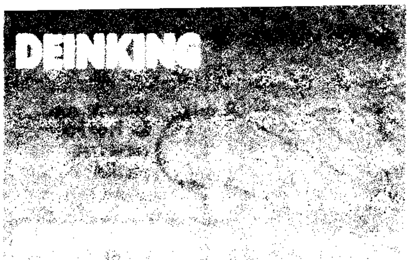


Agglomeration and magnetic deinking for office paper

MARIA AUGUSTA D. AZEVEDO AND JAN D. MILLER

The combination of toner agglomeration followed by magnetic separation provides a new deinking process strategy that should have significant impact on the office paper recycling industry. Agglomeration and magnetic deinking consist of agglomeration of magnetic and nonmagnetic toner particles to generate magnetic agglomerates that magnetic separation can remove. Single-stage, wet, high-intensity magnetic separation can achieve dirt removal of 91% and fiber recovery of 93% from office paper furnishes.

Application:

Toner agglomeration with magnetic separation is an effective deinking process strategy for recycling of office paper.

MAGNETIC DEINKING OF OFFICE paper (OP) is a promising technology for the production of high quality secondary fiber. The technique is possible because a significant portion of the toner in OP furnish has a magnetic character. Toner magnetic susceptibility can vary from weakly paramagnetic to ferromagnetic depending on the iron oxide content of the toner particles. The amount of iron oxide in toners varies. It can contain as much as 65% by weight (1) depending on the type of image development process used by electrophotography machines (2).

Previous work *(3)* has shown that wet, high-intensity magnetic separation (WHIMS) can successfully remove toner with at least a paramagnetic character from OP furnish. Achieving dirt removal of 97% in two stages is possible for a furnish made from OP containing toner with 30% iron oxide. Simultaneously, fiber loss is less (lower than 5%) than that achieved with the conventional technologies of flotation and washing (20%–25%). This is a remarkable result when compared with the conventional deinking process. To achieve the same extent of dirt removal, that process must have many stages of flotation, washing, or both. In practice, the recycling industry must deal with many different sources of OP. This OP varies considerably in toner magnetic character. At first glance, the use of magnetic separation would therefore seem to have limited use for the OP recycling industry.

Magnetic separation can combine with flotation to treat mixed OP. This combination can achieve dirt removal of 92.7% *(3)*. Although these results seem reasonable, achieving complete toner removal by magnetic separation alone would be more desirable. This is because magnetic deinking not only produces a high quality cellulose product but also improves the fiber recovery *(3, 4)*.

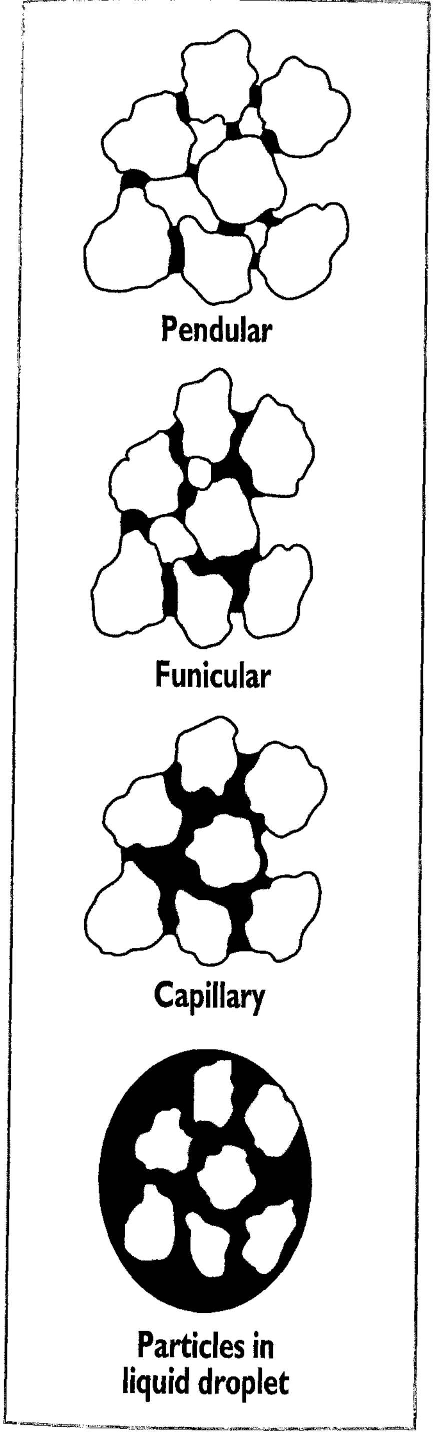
Magnetic deinking is possible by agglomeration of the magnetic and nonmagnetic toner particles. If the agglomerates have sufficient magnetic susceptibility—being at least paramagnetic, removing them by WHIMS should be possible. This eliminates the need for flotation, washing, or both. This work examines agglomeration and magnetic deinking to determine its potential use as a process strategy for the OP recycling industry.

