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Pacification Of Stickies By Fibre Loading

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Micro and Colloidal Stickie Pacification with Precipitated Calcium Carbonate

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ABSTRACT

Colloidal stickies that build up in mill process water during pulping are problematic and difficult to remove. We examined precipitated calcium carbonate (PCC) as a means to ameliorate process water stickies. The effectiveness of PCC added directly into a slurry of deinked pulp was compared with in situ precipitation of PCC by the fiber loading method. We found that without retention aids, fiber loaded PCC resulted in the greatest attraction of colloidal stickies to pulp following high-consistency refining required for fiber loading. Also, without retention aids, fiber loaded PCC was the most effective in masking stickies in handsheets. But under the conditions we used, PCC either added directly or fiber loaded was no more effective than retention aids in removing colloidal stickies from mill water.

INTRODUCTION

Stickie contaminants continue to plague the paper industry. Pervasive in both recycling and virgin fiber mills, stickies and their colloidal and dissolved counterparts cost the industry millions of dollars annually (1). Colloidal stickies originate from either natural sources, such as pitch in virgin mechanical pulp production or synthetic sources such as adhesives and papermaking chemicals in recycled fiber mills. Tightening the internal water loops of mill process water while decreasing fresh water intake has exacerbated the problem. Numerous approaches have been taken to minimize or pacify microstickies and colloidal particles that pass

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[1]The use of trade or firm names in this publication is for reader information and does not imply endorsement by the U.S. Department of Agriculture of any product or service.

through fine screens. Microstickies, often as small as 1 • m in diameter, result from and can be altered by pH, temperature, and shear of processing equipment creating colloidal or dispersed stickies. Advances in recycling equipment and processing generally have improved the quality of recycled fiber. However, the chemistry required to deal adequately with colloidal and dissolved stickie contaminants contained within process water is complex and difficult to resolve. Although colloidal microstickies cannot be removed by screening or cleaning, they can be treated in process water because of their chemical characteristics (2).

Traditionally, clay or talc has been used to control pitch deposition from process water in thennomechanical pulp (TMP) and paper mills. Banerjee and Merchant (3) observed–thattalc was ineffective for agglomerating stickies but was a powerful detackifer. That report also highlighted the effect of stirring speed and pH on stickie agglomeration. For printing and writing papers, researchers have reported the benefits of precipitated calcium carbonate (PCC) (4). Scientists at the Nippon Paper Industries laboratory have reported that both the surface area and charge of the PCC influence pitch adsorption. They observed that although both anionic dissolved and colloidal substances in bleached TMP (BTMP) filtrate were adsorbed on PCC, colloidal substances were more preferentially adsorbed (5).

This study concentrated on PCC and its ability to pacify colloidal stickies in recycled fiber process water and microstickies in semi-deinked pulp (deinked pulp obtained prior to flotation). We compare the performance of commercial PCC with PCC made by fiber loading. Fiber loading (FL) is a method developed at the USDA Forest Service, Forest Products Laboratory (FPL) for in situ formation of PCC. The FL process consists of two separate steps (6). Calcium hydroxide is mixed thoroughly into moist pulp and then the $Ca(OH)_2$-containing pulp is reacted within a high-consistency refiner or disk disperser pressurized with CO_2 to precipitate calcium carbonate. Freshly formed and highly charged $CaCO_3$ is deposited both within and on the exterior surfaces of the fibers (7).

We have previously investigated and reported the advantages of the FL process compared with the conventional practice of adding PCC to the wet end of the paper machine, a method we refer to as direct loading (DL). These studies have shown superior paper strength properties, recyclability, and energy and money savings made possible by substituting filler for fiber using fiber loaded pulp (8, 9, 10). The study reported here examines another aspect of PCC: the possibility to pacify or minimize colloidal and dissolved microstickies in process water from recycled pulp.

EXPERIMENTAL

We compared two batches of pulp at three different conditions for this study: 1) FL with and without retention aids, 2) DL of PCC into pulp samples with and without refining and with and without retention aids, 3) control pulp with and without refining and with and without retention aids. Handsheets were prepared and analyzed for dirt and stickies, and the associated water samples were analyzed for colloidal stickies.

