FLOTATION DE-INKING OF 50% ONP/ 50% OMG RECOVERED PAPERS MIXTURES USING NONIONIC SURFACTANT, SOAP, AND SURFACTANT/SOAP BLENDS

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A laboratory flotation column equipped with Venturi aerators and an adjustable froth removal system was used to study the effect of calcium soap and a mixture of calcium soap/alkyl phenol ethoxylate surfactant on ink and fibres transfer during flotation de-inking of a 50% old newprint (ONP) / 50% old magazines (OMG) recovered papers mixture. Mass transport phenomena determining the yield of the flotation process were interpreted using model equations describing particle removal in terms of flotation, entrainment, and drainage in the froth. A decrease in the ink and mineral fillers flotation rate constant, drainage through the froth, and in fibre entrainment was observed when increasing the surfactant concentration. These trends were consistent with the typical dispersing action of the studied nonionic surfactant. An opposite effect on ink and fillers was observed when using calcium soap alone, and the increase in the flotation rate constant and drainage through the froth were consistent with the collecting and defoaming action of the calcium soap. Moreover, fibre entrainment decreased when increasing the soap concentration. The study of the surfactant/soap mixture highlighted the absence of synergy between the calcium soap and the surfactant.

Keywords: Flotation de-inking; Nonionic surfactant; Calcium soap; Separation selectivity

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INTRODUCTION

During the last thirty years, froth flotation has become an established technology for the removal of ink particles from waste paper slurries, allowing the production of de-inked pulps with acceptable optical properties, a decreased loss of cellulosic material (Scott and Smith 1995; Beneventi et al. 2007a), and an ever-increasing use of de-inked pulp for paper manufacturing. The utilization rate of de-inked fibres for manufacturing of newsprint and graphic papers reached in Europe 92% and 10% respectively (CEPI 2009). However, the amount of residual ink still present in de-inked pulps (Lapierre et al. 2004; Zhu et al. 2005) still limits their use for manufacturing high quality grade papers. Presently these grades require high brightness, discriminating against the use of de-inked fibre in favour of virgin cellulose fibres. In order to overcome these difficulties and to extend the use of recycled fibres to high quality grades, higher ink removal is needed.

However, this usually achieved at the expense of the process yield because, in general, an increase in ink removal corresponds to a decrease in fibre, cellulose fine elements, and mineral fillers recovery (Zhu et al. 2005; Beneventi et al. 2007a). Thus, the improvement of ink selective removal from recovered papers slurries appears necessary for further enhancing the efficiency of the fibre recycling technology and of the de-inked pulp quality.

Recent research showed that ink removal selectivity can be improved by optimizing the layout of flotation deinking banks (Beneventi et al. 2009), controlling ink/fibre drainage in the froth phase (Zhu and Tan 2005; Beneventi et al. 2006), or using chemical additives such as nonionic surfactants (Beneventi et al. 2008), commercial soap/nonionic surfactant blends (Beneventi et al. 2007b), or natural polymeric dispersants (Zeno et al. 2010). Recently, soap/nonionic surfactant blends gained a rather wide usage in flotation deinking mills owing to their positive impact on the ink removal selectivity. Nevertheless, most of the time soap/nonionic surfactant blends are delivered to deinking mills as proprietary pre-formulated batches, and the action mechanisms of these chemicals remain incompletely understood (Theander and Pugh 2004).

The effect of single component deinking chemicals on ink removal from model mixed office wastepaper (MOW) has been thoroughly investigated (Azedevo et al. 1999; Epple et al. 1994; Zhu et al. 1998), and the higher deinking performance of nonionic surfactants when compared to calcium soaps is well documented. Nonionic surfactant addition in MOW slurries allows the stabilizing of air bubbles, the generation of a froth layer sufficient to prevent ink drop back in the pulp slurry, and finally promotion of ink removal. By contrast, according to their defoaming action (Zhang et al. 2003), soaps addition does not improve bubble/froth stability, and ink removal is impaired by the presence of large air bubbles and unstable froth.

Explicit structure/performance correlations have been identified when processing MOW because of the small release of surface active contaminants in process waters by this kind of recovered papers grade and the intrinsic hydrophobic character of toner inks (Drelich et al. 1996; Beneventi et al. 2004). In the presence of recovered papers grades releasing higher amounts of surface active and dissolved-colloidal substances, such as old newspapers (ONP) and old magazines (OMG), soap and nonionic surfactant action can be impaired by the released contaminants. Due to the lack of systemic studies correlating deinking chemicals performance to recovered papers composition, most of the general rules used for the optimization of the deinking chemistry are based on empiricism and mill practice.

Thereafter, as a first step to gain a deeper understanding on soap/nonionic surfactant systems performance in flotation deinking, this work evaluated the contribution of nonionic surfactant, soap, and soap/surfactant mixtures to ink and fibre transport in a laboratory flotation column when processing a 50% ONP/50% OMG mixture. Flexo-printed newspapers were deliberately excluded from the composition of recovered papers used in this study in order to avoid specific neutral-alkaline flotation deinking stages (Galland et al. 1997) that are necessary to improve the low flotability of flexo inks (Galland and Vernac 1993; Dorris and Nguyen 1995).

EXPERIMENTAL

Experimental Procedures

Repulping

A recovered paper mixture of 50% ONP (offset-printed) and 50% OMG (25% rotogravure- and 25% offset-printed, as determined by the visual analysis of the print texture) was repulped in a 20 L capacity helico pulper (Kadant Lamort) during 15 min at 13% consistency and 45°C (Fabry et al. 2001). A flotation deinking chemical formulation (i.e. an alkaline chemistry typically used in European deinking mills processing ONP/OMG mixtures), namely 0.7% NaOH, 0.7% SERFAX MT 90 (mainly composed of sodium oleate), 1% H_2O_2 and 2% Na_2SiO_3 (all dosages are given with respect to dry paper) was added in the pulper in order to promote ink detachment from cellulose fibres, its subsequent agglomeration, and to limit the yellowing of fibres. Then, the pulp was diluted to 0.8% and stored in a chest at 45°C. The calcium ion concentration of tap water used during the repulping and the subsequent dilution was adjusted to 150 mg/L by adding $CaCl_2$.

Flotation

Before running flotation trials, an aliquot sample of the pulp slurry, 150 L, was separately pre-conditioned for 15 minutes with a nonionic surfactant, namely nonylphenol ethoxylate 20EO (NP20EO) at concentrations ranging between 0 and 16 µmol/L, with the sodium soap used during the re-pulping stage (SERFAX MT 90) at concentrations ranging between 0 and 0.4 g/L or a mixture of both. Both nonionic surfactant and soap dosages were selected in order to cope with chemicals dosage recommended by deinking chemicals suppliers, i.e. 0.01 to 0.1% and 0 to 2% (given with respect to dry paper) for nonionic surfactant and soap, respectively. Relevant properties of the surfactant and of the sodium soap used in this work are given in Table 1.

