PURIFICATION OF WHITE WATERS BY SELECTIVE FLOTATION

Antti Haapala,[a] Mika Körkkö,[a] Kalle Kemppainen,[a] Donald MacNeil,[b] and Jouko Niinimäki [a]

Removal of detrimental contaminants from paper machine circulation waters is known to benefit process runnability and paper quality. The applicability of selective flotation to remove substances of a hydrophobic nature from paper machine circulation waters was investigated in laboratory-scale experiments. The separation efficiency of ink, stickies, and wood extractives was studied by using a flotation scheme in which the froth was generated by the white water's inherent surface active components without any chemical addition. The removal efficiency of detrimental contaminants was considered in relation to total losses of solid materials. The results showed that while not all white waters were able to produce stabile froth, those that generated froth also exhibited substantial separation of contaminants in the froth. With a moderate removal of 10% of total solids from white waters, removal of 45% of stickies, 27% of ink, and 20 to 50% of wood extractives was observed. Higher removal of contaminants resulted in solids losses at levels that are not economically feasible in paper production. The results showed that selective white water flotation can have beneficial results for papermaking processes.

Keywords: Process water; Separation; Froth; Extractives; Ink; Pitch; Stickies; Extraction

Contact information: a: Fibre and Particle Engineering Laboratory, Department of Process and Environmental Engineering, P.O. Box 4300, FI-90014 University of Oulu, Finland; b: Laboratory of Wood and Paper Chemistry, Åbo Akademi University, Porthansgatan 3, FI-20500 Turku, Finland;
** Corresponding author: antti.haapala@oulu.fi*

INTRODUCTION

Increasing closure of water circulations of paper and board machines has raised the levels of dispersed extractives, adhesives, ink, and other pulp contaminants in process waters. Their potentially adverse effects on runnability and quality problems in papermaking processes have been noted and addressed in several fairly recent studies (Sundberg et al. 2000; Holmbom and Sundberg 2003; Hubbe et al. 2006; Haapala et al. 2010; Valto et al. 2010). The environmental and economical drivers, however, rule out a return to high fresh water usage levels as the solution to the problem. Therefore, a wide selection of cleaning processes and chemical aids (e.g. fixatives and flocculants) are being developed to manage the concentration of dissolved and solid contaminants.

Even a moderate, continuous removal of accumulating material from the dispersed phase can substantially slow down the build-up of contaminants, reduce the equilibrium level of detrimental substances, and improve runnability and product quality (Xu and Deng 2004; Hubbe et al. 2006). Several methods to reduce the levels of accumulating substances have been presented in the literature (Sitholé and Allen 2002;

Gabl et al. 2006; Hubbe 2007b), but like all processes, these tend to have their drawbacks, such as a need for additional unit processes that add complexity and costs both in installation and operation.

Generally the process most used for water purification in papermaking applications has been dissolved air flotation (DAF). It is, however, considered unfit for the paper machine loop due to its high removal rate of all solids, including fillers and fiber fines (Røring and Wackerberg 1997; Richardson and Grubb 2004; Sarja 2007). Another different flotation concept, *selective flotation,* is in turn widely used to remove contaminants from the recycled paper during deinking. With this process a higher selectivity for removing hydrophobic contaminants, i.e. ink, stickies, and wood extractives can be achieved than with DAF, which removes also the precious fillers or wood fines (Sarja 2007; Körkkö et al. 2008). Many white waters also have a tendency to produce froth without flotation chemicals due to the presence of calcium and surface-active extractives. Selective flotation removes contaminants at a low expense of yield, and in the case of white waters, would also tend to reduce the need for defoamers.

Although the concept of white water flotation is not novel, only a few publications are available regarding its application for waters in the paper machine loop. Recent studies utilizing column flotation discuss a similar approach as in this study (Dionne et al. 2007; Ricard et al. 2008; De Grado et al. 2010), but focus, however, on the effects of water purification on paper properties but only to a limited extent on the solids losses and removal efficiencies of different components. Thus, there is a scarcity of information on the applicability of flotation in white water purification and efficiency of component removal with respect to unwanted solid losses caused by frothing.

The aim was to study the applicability of selective flotation in the environment of the paper machine's short circulation system, as well as relating the removal efficiency of contaminants to yield losses. Removal efficiencies of wood extractives (triglycerides, steryl esters, resin acids, fatty acids, and sterols) and, in the case of recycled paper process, also ink particles and stickies, are presented. The removal of undesired components is characterized by extraction methods and optical analyses and discussed in relation to total yield losses of solids that also contain the fiber and filler material.

EXPERIMENTAL

White Water Characterization

White water samples were obtained from European paper and board mills. White water denoted as WW-OCC originated from a board machine utilizing 100% old corrugated containers, WW-DIP came from a newsprint machine using 100% deinked pulp, and WW-MP came from a paper machine using mechanical virgin pulps. The paper machine fed with WW-MP used pressurized groundwood (PGW) and thermomechanical pulp (TMP) as a raw material for its production.

Properties of white waters are presented in Table 1. Measurement of pH (SFS 3021) and conductivity (SFS 27888) were made with a Denver Instrument Model 50 instrument. Dry matter content (DMC, SFS-EN 20638) from suspension mass and ash content (ISO 1762) from bone dry suspension mass were obtained using a Precisan prepASH 129. Suspended solids were analyzed according to SFS-EN 872 in relation to suspension mass. Water hardness, i.e. net concentration of calcium plus magnesium ions, was measured using a Perkin Elmer AAnalyst 600 atomic absorption spectrometer according to SFS 3044 and SFS 3018.

Table 1. Properties of White Waters

White water	Product / Pulp	Suspended solids [%]	DMC [%]	Ash [%]	Hardness [ºdH]	pH	Conductivity [mS/cm]
WW-OCC	OCC	0.27	1.12	42.8	171	6.4	4.7
WW-DIP	Newsprint / DIP	0.38	0.51	57.1	6.5	7.5	1.6
WW-MP	Newsprint / MP	0.47	0.70	26.3	2.3	4.2	2.0

Flotation

White water flotation was studied in a Voith Delta25 batch laboratory flotation cell. White waters in 20 L batches were pre-heated and held at 45°C for 15 minutes before weighing a sample batch for the flotation cell. No adjustments of pH and chemicals were used. Batches were floated with residence times of 0.5, 1, 3, and 5 min, while the air feed was set at 7.4 L/s (mode 10). The generated froth was continuously removed, and the liquid phase was studied for detrimental substances content while the liquid head was maintained constant during frothing. Each batch volume and the removed froth were weighed, and samples were taken before and after flotation for analysis.

Each sample was studied for dry matter and ash content, while the amount of stickies and extractives analyses was limited to points after flotation and on a few froth samples. Analysis of flotation removal efficiency was based on the removal of white water solids in relation to the contents of analyzed detrimental substances. Yield of flotation solids was related to the flow and dry matter content of removed froth reject to respective feed values, as given in Eq. (1), and the separation efficiency of contaminants according to Eq. (2). The selectivity of white water flotation was estimated in a similar way to Körkkö et al. (2008) according to a Q-index, originally introduced by Nelson (1981), given in Eq. (3):

$$Yield = 1 - RR_{\mathrm{m}} = 1 - \left(\frac{m_{\mathrm{R}} \cdot dmc_{\mathrm{R}}}{m_{\mathrm{F}} \cdot dmc_{\mathrm{F}}} \right), \tag{1}$$

$$E_{\mathrm{r}} = \frac{m_{\mathrm{R}} \cdot x_{\mathrm{R}}}{m_{\mathrm{F}} \cdot x_{\mathrm{F}}}, \tag{2}$$

$$E_{\mathrm{r}} = \frac{RR_{\mathrm{m}}}{1 - Q + Q \cdot RR_{\mathrm{m}}}, \text{ with } \quad Q = 1 - \frac{x_{\mathrm{A}}}{x_{\mathrm{R}}}, \tag{3}$$

where m_{R} and m_{F} are the masses of reject (froth) and feed (white water), RR_{m} is the mass reject rate, dmc_{R} and dmc_{F} are, respectively, the dry matter content of these samples and x_{R}, x_{F}, and x_{A} are the content of studied components in the reject, feed, and accept. Q is the selectivity index ranging from zero to one, where a value of zero indicates an equally split flow and positive values indicate the level of component enrichment in the froth.