MATERIALS

Pulp and Process Water

Two batches of pulp were obtained from a mill (Stora Enso North America, Duluth, MN) that produces a high quality, postconsumer deinked pulp. Mill personnel collected the pulp prior to flotation in the recycling process to provide a sample that still contained both dirt and stickies. Batch I pulp was sent to FPL as a slurry at ~0.8% consistency. This stock was subsequently dewatered in a 200-mesh screen box (0.074-mm openings) at FPL. The water was collected to simulate mill process water and used as the water supply for handsheets. Batch II pulp was dewatered at the mill in a 100-mesh screen box (0.149-mm openings) followed by additional dewatering. This wet lap (−25% solids) pulp was sent to FPL along with 20 L of deinked stock at −0.8% consistency, which was dewatered at FPL in a 200 mesh screen box (0.074 mm) to provide process water for the colloidal water analyses and to dilute pulps for handsheet preparation.

Chemicals

The calcium hydroxide was an industrial grade hydrated lime from Mississippi Codex (Alton, IL). The PCC used for direct loading was HO rhombohedral PCC from Specialty Minerals Inc. (New York, NY). Retention aids, cationic polyacrylamide (EKA PL 2310) and anionic colloidal silica (EKA BMA 780), were from Eka Chemicals, Inc. (Marietta, GA).

Equipment

Hobart dough mixer (Troy, OH)

Sprout Bauer (Springfield, OH) 305-mm pressurized batch disc refiner equipped with pattern D2B505 refiner plates.

METHODS

Fiber   Loading

A 500-g (ovendry basis) pulp sample was adjusted to 20% solids with deionized water, and 20% (based on dry fiber) calcium hydroxide was added to the pulp and blended in a Hobart mixer for 15 min using a flat stainless paddle. The pulp was placed in the holding chamber of the pressurized refiner, which also served as the reaction vessel. The chamber was pressurized with CO_2 at 172 to 207 kPa for 3 min before the pulp was screw-conveyed to the refiner zone where it passed through refiner plates at a 0.63-mm gap into the pressurized receiver tank. The reacted pulp was held an additional 12 min under CO_2 pressure to assure complete conversion to PCC. The total time for fiber loading was 15 min.

Process   Water

Water samples were collected for colloidal stickie analysis from both batches of pulp. Three grams (dry weight) of fiber were diluted to 1 L with mill process water. They were then mixed and poured into a Canadian Standard Freeness tester. All the effluent was collected, transferred to 500-mL polyethylene bottles, and sent to an outside laboratory for colloidal stickie analysis. In all cases, the slurries were made with 3 g (dry fiber), irrespective of the ash content, to provide a uniform filtering effect. When retention aids were used, the slurries were treated with 3-mL doses of cationic polymer (EKA PL 2310) at 0.05% concentration and mixed ~10 seconds with an air-driven mixer. Next, 450-• L doses of an anionic polymer (EKA BMA 780) at a 0.5% concentration were added to the slurries and mixed an additional 10 seconds. The slurries were

immediately transferred to the freeness tester. For the DL conditions, commercial PCC was added to the slurries during mixing. The PCC was added at a rate of 25% based on the dry weight of the fiber and was mixed thoroughly for 5 min to assure uniform distribution.

Refining

Refined pulps used for DL and controls received the same mechanical treatment as the fiber loaded pulp. A pulp sample of 500 g (ovendry) was adjusted to 20% solids with deionized water, mixed in the Hobart for 15 min, and passed through the refiner at a 0.63-mm gap. No pressurization or additional retention time was used.

Handsheets

The processed pulps were used to make 1.2-g handsheets (60 g/m^2) for both dirt and stickie quantification. All pulps were processed in a British disintegrator for 10,000 revolutions, transferred to a doler tank, and diluted to 0.15% consistency. The sheets were produced using a slightly modified process of Tappi 205 in which the sheets are speed dried between blotters on a hot plate (1 1). For Batch I handsheets, 100% process water was used for dilution water in de doler tank; only 12% of the dilution water was process water in Batch II pulp.

