Flotation Deinking- A Review of the Principles and Techniques

P. Somasundaran, Lei Zhang, S. Krishnakumar and Richard Slepetys

ABSTRACT

Deinking is one of the most important steps in waste paper recycling and a variety of techniques including conventional froth flotation and washing are being used currently to deink secondary fibers. This review encompasses the surface chemical and hydrodynamic principles underlying the flotation deinking process and considers various reagent schemes and parameters for controlling the process. The effects of surfactants, calcium ion concentration, pH, temperature, ink particles size, bubble size and other parameters on the deinking efficiency are discussed. Specifically, problems in deinking the flexographic and toner inks are addressed. Possibilities of modifying existing flotation techniques to achieve better deinking of fibers are indicated.

KEYWORDS

Bubbles, Contact angle, Deinking, Flotation, Ink Particle size, Surfactant, Toners, Waste paper.

INTRODUCTION

Recycling of recovered paper has become a major issue in the paper industry as a result of decreasing landfill space, diminishing supply of wood and environmental concern over deforestation. Paper fibers can be recycled and reused in paper making. Since ink is one of the major deleterious contaminants in the recovered paper due to its darkness, the quality of the secondary pulp is determined largely by the extent of ink removal. The most commonly used techniques for ink removal are washing, flotation, cleaning and screening. Among them, flotation is a process that utilizes the differences in surface physicochemical properties of various particles to separate them. In this process, hydrophobic particles, or hydrophilic particles that are made hydrophobic by surface-active reagents (surfactants), attach to the gas bubbles in the pulp and are carried with the froth and separated from other particles which remain in the bulk. The former particles can then be separated from the matrix by removing the froth from the bulk pulp (1). Compared to other physical separation methods, flotation features high selectivity and relatively low cost and is an economical process for deinking.

Flotation is essentially controlled by the physicochemical and hydrodynamic properties of the pulp, which is reviewed in this paper along with the effect of various parameters in flotation deinking. Possible extension of other techniques for improving deinking efficiency will also be discussed.

DISCUSSION

Unit Processes in Deinking

The main task in the deinking of printed papers is to detach the ink from the paper fiber and then to separate the ink from it. Detachment of the ink from the fiber is achieved by a combination of physical and chemical actions (2, 3). The first step, pulping, involves mechanical agitation of the recovered paper in a mixing unit at consistencies ranging from

---

Somasundaran and Zhang are with NSF IUCR Center for Surfactants, Columbia University, 500 West 120th Street, 911 SW Mudd Building, New York, NY 10027, USA.

Krishnakumar is with Unilever Research US, 45 River Rd, Edgewater, NJ 07020, USA.

Slepetys is with Engelhard Corporation, 101 Wood Ave., Iselin, NJ 08830, USA.

8-16% solids, with the addition of a few chemicals to facilitate ink detachment from the fiber. A combination of physical and chemical actions causes the ink to be detached from the fiber surface. In deinking, the pulping unit is usually operated in batches at temperatures ranging from 55-70 °C and at pH 9-11, which have been found to be the optimum for ink detachment. The pulper is also an ideal point for the addition of chemicals required in the subsequent stages as the mechanical action helps to mix them into the pulp for maximum effectiveness. A following step, screening, is designed to remove contaminants like staples, paperclips, gums etc., that are present in the pulp. Coarse screens are used to remove staples, paperclips and stones while fine pressure screens are used to remove light contaminants like plastics, stickies, etc. that are commonly found in recovered ONP, OMG, MOW, etc.

The most commonly used techniques for ink separation, which is the key step in the deinking process, are washing and flotation. In the washing process, the fine ink particles in suspension are washed away in a water stream and the ink is subsequently removed from the filtrate by flocculation using polymers. Washing is efficient only for removing the finer ink particles. It uses large volumes of water and the fiber yield can be low. Flotation deinking is similar to conventional mineral flotation (1, 4) where the hydrophobic particles are removed by their attachment to a stream of rising air bubbles. Flotation is usually less sensitive to particle size and results in a higher fiber yield (5, 6). As can be seen from Fig. 1, flotation is more effective in the size range of 15-150 microns, and below this range washing is more effective (7, 8). A combination of the two processes is found to be ideal for most type of furnishes (9-12). Dispersion is effective in detaching difficult inks such as toners or UV-cured inks from fiber. The ink particles are dispersed in this case by chemical addition, steam injection or vigorous mechanical mixing units.

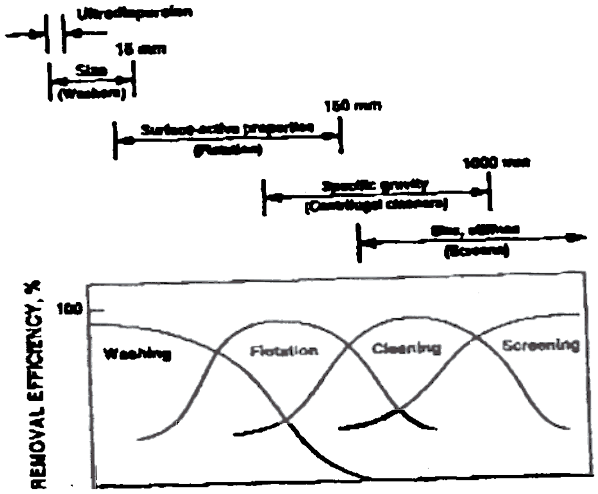

Figure 1: General scheme of particle size dependence of the removal efficiency by various deinking operations (8).

Large quantities of water used in the deinking process are usually reused by employing water recirculation techniques. Control of water hardness and pH is critical for the recirculation of water in deinking plants.

Physical Chemistry of Flotation Deinking

The principles of flotation deinking are similar to those of conventional mineral flotation wherein the particles to be removed are naturally hydrophobic or are rendered hydrophobic by the adsorption of molecules of surface active reagents (surfactants) on their surfaces. Adsorption of surfactants at the solid-liquid interface can alter the surface properties sufficiently to affect hydrophobicity and thus the flotation. Separation of one particle from another is dependent on selective adsorption of surfactants on only the particles which are to be floated.

Adsorption is essentially selective partitioning of the surfactant into the interfacial region. If the interactions between the surfactant and the solid are more energetically favorable than those between the surfactant and the solution, adsorption can take place. The contributing forces for adsorption include covalent bonding, coulombic interaction, ion exchange, desolvation of the polar group of the surfactant, desolvation of the surface, hydrogen bonding, hydrophobic interaction and van der Waals interactions. For each surfactant-solid system several of the above factors can be contributing depending on the solid and the surfactant type, surfactant concentration, temperature, etc. An understanding of the mechanisms of adsorption is therefore essential in order to select appropriate conditions for flotation separation (13-15).

The ink separation process requires specific chemical conditions which are created by adding the appropriate chemicals prior to flotation. Flotation reagents added in the deinking process include collector, frother, pH regulator, particle size controller and dispersant. Depending on the type of raw material to be deinked, the nature and dosage of chemicals are varied. Typical chemicals used for deinking flotation are shown in Table 1 along with their function and dosage (16, 17). For enhanced

Table 1. Chemicals Used as Flotation Reagents and Their Functions (16).

Deinking Chemical	Structure Formula	Function	Furnish Type	Dosage (% of fiber)
Sodium hydroxide	$NaOH$	Fiber swelling, ink break up, saponification, ink dispersion.	Wood-free grades	3-5%
Sodium silicate	Na_2SiO_3 (hydrated)	Wetting, peptization, ink dispersion, alkalinity and buffering, peroxide stabilization, by preventing decomposition by metals.	Ground wood grades, lightly inked ledger	2-6%
Sodium carbonate	Na_2CO_3	Alkalinity, buffering, water softening.	Ground wood grades, lightly inked ledger	2-5%
Sodium or Potassium phosphates	$(NaPO_3)_n$ $n = 15$	Metal ion sequestrant, ink dispersion, alkalinity, buffering, detergency, peptization.	All grades	0.2-1%
Nonionic surfactants	$CH_3(CH_2)mCH_2$- $O(CH_2CH_2O)_xH$ Ethoxylated linear alcohols	Ink removal, ink dispersion wetting, emulsification solubilizing	All grades	0.2-2%
Solvents	C_1-C_{14} aliphatic saturated hydrocarbons	Ink softening solvation	Wood-free grades	0.5-2%
Hydrophilic polymers	$CH_2CHC{=}OOH$ (Na)n polyacrylate	Ink dispersion anti redeposition	All grades	0.1-0.5%
Fatty acid	$CH_3(CH_2)_{16}$ COOH steric acid	Ink flotation aid collector	All grades	0.5-3%
Hydrogen peroxide	H_2O_2	Prevention of yellowing of fiber, ink lifting	All grades	0.5-1.5%
Chelating agents		Preventing of H_2O_2 decomposition by metals	All grades	0-0.5%
FAS	$HO_2SC(NH)NH_2$	Reductive bleach	All grades	0.3-0.6%
Sodium hydrosulfite	$Na_2S_2O_4$	Reductive bleach	All grades	0.5-1%

deinking performance, the flotation machines used for deinking are also modified from those used for mineral processing (18).

