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Brightness development of a hydrogen peroxide bleached spruce TMP. Comparisons of pre-treatments with DTPA and a separable chelating surfactant

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KEYWORDS: Thermomechanical pulp, Hydrogen peroxide bleaching, Manganese, DTPA, Chelating surfactant, Flotation

SUMMARY: In this investigation a new type of recoverable complexing agent (chelating surfactant) has been compared with a conventional complexing agent; diethylenetriamine pentaacetic acid (DTPA), in the metal ion sequestering of thermomechanical pulps (TMP) to be hydrogen peroxide bleached. After different degrees of washing of the pulps, bleaching experiments at different total alkali charges were performed with and without sodium silicate additions, and the ISO brightness of hand-made sheets was measured. The residual hydrogen peroxide in the bleaching liquor was also determined. No significant difference in either the brightness development or the residual hydrogen peroxide content could be detected between the pulps treated with equivalent molar ratios of the different complexing agents. Furthermore, the recovery of the chelating surfactant-manganese complexes from laboratory made white water by froth flotation was also studied. Two different foaming agents; sodium dodecyl sulphonate (SDS) and dimethyldodecylamine oxide (DDAO), were tested in the froth generation. After an addition of 160 ppm of DDAO, more than 80% of the manganese chelates could be recovered in the foam, containing 3% of the initial water mass.

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In wood, different metal ions are bound to acidic groups (carboxylic and phenolic) in the fibre walls. Transition metals such as iron, manganese and copper decompose hydrogen peroxide under bleaching conditions leading to lower bleached pulp brightness (Colodette et al. 1988). Thus, for successful bleaching these metal ions need to be removed from the pulp fibres. This can be obtained in several different ways. Washing the wood chips with an acidic aqueous solution, which induces protonation of the acidic groups and thereby liberates the metal ions into the washing solution, is one example of a simple ion-exchange approach that has been applied (Lundqvist et al. 2006). This works reasonably well if the chips are going to be digested, e.g. in kraft pulping. In mechanical pulping where hydrogen peroxide is used as a bleaching chemical the conditions are alkaline, and the method of acid washing is not preferable since a lot of alkali is then spent to reach and maintain the optimum pH-value. Prior to alkaline hydrogen peroxide bleaching, the chips or the pulp fibres can be impregnated or washed with electrolyte solutions, e.g. magnesium sulphate, to perform an exchange of the detrimental ions at neutral conditions (Li et al. 2001).

A more conventional way to minimise the influence of unwanted metal ions is to wash the pulp fibres with sequesters (complexing agents, chelators) before the bleaching operation. Synthesised complexing agents, e.g. nitrilotriacetic acid (NTA), ethylenediamine tetraacetic acid (EDTA) and diethylenetriamine pentaacetic acid (DTPA), are among the most commonly used (Pirkanniemi 2007).

The stability constants (K) of the different metal ion chelates vary and are dependent on the overall conditions in the system, such as the presence of other electrolytes, the pH-value and the temperature (Hughes, Martell 1956, Arena et al. 1983, Dow 1990, Wu, Horrocks 1996, Pirkanniemi et al. 2003, Tei et al. 2011). Other factors influencing the stability constants are the size and charge of the (hydrated) metal ion (Hughes, Martell 1956), as well as if the water environment can be characterised as reductive or oxidative (Wulfsberg 1991). Generally, very high stability constants i.e. in the log K range of 5 to 30 are to be expected (Furia 1972). The fundamental reason behind the gross complexing affinity for certain metal ions is the presence of multiple donor atoms in the complexing agent that bind to more than one coordination site on the metal ion. Due to that it is necessary to break all the bonds to the central atom for the ligand to be displaced, an increase in the free energy is required to increase the number of separate species.