For the DL handsheets, papermakers PCC was added at the 25% level (based on dry fiber weight) into the British disintegrator prior to the sheet making. Where designated, two polymer retention aids were used: cationic (polyacrylamide, PL 2310) and anionic (colloidal silica, BMA-780). The concentrations of the polymers, based on dry fiber weight, were 0.05% for the cationic polymer and 0.075% for the anionic polymer. The dilute polymers were added to each individual aliquot and were mixed together for 10 seconds before pouring into the sheetmold.

ANALYSES

Colloidal Stickie Analysis

Water samples generated by drainage through the freeness tester were analyzed for colloidal stickies by BASF-Canada (Toronto, Ontario). The procedure used a proprietary laser-based particle sizing and counting system developed by BASF. The detectable particle sizes are 1 to 10 • m. The water sample is first filtered through 100-• m and den 40-• m screens. A dye, which

attaches to hydrophobic particles, is added to the filtered sample. The sample is drawn into a capillary-measuring cell where the laser emits a specific wavelength that selectively causes the dye to fluoresce. Fluorescence is measured by a detector and provides both size and particle counts. The results are stored to a spreadsheet to tabulate both a particle size and a volume histogram An overall concentration is also calculated, for which the units are expressed as $\mu m^3/\mu L$. These units are equivalent to parts per billion (11).

Hand Sheet Stickie and Dirt Analysis

Handsheets were analyzed for dirt and stickies using image analysis systems. Because of equipment availability, Batch I handsheets were analyzed with an Apogee Spec*Scan 2000 V. 1.2.26 system (TCE Limited, Milwaukee, WI), whereas Batch II handsheets were evaluated with a Verity IA Size and Shape V.4.2 system (TCE Limited). The Apogee system utilizes an Hewlitt Packard (Palo Alto, CA) Scanjet 6100C flatbed scanner set to 600 dpi. The Apogee software was set to measure down to $0.001\text{-}mm^2$ particle area size with a gray level threshold setting of 127. The Verity system uses an AGFA ArcusII flatbed scanner set to 600 dpi. The Verity system was set to measure down to $0.005\text{-}m^2$ particle area size. The threshold was set to 80% of the mode of the background gray level for stickies. For dirt, the threshold was set to be equivalent to the threshold used for stickie analysis for each condition. Batch I and II data should be considered independently.

For stickie analysis, the sheets were dyed according to the FPL alternative dye method (12). This procedure entails dyeing the sheets (still attached to backing blotters) in a solution of Morplas Blue 1003 dye dissolved in heptane. The dyed sheets and blotters were speed dried on a hot plate. The backing blotter absorbs excess dye.

In all the handsheet analyses, we assumed that total contaminants detected on the dyed sheets include dirt as well as stickies. Under this presumption, we subtracted the large and small fractions of dirt counted on the undyed sheets from the total contaminants counted on the dyed sheets to obtain approximate contributions of each category of contaminant. All dirt and stickie graphs are plotted in this manner.

Ash   Testing

Handsheets were ashed at high temperature using a Senn (Portage, MI) ash tester. Dry samples were ashed in an oxygen-rich chamber that reduces the $CaCO_3$ to CaO. The ash weight was multiplied by a factor of 1.78 to convert the ash to percentage calcium carbonate.

DISCUSSION   OF   RESULTS

Figure 1 summarizes the results of Batch I pulp handsheets prepared using 100% process water in the doler tank. The initial pulp (control) had a total dirt count of approximately 800 ppm; the stickie content was about 300 ppm The deinked control pulp contained only minimal (0.06%) ask When PCC was added into the doler tank without retention aid, the dirt count was not substantially reduced because little PCC was retained in the handsheets. However, considerably more stickies were detected, especially in the larger than 0.02-mm^2 size range, even though the handsheet ash increased to 2.1% (Table 1). The fiber loaded handsheets (containing 12.7% ash) had significantly decreased dirt counts, approximately 425 ppm, but stickie counts remained at 300 ppm Large dirt particles were most dramatically reduced.