Caustic soda is one of the most important chemicals used in the deinking process. The high concentration of the alkali hydrolyzes the ink vehicles and causes swelling of the fibers which helps to release the ink particles from the fiber. The amount of sodium hydroxide added should be optimized to provide sufficient alkalinity for good saponification and hydrolysis of the resins while minimizing the formation of chromophores that cause yellowing of the fibers (19). Mechanical or groundwood-containing pulps such as ONP and OMG are vulnerable to the yellowing effects of excessive alkali. Bleaching agents like peroxides are also added to improve the brightness of the fiber and to neutralize the yellowing effect of certain added chemicals (20). Sodium carbonate and sodium silicate are often used in conjunction with NaOH to provide the desired alkalinity to the medium with minimum fiber damage. The use of silicates and carbonates allows deinking to be achieved at a lower pH which reduces yellowing of the fiber. Other alkalis which are more environmentally benign than NaOH such as MgO, $Mg(OH)_2$, $NaHCO_3$, $Ca(OH)_2$ can also be used for the same purpose (21). In addition to providing alkalinity, silicates aid in deinking by providing an ink dispersant action and by preventing ink redeposition on the fibers. Silicates also help to stabilize the peroxide by complexing with the metal ions that would otherwise decompose them (5, 16, 22, 23). Polyphosphates are added to sequester excessive Mg^{++} and Ca^{++} ions. They also form uncolored complexes with cations such as iron (16) and thereby help to improve the brightness of the final fiber. Chelating agents like DTPA (diethylenetriaminepentaacetic acid) and EDTA (ethylenediaminetetraacetic acid) are also used to form complexes with the heavy metal ions which impair the performance of the peroxide (24, 25). Nonionic surfactants like ethoxylated alkyl phenols and ethoxylated linear alcohols, function in the deinking system by lowering the surface tension of water, enabling efficient wetting of the fibers which in turn aids the removal of ink from the fibers and its dispersion by solubilization and emulsification. Solvents are available for dissolving most inks, but their use is restricted by their prohibitive costs and environmental concern. Also, they have to be relatively insoluble in water in order that they may form solvent-water emulsions. Hydrophilic polymers aid in dispersion and can also act as anti-redeposition agents. The two most common types of polymers used are polyacrylates and carboxymethylcellulose. Fatty acids, which are primarily blends of 16-18 C atom chains, are widely used collector chemicals in ONP/OMG deinking. They complex with the Ca^{2+} ions in the system to form calcium soaps which can adsorb on to the ink surface and provide the collector action. $CaCl_2$ is often added to provide sufficient Ca^{2+} activity in the system. Low molecular weight cationic polymers are often used as coagulants in conjunction with high molecular weight anionic polymers in the water recycling stage for clarification purposes (8). Clays are added in the pulp to improve the ink removal, although their function is not fully understood (7). Agglomerating chemicals are used now to treat the electrostatic printing inks (toner inks) (19).

Calcium-soap formation is the most important step in deinking flotation of old newspapers. The mechanism by which calcium improves the flotation efficiency of ink particles has been a subject of considerable research (26-29). Under the alkaline conditions existing in the flotation cells, the ink particles are negatively charged due to the ionization of the organic acids on their surface layers. It has been suggested that Ca^{2+} may interact with the negatively charged particles through carboxylic bridging mechanism and reduce the surface charge, leading to bridging between adsorbed Ca^{2+} and anionic fatty acids. Another possibility is the bulk precipitation of calcium soap that can cause heterocoagulation of ink particles and calcium soap particles and thus result in the buildup of calcium soap on ink particles by a microencapsulation mechanism. The ink particles become hydrophobic and hence are readily floatable (26). The third mechanism involves reduction of the negative charge of the ink particles by Ca^{2+} and resultant less repulsive force between the ink particles and easy aggregation. These aggregates acquire hydrophobic properties upon fatty acid adsorption and are easily floated out. These proposed mechanisms are summarized in Fig. 2 (27).

Rutland et al. used a surface force apparatus to study the interaction of fatty acid collector and calcium ions with a negatively charged mica substrate at high pH to simulate the flotation deinking process. They found no evidence of the bridging mechanism by the calcium ions under alkaline conditions. The calcium dehydration/destabilization mechanism was observed only at low concentrations of fatty acid (below calcium soap solubility limit) where calcium species adsorb on ink particles and lower the surface charge of them. At higher fatty acid and calcium concentrations, calcium soap was precipitated in the bulk solution. Under high shear

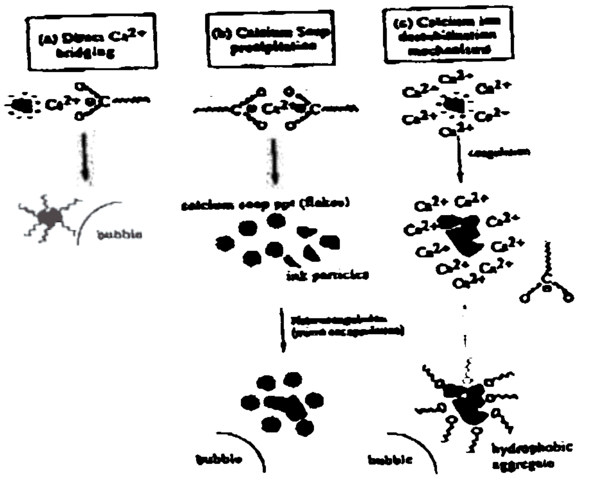

Figure 2: Schematic representation of possible mechanism of calcium-fatty acid interaction in deinking flotation (27).

conditions, the precipitated calcium soap can heterocoagulate with the ink particles, resulting in their coating with a hydrophobic layer. These hydrophobic aggregates can easily attach to air bubbles (27). A study on ink particles suspension without fiber shows that ink agglomeration is totally dependent on the calcium-soap formation and precipitation with the heterocoagulation starting only after calcium soap formation. The adsorption of free fatty acid anions on ink particles, on the other hand, is negligible as most fatty acid is precipitated as calcium soap (28). Harwot et al. studied the deposition of calcium oleate particles on latex particles with carboxylated charge groups on the surface to simulate the ink-calcium soap interaction. They also found heterocoagulation to be the main interaction mechanism between calcium oleate and carboxylated latex particles (29). While all the above studies suggest heterocoagulation to be the mechanism of interaction between ink particles and calcium-fatty acids system, it is to be noted that these experiments were done either with model systems or in the absence of fibers and other chemicals in the pulp. In real deinking pulp, interactions among ink particles, calcium ions and fatty acids are expected to be more complicated.

Advances in the understanding of the mechanisms underlying deinking have helped in the development of special chemicals for maximum benefit. One type of such chemicals called "displectors" (dispersant/collector), usually proprietary formulations of alkoxylated fatty acid derivatives, displays properties of both dispersants and collectors thereby improving the performance in both the flotation and the washing stages of deinking (30). They do not require calcium addition and thus reduce the problem of unwanted scale deposition in the mill. Newer flotation collector chemicals based on modified polyester resins have also been developed. They tend to act in low dosages as foaming collectors and do not require the presence of hardness ions (9).