TONER AGGLOMERATION

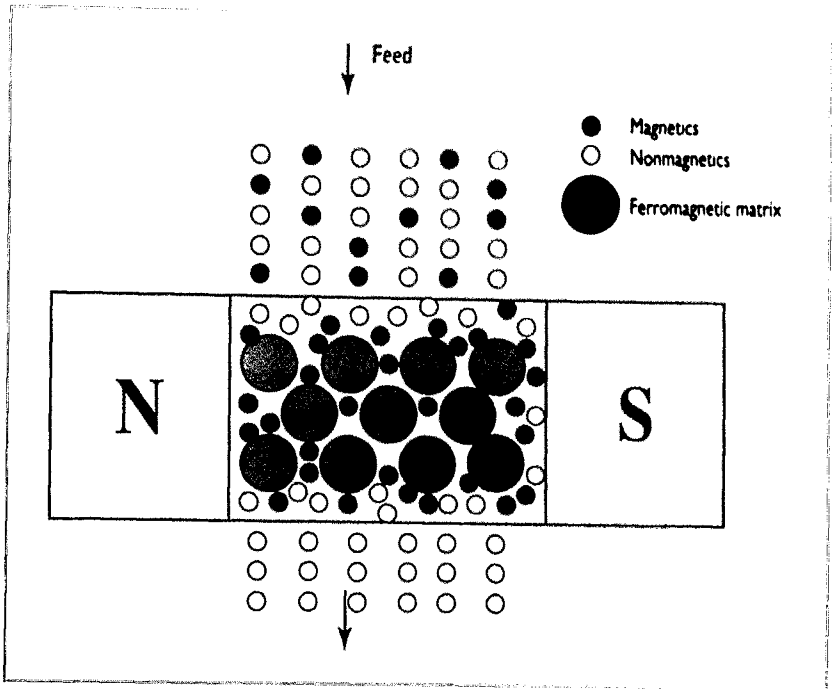
Toner agglomeration can occur in many ways depending on the particular application. For magnetic separation where the aggregates must stay in a state of agitation, the aggregates must exhibit good stability and remain intact during the entire separation process. Efficient agglomeration is possible here using an immiscible liquid or bridging agent to form strong and dense agglomerates selectively while the cellulose fibers remain in a dispersed state.

Immiscible liquid agglomeration involves the addition of a bridging agent that preferentially wets the toner particles and causes adhesion by capillary forces. This method depends on the amount of bridging liquid added to a particulate suspension as **Fig. 1** shows. At low levels of immiscible liquid, only pendular bridges connect the particles. This forms an unconsolidated floc structure. As liquid bridging becomes more extensive, the funicular region is reached, and the flocs consolidate moderately. When the amount of bridging liquid increases even more, the agglomerates eventually grow and reach maximum strength and sphericity in the capillary region. Beyond this region, the bridging liquid is in excess, and the solids are essentially dispersed into bridging liquid drops *(5)*.

Many bridging liquids can agglomerate toner particles. Kerosene and n-heptane *(6, 7)* promote the agglomeration of toner particles, but the agglomerates are weak. The presence of highly sized fibers and starch disrupts the process. Snyder *et al. (8)* recently found that the inhibition of toner-oil agglomeration by starch



1. States of agglomeration with immiscible liquid



2. General principle of WHIMS

relates to its adsorption at oil and toner particle interfaces to generate steric layers that cause repulsion on close approach.