Similarly, process water analysis showed comparable reduction in the number of counts of colloidal particles per microliter from the fiber loaded pulp compared with process water from the control and direct loaded pulp samples. The profile of colloidal particle size distribution (Fig. 2) shows the highest concentration of particles in the range under 5 • m Above 5 • m, the fiber loaded and direct loaded curves are essentially identical but lower than those for the process water from the control pulp with no PCC. Process water for control 2 (Fig. 2) was sampled after storage at approximately 5°C. As expected, fewer colloidal particles were detected in the water after cooling, and the particle size distribution shows substantially fewer stickie particles larger than 4 • m compared with control 1, indicating agglomeration and removal of the larger colloidal particles during screening through the freeness tester. Because the colloidal stickie profile of the pulp and process water had changed by cold storage, we requested another batch of fresh pulp and process water.

Because fiber loading requires high-consistency mixing and passing though a pressurized refiner, we used Batch II pulp to investigate the role of the high-consistency refiner and retention aid on handsheet contaminants and colloidal particles in process water. Although "refining" per se was

not done on the samples because of the high-consistency processing through a wide plate gap, additional fibrillation did occur, which increased fiber surface area and bonding. Roberts (13) states that filler is rarely attached to actual fiber surfaces but rather attaches primarily to fibrils and fine fragments by electrostatic forces that fix filler particles. Filler may also provide more area for adsorption of microstickies when retention aids are used. All of the experiments run on Batch II were done on the same day to eliminate any effects of cold storage. Some pulp was passed through the high-consistency refiner prior to making handsheets for both the control and direct loaded sheets; the fiber loaded sample was prepared according to the usual protocol. A profile of the contaminants contained in the handsheets made from these pulps is shown in Fig. 3. As with Batch I (Fig. 1), no retention aid was used; however, no process water was included in the handsheet preparation. Process water was analyzed separately.

After Batch II pulp passed through the high-consistency refiner, we measured 936 ppm total contaminants with a high concentration of stickies. As in Fig. 1, the fiber loaded pulp was more effective in reducing contaminants, especially the microstickies and dirt, than was the direct loaded pulp. Residual contaminants were 800 ppm for the DL and 580 ppm for the FL sheets. Ash contents measured in these handsheets were 0.2%, 3.5%, and 7.7% for the control, DL, and FL, respectively. Data suggest that the high-consistency refiner does reduce the particle size of . larger dirt and stickie contaminants even though a wide gap was used.

Because the DL and FL handsheets in Figs. 1 and 3 did not include a retention aid, they were not measured at comparable ash. Experiments on Batch II handsheets were repeated using the refiner prior to handsheet preparation and with retention aid. This time, 12% of the total dilution water was supplied from previously collected process water. Figure 4 primarily illustrates the effect of retention aid to incorporate higher ash into the handsheets but also gives a baseline for the unrefined control plus 12% process water. Total contaminants in the unrefined control, approximately 1,000 ppm at 0.2% ash, was reduced to 7 12 ppm at 1.1% ash by the refiner plus the use of retention aid, which incorporated the semi-deinked pulp ash into the sheet.

When we added retention aid in the preparation of the direct and fiber loaded sheets, the DL out performed the FL in contaminant pacification. However, the DL handsheets contained 20.8%

ash, which is 3% more than the 17.9% contained in the FL sheets. However, the superiority of the DL in reducing contaminants in Fig. 4 can be explained by several factors other than total ask The FL process incorporates some PCC inside the fiber lumens where it was unavailable for pacification of slurried contaminants or for masking handsheet contaminants. The FL PCC crystals are slightly larger, approximately 1.5 • m in diameter, than the commercial papermaking PCC used here, which was 1.4 • m Smaller PCC particles have a larger surface area on which stickie contaminants may be adsorbed when retention aids are used. Roberts (13) contends that because filler retention is dependent on surface chemistry, the influence of particle size and number is very important. Also, when PCC is added in a mill, it is added at the papermachine without the advantage of high-consistency refining. Therefore, the more accurate comparison is shown in Fig. 4 where unrefined pulp is direct loaded. These DL handsheets made without refining contained 17.4% ash and were significantly less effective in decreasing contaminants than were the FL sheets at comparable ash content.