Contaminant Analyses

The wood extractives and stickies content in the samples was obtained by extraction with methyl *tert*-butyl ether (MTBE) followed by analysis by high performance liquid chromatography (HPLC). This method was modified from MacNeil et al. (2006), and Örså and Holmbom (1994). Each 5 ml sample was first acidified to less than pH 4 by addition of 0.05 M H_2SO_4 using bromocresol green as an indicator, in order to ensure that the wood extractives were no longer dissolved in the water phase and extracted into the organic solvent phase. The acidified sample was sequentially extracted three times with 4 mL of MTBE. Samples were vigorously shaken for 1 minute before centrifugation to separate the solvent and water phases. The solvent was removed and combined with the other extractions in the sequence. The solvent was evaporated under nitrogen gas until dry and re-diluted in 1 mL of tetrahydrofuran (THF). A similar method was previously used e.g. by Sarja (2007). 5 mL of each water sample were freeze-dried before extraction by reflux with 20 ml THF for 1 hour. The THF was evaporated to concentrate the sample to within the required concentration range for HPLC analysis. This allowed quantification of component groups with concentrations exceeding 1.5 mg/L, which in most cases corresponds to approximately 0.5 mg/g. Variance of measurement reported by Johansson et al. (2003) for similar extraction gives the repeatability of analysis as 4.6%.

The samples solved in THF were injected into an HPLC system consisting of a size-exclusion column (Jordi 550A), and an evaporating solvent light scattering (ELS) detector (Sedex 80) with a nebulizer temperature of 40°C. The eluant was THF at 1.0 mL/min. External calibration was made by a prepared solution of C21:0 in THF. Total extracted material was obtained by quantification of HPLC-SEC chromatograms for the 5 main groups individually and presented in relation to white water solids as mg/g. A sample chromatogram with the 5 groups is shown in Fig. 1. Peak separation was obtained by using peak fitting software in Origin 8.0.

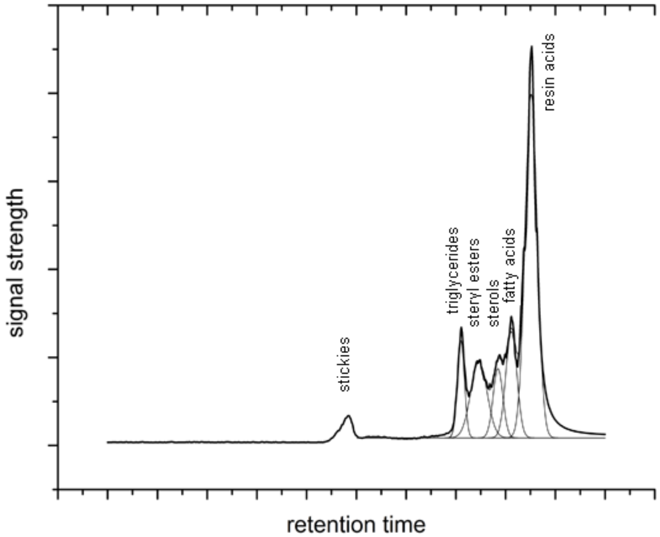

Fig. 1. Typical chromatograph from WW-DIP sample with detected contaminant group peaks. Retention time depends on molecular weight, and material content is defined by peak area.

Ink particle removal in flotation was measured with a Lorentzen & Wettre Elrepho 070 spectrophotometer from 40 g/m^2 handsheets according to the method for residual ink determination (RI$_B$ value, obtained with 5.1% repeatability) from process waters, as described by Haapala et al. (2009). Sheets were made from a mixture of 90% eucalyptus pulp and 10% white water based on their dry weights. The absorption coefficient of the used fiber, k_{fiber} was measured as 0.12 m^2/kg. Prepared sheets satisfied the opacity limitation (below 97%) for scattering coefficient measurement.

RESULTS

Froth Formation and Solids Losses

The froth formation was good with WW-DIP and WW-MP, but in the case of WW-OCC, no froth was obtained. Water hardness and other reasons for this are presented later in Discussion. Hence, results are only presented for WW-DIP and WW-MP. For them, the froth build-up took place in just a few seconds of air feed into the cell. In addition, in the case of WW-DIP, immediately after froth build-up a clearly visible red layer of fine ink and toner residue was formed on top of the froth layer (see Fig. 2).

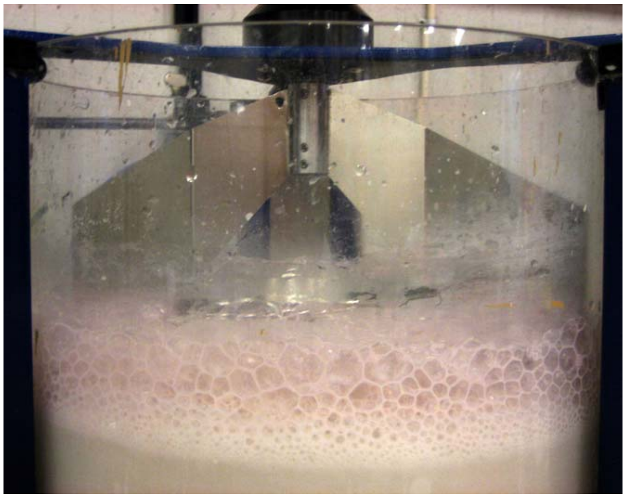

Fig. 2. Distinct layers of colored ink, white froth, and contaminated water could be observed during the froth build-up and early stages of frothing (WW-DIP).

The yield values according to Eq. (1) for WW-DIP and WW-MP, obtained for the flotation time range up to 5 minutes, are summarized in Table 2. Removed total solids had in all cases a higher content of inorganic material than organic, e.g. fiber fines. For example, the share of inorganic and organic material was 70/30 (%) for the WW-DIP froth and 55/45 (%) in untreated white water (flotation feed). For WW-MP the relation in froth was around 30/70 (%), while it was 25/75 (%) in the water. The visually observed differences between water frothing were substantial: WW-OCC produced no froth at all, whereas WW-DIP showed a consistently higher relative frothing tendency than WW-MP, hence also showing a lower yield of solids. All results for removal of measured functional materials in selective flotation are further summarized in Table 3 at the end of the Results section.