Effective bridging agents *(9, 10)* reported to agglomerate toner particles are the saturated aliphatic primary alcohols commonly called fatty alcohols. The principle of toner agglomeration by fatty alcohols is approximately similar to agglomeration by n-heptane. The long chain alcohols and n-heptane are insoluble in water. At room temperature, the alcohols are in a solid state. Heating the OP furnish to a temperature a few degrees above the melting point (MP) of the fatty alcohol is therefore necessary to liquefy the alcohol. In the liquid state, the alcohol wets the toner particles that then become coated with the alcohol. When such toner particles collide, the alcohol holds the toner particles together by forming a liquid bridge between them. The process continues until many toner particles collect into a large agglomerate. Such an agglomerate might be 1 cm or more in diameter. After agglomeration, the furnish must undergo quenching. The cooling of the OP furnish produces solidification of the toner agglomerates. This strengthens the bonding between toner and alcohol and densifies the agglomerate. Cooling of the agglomerates is the basis for the efficiency of the fatty alcohol agglomeration process.

The selection of fatty alcohols for use in toner agglomeration depends on the toner softening point. Usually, the softening point is 58°C–70°C. For this temperature range, the appropriate fatty alcohols are those with a carbon chain length of 11–18 carbons. Small *et al. (11)* investigated toner agglomeration with and without the addition of a fatty alcohol, 1-octadecanol ($C_{18}H_{38}O$), at a temperature of 85°C. They observed that agglomeration of toner particles without the presence of the alcohol led to formation of weak agglomerates. The shape of the individual toner particles was still apparent, but they had slightly rounded edges. With the addition of 1-octadecanol (MP 60°C), the toner particles agglomerated into a distinctly spherical shape.

Deinking surfactants also have use as bridging agents *(12-14)*. Those having an admixture of nonionic surfactants and alcohols are especially effective. Due to the presence of alcohols, this type of reagent promotes the agglomeration of toner particles *(15, 16)*.

EXPERIMENTAL

Material

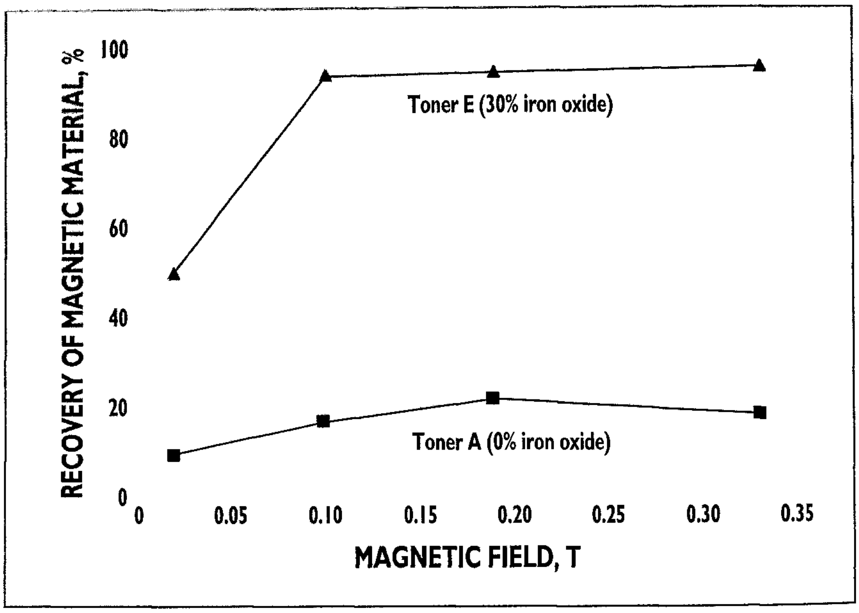
Commercial toners with iron oxide content varying from 0%–55% by

Commercial toners	Iron oxide, %	Specific (mass) magnetic susceptibility, $m^3/kg \times 10^{-9}$	Magnetic susceptibility
A	0.0	14	Weakly paramagnetic
B	<10	35276	Paramagnetic
C	15-20	104790	Ferromagnetic
D	25-30	123085	Ferromagnetic
E	30-40	174272	Ferromagnetic
F	40-45	205001	Ferromagnetic
G	45-50	282005	Ferromagnetic

I. Magnetic susceptibility of commercial toners

Bridging reagent	Average agglomerate size, µm
Primary alcohol	66.5
1-Octadecanol	120.5

II. Average agglomerate size



3. Separation of toner particles by WHIMS with ferromagnetic matrix of steel balls 19 mm in diameter

weight were examined for magnetic susceptibility and agglomeration behavior. **Table I** lists these toners.

The efficiency of toner agglomeration relies on the appropriate choice of a bridging liquid. **Table II** shows the two types of bridging liquid investigated—commercial surfactant and pure fatty alcohol. The commercial surfactant was a primary alcohol. This surfactant was selected because it can promote agglomeration of toner particles *(17)*. The fatty alcohol used was 1-octadecanol.

