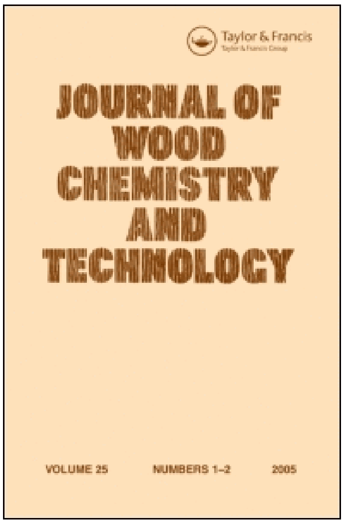

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Removal of Resin from Mechanical Pulps by Selective Flotation: Mechanisms of Resin Flotation and Yield Loss of Fibers

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Abstract: The amount of wood resin in mechanical pulp suspensions could be decreased using a selective flotation process. In selective flotation air-bubbles are dispersed into low consistency pulp suspensions mechanically by an impeller or by injectors. Resin particles attach to the air-bubbles and are lifted to the top of the pulp suspension from where they are removed, along with the flotation froth. The very small size of the resin particles (average diameter <1.0 micron) suggests that they are driven toward the air-bubbles mainly by Brownian diffusion and that attachment of the resin particles to the air-bubbles takes place through colloidal interactions. The resin flotation followed approximate first-order kinetics. The mechanism of yield loss of fibers was entrainment, whereby they were hydraulically transported into the froth along with the water.

Keywords: Flotation, mechanism, collection, entrainment, particle size, resin, extractives, pitch control, deresination, yield, mechanical pulp

BACKGROUND

The resin content of most softwoods used for papermaking is in the 1–4% range.[1] During mechanical pulping the resin is liberated from resin canals and parencyhma cells and dispersed into the pulp suspension as spherical droplets.[2,3] Some of the dispersed resin particles precipitate on fiber

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surfaces impairing fiber-to-fiber bonding and therefore the strength properties of the paper.[4–6] Resin particles depositing later in the pulping and papermaking processes causes diverse runnability and product quality problems.[7] The problems are particularly prevalent when using resin-rich pine species in mechanical pulping. For a long time the paper industry has been trying to develop effective and environmentally friendly technologies to remove and control the resin. Recent laboratory-scale experiments showed that dispersed resin particles can be removed from mechanical pulps by a selective flotation method resembling ink flotation used for deinking of waste paper pulps.[8] The present study provides additional clarification of the mechanism of resin removal and yield loss of mechanical pulp fibers in a flotation processes.

In selective flotation processes, air bubbles are mixed into an aqueous suspension of solid particles by feeding air through an impeller or by creating the bubbles by injectors. In the suspension the air-bubbles and particles collide causing attachment of hydrophobic particles to the air-bubbles. After the attachment the particles are lifted to the surface of the suspension with the air-bubbles and removed with the flotation froth.[9,10]

The basic mechanism of mineral and ink flotation has been thoroughly studied.[9–13] The theories state that as the particle enters the vicinity of an air-bubble a thin water film is formed between the particle and the bubble. The disjoining pressure is a measure of the strength of this water film. Hydrophilic particles have a water film that exhibits a high disjoining pressure whereas the disjoining pressure of hydrophobic particles is small, enhancing rupture of the liquid film and attachment of the particle to the bubble, and further, selective removal of hydrophobic particles from the suspension. It has been generally established that both mineral and ink flotation are first-order kinetics processes.[10,13] The first-order rate equation can be written as:

$$\ln C = -kt + \ln C_0 \qquad (1)$$

where $t =$ reaction time (flotation time), $k =$ the rate constant, $C =$ concentration at $t = t$ and $C_0 =$ concentration at $t = 0$.

Schmidt and Berg[14] expressed the rate constant k for ink flotation processes as:

$$k = (3G_{fr}EL)/(2D_bV_r) \qquad (2)$$

where G_{fr} is the gas volumetric flow rate, L is the length of the bubble rise (approximately the same distance as the cell height), V_r is the cell volume, D_b is the diameter of the bubble, and E is the overall collection efficiency which can be expressed as:

$$E = E_cE_aE_sE_f \qquad (3)$$

where E_c is the collision efficiency, E_a is the attachment efficiency, E_s is the stability efficiency of the particle/bubble aggregate, and E_f is the efficiency of particle transfer to the froth.