Hydrodynamics of Deinking Flotation

The basic mechanisms of flotation include the collision between the particles and bubbles in the liquid suspension, the attachment of the particles to the bubbles and the rising of the particle/bubble aggregates to the surface of the suspension. The collision, attachment and stability of the aggregates depend on the hydrodynamics in the flotation cell. Thus, flotation is a dynamic process that involves many hydrodynamic phenomena in a system containing solid, liquid and gas in a state of varying turbulence. Apart from the physical chemistry of the interfaces, parameters such as pulp aeration, bubble mineralization, agitation intensity, bubble size and particle size have an effect on the flotation efficiency.

The attachment of particles to bubbles has been treated using the DLVO theory involving electrical double layer forces between the particle and the bubble (with adsorbed surfactant on both) and van der Waals forces, modified to include hydrophobic attractive force arising from the transfer of the surfactant chains from the solid-liquid interface to the liquid-air interface and repulsive interactions due to possible steric hindrance between adsorbed surfactant layers on the interacting bubbles and particles (31).

The above treatment does not consider the hydrodynamic conditions of the cell. Particle/bubble collision is indeed affected by the hydrodynamic characteristics of the flotation cell (32, 33). The overall probability P of particle-bubble attachment can be represented by the product of three separated probability terms (1):

$$P = P_c \times P_a \times P_d \qquad [1]$$

where P_c is the probability of collision between the particle and the bubble, P_a is the probability of adhesion after collision, and P_d is the probability of maintaining the adhesion. The first term, P_c, depends mainly on the hydrodynamic conditions of the flotation cell. For large particles and large bubbles, collision will depend greatly on the inertial forces. For small particles and medium size bubbles, particle-bubble collision will occur with the sinking particles encountering rising bubbles. Extremely fine particles are carried along the streamlines and will not make a close encounter with bubbles, unless they can cross the streamline by diffusion (34). Thus, for different systems, hydrodynamic conditions in the cell play a vital role in affecting the particle/bubble collision in different ways.

The relationship between P_c as a function of bubble size (D_b) and particle size (D_p) can be expressed as (35):

$$P_c = a\left(\frac{D_p}{D_b}\right)^n \qquad [2]$$

in which a and n are parameters that vary with flow conditions. It is clear that P_c varies approximately with the square of particle size, D_p, and inversely as the square of the bubble size, D_b.

For large particles, inertia force plays a key role in causing particles to deviate from fluid streamlines around the bubble and cause the collision. The large inertia force may cause detachment of the particles as well. Fine particles have very small inertia and follow the streamline around the bubbles unless their hydrodynamically determined trajectories come within one particle radius of the bubble surface. On the other hand, fine particles have a low detachment probability. It has been reported that while for ensembles of particles larger than 100 μm the attachment of particle ensembles to bubbles can be predicted by the theory (36), for particles of smaller than 100 μm the force of attachment is 300-400% higher than that predicted (37).

Flotation is most effective for the removal of ink particles in the range of 10-150 μm. A theoretical analysis of the particle/bubble attachment by collision suggests that when particles are large enough to be unaffected by Brownian motion, the flotation rate should increase roughly with the square of the particle size (38). Similar results have been reported for the flotation of model ink particles with the flotation rate proportional to the ink particle diameter raised to the power of 1.8 (26). The flotation removal of fine particles, based on Equation 2, can be enhanced by reducing the bubble size.

The turbulent conditions in the flotation cell also control the particle/bubble attachment and detachment. For deinking cells, due to the small size of ink particles and the lower concentration of solids, a comparatively quiescent condition is usually used. While good mixing is necessary for efficient particle/bubble collision, it should not be so strong as to cause the detachment of particle/bubble aggregates and the collapse of bubbles. Also, in deinking, the floated material is often an aggregate of ink particles rather than a dispersed particle. High shear rate must be avoided in such cases in order to keep from destroying the aggregates. A kinetic model that takes into account both particle/bubble adhesion and breakage has been developed by Bloom et al. for the deinking flotation (39).

Effects of Process Variables in Flotation Deinking

In the following section, effects of various physicochemical and hydrodynamic parameters on flotation deinking are discussed.

a) Surfactant type

A comparative study of several types of surfactants reveals that soaps of fatty acids yield good ink removal and minimal fiber loss (Fig. 3) (40). Ampholytic surfactants exhibit good filler flotation but cause excessive fiber loss. Nonionic surfactants give good foaming effect but inadequate flotation. The better collecting action of soaps compared to that of nonionic surfactants is probably due to the charge neutralization effect of calcium ions. Cationic surfactants yield good filler flotation but only moderate ink removal. The chain length of the surfactant can also affect the flotation response. It has been found that the absence of double bonds in the carbon chain helps the removal of ink from the fibers while the presence of double bonds helps the flotation process itself (41). Tests have also indicated maximum brightness levels to be obtained with C_{14} to C_{18} fatty acids (Fig. 4) (42).

b) Surfactant / soap concentration

It has been observed that in the presence of Ca^{++}, the floatability of ink particles increases with

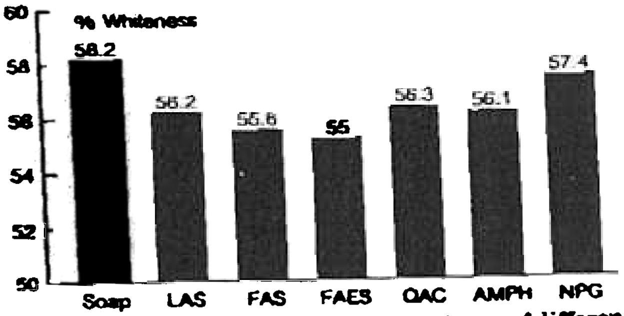

Figure 3: A comparison of deinking efficiency of different surfactants: Soap - fatty acids; LAS - linear alkylbenzene sulfonate; FAS-fatty alcohol sulfate; FAES - fatty alcohol ether sulfate; QAC - quaternary ammonium compound; AMPH - ampholytic surfactants; NPG - nonylphenol ethoxylate (40).

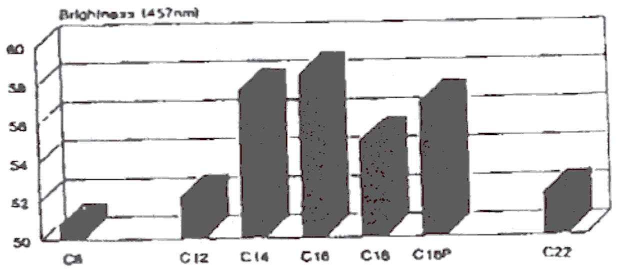

Figure 4: Brightness as a function of the hydrocarbon chain length of fatty acids (42).

increasing addition of soap (26) (Fig. 5). There is an optimum soap concentration beyond which bilayer adsorption of surfactants may occur rendering the particles hydrophilic and hence less floatable (43). The soap concentrations used are usually well below the critical micelle concentrations. Micelles, however, are useful in dispersing pigment particles of low water solubility by solubilizing them. In such cases nonionic surfactants which have a much lower critical micelle concentration than the ionic surfactants may be used (40). High dosages of nonionic surfactants have been found to decrease the ink flotation efficiency, possibly due to the reverse orientation of the adsorbed surfactant (44, 45) as well as increased steric repulsion between the ink particles and the bubbles and increased elasticity of thin films between ink particles and bubbles. They also decrease the surface tension of the pulp and reduce the air-liquid-particle contact angle (46). Since soap has to act together with Ca^{++} to be effective, the optimum soap concentration is also dependent on the water hardness. Figure 6 shows the effect of soap concentration on the brightness of the deinked fibers at different water hardness levels (47).

Although calcium soap formation is essential for the deinking flotation, the quality of the deinked fiber is impaired by the retention of the Ca soap in the pulp. In this regard, alkyl polyglycol ether can retard collector retention in the fibers. Soap retention can also be minimized by optimizing the dewatering conditions during which the Ca soap deposited on the fibers can be washed away. However, experiments have shown that under normal deinking conditions only a small fraction of the Ca soap is actually retained on the fiber, and the high retention found in the mills has been attributed to mechanical entrapment (48, 49). The quality of recycled paper is also affected by the residual fatty acid on fibers. It has been suggested that fatty acid may be at least partly responsible for the low coefficient of friction (COF) of recycled newsprint papers. Other collectors such as tall oil have been proposed for raising the COF of papers made from recycled pulp (50).