Table 2. Obtained Yield Range of Floated White Waters with Variable Flotation Times

	Yield [%]	
Flotation time	WW-DIP	WW-MP
30 sec	> 92	> 95
1 min	> 88	> 92
3 min	> 65	> 75
5 min	> 50	> 65

WW-DIP Purification in Flotation

WW-DIP, coming from a newsprint machine, contained some ink and stickies in addition to wood-originating extractives. An ink content reduction was observed as the flotation progressed, from 520 ppm down to the level of 300 ppm, as shown in Fig. 3. The structure of the froth was visually assessed as weak in relation to e.g. conventional deinking flotation. Removal of ink appeared to be selective even without added flotation chemistry, as the measured ink content showed a nonlinear decline when the flotation progressed and more solids were removed with in the froth. With 10% solids losses, a reduction of ink content down to less than 400 ppm (or relatively, ca. 27% removal) was observed. After the first 10% drop in yield the removal trend appeared to be fairly linear to the end of flotation, being reduced by 45% to 290 ppm.

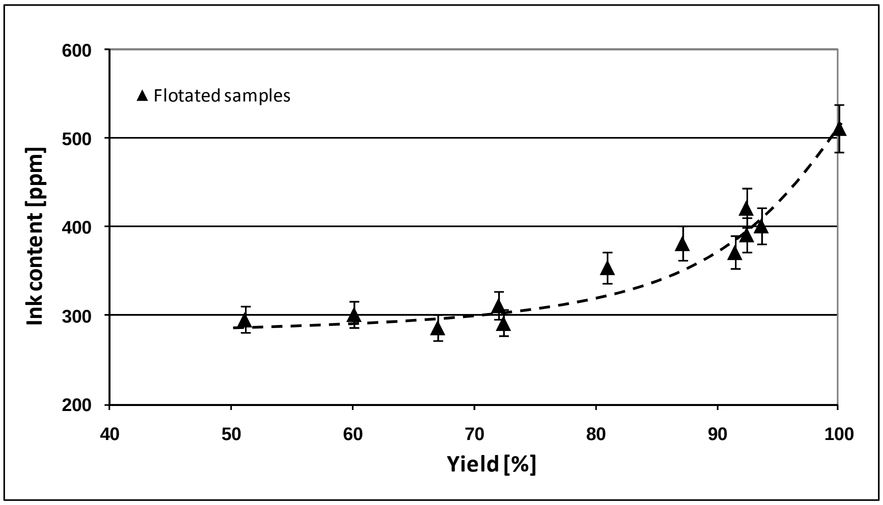

Fig. 3. Ink particle removal in WW-DIP frothing (indicative trend line)

The stickies and extractives are considered here in unison as extracted materials content. The concentration of contaminants is related to total solids in white waters and given as mg/g. The content of overall detrimental extracted materials containing stickies and all extractives is shown in Fig. 4. Their removal rate in relation to solids losses can be considered almost linear, with some difference between components. At 90% yield level there was a decrease of 26% in all extracted materials content, which developed further down to 7.2 mg/g (65% reduction).

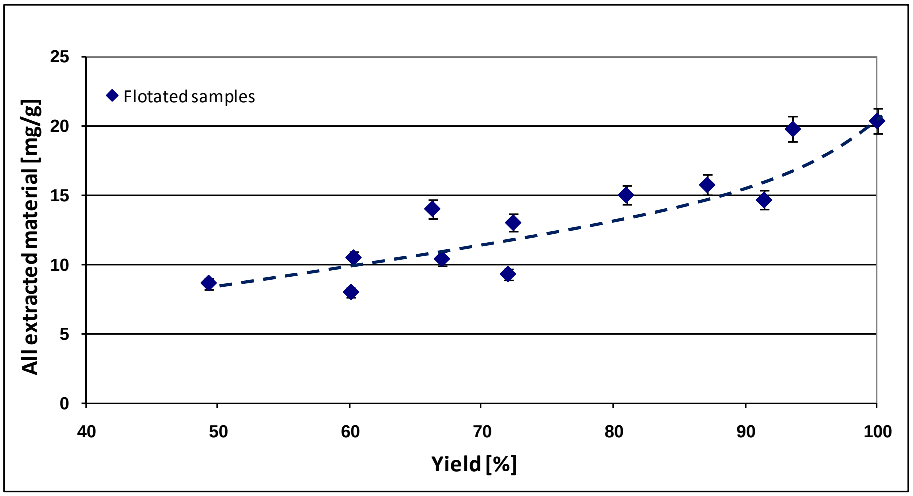

Fig. 4. Total extracted materials removal in WW-DIP frothing (indicative trend line)

Removal rates of extracted stickies and various extractive groups are presented in Fig. 5. It is apparent that the bulk of the extractives consisted of fatty acids (FA), either from the wood fibers or from deinking chemicals, resin acids, and sterols, and the most rapid decrease in their concentration was observed in the initial stages of flotation. This indicated a good selectivity of removal.

Especially stickies, triglycerides, and steryl esters appear to be efficiently removed (Fig. 5A). Stickies content was reduced 45% from 2.4 mg/g measured for untreated white waters at 90% yield, and the content of triglycerides was reduced 51%, from 3.5 mg/g. At the end of the flotation runs the concentration was down to 0.7 mg/g for stickies and 0.8 mg/g for triglycerides, indicating removal efficiencies of around 70% and 75%, respectively. Similarly, we observed the removal of steryl esters at down to a 72% reduction.

Fatty acids (FA) and sterols content (Fig. 5B) were reduced 40% from a concentration of 8.0 mg/g at 90% yield, and the removal continued to the level of 2.0 mg/g at 50% yield (removal of 75%). The analysis method was not able to quantify the content of resin acids (RA) from a few samples due to the poor separation between components and posed a much higher error to measured data than for other wood components. Still, assuming a first order kinetics of separation (Korpela 2006), we obtain a 26% reduction in resin content from 11.5 mg/g to at 90% yield with a trend descended down to 3.5 mg/g concentration at 50% yield (removal of 70%).

WW-MP Purification in Flotation

WW-MP, coming from the newsprint paper machine utilizing only virgin mechanical pulps, contained a variety of wood-originating extractives, but not stickies or ink. Froth of WW-MP was fairly weak, similar to the WW-DIP, but the froth layer thickness in the flotation cell was slightly higher. Removal of solids and hence the lowering of process yield was very similar with both white waters. Similar to the WW-DIP flotation case, the removal of extracted components was slightly pronounced during the first 10% drop in yield (Fig. 6) but after this the removal trends seemed fairly linear to the end of flotation, which was at around 67% yield for WW-MP.

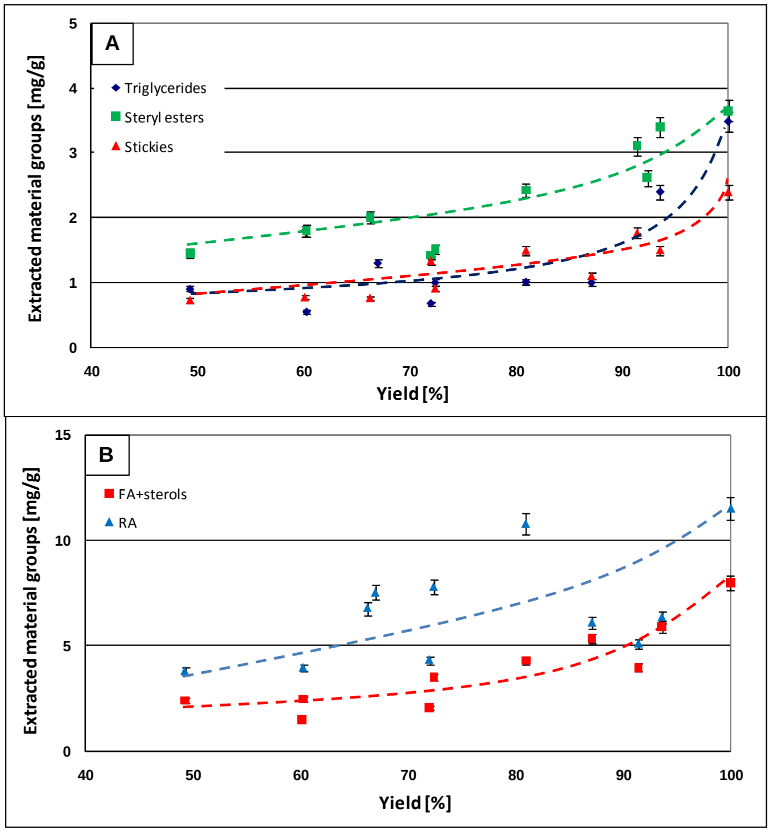

Fig. 5. A) Removal of extracted stickies, triglycerides and steryl esters, B) fatty acids (FA) and sterols, and resin acids (RA) in WW-DIP frothing (indicative trend lines)

