

## USE OF A VOITH FLOTATION CELL FOR REMOVAL OF LIPOPHILIC EXTRACTIVES AND Mn IONS FROM SPRUCE THERMOMECHANICAL PULPING PROCESS WATERS

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The effects of a chelating surfactant and different foaming agents on the efficiency of cleaning process waters from a thermomechanical pulp (TMP) mill were studied in a Voith flotation cell. Turbidity measurements and gas chromatography were used to determine the removal extent and characteristics of dissolved and colloidal substances (DisCo). The metal ion content in the process waters before flotation and the metal chelate removal after flotation were determined using inductively coupled plasma-optical emission spectrometry (ICP-OES). FiberLab™ equipment was used to characterize changes in the size of fibers present in the process waters. The results indicate that a decrease in turbidity of up to 91% and the removal of 80% of lipophilic extractives in the TMP water could be obtained using a single-stage flotation unit. Furthermore, the foam fraction was within 5% of the initial volume, and 100% of the Mn<sup>2+</sup>/chelating surfactant complex added to the TMP water was removed.

*Keywords:* Flotation; Extractives; Foaming agents; Chelating surfactant; Purification; Internal cleaning stage

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### INTRODUCTION

During the mechanical pretreatment of wood, dissolved and colloidal (DisCo) substances and metal ions are liberated to the process water (Tanase *et al.* 2009). Closing the water system in a paper mill results in the accumulation of these detrimental substances, possibly negatively affecting the papermaking process and final product properties.

Lipophilic extractives belonging to colloidal substances account for production process disturbances, such as deposits on the paper machine (Sundberg *et al.* 2000; Vähäsalo and Holmbom 2006). Such lipophilic extractives also increase the consumption of cationic process chemicals (Shevchenko and Duggirala 2009) and decrease the efficiency of biological effluent treatment (Zhang and Sain 2002; Wang *et al.* 1995). Impaired final product quality, such as decreased strength, impaired optical properties, and the presence of dirt and holes, are connected with the presence of lipophilic extractives (Back and Allen 2000; Holmbom and Sundberg 2003; Kokkonen *et al.* 2004; Lindström *et al.* 1977; Otero *et al.* 2000; Sjöström 1993; Sjöström and Alen 1998; Tammelin *et al.* 2007). The influence of the dissolved part of wood components is not as well known as that of lipophilic extractives, but research is increasingly revealing their positive effects on the production process. For example, hemicelluloses dissolved in the

process water are believed to sterically stabilize lipophilic extractives dispersion, possibly preventing uncontrolled aggregation (Johnsen *et al.* 2004; Kokko *et al.* 2004; Kokkonen *et al.* 2002; Sihvonen *et al.* 1998; Sundberg *et al.* 1994; Sundberg *et al.* 1996).

Since new bleaching methods have been developed recently, process disturbances due to metal ions located in the fiber walls have been experienced. Special attention has been paid to the ability of transition metal ions to catalyze hydrogen peroxide decomposition. Increased bleaching cost and impaired optical properties are noted when such decomposition occurs (Kujala *et al.* 2004; Norkus *et al.* 2006). To prevent H<sub>2</sub>O<sub>2</sub> decomposition, the manganese ions naturally present in relatively large amounts in the wood are neutralized by adding chelating agents to the pulp fiber suspensions.

The biodegradation of these added chelating agents is relatively low, which is regarded as an imminent problem in terms of heavy metal release over large water areas (Nörtemann 2005; Sillaanpää 1996). In this context, an efficient chelating agent that is separable from the process water could be an interesting alternative.

Accumulation of non-adsorbed lipophilic substances increases the risk of uncontrolled lipophilic extractives aggregation and process disturbances (Basta *et al.* 2004; Holmbom and Sundberg 2004; Johnsen and Stenius 2007). Johnsen and Stenius (2007) demonstrate that only approximately 30% of the lipophilic extractives can be retained in the paper. In light of this, treatment methods that decrease the harmful effects of lipophilic substances and decrease the emissions of chemicals and released wood substances to the environment would be desirable (Pirkanniemi *et al.* 2007; World Health Organization 2008).