The OP furnish prepared at the University of Utah contained 50% paper copied in a commercial photographic machine and 50% paper printed by a commercial laser printer. The photocopy machine uses a toner with 0% iron oxide, and the laser printer uses a toner with 30% iron oxide. For each machine, the same text was fully printed on one side of the paper. Sufficient copies were made as necessary to prepare the OP furnish.

Magnetic susceptibility

A commercially available susceptometer using the alternating current method measured the magnetic susceptibilities of the commercial toners. The susceptometer has high accuracy and a rapid measuring rate. It can determine magnetic susceptibility of materials that range from diamagnetic to ferromagnetic. The measurements yield units normalized to mass magnetic susceptibility.

WHIMS

A commercially available batch type WHIMS separated magnetic toners from nonmagnetic cellulose fibers. The principle of operation is available in the literature *(18, 19)* and is illustrated in **Fig. 2**. The pulp is fed into the chamber containing a ferromagnetic matrix (steel balls) in-place with coil current at the desired setting. Magnetic material is retained in the chamber after flushing with water, and nonmagnetic material is washed through the chamber. The magnetic fraction can then be washed from the ferromagnetic matrix after turning off the coil current.

The WHIMS unit was operated with soft iron balls of a 19-mm diameter. The pulped wastepaper was fed continually into the WHIMS at a consistency of 1%. The magnetic fraction (toner particles) and a nonmagnetic fraction (cellulose fibers) were collected, filtered, and stored for analysis.

RESULTS AND DISCUSSION

Toner particles

Table I shows the specific (mass) magnetic susceptibilities of the commercial toners. The table shows that magnetic susceptibility progressively increases as the content of iron oxide increases. For magnetic separation in a high gradient field, toners with at least 10% iron oxide have sufficient magnetic character for magnetic separation.

To study the behavior of toner particles in the WHIMS, two toners were selected to represent the toners normally found in OP furnish. One was a commercially available nonmagnetic toner used in copy machines. The other was a commercially available magnetic toner frequently used in laser printers.

Figure 3 shows the weight recovery of these toners vs. applied magnetic field. Due to the difference in magnetic susceptibility between these toners, the weight recovery of a magnetic toner (30% iron oxide) is greater than that of a nonmagnetic toner (0% iron oxide). The results clearly show that agglomeration is necessary to remove both magnetic and nonmagnetic toner particles by WHIMS.

Toner-only agglomeration studies

For magnetic deinking, toner agglomerates must have sufficient magnetic character for successful removal from the nonmagnetic cellulose fiber. At least a paramagnetic state is necessary to overcome the drag and gravitational forces (competing forces) that act against the magnetic force during magnetic separation.

During the process of agglomeration, toners of different magnetic character are randomly assembled. The magnetic susceptibilities of the agglomerates will therefore depend on the combination of the individual toner particles in the agglomerate. In other words, many strongly magnetic toner particles must be present in each agglomerate to give that agglomerate at least a paramagnetic character.

To estimate the magnetic susceptibility of an agglomerate, a theoretical calculation was made for an agglomerate composed of nonmagnetic (0% iron oxide) and magnetic (30% iron oxide) toner particles. **Table III** shows the theoretical magnetic susceptibility of toner agglomerates. The results show that the agglomerates become richer in magnetic toner as the magnetic susceptibility of the agglomerate increases.

