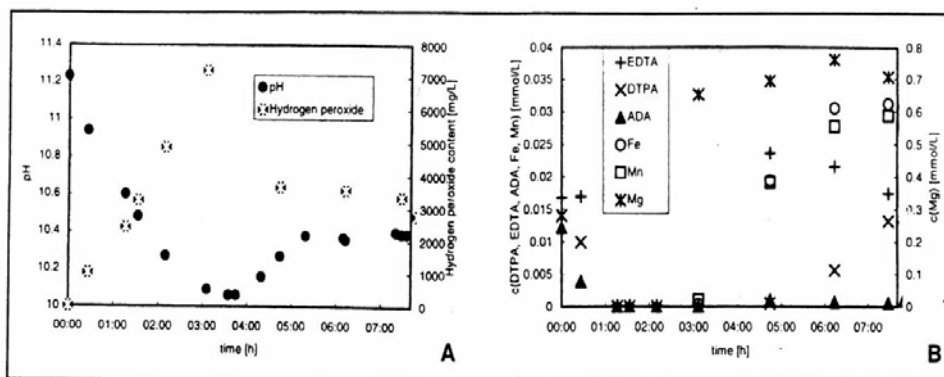
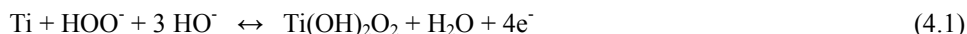


Fig. 4. Results for the experiment where EDTA, DTPA and ADA were used simultaneously: A) pH and total hydrogen peroxide concentrations as a function of time; B) total concentrations of metals and concentrations of soluble EDTA, DTPA and ADA [III]. Reproduced by permission of PAPTAC.

## 4 Uniform corrosion of titanium in alkaline hydrogen peroxide environments

Unalloyed titanium has good corrosion resistance in a highly oxidizing low pH environment and so it has been a traditional material for Cl<sub>2</sub> and ClO<sub>2</sub> bleaching stages. It is also a suitable material in alkaline environments. Corrosion resistance has been reported to be under 0.1 mm/y in 5% NaOH 40% NaCl solution at 108 °C [65].

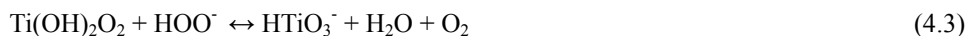
However, hydrogen peroxide in alkaline conditions is known to corrode titanium, and since the beginning of the utilization of hydrogen peroxide stages in pulp bleaching, practical corrosion problems have arisen. A proposed corrosion mechanism is an attack of the hydrogen peroxide anion [66]. The HOO<sup>-</sup> anion can break the oxide layer and form a complex, Ti(OH)<sub>2</sub>O<sub>2</sub> in which titanium is probably in its most important state, IV [67]. A dehydrated form of this complex, TiO<sub>2</sub>O·H<sub>2</sub>O, may also exist.



The Ti(OH)<sub>2</sub>O<sub>2</sub> complex may then hydrolyse to form titanium hydroxide and hydrogen peroxide.



Also, further reaction with the HOO<sup>-</sup> ion may occur [68].



Although it is possible that radicals forming in certain conditions, mainly in the presence of copper, may also cause corrosion damages, hydrogen peroxide anion is generally considered the corrosive agent [68-70]. It has been shown that when decreasing the amount of hydrogen peroxide, the critical pH value for corrosion of titanium is increased [71] and the increase in the pH value can be compensated for by decreasing the concentration of hydrogen peroxide [72]. This is evident on the basis of equation (2.1).

The purpose of the research in this study was to determine the critical corroding levels of the hydrogen peroxide anion. It has been found earlier that silica, magnesium and

especially calcium inhibit the corrosion [73-75] and so their influence on the critical level of  $\text{HOO}^-$  was taken into consideration. Due to the strong impact of transition metals on the behaviour of hydrogen peroxide and due to their presence in real bleaching processes, the effect of iron and manganese was also investigated.

In addition to unalloyed Grade 2, we studied aluminum and vanadium alloyed two phase Grade 5, which has good mechanical properties (yield strength is over 800 MPa) [69].

The experiments were started by recirculating solutions containing chemicals other than hydrogen peroxide and calcium between the reservoir and the autoclave (Fig. 1.). This was followed by starting the hydrogen peroxide pump to enhance the hydrogen peroxide level to the desired steady state. Calcium was fed with the hydrogen peroxide stream in which it was in a soluble form. When the steady state value was achieved, only slight regulation of the hydrogen peroxide pump was needed to compensate for the decomposition. It took approximately 100 min to reach the steady state after which the experiment was continued for at least two hours. The corrosion rates were determined according to the steady state. The potentials of titanium and platinum wires were followed against 0.1 molar KCl Ag/AgCl internal reference electrode.

Chloride, magnesium and DTPA concentrations were the same in all experiments, 200, 100 and 100 mg/l, respectively, and the experimental temperature was 85 °C. The pH in the steady state of the different experiments was 9.6 to 10.3 and the total hydrogen peroxide concentration ( $\text{HOO}^- + \text{HOOH}$ ) varied between 2600 to 3600 mg/l. Hence, the hydrogen peroxide anion concentration calculated by equation (2.1) was from 0 to 1200. Because calcium was fed with the peroxide, its concentrations also varied; the steady state values were from 70 to 120 mg/l.

Otherwise the chemical environments were as follows and they are presented in Table 2.

Group 1. Experiments without inhibitors or transition metals: no other chemicals.

Group 2. Experiments with inhibitors: calcium 77-95 mg/l (added as calcium acetate), silica 100 mg/l as  $\text{SiO}_3^{2-}$  (added as sodium silicate,  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ ).

Group 3. Experiments with inhibitors and transition metals: calcium 70-120 mg/l, silica 100 mg/l as  $\text{SiO}_3^{2-}$ , iron 2 mg/l (added as ferrous sulphate), manganese 1 mg/l (added as manganese sulphate).

Table 2. Rate of corrosion of titanium under different experimental conditions [IV, V].