As seen from Fig. 6, the total concentration of extracted material in white water (around 224 mg/g in untreated white water) was high in relation to the WW-DIP case of 20.3 mg/g of total extract detected in an untreated white water. For WW-MP the separation of total extracted material resulted in a reduction of 50% of extractives at 70% yield.

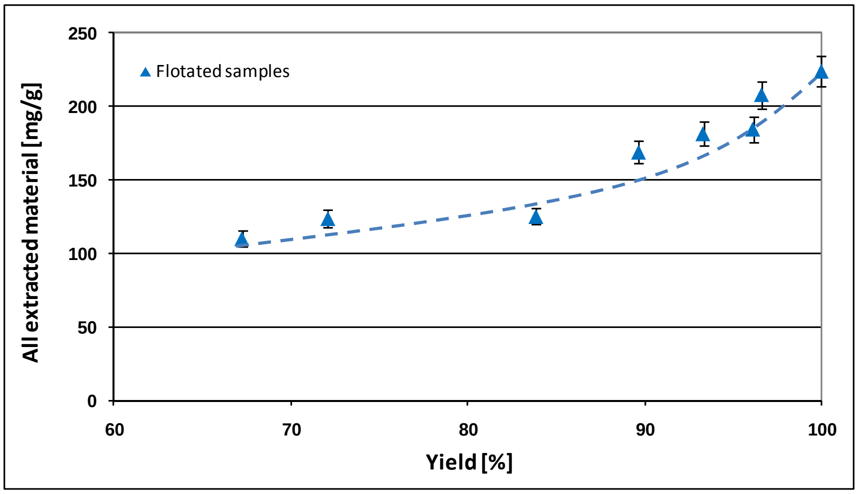

Fig. 6. Total extracted materials removal in WW-MP frothing (indicative trend line)

Separation efficiencies divided according to constituent groups are given in Fig 7. The extractives content in WW-MP as presented in Fig. 7 appears to consist mainly of triglycerides and resin acids, which are commonly found at high concentrations in mechanical pulps. They also showed the highest tendency to become evacuated in froth at brief flotation times.

The triglycerides content was seen to decrease 33% from an initial level of 123 mg/g at 90% yield, further decreasing by 53% as the flotation continued up to a yield of 70%. A reduction in resin acids (RA) content was initially 74 mg/g, from which a removal of 22% at 90% yield descended to 40% removal at 70% yield. The content of steryl esters and fatty acid groups was small in comparison. Their content was reduced by 27% and 28% from 15.1 mg/g and 9.4 mg/g at 90% yield, and 45% and 46% at 70% yield, respectively. All results obtained by estimating the concentration rates of reduction are summarized in Table 3.

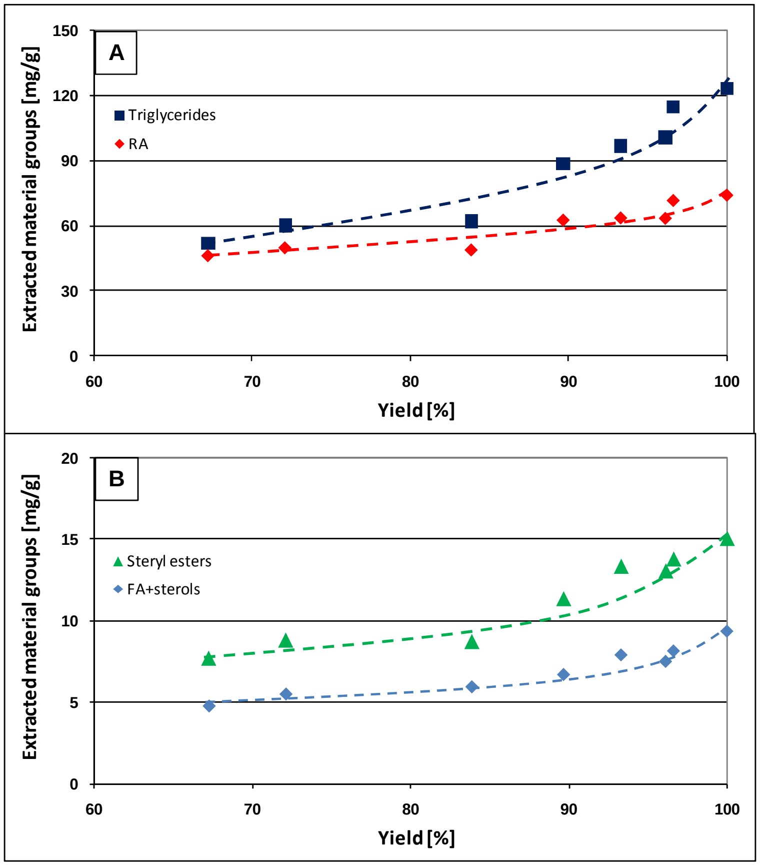

Fig. 7. Removal of extracted triglycerides, steryl esters, fatty acids (FA) and sterols, and resin acids (RA) in WW-MP frothing (indicative trend lines)

Removal of detrimental substances from the water phase to froth was seen to occur for all identified component groups, as summarized in Table 3. Estimations on reduction of contaminants at each yield level were obtained by interpolation between measured values, assuming first order kinetics on component removal. Removal of stickies was better than ink. The evacuation tendency within wood extractives was the highest for groups of triglycerides and combined fatty acids and sterols in both observed cases. Evidence of good froth generation of WW-DIP was also seen in the somewhat better removal efficiency of all functional contaminant groups.

Table 3. Reduction (%) of White Water Component Concentration in Selective Flotation

	Yield [%]	Reduction of material concentration in frothing [%]						
		Ink	Stickies	Triglycerides	Steryl esters	FA and sterols	Resin acids	Total extracts
WW-DIP	90	27	45	51	30	40	26	26
	70	40	62	71	50	68	50	45
	50	45	70	75	72	75	70	65
WW-MP	90	na	na	33	27	28	22	33
	70	na	na	53	45	46	40	50

Selectivity of White Water Flotation

Flotation efficiency for each contaminant group was evaluated via a selectivity index *Q* as presented by Nelson (1981), which is given in Eq. (3). As a sample, the ink removal efficiency (Eq. 2) and its *Q* index of selectivity are shown in Fig. 8. Selectivity of all components is given in Table 4.