Table 1. Relevant Properties of Chemicals Used **

Product Name	HLB	M_w (g/mol)	T_{cloud} (°C)	CMC (µmol/L)	Γ_∞ (mol/m^2)	D_{app} (m^2/s)
NP 20 EO	16	1112.5	~72	100	$1.6.10^{-6}$	$2.5.10^{-9}$
SERFAX MT90		284*		~700*	$3.5.10^{-10}$*	$4.6.10^{-10}$*

* Data referring to pure sodium oleate.

** D_{app} is the apparent diffusion coefficient, Γ_∞ is the molecule surface excess at the saturation of the air/water interface and Cmc is the critical micellar concentration in deionised water.

Table 2. Composition of Surfactant/Soap Mixtures used during Flotation Trials

C_{soap} (g/L) \ $C_{surfactant}$ (µmol/L)	0	1.6	3.2	6.4	16
0	X	X	X	X	X
0.05	X	X		X	X
0.1	X			X	
0.2	X			X	
0.4	X	X		X	X

The compositions of the soap/nonionic surfactant blends used during the flotation trials are summarized in Table 2. Continuous flotation experiments were performed using a laboratory flotation column operated in continuous mode (Beneventi et al. 2006). For all tested chemistries, the flotation cell was fed with a constant pulp flow of 2 L/min and an air flow of 4 L/min, which was injected via the static injectors placed at the base of the column. For each chemical formulation, the froth removal thickness was adjusted by placing a vacuum funnel 1 cm above the pulp/froth interface. Pulp samples were collected after 15 min flotation, and the froth removal thickness was subsequently increased to 2 cm. This procedure made it possible to collect pulp samples under steady state conditions (Beneventi et al. 2006). Then, the froth removal thickness was increased to 4 cm and finally to the maximum froth thickness attainable. Again, pulp samples were collected after 15 min flotation and for each removal thickness. At each froth removal thickness, froth samples were collected during 5 min after 10 min flotation.

Flotation trials corresponding to each chemical condition were duplicated, and particle removal data displayed a scatter of less than 10 %. The average value of two runs was therefore considered for data processing.

Pulp characterization

In order to establish a complete mass balance, the consistency and the weight of pulp samples were measured. To avoid ink and fillers washing during filtration, pulp pads of ca. 400 g/m^2 were prepared by filtrating pulp/froth slurries on a Büchner funnel (Whatman grade 2 paper filter) after pre-conditioning with aluminium sulphate and cationic polyacrylamide (Carré et al. 1994). For each sampling point, one and three pulp pads where prepared for the froth and the floated pulp, respectively. The residual ink content (ERIC) in pulp pads was determined by measuring pad reflectance at 950 nm (Jordan and Popson 1994) (3 measurements for each pad side), and the ink concentration in the pulp slurry was estimated by using Eq. (1) (Beneventi et al. 2006),

$$c_{ink} = ERIC \cdot c_{pulp} \frac{r_{ink}}{r_{flexo}} \tag{1}$$

where c_{pulp} is the pulp concentration, r_{ink} is the average diameter of ink particle, and r_{flexo} is the average diameter of reference ink particles, viz. ~13 and 0.5 µm (Dorris and Nguyen 1995; Chabot et al. 1996), respectively. Fibre and mineral fillers fractions in the pulp composition were determined by weighing long fibres remaining on a 200 mesh wire screen after thorough washing and by dry pulp/froth ignition and overnight storage in an oven at 425 °C, respectively. The composition of the recovered pulp slurry before flotation is given in Table 3.

Table 3. Pulp Properties Before Flotation

Consistency (g/L)	Ash (%)	Fines (%)	Fibre (%)	ERIC (ppm)	Ink* (%)
8	20.1	22.3	57.6	900	2.1

*Ink fraction calculated from ERIC measurement using Eq. (1).

Online gas hold-up and fibre flocculation measurement

The gas hold-up in the flotation cell was measured after pulp sampling using a commercial gas hold-up sensor (ACS 8-P, PMC, Danbury CT, USA) (Dorris et al. 2006) composed of a rigid hose with 2 pressure gauges spaced at 50 cm. The sensor was installed vertically in the flotation cell, it was calibrated with the pulp slurry before aeration, and the pressure difference was measured after air injection and used to calculate the gas hold-up,

$$\varepsilon_g = 1 - \frac{\Delta P}{\rho_{H_2O} \cdot g \cdot \Delta h} \tag{2}$$

where ΔP is the differential pressure, Δh is the distance between pressure gauges, and ρ_{H2O} is water density.

In order to evaluate the effect of surfactant/soap concentration on pulp flocculation, a simplified device to collect images of the pulp slurry was implemented at the inlet of the flotation column (Allix et al. 2010). Pictures of the pulp slurry were taken in light transmission mode using a digital photo camera (DSC H-5, Sony), and image analysis was used to evaluate the flocculation index, F, which was calculated as the raw moment of second order of the flocs size distribution (Huber et al. 2006),

$$F = \sum_i S_i \cdot D_i^2 \tag{3}$$

where S_i is the global surface of class size floc i, and D_i is the average floc diameter of class size i. The effect of soap and surfactant addition on pulp flocculation was represented by the difference between flocculation indexes measured without chemicals addition (F_0) and after pulp preconditioning with soap/surfactant (F).

Particle Transport Mechanisms

The equations that follow present a transport-based approach to several of the phenomena associated with flotation deinking (Beneventi et al. 2006, 2007a). Suspended solids separation occurring in a flotation deinking column was interpreted using equations modelling transport phenomena in terms of the following unit processes:

Flotation in the aerated pulp slurry.

Particle flotation was described by the typical first order equation (Julien Saint Amand 1999),

$$\left(\frac{dc}{dt}\right)_{flot} = -k \cdot c \tag{4}$$

where c is the concentration of the suspended material subject to flotation (i.e. ink or mineral fillers), and k is its corresponding flotation rate constant.

Large hydrophilic cellulose fibres were not subjected to flotation, and their flotation rate constant was forced to zero when fitting experimental data.

Entrainment in the aerated pulp slurry.

The hydraulic transfer of suspended solids was correlated to their concentration and the water upward flow in the froth,

$$\left(\frac{dc}{dt}\right)_{entr} = -\frac{\phi \cdot Q_f^0}{V} c \tag{5}$$

where ϕ is the entrainment coefficient, $Q^0{}_f$ is the water upward flow in the froth in the absence of drainage (i.e. the froth is removed at the surface of the aerated pulp slurry), and V is the pulp volume in the flotation cell. Since ink and mineral fillers are subjected mainly to flotation (Beneventi et al. 2006), the entrainment contribution in the transport of these two types of particles was neglected. Equation (5) was therefore used to describe fibre transport, and c represents fibre concentration in the pulp slurry.

