Evaluation of carbon dioxide as a carrier gas in flotation deinking

Lorenzo Marchildon, Carlos C. Castro, Marcel W. Lapointe, and Claude Daneault

ABSTRACT: Experimental results revealed no significant differences in the optical and mechanical properties of pulps deinked by flotation using air, O_2, or N_2 as carrier gases. Pulps deinked by flotation with CO_2 showed improvement in optical properties (greater brightness and luminosity, less yellowing) but suffered losses in mechanical properties (breaking length and burst index). The results obtained with CO_2 were attributed to the acidification that occurs when this highly soluble gas bubbles upward through the pulp suspension. The drop in breaking length for pulps deinked with CO_2 gas can be recovered by an alkaline wash stage after flotation.

KEYWORDS: Acidification, air, carbon dioxide, deinking, flotation, gas, handsheets, mechanical properties, newsprint, optical properties, paper properties.

The adoption of new laws governing the use of recycled fiber in the United States is having a ripple effect on papermakers in Canada, where the use of secondary fiber is more of an obligation than a matter of choice. To remain competitive, Canadian producers of newsprint will have to begin using recycled fibers in their papermaking furnishes. Effective deinking of secondary fiber is a key factor in producing paper of acceptable quality at a competitive cost.

This report presents the results of a study into the effects of different carrier gases on the mechanical and optical properties of flotation-deinked pulp. The gases studied in this work were air, carbon dioxide (CO_2), oxygen (O_2), and nitrogen (N_2).

Deinking process

Deinking is the process of removing ink and other contaminants from printed paper. Inks are separated from the pulp suspension by flotation, by washing, or by a combination of flotation and washing.

Chemicals

A wide variety of chemicals are used to facilitate the deinking process (*1–3*). The choice is based mainly on the type of raw material to be treated, the separation method (flotation or washing), and the desired quality of the end product. Alkali and surfactants are widely used in deinking.

Alkali. Alkali causes fibers to swell and helps remove the resins and oils that serve as binding agents for printing inks (*4*). The most common alkaline reagents are sodium hydroxide and sodium silicate. The latter has an advantage in that it prevents redeposition of ink on the fibers and acts as a stabilizer for any hydrogen peroxide that may be added to the pulp suspension.

Surfactants. Surfactants, or surface-active agents, are chemicals that alter the interfaces in a system. A surfactant molecule typically has one extremity that is polarized and another that is not. The nonpolarized portion of the surfactant is adsorbed by hydrophobic substances (ink particles, fibers, fillers). The polarized portion is directed outward, thus enhancing the wettability and dispersion of hydrophobic substances in an aqueous environment.

The polarized and nonpolarized portions of a typical surfactant, in this case sodium oleate, are illustrated in **Fig. 1**. The figure also depicts an ink particle and an air bubble with the polarized portions of the surfactant directed outward. During the deinking process, surfactants are adsorbed by the solids (fibers, ink, fillers), which enhances fiber swelling and expedites dispersion of the ink after separation from the fiber.

Surfactants are classified as cationic, anionic, or nonionic. Each category has distinctive characteristics.

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Cationic surfactant [e.g., hexadecyl trimethylammonium bromide (*5*)]:

- Insensitive to pH variations
- Good foam formation
- Better adsorption by negatively charged particles (ink).

Anionic surfactant [e.g., sodium oleate (*5*)]:

- pH must be alkaline
- Good foam formation
- Strong bonding with ink.

Nonionic surfactant [e.g., polyglycolether alkyl (*5, 6*)]:

- Insensitive to pH variations
- Little foam formation
- Weak bonding with ink
- Excellent dispersion of ink particles.

This study was limited to anionic and cationic surfactants in an effort to simplify the process and ease data interpretation.

Flotation deinking

Flotation deinking involves two fundamental steps: ink–fiber separation and elimination of ink by flotation.