In mineral and ink flotation processes particles with a diameter of around 10–100 μm are removed most efficiently. According to general flotation theories, very small and light particles tend to follow the streamlines of water in the pulp suspension and thus avoid attachment to the bubble surface. On the other hand, the flotation efficiency of large and heavy particles is claimed to be impaired by strong detachment forces between particle and bubble in turbulent mixing conditions prevailing in the pulp suspension.[10–12]

In practice, prediction of the parameters affecting overall collection efficiency E (equation (3)) is most difficult. However, equation (2) suggests that the rate constant of flotation can be increased by increasing the airflow rate or by decreasing the average bubble diameter. In ink flotation a general concept of flotation cell design is not to generate very small air-bubbles. This is because these tend to adhere to the fibers causing the fibers to float and be rejected in the froth. On the other hand, large air-bubbles are needed to lift the largest and heaviest ink particles through the pulp suspension.[10–12] The major drawback of ink flotation processes is yield loss of fibers. It has been shown that the dominant yield loss mechanism in ink flotation is not a real flotation emerging from attachment of air-bubbles on fibers, but entrainment, whereby pulp fibers are hydraulically transported into the froth along with the water.[15,16] None of the earlier publications concerning selective flotation of resin from wood pulps discuss the mechanism of resin removal in detail.[8,17–19] In the present study resin flotation trials were performed using laboratory-scale flotation apparatus. Resin particle size distribution measurements, giving information on possible resin droplet aggregation and, indirectly, information on the flotation mechanism of resin particles, were carried out using flow cytometry (FCM). In order to verify that the mechanism of yield loss of fibers was physical entrainment, yield loss was considered as a function of water loss.

EXPERIMENTAL

Pulps

The thermomechanical pulps (TMP) from *Pinus silvestris* and *Picea abies* were produced in the KCL pilot-plant using a RGP 44 high consistency refiner. The Canadian standard freeness of pine and spruce TMP were 84 mL and 48 mL, respectively. The length-weighted average fiber length determined on a Kajaani FS-200 instrument was 1.71 mm for spruce TMP and 1.59 mm for pine TMP. The pulps were stored frozen before use. The content of lipophilic extractives in the spruce and pine TMP were 0.94% and 2.77%, respectively.

Flotation

The flotation trials were carried out using a laboratory-scale Outokumpu flotation cell (15 L).[8] In the cell the air-bubbles are formed and mixed into the pulp suspension via an impeller. Dilution of the pulp was carried out using ion-exchanged water adjusted to a temperature of 55°C. The cell was filled with the pulp suspension so that the surface of the pulp was 0.5 cm below the edge of the cell. The pH values of the suspensions were around 5. After addition of $CaCl_2 \cdot 2H_20$ and mixing of the pulp for 10 min with the impeller (2400 rpm), the airflow valve was opened (6 L/min), and removal of the froth was started. Removal of the froth to a reject vessel was accomplished manually with a plastic scraper. The pulp level was kept constant in the cell by addition of ion-exhanged water (50°C).

Measurement of Size Distribution of Resin Particles

The size distributions of resin particles in the mechanical pulp suspensions and in the flotation froths were studied using flow cytometry (FCM). In FCM, the sample is fed into a measurement cell illuminated by a laser beam. From the scattered light intensity and pulse data an approximate particle size can be calculated. The method is described in detail by Vähäsalo et al.[20] All samples were filtered through a 30-mesh wire prior to FCM-analysis and diluted by a factor of 10.

Measurement of Resin Removal and Fiber Yield Loss

The total content of lipophilic extractives in the pulp suspensions were determined by cyclohexane-acetone (9 : 1, vol) extraction according to SCAN-CM 50 : XE. The compositions of acetone-soluble resinous compounds extracted according to SCAN-CM 49 : 93 were determined by gas chromatography using the short column technique described by Holmbom and Örså.[21] The major difference between the two extraction procedures is that in the acetone extraction phenolic compounds such as lignans are also dissolved and extracted.

To determine the yield loss of fibers caused by the flotation treatment, the froth removed from the cell was filtered in a Büchner-funnel using S&S 589[1] filter paper. The filter cake was dried overnight at 60°C and extracted with acetone to remove resinous compounds. The residue represented the fiber yield loss that had occurred during the flotation treatment.