Flotation is an interesting method for use as an internal cleaning stage to remove lipophilic substances. Flotation has been used in the mining industry for over 80 years. Due to its simplicity, flotation has been rapidly adopted by the paper industry, where it is used in deinking waste paper and has been suggested as an internal method for cleaning process water in a mechanical pulp mill (Woodward 1986; Saarimaa *et al.* 2006).

To our knowledge, relatively few published articles describe an internal cleaning stage based on flotation. Lipophilic extractives aggregated with cationic polyelectrolytes can largely be removed from the process waters from a recycled paper-based newsprint mill (Miranda *et al.* 2008, 2009) and a eucalyptus mill (Negro *et al.* 2005) by dissolved air flotation (DAF).

The present paper explores a new way of removing of lipophilic extractives and manganese ions by induced air flotation (IAF). The use of a Voith flotation cell as an internal cleaning stage, in combination with a separable chelating surfactant (Högberg *et al.* 2011, 2012) and foaming agents, is investigated. The influence of different foaming agents and complexing agents on the IAF efficiency is discussed.

## EXPERIMENTAL

### Materials

#### *Chemicals*

The full names, abbreviations, and suppliers of the chemicals used in the experiments are presented in Table 1.

**Table 1.** Abbreviations, Full Names, and Suppliers of the Foaming agents (f.a.), and Complexing Agents (c.a.) and other chemicals (o.c.) Used

Abbreviation	Name	Supplier	Type
DDAO	N,N-Dimethyl dodecylamine-N-oxide (amphoteric)	SIGMA	f.a.
DoTAC	Dodecyltrimethylammoniumchloride (cationic)	FLUKA	f.a.
SDS	Sodium dodecyl sulfate (anionic)	CALBIOCHEM	f.a.
4-C12-DTPA	4-dodecyl-3,6,9-tri(carboxymethyl) -3,6,9-triazaundecane diacid	MID SWEDEN UNIVERSITY	c.a.
DTPA	Diethylenetriaminepentaacetic acid	FLUKA	c.a.
MnSO <sub>4</sub> ·H <sub>2</sub> O	Manganese sulfate monohydrate	Merck	o.c.

*Spruce TMP water*

The samples of the spruce TMP water were taken from the wire press section before the bleaching tower at SCA Graphic Sundsvall, Ortviken mill, Sweden. The pulp consistency after the wire press is 35%. TMP water is called O-water in this study.

**Methods***Preparation of the Mn<sup>2+</sup>/4-C12-DTPA complex*

A complex of 4-C12-DTPA and Mn<sup>2+</sup> ions in 60 mL of distilled water, corresponding to 10 mg/L of extra bonded Mn<sup>2+</sup> ions in 6 L TMP water was prepared by mixing together a 30 mL solution of MnSO<sub>4</sub>·H<sub>2</sub>O corresponding to 36.3 mM of Mn<sup>2+</sup> and a 30 mL of 43.6 mM solution of 4-C12-DTPA. The molar ratio of 4-C12-DTPA and Mn<sup>2+</sup> ions was 1.2:1.

*Pretreatment of spruce TMP water*

The fibre fraction was removed by filtration through a plastic Büchner funnel equipped with a 100 mesh filter. The filtrate was stored in a refrigerator at 6 °C. Before flotation, the filtrate was diluted 1:1 with distilled water. Table 2 presents the initial process parameters and chemical characteristics of the waters studied. The water after pretreatment is called P-water in this study.

**Table 2.** Initial Parameters of Studied Waters

Analysis	TMP water "O-water"	TMP water after pretreatment "P-water"
pH	5.0	5.5
Turbidity (NTU)	2400	1060
Carbohydrates (mg/L)	1780	920
Total concentration of Extractives (mg/L)	738	207
Fatty and resin acids (mg/L)	73	26
Lignans (mg/L)	10	4
Sterols (mg/L)	11	4
Steryl esters (mg/L)	88	25
Triglycerides (mg/L)	137	47
Mn <sup>2+</sup> (mg/L)	11.2	5.9

### Flotation of process waters

P-water and O-water were tested in the Voith cell. 6 L samples of waters were used during flotations. The flotation time for P-water was 5 min, while the flotation of O-water continued until the formation of stable foam ended. The flotation times ranged from 60 min at 32 ppm of DoTAC to 130 min at 180 ppm of DoTAC. The foam fraction was weighted after the flotations.