Ink–fiber separation. Ink particles are separated from fibers in a pulper operated under alkaline conditions (pH 10–11) at low temperature (30–60°C). Chemicals are added to help destroy the ink's binding agent and promote the swelling of the fibers, which creates a shearing action at the ink–fiber interface. The strong agitation in the pulper creates friction between fibers and generates hydrodynamic forces, both of which promote separation of ink particles from the fiber surface. Once the ink particles have been separated, they are coated and stabilized by the surfactant. This process is illustrated in **Fig. 2** (*4*).

Elimination of ink. The flotation process removes ink from the fiber suspension by exploiting physical differences (density) and physico-chemical properties (wettability, interface tension). Once the ink has been separated from the fiber surface, the surfactant is deposited on the surface of the ink particles. The surfactant then reacts with calcium ions that are added to the suspension, thus lowering the charge on the ink particles. This allows the small ink particles to agglomerate and form larger particles that can more easily latch onto gas bubbles rising from the bottom of the vessel (*7*). The ink-laden bubbles rise to the surface, where they create a black foam that is raked off and separated from the suspension. This process is illustrated in **Fig. 3**.

CO_2 as a carrier gas in flotation deinking

The use of CO_2 as a carrier gas probably results in smaller bubbles because of the affinity between the gaseous and liquid phases. The layer of surfactant deposited on the bubble surfaces also is likely to be more unstable because of the mass transfer that occurs at the interface of the gaseous and liquid phases.

Ordinarily, flotation is performed under alkaline conditions (pH 8–10). However, the use of CO_2 as the carrier gas acidifies the process. Carbon dioxide is quite soluble in water, with the quantity of CO_2 that can dissolve in one liter of water ranging from 15 mg at 80°C to 75 mg at 30°C (*8*). This dissolution forms a mild acid of pH 5 (*9*).

$$CO_2 + H_2O \leftrightarrow H_3O^+ + HCO_3^- \quad pK = 6.4$$

$$HCO_3^- \leftrightarrow H_3O^+ + CO_3^- \quad pK = 10.2$$

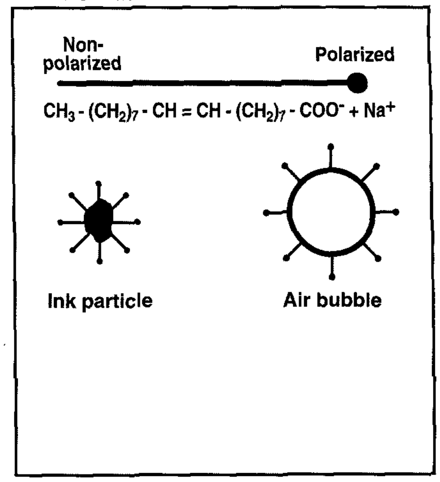
Conventional deinking chemicals, such as sodium silicate and oleic acid, do not work well in an acidic environment. During preliminary trials using CO_2 as a carrier gas, no foam was produced during flotation using these chemicals. Consequently, there was virtually no ink removal.

The acidic environment affects the surfaces of the solid particles (fiber, ink) and modifies their ability to adsorb ionic surfactants. At lower pH, the solid's surface becomes more positive (or less negative) as protons in the solution are adsorbed onto charged sites on the surface. The result is an increase in the adsorption of anionic surfactants and a decrease in the adsorption of cationic surfactants.