Drainage in the froth.

The hydraulic entrainment of solids dispersed in the froth was correlated to the water drainage flow, Q_d, by the equation,

$$\frac{dM_f}{dt} = -\delta \cdot c_f \cdot Q_d \tag{6}$$

where dM_f/dt is the downward flow from the froth to the pulp due to drainage of the considered solid (i.e. ink, mineral fillers or fibres), δ is particle drainage coefficient, and c_f is the particle concentration in the liquid phase in the froth.

Equations (4-6) and the typical exponential equation used to model the effect of the froth removal thickness on the water reject stream (Gorain et al. 1998; Zheng et al. 2005) were combined in order to establish a mass balance for water and solids transfer in the aerated pulp slurry and in the froth. Under the assumption of perfect mixing in the aerated pulp slurry and plug flow in the froth, discretized solutions of the equations system where used for the numeric fit experimental data and for extracting transport coefficients. Details of the procedure used for data processing and model assumptions have been described in a previous work (Beneventi et al. 2010). However a simplified rule can be derived from the numeric fit: the flotation rate constant and the entrainment coefficient can be calculated using ink, mineral fillers and fibre concentration variations, Eq. (4) and Eq. (5), respectively, when the froth is removed close to the surface of the aerated pulp (ca. 1 cm in this study). On the other hand, the solid drainage coefficient can be estimated using Eq. (6) and solid material (ink, mineral fillers, fibres) and water reject flows obtained with different froth removal thickness.

RESULTS AND DISCUSSION

Single-Component Systems

Effect of non-ionic surfactant on ink removal and fibre loss.

Figure 1 shows that the addition of nonionic surfactant alone to the pulp slurry depressed ink floatability with a subsequent drop of the flotation rate constant. Above ca. 6 µmol/L, the ink flotation rate constant reached a plateau value. The decrease of the ink flotation rate constant at increasing surfactant concentration was associated with surfactant adsorption at both the bubble/ and ink/water interface, the decrease of air bubble surface tension, ink/water contact angle (viz. ink adhesion to air bubbles) (Beneventi et al, 2008), and to the depression of ink collection by calcium soaps (Johansson and Johansson 2000). In the froth phase, the non-ionic surfactant improved bubble stability and water hold-up, reducing ink re-dispersion and drainage (Fig. 2).

Flotation rate constants and drainage coefficients obtained for mineral fillers (not shown for brevity) displayed trends similar to those obtained for ink particles. This similarity was attributed to the intrinsic good flotability of fillers and the absence of a selective interaction of the nonionic surfactant with ink or mineral particles.

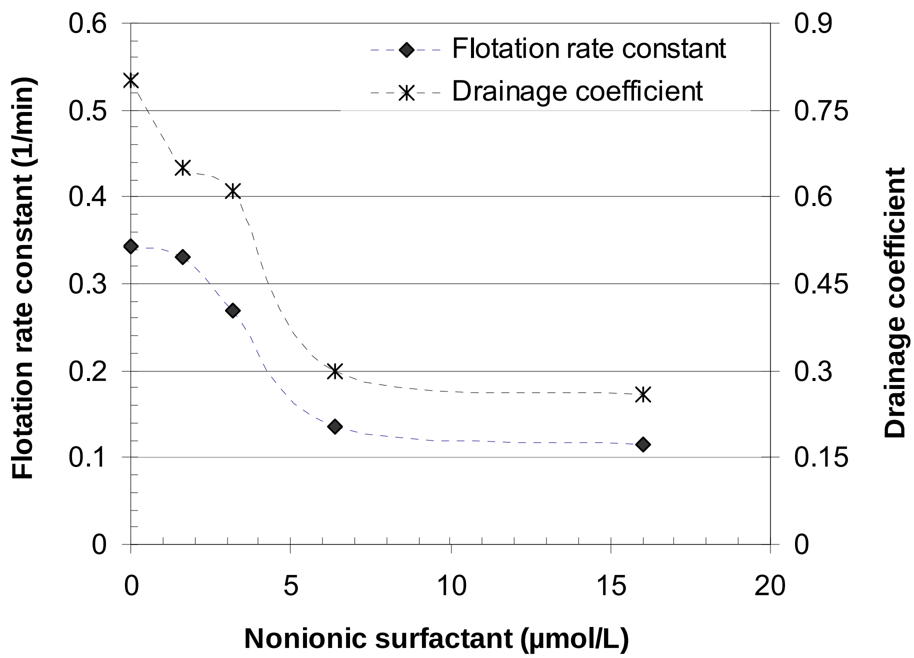


Fig. 1. Ink flotation rate constant and drainage coefficient plotted as a function of surfactant concentration. Dotted lines were added to guide the eye.

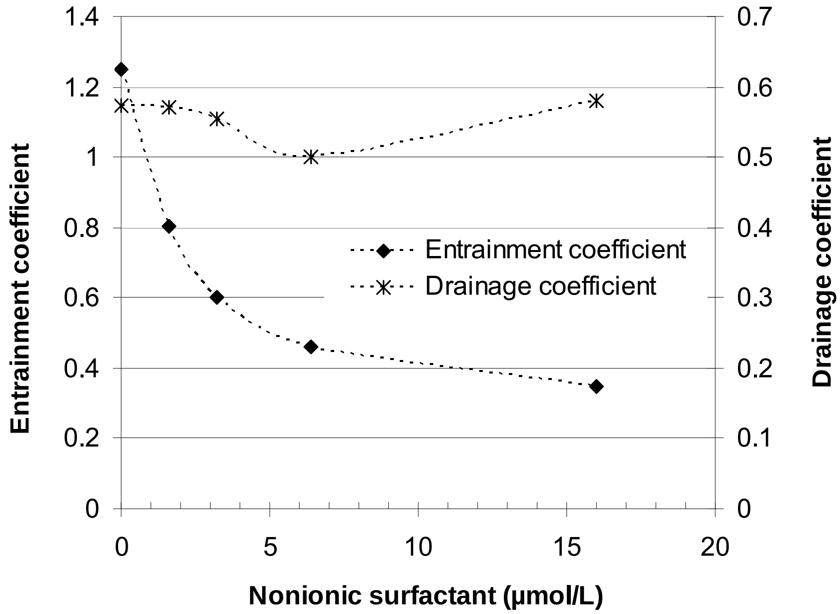


Fig. 2. Fibre entrainment and drainage coefficients plotted as a function of surfactant concentration. Dotted lines were added to guide the eye.