The flotation time and DoTAC concentration were 60 min and 80 ppm, respectively, for two investigations of removal of complex of  $Mn^{2+}$  ions with 4-C12-DTPA and DTPA.

In Fig. 1 a customized 1 L flotation cell used in a previous investigation and a Voith flotation cell used in this study are presented. The customized 1 L flotation cell is built of a plexiglass cylinder with an inner-diameter of 80 mm equipped with a sintered glass frit of diameter 60 mm (porosity 4, VWR, Sweden) placed at the bottom of the cell. In order to induce the flotation process, a nitrogen gas flow of 5 L/min was applied. The Voith flotation cell consists of a plexiglass cube with a length side of 30 cm. Additionally the cell is equipped with a motor delivering a rotational speed of 1340 rpm of an impeller. In each corner of the cube plexiglass plates in the size of 6 cm x 13 cm are located. The flotations were induced only by switching on the impeller.



Fig. 1. Induced air flotation: a) customized 1 L cell (Zasadowski *et al.* 2012) and b) Voith cell

## Analyses

### Carbohydrates in spruce TMP process water

The carbohydrate content was determined using the Orcinol method based on a colour reaction of carbohydrates with 0.2% orcinol reagent solution in concentrated sulphuric acid. 5 mL of water sample was heated for 25 min in a water bath after the addition of 10 mL of orcinol reagent. The solution was cooled down to room temperature and analyzed according to SCA-F W 15:77 on a Varian 100 Bio UV-Vis spectrophotometer at 540 nm of wavelength.

*Lipophilic extractives in spruce TMP process water*

The total concentration of extractives was determined gravimetrically according to the SCA-F W 35:97 method based on a solid phase extraction (SPE), which was preceded by addition of methanol to a concentration of 15% in the water sample and pH adjustment to pH 2. Before extraction, a SPE disc (3M Empore, SDB-XC, 47 mm, Scantec Lab) was washed with 10 mL of methyl tert-butyl ether (MTBE) followed by 10 mL of methanol and then 10 mL of distilled water. During the extraction, small amounts of water samples were added so that the flow did not exceed 2 mL/min. Then after the extraction the SPE disc was washed with 2 portions of 10 mL of 40% methanol and vacuum-dried for 30 min. The disc is eluted with 3 portions of 30 mL of MTBE. The received solution is vacuum-dried at 40 °C for 3 h and then weighted.

The main groups of lipophilic extractives were investigated by gas chromatography (GC) analysis using an Agilent 6980 instrument according to SCA-F G15:95 method based on a protocol presented in Örså and Holmbom (1994) with small changes in GC instrument parameters. The water samples were extracted with MTBE and silylated with bis-(trimethylsilyl)-trifluoro-acetamide (BSTFA) and trimethylchlorosilane (TMCS) before analysis. The temperature of the injector during the injection was programmed from 53 °C to 343 °C at a rate of 16 °C/min. The detector temperature was held at 350 °C. The column was a 5 m/0.53 mm i.d. wide-bore capillary column (DB-1) having a film thickness of 0.15 µm.

*Lipophilic extractives in fibre fraction from spruce TMP process water*

The fibre fraction was separated from spruce TMP process water by filtration through a plastic Büchner funnel having a diameter of 24 cm equipped with a 100 mesh as a filter. Small amount of water was used at once to avoid formation of a fibre filter which may influence the concentration of lipophilic extractives in the fibre fraction. The fibre fraction was freeze-dried overnight before extraction.