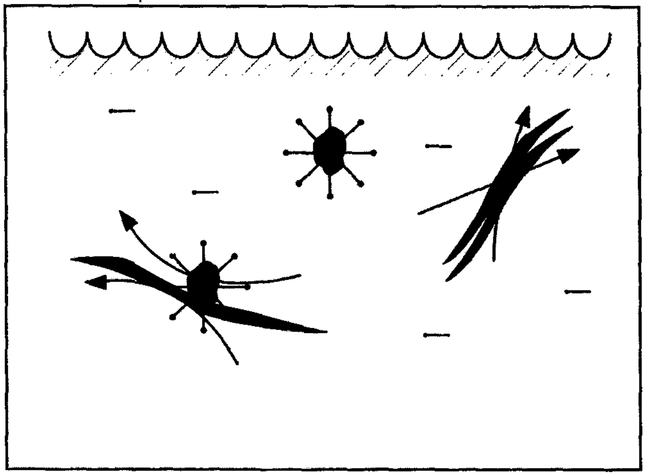
The acidic environment also modifies the surfactant molecules, especially those containing carboxylate groups (soaps, e.g., sodium oleate). In an acid environment, sodium oleate becomes nondissociated oleic acid (neutral molecule), and its adsorption ability is only effective through hydrogen bonding. An alkaline environment, on the other hand, allows the ionization of the polar group R-COONa into $R\text{-}COO^- + Na^+$, which promotes adsorption.

Based on these observations, the surfactant was switched from sodium oleate to hexadecyl trimethylammonium bromide (HTAB). This surfactant has characteristics that make it suitable for use in an acidic environment. Because it is a cationic surfactant, the hydrophilic group carries a positive charge, as opposed to the negative charge carried by the sodium oleate, an anionic surfactant. The main advantage of a cationic surfactant is that it is insensitive to pH variations and retains its positive charge in acidic, neutral, or alkaline environments. HTAB improves the collection of ink particles by making their surfaces hydrophobic.

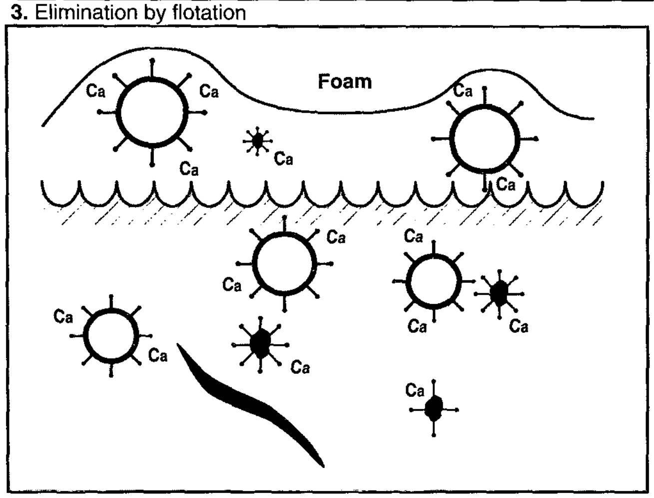
1. The surfactants as collector



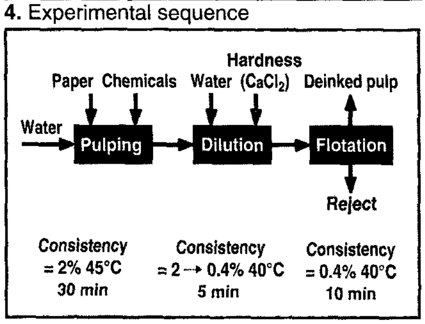
2. Ink–fiber separation



3. Elimination by flotation



4. Experimental sequence



Experimental

All experiments were performed using newsprint furnished by a single printer. All papers were printed fewer than 14 days prior to laboratory deinking. Flotations were carried out in a Voith laboratory cell. Handsheets were prepared from pulp samples before and after flotation in order to measure changes in mechanical and optical properties.

Figure 4 illustrates the sequence that was used for all experiments. The chemicals used in the laboratory deinking were sodium silicate, oleic acid, and the foaming agent HTAB.

First series of experiments

During the first series of experiments, flotation was carried out using four different gases (air, O_2, N_2, CO_2), two levels of oleic acid (0 and 2%), and three levels of foaming agent (0, 0.6%, 1.2%). Sodium silicate content was held constant at 3% during all experiments. The pH before flotation was maintained at a constant level (pH 9–10) and remained unchanged for the flotation runs using air, O_2, and N_2. During the runs with CO_2, the pH rapidly dropped to 4–5.