The decrease in the fibre entrainment coefficient shown in Fig. 2 was associated with the fibre dispersing action of the nonionic surfactant, the suppression of fibre flocculation by calcium soap, with a decrease of bubble entrapment in fibre flocs, and with the convective motion of fibre/bubble flocs towards the froth (Beneventi et al. 2008; Zeno et al. 2010).

According to the error estimated for experimental data (ca. 10%), fibre drainage coefficients shown in Fig. 2 displayed a nearly constant value, indicating that fibre drainage was mainly governed by the intensity of the water drainage flow (Zhu and Tan 2005). Indeed, contrary to ink particles, which are re-dispersed in the froth and subjected to drainage when bubbles burst, hydrophilic fibres do not adhere to froth bubbles and are assumed to be subjected only to hydraulic transport.

Effect of calcium soap on ink removal and fibre loss

Figure 3 indicates an increase of the ink flotation rate constant and a slight increase of the ink drainage coefficient, when adding soap alone. The progressive increase of the ink flotation rate constant with soap dosage was ascribed to the typical coagulation of calcium soap on ink particles and their subsequent agglomeration into calcium soap/ink aggregates, which are hydrophobic and highly floatable (Rutland and Pugh 1997). In the froth phase, the addition of calcium soap progressively increased ink drainage (Fig. 3). A possible explanation for this trend is that the characteristic defoaming action of calcium soap (Zhang et al. 2003) promoted bubble bursting, ink detachment, re-dispersion in the liquid phase surrounding froth bubbles, and its drainage down to the pulp slurry. The present findings show that calcium soap promotes ink removal from the aerated pulp slurry while depressing ink transport in the froth phase.

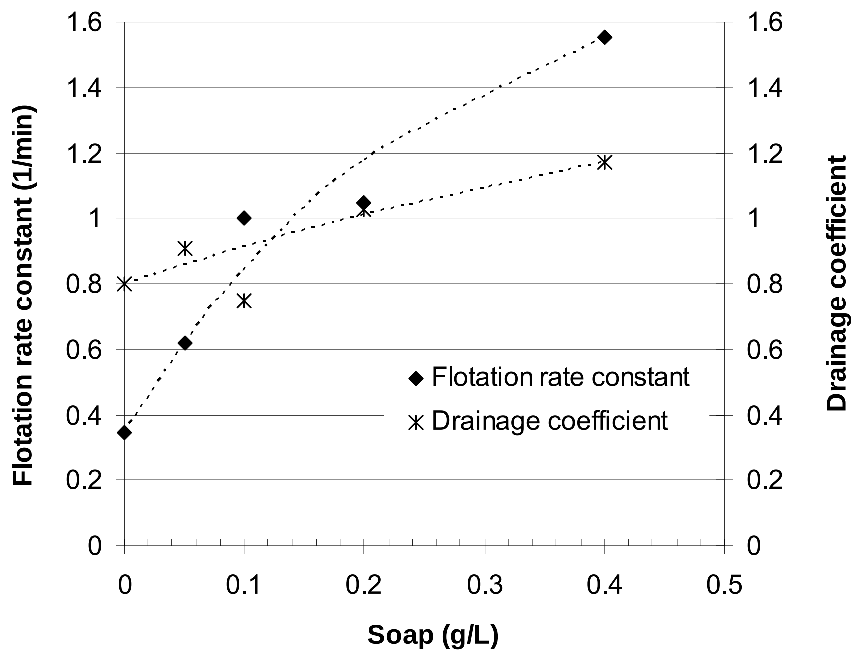


Fig. 3. Ink flotation rate constant and drainage coefficient plotted as a function of surfactant concentration. Dotted lines were added to guide the eye.

The presence of these two concurrent effects on ink transport indicates that optimal conditions for efficient ink removal rely on a delicate balance between: i) ink particles collection by air bubbles in the pulp slurry, which can be tuned by adapting the soap concentration, and ii) ink transport in the froth phase, which can be adjusted by modifying both soap concentration and the froth retention time in the flotation cell. Similarly to ink particles, the addition of soap boosted fillers flotation and drainage (not shown for brevity). As for the nonionic surfactant, this was correlated to the absence of a selective interaction between the calcium soap and pulp components.

Figure 4 highlights a decrease of the fibre entrainment coefficient at increasing soap concentration. This decrease can be explained by the soap effect on the pulp slurry. Indeed, soap addition can lead to both pulp flocculation and bubble coalescence. According to basic mechanisms at the origin of fibre transport in aerated pulp slurries (Ajersc and Pelton 1996; Tang and Heindel 2005), with constant bubble size, pulp flocculation should lead to an intense entrainment of cellulose fibres caused by the entrapment of air bubbles in fibre flocs and the convective motion of fibre flocs/bubble clusters towards the pulp surface. However, under the tested conditions, larger bubbles due to soap-induced coalescence were supposed to break fibre flocs, thus decreasing bubble entrapment and fibre entrainment.

Figure 4 shows that the presence of soap doubled the coefficient value, but increasing concentration of soap had no effect. As observed for ink drainage, this trend was attributed to the defoaming action of calcium soap which, inducing bubble burst and coarsening the froth texture (from visual analysis), was supposed to favour fibre motion in inter-bubble liquid films and their entrainment by the water drainage stream.