Distribution curves for colloidal particle size contained in the process water from the pulps made from Batch II are shown in Fig. 5. As expected, the process water from the unrefined control pulp displayed a similar profile and total number of colloidal particles per microliter as that obtained for the Batch I control. When the control was refined and retention aid was added, the number of colloidal particles in the process water was dramatically reduced. We suggest this was due to increased fibrillation from refining and a receptive, increased surface area to attach colloidal particles with retention aid. Because the DL and FL samples contained relatively high ash, the total number of microparticles (2 • m) detected was significantly lower (approximately 0.5/• L) than the process water collected from the unrefined control (2.5/• L). Distribution curves are essentially identical for colloidal stickies remaining in process water after DL or FL followed by retention aid. No attempt was made to optimize retention aid requirements, so it is entirely possible that if it were applied differently, the effect of the PCC and method of addition might be more pronounced. Also, order of addition and shear levels used in manufacturing could alter the results.

CONCLUSIONS

Our results indicate

- fiber loading (FL) is more effective than direct loading (DL) (without refining) for decreasing detectable microstickies in handsheets made from deinked pulp (no retention aid);
- at the level applied, retention aids are very effective in removing colloidal microstickies from process water; and
- high-consistency mixing and refining enhances adsorption of microstickies on PCC and fibers.

Table 1. Content of ash in handsheets (NA, data not available)

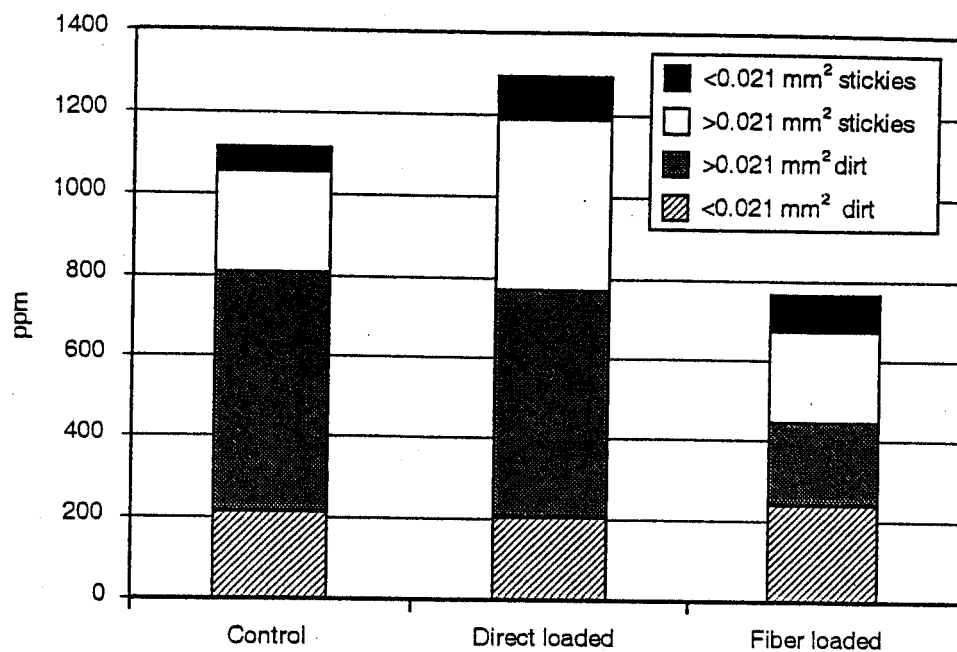|	Handsheet ash content (%)	
	Batch I	Batch II
Control (no refiner, no retention aid)	0.06	0.2
Direct load (no refiner, no retention aid)	2.1	3.5
Fiber load (no retention aid)	12.7	7.7
Control (refiner, no retention aid)	NA	0.2
Direct load (no refiner, with retention aid)	NA	17.4
Direct load (with refiner, with retention aid)	NA	20.8
Fiber load (with retention aid)	NA	17.9