Experiment	HOO <sup>-</sup>	Ca <sup>2+</sup>	Silicate	Fe	Mn	E Gr.2	Rate of	Rate of
	level	level	as SiO <sub>3</sub> <sup>2-</sup>				Gr.2	Gr.5
	mg/l			mV			mm/y	
<i>Group 1. No inhibitors or transition metals</i>								
1 / 1	200	0	0	0	0	-150	0.4	1.4
1 / 2	1200	0	0	0	0	-300	12	33
<i>Group 2. Inhibitors</i>								
2 / 1	300	80	100	0	0	250	0	2.4
2 / 2	440	95	100	0	0	210	0.1	9
2 / 3	470	95	100	0	0	210	0.3	8
2 / 4	470	77	100	0	0	90	2.1	14
2 / 5	480	80	100	0	0	220	0.8	12
2 / 6	540	80	100	0	0	190	0.5	9
<i>Group 4. Inhibitors and transition metals</i>								
3 / 1	420	120	100	2	1	50	0	0.7
3 / 2	800	100	100	2	1	-40	0.1	2
3 / 3	900	70	100	2	1	0	0.1	13
3 / 4	1000	80	100	2	1	-30	0.4	18

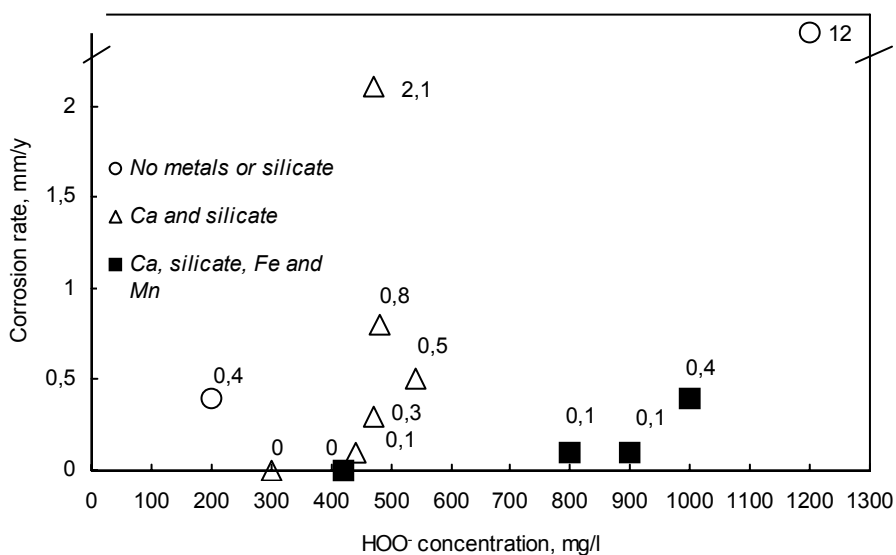
#### 4.1 Critical hydrogen peroxide anion levels and the influence of inhibitors and transition metals

In addition to experimental conditions, Table 2 presents the potentials of titanium and the corrosion rates. The results are also in Figs. 5 and 6 for titanium Grade 2 and Grade 5, respectively, for which comparison of the rates in different environments can be performed.

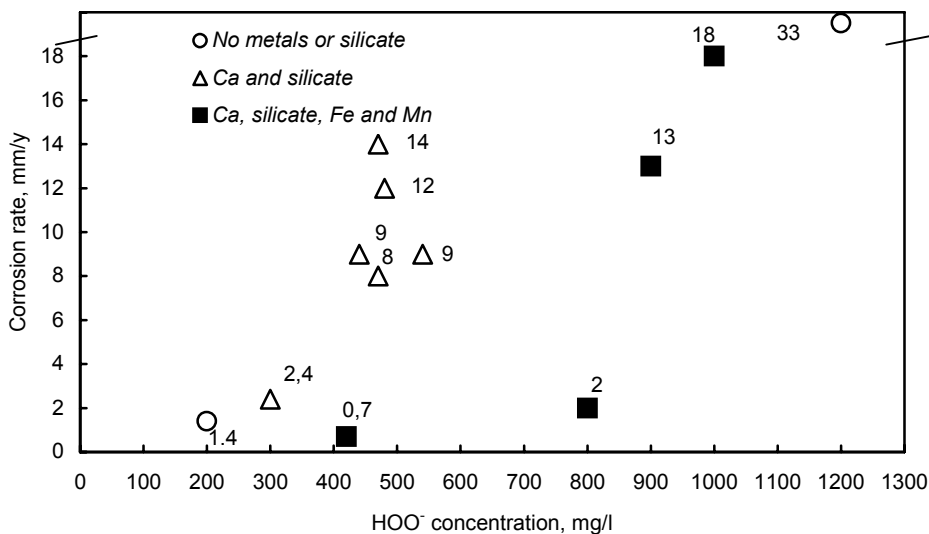
With the unalloyed titanium (Fig. 5) and no inhibitors or transition metals present, notable corrosion of 0.4 mm/y occurred at a hydrogen peroxide anion concentration as low as 200 mg/l and rapid corrosion of 12 mm/y occurred at concentration 1200 mg/l. Calcium and silica (Group 2) were able to protect the unalloyed titanium at hydrogen peroxide concentration 300 mg/l, and corrosion was still only slight at the concentration level 440 mg/l. Above this level, rates rose rapidly. With the transition metals present in addition to the inhibitors, no corrosion occurred even at the hydrogen peroxide level of 420 mg/l and the rates were low up to a concentration of 900 mg/l.

The results for the alloyed titanium are illustrated in Fig. 6. In general, corrosion rates were much higher than those of the unalloyed grade, but the effects of the inhibitors and the transition metals were similar. Without inhibitors or transition metals, the corrosion

rate was considerable (1.4 mm/y) already when the hydrogen peroxide anion level was 200 mg/l. A rate as high as 33 mm/y was observed at hydrogen peroxide anion concentration of 1200 mg/l. In the presence of calcium and silicate, Grade 5 corroded 2.4 mm/y at the  $\text{HOO}^-$  anion level of 300 mg/l. Together with the inhibitors, iron and manganese offered slight but clear protection properties up to the concentration level 420 mg/l, but in the range above 800 mg/l, corrosion was damaging.



**Fig. 5. Corrosion rates of the unalloyed titanium (Grade 2) as a function of hydrogen peroxide anion ( $\text{HOO}^-$ ) concentration.**



**Fig. 6. Corrosion rates of the alloyed titanium (Grade 5) as a function of hydrogen peroxide anion (HOO<sup>-</sup>) concentration.**

Several explanations may be suggested for the inhibition of silica and calcium. Silicate is sometimes added in bleaching to protect the hydrogen peroxide against decomposition. While the contamination it causes to fibres and process equipment is generally undesirable, from the point of view of protection against titanium corrosion the contamination may be beneficial. In the investigation of this work, added form of silicate was sodium metasilicate nonahydrate  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$  actual structure of which being probably  $\text{Na}_2[(\text{HO})_2\text{SiO}_2] \cdot 8\text{H}_2\text{O}$  [76]. In general, the silicate ions in solution or in crystals appear to contain silicon with a coordination number four [76]. In solutions of sodium silicates, there are mainly ions of  $(\text{HO})_2\text{SiO}_2^{2-}$  with some cyclic tetramer  $(\text{HO})_4(\text{Si}_4\text{O}_4)\text{O}_4^{4-}$  [76]. In the pH range investigated (9.6 – 10.3) it is also possible that a part of silica formed a sol [76]. It is unclear whether the anions or the sol provide notable protection against corrosion or even whether they exist in the conditions investigated, because magnesium forms a variety of silicates, for example  $\text{MgSiO}_3$ ,  $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ ,  $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ ,  $\text{Mg}_2\text{SiO}_4$ ,  $(\text{MgO})_2(\text{SiO}_2)_3(\text{H}_2\text{O})_8$ ,  $\text{CaMg}(\text{SiO}_3)_2$  and  $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$  [77]. The  $(\text{MgO})_2(\text{SiO}_2)_3(\text{H}_2\text{O})_8$ , is extremely insoluble, solubility product being lower than  $10^{-37}$  in the temperature of the experiments (85 °C) [77]. In addition, silica in both the monomeric and the polymeric state, has a strong tendency to precipitate with magnesium hydroxide [76, 78], and the conventional method of precipitating silica has been co-precipitation with magnesium [78]. Magnesium hydroxide existed at considerable level in the systems investigated. Hence it is very likely that silicate was bound to magnesium forming a system which might have some protecting properties. In an earlier in-depth study of the interactions between silicate, magnesium and calcium in peroxide brightening, silicate preferred to react with