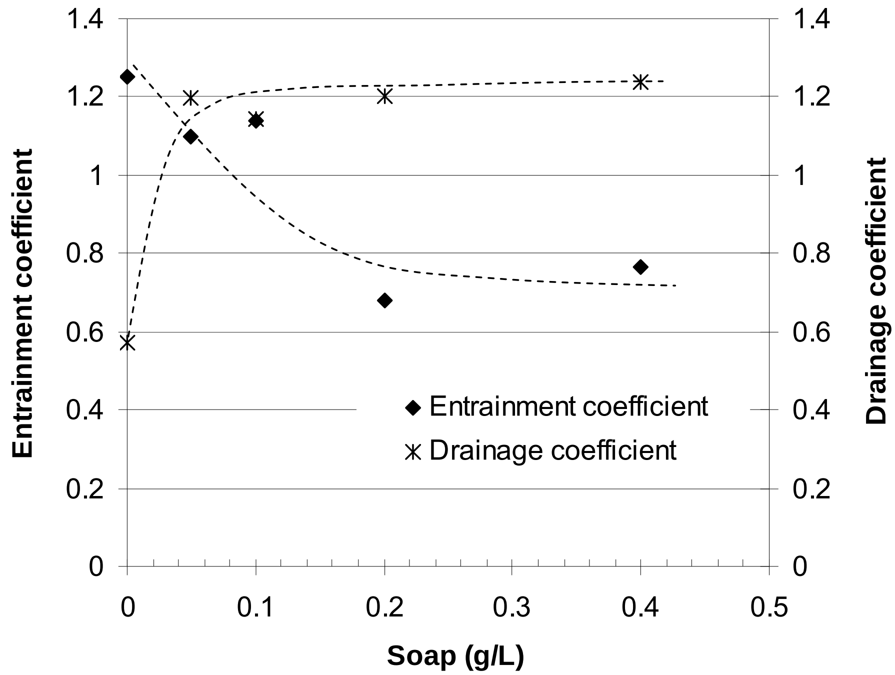
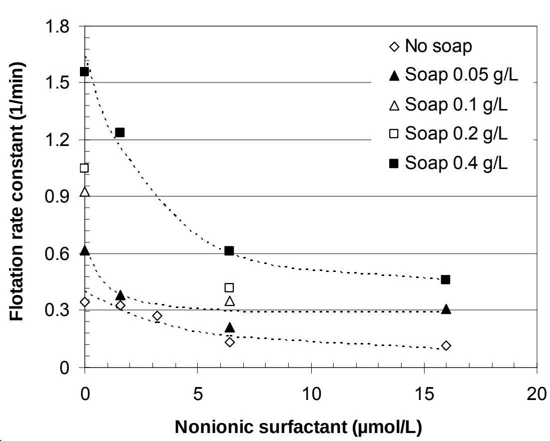


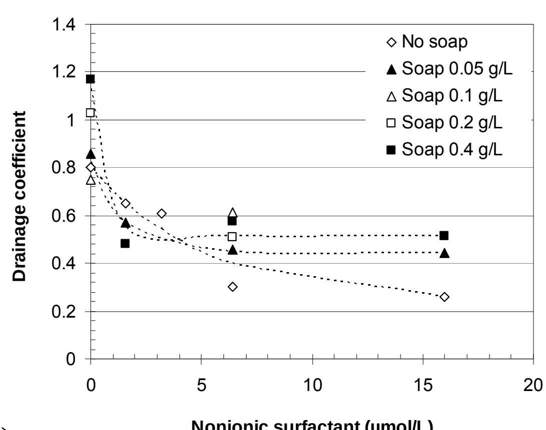
Fig. 4. Fibre entrainment and drainage coefficients plotted as a function of surfactant concentration. Dotted lines were added to guide the eye.

Multi-Component Systems

Figure 5a shows that, whatever the soap dosage, the ink flotation rate constant monotonically decreased at increasing surfactant concentration. A general shift towards higher flotation rate constant values was observed when increasing the soap concentration. Similarly, ink drainage decreased (Fig. 5b) for increasing surfactant concentration, while soap poorly affected ink drainage inducing a slight increase of the drainage coefficient at high surfactant concentration, as obtained for soap alone (Fig. 3).



a)



b)

Fig. 5. Ink flotation rate constant (a) and drainage coefficient (b) plotted as a function of nonionic surfactant and soap concentration. "No Soap" data are replotted from Fig. 1.

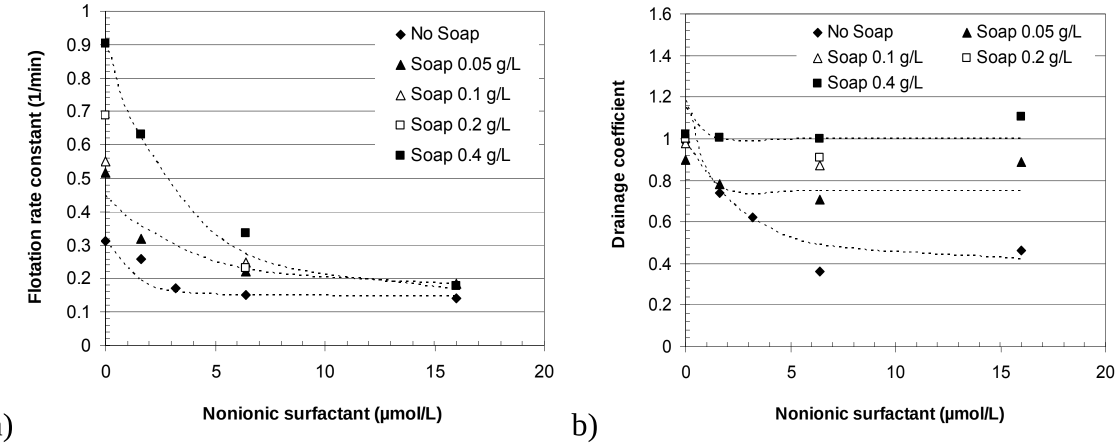


Fig. 6. Mineral fillers flotation rate constant (a) and drainage coefficient (b) plotted as a function of nonionic surfactant and soap concentration

As observed for single component systems, the composition of the surfactant/soap mixture affected mineral fillers flotation (Fig. 6a) in the same way as for ink flotation. For all tested surfactant concentrations, soap addition caused a sizeable increase of fillers drainage (Fig. 6b) which was consistent with both the froth destabilization by calcium soap and the high density of mineral particles.

Fibre entrainment (Fig. 7a) was mainly affected by the nonionic surfactant. Indeed, as observed for the single component system (surfactant only), fibre entrainment dropped off when increasing the surfactant concentration. Moreover, at high surfactant dosage, the slight contribution of calcium soap on the entrainment coefficient was suppressed. In the froth phase the nonionic surfactant accentuated the defoaming action of the calcium soap. Indeed, Figure 7b shows that below 5 µmol/L of surfactant, the fibre drainage coefficient doubled whatever the soap concentration. While, above 5 µmol/L the increase in the calcium soap concentration boosted fibre drainage.

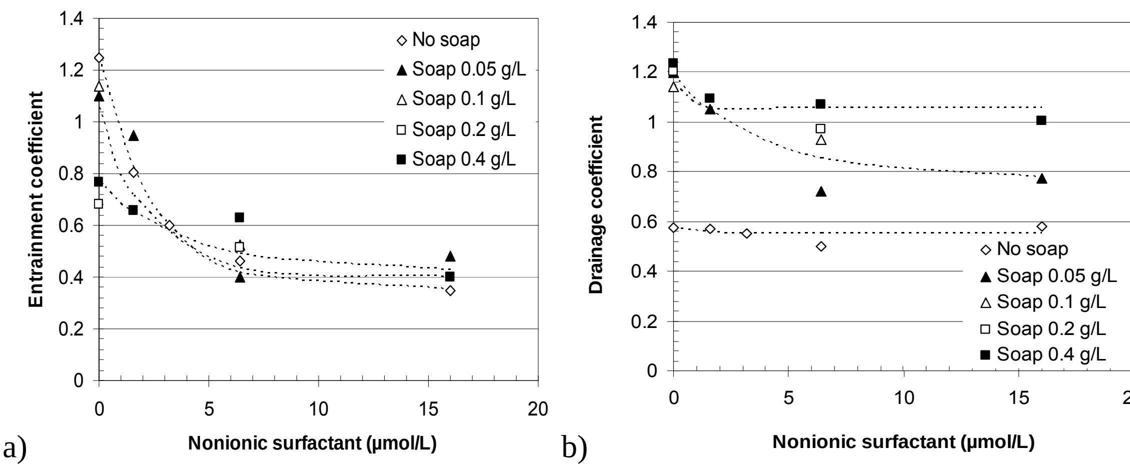


Fig. 7. Fibre entrainment coefficient (a) and drainage coefficient (b) plotted as a function of soap concentration. “No soap” data are replotted from Fig. 2.