Today, compared with many other manufacturing industries, the use of complexing agents as metal ion catchers in production of bleached pulps is relatively large, and EDTA and DTPA totally dominates the complexing agent sales in Sweden and Finland (Pirkanniemi 2007). DTPA has generally higher stability constants for its transition metal ion complexes than EDTA (Dow 1990) and is also more frequently used than EDTA in the pulp and paper industry in the Nordic countries (Pirkanniemi 2007). A general drawback of the use of complexing agents, such as EDTA and DTPA, is related to environmental concerns, since their biodegradation is relatively slow (Means et al. 1980).

Due to very strong complexing efficiency, the risk of releasing and spreading heavy metal ions, e.g. buried in bottom sediments, to the ecosystem by these sequesters is imminent (Laamanen et al. 2005). There are indeed some complexing agents on the market accepted as readily biodegradable, for instance 1,3-propylenediamine tetra-acetic acid (1,3-PDTA), methylglycine diacetic acid (MGDA) and ethylenediamine disuccinate (EDDS). However the use of these complexing agents is relatively low, especially within the pulp and paper industry (Pirkanniemi 2007), which may be due to low performance or high pricing, or a combination thereof.

Besides making complexing agents biodegradable, another way to tackle the problem of emissions is through introduction of specific functionality to complexing agents that enables separation of the chemicals from different waters/effluents. Moreover, this could also make recycling, i.e. separation, isolation and regeneration, of the complexing agents (and collection of the metal ions) possible and thus, clearly contribute to make the processes more sustainable. Moreover, new disruptive utilisation of strong complexing agents in other sectors than the pulp and paper industry, where conventional complexing agents cannot be used due to their water solubility, may arise. For instance, as separable heavy metal catchers in the decontamination industry with low secondary waste generation, or as specific rare metal collectors in the electronic and surface treatment industry.

A new class of hydrophobically modified complexing agents, chelating surfactants, was recently designed, synthesised and characterised in our laboratories (Högberg et al. 2011). In the present investigation, the transition-metal ion complexing efficiency during washing and hydrogen peroxide bleaching of thermo-mechanical pulps (TMP), using these new complexing agents, are compared with pulps conventionally treated with DTPA. Moreover, initial results from recovery studies of manganese chelates after froth flotation of the white water, are reported.

Materials and Methods

Chemicals

Na_5DTPA (Versenex 80) was delivered from Dow, (Sweden). 4-Dodecyl-3,6,9-tri(carboxymethyl)-3,6,9-triaza-undecane diacid (4-C12-DTPA) was synthesised in our laboratories (Högberg et al. 2011) and the molecular structure is shown in *Fig 1*.

Sodium silicate (S38), with a weight ratio between SiO_2 and Na_2O of 3.25, was supplied by PQ Europe (Sweden) and used as received. Sodium dodecyl sulphate (SDS, ≥99%) and dimethyldodecylamine-N-oxide ~30% in water (DDAO, purum), were delivered by Sigma Aldrich (Germany).
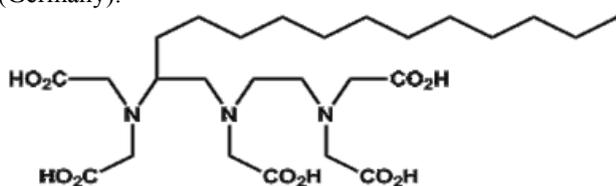
Fig 1. Molecular structure of the studied complexing surfactant, 4-C12-DTPA (M = 561 g/mol).

Pulp fibres

Unbleached commercial thermomechanical pulp, with a manganese content determined to 104 ppm, produced from Norway spruce (*Picea abies*) by SCA was used as received.