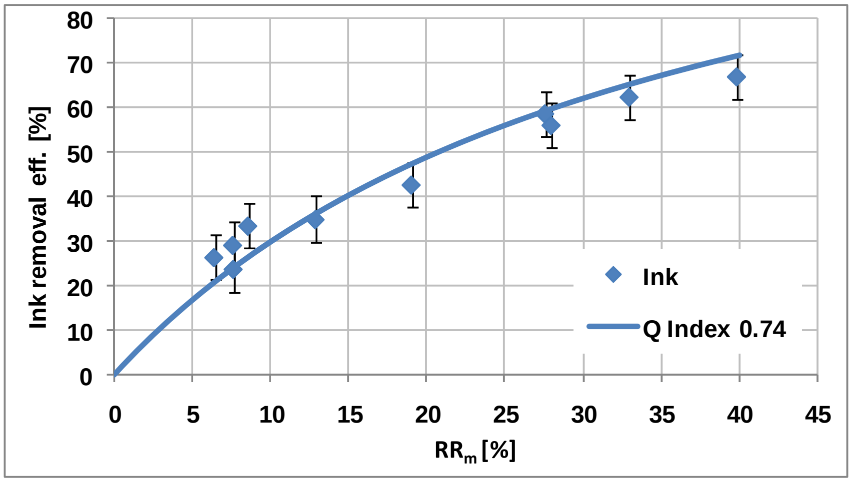

Fig. 8. Ink removal efficiency from WW-DIP. Trend line set with separation selectivity index 0.74.

Table 4. Selectivity Indexes For White Water Contaminant Removal

	Ink	Stickies	Triglycerides	Steryl esters	FA and sterols	Resin acids	Total extracts
WW-DIP	0.74	0.87	0.87	0.78	0.87	0.63	0.79
WW-MP	na	na	0.83	0.76	0.75	0.69	0.77

The results show that all components were selectively removed, while the highest selectivity at 0.87 was obtained for stickies, triglycerides, fatty acids, and sterols. Selectivity of components was similar in both studied white waters, although the removal of fatty acids and sterols in WW-DIP showed higher selectivity than in WW-MP. Resin acids had the lowest selectivity of all components. The stickies and ink, which are present in practically all recycled pulp processes, were also selectively removed.

DISCUSSION

Removal of Contaminants from Process Waters by Flotation

Different possibilities for managing the adverse effects of accumulated contaminants in paper machine circulation have been studied extensively, as summarized by e.g. Gabl et al. (2006) and Hubbe (2007b). Paper machine loop purification stages have commonly been referred to as “kidneys”, emphasizing their intended function as internal purification. Removal of contaminants from internal loops must also maintain the economical production levels and product quality, and thus viable processes must provide a high level of selectivity towards detrimental materials removal.

Flotation applications for internal water purification in the paper machine loop have not been widely promoted. Air has commonly been taken out of the short circulation and not fed in; also the frothing of white waters is easily associated with problematic deposit formation and not considered beneficial in terms of water purification. Also the occurring froth is commonly dispersed with defoamer chemicals or mechanically by water showers (Allen et al. 1993; Stoor 2006; Helle 2008).

Deresination of mechanical pulps by natural flotation has been a familiar notion for quite some time, being first introduced by Brune (1917), but the recent studies by Dionne et al. (2007), Ricard et al. (2008) and De Grado et al. (2010) have shown its potential when adapted to white water purification. Considerable benefits were reported in their studies for web strength and optical properties of handsheets made from white water fines from which the content of ink and wood extractives has been reduced. A similar linkage has previously been presented from the pulp treatment point of view (Eklund and Lindström 1991). Improvements in optical properties will have to be balanced between removal of ink and losses of bright fillers (Ben et al. 2003, 2004). Our previous study on paper machine runnability (Haapala et al. 2010) indicates that gains in extractives and stickies content reduction can also be significant through the reduced rate of deposit formation and concurring web breaks.

Although flotation studies aimed at water purification are scarce, some references can be made to deinking flotation, which has the same operational principle. Both pulp and process water flotation appear to follow first order kinetics, and thus removal of contaminants is dependent directly on flotation time and component concentration (Korpela 2006; Ricard et al. 2008). However, the issue remains that the vast majority of available flotation studies have been made using chemicals to promote selective separation of contaminants, making the comparison of results troublesome.

White Water Flotation and Solids Losses

As stated before, in addition to contaminant removal in flotation some valuable material, such as fibers and minerals, are lost in froth, which lowers the yield and thus decreases the profitability of the process. In industrial processes the solid losses are controlled with e.g. soap addition, air to water feed ratio, froth layer height, and froth washing. Surfaces of filler components in deinking processes are considered more contaminated by hydrophobic contaminants, and thus their removal can be well justified by gains in optical pulp properties (Carré et al. 2001; Røring et al. 2002). The highest total losses come from the mineral fillers and to some extent from fiber fines (Carré et al.

2001; Røring et al. 2002; Körkkö et al. 2008). Fiber component losses have been reported to occur linearly to the volume of water removed in flotation (Ajersch and Pelton 1996). While the fibers and fiber fines are hydrophilic in nature, and it is widely believed that they are removed only by entrainment, it has been suggested that sticky, calcium-precipitated particles can attach onto them and assist in especially the removal of fine particles (Drabek et al. 1998). Also the contamination of fines and fiber makes their surface more hydrophobic and favors their entrainment in froth (Rundlöf et al. 2000a,b; Ricard and Dorris 2007).

In our case the froth was allowed free buildup, and it led to a rapidly increasing solids removal. The flotation performance was not optimized by any external process aid. Losses of total solids in white water flotation appeared to be reasonable for very brief flotation times, resulting in losses of around 10% for both WW-DIP and WW-MP (Table 2) at just after one minute. With longer treatments the losses accumulated rapidly to levels that were not appropriate for practical papermaking operations, although at the same losses, an increased reduction in the concentrations of all monitored detrimental substances was observed. In the case of WW-DIP the removed froth contained 70% of inorganic filler, while in WW-MP the level of ash in the process was in general low and the removed froth contained only 30% of filler. Thus, the costs in terms of solid losses are likely to be higher in the mechanical pulp rather than in recycled paper processes.

In our studies the range of total solid losses studied gives a fairly good insight into the efficiency limits of non-chemically aided white water flotation. The target losses in process scale flotation are case sensitive but should always be low, likely around a few percentage units of total solids. However, as usual in flotation processes, the losses of solids and the final removal efficiency gained on a component level can be obtained more easily when arranging a secondary flotation (or some other separation process) stage in a cascade mode. Also, as pointed out by e.g. Ricard et al. (2008), even a partial treatment of white water volume removes unwanted components and provides beneficial effects.

White Water Frothing

The single most definite physicochemical prerequisite for white water flotation to work is the ability of water to produce froth and a froth layer stabile enough to trap particles. The presence of calcium ions is generally required for the collecting effect of hydrophobic particles. The accumulated fillers in white waters provide sufficient levels of calcium ions, which are also reacting with anionic surface active compounds by precipitating them into solid particles that are believed to be part of the collector system commonly used for deinking applications. However, a certain amount of soluble surface active compounds must also be present to create foam on top of the flotation cell where floated materials will be suspended. Commonly these are provided by coating components, wood extractives, and deinking chemical residue (Hubbe 2007a). Hence, the stability of white water to froth is very case dependent and generalizations can be hazardous.