The total concentration of extractives was determined gravimetrically according to the SCAN-CM 67:03 method. The extraction of fibre fraction was carried out in a Soxhlet apparatus with a cyclohexane:acetone ratio of 9:1. The extract was transported to an aluminum form, evaporated for 30 min at 105 °C, and weighed.

The main groups of lipophilic extractives in fibre fraction from spruce TMP process water were investigated according to the same procedure used to investigate spruce TMP process water.

*Turbidity*

The turbidity was analyzed using a HACH RATIO/XR 43900 turbidimeter. The TMP water contained fibres and fines that significantly influenced the turbidity measurements. The measurements of the water before and after flotation were made after 1 h of sedimentation.

*Fibre distribution*

Optical measurements to determine the geometry of each fiber were made in the Metso Automation FiberLab™ equipped with a sampling carousel and software display. The measurements were made using two CCD cameras that measured the fibres in a 50-

µm-wide chamber. The procedures for fibre and image processing needed to determine the fibre properties are described in detail elsewhere (Metso Automation 2001).

#### *Residual foaming agent*

The residual foaming agent contents (DoTAC) in the water samples after flotation experiments were determined using mass spectrometry (MS) measurements made on an ESI-MS Quattro II instrument equipped with MassLynx™ 4.0 software. The following instrument parameters were used during the measurements: source temperature 60 °C, drying gas flow 250 L/h, nebulising gas flow 10 L/h, capillary voltage 4.5 kV, HV lens voltage 0.5 kV, and sample cone voltage 30 V. The fibres and fines from the water samples were removed by filtration through a 0.22 µm MILLEX®-GS filter. Methanol was added to the water samples to a concentration of 50%. Three standard DoTAC solutions with concentrations of 1.1, 2.2, and 5.5 ppm were prepared. A calibration curve was obtained with a linear relationship between the signal at  $m/z$  228.1 and the concentration of DoTAC ( $R^2 = 0.9968$ ). The water samples were measured in ES+ mode.

#### *Metal ion contents*

A 10 mL sample of water was refluxed for 5 minutes with 2.5 mL of concentrated nitric acid and 2 mL of 30% hydrogen peroxide in order to digest the fibre fraction. The solution was filtered through a Munktell 00H paper filter and adjusted to 25 mL. The metal ion contents in waters before and after flotation were analyzed according to SCAN standard method CM 38:96 on a Varian ICP-OES 720 inductively coupled plasma spectrometer and optical emission spectrometry.

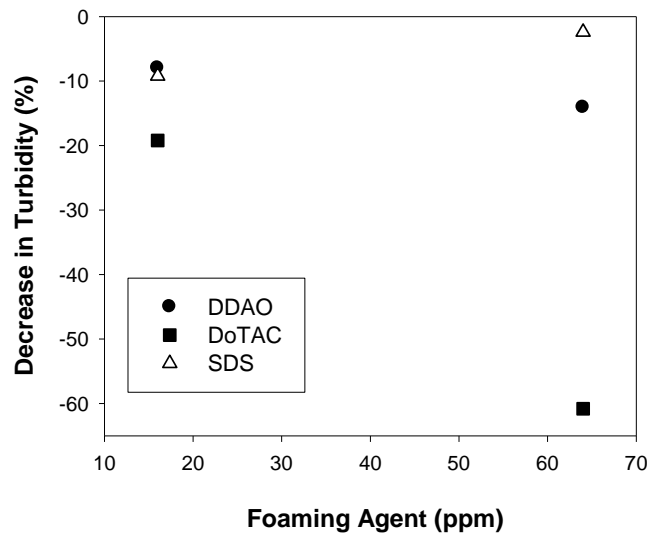
## RESULTS AND DISCUSSION

### **Effects of Different Foaming Agents on the Removal Efficiency of DisCo Components from P- and O-water**

Figure 2 shows the decrease in turbidity of the P-water as a function of different foaming agents. The figure indicates that DoTAC yielded a larger decrease in the turbidity compared to SDS or DDAO. This is because DoTAC is a cationic foaming agent that is likely adsorbed on negatively charged double-layered lipophilic extractives droplets, creating stronger interactions than the zwitterionic foaming agent DDAO (Nelson 2003). DoTAC modifies the lipophilic extractives droplet's surface properties so that the lipophilic extractives may create small aggregates based on weak electrostatic interactions that facilitate their removal from the process waters by flotation (Zasadowski *et al.* 2012).