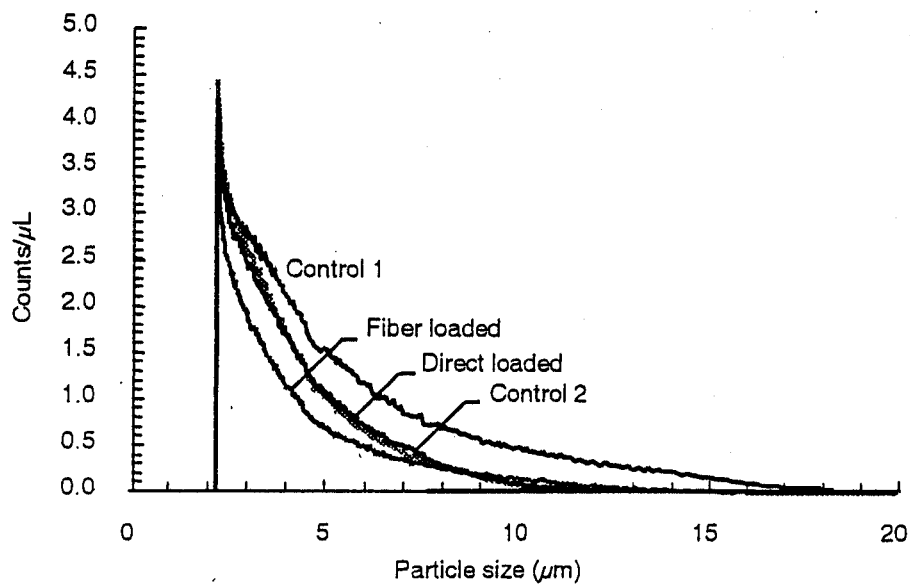Figure 1 — Components of total stickies and dirt, Batch I handsheets (no retention aid).

Figure 2 — Colloidal particle size distribution curves, Batch I process water (refined with no retention aid).
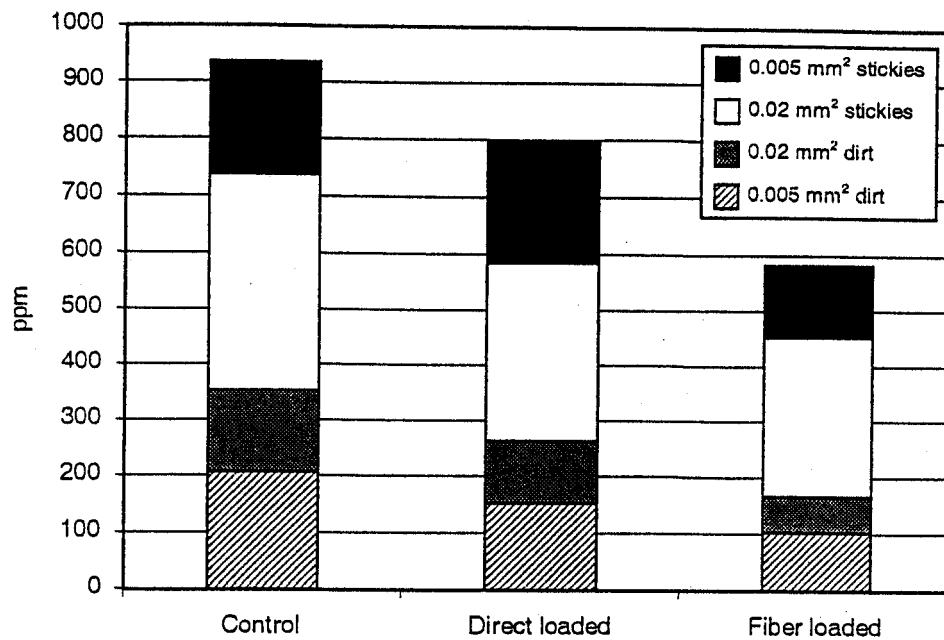
11