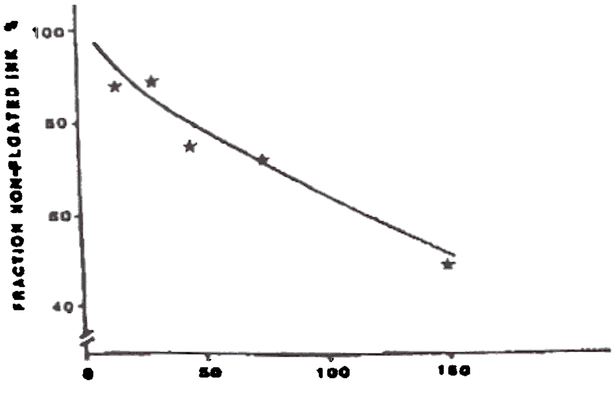

Figure 5: **Influence of soap concentration on the floatability of ink particles (26).**

c) Effect of calcium and water hardness

Flotation response was observed to be inadequate at hardness levels below 180 ppm, above which maximum flotation efficiency was obtained. The brightness of fiber is also affected by water hardness with the brightness increasing with water hardness (42, 47) (Fig. 7). Generally higher water hardness level is required for flotation deinking with fatty acids. Other metal ions such as Mg^{2+}, Al^{3+} also contribute to enhanced ink flotation (51).

In deinking pulp the hardness is regulated by the addition of calcium ion in the form of CaCl$_2$. It has been clearly shown in the past that in the absence of calcium the ink particles do not float and even small additions of it improve the flotation considerably (Fig. 8). The mechanism by which calcium improves the flotation efficiency of ink particles using fatty acid as collector has been discussed in the previous section. Excessive Ca^{++} concentrations must be avoided as it can promote scaling in the

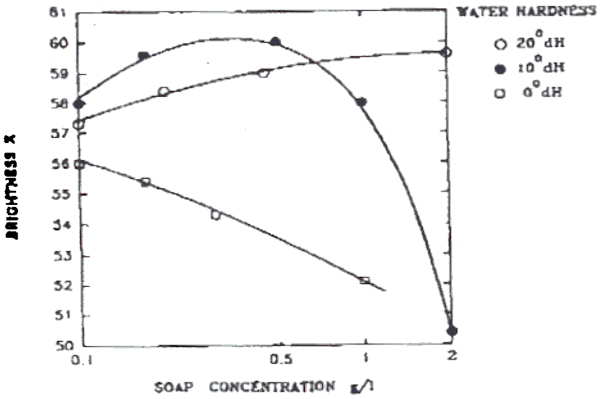

Figure 6: **Effect of soap concentration on the brightness at different hardness levels (47).**

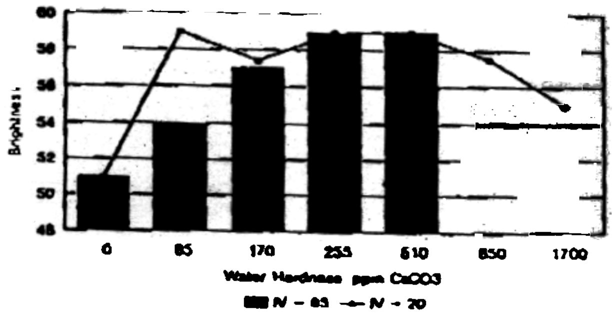

Figure 7: **Effect of water hardness on the brightness of the deinked fiber (47).**

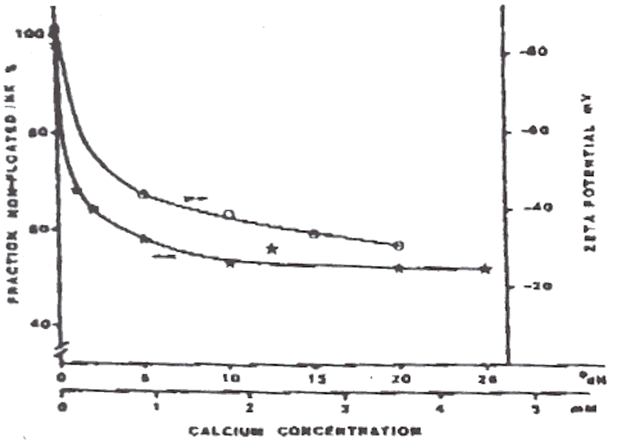

Figure 8: Influence of Ca^{++} concentration on ink particle floatability and zeta-potential (26).

flotation cell. Also, it has been suggested that calcium ions can attach themselves to the fibers and render the fiber hydrophobic. Thus, the presence of calcium ions can contribute to the loss of fiber in the flotation (52, 53).

d) Effect of pH

A high pH is necessary for fiber swelling which improves ink detachment. Generally a pH of 8-10 is reported to be the optimum for the ink flotation, above which the floatability of ink particles has been found to decrease (Fig. 9) (19, 26, 54, 55). This is probably due to the increased surface charge which keeps the ink particles in a highly dispersed state and difficult to float. pH also affects flotation due to its effects on solubility of fatty acids and other chemicals.

e) Effect of temperature

Deinking flotation is usually done at 40-60 °C. Larsson et al. have reported floatability of model ink particles to decrease slightly with increase in temperature (26). Marchildon et al., on the contrary, have found the ink removal to be enhanced with increase in temperature (Fig. 10) (56). Generally, an increase in temperature can facilitate the detachment of ink particles from fibers which contributes to an increase in deinking efficiency. However, elevation in temperatures can also increase the solubility of various chemicals that can either enhance or hamper the deinking process.

Cloud point is a property of nonionic ethoxylated surfactants above which the surfactant solutions become cloudy as a result of phase separation. It has been found that deinking efficiency in washing is strongly dependent on the cloud point of the surfactants used. The highest deinked sheet brightness values were obtained when the process temperature was within 5 °C of the surfactant cloud point (57, 58). The importance of this relationship is to be noted in deinking flotation when nonionic ethoxylated surfactants are present in the pulp.

f) Role of clay and other mineral additives

It has been found that in traditional deinking flotation scheme (Ca soap-fatty acids), ash in the feed

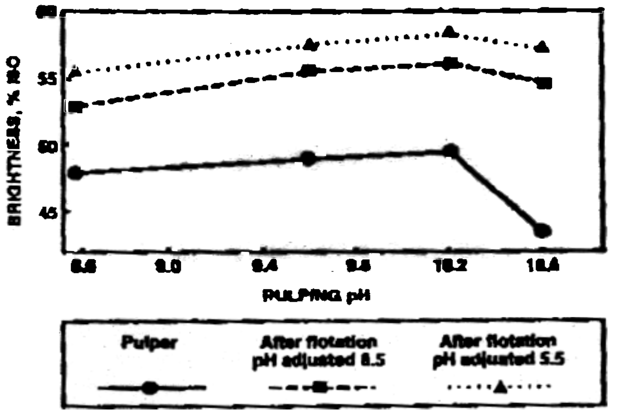

Figure 9: **Effect of pH on ink flotation (19).**

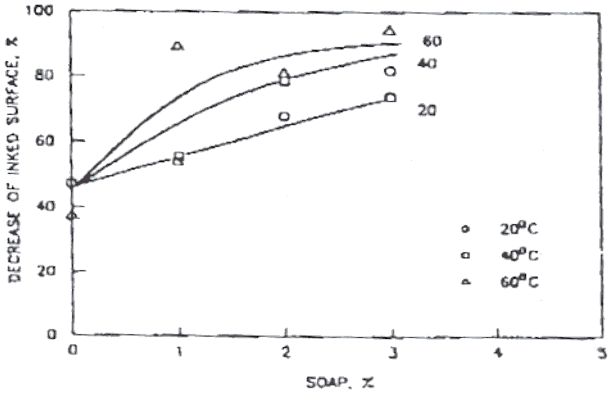

Figure 10: **Decrease of inked surface as a function of temperature at different soap concentrations (56).**

can be optimized for ink removal. It used to be the practice to add ash by blending coated materials such as magazines with the newsprint (7). Due to rapid growth in newsprint deinking by flotation techniques, the demand for coated material is fast exceeding the supply. Moreover the ash content in the coated materials varies widely giving rise to significant swings in the ash content of the feed. Direct addition of clays or some other minerals such as calcite and zeolite in the flotation cell has been explored. These materials have been found to have a positive effect on ink flotation. Schriver et al. reported that among 10 different mineral additives, calcined filler clays give maximum brightness when used in conjunction with either fatty acids or dispersant/collector combinations (59). It is to be noted that role of ash in flotation deinking is also not very well understood. Grant et al. speculated that ink particles may adsorb onto the surface of the inorganic material. The resulting particle complex is larger in size and more hydrophobic and hence floated more efficiently (60). This phenomenon is akin to carrier flotation or piggy-back flotation used in mineral processing in which very fine particles are attached to bigger carrier particles and floated (61). Grant et al. also showed that size of agglomerate formed by ink particles and clay particles is dependent on the type of minerals and the ratio of inks to mineral fillers.