magnesium when both the magnesium and the calcium were present. The resulted magnesium silicates, however, appeared to be soft talc-like precipitates which did not stick to stainless steels [79]. This might concern also titanium. It must be noted that silicate may form also soluble positively charged complexes with magnesium and calcium, namely  $\text{MgHSiO}_3^+$  and  $\text{CaHSiO}_3^+$ [77], which may have assisted in the protection.

Divalent  $\text{Ca}^{2+}$  ions may adsorb physically on to the surface of titanium, which is at a low potential. The adsorption layer may protect the surface against attacks of the  $\text{HOO}^-$  anions. To be useful in the protection of surfaces, calcium needs to exist as free  $\text{Ca}^{2+}$  ion. The hydrolysis of calcium is low, which means that it does not precipitate as hydroxide in the conditions of our investigations or in real bleaching. Calcium did not precipitate as carbonate because it was fed to the closed autoclave with the acidic solution of the hydrogen peroxide (Fig. 1). In real bleaching conditions formation of carbonate is kinetically hindered by the DOC [13, 80], as discussed in the earlier chapter. Sulphate concentration in the experimental system was not adequate to precipitate calcium as gypsum, and due to its molar minority, DTPA could bind only small part of calcium. Silica was very likely bound with magnesium, as noted above. In addition, calcium silicate does not form rapidly except at very high temperatures [76]. It is possible, although unlike, that low amounts of  $\text{CaHSiO}_3^+$  complex [77] or solid calcium silicate particles have enhanced the protection to some extent. In mill conditions calcium silicate scaling has been observed, although presence of magnesium has dramatically diminished the effect [79]. In the possible sol mentioned in the previous chapter,  $\text{Ca}^{2+}$  ions may adsorb on the surface and displace one hydrogen converting OH group into  $\text{OCa}^+$  group [76] and form a particle, which might have also protective properties against the corrosion. The protecting power of the calcium ions may be enhanced also by the formation of calcium peroxide in the adsorption layer reducing surface concentration of  $\text{HOO}^-$  ions [75].



Formation of calcium titanate,  $\text{CaTiO}_3$ , is also thermodynamically possible in aqueous alkaline hydrogen peroxide environments. However, no evidence of calcium in the surface film has been found by atomic emission spectrometry (AES), X-ray photoelectronic spectrometry (XPS) or secondary ion mass spectrometry (SIMS) with depth profiling in a coupon inhibited by calcium, making this mechanism questionable [75].

Due to the ability of the calcium ion to protect titanium, it might be beneficial to determine its concentration in real processes. Immediate or even in-line ion selective electrode analysis (subsection 5.1.3) could be a good analysis method.

The inhibiting effect of iron and manganese was also clearly observable in this work. Due to decomposition of the hydrogen peroxide in the presence of these metals, the amount of oxygen bubbles is high, and this may contribute to the formation of a tight protective titanium oxide layer at elevated temperatures. The bubbles themselves may also adhere to the surface, diminishing the contacts of the titanium layer and the  $\text{HOO}^-$  ions. It is possible that a part of the decomposition of the hydrogen peroxide occurred with the free radical mechanism in the experiments in which iron was present. Due to the

observed slow corrosion rates, however, it may be concluded that the possible radicals have no significant role in the corrosion of titanium.

## **4.2 The relationship between the corrosion rate and potential**

Experiment 1/2 in Table 2 suggests that in case of very damaging corrosion, the potential of titanium is low. To confirm this hypothesis, corrosion rates of the unalloyed titanium (Grade 2) were compared to the potentials in 36 different simulated alkaline hydrogen peroxide environments. The results in Fig. 7 reveal that low potential of titanium clearly indicated high corrosion rates, but it must be noted that high corrosion potentials did not guarantee that titanium is protected. Platinum electrode was added to some systems to indicate whether the low potentials during rapid corrosion rates resulted from surface reactions. With three exceptions, the potential of titanium was clearly below that of platinum suggesting that the corrosion occurred by mechanisms presented in equations (4.1), (4.2) and (4.3). (When no corrosion was observable, there were four additional cases, in which the potential of platinum was lower than that of titanium.)

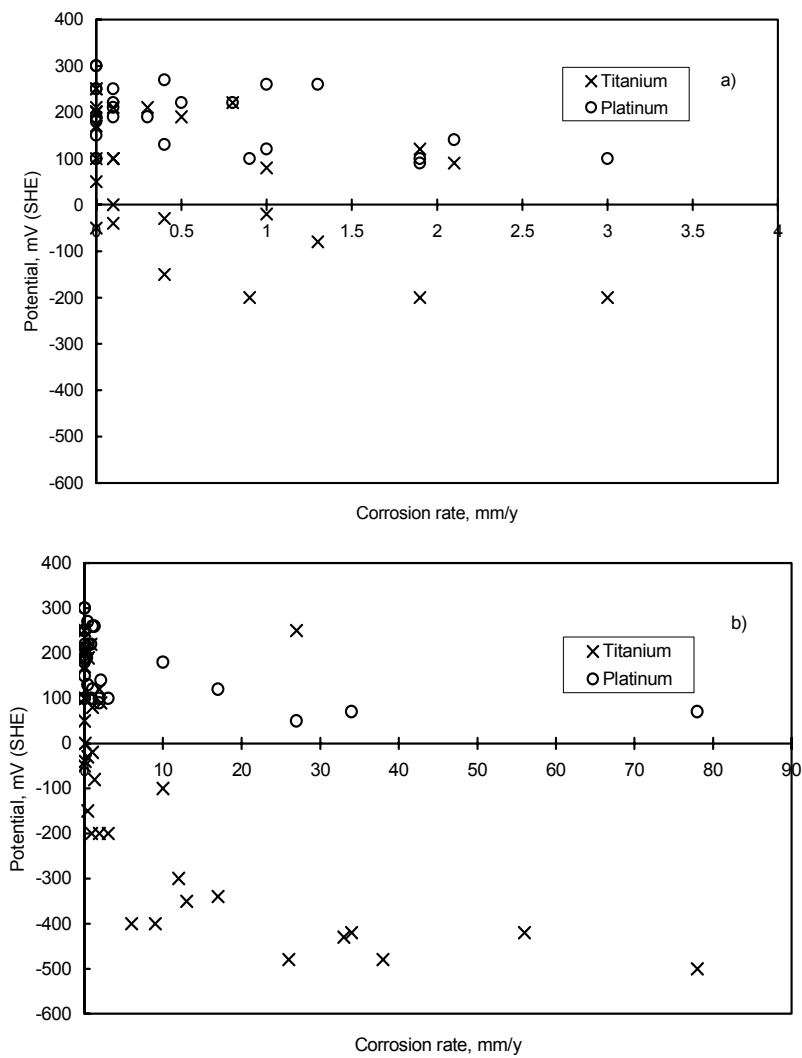


Fig. 7. Corrosion potential vs. corrosion rate of titanium Grade 2; a) 0-4 mm/y, b) 0-90 mm/y.