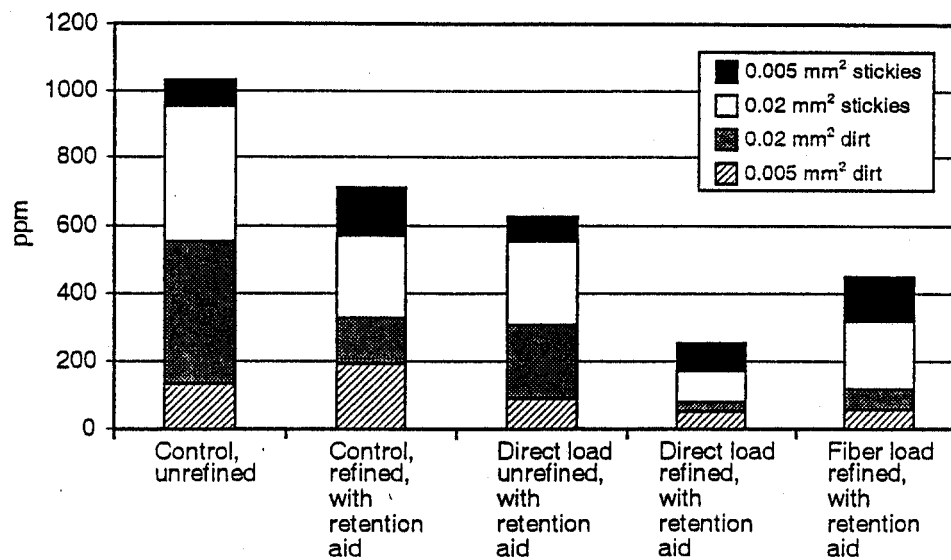Figure 3 — Components of total stickies and dirt, Batch II handsheets (refined with no retention aid).

Figure 4—Components of total stickies and dirt, Batch II handsheets.
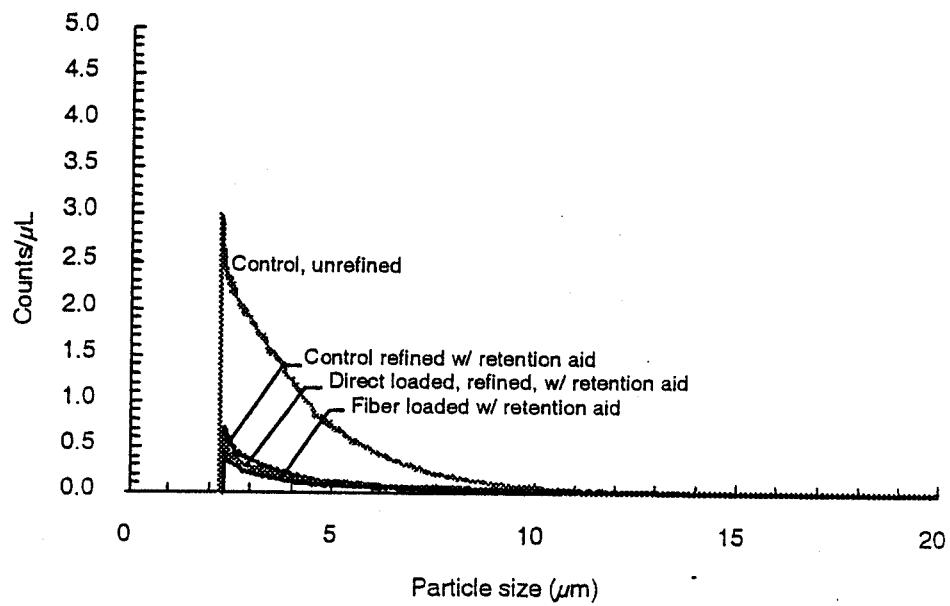
Figure 5—Colloidal particle size distribution curves, Batch II process water.

ACKNOWLEDGMENTS

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