Froth produced by the studied WW-MP was fairly weak, but the layer thickness in the flotation cell was visually noted as slightly higher than in WW-DIP. This could be an effect of the water hardness. The softer water of WW-MP results in a low concentration of calcium soaps, which can otherwise have defoaming effects in suspensions (Zhang et al. 2004; Lim 2009). As seen in the case of WW-OCC, the frothing tendencies of white waters are not always suited for spontaneous frothing, which means that the flotation treatment cannot be applied to all mill cases. The reason behind the defoaming effect of OCC water remains unclear, as froth generation is dependent on several physicochemical factors. The most important factor is of course the presence of surfactants required for froth generation. Thus, one possibility is the overall low concentration of surfactants in the white water, as OCC does not contain two major sources of surfactants present in DIP process: deinking chemicals (OCC lacks deinking flotation) and coating colors and fines from recycled coated paper. However, no data can be presented to support this theory.

The only significant difference in the properties of WW-OCC was its unusually high hardness, 171 °dH, or 1220 ppm as calcium concentration. As reported elsewhere (Zhang et al. 2004; Lim 2009), froth stability can be weakened by the presence of calcium soaps, possibly caused by the interaction between the calcium ions in the process water and fatty acids, such as oleic acid, originating from the wood fibers or the deinking chemicals (such as in WW-DIP). This defoaming effect of calcium and magnesium soaps is well known but not well understood. The content of fatty acids was very similar in both white waters, so its relation to water frothing cannot be determined in this study.

In addition, the commonly used defoamer chemicals are likely to hinder froth formation. As no information was obtained from their dosing to process waters, they can also be considered as a likely candidate for poor froth formation. This aspect should also be considered when different white waters are tested for their frothing capabilities in order to obtain realistic estimates on the potential of selective flotation usage, as no defoamer would be present if such a process was actively in use at paper machine loop.

Removal of Ink in White Water Flotation

Ink removal from WW-DIP can be considered effective even for short flotation times, where a reduction of 27% was observed. It was considered that the most hydrophobic inks and toner particles were removed most quickly during the first few minutes of flotation. This was confirmed by visual observation of the froth buildup, where the colored ink residue (Fig. 2) was no longer present or visible to naked eye after froth had been removed for more than a minute.

Moderate ink removal can also result from fragmentation of ink present in process waters (Ricard et al. 2008). The bulk of the ink particles circulating in the paper machine loop are constantly affected by stresses in pumping, screening, and filtration through a fiber mat in the former. They must therefore be very small in size and, as shown in Fig. 3, their removal decreases after a certain extent of flotation. This supports a conclusion that most of the free ink in process waters is below 10 μm, the size range that is reportedly poorly removable in flotation (Holik 2000).

The results differ slightly from the column flotation trials reported by Dionne et al. (2007). Interpolation of their data shows a less than 10% reduction after one minute of column flotation, reaching down to 64% after 6 minutes, although no information on corresponding solids losses is reported. Similarly for Ricard et al. (2008) no promoted ink removal was observed in the beginning of the flotation. Their results indicate poor ink removal in short flotation (~5%), reaching 33% after 11 minutes with 47% removal of ash, while the total solids removal is not reported. In addition, the variance between separation efficiencies as well as the kinetics of flotation differs slightly, as both column flotation trials reported a linear removal of ink with respect to flotation time. This can be attributed to the dynamic nature of column flotation, which does not allow separation of hydrophobic material at the air-water interface prior to experiments, as in batch laboratory flotation. The higher removal of ink obtained by Dionne et al. (2007) can be attributed to a longer residence time of froth and froth washing in the column that are known to promote ink removal.

Removal of Stickies in White Water Flotation

In addition to ink particles, recycled pulp usage leads to accumulation of adhesives and hot melt glues in the paper machine circulation. These are tacky, easily depositing materials with a high potential to result in serious runnability problems on paper machines (Hubbe et al. 2006; Sarja 2007). Despite the need for their removal, no previous results have been reported on stickies removal by selective flotation from white waters at the paper machine loop.

The good floatability of micro stickies and ink is due to the same mechanism for removal: they are both hydrophobic and have optimal size distributions for flotation – from a few micrometers up to about 100 μm (Sarja 2007). The flotation performed well in our white water flotation (Fig. 5): a rapid initial drop of 45% in stickies concentration at a 10% solids loss was followed by a lower but consistent decrease in stickies content. The stickies content was initially quite low, 8.5 mg/L (2.4 mg/g) relative to e.g. effluent waters from a deinking line which have been measured at 15–45 mg/L (Sarja 2007).

As a reference, reduction in stickies concentration in deinking flotation was reported in a study of eight mills, and it varied from 48 to 81% (Sarja 2007). When the separation was continued in a second flotation stage, screening, cleaning, dewatering, etc., the total reductions in stickies concentrations varied from 74 to 92%. This indicates that a considerable amount of stickies are being carried over to the paper machine and that the removal of stickies by selective flotation is good from both pulp and water. Hence, the applicability of selective flotation in paper machine environment appears reasonable, although so far the related research has concentrated on their separation in pulping (Johansson et al. 2003; Lee and Kim 2006) or effluent water treatment in DAF (e.g. Ben et al. 2003; Perrin and Julien Saint Amand 2006).

Removal of Wood Extractives

Wood extractives, i.e. pitch components, accumulate in process streams, commonly originating from mechanical pulp or recycled pulp, where the share coming from chemical pulp is commonly quite small. They are partially removed from the process already in pulping or deinking via washing, thickening, or microflotation. Alternatively, the extractives are further treated in paper machines with passivation agents or fixatives, although according to a recent study (Murray et al. 2009) pitch has a stronger affinity for pitch-covered surfaces than for polysaccharides. Hence the pitch particles can serve as nucleation centers for further pitch adsorption rather than attaching onto fibers, depending e.g. on pH and suspension composition, which have substantial effects on the precipitation of pitch components. Due to the hydrophobic nature of extractives, flotation has high potential for their removal from process streams. As seen from Fig. 6, the total concentration of extractives in WW-MP was high in relation to the

WW-DIP in total extracts detected in an untreated white water. This is common for mechanical pulps, as the pulping lines contain fewer cleaning stages than the deinking lines used for recycled fibers (MacNeil et al. 2004).

Richardson and Grubb (2004) reported an 80 to 90% removal of fiber-bound and colloidal wood extractives in a DAF unit. Saarimaa et al. (2006) reported that up to 90% of pitch could be removed by DAF at pH 5, when most of the extractives are in colloidal form. MacNeil et al. (2004) showed very good fatty acid removal in flotation, but quite poor resin acid removal from DIP furnish when investigating three deinking lines. Similarly Korpela (2006) showed that with a chemically aided laboratory flotation, up to 85% of total resin can be removed from mechanical pulp.

These processes, however, were chemically aided to obtain maximum removal efficiency. Recent studies utilizing column flotation of white waters without chemicals present, with extended treatment times of 6 to 11 minutes, showed a dissolved and colloidal material (DCM) removal of 73% (Ricard et al. 2008) and 85% (Dionne et al. 2007). Our results showing a total extractives reduction up to 65% and 50%, as summarized in Table 3, appear to be in good agreement with these results, given the briefer flotation times used. Results from Dionne et al. (2007) and Ricard et al. (2008) corresponding to 1 minute of flotation show DCM removal of 30% and 22%, respectively. In our studies, the total extractives removal at around 1 minute of flotation was 26% (WW-DIP) and 33% (WW-MP).