Letscher et al., on the other hand, reported that fillers do not play a significant role in improving the flotation deinking (as measured by brightness) (62). Retention of kaolin clay fillers did not improve the brightness of the stock. The increase of brightness with silica filler was due to filler retention instead of improved flotation efficiency. However, their tests were carried out with a displector chemistry that is quite different from fatty acid chemistry. It may be one of the reason as to why fillers are not beneficial for efficient deinking.

g) Effect of particle size

It is well known that for small particles in the range of 1-50 µm, floatability decreases with particle size (63). The larger particles are usually easily floated and can be separated in a short time (56). The flotation rate of small particles is rather slow and they cannot be easily removed even by prolonged flotation. Figure 11 shows the ink particle size distribution before and after flotation and clearly indicates the higher floatability of the coarse particles. (The number of particles as shown in the figure is a particle count on a fixed area after deposition on a filter.) The main reason for the poor flotation response of the small particles is the hydrodynamic effect (reduced momentum) that decreases the particle-bubble attachment efficiency. The presence of small particles affects the brightness of the recovered fiber adversely. Figure 12 indicates the effect of particle size on the brightness of the fiber. As can be seen, as the size of the ink particles generated becomes smaller the

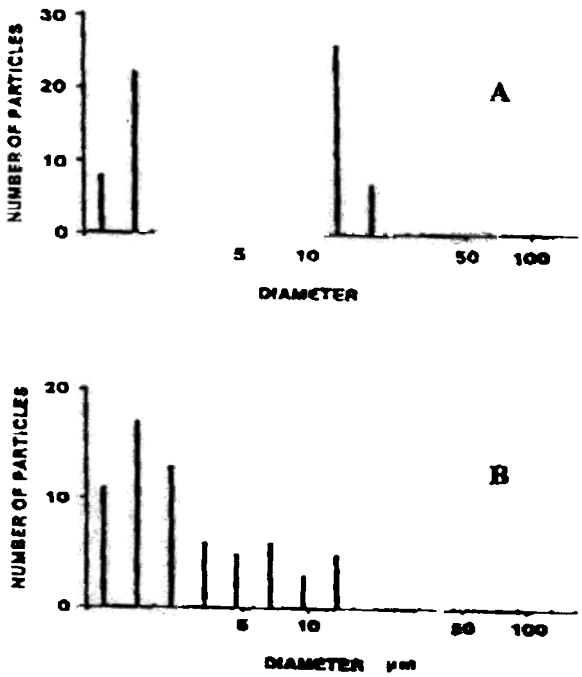

Figure 11: **Effect of particle size on flotation kinetics. A) Ink particle size distribution before flotation; B) Ink particle size distribution after 10 min flotation (63).**

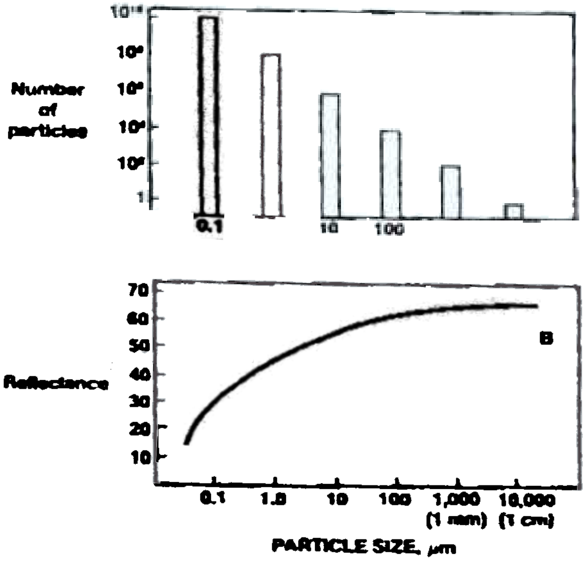

Figure 12: **Effect of particle size on brightness of deinked fiber (7).**

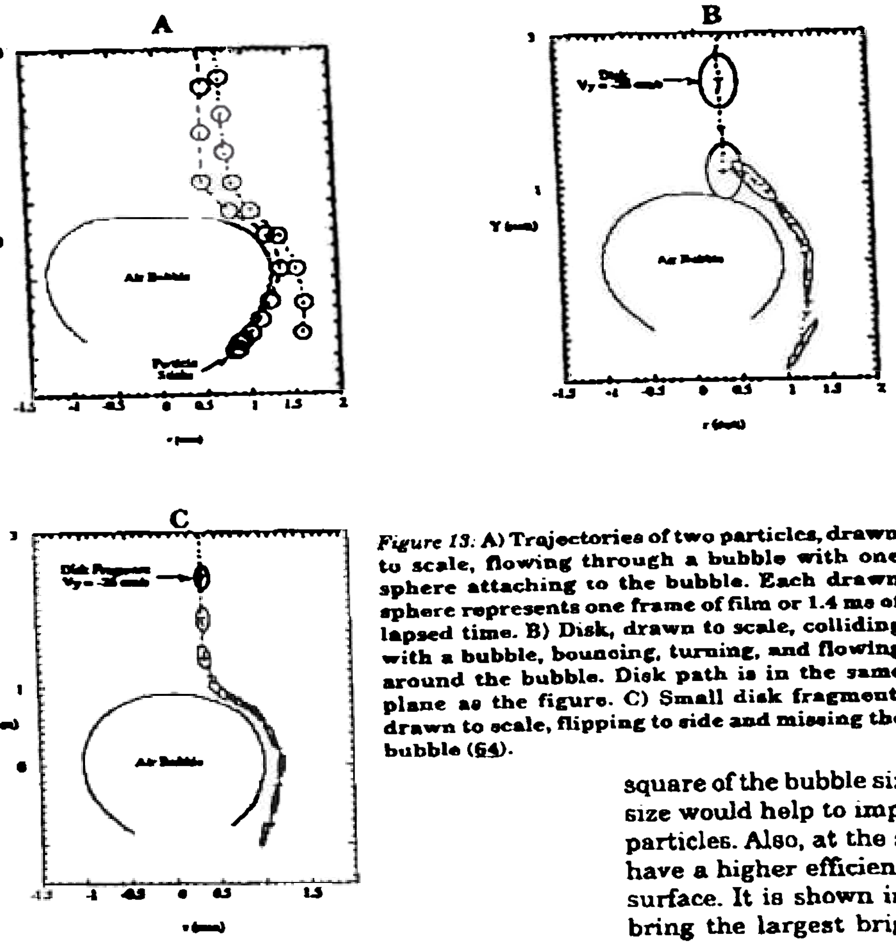

Figure 13: **A) Trajectories of two particles, drawn to scale, flowing through a bubble with one sphere attaching to the bubble. Each drawn sphere represents one frame of film or 1.4 ms of lapsed time. B) Disk, drawn to scale, colliding with a bubble, bouncing, turning, and flowing around the bubble. Disk path is in the same plane as the figure. C) Small disk fragment, drawn to scale, flipping to side and missing the bubble (64).**

reflectance of the fiber also decreases. Thus, for efficient deinking, the process variables should be adjusted to minimize the generation of fine particles and also to achieve maximum removal of the particles generated. Small particles are formed when the inks are aged or when strong mechanical action is used to detach the difficult to remove, offset inks. Repulping of the flexographic printing papers also generates fine particles under the common alkaline conditions used. The probability for producing small particles increases with the difficulty of ink separation. However the presence of both calcium and soap in the pulp induces agglomeration of offset ink particles and increases the average particle size. Also, the possibility of using polymers to flocculate the fines prior to flotation needs to be further investigated.