Metal sequestering

The TMP was divided into two different batches for treatment with either DTPA or 4-C12-DTPA. The moisture content of the pulp was measured with a Mettler Toledo, HR73 Halogen Moisture Analyzer, (Mettler Toledo, Sweden). 100 g of the pulp (dry pulp weight) was dispersed in Milli-Q water at room temperature to a consistency of 5% and disintegrated at 3000 rev on an App. 03, Type 8-3, No. 723 disintegrator (AB Lorentzen & Wettre, Sweden). The pulp was dewatered on a polyamide wire (125 µm) in a Büchner funnel, the filtrates being recirculated twice through the filter cake to avoid the loss of fibres and fines material. The pulp was re-dispersed to a consistency of 5% in Milli-Q water of ~60ºC, disintegrated and soaked for 1 h before dewatering as described above. The last procedure was then performed with addition of the studied complexing agent. The charge of complexing agent added corresponded to a molar ratio of complexing agent:Mn of 1.2:1 or 1.5:1 of the untreated pulp. In the investigation of the effects of complexing agent carry-over to the bleaching, the pulp was thereafter centrifuged to meet a consistency of 34%, accurately adjusted with the filtrate when needed. In the studies of maximum removal of manganese chelates, the pulps were re-dispersed to a consistency of 5% in Milli-Q water of ~60ºC, disintegrated and soaked for 1 h before dewatering, as described above, and finally centrifuged to meet a consistency of 34%, accurately adjusted with the filtrate when needed. Metal ion contents in the pulps before and after metal sequestering, were analysed according to SCAN standard method CM:38:96 on an ICP-OES (Thermo Jarrel Ash, Metric Analys, Sweden).

Hydrogen peroxide bleaching

High consistency hydrogen peroxide bleaching was performed at a pulp consistency of 28%. 5 g of pulp (oven-dry) was mixed with the bleaching chemicals at room temperature for one minute using a stainless steel coffee grinder. The pulp was thereafter immediately placed into a polyethylene plastic bag (thickness 90 µm, Genpack A/S, Denmark), which was sealed and immersed into a thermostatic water bath. The hydrogen peroxide (H_2O_2) charge was 45 kg/ton and the sodium hydroxide (NaOH) charge was optimised and varied between 9 and 24 kg/ton with the purpose to reach the highest possible brightness. The sodium silicate charge was kept constant and was 29 kg/ton. The manganese and copper contents were less than 1 ppm and the iron content was 51 ppm in the sodium silicate used. The bleaching trials were performed at 70°C with a retention time of 120 min. After the bleaching stage, the pulp was cooled to room temperature. 1 g of pulp (oven-dry) was diluted with 50 g deionised water and after 5 min, the pulp suspension was dewatered in a Büchner funnel on a Munktell 3 filter paper. The filtrate was collected and

used to determine residual hydrogen peroxide by iodometric titration, where the liberated iodine was titrated with 0.1 M sodium thiosulphate, where starch was used as indicator of the stoichiometric point. Sodium silicate was added as technical quality. Hydrogen peroxide and sodium hydroxide charges are given as 100% active component.

Brightness measurements

Sheets for brightness determination (approximately 200 g/m^2, oven-dry) were prepared according to ISO standard method 3688. The brightness was measured according to ISO 2470 on a LoW Elrepho (AB Lorentzen & Wettre, Sweden).