Removal rates of all white water schemes can be considered good, given the short treatment times and lack of flotation aids. The extractives content in WW-MP presented in Fig. 7 appears to consist mainly of triglycerides and resin acids, which are commonly found at high concentrations in mechanical pulps, due to the lack of breakdown of the triglycerides to fatty acids during storage (Ekman 2000) or the alkaline environment found in recycled fiber processes. Our results indicate that flotation removal slightly promotes the removal of triglycerides above other extractive groups. The fact that the decrease in triglyceride content is highest is likely due to the near-insoluble nature of the triglycerides and the quite high solubility of resin acids, even in hard water (MacNeil et al. 2010). In the case of WW-DIP, also the fatty acids and sterols group had better removal than resin acids or steryl esters. The practical conclusions from the papermaking point of view can be drawn from the removal of total extracts content. The total extracts content can be indirectly determined through standard mill measurements, such as turbidity (Sarja 2004). Other indirect methods also exist, such as determination of total organic content in a particular size range (Haynes 2003). However, access to more advanced instrumentation in this study allowed for more direct and accurate determination of both total extract content as well as different component groups.

Selectivity of White Water Flotation

Previous studies of deinking flotation of pulps have shown that selectivity of component removal descends in the following order: ink, fiber fines, ash, short fibers, and finally long fibers (Körkkö et al. 2008). While the selectivity of ink was fairly high at a Q index value 0.74, considerably higher selectivity was obtained for stickies (0.87) and wood extractives, excluding the resin acids. The results for resin removal were, however, somewhat biased due to the inaccuracies in their measurement.

Sarja et al. (2007) reported that in deinking flotation, stickies are removed in pulp flotation faster or at the same rate as ink. The result is in good agreement with our results that indicate that stickies are readily removed from white waters by frothing. In another previous study (Korpela 2006) reports that typical pitch components are all removed at the same rate in flotation. In our case, only steryl esters (*Q* 0.76-0.78) and the resin acids were (*Q* 0.63-0.69) deviated from other wood components. As a group, the wood extractives had a fairly high selectivity, and all tested components had a selective nature of removal. The good selectivity obtained for component removal indicates that even a brief flotation and low froth removal results in a considerable removal of contaminants.

Benefits from White Water Purification

Problems in paper production related to various hydrophobic contaminants present in paper machine stock streams and white water are widely recognized. The removal efficiencies of these detrimental components in our flotation trials can be considered sufficient to significantly improve paper process efficiency, as it reduces the rate at which materials accumulate and lowers the highest and most problematic contaminant concentrations. For example, the rate at which stickies and extractives plug the press felts will be reduced, providing more production time in between machine washes.

The financial benefits of such purification schemes must be considered individually for each case, but experience has shown that continuous savings add up considerably over long periods of time. If the smaller content of stickies and extractives saves one web break and 20 minutes of production in a week and one wash break per year, this gives one extra day of production per year. The impact and benefits obtained are likely to be highest on paper machines suffering the most with their detrimental contaminants load.

CONCLUSIONS

1. With white waters that generate froth, a significant separation potential of contaminants with selective flotation exists for cleaning process waters. Some waters may, however, be unable to produce enough stabile froth to be rejected in flotation, and hence the matter remains case-sensitive. Reasons for this can be either absence of surfactants, a defoaming effect of a high calcium and magnesium concentration through precipitation with fatty acids, or the use of defoamer chemicals.
2. Purification of white waters in a chemically unaided selective flotation can remove significant amounts of hydrophobic contaminants from the paper machine short circulation: Reductions of 27% of ink, 45% of stickies, and 26% in total wood extractives content were observed in laboratory trials with a reasonable 10% loss of total white water solids after just one minute of flotation. The best removal of wood extractives was seen for triglycerides and the group of fatty acids and sterols. Along with stickies they also had the highest removal selectivity. Continuing the flotation process to higher levels increases the contaminant removal but also results in yield losses that are not economically sustainable.

ACKNOWLEDGEMENTS

Financial support from Metso Inc. paper group and the international PaPSaT doctoral program are gratefully acknowledged. Also the patient assistance during flotation trials by Ms. Terhi Suopajärvi and Mr. Tommi Niskanen are greatly appreciated.

REFERENCES CITED

Allen, S. L., Allen, L. H., and Flaherty, T. D. (1993). "Defoaming in the pulp and paper industry," in: *Defoaming: Theory and Industrial Applications*, Garrett, P. R. (ed.), CRC Press, 344 pp.

Ajersch, M., and Pelton, R. (1996). "Mechanisms of pulp loss in flotation deinking," *J. Pulp Pap. Sci.* 22(9), 338-345.

Ben, Y., Dorris, G., Hill, G., and Allen, J. (2003). "Contaminant removal from deinking process water, Part I: Mill benchmarking," *Pulp Pap. Can.* 104(1), 42-48.

Ben, Y., and Dorris, G. (2004). "Characterization of dissolved air flotation rejects," *Pulp Pap. Can.* 105(11), 28-33.

Brune, O. (1917). "Verfahren zum Ausscheiden von Harzen, Fetten und Ölen aus Zellstoff, Holzstoff und aus Holz erzeugten Papierstoffen," D.R.P. 310554.

Carré, B., Vernac, Y., and Beneventi, D. (2001). "Is there something interesting to recover in flotation deinking froths?," *Pulp Pap. Can.* 102(6), T152-T155.

De Grado, A. F., Lascar, A., Pottier, S., Carré, B, and Zeno, E., (2010). "How to improve paper mill efficiency by a global control of surface active substances S.A.S," *Conf. Proc. of PTS-CTP Deinking Symposium*, Munich, Germany, 27-29 April, Paper 20.

Dionne, Y., Ricard, M., Dorris, G., and Daneault, C. (2007). "Flotation column: A process unit for cleaning up paper machine whitewater circuits," *Conf. Proc. of 8th Research Forum on Recycling*, Niagara Falls, Canada, 23-26. September, 321-328.

Drabek, O., Sterne, J., and van de Ven, T. G. M. (1998). "Effect of deinking chemicals on the deposition of fines and fillers on an air-water interface," *J. Pulp Pap. Sci.* 24(4), 116-120.

Eklund, D., and Lindström, T. (1991). *Paper Chemistry, an Introduction*, DT Paper Science Publications, Grankulla, Finland, 305 p.

Ekman, R. (2000). "Resin during storage and in biological treatment," in *Pitch Control, Wood Resin and Deresination*, Back, E. L., and Allen, L. H. (eds.). TAPPI Press, Atlanta, 185-204.

Gabl, H., Hamm, U., Bobek, B., Putz, H-J., Schabel, S., Hamann, L., Cordier, O., Kappen, J., and Pauly, D. (2006). "Sticky and trash removal techniques for water loops in paper mills," *Paper Tech.* 47(September), 31-34.

Haapala, A., Körkkö, M., Laitinen, O., and Niinimäki, J. (2009). "Methods for process water ink content analysis," *Conf. Proc. of TAPPI EPE*, Memphis, TN, USA, October 14-16.

Haapala, A., Liimatainen, H., Körkkö, M., Ekman, J., and Niinimäki, J. (2010). "Runnability upgrade for a newsprint machine through defect identification and control - A mill case study," *Conf. Proc. of 64th Appita Annual Conf.*, Melbourne, AUS, April, 18-21.

Haynes, D. (2003). "Measurement of micro stickies formation," *Prog. Pap. Recycl.* 12(2), 19-26.

Helle, T. (2008). "Characterization and removal of gas in papermaking," Dissertation, Helsinki University of Technology, Finland, 51 pp.

Holik, H. (2000). "Unit operations and equipments in recycled fiber processing", In: Göttsching, L. and Pakarinen, H., *Recycled Fiber and Deinking*, Fapet Oy, Jyväskylä, Finland, 94 p.