## 5 Analytical techniques in pulp and water matrices

In pulp bleaching, waste water treatment and the receiving aquatic environment, the importance of analytics is increasing due to technical development, including diminished water amounts, and due to strengthened environmental demands. The analytical research of this dissertation focused on metals in pulp matrix (5.1) with several techniques [VI-IX], but also determinations of hydrogen peroxide (5.2), pH [VIII] (5.2) and chelating agents ADA [X] and NTA [XI] (5.3) were investigated.

### 5.1 Metals

Transition metals have an outstanding impact on the peroxide stages of modern ECF and TCF bleaching sequences. Although under certain conditions they may have a stabilising effect [2] and add to the final brightness gain [81, 82], in general they are unwelcome because of the tendency to catalyze the decomposition of hydrogen peroxide, as discussed in chapter 1 [2-7]. Their rapid analysis, especially Mn, could assist in keeping the use of the chelating agents and the bleach itself to a minimum. In addition, if transition metal concentrations are known before the O<sub>2</sub> stages, the use of magnesium sulfate, which is added to the O<sub>2</sub> stage as a stabilizer, could be optimized.

In addition to transition metals, considerable amounts of alkaline and alkaline earth metals are introduced to the bleaching processes. Excessive amounts of free calcium ions interfere strongly with the functioning of complexing agents, restricting the chelation of iron and manganese in particular [13]. Abundance free Ca<sup>2+</sup> ions may exist in bleaching systems, because their hydrolysis is low [45] and the formation of CaCO<sub>3</sub> is kinetically hindered due to the presence of DOC [13, 80]. On the positive side, free calcium also has protective properties on titanium structures in the alkaline hydrogen peroxide bleaching stages (chapter 5) [V]. Sodium is a major part of the load of NPE in pulping and bleaching. Increased system closure leads to an accumulation of NPE, with a build-up of harmful deposits and corrosion problems [83-85].

In this thesis, performances of three analytical techniques, ICP-AES [VI], XRF [VII] and ISE [VIII] were studied focusing on feasibility for on-line techniques. Comparison of

these methods was made from a practical point of view, and several advantages and disadvantages of each technique were discussed.

### ***5.1.1 ICP-AES***

The ICP-AES method has low detection limits and permits several metals to be determined simultaneously. It is a typical liquid analysis method and so the pulp sample has to be wet ashed or metals have to be extracted into the aqueous phase. Since the wet ashing would be difficult to perform on-line, this work focused on developing a simple but reliable method for the extraction [VI]. Target metals were Al, Ba, Ca, Cr, Cu, Fe, Mg, Mn, Ni, Ti, Zn and the performance of four different chelating agents (EDTA, DTPA, nitrilotriacetic acid NTA and diethylenetriamine pentakis (methylenephosphonic acid) DTPMP) was compared. In addition, acid hydrolysis without any chelating agent was performed.

As an experimental procedure, 20 g of pulp (dry matter about 10%) was added to 150 ml of extraction solution in which the dosage of chelating agent was 1.83 mmol. This amount was approximately ten times higher than the molar concentration of the metals. Nitrogen bubbles carried out mixing. After the extraction, 20 ml liquid was bled with a filtrated syringe, to which 1 ml concentrated nitric acid had been added, to adjust acid concentration corresponding that of ICP standards. To determine the total contents of metals in the pulp, the samples were dry-ashed and the recovery of the extraction was calculated by comparing the amount of metals in the extraction solution to the total content.

Regarding the experiments with the chelating agents, optimal recoveries were obtained using DTPMP at 85 °C and pH 3. A contact time of 15 minutes was sufficient. In general, recoveries increased as a function of stability constants of the chelating agents and temperatures. When the temperature approached 100 °C, mixing was complicated due to swelling of fibres. Overall, the best extraction method was acid hydrolysis [86, 87] by 0.1 mol/l HCl at 95 °C, but this kind of solution may cause corrosion damages, if metal constructions are used in on-line equipment.

Over 95% recoveries were obtained for Mn and also for Ba, Ca, Mg, Zn. Recoveries for iron and aluminum were matrix dependent, 40-80% and 15-40%, respectively. Samples contained very little Cr, Cu Ni and Ti and so conclusions for these metals were difficult to draw. Mn, Ca, Mg and Zn showed no differences between pulp types. However, Al and Fe were easier to extract from softwood pulp than from hardwood pulp. The method was linear in the range of investigations. The reproducibilities, repeatabilities and determination limits varied between 1.7 and 7.0 %, 0.3 and 1.7 % and between 0.05 (Mn) and 2.1 (Al) mg/kg, respectively.

### 5.1.2 X-ray fluorescence

Besides being rapid, the XRF-technique requires little or no sample pretreatment, so that process control can be achieved with a minimal delay. This study concentrated on the three technically most important metals, Mn, Fe and Cu [VII]. As a complex matrix, pulp makes demands on the XRF, too. The solid content of pulp taken from bleaching lines is typically 10%, the distribution of metals between fibres and the aqueous phase may differ and precipitation may occur [10, 88]. Differences in distribution of fibres on the sample film might also influence on the detected fluorescence.

To avoid matrix effects, a standard addition method was investigated. Preparation of addition standards and samples was commenced by weighing 10.00 g hardwood pulp into a polypropylene decanter. Further, to avoid the distribution problems, concentrated nitric acid was added to all addition standards and samples to enhance solubility and equalize the distribution. The target metals were added to the standards as 15-300 mg/l solutions. The total solution addition to the 10.00 g of pulp was always 2 ml. The solution added to the samples consisted of pure nitric acid. Five standard addition calibration lines were prepared for Mn, Fe and Cu in their realistic concentration ranges; 0-15 mg/kg for Mn and 0-5 mg/kg for Fe and Cu. The pulp to which the additions were made was taken from a final wash of an ECF line and contained very low amounts of metals initially.