Preparation of laboratory white water

For the investigation of recovery of metal chelates, a laboratory made white water was prepared using a method developed by Holmbom and Örså (1994). A portion of unbleached TMP was diluted with distilled water to 1% consistency and agitated (100-150 rpm) at 60°C for 4 h. The final pH was around 5. The suspension was centrifuged at 500 g and the supernatant containing the dissolved and colloidal substances was separated by decantation and stored in a refrigerator at 10°C. This method was shown to produce water samples containing dissolved and colloidal substances in a reproducible way and gave white waters with a manganese content of 1.3 ± 0.2 ppm, a turbidity of 204 ±10 NTU, carbohydrate content according to the Orcinol method (SCA-F W 15:77) of 336 ±11 mg/l, total organic carbon (TOC) of 258 ±10 mg/l and a pH-value of 5.6 ±0.1. To sequester the manganese in the prepared white water, a chelating surfactant (4-C12-DTPA) was added at a molar ratio of 1.5:1 to the manganese content.
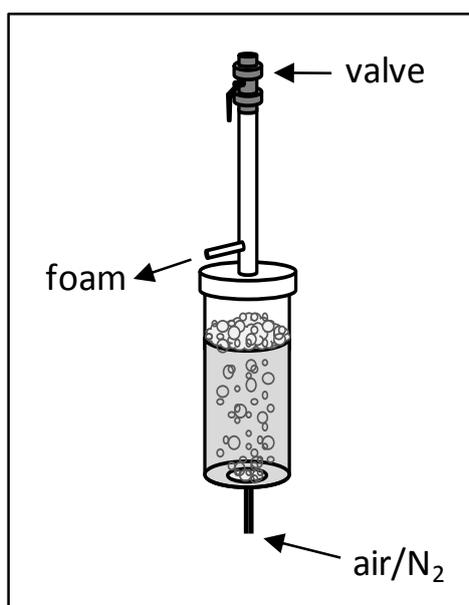
Fig 2. Illustration of the customised flotation cell; air is injected through a glass frit in the bottom of the cell to create small air bubbles. The foam, formed at the top of the solution, is collected through the horizontal tube. The pressure in the cell is controlled by the top valve.

Froth flotation

Froth flotation of white water was performed at room temperature in a customised flotation cell with a volume of 1.6 l (*Fig 2*), consisting of a plexiglass cylinder with an inner-diameter of 80 mm and a sintered glass frit of diameter 60 mm (porosity 4, VWR, Sweden) mounted at the bottom of the cell. A nitrogen flow of ~5 l/min through the frit, to induce the bubbles, was applied. A valve on the top of the cylinder was used to control the rate of the foam transport out of the flotation unit. Flotation proceeded until the formation of stable foam stopped, and the flotation time was found to correlate to the amount of added foaming agent and varied from 35 min for the lowest additions up to 70 min for the highest additions. The foam was collected and accurately weighed, and the manganese content in the foam was analysed on an ICP-OES (Thermo Jarrel Ash, Metric Analys, Sweden).

Results and Discussions

From the results of the complexing agent washing of the TMP shown in *Table 1*, it is found that especially the manganese content is slightly higher after treatment with the chelating surfactant, 4-C12-DTPA, than after conventional DTPA treatment. The greatest effect is seen in the carry-over experiments, where the pulp is not efficiently washed after treatment. Initial results from competitive studies monitored by electrospray ionization mass spectrometry (ESI-MS) using an evaluation method developed by Kempen and Brodbelt (2000) show that 4-C12-DTPA and DTPA have very similar stability constants, which is expected from the related chemical structures. This indicates that a likely explanation for the slightly higher manganese content is that the chelating surfactant-manganese complexes interact stronger with the molecular constituents of wood than the DTPA-manganese complexes do. The nature of 4-C12-DTPA facilitates interactions of hydrophobic origin between the hydrocarbon tail and wood surfaces, especially where the hydrophobic extractives are located. Due to hydrophobic interactions, surfactants can be adsorbed at surfaces in porous materials and these interactions have been shown more important for the retention of the surfactants than the material's pore size distribution (Wu, Pendleton 2001). In the present study, the hydrophobic interactions between the chelating surfactant and the wood material could induce a slower transport of the chelating surfactant through the fibre wall. However, from a metal ion handling perspective, the transition metal ions can still be chelated by the complexing agents within the fibre walls. The metal ions can thereby be prevented from taking part in the catalysis of hydrogen peroxide decomposition under bleaching, as long as the metal chelate itself is not oxidised and degraded by the bleaching chemicals (Pirkanniemi et al. 2003).

The results from the hydrogen peroxide bleaching of TMP pulps at different total alkali charges, after pre-ment with different complexing agents, are shown in *Figs. 3-5*.

Table 1. Metal content[a] in TMP fibres before bleaching.

