

The Influence of Clay Addition on Flotation Deinking

Jie 'Fred' Shen
Graduate Student
Miami University
Oxford, OH 45056

Said Abubakr
USDA Forest Service
Forest Products Laboratory
One Gifford Pinchot Drive
Madison, WI 53705

Allan M. Springer
Professor
of Paper Science and Engineering
Miami University
Oxford, OH 45056

Fiber loss is a major concern in deinking operations. In the current laboratory investigation, ledger grade paper underwent a laboratory deinking process that included alkaline pulping, screen washing and dispersed air flotation. High levels of clay added into the flotation cell significantly decreased the fiber loss in the flotation rejects. Yet, the clay added did not interfere with flotation deinking performance as measured by brightness, dirt count and Effective Residual Ink Concentration.

INTRODUCTION

Most recently constructed deinking facilities have taken measures to preserve or recycle process water in response to tighter discharge water regulations. A number of technical issues related-to closure of process water loops have not been fully addressed. One of the timely topics that lacks sufficient investigation is the impact of process water quality on flotation deinking performance.

Dissolved air flotation (DAF) clarifiers are widely installed in deinking plants to remove suspended solids. The incapability of DAF units in removing dissolved solids will result in the accumulation of the latter in the water loop. Accumulation of fine suspended solids may also occur when the DAF clarifiers are operated at low

removal efficiency due to economic considerations. This work is a part of a project that is designed to screen these impurities in the water loop for their effect on a flotation deinking process. Evaluations of their effect are based equally on ink removal and fiber loss across the flotation process. It is well known that brighter and cleaner paper can be produced from waste stock at the cost of yield (1). Yield loss, sometimes as high as 12% (2), is a primary concern of any deinking mill in addition to deinking quality. Some contaminants, such as calcium ions, can cause excessive fiber losses in flotation loops (2).

The impurity studied in this work is clay. The source of clay can either be from tiller or coating of the paper. Only coating clay was the subject of study in this paper.

EXPERIMENTAL

Stock Preparation

Stock variation is a major source of error in deinking studies. In the current study, a universal stock was used in all experiments. Preparation of these waste paper stocks started with COMPAT XOS, a non-coated xerography and laser printing grade paper from Nationwide Paper. This paper was then sent to the Office of Applied Technologies at Miami University to be printed with Soy-A-Lith Duplicator Inks, a soybean oil based offset ink from Braden Sutphin. The image on each sheet of paper was two 3" x 5" pictures, half a page of text and a .5" x 10" dark bar in order to represent a moderate to intensive ink coverage.

Pulping

To eliminate variables, deionized water with 50 ppm (as CaCO_3) of added hardness was used to pulp the stock in a British Disintegrator running at 3,000 rpm. Unless otherwise noted, all the DI water used was prepared with 50 ppm hardness. Waste paper stocks were cut into 1 square inch pieces and pulped at 5% consistency. There was 8.6% filler content in the paper. However, for the convenience of discussion, all consistencies in this paper are calculated based on the total stock added. Sodium hydroxide was used to adjust the initial pH to 10.5. A TEXO surfactant, TEX-D-INK 1621, was also added at 880 mg/kg to aid the dispersion of ink particles. The surfactant was a blend of nonylphenol ethoxylate and phosphate compounds. Pulping was carried out at 45 °C for 25 minutes.

Washing

Defibered pulps were washed before being subjected to the flotation process. Pulps removed from the British Disintegrator were diluted to 1% consistency and placed onto a 100 mesh screen. The concentrated pulp (8 - 10% consistency) was again diluted to 1% consistency and used in flotation studies.

Flotation

A HENKAL flotation aid, OLINOR 1200, was added to the 1% pulp at 2 g/kg. The flotation aid is a blend of polyoxyethylenated fatty acid esters. It aids the foam generation and increases the hydrophobicity of ink particles. Flotation runs were conducted in a WEMCO laboratory flotation unit with an automatic skimmer. Clays were blended with the pulp using an electric stirrer. The consistencies of fiber were kept constant at 1% while different levels of clays were added. Therefore, the consistencies of the final stocks in the flotation cell were in fact altered by clay addition. Total volume of the pulp added to the flotation cell was 5.5 l. Flotation conditions were: 35 °C, 10 min, 1,500 rpm and 471 ml/sec air injection. Solid contaminants were mixed with the stock by a Warton RZR50 stirrer rotating at 400 rpm.

Reject Solid Content and Ash Determinations

Overflow from the flotation cell was collected as rejects. The volumes of overflow were recorded for each flotation run. The solids content in the rejects was determined by drying 150 ml overflow in a 95 °C oven for 24 hr. The 150 ml of rejects were placed in 15 cm petri-dishes and the final solids were scraped with a blade and weighed on a balance.

The solids collected were ashed in a muffle furnace according to T211. The ash left in crucibles was weighed and recorded.