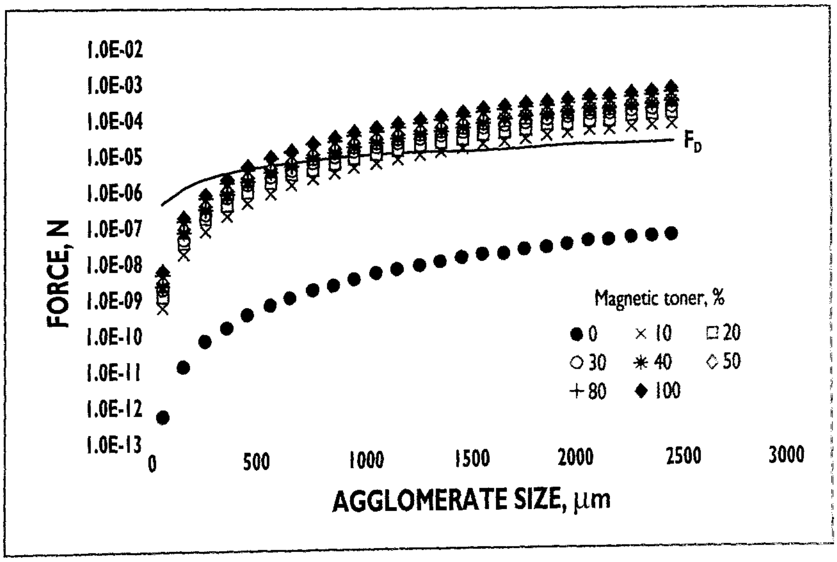
Agglomerate, % ferromagnetic toner	Specific (mass) magnetic susceptibility, m³/kg
0%	1.40 × 10^{-8}
10%	1.74 × 10^{-5}
20%	3.49 × 10^{-5}
30%	5.23 × 10^{-5}
40%	6.97 × 10^{-5}
50%	8.71 × 10^{-5}
60%	1.05 × 10^{-4}
70%	1.22 × 10^{-4}
80%	1.39 × 10^{-4}
90%	1.57 × 10^{-4}
100%	1.74 × 10^{-4}

Agglomerates prepared as mixtures of toner A (0% iron oxide) and toner E (30% iron oxide)

III. Theoretical magnetic susceptibility for toner agglomerates

How will the agglomerates behave during WHIMS? Will the size of the agglomerates influence the separation efficiency? The answer to these questions can be predicted by comparing the forces that act on agglomerates during WHIMS separation. **Figure 4** shows the results for agglomerates of different toner composition—mixtures of magnetic, 30% iron oxide, and nonmagnetic toner particles—passing through a theoretical magnetic field induction of 2T at a velocity 0.1 m/s with the field gradient generated by a matched steel ball matrix. For typical agglomerates greater than 1 mm, the results show that the magnetic force should exceed the drag and gravitational forces for agglomerates containing at least 20% magnetic toner. In other words, achieving the removal of agglomerates having a composition of at least 20% magnetic toner is theoretically possible.

To verify the actual organization of toner particles in the agglomerates, agglomerations were carried out using nonmagnetic and magnetic toners. To observe the individual toner particles, the agglomeration was made in the funicular state. The agglomerates were subsequently measured by SEM. **Figure 5** shows the SEM picture of a typical agglomerate with primary alcohol. Toner particles in the agglomerate having a smooth surface are the nonmagnetic toners, and the toner particles having a rough surface



4. Plot of magnetic force and drag force vs. agglomerate particle size for agglomerates flowing through the steel ball matrix in a magnetic field of 2T at an interstitial velocity 0.1 m/s (Agglomerate composition is numerical percentage of magnetic toner particles containing 30% iron oxide)

5. Funicular state of toner particles agglomerate with 0% iron oxide content (smooth surface) and 30% iron oxide content (rough surface) with agglomeration at 72 °C with primary alcohol

represent the magnetic toners. The agglomeration of magnetic with nonmagnetic toner particles is evident. On this basis, toner agglomeration and magnetic deinking should be possible.

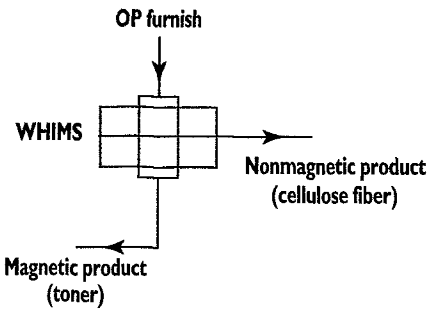
Agglomeration and magnetic deinking O + OP furnish

Figure 6 shows the results for a single-stage WHIS for furnish in which the toner particles were agglomerated. In these experiments, agglomeration with primary alcohol provides dirt removal of 82.3%. Agglomeration with 1-octadecanol gives dirt removal of 90.8%. In both cases, agglomeration does improve removal of toner particles with a gain of almost 40% in dirt removal. The fiber lost in both agglomeration experiments was approximately 7%.

We investigated the effect of different bridging reagents on agglomerate size, form, and structure. Table II shows the average agglomerate size for both bridging reagents. The primary alcohol generates smaller agglomerates than the 1-octadecanol. **Figures 7 and 8** show the same results for SEM examination. The reason for this behavior might be the melting point of the bridging reagents. 1-octadecanol has a melting point of 60°C. The primary alcohol has a melting point of 9.4°C. After quenching, the primary alcohol therefore remains in the liquid state. This probably accounts for the weaker agglomerates. To verify this statement, additional experiments used a high molecular weight surfactant with a melting point of 35°C. With this material, the average agglomerate size increased and dirt removal improved. These results therefore suggest that the solidification of the bridging liquid after quenching plays a major role in toner agglomeration and magnetic separation efficiency.