The averages of squares of the linear correlation coefficients between measured intensity and added metal concentrations were 0.994, 0.950 and 0.932, for Mn, Fe and Cu, respectively. The reproducibilities and repeatabilities turned out to be concentration dependent and varied between 3 and 19 % and between 1 and 17%, respectively. The quantification limits were 2-3 mg/kg.

To find out whether the analysis could be carried out without the addition of acid, which would simplify on-line construction, four different process samples were analysed. The results are given in Table 3 in which "Result without pretreatment" refers to the situation where no nitric acid was added. In that case, the pulp was simply pressed lightly onto the Mylar film. The difference between the two measurements is not considered to be significant and evidently manganese is distributed uniformly in the samples.

*Table 3. Comparison of results of manganese analyses with and without pretreatment, mg/kg [VII].*

Pulp type	Result with pretreatment	Result without pretreatment
Hardwood	1.8	1.9
Hardwood	14	12
Softwood	11	11
Softwood	7.8	8.1

Using air instead of helium as a chamber gas would also simplify the on-line equipment construction. To study this, acidic metal solutions of 4 mg/l were measured as before, the only difference was the chamber gas. The measured intensities with air were 60% of the intensities with helium, indicating that air does attenuate the fluorescence of the elements. This effect could be minimized if the path length of the X-rays before and after the sample could be shortened.

On-line XRF spectrometry has been successfully applied in the mining industry for a long time. In these applications slurry courses are driven continuously in a cuvette containing a sample window with changeable film. With the wet pulp matrix this is problematic, because the aquatic phase easily separates from the fibres. A screw pump might be the choice with the most potential. Discrete pulp dosages could be possible to move on to an XRF sample window. There could be also another way to analyse metals on-line in pulp. Present pulp sampling technology allows preparation of a dry briquette in five minutes. Only simple robotics would be needed to move the briquette to the sample window of an XRF-spectrometer.

### 5.1.3 Ion selective electrodes

As a cost effective technique, potentiometry is a noteworthy alternative for on-line determination of  $K^+$ ,  $Ca^{2+}$ ,  $Na^+$  and  $Cl^-$  ions. In this study, a series of ISE measurements of calcium and sodium from pulp samples taken from a TCF bleaching line was performed [VIII, IX]. The purpose of these measurements was to compare ISE measurements carried out in different ways and to create information about the distribution of these metals. The total concentrations were measured by AAS. The results for calcium are presented in Table 4. The "ISE in line" column refers to a measurement without any sample preparation. This type of measurement can be thought to represent a situation in which an ion selective electrode is placed directly in a process stream or in a separated side stream. The ionic strength of the calibration standards was 0.1, which is typical of bleaching lines, and the error resulting from differences in activity coefficients can thus be assumed to be insignificant. Considering the results in the "ISE on line" column, an ionic strength adjustor was used. These measurements simulate a situation in which a sample has been taken from a process stream into a separated vessel in which potassium chloride solution has been added to adjust the total ionic strength to unity, which was now the ionic strength of the calibration standards, too.

Table 4. Measurements of calcium in a TCF bleaching line, using an ion selective electrode with and without an ionic strength adjustor, and by AAS ( $x$  = average,  $s$  = standard deviation,  $n$  = sample amount).

Sample	pH (23°C)	ISE in line (mg/kg)			ISE on line (mg/kg)			Total concentration (mg/kg) by AAS
		$x$	$s$	$n$	$x$	$s$	$n$	
Z/Q	7.1	55	1	3	85	1	3	270
Z/Q	8.1	50	3	3	55	3	3	110
P	10.2	1	0	3	5	0	3	275
P	10.3	9	1	3	15	1	3	45

The P-phases were alkaline in which only a negligible amount of calcium can exist as free ions in solution according to thermodynamics [89]. Perhaps due to kinetic hindering by the DOC, however, [13, 80] a certain amount of calcium could be detected in a solution, as Table 4 reveals. The pH in the Z/Q phases was adequately low to allow measurements in the atmosphere (solubility of the free  $\text{Ca}^{2+}$  ion is about 80 mg/l at pH 8 [89]), and it can be seen that a considerable part of calcium indeed exists as free  $\text{Ca}^{2+}$  ions. A similar observation has been made earlier under paper machine conditions [90]. It deserves to be mentioned that in the absence of the DOC, precipitation of calcium carbonate increases very rapidly as a function of pH [VIII].

As an interesting observation, the results obtained without using the ionic strength adjustor were lower than those obtained with the adjustor. The reason might be that a part of the ionic strength adjustor adsorbed to the fibres. Because of this, activity coefficients in samples were higher than those in the calibration standards and the measured concentrations were thus higher.

Since glass electrodes bearing high temperatures have been developed, the ISE technique allows good facilities also for monitoring sodium ion levels. A series of sodium ion selective measurements similar to that of calcium was performed in this work. The results are presented in Table 5. Considering on-line measurements, the same systematic error as in the case of calcium was observed. The ion strength was adjusted with an  $\text{NH}_4\text{Cl}+\text{NH}_4\text{OH}$ , solution which also ensured pH values high enough to avoid interference of the hydrogen ions. Table 5 reveals that both the in-line and the on-line measurements are reliable corresponding well to the total concentrations analysed by AAS. Thus, the main part of the sodium existed as a free or weakly adsorbed  $\text{Na}^+$  ion.

*Table 5. Measurements of sodium in a TCF bleaching line, with an ion selective electrode with and without an ionic strength adjustor, and by AAS (x = average, s = standard deviation, n = sample amount).*

Sample	pH (23°C)	ISE in line (mg/kg)			ISE on line (mg/kg)			Total concentration (mg/kg) by AAS
		x	s	n	x	s	n	
Z/Q	7.1	1250	32	3	1370	0	3	1200
Z/Q	8.1	650	18	3	780	0	3	710
P	10.2	1700	18	3	1950	5	3	1850
P	10.3	620	20	3	750	0	3	680

#### **5.1.4 Comparison of metal analysis methods**

The main points of the methods discussed above are summarized in Table 6 to which have been included some practical expert opinions dealing with on-line feasibility.



Table 6. Comparison of metal analysis methods.