Fiber loss in the flotation overflow was calculated as follows:

$$(A - B) \times \frac{C}{150}$$

A = solid contents in 150 ml overflow, g

B = ash contents in 150 ml overflow, g

C = total volume of overflow, ml

Deinking Performance Evaluation

Pulp handsheets were formed from 150 ml samples of flotation accepts using Fisher P8 15 ml qualitative filter paper in a Buchner funnel. The handsheets were pressed and dried according to T218. For comparison, handsheets were also made from the pulp before and after washing. Five handsheets were made from each pulp sample.

Deinking performance was evaluated by three methods that were available. Dirt counts were done using an OPTOMAX Dirt Counter unit. All images on the unit were acquired with a 300 dpi scanner (Hewlett Packard ScanJet Plus). The unit was capable of detecting ink particles down to 0.04 mm², which is equal to ink particles with 200 µm diameters. It was necessary to detect ink particles smaller than 0.02 mm² in the current work, therefore, the software settings were changed to interpolate to 600 dpi. The accuracy of interpolation is a subject for extensive discussion today (3), however, we believed that the data were still valid for internal comparison. A second method, the Effective Residual Ink Concentration (ERIC), measured by a Technidyne Technibrite Micro TB- 1C, was also used. ERIC measures the accumulative effect of residual ink particles in the handsheets at infrared spectrum (950 nm) and manipulates these reflectances via Kubelka-Munk analysis until the Effective Residual Ink Concentration is computed. A third evaluation method used was handsheet brightness. Brightness was measured at 457 nm using a Technidyne S-4 Brightness Tester and Colorimeter according to T452. Measurements were done at four different spots on each handsheet. It is commonly accepted that finer ink particles in the handsheets have stronger influence on brightness.

RESULTS

The initial pulp after alkaline pulping in the Morden slusher had a TAPPI brightness of 68. The laboratory deinking sequence yielded a 13 unit increase in pulp brightness (Fig. 1). Therefore, it was valid to study the influence of clays using this sequence.

One of the initial hypotheses was that the size of clay particles may play a significant role (4). Therefore, two coating clays of different size from J. M. Huber were studied. HYDRAGLOSS 90, an ultrafine coating clay, had 96 - 100% particles finer than 2 µm and a TAPPI brightness of 90. HYDRASPERSE, a #2 coating clay, had 80 - 85% particles finer than 2 µm and a TAPPI brightness of 86.

There was 5.6% clay in the original sheets of COMPAT XOS paper. A majority of these clays were lost during washing on the 100 mesh screen (data not shown). All data were plotted against the amount of clay additions instead of the actual amount of clay in the pulp.

Fiber Loss Reduction

Both coating clays reduced fiber loss in flotation overflows (Fig. 2a,b). The magnitude of decrease was about 50 - 70%. It was reasonable that the ash contents in the total reject increased as greater amounts of clays were added. Yet, the total solids content in the rejects did not increase. It either slightly decreased or remained constant, consequently leading to a decrease in fiber loss.

Total volumes of the overflow from the flotation cell were reduced upon additions of clays (Fig. 3). The fiber loss reductions in rejects were clearly associated with this decrease in rejects volumes.

Similar fiber loss reductions in flotation rejects were observed when a 'clean' furnish was mixed with the #2 coating clay (Fig. 4). The 'clean' furnish was repulped from the original unprinted sheets and was subjected to same deinking processes. Flotation of the 'clean' furnish resulted in about 8% fiber loss. Lack of ink particles in the furnish did not prevent 10 g/l of #2 coating clay from reducing fiber loss by more than 50%.

Deinking Performance

With respect to dirt counts, neither ultratone coating clay nor #2 coating clay exhibited any detrimental effect on the flotation deinking. Addition up to 10 g/l of coating clay in the flotation cell did not significantly increase the dirt counts of handsheets (Fig. 5a). Due to the nature of the measurements, deviation of the data was substantial. Therefore, it was concluded that the downward trends of dirt counts on handsheets were not statistically significant either.

Similarly, ERIC measurement indicated the addition of either clay did not negatively affect the ink removal (Fig. 5b). No substantial difference in ERIC values of handsheets was observed upon the addition of coating clays. The slight increases at high clay addition were not statistically significant.

Brightness of the handsheets was constant when different levels #2 coating clay were added (Fig. 5c). Addition of ultratone coating clay resulted in a one point brightness increase (Fig. 5c). However, it was not significant.

The handsheet retention of the two coating clays were about 20% and 50%, respectively (Fig. 6a,b). The clay constituted up to 30% of the handsheet weight. As brightness of both clays was higher than 85, it was necessary to determine whether there was any brightness enhancement due to the inclusion of clays. Flotation accepts (w/o clay) were mixed with 10 g/l ultratone and #2 coating clays. Surprisingly, inclusion of the high brightness clays failed to enhance the handsheets' brightness (Fig. 7). Instead, slight decreases were observed.