RESULTS AND DISCUSSION

Flotation trials were carried out using three pulp consistencies (see Figures 1 and 2). For pine and spruce TMP the resin removal was most efficient at 0.4%

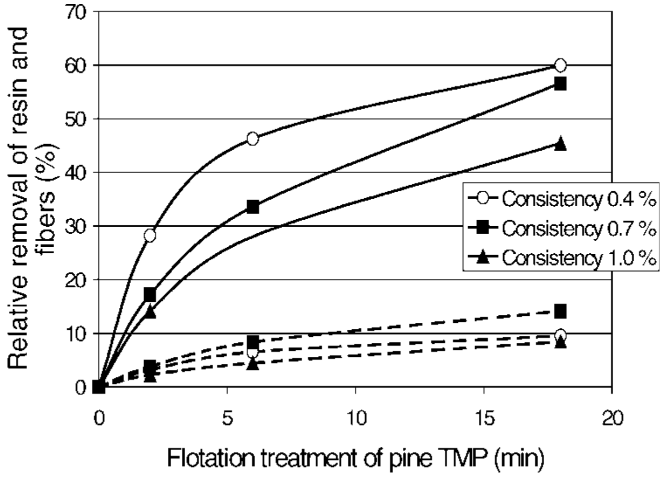

Figure 1. Resin (solid lines) and fibers (broken lines) removed in flotation treatment of pine TMP at three different pulp consistencies ($CaCl_2 = 1.8\,mM$, $pH = 5$, $T = 50°C$).

pulp consistency. Measurement of the size-distribution of air-bubbles in the pulp suspension was difficult. However, it was evident that fiber flocks forming in thicker consistency pulps prevented the efficient dispersion of air-bubbles throughout the pulp suspension, causing the total surface area of the air-bubbles to decrease, and further, the resin removal efficiency to

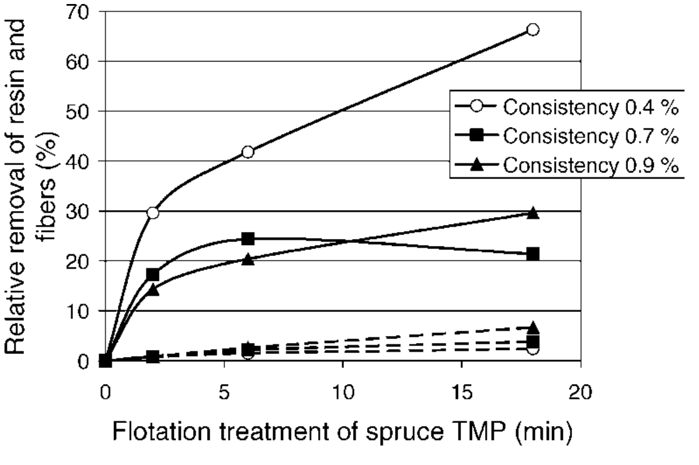

Figure 2. Resin (solid lines) and fibers (broken lines) removed in flotation treatment of spruce-TMP at three different pulp consistencies ($CaCl_2 = 1.8\,mM$, $pH = 5$, $T = 50°C$).

drop. With spruce TMP the turbulent pulp flow stagnated when the pulp consistency was increased to 1.0%. Discontinuous pulp flow significantly deteriorated repeatability of flotation trials. The results concerning yield loss of fibers were somewhat inconsistent.

As indicated in Figure 3, resin removal by selective flotation at 0.4% pulp consistency followed first-order kinetics (equation (1)) to a good approximation. It therefore resembles the kinetics of ink and mineral flotation. The fact that ln C/C_o plots give a positive value when extrapolated to $t = 0$ is probably due to the formation of resin-rich froth during the mixing step, that is, prior to opening the air valve.

In softwoods the resin is located in resin canals and in parenchyma cells. The resin canals are rich in resin acids whereas the parenchyma resin is mainly fatty acid esters and sterols.[1] The results in Figure 4 show that the resin flotation process removes all the types of resin compounds approximately to the same extent, that is, there is no significant difference in terms of removal rate for canal resin or parenchyma resin.

The number-based size distributions of the resin particles in the pulp suspension and in the flotation froth were determined using flow cytometry. The size distribution of the resin droplets in the pulp suspension showed a maximum far below 1.0 μm (Figure 5). Calcium ions did not influence the particle size distributions. However, large resin agglomerates existed in the flotation froth (see Figure 6). This observation was in accordance with earlier findings.[8] The size distribution curves in Figure 7 indicate that the particle size of the resin in the suspension reduces with flotation slightly but an in-depth study would be needed to confirm the observation.