The shape of the particles also plays a role in determining their floatability by affecting the probability of particle-bubble collisions. The toner particles are usually present as plate or disk-like particles of various sizes in the deinking pulp. It is reported that when plate or disk shape particles interact with a bubble, larger particles collide with the bubbles edge-on and bounce off before attachment can take place, while small particles can flip onto the side resulting in a larger contact area which cannot drain and rupture during the time of contact. In both cases, the particles have a much smaller probability of attachment than does a similar size sphere (64) (Fig. 13).

h) Effect of bubble size

Equation 2 states that collision probability, P_c, varies inversely with the square of the bubble size, D_b. The decrease of bubble size would help to improve the removal of fine ink particles. Also, at the same air rate, small bubbles have a higher efficiency due to the higher specific surface. It is shown in Fig. 14 that small bubbles bring the largest brightness gain (65). However, small bubbles can also cause an increase in fiber loss due to the entrainment (66).

The bubble size is affected to a greater extent by the chemistry of the deinking pulp. Rao et al. showed that as the surface tension of the pulp decreases, average bubble size as well as maximum bubble size decreases. Thus, the chemicals used in the deinking process can be expected to affect flotation by affecting bubble size distribution (67).

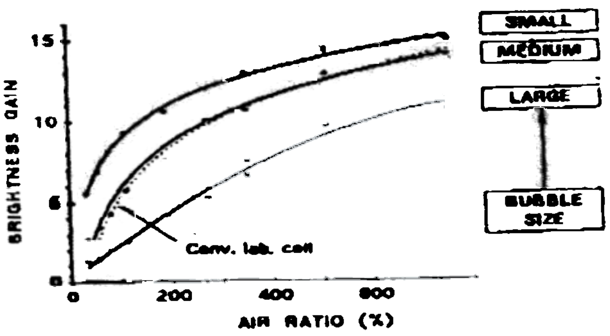

Figure 14: **Effect of bubble size on ink flotation (65).**

Treatment of Flexographic and Toner Inks

Water-based flexographic inks and electrostatic inks (toner) are relatively new types of printing inks which occur more and more often in recycled paper, especially the mixed office papers. They have quite different composition from traditional printing inks and are not readily removed by flotation using conventional flotation chemistry discussed above, e.g., calcium-soap chemistry. The presence of these inks has become one of the major problems in the deinking flotation and processes dependent on different specific physicochemical properties are required to treat papers printed with these inks.

Flexographic printing uses water-based inks and is environmental-friendly due to reduced emission of volatile organic compounds during the printing process. It is also economical compared with the traditional offset and letterpress printing. After repulping, flexographic inks form very fine particles (< 5 µm) and due to the small particle size, plus the hydrophilic nature of the inks, it is rather difficult to remove them by flotation. They form very stable colloidal dispersion. It is reported that the conventional calcium soap of fatty acids are effective for the laboratory flotation of model flexo inks. Calcium soap and flexo inks can form aggregates (68, 69). The problem with flexo inks may thus be due to the complex chemistry involved in the actual mill with fibers and other constituents, redeposition of the inks onto fibers, and entrapment (70).

As flexographic inks contain acrylic resins that are water soluble under alkaline conditions, repulping the recovered paper under acidic or neutral conditions can reduce the ink dispersion. It can be seen from Fig. 15 that with a standard deinking chemical mixture, the brightness of the pulp increases with the decrease in pulp pH (71). Based on this, a two stage deinking process has been proposed to treat mixed recovered paper, with a neutral stage before the conventional alkaline deinking stage. This process causes less dispersion of flexo inks and reduces ink redeposition (72, 73). Other approaches include adding a washing stage to the flotation process, or modifying the composition of flexographic inks to improve their flotation deinkability (74, 75).

Photocopying and laser printing processes use thermoplastic powders, termed toners, instead of conventional inks. They are electrostatically placed on the paper and then fused in place. Upon repulping, the toner particles break into plates or disk-like particles of various sizes. They are not easily removed by conventional washing, flotation, cleaning or screening processes.

Although the toner particles are generally hydrophobic (74), the flotation removal of them has been reported to be poor compared to that of conventional inks. One reason may be the attachment of fibers to the toner particles after repulping, as toners are fused to the paper surface and are difficult to detach from the fiber. The attached fiber makes it hydrodynamically very difficult for particle/bubble attachment to occur. Furthermore, the attached fiber renders the toner/ink aggregates more hydrophilic and thus less floatable (77, 78).

The printing parameters for toners such as the thickness of print, degree of bonding to paper, and the speed of printing are found to affect subsequent deinking. Slow-printing machines usually produce larger toner particles that contain attached fibers upon repulping and negatively affect the flotation deinking (79). It is hard to break up thick prints in the repulping stage due to their stronger cohesiveness (80). As mentioned in the above sections, the shape of the toner particles may also play an important role in affecting the flotation of toners (64).

A number of techniques have been proposed to treat the toner particles. It is suggested that toner flotation can be enhanced by simply improving the chemical and hydrodynamic conditions of the pulp to generate smaller ink particles that are free of attached fibers (81). The addition of chemicals such

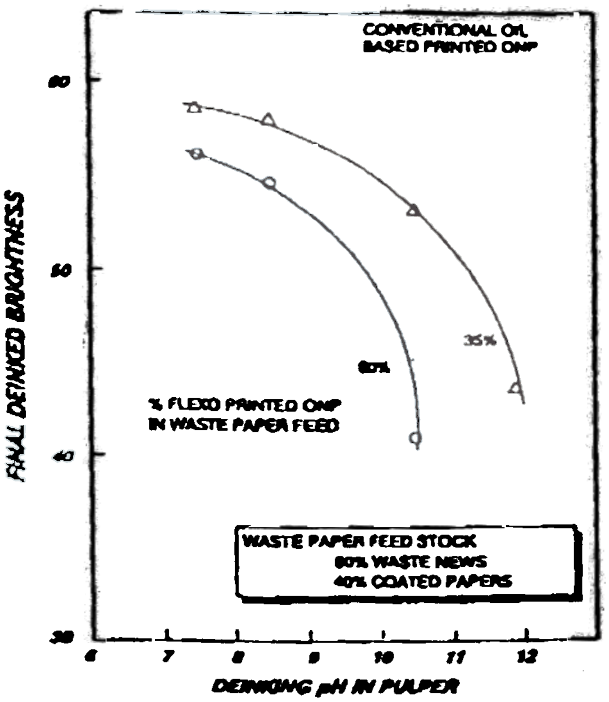

Figure 15: **Effect of decreasing pH on flexographic ink deinking (71).**

as mineral oil and polymers to agglomerate the toners into larger particles and their subsequent removal by fine screening and centrifugal cleaning have been proposed (82-84). Pulping under acidic conditions could cause toner to be released as small particles and increase the effectiveness of toner removal (85). Two-stage treatment (washing/flotation and two stage flotation) (86), densification and forward cleaning also gives better flotation results.

Despite the advances in understanding the deinking of flexographic and toner inks, experimental results reported for flexographic and toner deinking often are conflicting, probably due to the differences in the printing process and the composition of the printing inks. Clearly more work is needed to elucidate interactions between these types of inks and deinking chemicals and to derive a general protocol for deinking based on such information.

SUMMARY

Flotation is an effective method for deinking and when combined suitably with other processes like washing, can remove a wide variety of inks in a large range of sizes. However, flotation is a complex process that involves many physicochemical and hydrodynamic parameters at the solid/liquid/gas interface. The flotation deinking efficiency can be affected by a large number of factors. Process variables such as collector type, collector concentration, Ca^{++} concentration, pH, temperature, clay minerals, particle size and shape and bubble size are shown in this discussion to have significant effects. The mechanism of calcium-soap formation and its effect on flotation deinking has been reviewed. It is clear that clarification of the underlying mechanisms in deinking flotation offers an opportunity to optimize the deinking process and help to develop special chemicals for the maximum benefit.

Although significant advances have been made in elucidating the mechanisms of deinking conventional newsprint and process schemes for treating such inks are well established, flotation deinking of flexographic and toner inks still face difficulties particularly due to lack of understanding of the processes involved.