DISCUSSION

Effect of Clay on Deinking Performance Evaluation

Law et al. (5) developed a method to chemically remove most components of a handsheet so that the mass of toner ink particles that were left intact could be measured. Clay was claimed as one element of a handsheet that was not readily removed by any chemical means. Clay can be removed from pulp by extensive washing; however, this can not be done without losing a large number of the ink particles. Most particles of the clay used in this study had a diameter smaller than 2 μm . They should be able to pass through the qualitative filter paper for handsheet making. However, the fiber in the pulp formed a dense mat on the filter paper that caught up to 50% of clay particles (Fig 6). Fortunately, results in this study have shown that inclusion of coating clay in the handsheet did not increase the handsheet brightness (Fig. 7). Probably the optical performance of a filler is not dependent on its brightness alone, but is also determined by its particle size, morphology and packing ability (6).

Effect of Clay on Removal of Ink Particles

It is well known that efficient newsprint deinking requires inclusion of old magazine (OMG). Credit for the improved ink removal used to be given to the high clay loading in the OMG coating. Experiments by Sutman and Letscher (10), nevertheless, indicated that kaolin clays were incapable of consistently improving flotation accepts brightness. They suggested that agglomeration of clay and ink did not occur during the collection process.

The amount of clay added to the flotation cell in this study was far greater than the amount added by Sutman

and Letscher. The experimental results in this study indicated that high loading of clay up to 100% (to fiber) in the flotation cell had no detrimental effect on deinking performance. Schriver et al. added up to 12% (of oven dry fiber) coating clay to newsprint stock, without observing any negative effects (7).

Flotation selectively removes particles that are hydrophobic. Both particles of ink and clay are hydrophobic. However, flotation can effectively remove ink particles that are larger than 20 μm (8). The removal efficiency reaches maximum at 80 - 100 μm , which are far larger than clay particles (9). Preferential removal of clay alone into the froth layer was not observed in a previous study (10), while Liphard et al. reported the enhancement of clay removal in flotation with an anionic surfactant and a cationic polymer (11).

Effect of Clay on Flotation Overflow Volume

Large amounts of clay in the pulp significantly decreased the overflow volume (Fig. 3). It is obvious that addition of clay caused the reduction in foam generation. Clay reduces foam volume either by interfering with the mechanical process for foam formation or destabilizing the air bubbles so that they rupture after they are formed.

Foam is formed in the flotation cell by agitation and air injection. Addition of clay without reduction in fiber will considerably increase the consistency of the pulp in the flotation cell. One may suspect that consistency of the pulp should have substantial impact on agitation. However, this did not appear to be a factor, because adding the same amount of calcium carbonate into the flotation cell did not reduce total overflow volume in later studies (data not shown).

Foam formation requires liquid surface elasticity so that foam film can resist excessive localized thinning (12). This surface elasticity is usually provided by a surfactant with high surface activity. Calcium salt of fatty acid soap, a widely used deinking collector in Western Europe, is also well known as a defoamer (13). Fine solid particles of calcium soap precipitate on the ink particles to provide them with hydrophobic surfaces so that they can be better collected on to air bubbles. Meanwhile, these fine particles also replace the surfactant molecules on the surface of air bubbles so that it forms a 'solid', brittle and close-packed film having no elasticity (12). The foam formation is thus retarded. The coating clays used in the current study were similar to calcium soaps in that they both had fine particles that were moderately hydrophobic.

Therefore, it is possible that clay particles reduce the foam formation by the same mechanism.

Flotation efficiency of ink particles is a function of collision, attachment and detachment between ink particles and air bubbles (14). Reducing foam formation clearly decreased the probability for collision. However, in the current study, clay did not show any negative effect on ink removal. Further study is necessary to address this phenomenon.

The mechanism for fiber loss in the flotation process is not clear. Turvey concluded that newsprint fibers attached to air bubbles because they became hydrophobic when ink particles redeposit onto their surfaces in the presence of the calcium ions (2). However, the current study suggests that fiber loss was irrelevant to ink particles (Fig. 4). It also suggests that the reduction in fiber loss by clays was not connected to clay-ink interaction either.

It was also suggested that fibers are not floated by attaching to individual air bubbles, but by becoming trapped between aggregated air bubbles. Collisions of air bubbles with fibers and other air bubbles are essential for the formation of the aggregates. Since clay 'solidifies' the surface film of air bubbles, it might reduce fiber loss by causing rupture of air bubbles upon the collisions. Meanwhile, effective ink removal was preserved because ink particles are too small to break the air bubbles during the collisions.

Recommendation

The trade-off between deinking quality and yield loss is an everlasting dilemma for a deinking mill. Yield loss across most mill flotation cells is 5 - 12% of the incoming waste. Fiber loss makes up a large part of the total yield loss.

The goal of any separation process is to maximize contaminant removal and minimize the reject rate. In the current study, clay additions were able to achieve up to 50 - 70% reduction in fiber loss across the flotation cell without decreasing ink removal. This will represent a 1 - 5% increase in production or decrease in waste paper cost in a deinking mill. However, further investigation is required to determine whether the same approach can exhibit a similar effect in pilot scale or mill scale flotation cells.