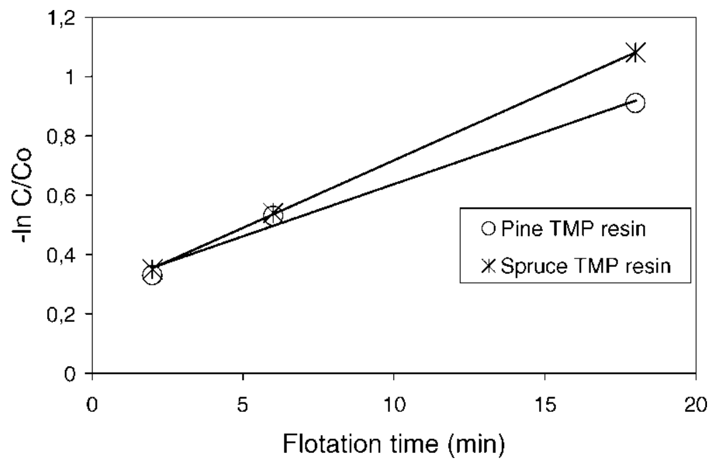

Figure 3. First-order kinetic plots for resin removal in flotation treatment of pine- and spruce-TMP pulps ($c_{pulp} = 0.4\%$, $CaCl_2 = 1.8$ mM, pH = 5, T = 50°C).

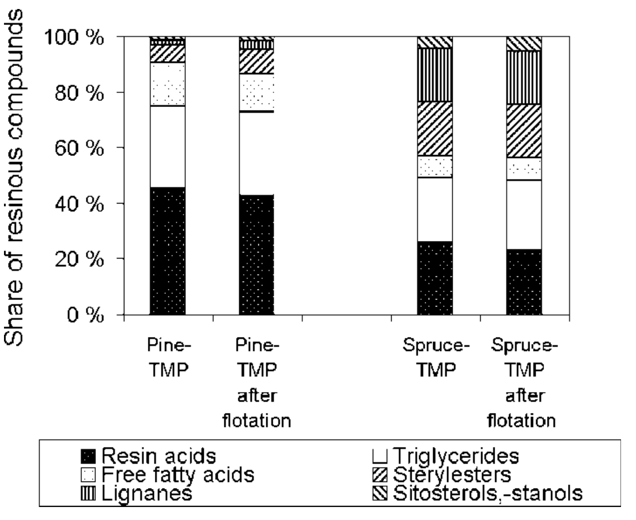

Figure 4. Percentage composition of resinous compounds (acetone-soluble extractives) in pine- and spruce-TMP prior to and after 18 min flotation treatment ($c_{pulp} = 0.4\%$, $CaCl_2 = 1.8$ mM, pH = 5, T = 50°C).

An initial hypothesis based on a previous study[8] was that calcium ions induce agglomeration of the resin particles and that the resulting increase in the particle size enhances their attachment to air-bubbles. In a mechanical pulp suspension the dispersed resin particles are sterically stabilized against agglomeration by carbohydrate chains.[3,22] Probably because of the steric stabilization, resin particles do not agglomerate in the flotation cell either, despite the presence of calcium ions and the vigorous mixing conditions in the pulp suspension. Agglomeration of the resin particles in the flotation

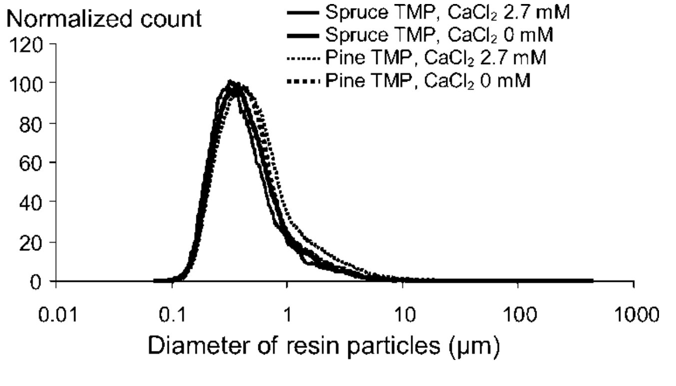

Figure 5. Diameter of resin particles in pine- and spruce-TMP ($c_{pulp} = 0.8\%$, pH = 5, T = 50°C).