In the experiments where oleic acid was used, it was necessary to add calcium chloride to harden the water to a hardness of 180 ppm calcium. The calcium chloride reacts with oleic acid to form a calcium soap that acts as a collecting agent.

Second series of experiments

During the second series of experiments, flotation was carried out using four different gases (air, O_2, N_2, CO_2) and three levels of pH prior to flotation (9.8, 6.9, 4.8). The quantities of oleic acid, foaming agent HTAB, and sodium silicate were held constant at 2%, 0.6%, and 3%, respectively. Calcium chloride was added to obtain a water hardness of 180 ppm calcium.

Results

The experimental results were treated statistically in an effort to determine the correlations between different variables. The equations obtained were used to generate the continuous curves in Figs. 5–15.

First series of experiments

Optical properties. Pulp brightness achieved without oleic acid is shown in **Fig. 5**. Addition of oleic acid improved brightness for all carrier gases (air, O_2, N_2, CO_2), as seen in **Fig. 6**. Pulps floated with CO_2 as a carrier gas had superior brightness in both cases.

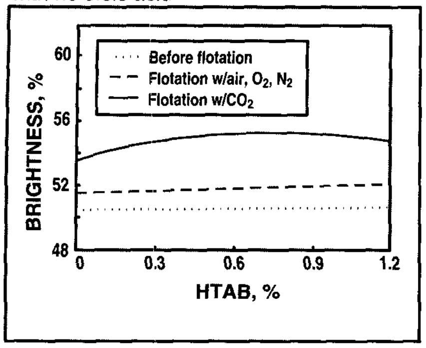
The foaming agent was more effective when added at the same time as the oleic acid. We presume that the oleic acid acts as a collector and the foaming agent helps remove the collected ink.

The trend for luminosity (L^*) was similar to that observed for brightness, as seen in **Fig. 7**.

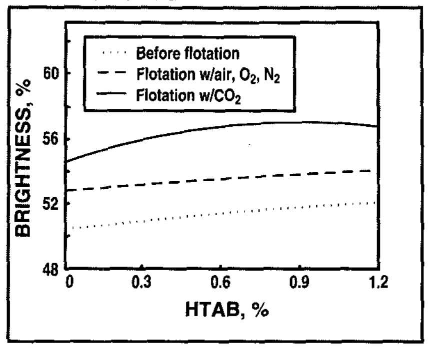
The results in **Fig.** 8 indicate that pulps floated with CO_2 showed less yellowing (b^*) than the pulps floated with the other gases. This performance can be attributed to the acidification caused by solubilization of the CO_2 gas. A slightly acidic environment helps prevent the formation of chromophoric groups, which cause yellowing (*10*).

Mechanical properties. Breaking length for pulp handsheets without addition of oleic acid is shown in **Fig. 9**. Results obtained with addition of 2% oleic acid are illustrated in **Fig. 10**. As seen earlier in Figs. 5 and 6, pulp brightness increased in the presence of oleic acid. However, addition of oleic acid also lowered the breaking length, as evidenced by the results in Figs. 9 and 10. Flotation with CO_2 as a carrier

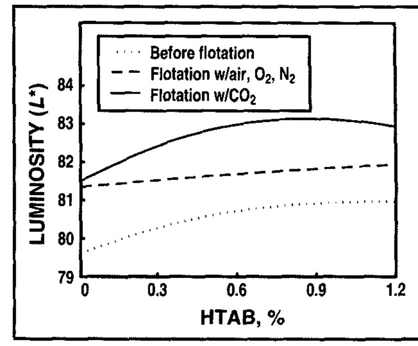
5. Brightness as a function of HTAB addition with no oleic acid