ACKNOWLEDGMENT

The authors acknowledge financial support of the National Science Foundation (CTS-9622781, CTS-9632479 and EEC-9804618).

LITERATURE CITED

1. Gaudin, A. M. Flotation. McGraw Hill, New York, NY (1957).

2. Crow, D.R.; Secor, R.F. The ten steps of deinking. Tappi J. 70 (7): 101 (July 1987).

3. Secondary Fiber Recycling (Spangenberg, R. J., Ed.) TAPPI Press, Atlanta, GA (1993).

4. Somasundaran, P. Foams and flotation. *In* Theory, Practice and Process Principles for Physical Separations, p 237 (M.P. Freeman, J.A. Fitzpatrick (Ed.)) Engineering Foundation, New York, NY (1981).

5. Read, B.R. Selection of chemicals within a modern deinking plant. Paper Technology and Industry, p. 339 (Nov. 1985).

6. Harrison, A. Flotation deinking is critical in unit process method of deinking. Paper & Pulp, p. 60 (March 1989).

7. Zabala, M.; McCool, J. Deinking at Papelera Peninsular and the philosophy of deinking system desige. Tappi J. 71 (8): 62 (Aug. 1988).

8. Ferguson, L. D. Deinking chemistry: Part II Tappi J. 75 (8): 49 (Aug. 1992).

9. Schriver, K.E. Mill chemistry must be considered before making deink line decision. Pulp & Paper, p. 76 (March 1990).

10. Koffinke, R. A. Modern newsprint system combines flotation and washing deinking. Tappi J. 68 (2): 61 (Feb. 1985).

11. Borchardt, J. K.; Matalamaki, D. W. Newsprint deinking: unit operations studies of flotation-wash deinking, a comparison of commercial and proprietary surfactants. Pulp and Paper Canada 95 (10): T374 (1994).

12. Horacek, R. G.; Jarrehult, B. Chemical application expands in washing/flotation deinking systems. Pulp and Paper, p. 96 (March 1989).

13. Fuerstenau, D. W. The adsorption of surfactants at solid/water interfaces. *In* The Chemistry of Biosurfaces, Vol. 1, p. 143-176 (M. L. Hair, Ed.) Marcel Dekker, New York, NY (1971).

14. Goddard, E.D.; Somasundaran, P. Adsorption of surfactants on solids. Croatica Chemica Acta 48: 451 (1976).

15. Somasundaran, P. Physico-chemical aspects of surface active agents on minerals. Croatica Chemica Acta 52, p 67 (1979).

16. Woodward, T. W. Appropriate chemical additives are key to improved deinking operations. Pulp and Paper, p. 59 (Nov. 1986).

17. Woodward, T. W. Deinking chemistry. 1991 Chemical Processing Aids Short Course, No. 281, TAPPI Press, Atlanta, GA (1991).

18. McCool, M. A. Flotation deinking. *In* Secondary Fiber Recycling, p. 141-162 (R. J. Spangenberg, Ed.) TAPPI Press, Atlanta, GA (1993).

19. Ferguson, L. D. Deinking chemistry: Part I. Tappi J. 75 (7): 75 (July 1992).

20. Renders, A. Hydrogen peroxide and related chemical additives in deinking processes. Tappi J. 76 (11): 155 (Nov. 1993).

21. Nystrom, M.; Pykalainen, J.; Lehto, J. Peroxide bleaching of mechanical pulp using different types of alkali. Paper and Timber 75 (6): 419 (1993).

22. Ali, T.; Mclellan, F.; Adiwinita, J.; May, M. Functional and performance characteristics of soluble silicates in deinking. Part 1: alkaline deinking of newsprint magazine. Proc. 1st Recycling Forum, p. 21, Technical Section CPPA, Montreal, PQ, Canada (1991).

23. Colodette, J. L.; Rothenberg, S.; Dense, C. W.Hydrogen peroxide stability in presence of sodium silicate. JPPS 15 1:J3 (1989).

24. Bambrick, D. R. The effect of DTPA on reducing peroxide decomposition. Tappi J. 68 (6): 96 (June 1985).

25. Mathur, I. Chelant optimization in deinking formulation. Proc. 1st Recycling Forum, p. 49, Technical Section CPPA, Montreal, PQ, Canada (1991).

26. Larsson, A.; Stenius, P.; Odberg, L. Surface chemistry in flotation deinking - Part I. Svensk Papperstidning 18, p. 158 (1984).

27. Rutland, M.; Pugh, R. J. Calcium soaps in flotation deinking; fundamental studies using surface force and coagulation techniques. Colloids and Surfaces, A 125, p. 33 (1997).

28. Johansson, B.; Wickman, M.; Ström, G. The mechanism of offset ink particles agglomeration in a calcium-fatty acid collector system. Proc. 3rd Recycling Forum, p.51, Technical Section CPPA, Montreal, PQ, Canada (1995).

29. Harwot, P.; van de Ven, T. G. M. Effects of sodium oleate and calcium chloride on the deposition of latex particles on an air/water interface. Colloids and Surfaces A, 121, p. 229 (1997).

30. Horacek, R. G.; Jarrehult, B. Chemical application expands in washing/flotation deinking systems. Pulp & Paper, p. 97 (March 1989).

31. Somasundaran, P.; Chardar, P.; Chari, K. A study of the interactions between particles and bubbles in surfactant solution. Colloids and Surface A, 8, p. 121 (1983).

32. Schulze, H. J. . The fundamentals of flotation deinknig in comparison to mineral flotation. Proc. 1st Recycling Forum, p. 161, Technical Section CPPA, Montreal, PQ, Canada (1991).

33. Paulsen, F. G.; Pan, R.; Bousfield, D. W.; Thompson, E. V. The dynamics of bubble/particle approach and attachment during flotation and the influence of short-range nonhydrodynamic forces on disjoining film rupture. Proc. 2nd Recycling Forum, p. 1, Technical Section CPPA, Montreal, PQ, Canada (1993).

34. Matis, K. A.; Zouboulis, A. I. The role of bubble/particle size. *In* Flotation Science and Engineering, p. 63 (Matis, K. A., Ed.) Marcel Dekker, New York, NY (1995).

35. Yoon, R. H.; Luttrell, G. H.; Adel, G. T. Advances in fine particle flotation. *In* Challenges in Mineral Processing, p. 487 (K. V. S. Sastry, M. C. Fuerstenau, Eds.) SME, Denver, CO (1989).

36. Nutt, C. W. Froth flotation, the adhesion of solid particles to flat interfaces and bubbles. Chem. Eng. Sci. 12, p. 133 (1960).

37. Somasundaran, P.; Varbonov, R.; Tchaliovska, S.; Nishkov, I. Ensemble effects in the detachment if floating microspheres. Colloids and Surface A, 64, p. 35 (1992).

38. Reay, D.; Ratcliff, G. A. Removal of fine particles from water by dispersed air flotation: Effects of bubble size and particle size on collection efficiency. Canadian J. Chem. Engr. 51, p. 178 (1973).

39. Bloom, F.; Heindel, T. J. A theoretical model of flotation deinking efficiency. Journal of Colloid and Interface Science 190, p. 197 (1997).

40. Balos, B.; Patterson, J.; Hornfeck, K.; Liphard, M. Flotation deinking chemistry. Paper Age Recycling Annual, p. 15 (1990).

41. Read, B. R. Proc. TAPPI Pulping Conf., p. 851, TAPPI Press, Atlanta, GA (1991).

42. Mak, N.; Stevens, J. Characteristics of fatty acid as an effective flotation deinking collector. Proc. 2nd Recycling Forum, p. 145, Technical Section CPPA, Montreal, PQ, Canada (1993).

43. Somasundaran, P.; Kunjappu, J. T. In-situ investigation of adsorbed surfactants and polymers on solids in solution. Colloids and Surfaces 37, p. 245 (1989).

44. Somasundaran, P.; Snell, E.D.; Xu, Q. Adsorption behavior of alkylarylethoxylated alcohols on silica. J. Colloid and Interface Science 144, p. 165 (1991).

45. Zhang, L.; Somasundaran, P.; Maltesh, C. Adsorption of n-dodecyl-ß-D-maltoside on solids. J. Colloid and Interface Science 191, p. 202 (1991).