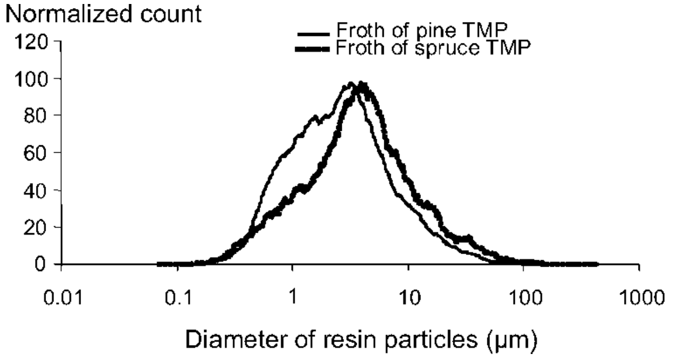

Figure 6. Resin particle size distributions in flotation froth of pine- and spruce-TMP ($c_{pulp} = 0.8\%$, $CaCl_2 = 2.7$ mM, pH = 5, T = 50°C).

froth occurs possibly as a result of drainage and collapse of the froth causing a high local concentration of resin particles leading to agglomeration. A similar mechanism for resin agglomeration occurring on the surface froth of paper mill white waters was suggested earlier by Allen.[23]

According to prevailing flotation theories, the movement of very fine particles to the vicinity of air-bubbles is mainly by Brownian diffusion, not by large-scale mutual movement and collisions of particles and air-bubbles that occurs in conventional ink and mineral flotation processes (particle size typically 5–100 μm).[24–26] Reay and Ratcliff[26] have stated that when the particles are large enough to be unaffected by Brownian diffusion (particles larger than around 3.0 μm in diameter), the flotation rate increases approximately with the square of the particle diameter. According to the theory, with sub-micron particles moved by Brownian diffusion the flotation rate is

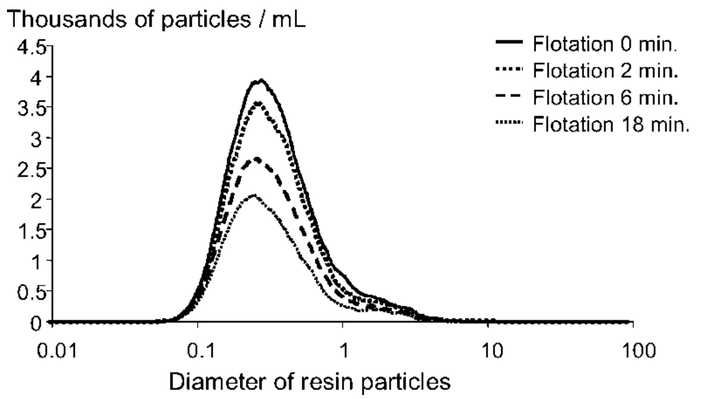

Figure 7. Resin particle size distribution of spruce TMP after different flotation times ($c_{pulp} = 0.4\%$, $CaCl_2 = 1.8$ mM, pH = 5, T = 50°C).

inversely proportional to the particle diameter. Thus, in the intermediate region where both diffusion and collision mechanisms contribute to particle attachment, the flotation efficiency should be at a minimum.

In mineral flotation and in flotation deinking the attachment of particles to air-bubbles occurs through film rupture of the air-bubbles. Derjaguin[27] has stated that because of the energy barrier very fine and light particles do not form a three-phase wetting perimeter when attaching to the bubble. According to Derjaquing, the primary mechanism of flotation of sub-micron particles is "contactless flotation" where the particle is held in the vicinity of the bubble by London-van der Waals forces of molecular attraction. Therefore the stability of the attachment should obey the general principles of the stability of colloids controlled by surface forces.[27] In accordance with Derjaquin's statement it has been shown that electrostatic interactions between particles and air-bubbles play an important role in the flotation of fine particles. The reduction in zeta-potential as a result of electrolyte addition reduces electrostatic repulsion between particles and air-bubbles resulting in a more stable colloidal attachment and more efficient flotation of the particles.[28,29] Electrolytes may, according to Paulson and Pugh,[28] improve flotation of hydrophobic particles by making the size of the air-bubbles smaller. Addition of calcium ions into the mechanical pulp suspensions improves resin removal in the flotation treatment significantly.[8] However, enhancement of resin removal by the presence of calcium ions is not necessarily linked solely to the charge neutralization or possible reduction in air-bubble size. The calcium ions also have a significant effect on enhancing the froth stability.[8] Froth formation and its influence on flotation efficiency is a complex matter and is the subject of further studies.