Clays are readily removed by any thickening operations. Therefore, removal of the clays from the fiber should not pose a serious problem for the mill. Reuse of the clay can be done by carefully designing the process

water loops to ensure the clay separated from the pulp is relatively clean.

CONCLUSIONS

The laboratory study on ledger paper deinking has led us to the following conclusions:

- Coating clays added directly to the flotation cell reduce the fiber loss in rejects and the overflow volume.
- High levels of clay additions in flotation cell do not prevent ink removal.
- Ink-fiber interaction is not essential for fiber to float.
- Clay reduces fiber loss and foam formation by decreasing the film elasticity of the air bubbles.
- Clay inclusions in the handsheets do not interfere with brightness measurements.
- By adding a high levels of coating clay, fiber loss reduction without negative effect on ink removal can be achieved in bench scale flotation trials.

REFERENCES

1. McCool, M. A., "Flotation deinking", Secondary fiber recycling, Tappi Press, Atlanta, GA, p.141-162, 1993
2. Turvey, R. W., "Why do fibers float", *Journal of Pulp and Paper Science*, 19:2, J52-J56, 1993
3. Zeyer, C., Heitmann, J. A., Venditti, R. and Joyce, T. W., "Image analysis with an optical scanner", *Progress in Paper Recycling*, 3:3, 29-38, 1994
4. Rogers, R. M., Water quality attributes that impact deinking performance, M. S. Thesis, Miami University, OH, 1993
5. Law, K. N., Jiang, Z. H. and Valade, J. L., "A method for measuring the mass of nondispersible ink", *Tappi Journal*, 77:4, 181-184, 1994
6. Gill, R. and Scott, W., "The relative effects of different calcium carbonate filler pigments on optical properties", *Tappi Journal*, 69:1, 93-99, 1987
7. Schriver, K. E., Bingham, S. J. and Fraizer, M. W., "The function of clay in flotation deinking", *Proceedings of 1990 Tappi Pulping Conference*, Tappi Press, Atlanta, GA, p.133-143, 1990
8. Larsson, A., "Surface chemistry in flotation deinking, Part 2., the importance of ink particles size", *svensk papperstidning*, no.18, R165-R169, 1984
9. Woodward, T. W., "New ways to deink office waste", *PIMA Magazine*, 75:1, 49-51, 1993
10. Letscher, M. K. and Sutman, F. J., "The effects of magazine and filler on the flotation deinking of newsprint", *Journal of Pulp and Paper Science*, 18:6, J225-J230, 1992
11. Liphard, M., Schreck, B. and Hornfeck, K., "Surface-chemical aspects of filler flotation in waste paper recycling", *Pulp and Paper Canada*, 94:8, 27-31, 1994
12. Rosen, M. J., Surfactants and interfacial phenomena, John-Wiley & Sons, New York, p.200-220, 1978
13. Turvey, R. W., Paper recycling technology, ed: McKinney, R. W. J., Blackie Academic and Professional Publishing, to be published, 1994
14. Thompson, E. V., R. Pan, and D. W. Bousfield, "Modelling particle-bubble dynamics and adhesion in air bubble/solid particle/liquid systems", *Proceedings of 1992 Tappi Pulping Conference*, Tappi Press, GA, p.941-956, 1992

ACKNOWLEDGMENTS

This work was supported by Miami University as part of the education process for a M.S. degree. Thanks are also extended to David DiGiacomo for his assistance in the preparation of this manuscript.

Fig. 1. Brightness Increase after Deinking

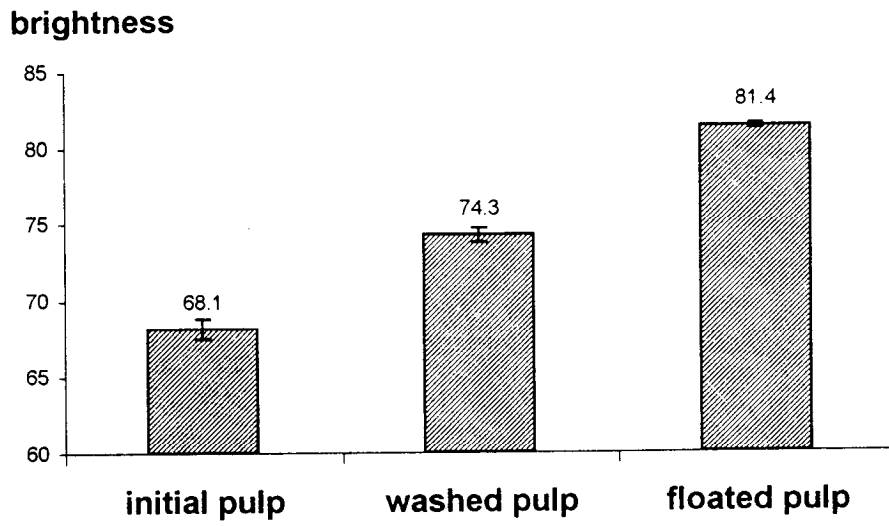


Fig. 2a. Reject Analysis (ultrafine coating clay)