	ICP-AES	XRF	ISE
Determinable metals	Over 60 elements	Mg semi-quantitatively, other metals quantitatively	Na <sup>+</sup> , K <sup>+</sup> , Ca <sup>2+</sup> , Cl <sup>-</sup>
Correspondence to the total concentration	Soluble and total concentrations	Total concentration	Concentration of free ion
Determination limits	Soluble: 0.01-1 mg/l Total: 0.1-10 mg/kg	Mn 2 mg/kg, Fe and Cu 2-3 mg/kg, K and Ca 15 mg/kg	Na <sup>+</sup> 0.4 mg/kg, K <sup>+</sup> 0.03 mg/kg, Ca <sup>2+</sup> 0.02 mg/kg (Cl <sup>-</sup> 0.3mg/kg)
Demand for sample pretreatment	When measuring the total concentrations elements have to be extracted to solution	Direct measurement, acid increment before analysis or analysis from briquette	Analysis from suspension up to 80 °C
General on-line feasibility	Good, commercial equipments available	Good, commercial equipments available	Good, commercial equipments available
Cost of investment	Equipment: 85-125 kEURO; pretreatment 15-30 kEURO	ED: 200 kEURO WD: 300 kEURO	10-30 kEURO
Operating cost	25 kEURO/year	4.5 kEURO/line/year	10-40 kEURO/year
Required education of operation staff	Process worker, chemist in background	Process worker, for calibration person from laboratory	Process worker, chemist in background
Estimated working hours required	1-2 h/d	15-90 min/d Calibration: 4 h/month	60 min/week
Benefits	Multielemental analysis, low determination limits, rapid measurements, possibility to analyse both the total and the soluble content	Simple pretreatment, possibility to direct measurement, good experiences in mining industry	Small size, cheap, rapid, low consumption of energy, large range, no pretreatment re-quired
Disadvantages	Complexity of the pretreatment, operating and investment costs, large size at the present	Determination limits, large size	Contamination problems of electrode surface

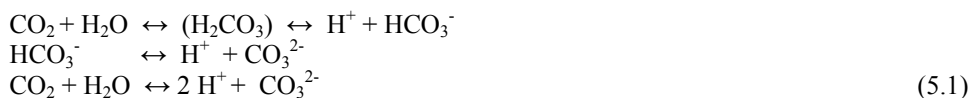
## 5.2 pH and hydrogen peroxide

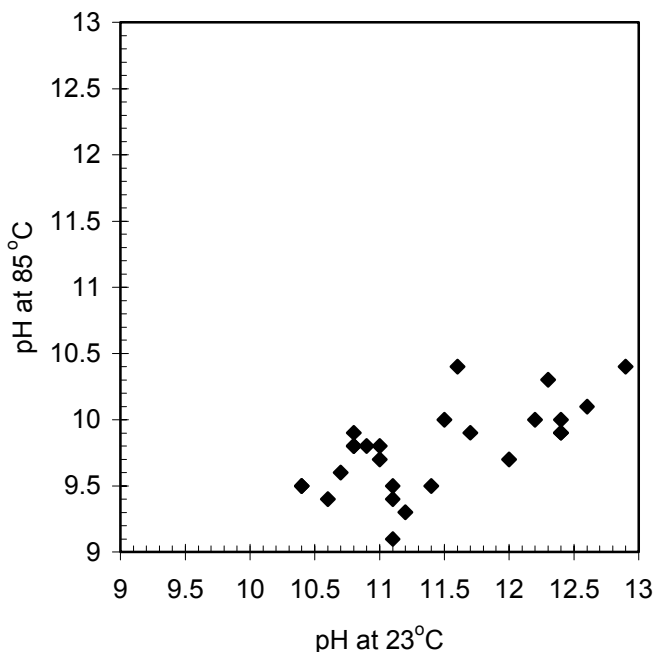
pH data are needed to maintain the pH of unit operations at target values, which in chloride dioxide and chelation stages are usually in the acidic region and in hydrogen peroxide stages usually in the alkaline region. pH measurement, especially in the alkaline region is not easy to perform, and several factors have to be taken into account.

Reality in industrial processes is that an accuracy of 0.25 units in pH measurements is rarely achieved [91]. Contamination of the electrode surface is a major problem, but temperature differences and atmospheric carbon dioxide are also notable error sources, the significance of which was investigated in this study [VIII].

Under alkaline conditions, such as those that prevail in hydrogen peroxide bleaching stages, hydroxide ion concentration is mostly determined by the amounts of added sodium hydroxide and hydrogen peroxide, the latter functioning as an acid that partly neutralises the OH<sup>-</sup> ions. Due to the fact that the activity of the H<sup>+</sup> ions is the ionic product of water divided by the activity of the OH<sup>-</sup> ions, a sample taken from a process and left to cool down to room temperature cannot be used to evaluate the real process pH. In this study this effect was evaluated. Figure 8 shows the difference between the results with pH measurements carried out at 85 °C and 23 °C. The vertical axis represents the pH values obtained with an electrode located in simulated hydrogen peroxide bleaching solutions at 85°C, while the values of the horizontal axis are the room temperature values of the same experiments. As can be seen, the difference may be as much as 2.5 pH units. Much of the deviation can be attributed to the ionic product of water, which is 10<sup>-14</sup> at room temperature but considerably higher, 10<sup>-12.5</sup>, at 85°C.

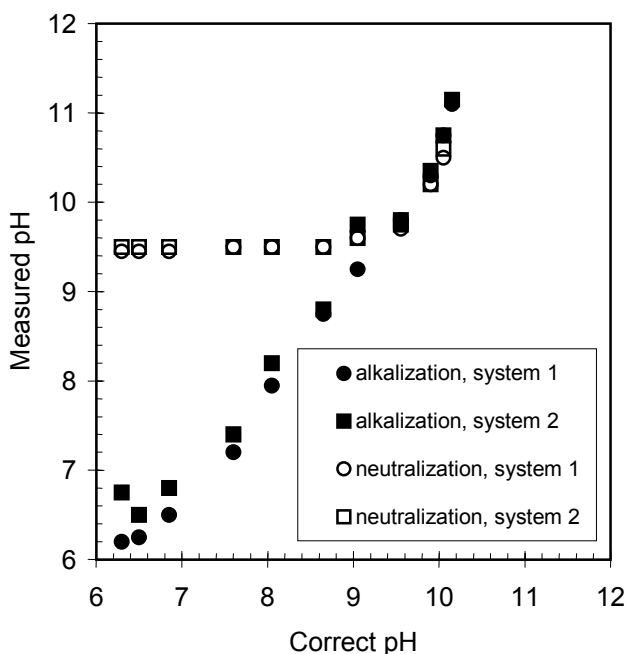
In conclusion, if a pH electrode cannot be placed in the process itself, rapid measurement before cooling is recommended to obtain more accurate results. There is also another reason for rapid measurement, namely, the formation of a carbonate buffer with atmospheric carbon dioxide:





**Fig. 8. pH values measured using an ion selective electrode on-line in the process as a function of values measured later at room temperature. Reproduced by permission of APPITA.**

To investigate this source of error, a series of experiments in which the pH of an aqueous solution at 80°C was measured by two similar but independent pH measuring systems with glass electrodes was studied. The pH of the solution was increased step by step to a theoretical value of 10.1 with the addition of sodium hydroxide (Fig. 9: alkalization, systems 1 and 2). After that, corresponding amounts of hydrochloric acid were added to neutralise the solution (Fig. 9: neutralization, systems 1 and 2). The results presented in Fig. 9 reveal that the measurement was reliable up to a theoretical pH value 9, after which the measured values began to be higher than the real values. When the solution was neutralised, both measuring systems were reversible down to a pH value of 9, after which the system no longer responded to the added acid, because of the formation of the carbonate buffer described by the reaction (5.1).