Figures 8 and 9 show that loss of fibers correlates with water loss whereas resin removal and water loss seem not to have as strong a mutual correlation. The correlation between loss of fibers and water loss suggests that the mechanism is the same as that reported to be occurring in ink flotation, that is entrainment, whereby pulp fibers are hydraulically transported into the froth with the water.[15,16] The fact that the resin removal rate does not correlate strongly with water loss indicates that the primary mechanism of resin removal is not solely entrainment, and that in terms of resin removal other factors such as the interaction of air-bubbles and resin particles (i.e., collection, attachment, and detachment processes) are of great importance.

CONCLUSIONS

As with ink and mineral flotation processes the resin flotation is a first-order kinetic process. Collection of resin droplets with average diameters below 1.0 μm on air-bubbles is mainly driven by Brownian diffusion, not by large-scale mutual movement and collisions of particles and air-bubbles as in the case of ink and mineral flotation.

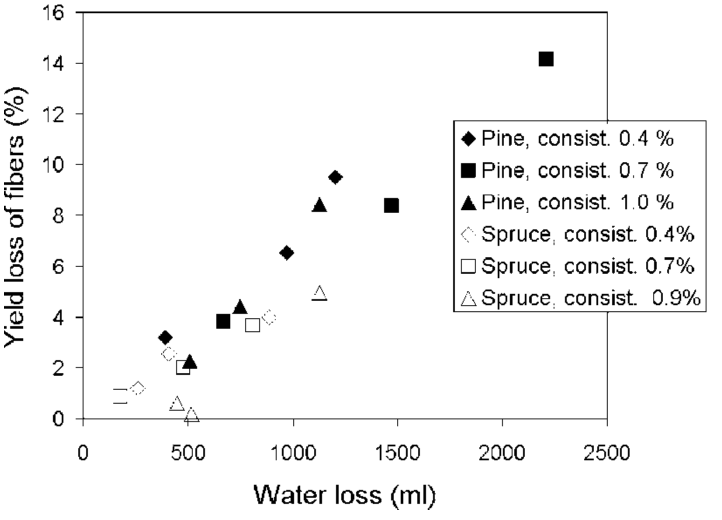

Figure 8. Fiber loss vs. water loss in flotation treatment of spruce- and pine-TMP ($CaCl_2 = 1.8\,mM$, $pH = 5$, $T = 50°C$).

The stability of the attachment of the resin droplets to the air-bubbles obeys the general principles of the stability of colloids controlled by surface forces, whereas in mineral flotation and in flotation deinking, the attachments occur mainly through film rupture of the air-bubbles.

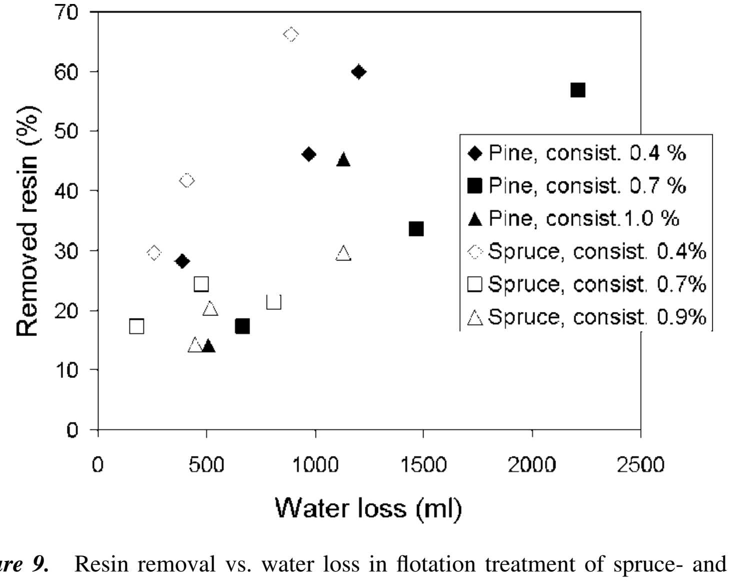

Figure 9. Resin removal vs. water loss in flotation treatment of spruce- and pine-TMP ($CaCl_2 = 1.8\,mM$, $pH = 5$, $T = 50°C$).

Flotation removes all types of resin compounds approximately to the same extent. The results indicate that there is no selectivity in terms of removal of canal and parenchyma resin.

The mechanism of fiber loss is similar to that in flotation deinking, that is, entrainment, whereby pulp fibers are hydraulically transported into the froth with the water.

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