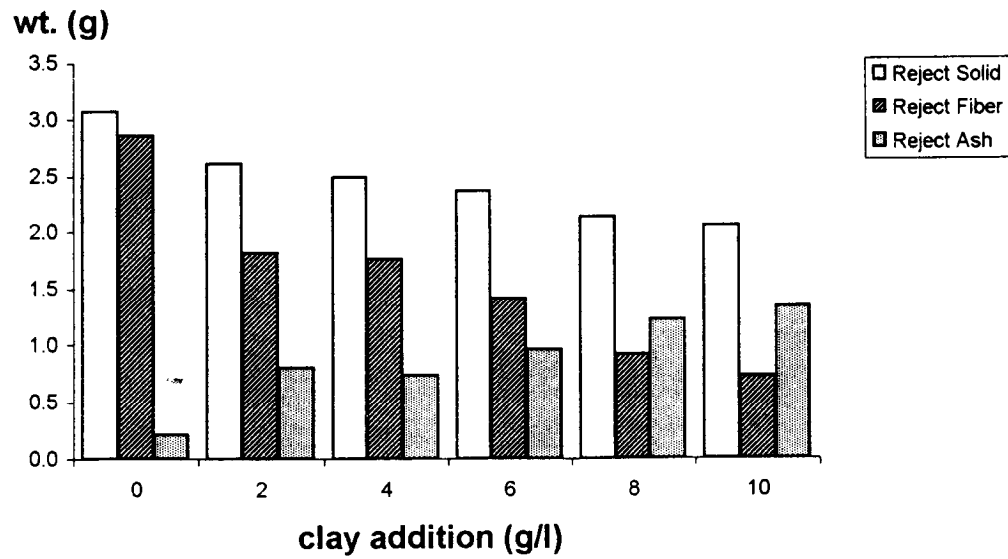


Fig. 2b. Reject Analysis (# 2 coating clay)

wt. (g)

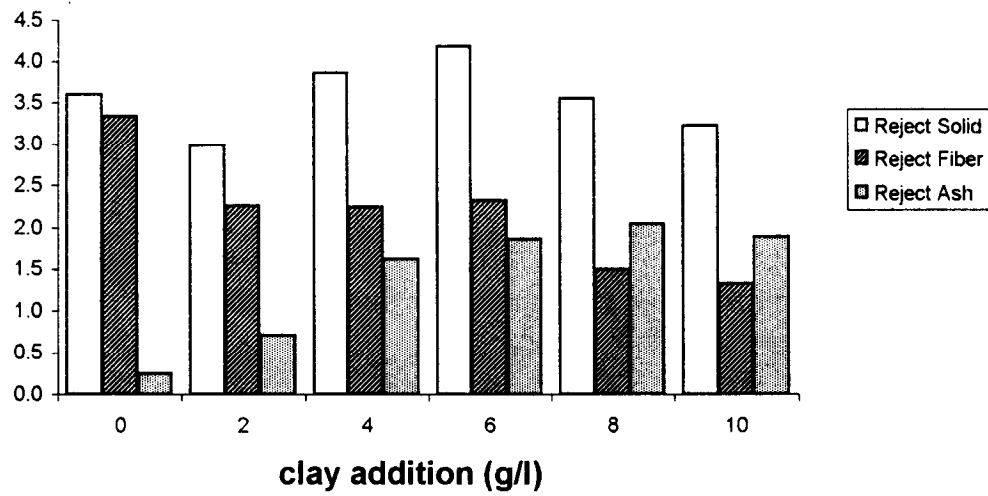


Fig. 3. Flotation Reject Volume

reject volume (ml)

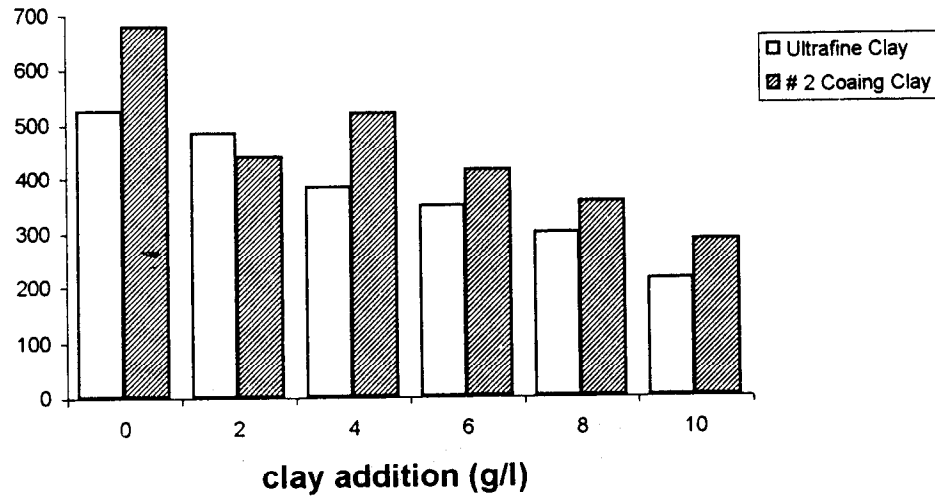


Fig. 4. Reject-Analysis (unprinted sheets)