Treatment[b]	Addition[c]	Mn (ppm)	Cu (ppm)	Fe (ppm)	Ca (ppm)	Mg (ppm)	Na (ppm)	K (ppm)
untreated	–	104	0.56	4.1	890	110	46	380
4-C12-DTPA	1.5:1	7.0	<0.10	3.6	810	93	61	30
4-C12-DTPA, CO	1.5:1	17	<0.10	3.6	790	90	140	44
DTPA	1.5:1	5.1	<0.10	3.2	810	96	54	34
DTPA, CO	1.5:1	9.1	<0.10	3.7	790	94	84	54
4-C12-DTPA, CO	1.2:1	17	<0.10	4.9	770	87	97	49
DTPA, CO	1.2:1	13	<0.10	2.8	850	98	76	57

[a] Determined by ICP-OES (SCAN CM:38:96), [b] CO indicates the carry-over experiments, [c] Molar ratio complexing agent:Mn(untreated).

In *Fig 3*, the ISO brightness of the pulps bleached after treatment with the two different complexing agents at a molar ratio of 1.5:1 and different degrees of washing is found to vary within 0.4% ISO-units at a total alkali charge of 21 kg/ton, where the maximum brightness is obtained. The individual values of brightness are reported as 79.4% ± 0.1 for DTPA, CO 1:1.5, 79.4% ± 0.0 for 4-C12-DTPA, CO 1:1.5, 79.2% ± 0.1 for DTPA 1:1.5, and 79.0% ± 0.0 for 4-C12-DTPA 1:1.5. The results do not indicate any significant difference in the complex binding efficiency between the chelating surfactant and the conventional complexing agent. As expected, when treated with a lower ratio of complexing agent (1.2:1), and applying carry-over conditions, the bleaching curves show slightly different brightness development and the maximum brightness is obtained at a total alkali charge of 18 kg/ton. Thereafter, a decrease in brightness at higher total alkali charge is indicated.

Fig 4 shows the brightness development when sodium silicate is added to the bleaching liquor. The maximum brightness is increased about 1.7% ISO-units to 81.1% ±0.1 at the same total alkali charge as before for 4-C12-DTPA, whereas the maximum brightness is found shifted towards a total alkali charge of 24 kg/ton for DTPA and is 81.0% ±0.1. It is also found from *Figs 3-4* that pulps pre-treated at the same molar additions of the different complexing agents and washed to different degrees, giving different residual metal content in the pulps, still

develop very similar brightness after bleaching. This refers to the fact that even if there is a carry-over of manganese that could be detrimental for the brightness development under bleaching conditions, the manganese is inaccessible for catalysis of hydrogen peroxide decomposition, due to very strong chelate formation. Moreover, the results indicate that the applied bleaching conditions do not induce any differences in hydrogen peroxide decomposition between pulps treated with DTPA and the chelating surfactant, at equivalent molar ratios. The latter is also confirmed in *Fig 5*, where the residual hydrogen peroxide in the bleaching liquor is plotted as a function of the total alkali for the different pulp samples.

The main idea of using chelating surfactants in metal ion management relates to that the surface activity provides possibilities for separation of the complexing agent from the water. Since surfactants adsorb at air-water interfaces, flotation is a viable method of choice to separate the surface active metal chelates from the aqueous bulk phase and concentrate them as a foam that can be removed. In *Fig 6*, some results from initial studies of the removal efficiency of highly soluble chelating surfactant-manganese complexes from laboratory white waters are shown.