This trend was supposed to be due to the onset of different froth stabilization mechanisms, i.e. by particle stabilization and by surfactant stabilization at low and high surfactant concentration, respectively.

In the absence (or at low concentration) of surfactant, a rather unstable froth was generated during flotation. It can be supposed that the froth was stabilized by surfactants released by recovered papers and mostly by the mechanical action of hydrophilic particles (viz. cellulosic and mineral particles). In this condition, a low amount of calcium soap was sufficient to destabilize liquid films between froth bubbles, but the complete collapse of the froth was prevented by the rigid backbone of cellulosic and mineral material. At high surfactant concentration a stable froth with fine texture was generated. A possible explanation is that the froth was stabilized mainly by surfactant molecules adsorbed on bubble surfaces, and the addition of soap progressively destabilized the froth. The visual analysis of the froth (top layer and on column walls) showed that soap addition promoted froth bubble coalescence and the formation of fibre flocs flowing down in the pulp slurry. It was therefore supposed that the increase of fibre drainage shown in Figure 7b was due to both an increase in water drainage and the formation of fibre/soap flocs which where entrained by the water drainage stream.

Gas hold-up and pulp flocculation shown in Figs. 8 and 9 are in line with trends obtained for fibre transport coefficients (Fig. 7) and for bubble/fibre interactions in flotation de-inking systems (Ajersch and Pelton 1996; Tang and Heindel 2005; Allix et al. 2010). The general decrease of the gas hold-up caused by soap addition (Fig. 8) was supposed to be induced by bubble coalescence, the progressive flocculation of the pulp slurry (Fig. 9), the onset of bubble channeling between fibre flocs, and the ensuing increase of bubble rising velocity through the pulp slurry.

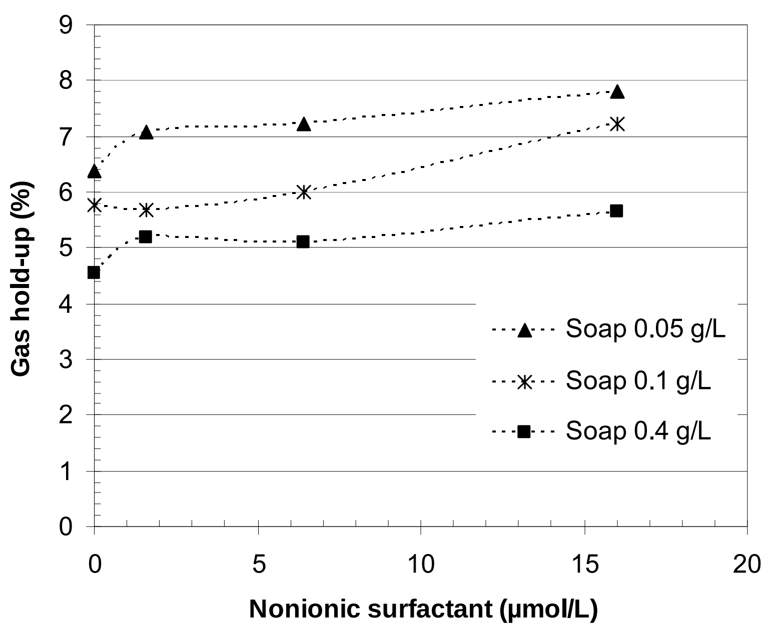


Fig. 8. Effect of soap and nonionic surfactant concentration on gas hold-up

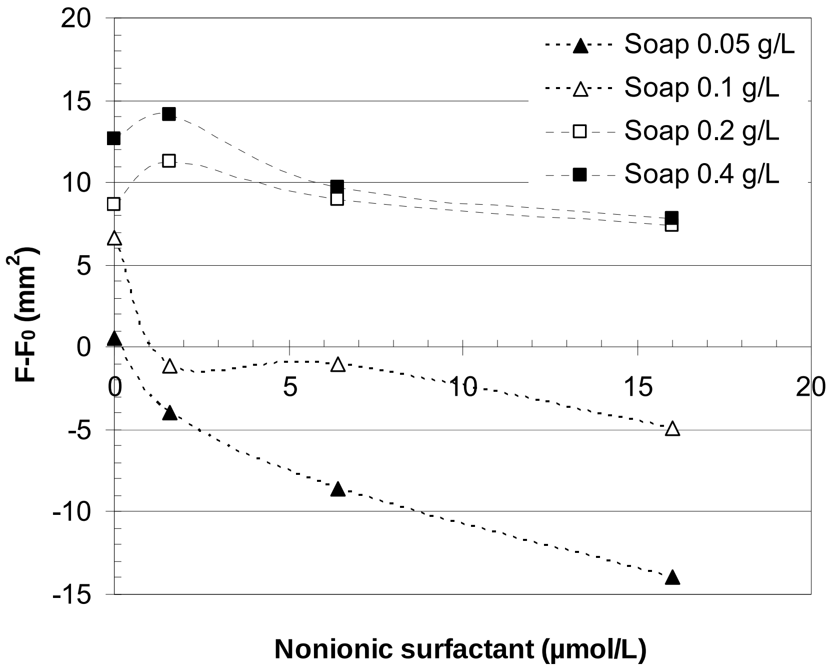


Fig. 9. Variation of pulp slurry flocculation after soap and nonionic surfactant addition

Despite the drop of the gas surface area flux due to bubble coalescence and reduced gas hold-up (which should lead to a decrease in the flotation rate constant) (Heiskanen 2000), soap addition boosted ink and mineral fillers flotation (Figs. 5 and 6). These apparently contradictory results demonstrate that, under tested conditions, ink/fillers flotation is governed by the collecting action of calcium soap (improvement of ink/fillers adhesion to air bubbles), whereas soap's negative impact on the surface area flux has a secondary role.