Besides information regarding particle size, SEM provides information about the form and structure of the agglomerates. Figures 6 and 7 show that the agglomerates have a well-defined spherical shape. This means that the agglomeration occurred between the capillary and liquid drop states. The toner agglomerates also contain some fiber and filler particles.

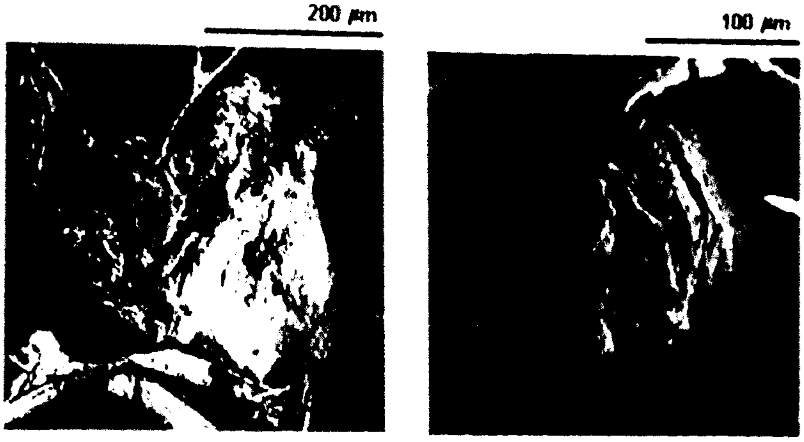
Recent work has reported characterization of the rate and extent of consumption of 1-octadecanol by different components of the OP furnish, e.g., toner, fiber and filler (calcium carbonate, $CaCO_3$) *(20)*. These experiments showed that fibers and especially filler particles both consume the 1-octadecanol. The presence of filler particles in the agglomerates should not hurt the magnetic separation process if the agglomerates maintain sufficient magnetic character. Removal by agglomeration and magnetic separation of toners and filler particles is beneficial. The real concern is the locking of the fibers in the agglomerates that represents a fiber loss. Fortunately in these experiments, the extent of fiber distribution in the agglomerates is not significant.



Furnish	Dirt removal*
Dispersed toner (no reagent)	51.0%
Agglomerated toner (primary alcohol - 2% dry fiber)	82.3%
Agglomerated toner (1-octadecanol - 2% dry fiber)	90.8%

$$\text{*Dirt removal} = 100\left(1 - \frac{\text{Handsheet area covered by ink after treatment}}{\text{Handsheet area covered by ink before treatment}}\right)$$

6. Single state WHIMS for office paper (50% laser printer + 50% photocopy) with ferromagnetic matrix, 19 mm steel balls, and a magnetic field of 0.3 T



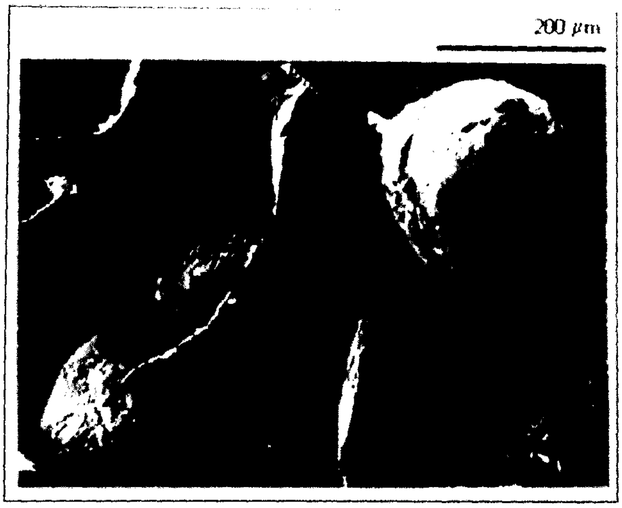
7. Toner agglomerates produced with 1-octadecanol from OP furnish

INDUSTRIAL CONSIDERATIONS

Agglomeration and magnetic deinking are currently technically successful at the laboratory scale. Scaling to an industrial level will require additional study to optimize the total economics. Factors such as energy consumption, availability, and the size of the machine per unit mass of material treated (specific capacity) require consideration. Note also that different separators will give different separation efficiencies. Consequently, an incorrect choice can severely influence the economics and the efficiency of the magnetic separation. For a realistic cost estimate, pilot plant trials are necessary. A detailed description of the economics of magnetic separation is beyond the scope of this paper.