The degree of removal is dependent on a number of different parameters; the design of the flotation cell, flotation time, water composition, pH, ionic strength,
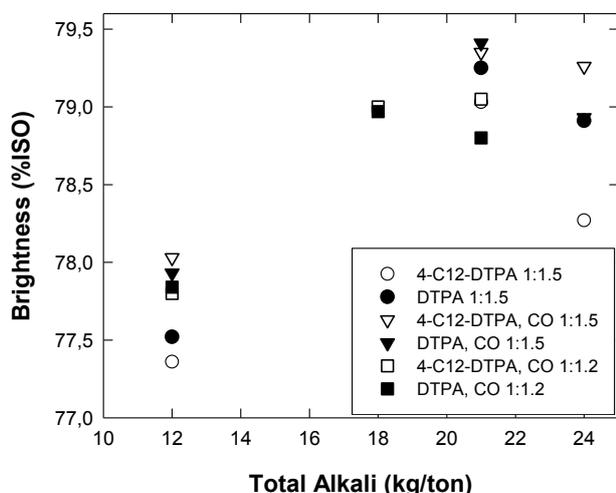
Fig 3. Brightness development of hydrogen peroxide bleached TMP versus total alkali. Before the bleaching the pulps were treated with equal charges (1.5:1 or 1.2:1) of 4-C12-DTPA and DTPA, respectively, and washed to different degrees.
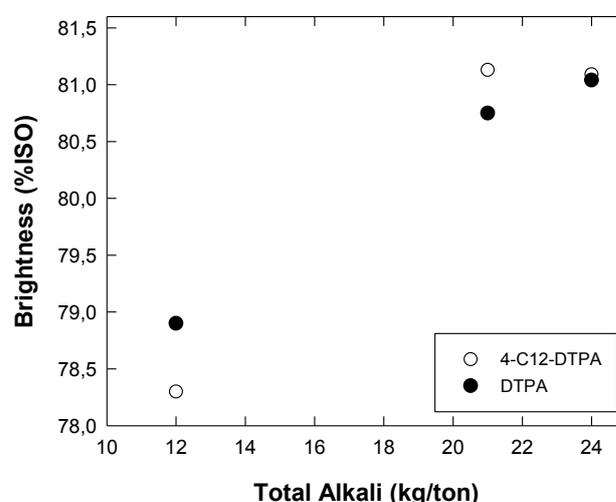
Fig 4. Brightness development of hydrogen peroxide bleached TMP with constant charge of sodium silicate (29 kg/ton) vs total alkali. Before the bleaching, the pulps were carefully washed with chelating surfactant and DTPA at a molar ratio of 1.5:1.
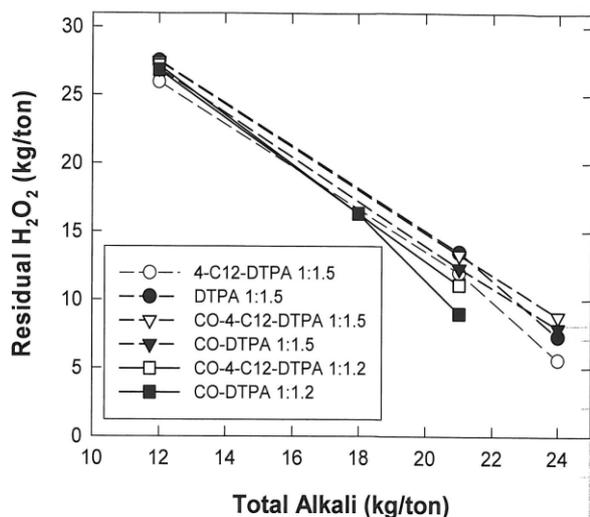
Fig 5. The removal efficiency of manganese-4-C12-DTPA chelates (determined as Mn by ICP-OES) from laboratory white waters by froth flotation. Two foaming agents at different additions are compared. The lines shown are only for the guidance of the eye.

Table 2. Water content of the foams.

Foaming agent [a]	Addition (ppm)	η
SDS	8	0.01
SDS	16	0.01
SDS	40	0.08
SDS	80	0.14
SDS	160	0.22
DDAO	8	0.01
DDAO	16	0.01
DDAO	40	0.04
DDAO	80	0.03
DDAO	160	0.03

ionic charge of the foaming agent head group, concentration of the foaming agent, hydrocarbon chain length and critical packing parameter of the chelating surfactant and the foaming agent, etc. This also implies that a lot more can be done to optimise the metal chelate removal and water content of the foam.