The increase in gas hold-up after nonionic surfactant addition was correlated to both bubble stabilization and pulp deflocculation, which, generating an homogeneous fibre network, hampers bubble motion in the pulp slurry (Zeno et al. 2010; Allix et al. 2010) with a subsequent increase in gas hold-up. As observed for soap, gas hold-up and bubble stabilization cannot be directly correlated to ink and mineral fillers flotation. The drop in the flotation rate constant after nonionic surfactant addition (according to gas hold-up increase one would expect a flotation rate constant increase) shows that ink/fillers flotation was governed by the surfactant dispersing action, and its positive impact on gas hold-up and the gas surface area flux has a secondary role (Beneventi et al. 2008).

The direct correlation found for fibre entrainment and pulp flocculation (Figs. 7 and 9) was in line with previous studies in which both a nonionic surfactant and polymeric dispersants were used to modify pulp flocculation (Zeno et al. 2010; Allix et al. 2010). However, in the presence of soap this correlation was not confirmed, and the increase in pulp flocculation induced by the calcium soap (Fig. 9) was not associated with an evident increase in fibre entrainment (Fig. 7a).

The present results do not make it possible to provide a comprehensive understanding of the effect of calcium soap of fibre transport during the flotation de-inking process, and a deeper study on fibre/calcium soap flocs properties and their interactions with air bubbles would be required.

Figure 10 summarizes the role of nonionic surfactant and soap during the flotation deinking process according to previous investigations (Borchard 1994; Zhao et al. 2004; Theander and Pugh 2004) and results obtained in this study.

		Nonionic surfactant	Calcium soap
Physical action	Ink	- Dispersion - Decrease of surface hydrophobicity	- Agglomeration - Increase of surface hydrophobicity
	Mineral fillers	- Dispersion - Decrease of surface hydrophobicity	- Agglomeration - Increase of surface hydrophobicity
	Fibres	- Pulp deflocculation*	- Pulp flocculation*
	Bubbles	- Bubble stabilization (both dispersed and froth bubbles)	- Bubble destabilization (both dispersed and froth bubbles)
		⇩	⇩
Effect on particle transport	Ink	- Decrease of ink attachment to air bubbles - Decrease of the flotation rate constant*	- Increase of ink attachment to air bubbles - Increase of the flotation rate constant*
	Mineral fillers	- Decrease of filler attachment to air bubbles - Decrease of the flotation rate constant*	- Increase of filler attachment to air bubbles - Increase of the flotation rate constant*
	Fibres	- Decrease of bubble entrapment in fibre flocs - Decrease of fibre entrainment*	- No clear effect detected*
	Bubbles	- Slower rising motion in the pulp slurry (bubble size and pulp deflocculation effect) - Increase of gas hold-up*	- Faster rising motion in the pulp slurry (bubble size and pulp flocculation effect) - Decrease of gas hold-up*

Fig 10. Overview of the physical action and the effect on particle transport of nonionic surfactant and soap. This overview was drawn from review papers of Borchard 1994, Zhao et al. 2004, Theander and Pugh 2004. * Indicates nonionic surfactant and soap effects observed in this study. In the presence of surfactant/soap mixtures each component maintains its action, which can be attenuated by the presence of the second component.

CONCLUSIONS

Effect of nonionic surfactant alone. Depending on particle type (ink or fibre) and their location (in the pulp or in the froth), the surfactant had a positive or negative impact. For ink particles the surfactant had a negative impact in the pulp by depressing ink floatability, and a positive impact in the froth by decreasing the ink drainage. For fibres, the surfactant had a positive impact in the pulp by depressing the fibre entrainment. These effects were correlated to the typical dispersing action of the tested surfactant, which redispersed both ink particles and cellulose fibres, thus limiting their transport by air bubbles.

Effect of soap alone. Soap also affected particle transport as a function of particle types (ink or fibre) and their location (in pulp or in froth). In the pulp slurry soap boosted ink flotation while depressing fibre entrainment. In the froth both ink and fibre drainage were promoted by soap addition. Results obtained for ink transport were in line with the well established role of soap in flotation de-inking. However, the depression of fibre entrainment was not in line with the corresponding increase in pulp flocculation and the expected increase in fibre entrainment. This mismatch was associated with bubble coalescence induced by the calcium soap, the breakage of fibre flocs by large bubbles, and the decrease of fibre entrainment due to bubble capture in fibre flocs.

Effect of soap/surfactant mixture. The effect on ink removal of the soap/surfactant dosage used together was similar to that observed with each chemical used alone, i.e. for ink the surfactant depressed floatability, while calcium soap boosted it. For fibres the surfactant depressed entrainment, while calcium soap had a limited effect. Despite the absence of synergism, particle removal appeared to be sensitive to the composition of soap/surfactant mixtures, thus showing that mixtures formulation can be effectively used to adjust ink removal and yield during flotation de-inking.

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REFERENCES CITED

Ajersch, M., and Pelton, R. (1996). “Mechanisms of pulp loss in flotation deinking,” *J. Pulp Paper Sci.* 22, 338-435.

Allix, J., Zeno, E., Nortier, P., and Beneventi, D. (2010). “Impact of fibre and surfactant concentration on mixing and fibre transport in a flotation deinking column,” submitted for evaluation for publication.

Azedevo, J., Drelich, J., and Miller, J. D. (1999). “The effect of pH on pulping and flotation of mixed office wastepaper,” *J. Pulp Paper Sci.* 25, 317-320.

Beneventi, D., Benesse, M., Carré, B., Julien Saint Amand, F., and Salgueiro, L. (2007a). “Modelling deinking selectivity in multistage flotation systems,” *Sep. Purif. Technol.* 54, 77-87.

Beneventi, D., Carré, B., Hannuksela, T., and Rosencrance, S. (2007b). “Assessment of deinking chemistry performance: From laboratory flotation tests to the simulation of an industrial pre-flotation line,” *8th Research Forum on Recycling*, Niagara Falls, September 25th-29th, 1-13.

Beneventi, D., Allix, J., Zeno, E., and Nortier, P. (2008). "Influence of surfactant concentration on the ink removal selectivity in a laboratory flotation column," *Int. J. Mineral Process.* 87, 134-140.

Beneventi, D., Rousset, X., and Zeno, E. (2006). "Modelling transport phenomena in a flotation de-inking column: Focus on gas flow, pulp and froth retention time," *Int. J. Mineral Process.* 80, 43-57.

Beneventi, D., Zeno, E., Nortier, P., Carré, B., and Dorris, G. (2009). "Optimization and management of flotation deinking banks by process simulation," *Ind. Eng. Chem. Res.* 48, 3964-3972.