Magnetic separation has extensive use in industrial applications. In the production of final clay products such as kaolin for example, WHIMS has use for the removal of contaminants to meet brightness specifications for the kaolin filler and coating products. These kaolin plants have a capacity of 160-400 gal/min and an average energy consumption corresponding to a cost of US$ 0.0017/gal. Today, the kaolin industry is substituting WHIMS with a superconducting technology that provides a significant reduction in power rating from 400 kW to less than 10kW *(21)*. As a result, the energy cost for brightening the final kaolin product becomes almost insignificant. Especially for energy consumption, a careful study is therefore necessary for the proper design and selection of magnetic separator equipment for recycling mills.

Justification for the replacement of conventional separation technologies with magnetic separation may seem difficult. This possibility should not be dismissed because of the superior quality of the secondary fiber product that can occur with agglomeration and magnetic deinking. The use of agglomeration and magnetic deinking not only improves the ink removal but also significantly reduces the amount of fiber loss to less than 5%. Another important aspect for consideration is that magnetic deinking can operate at high consistency. For instance, experiments showed the possibility to operate a ball matrix WHIMS at a consistency up to 2%. For consistency higher than 2%, the fiber loss increases due to entrapment of cellulose fiber between the balls. Note that the WHIMS used in these experiments was designed for mineral particles. Achieving a better separation at consistency close to 3% should be possible if an advanced design for the magnetic separator can be developed to fit the characteristics of the OP furnish. Operating at high consistency will improve capacity and provide a higher recovery rate of cellulose fibers.



8. Toner agglomerates produced with primary alcohol from OP furnish

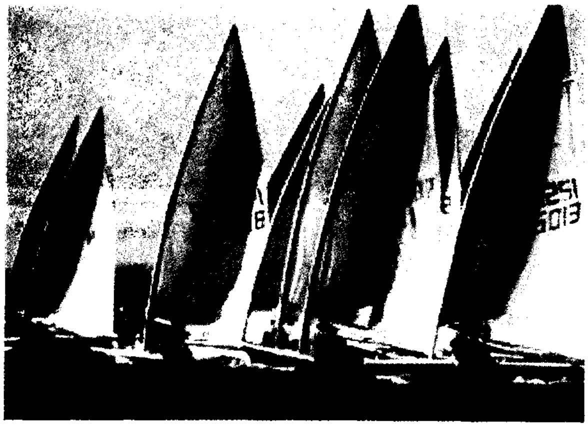
In a conventional deinking process, the furnish must undergo different unit operations to achieve reasonable ink removal. This is because most deinking techniques are limited regarding ink particle size. Washing is more effective for the removal of ink particles smaller than 20 µm, and flotation gives optimum ink removal for ink particles of 10-100 µm *(22)*. Centrifugal cleaners are most efficient on particles of 80-300 µm *(22, 23)*. Particle size is also an important factor in magnetic separation. The optimum particle size range for magnetic deinking will depend on the type of separator, the magnetic susceptibility of the toners, and competing forces present in the separation chamber. For WHIMS, the particle size range can be 0.1-1000 µm *(18)* depending on the magnetic susceptibility of the toner particles. This work did not determine the optimal particle size range. Agglomeration can control the toner particle size to optimize separation efficiency.

Scaleup of agglomeration and magnetic deinking to an industrial level will require design of a system to fit the unique features of OP furnish. Careful consideration of savings in capital and operating costs and improved separation efficiency will make magnetic deinking a promising process alternative.

CONCLUSION

Toners with at least 10% iron oxide are sufficiently paramagnetic for separation by WHIMS. Calculations from first principle suggest that agglomerates containing at least 20% magnetic toners are necessary for an efficient separation.

Magnetic deinking is successful to remove magnetic and nonmagnetic toners by appropriate agglomeration of the toner particles. After agglomeration, a single-stage dirt removal of almost 91% is possible by WHIMS with a fiber loss around 7%. Such a process should have industrial significance and could eliminate the need for extensive flotation, washing, or both in the treatment of OP furnishes. **TJ**



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