The carbohydrate analysis indicated that DoTAC might also be associated with dissolved carbohydrates, but not as much as with the lipophilic extractives. Adding 64 ppm of DoTAC gave a 65% decrease in the turbidity (Fig. 2) and a 20% decrease in the carbohydrate content of the P-water determined with the Orcinol method (Fig. 3).

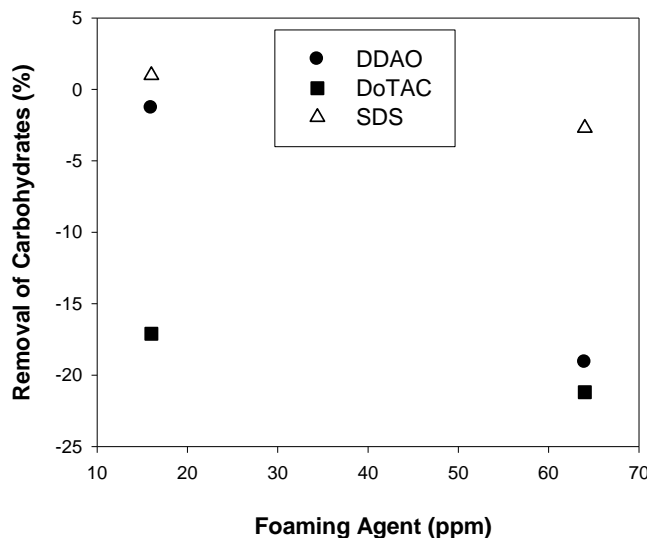
Due to the experimental setup, it was noted that foam formation was not completed at foaming agent concentrations above 18 ppm. This suggests that the flotation times should either be increased or that a flotation unit providing more turbulent conditions should be used.



**Fig. 2.** The decrease in the turbidity in the P-water (%) as a function of different foaming agent concentrations (ppm) after flotation at pH 5.5 and 21 °C

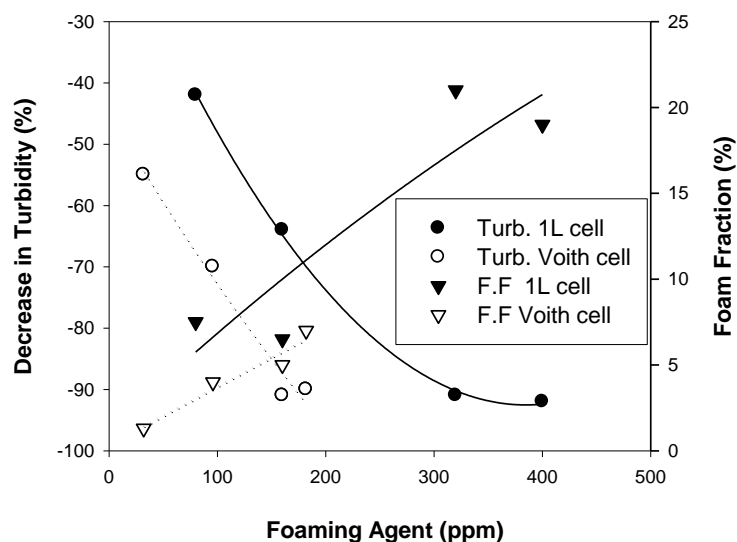
A significant difference was noted between the influence of the Voith cell and of a 1 L cell (Zasadowski *et al.* 2012) with respect to the turbidity of the treated waters and on the removal of extractives from O-water, so these two flotation cells are compared in Fig. 4 and Table 3, respectively.