Holmbom, B., and Sundberg, A. (2003). "Dissolved and colloidal substances accumulating in papermaking process waters," *Wochenblatt für Papierfabrikation*, 131(21), 1305-1311.

Hubbe, M. A. (2007a). "Water and papermaking 2. White water components," *Paper Tech.* 48(2), 31-40.

Hubbe, M. A. (2007b). "Water and papermaking 3: Measures to clean up process water," *Paper Tech.* 48(3), 23-30.

Hubbe, M. A., Rojas, O. J., and Venditti, R. A. (2006). "Control of tacky deposits on paper machines – A review," *Nord Pulp Pap. Res. J.* 21(2), 154-171.

Johansson, H., Wikman, B., Lindström, E., and Österberg, F. (2003). "Detection and evaluation of micro-stickies," *Prog. Pap. Recycl.* 12(2), 4-12.

Korpela, A. (2006). "Removal of resin from mechanical pulps by selective flotation: Mechanisms of resin flotation and yield loss on fibers," *J. Wood Chem. Tech.* 26(2), 175-186.

Käyhkö, J. (2002). "The influence of process conditions on the deresination efficiency in mechanical pulp washing," Dissertation, Lappeenranta University of Technology, Digipaino, 112 pp.

Körkkö, M., Laitinen, O., Vahlroos, S., Ämmälä, A., and Niinimäki, J. (2008). "Components removal in flotation deinking," *Prog. Pap. Recycl.* 17(4), 15-22.

Lee, H. L., and Kim, J. M. (2006). "Quantification of macro and micro stickies and their control by flotation in OCC recycling process," *Appita J.* 59(1), 31-36.

Leiviskä, T., and Rämö, J. (2008). "Coagulation of wood extractives in chemical pulp bleaching filtrate by cationic polyelectrolytes," *J. of Hazardous Materials* 153, 525-531.

Lim, J. C. (2009). "Effect of formation of calcium carbonate on foam stability in Neodol 25-3S anionic surfactant Systems," *J. Ind. Eng. Chem.*, 15, 257-264.

Ljunggren, M., and Jönsson, L. (2003). "Separation characteristics in dissolved air flotation – Pilot and full-scale demonstration," *Water Sci. Tech.* 48(3), 89-96.

MacNeil, D., Holmbäck, Å., Lassus, A., Hoel, H., Røring, A., and Holmbom, B. (2004). "Removal of fatty and resin acids in European deinking processes," *Prog. Pap. Recycl.* 14(1), 6-13.

MacNeil, D., Sarja, T., Reunanen, M., Xu, C.-L., and Holmbom, B. (2006). "Distribution of stickies in deinked pulp, Part I: Methods for extraction and analysis of stickies," *Professional Papermaking* 1/2006, 10-14.

MacNeil, D., Sundberg, A., Vähäsalo, L., and Holmbom, B. (2010). "Effect of calcium on the phase distribution of resin and fatty acids in pitch emulsions," *J. Disp. Sci. Tech.*, (In press)

Murray, G., Stack, K., McLean, D. S., Shen, W., and Garnier, G. (2009). "Dynamics of colloidal pitch adsorption at the solid–liquid interface by surface plasmon resonance," *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 341, 127-133.

Nelson, G. L. (1981). "The screening quotient: a better index for screening performance," *Tappi Journal*, 64(5): 133-134.

Perrin, B., and Julien Saint Amand, F. (2006). "Deinking rejects analysis in newsprint and copy paper mills," *Conf. Proc. of 12th PTS-CTP Deinking Symposium*, Leipzig, Germany, 25-27 April, Paper 31.

Ricard, M., and Dorris, G. (2007). "Recirculation contaminates whitewater solids. Part II: Contamination of fines and fillers by extractives and metals," *Preprints of 93rd an. meeting of the Pulp and Paper Technical Association of Canada*, v B, p B263-B270.

Ricard, M., Dorris, G., Lapointe, C., Dionne, Y., and Daneault, C. (2008). "Prospects of using column flotation to decontaminate paper machine whitewater," *Conf. Proc. of PTS-CTP Deinking Symposium*, Leipzig, Germany, 15-17. April, 34, 1-16.

Richardson, D., and Grubb, M. (2004). "Extractives removal from newsprint mill process waters by dissolved air flotation," *Conf. Proc. of 58th Appita Annual Conf.* Canberra, Australia, 19-21 April, 79-84.

Røring, A., and Wackerberg, E. (1997). "Characterization of deinking white water – Influence on flotation and bleaching efficiency," *Pulp Pap. Can.* 98(5), 17-21.

Røring, A., Øvrum, T., Røstad, T., and Harbak, G. E. (2002). "Hunting high yield," Proc. of PTS-CTP Deinking Symposium, Munich, Germany, 23-26 April, 19, 1-13.

Rundlöf, M., Htun, M., Höglund, H., and Wagberg, L. (2000a). "Mechanical pulp fines of poor quality - characteristics and influence of white water," *J. Pulp Pap. Sci.* 26(9), 308-316.

Rundlöf, M., Sjölund, A-K., Ström, H., and Asell, I. (2000b). "Effect of dissolved and colloidal substances released from TMP on the properties of TMP fines," *Nord Pulp Pap. Res. J.* 15(4), 256-265.

Saarimaa, V., Sundberg, A., Holmbom, B., Blanco, A., Negro, C., and Fuente, E. (2006). "Purification of peroxide-bleached TMP water by dissolved air flotation," *Tappi J.*, 5(5), 15-21.

Sarja, T., Zabihian, M., Kourunen, P., and Niinimäki, J. (2004). "New method for measuring potential secondary stickies in deinked pulp filtrates," *Water Sci. Technol.* 50(3), 207-215.

Sarja, T. (2007). "Measurement, nature and removal of stickies in deinked pulp," dissertation, University of Oulu, Finland, 82 pp.

Sarja, T., MacNeil, D., Huber, P., and Niinimäki, J. (2007). "Removal of stickies in flotation," *Prog. Pap. Recycl.* 16(3), 5-11.

Sitholé, B. B., and Allen, L. (2002). "The effects of wood extractives on system closure," *Tappsa J.* 105(7), 22-30.

Stoor, T. (2006). "Air in pulp and papermaking processes," Dissertation, University of Oulu, Finland, 66 pp.

Sundberg, A., Holmbom, B., Willför, S., and Pranovich, A. (2000). "Weakening of paper strength by wood resin," *Nord Pulp Pap. Res. J.* 15(1), 46-53.

Valto, P., Knuutinen, J., Alén, R., Rantalankila, M., Lehmonen, J., Grönroos, A., and Houni, J. (2010). "Analysis of resin and fatty acids enriched in papermaking process waters," *BioResources* 5(1), 172-186.

Xu, Y., and Deng, Y. (2004). "The buildup of dissolved solids in closed white water systems," *Tappi J.* 3(8), 17-21.

Zhang, H., Miller, C., Garrett, P., and Raney, K. (2004). "Defoaming effect of calcium soap," *J. Colloid Surf. Chem.* 279, 539-547.

Örså, F., and Holmbom, B. (1994). "A convenient method for the determination of wood extractives in papermaking process waters and effluents," *J. Pulp Pap. Sci.* 20(12), J361-J365.

Article submitted: June 18, 2010; Peer review completed: July 14, 2010; Revised version received and accepted: August 11, 2010; Published: August 12, 2010.