**Fig. 9. Formation of a carbonate buffer shown as inaccuracy of the pH values measured in solutions after alkalization with NaOH and neutralization with HCl. Reproduced by permission of APPITA.**

The total hydrogen peroxide content can be analysed using two stage iodometric titration [92, 93] in which hydrogen peroxide first oxidizes iodide to iodine, which is further titrated by thiosulphate. Starch may help in the indication of the endpoint, if added when the dark color of iodine is hardly seen. This titration is excellent in the investigation of hydrogen peroxide solutions, but interferences need to be taken into account in applying it to real industrial solutions. Other oxidizing agents will also produce iodine, whereas reducing agents like organics with double bonds will react with the liberated iodine. Hydrogen peroxide can be titrated also directly by potassium permanganate in which hydrogen peroxide reduces purple permanganate to colorless manganese ions [94].

Changes in the hydrogen peroxide levels can be followed voltammetrically. Glassy carbon is a good electrode material: Voltammograms with good reproducibility and a peak current proportional to hydrogen peroxide concentrations have been obtained in concentrations higher than 3.4 mg/l [95]. It has also been shown that mechanically and thermodynamically correctly handled glassy carbon is a good working electrode material

in concentration ranges from 3400 to 10 000 mg/l in many industrial applications. The specific voltammetric reaction is characterized as seven-phase oxidation reaction [96]. Polarizing glassy carbon (Sigradur G) 1500 mV over silver/silver chloride has shown good responses to hydrogen peroxide level changes [97]. Platinum as a working electrode has also shown to be feasible when polarized 200 mV under free potential [97]. Very recently, ruthenium/rhodium modified gold electrodes have been successfully applied in determination of hydrogen peroxide at low potentials [98]. Commercial voltammetric equipment also feasible for chloride dioxide determinations [99] are widely in use. Determination of hydrogen peroxide using Fourier transform infrared spectroscopy (FTIR) could also be possible.

### 5.3 Chelating agents ADA and NTA

There exist several direct and indirect analytical methods for DTPA and EDTA, including chromatography, voltammetry, potentiometry, spectrophotometry and AAS [100]. As an exact, practical and versatile technique, chromatography is probably the most widespread. Gas chromatographic (GC) methods are far more sensitive than liquid chromatographic (LC) methods [100]. A main benefit of GC is the fact that the same method can be used during the whole operation cycle of the chelating agents, from their addition into the process to the final environmental fate. As drawbacks of the GC methods, a required derivatization step is time consuming and, in contrast with LC [101, 102] and capillary electrophoresis CE [103, 104], only total amounts can be determined.

Since GC analytics of DTPA and EDTA have been well established earlier [100, 105, 106], this study focused on the development of analytical methods for ADA [X] and NTA [XI]. Use of NTA has attracted criticism because it is considered to be poorly biodegradable [24], and it has been classified as possibly a carcinogenic substance [107]. On the other hand, it has been observed to degrade well in normal waste water treatment [35, 108] and, in a long-term study, it has been concluded that NTA is an ideal substitute for EDTA from the environmental point of view [109]. In any case, it has been used for a long time in the EU area (mainly in detergents), which increases the need for a sensitive analytical method.

In the GC-procedures developed in this dissertation [X, XI], the water sample is first evaporated to dryness, followed by the addition of the esterification reagent consisting of alcohol and sulphuric acid. Further, a sample is extracted to toluene and neutralized with  $\text{KHCO}_3$ . The organic phase is dried with  $\text{Na}_2\text{SO}_4$  before the GC-NPD analysis. The optimum sample pretreating conditions for both analyses are presented in Table 7. For ADA, the analysis of lake sediment samples, after extraction with  $\text{NaH}_2\text{PO}_4$ , was also studied.

Table 7. Optimized sample pretreating conditions and analytical parameters [X, XI].

	ADA	NTA
<i>Optimized sample pretreating conditions</i>		
Sample amount	20 ml	10 ml
Derivatization - conditions and added reagent	86 °C, 2 h 1 ml 5 vol% H <sub>2</sub> SO <sub>4</sub> 0.5 mg/l HDAN Ethanol	78 °C, 6 h 3 ml 5 vol% H <sub>2</sub> SO <sub>4</sub> 5 mg/l HDAN 0.05 vol% acetic acid catalyst Ethanol or propanol
Extraction	1.5 ml toluene	0.75 ml toluene
Neutralization	10 ml 1 mol/l KHCO <sub>3</sub>	20 ml 1 mol/l KHCO <sub>3</sub>
<i>Statistical data</i>		
Reproducibility	Lake water 4.1-14.2 % Sea water 5.7 –21.7 % Waste water 4.4 –12.3% Sediments 9-30%	Distilled water under 2.1 %
Repeatability	Distilled water under 7%	Distilled water under 2.1 %
Detection limit	Distilled water 2.0 µg/l Waste water 2.7 µg/l Lake water 2.5 µg/l Sea water 2.9 µg/l sediment 21 µg/g	Distilled water 6 µg/l
Linear range	0-10 mg/l Correlation coefficient 0.998-0.999	0.006-50 mg/l Correlation coefficient 0.9995-1
Observed interferences of metals	Cd(II), Ni(II), Pb(II), Cu(II), Hg(II), Mn(II), Cr(III) : no interference at 1mmol/l Fe(III): interference at concentrations over 10 mg/l	Cu(II) and Mn(II): no interference under 100 mg/l Fe(II):slight interference at concentrations over 10 mg/l
Recovery	Natural waters 49-111% Sediments: 19-21%	Lake water 105-123 % Waste water 113-124 %

The procedure for ADA is simple and suitable for the analysis of different water samples. Preparation of propyl ester instead of ethyl ester may be useful when the resolution needs to be improved. The influence of metals is low; iron disturbs only in concentrations of heavily contaminated waste waters matrices. Table 7 reveals that the recovery of the extracted sediment samples is low, only 19-21 %. Hence the extraction step should be improved.

The good reproducibility and recovery values of the determination of NTA suggest that the procedure is applicable for routine analysis of waste waters and for a natural aquatic environment. Importantly, the low detection limit at the sample amount of 10 ml shows the suitability of the method for trace analysis and the limit of determination can be further lowered by using higher sample volumes. This procedure may also allow simultaneous determination of DTPA, EDTA, ADA and NTA, as the high resolution in Figure 10 reveals.