46. Larsson, A. Surface chemistry in flotation deinking. PTI, p. 388 (Feb. 1987).

47. Bechstein, G.; Unger, E. Verfahrenstechnische Probleme der Entfärbung von Altpapier nach dem Deinking-Flotationsprozeß. Chem. Techn. 23, p 731 (1971).

48. Larsson, A.; Stenius, P.; Odberg, L. Surface chemistny in flotation deinking - Part 3. Svensk Papperstidning 3, p. 2 (1985).

49. Fernandez C.; Garnier, G. Adsorption and entrapment of calcium soaps using packed beds of pulp fibers. Proc. 3rd Recycling Forum, p. 45, Technical Section CPPA, Montreal, PQ, Canada (1985).

50. Dorris, G. M.; Dagenais, M.; Douek, M.; Boegh, K.; Allen, J. Use of distilled tall oil as a flotation collector in deinking mills. Pulp & Paper Canada 98 (12): 137 (1997).

51. Oliveira, A. P.; Torem, M. L. The influence of some metallic cations on deinking flotation. Colloids and Surfaces A, 110, p. 75 (1996).

52. Turvey, R. W. Stock loss as a function of water hardness in deinking. PTI, p. 366 (Feb. 1987).

53. Turvey, R. W. Why do fibers float? Journal of Pulp and Paper Science 19 (2): J52 (1993).

54. Sengupta, D. K.; Attia, Y. A.; Hamza, H. A. Flotation of ink particles from paper pulp. SME preprint, 93-81, SME, Denver, CO (1993).

55. Heimonen, J.; Stenius, P. The effects and behavior of different types of deinking chemicals in the deinking of coated and non-coated paper. Proc. 3rd Recycling Forum, p. 57, Technical Section CPPA, Montreal, PQ, Canada (1995).

56. Marchildon, M.; Lapointe, M.; Chabot, B. The influence of particulate size in flotation deinking of newsprint. Pulp & Paper Canada 90, p. 90 (1989).

57. Wood, D. L. Alcohol ethoxylates and other nonionics as surfactant in the deinking of waste paper. Proc. TAPPI Pulping Conf., p. 435, TAPPI Press, Atlanta, GA (1982).

58. Borchardt, J. K. Mechanistic insights into deinking. Colloid and Surface A, 88, p. 13 (1993).

59. Schriver, K.E.; Bingham, S.J.; Fraizer, M. The function of clay in flotation deinking. Proc. TAPPI Pulping Conf., p. 133, TAPPI Press, Atlanta, GA (1990).

60. Grant, J.; Blain, T. Short sequence recycling: the factors affecting ink agglomeration and stability. Proc. 3rd Recycling Forum, p. 247, Technical Section CPPA, Montreal, PQ, Canada (1995).

61. Wang, Y. H.; Somasundaran, P. A study of carrier flotation of clay. *In* Fine Particle Processing, Vol 2, p. 1112 (P. Somasundaran, Ed.) AIME, New York, NY (1980).

62. Letscher, M. K.; Sutman, F. J. The effects of magazine and filler on the flotation deinking of newsprint. Journal of Pulp and Paper Science 18 (6): 225 (1992).

63. Larsson, A.; Stenius, P.; Odberg, L. Surface chemistny in flotation deinking - Part 2. Svensk Papperstidning 18 p. 165 (1984).

64. Schmidt, D. C.; Berg, J. C. The selective removal of toner particles from repulper slurries by flotation. Proc. 3rd Recycling Forum, p. 227, Technical Section CPPA, Montreal, PQ, Canada (1995).

65. Julien Saint Amand, F.; Perrin, B. The effect on particle size on ink and speck removal efficiency of the deinking steps. Proc. 1st Recycling Forum, p. 39, Technical Section CPPA, Montreal, PQ, Canada (1991).

66. Ajersch, M.; Pelton, R. Mechanism of pulp loss in flotation deinking. Journal of Pulp and Paper Science 22, p. J338 (1996).

67. Rao, R.; Stenius, P. The effect of flotation deinking chemicals on bubble formation. Journal of Pulp and Paper Science 24 (5): 156 (1998).

68. Dorris, G. M.; Nguyen, N. Flotation of model inks, part II. Flexo ink dispersion without fibres. Proc. 2nd Recycling Forum, p. 13, Technical Section CPPA, Montreal, PQ, Canada (1993).

69. McLennan, I. J.; Pelton, R. Some factors influencing flexo ink calcium soap particle morphology in flotation deinking. Proc. 3rd Recycling Forum, p. 77, Technical Section CPPA, Montreal, PQ, Canada (1995).

70. Chabot, B.; Daneault, C.; Dorris, G. M. Entrapment of water-based inks in fibre mats. J. of Pulp and Paper Science 21, p. J296 (1995).

71. Mak, T.; Reid, F.; Yau, T. Deinking of flexographic ink by flotation process. 79th Annual Meeting, Technical Section CPPA, Montreal, PQ, Canada (1993).

72. Galland, G.; Vernac, Y. Deinking of wastepaper containing waterbased flexographic newsprint. Proc. 1st Recycling Forum, p. 31, Technical Section CPPA, Montreal, PQ, Canda (1991).

73. Galland, G.; Vernac, Y.; Carre, B. The advantages of combining neutral and alkaline deinking. Proc. 3rd Recycling Forum, p. 235, Technical Section CPPA, Montreal, PQ, Canada (1995).

74. Ackermann, C.; Putz, H.; Gottsching, L. Deinkability of waterborne flexo inks by flotation Proc. 2nd Recycling Forum, p. 201, Technical Section CPPA, Montreal, PQ, Canada (1993).

75. Upton, B. H.; Krishnagopalan, G. A.; Abubakr, S. Deinking flexographic newsprint: using ultrafiltration to close the water loop. Tappi J. 80 (2): 155 (Feb. 1997).

76. Snyder, B. A.; Schmidt, D. C.; Berg, J. C. Characterization and flotation studies of electrostatic inks. Prog. in Paper Recycl. 3 (1): 17-26 (1993).

77. Johnson, D. A.; Thompson, E. V. Fiber and toner detachment during repulping of mixed office waste containing photocopied and laser-printed paper. Tappi J. 78, p. 41 (1995).

78. Vidotti, R. M.; Johnson, D. A.; Thompson, E. V. Influence of toner detachment during mixed office waste paper repulping on flotation efficiency. Proc. 3rd Recycling Forum, p. 257, Technical Section CPPA, Montreal, PQ, Canda (1995).

79. Snyder, B. A.; Berg, J. C. Effect of particle size and density in flotation deinking of electrostatic papers. Tappi J. 77 (7): 157 (July 1994).

80. Dorris, G. M.; Page, M. Deinking of toner-printed papers. Part1: flotation kinetics, froth stability and fiber entrainment. Proc. 3rd Recycling Forum, p. 215, Technical Section CPPA, Montreal, PQ, Canada (1995).

81. Dorris, G. M.; Sayegh, N. N. The role of print layer thickness and cohesiveness on deinking of toner-printed papers. Tappi J. 80 (4): 181 (April 1997).

82. Snyder, B. A.; Berg, J. C. Liquid bridge agglomeration: a fundamental approach to toner deinking. Tappi J. 77 (5): 79 (1994).

83. Darlington, W. B. A new process for deinking electrostatically-printed secondary fiber. Tappi J. 72 (1): 35 (Jan. 1989).

84. Olson, C. R.; Richmann, S. K.; Sutman, F. J.; Letscher, M. B. Deinking of laser-printed stock using chemical densification and forward cleaning. Tappi J. 76 (1): 136 (Jan. 1993).

85. Azevedo, M. A. D.; Yalamanchili, M. R.; Drelich, J.; Miller, J. D. Flotation of toner particles and mineral filler particles during de-inking of laser printed wastepaper. SME preprint, pp. 97-112, SME, Denver, CO (1997).

86. Quick, T. H.; Hodgson, K. T. Xerography deinking - a fundamental approach. Proc. TAPPI Pulping Conf., p. 561, TAPPI Press, Atlanta, GA (1985). ■

Original Manuscript Received for Review on October 10, 1998
Revised Manuscripted Accepted on January 29, 1999