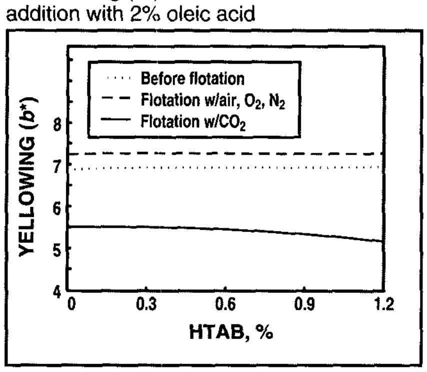
6. Brightness as a function of HTAB addition with 2% oleic acid



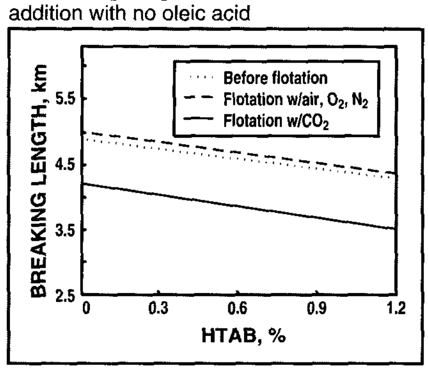
7. Luminosity (L^*) as a function of HTAB addition with 2% oleic acid



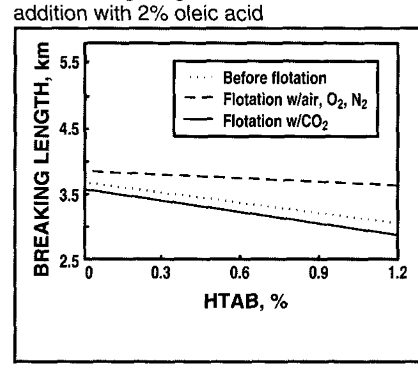
8. Yellowing (b^*) as a function of HTAB addition with 2% oleic acid



9. Breaking length as a function of HTAB addition with no oleic acid



10. Breaking length as a function of HTAB addition with 2% oleic acid



gas increases the acidity of the environment, thus increasing fiber degradation and further weakening the pulp's mechanical properties. The results for burst index in **Fig. 11** provide additional evidence that pulps floated with CO_2 suffer a loss in mechanical properties.

Mechanical properties are also reduced by the presence of surfactants, which disrupt interfiber bonding during paper formation. This effect is enhanced for pulps that are deinked in an acidic environment, which promotes adsorption of surfactants onto fibers. It is likely that the lower mechanical properties for the CO_2-floated pulps can be attributed to a combination of fiber degradation and enhanced adsorption of surfactant.

Second series of experiments

Optical properties. The results in **Figs. 12** and **13** show that acidification of the pulp prior to flotation improved the optical properties (greater brightness, reduced yellowing). This is because acidic environments inhibit the formation of chromophores. For flotation carried out at pH 4.8, there was no difference in optical properties for the various carrier gases. However, when flotation was carried out at neutral or basic pH, CO_2 provided the best results.

Mechanical properties. Mechanical properties of pulps increase with increasing pH prior to flotation, as seen in **Fig. 14**. At pH 4.8, there was no significant difference in burst index, regardless of which gas was used for flotation. Burst index for pulp samples floated with CO_2 varied very little, indicating that they were not influenced by the initial pH of the suspension. This phenomenon is attributed to the rapid acidification of the pulp suspension in the presence of CO_2 gas. The pH during batch flotation with CO_2 hovered around pH 5 within 2 min, regardless of the initial pH.

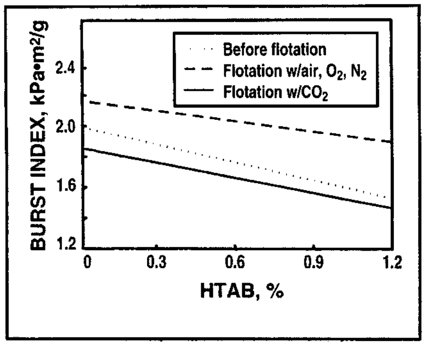
Figure 15 shows that the breaking length of CO_2-floated pulp can be recovered by an alkaline wash. A neutral wash (ca. pH 7) provides only a partial recovery of the breaking-length value. The improvement in breaking length occurs because the wash stage removes the excess surfactant adsorbed by the fibers, thereby increasing the number of sites available for interfiber bonds. Figure 15 also shows the effect of another variable, the dead time between flotation and washing. The results suggest that dead time has little effect on breaking length.