The main parameters used in investigating the 1 L cell are presented below, and the results obtained were used in the comparison. The flotation times for O-water in the 1 L flotation unit ranged from 40 min at 80 ppm of DoTAC to 240 min at 400 ppm (Zasadowski *et al.* 2012). In the Voith flotation cell, the flotation time ranged from 80 min at 32 ppm of DoTAC to 130 min at 180 ppm.



**Fig. 3.** The decrease in the content of carbohydrates (%) in the P-water as a function of different foaming agent concentrations (ppm) after flotation in the Voith cell at pH 5.5 and 21 °C

Figure 4 shows that the Voith cell removed more of the lipophilic extractives from the O-water than did the 1 L cell. After 110 min of flotation in the Voith cell at 160 ppm of DoTAC, a 90% decrease in the turbidity of O-water was obtained. In addition, the amount of foam fraction was within 5% of the initial volume, which indicated that the flotation process may be successfully used to purify the O-water. Further increasing the amount of DoTAC in the Voith cell resulted only in increased flotation time and more water in the foam fraction due to the high affinity of DoTAC for the water in the case of an overdose of DoTAC. When looking at the flotation experiments in the 1 L cell, higher concentrations of DoTAC and a longer flotation time is needed to obtain a 90% decrease in turbidity, which leads to high amounts of water in the foam fraction.

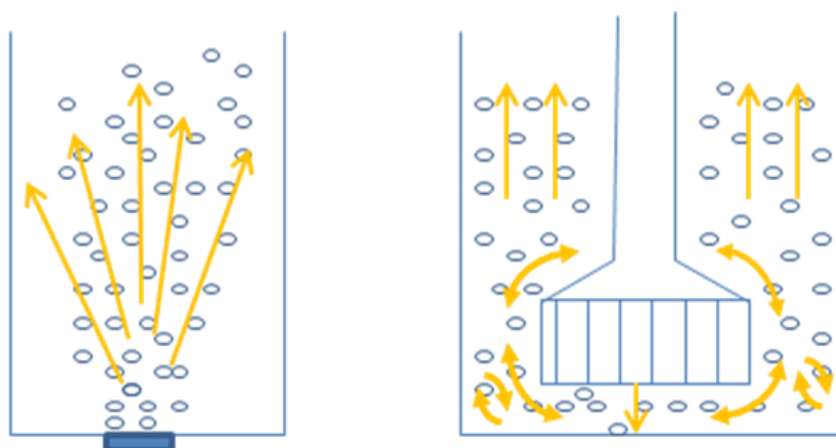


**Fig. 4.** The decrease in the turbidity (%) and the amount of foam fraction (wt%) in O-water as a function of different DoTAC concentrations (ppm) after flotation in the Voith cell and in the 1 L cell at pH 5.0 and 21 °C

The improved removal of lipophilic extractives in the Voith cell compared with the customized 1 L cell is probably related to the different froth generation techniques used. In the Voith cell, the air bubbles are formed and mixed into the solution by an impeller, whereas in the customized 1 L cell, the air bubbles are generated only by directly injecting air through a glass filter. This difference in the foam generation systems between the Voith cell and the customized 1 L cell results in various distribution of driving forces in the units, as shown in Fig. 5. The Voith flotation cell giving more turbulent conditions and a better distribution of driving forces has better removal efficiency of lipophilic extractives from process water.

The decreased turbidity, total extractive concentration, and major extractive group concentrations in O-water before and after flotation in both the Voith cell and 1 L cell are presented in Table 3. More extractives were removed in the Voith flotation cell at a lower DoTAC concentration and shorter flotation time than in the 1 L cell. The results confirm that a flotation unit delivering more turbulent conditions is more efficient in terms of shorter flotation time and lower foaming agent concentrations.