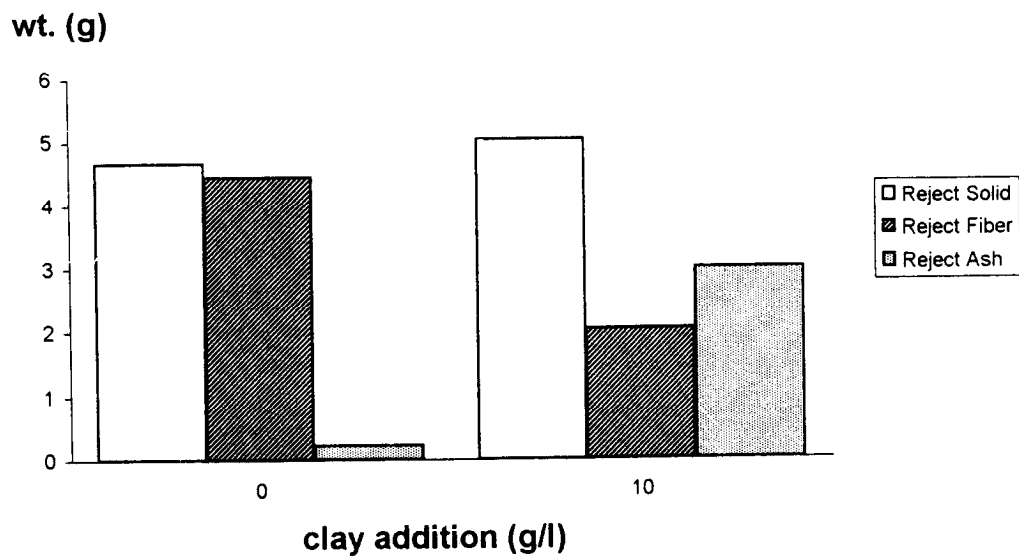


Fig. 5a. Flotation Accept Dirt Counts

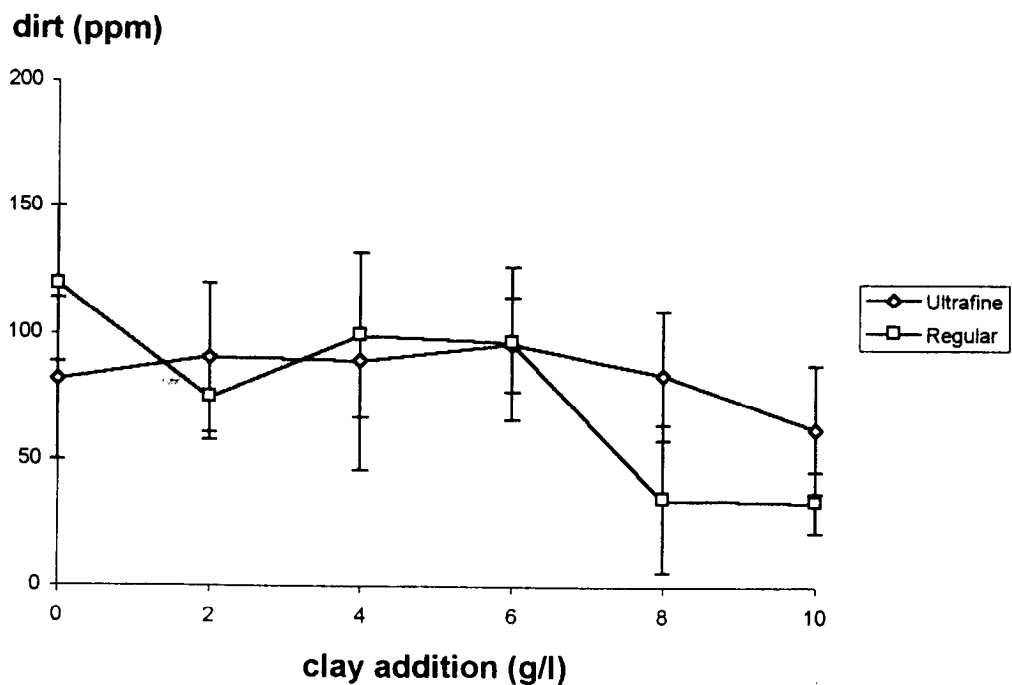


Fig. 5b. Flotation Accept ERIC