Conclusion

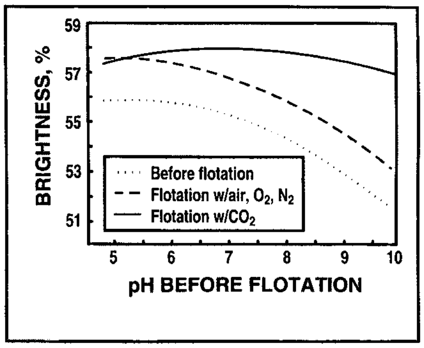
There were no significant differences in the optical and mechanical properties of pulps deinked by flotation using air, O_2, or N_2 as carrier gases. However, the use of CO_2 as a carrier gas for flotation deinking had a significant effect on pulp properties.

- Pulps had superior optical properties (greater brightness and luminosity, reduced yellowing).

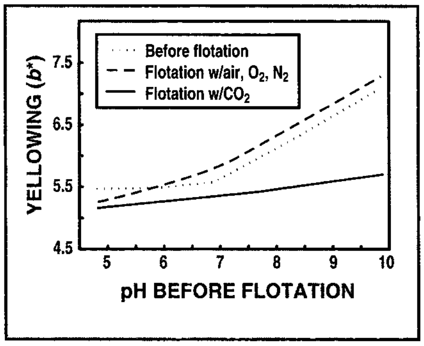
11. Burst index as a function of HTAB addition with 2% oleic acid



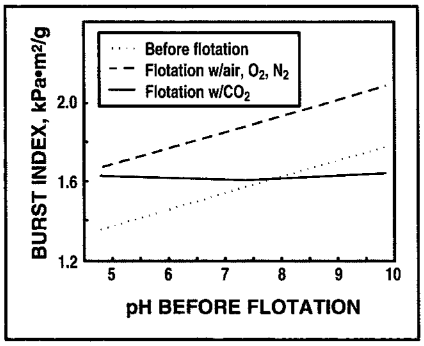
12. Brightness as a function of pH before flotation with 2% oleic acid and 0.6% HTAB



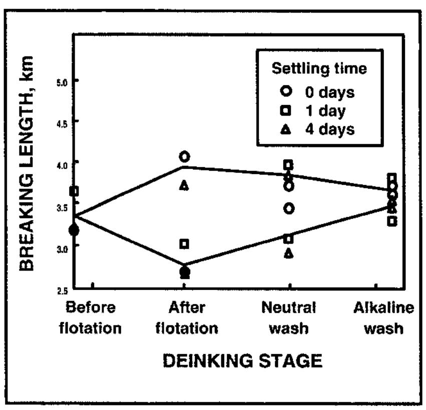
13. Yellowing (b^*) as a function of pH before flotation with 2% oleic acid and 0.6% HTAB



14. Burst index as a function of pH before flotation with 2% oleic acid and 0.6% HTAB



15. Breaking length before and after flotation, after washing at neutral pH, and after alkaline wash. Flotation carried out with 2% oleic acid and 0.6% HTAB.



- Pulps suffered a loss in mechanical properties (breaking length and burst index).

Because CO_2 gas is so soluble in water, the pulp suspension undergoes mild but rapid acidification. The acidity of the pulp suspension inhibits the formation of chromophores, thus enhancing the pulp's optical properties. However, the acid environment also promotes fiber degradation and enhances adsorption of surfactants onto the pulp fibers, resulting in a decline in the pulp's mechanical properties. Most of the mechanical properties can be recovered by passing the pulp through an alkaline wash stage. TJ

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