**Fig. 5.** A difference in the driving forces distribution between 1 L and Voith flotation cell

**Table 3.** Decrease in Turbidity (%) and Decrease Total Extractive and Major Extractive Group Concentrations (mg/L) in O-water Before and After Flotation in the Voith Cell and 1 L Cell at Different DoTAC Concentrations at pH 5.0, 21°C

Analysis	O-water	Voith cell DoTAC 160 ppm	1 L cell DoTAC 320 ppm
Decrease in turbidity (%)	-	92	91
Total concentration of extractives (mg/L)	738	114	149
Fatty and resin acids (mg/L)	73.1	2.4	2.8
Lignans (mg/L)	10	9.0	9.3
Sterols (mg/L)	11.8	2.8	3.2
Steryl esters (mg/L)	88.2	3.4	7.6
Triglycerides (mg/L)	137	2.1	7.7

In the GC analysis of the extractives, a large peak was found in the O-water, before and after flotation, in the lignans area, and small peaks were detected adjacent to the triglyceride area; these were assigned to the total extractive concentration, but not calculated or defined for the major extractive group concentrations. It should be noted that, despite the considerable decrease in turbidity after DoTAC treatment, high total concentrations of extractives remained in the water. This may indicate a selective DoTAC functioning. The low charge density of the lignans at the investigated pH contributed to their low removal efficiency by flotation, compared with the droplets of lipophilic extractives, which have high charges due to their chemical structure. The lipophilic extractives droplet has a two-layered structure: the middle of the droplet consists of neutral triglycerides and steryl esters, while the outer layer consists of resin and fatty acids anchored by tails in the inner part of the droplet (Sundberg *et al.* 2009; Strand *et al.* 2011).

Additionally, it should be noted that only 43% of the total concentration of extractives were accounted for in the group determination by GC, as shown in Table 3.

This is in agreement with results obtained in laboratories participating in the “COST E41 Joint Analysis Effort” (Willför *et al.* 2006)

From the ESI-MS analysis, the final results after the finished flotation experiment in the Voith cell indicated a 0.5% DoTAC content with an initial addition of 160 ppm. This indicates that both lipophilic extractives and added chemicals can be successfully removed from the O-water.

### Influence of Flotation on O-water Fibre Fraction

O-water initially contains 0.5 to 1% fibres and fines. This fibre/fines fraction remains in TMP water after flotation, with only individual fibres and fines being removed with the foam fraction. Deng (2000) demonstrated that fibres losses increase with an increasing foam fraction. The fiber length distribution changed during flotation, as shown in Table 4. The higher amounts of shorter fractions after flotation were generated by the stirring system in the Voith cell cutting the long fractions. The proportion of fibres in the 1.2 to 2 mm fraction decreased from 17.2% to 5.2%, whereas the proportion of fines material in the 0.2 to 0.5 mm fraction increased from 27.8% to 42.9% during flotation. While the mechanical properties of fibres were changed by fibres cutting, the fiber structure became more open, increasing the foaming agent penetration and facilitating the removal of the lipophilic extractives encapsulated inside and adsorbed on the fines and fibres. The results of GC analysis of the lipophilic extractives from the extraction of the fibres and fines from O-water before and after flotation are shown in Table 5.

**Table 4.** Distribution of Fibre Material (%) in O-water Before and After Flotation at a DoTAC Concentration of 160 ppm at pH 5.0 and 21 °C

Length [mm]	Before [%]	After [%]
0.1–0.2	11	18
0.2–0.5	28	43
0.5–1.2	32	32
1.2–2.0	17	5
2.0–3.2	9	1
3.2–7.6	3	1

**Table 5.** Major Extractive Group Concentrations (mg/L) and Extract Concentration (%) in the Fibres and Fines in O-water Before and After Flotation at a DoTAC Concentration of 160 ppm at pH 5.0 and 21 °C

Extractives	Before	After
Total concentration of extractives (mg/kg)	42200	16700
Fatty and resin acids (mg/kg)	15900	3110
Lignans (mg/kg)	698	781
Sterols (mg/kg)	1360	832
Steryl esters (mg/kg)	9060	5250
Triglycerides (mg/kg)	15100	6720

The results showed that over 80% of fatty and resin acids, 50% of triglycerides, and 30% of sterylcesters can be removed from O-water fibres by a single-stage flotation process. This indicates that the flotation process may be efficient at removing all forms of lipophilic extractives encountered in the production process, both as droplets and when they are absorbed on the fibres surfaces and encapsulated in the fibres.