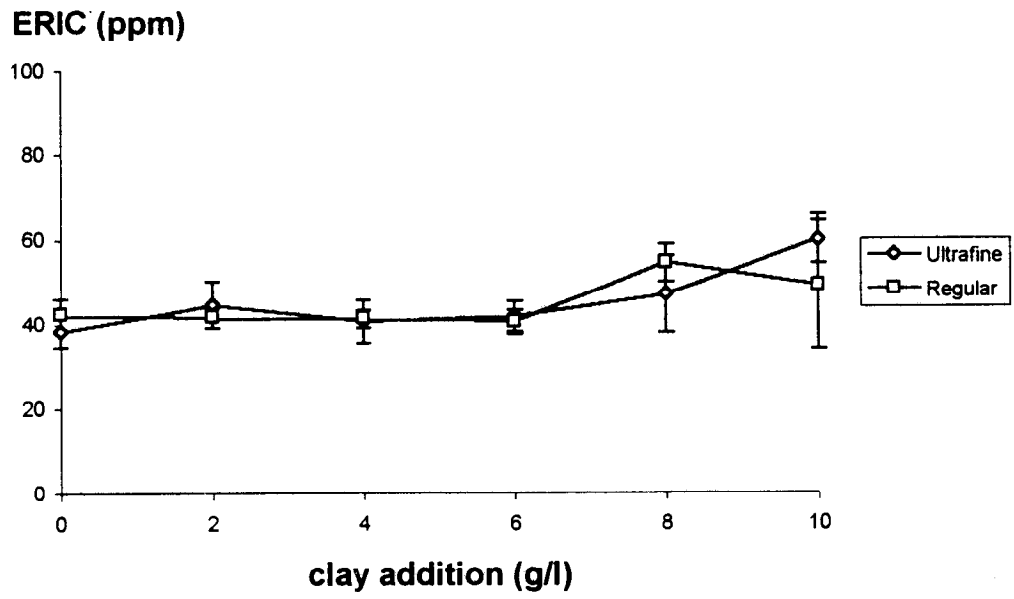


Fig. 5c. Flotation Accept Brightness

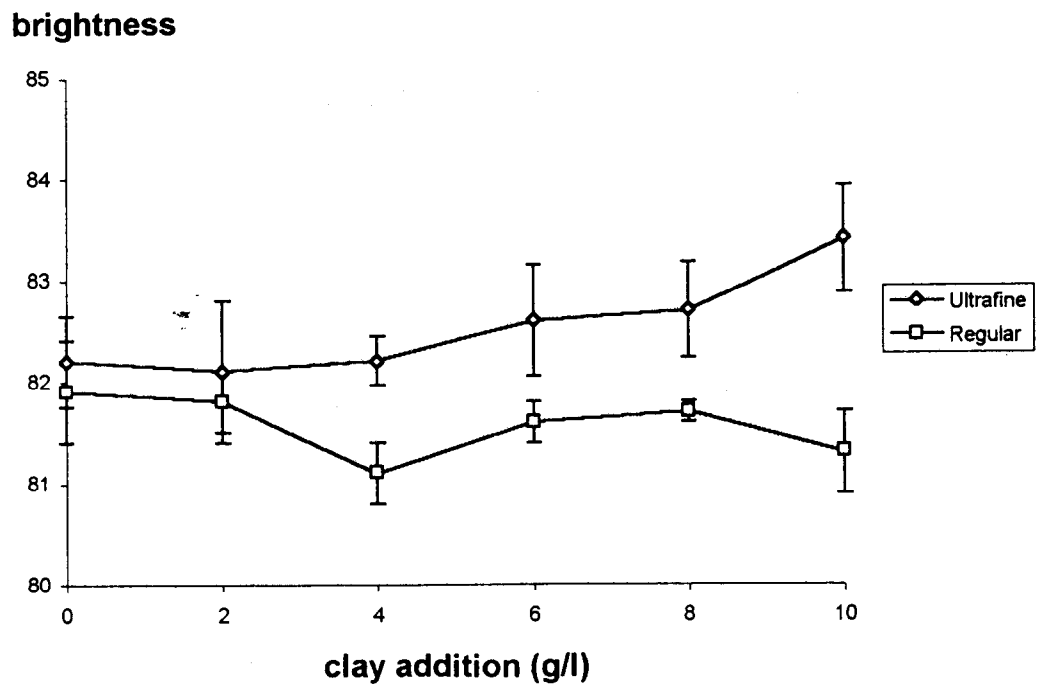


Fig. 6a. Handsheet Analysis (ultrafine coating clay)