Beneventi, D., Leroy, L., DeLuca, P. (2004). "Dynamic-surface tension and –contact angle as basic parameters for modelling toner flotation. I. Non-ionic surfactants action," *Progr. Paper Recycling* 14, 14-22.

Beneventi, D., Badouin, O., and Nortier, P. (2010). "Semi-empirical modelling and management of flotation deinking banks by process simulation," In: *Process Management*, Pomffyova, M. (ed.), INTECH, Chap. 7, 121-146. *http://sciyo.com/books/show/title/process-management* .

Borchardt, J. K. (1994). "Mechanistic insights into de-inking," *Colloid Surf. A: Physicochem. Eng. Asp*. 88, 13-25.

Carré, B., Galland, G., and Julien Saint Amand, F. (1994). "Estimation of ink detachment and removal," *Progr. Paper Recycling* 4, 80.

Chabot, B., and Krinshnagopalan, G. A. (1996). "Flexographic newspaper deinking: Treatment of wash filtrate effluent by membrane technology," 4th Research Forum on Recycling, Chateau Frontenac, Quebec, October 7-9, 233-242.

Confederation of European Paper Industries (CEPI). (2009). Key Statistics 2009 European Pulp and Paper Industry. http://www.cepi.org/, Brussels.

Dorris, G. M., and Nguyen, N. (1995). "Flotation of model inks. II: Flexo ink dispersions without fibres," *J. Pulp Paper Sci.* 21, 55-62.

Dorris, G. M., Pagé, N., Gendron, S., Murray, T., and Ben, Y. (2006). "On-line measurement of air content in pulping and papermaking systems. Application to flotation cells," *Prog. Pap. Recycling* 16, 31-40.

Dorris, G. M., and Nguyen, N. (1995). "Flotation of model inks. Part II. Flexo ink dispersions without fibres," *J. Pulp Paper Sci.* 21, 55-62.

Dorris, G. M., Page, N. (1997). "Deinking of toner-printed papers. Part I: flotation kinetics, froth stability and fibre entrainment," *J. Pulp Paper Sci.* 23, 206-215.

Drelich, J., Azedevo, M. A. D., Miller, J. D., and Dryden, P. (1996). "Hydrophobicity and elemental composition of laser-printed toner films," *Progr. Paper Recycling* 5, 31-38.

Epple, M., Schmidt, D. C., and Berg, J. C. (1994). "The effect of froth stability and wettability on the flotation of a xerographic toner," *Colloid Polym. Sci.* 272, 1264-1272.

Fabry, B., Roux, J-C., and Carre, B. (2001). "Characterization of friction during pulping: An interesting tool to achieve good deinking," *J. Pulp Paper Sci.* 27, 284-288.

Galland, G., and Vernac, Y., (1993). "Deinking of wastepaper containing water-based flexo-printed newsprint," *Pulp Paper Can.* 96, 181-185.

Galland, G., Vernac, Y., and Carré, B. (1997). "The advantages of combining neutral and alkaline deinking, Part I: Comparison of deinking of offset and flexo printed paper," *Pulp Paper Can.* 98, 46-49.

Gorain, B. K., Harris, M. C., Franzidis, J.-P., and Manlapig, E. V. (1998). "The effect of froth residence time on the kinetics of flotation," *Miner. Eng.* 11, 627-638.

Heiskanen, K. (2000). "On the relationship between flotation rate and surface area flux," *Miner. Eng.* 13, 141-149.

Huber, P., Roux, J.-C., Mauret, E., and Carré, B. (2006). "Characterizing the floc size distribution of flowing pulp suspensions: From fibre flocculation to sheet formation," *Appita J.* 59, 37-43.

Johansson, B., and Johansson, M. (2000). "Agglomeration of ink particles using a mixture of a fatty acid sodium salt and a non-ionic surfactant," *Nord. Pulp Paper Res. J.* 15, 243-250.

Jordan, B. D., and Popson, S. J. (1994). "Measuring the concentration of residual ink in recycled newsprint," *J. Pulp Paper Sci.* 20, 161-167.

Julien Saint Amand, F. (1999). "Hydrodynamics of deinking flotation," *Int. J. Mineral Process.* 56, 277-316.

Lapierre, L., Dorris, G., Merza, J., Haynes, R. D., Chezick, C., Allen, J., and Hill, G. (2004). "Mill trials on near-neutral sulphite deinking: Part II," *Pulp Paper Can.* 105, 47-52.

Rutland, M., and Pugh, R. J. (1997). "Calcium soaps in flotation de-inking fundamental studies using force and coagulation techniques," *Colloid and Surface A: Physicochem. Eng. Asp.* 125, 33-46.

Scott, G., and Smith, A. (1995). "Sludge characteristics and disposal alternatives for recycled fiber plants," Proceed. of the 1995 Recycling Symp., TAPPI, New Orleans, LA, Feb. 20-23, 239-249.

Tang, C., and Heindel, T. J. (2005). "Effect of fiber type on gas holdup in a cocurrent air–water–fiber bubble column," *Chem. Eng. J.* 111, 21-30.

Theander, K., and Pugh, R. J. (2004). "Surface chemicals concepts in flotation de-inking," *Colloids and Surfaces A: Physicochem. Eng. Asp.* 240, 111-130.

Zeno, E., Huber, P., Rousset, X., Fabry, B., and Beneventi, D. (2010). "Enhancement of the flotation deinking selectivity by polymeric dispersants," *Ind. Eng. Chem. Res.* 49, 9322-9329.

Zhang, H., Miller, C. A., Garrett, P. R., and Raney, K. H. (2003). "Mechanism for defoaming by oils and calcium soap in aqueous systems," *J. Colloid and Interface Sci.* 263, 633-644.

Zhao, Y., Deng, Y., and Zhu, J. Y. (2004). "Roles of surfactants in flotation deinking," *Progr. Paper Recycl.* 14, 41-45.

Zheng, X., Franzidis, J.-P., Johnson, N. W., and Manlapig, E. V. (2005). "Modelling of entrainment in industrial flotation cells: the effect of solids suspension," *Miner. Eng.* 18, 51-58.

Zhu, J. Y., Tan, F., Scallon, K. L., Zhao, Y. L., and Deng, Y. (2005). "Deinking selectivity (Z-factor): A new parameter to evaluate the performance of flotation deinking process," *Separation and Purification Technology* 43, 33-41.

Zhu, J. Y., and Tan, F. (2005). "Dynamic drainage of froth with wood fibers," *Ind. Eng. Chem. Res.* 44, 3336-3342.

Zhu, J. Y., Wu, G. H., and Deng, Y. (1998). "Flotation deinking of toner-printed papers using frother spray," *J. Pulp Paper Sci.* 24, 295-299.

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