### Effect of 4-C12-DTPA and DTPA in Combination with DoTAC on Manganese Ion Removal from O-water

Two complexing agents were studied during flotation: DTPA, a complexing agent usually used in the paper industry, and a chelating surfactant, 4-C12-DTPA, synthesized at Mid Sweden University. 4-C12-DTPA has surface-active properties due to the introduction of a carbon chain into its structure, though its affinity for metal ions is not affected (Högberg *et al.* 2011, 2012). Metal ions bound with 4-C12-DTPA can be easily removed in a simple flotation process by interactions between the chelating surfactant and the air bubble surface.

O-water is TMP press water before the bleaching stage and already contains DTPA. The study of the effect of DTPA on the flotation relied on the addition of DoTAC to the O-water. The study of the effect of 4-C12-DTPA on the flotation was preceded by the introduction of a complex of chelating surfactant and  $Mn^{2+}$  before the addition of DoTAC to the O-water. The results shown in Table 6 confirm that 4-C12-DTPA can successfully be used to remove  $Mn^{2+}$  ions from TMP water: 100% of the added  $Mn^{2+}$  complex was removed, while concentrations of the other metal ions remained almost unchanged. Only the  $Cu^{2+}$  ion concentration increased due to the release of  $Cu^{2+}$  ions from the copper component of the flotation cell. The application of DTPA in the flotation did not result in a decrease of  $Mn^{2+}$  concentration, as shown in Table 7. This indicates that DTPA has a lower affinity for the air bubbles than does 4-C12-DTPA. A 60% and 65% decrease in the turbidity of the O-water was observed for the 4-C12-DTPA/DoTAC and DTPA/DoTAC combinations, respectively.

**Table 6.** Concentrations of Metal Ions (mg/L) in O-water Before Flotation, After Complex Addition, and After Flotation at 80 ppm of DoTAC at pH 5.0 and 20 °C

Samples	$Cu^{2+}$ (mg/L)	$Fe^{3+}$ (mg/L)	$Mn^{2+}$ (mg/L)	$Zn^{2+}$ (mg/L)	$Ca^{2+}$ (mg/L)
O-water with DTPA	0.1	0.5	16	1.4	25.5
After $Mn^{2+}$ 4-C12-DTPA addition	0.1	0.5	25	1.4	23.7
After flotation	0.5	0.4	13	1.5	19.6

**Table 7.** Concentrations of Metal Ions (mg/L) in O-water Before and After Flotation at 80 ppm of DoTAC at pH 5.0 and 20 °C

Samples	$Cu^{2+}$ (mg/L)	$Fe^{3+}$ (mg/L)	$Mn^{2+}$ (mg/L)	$Zn^{2+}$ (mg/L)	$Ca^{2+}$ (mg/L)
O-water with DTPA	0.1	0.5	16	1.4	25.5
After flotation	0.2	0.4	14	1.3	24

The presence of a copper component in the Voith cell indicates that possible release of metal ions was not considered when designing the cell application. The deinking of waste paper is the main area of investigation for which the cell is used.

As the results show, 4-C12-DTPA may be successfully used as a chelating surfactant to remove metal ions from process waters by flotation. In comparison to 4-C12-DTPA, the chemical structure of DTPA is too hydrophilic and does not have any specific affinity to the air-water interfaces in the bubbles created during flotation.

## CONCLUSIONS

1. A 90% decrease in turbidity was obtained in the Voith cell with a shorter flotation time and lower foaming agent concentration than in the 1 L cell.
2. Concentration of carbohydrates was almost unchanged.
3. The stirring system of the flotation cell influenced the fiber length. Cutting effects open the fiber structure, increasing foaming agent penetration and facilitating removal of the lipophilic extractives encapsulated inside and adsorbed on the fines and fibers.
4. In an optimized flotation, high removal of lipophilic extractives can be obtained at a relatively low amount of foam fraction.
5. Flotation can remove 100% of the  $Mn^{2+}$ /4-C12-DTPA complex.

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