The results shown in *Fig 6* indicate that already at and addition of 40 ppm of DDAO it is possible to remove about 70% of the chelating surfactant from the white water with the simple customised flotation unit used, and at an addition of 160 ppm DDAO the degree of removal exceeds 80%.

In the flotation study presented in *Fig 6*, the water transfer due to foam removal during flotation is described as;

$$\eta = m_f/M \qquad [1]$$

where m_f is the mass of the foam and M is the total mass of the sample before flotation. In the case of white waters, the major part of both m_f and M is of course due to water.

In *Table 2*, the water content in the foam after flotation at different additions of the two foaming agents studied is shown. From the data it is clear that the foam developed during the flotation in the presence of a mixture of
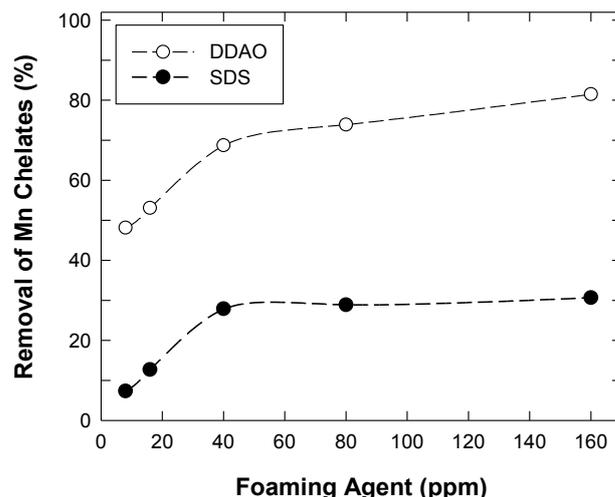
Fig 6. The removal efficiency of manganese-4-C12-DTPA chelates (determined as Mn by ICP-OES) from laboratory white waters by froth flotation. Two foaming agents at different additions are compared. The lines shown are only for the guidance of the eye.

DDAO and chelating surfactant is much dryer than if SDS is used as the foaming agent. The water content of the foams generated in the DDAO experiments never exceed 4%, whereas the SDS system shows water contents as high as 22% at 160 ppm. When taking the results plotted in *Fig 6* into account, the use of DDAO as foaming agent also promotes the removal of the manganese-chelating surfactant complexes to a much greater extent than additions of SDS does. One reason behind this is that the interactions between the chelating surfactant and the zwitterionic DDAO are stronger than between the chelating surfactant and anionic SDS. This is most probably due to presence of protonised nitrogen atoms in DDAO, making it cationic at the pH investigated.

The positive charge promotes an attractive head group interaction with 4-C12-DTPA, which has a net negative charge at the present pH. SDS on the other hand is anionic and the head group interactions with the chelating surfactant are probably much weaker.

Supportive results have recently been obtained in fundamental studies of the change in the interaction parameter, *β*, when mixed surfactant systems comprised of 4-C12-DTPA and dodecyltrimethyl-ammonium chloride (DoTAC) or SDS were compared (Högberg et al. 2011). Due to the same reasons, the presence of a cationic foaming agent may also result in foams of increased stability due to better surfactant packing, as well as less water, in the membranes of the formed soap bubbles.

Conclusions

It is concluded that the chelating surfactant studied can be efficiently used as a complexing agent in the metal ion removal of the spruce thermomechanical pulp (TMP) investigated prior to hydrogen peroxide bleaching. No significant differences in either the brightness development or the hydrogen peroxide consumption could be detected in comparison to pulps treated with the conventional complexing agent diethylenetriamine

pentaacetic acid (DTPA). It is also concluded that the chelating surfactant has a potential of being removed more efficiently from the white water by flotation if the system is further optimised. The findings provide some insights for future development of a different metal ion management in the pulp mills, and for disruptive use of strong complexing agents in other water-based, metal ion containing environments, where low emission of heavy metals is demanded.

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