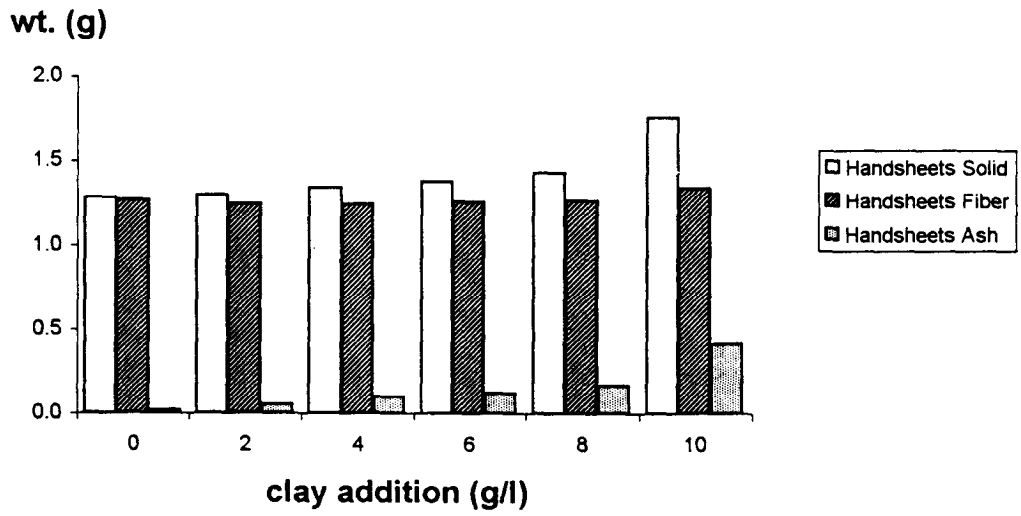


Fig. 6b. Handsheet Analysis (#2 coating clay)

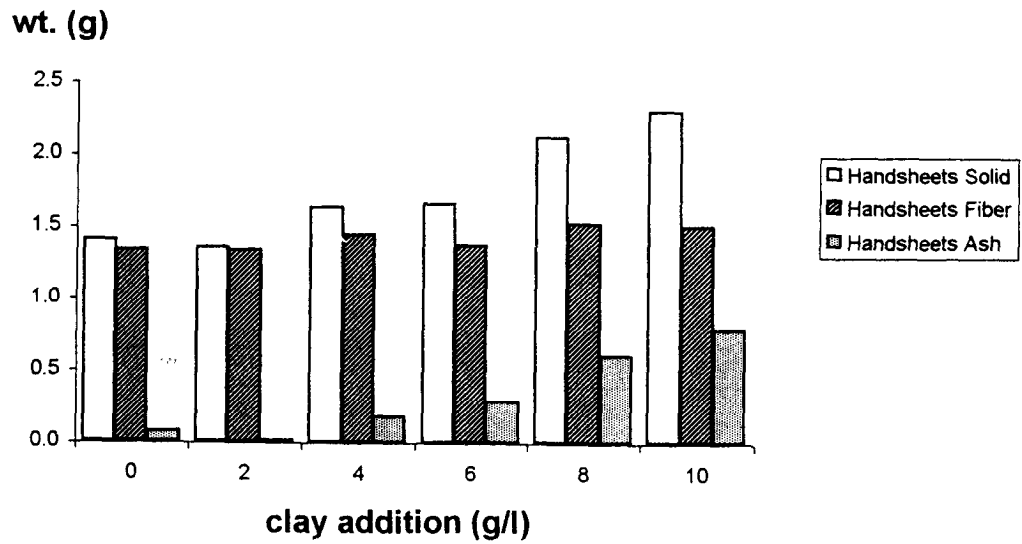
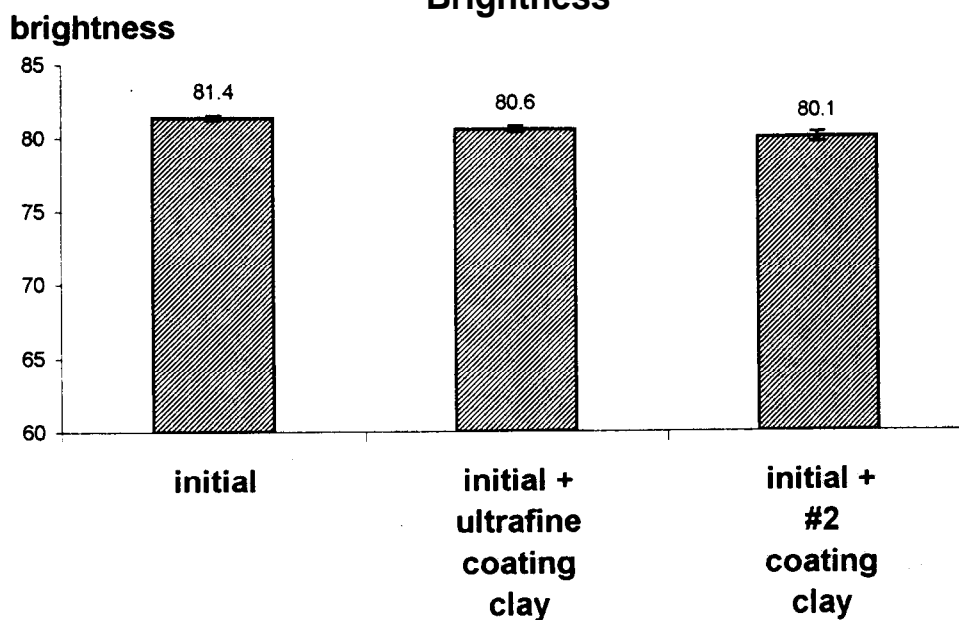


Fig. 7. Effect of Clay Inclusion on Handsheet Brightness



1995 Recycling Symposium Proceedings



Technology Park/Atlanta
P. O. Box 105113
Atlanta, GA 30348-5113, USA