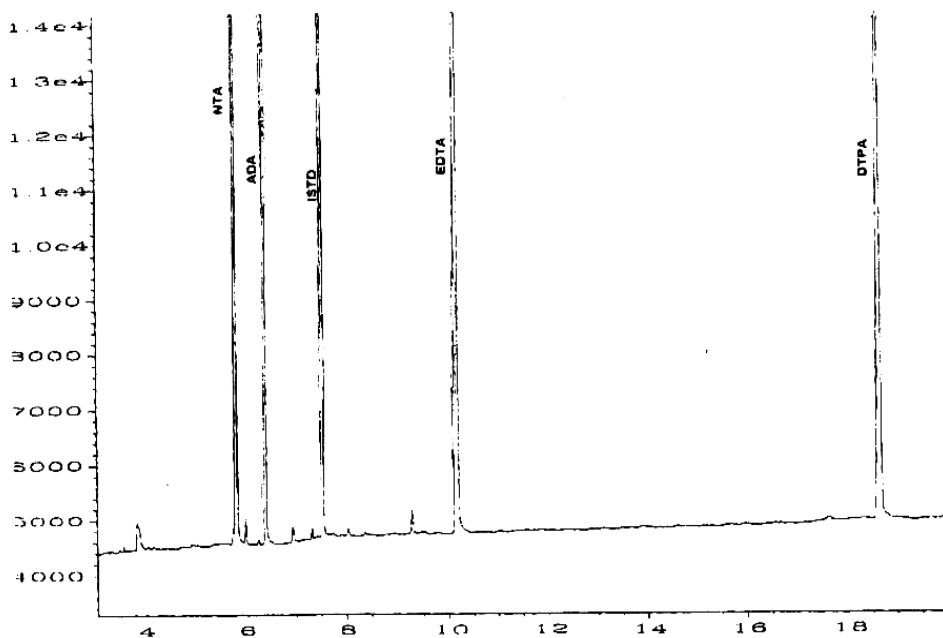


Fig. 10. Chromatogram of ethyl esters of DTPA, EDTA ADA and NTA. Reproduced by permission of Taylor & Francis Ltd.

## 6 Summary and conclusions

Exact knowledge on the behaviour of metal ions is needed to improve the efficiency and environmental aspects of modern pulp bleaching sequences, especially those including a hydrogen peroxide stage. The aim of this study was to extend this knowledge and it was based on practical phenomena and problems. First, the decomposition [I, II], thermodynamic chelating ability [I, II, III] and solubility [III] of chelating agents in simulated hydrogen peroxide conditions were investigated. Second, interactions between hydrogen peroxide and a typical construction material, titanium, were studied [IV, V] taking into account the influence of calcium and silicate inhibitors [V], as well as iron and manganese [IV, V]. The analysis of metals [VI-IX], pH [VIII], hydrogen peroxide and chelating agents ADA [X] and NTA [XI] formed the third part of the thesis.

Hydrogen peroxide anion was able to decompose ADA at a concentration level of 400 mg/l (60 °C, pH 10-11, total hydrogen peroxide concentration 1000 mg/l). The average residual percentage was 71. In similar conditions 94% of DTPA remained. The residual percentage of hydrogen peroxide was 40 for both the chelating agents. As a conclusion, degradation of ADA may beneficially occur already in the industrial process before WWTP. Further, EDTA was proved to be more recalcitrant against chemical decomposition compared to ADA. The percentage of residual was 94 at a hydrogen peroxide anion level of 1200 mg/l (60 °C, pH 10-11, total hydrogen peroxide concentration 5000 mg/l). Also decomposition of hydrogen peroxide was low, 74% remained when EDTA was the complexing agent. The reason for the observed higher decomposition of ADA compared to the other two chelating agents was probably the higher electron deficit in nitrogen or the existence of Mn(III) and Mn(IV) oxides. The observed high durability of EDTA supports aspirations for minimizing its utilization by using replacement ligands (ADA, S,S'-EDDS, hydroxycarboxylic acids) or by developing effective procedures for its removal.

The solubility of DTPA, EDTA and ADA in an alkaline hydrogen peroxide environment was limited but increased in the presence of transition metals, Fe and Mn. A possible explanation for the limited solubility is that the complexes, particularly the magnesium complex, are adsorbed on to magnesium hydroxide precipitate.

According to thermodynamic speciation in typical bleaching conditions, chelating agents exist mainly as calcium (70-80%), manganese (15-20%) and magnesium (0-5 %)



complexes, which is also relevant in the experiments of this study. Iron is thermodynamically more difficult to chelate due to its strong self-hydrolysis. As a suggestion for further investigations, the correspondence with species distribution calculations could be investigated experimentally using LC, CE or polarographic methods.

The typical construction material of bleaching lines, unalloyed titanium Grade 2, corroded in alkaline magnesium containing hydrogen peroxide solutions when the  $\text{HOO}^-$  anion level exceeded 200 mg/l. Vanadium and aluminum alloyed Grade 5 was inferior to Grade 2. The presence of calcium ions and silicate improved corrosion resistance by enhancing the critical anion levels. Proposed protection mechanisms for the observed inhibition were physical adsorption of the  $\text{Ca}^{2+}$  ions or Ca-silica compound as well as the formation of calcium peroxide near a metal oxide surface. The presence of iron and manganese further enhanced the critical levels; corrosion of Grade 2 was low, even at a hydrogen peroxide anion level of 800 mg/l. The corrosion potential of Grade 2 could be used as an indicator whether uniform corrosion of titanium took place. During rapid corrosion, potentials were under 200 mV (SHE), and clearly lower than the potentials of platinum.

A comparative study in pulp matrix between three different metal analytical methods, ICP-AES, XRF and ISE was performed. For the ICP-AES technique, investigations focused on the extraction of metals to aqueous solution by chelation or acid hydrolysis. Over 90% yields were obtained for Ba, Ca, Mg, Zn and, most importantly, Mn. Yields for iron and aluminum were matrix dependent, typically 40-60% and 15-40%, respectively. DTPMP appeared to be the best chelating agent, but overall the most effective extracting method was acid hydrolysis. A rapid X-ray fluorescence method with a quantification limit of 2-3 mg/kg was developed for Mn, Fe and Cu. As an undoubted benefit, direct analysis was successful. Dealing with ISE techniques, for  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and Cl<sup>-</sup> quantification limits under 1 mg/kg were reached and some important sources of error were elucidated. pH measured in room temperature may be more than two units higher than the real values of the process. Atmospheric carbon dioxide dissolves in the measuring systems forming a carbonate buffer and decreasing the reversibility of the measurements. It also may precipitate some part of  $\text{Ca}^{2+}$  ions as carbonate. When an ion strength adjustor is not employed, variations in the total ionic strengths of samples must be taken into account. Where the adjustor is used, its adsorption on to fibres may lead to elevated high values.

Sensitive GC methods for ADA and NTA were developed. Detection limits in water samples were under 6  $\mu\text{g/l}$  and reproducibilities were good, under 15% in distilled, lake and waste waters. However, the extraction step from sediments is to be improved. The procedure developed was suitable for simultaneous determination of DTPA, EDTA, ADA and NTA.

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