The Effect of Electrohydraulic Discharge on Flotation Deinking Efficiency

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The Effect of Electrohydraulic Discharge on Flotation Deinking Efficiency

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This thesis is dedicated with love to my wife, Maria, who has put up with me through it all. I couldn't have done this without her love and support.
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<thead>
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<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>A</td>
<td>Amperes</td>
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<td>AC</td>
<td>Alternating current</td>
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<td>ε₀</td>
<td>Permittivity of free space</td>
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<td>Electrohydraulic discharge</td>
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<td>ppm</td>
<td>Parts per million</td>
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SUMMARY

Firing an underwater spark discharge generates an expanding plasma which causes a spherical shockwave to propagate through the surrounding water. The shockwave can have many effects, including resonance effects on bubbles, mechanical destructive effects on solid surfaces and living organisms, and sonochemical oxidative effects on particles and chemical species present in the water.

This phenomenon has been shown to improve the efficiency of ink removal in a laboratory flotation deinking cell, while simultaneously decreasing fiber loss. These process improvements are attributed to the sonochemical oxidation of ink particle surfaces, caused by shockwave-induced cavitation. This finding is supported by zeta potential measurements. Sparking was found to reduce the zeta potential of ink particles by up to 20 mV.

When sparking was performed during deinking, no effect was found on either ink removal or solids loss. However, when the pulp was pretreated with sparking before flotation, a significant improvement was seen in the brightness gain. Further, fiber loss was decreased by up to 25% in a single flotation stage. The economics of this process are attractive; payback is on the order of three months based on fiber savings alone. Also, at about 1.5 kJ per spark, the power requirements are minimal with respect to the benefit derived.
1 INTRODUCTION

Flotation deinking is commonly used in paper recycling to remove ink and other contaminants from fiber[1-4]. This method involves bubbling air through the pulp in the presence of deinking chemicals. It is best for removing hydrophobic particles, which will preferentially attach themselves to the bubbles. Ink removal is inevitably accompanied by fiber loss[5], and a compromise is usually struck based on product specifications.

It has previously been shown that firing a high-intensity spark underwater creates a spherical shock wave that generates an acoustic field, which, in turn, breaks water into hydroxyl radicals[6]. The surfaces of acrylate particles suspended in water are mildly oxidized upon exposure, and their zeta potential and tack drop. These contaminants are commonly found in recycled paper process streams, and a reduction in tack minimizes deposits and other operational problems[7, 8].

In this work, the underwater sparking device has been shown to improve the efficiency of ink removal in a laboratory flotation deinking cell, while simultaneously decreasing fiber loss. These process improvements are attributed to the sonochemical oxidation of ink particle surfaces, caused by shockwave-induced cavitation.

It was found that sparking during flotation had no effect on the results, but sparking as a pretreatment before flotation promoted ink removal, while simultaneously decreasing fiber loss during flotation deinking. It was therefore determined that the beneficial
effects of sparking were due not to the mechanical effects of the shockwave on bubbles, but rather to sonochemical reactions on the surface of the ink particles. When the spark pretreatment was performed, oxidation due to cavitation reduced the zeta potential of the ink particles, leading to a decrease in ink redeposition, and an increase in ink removal efficiency. Sparking during flotation led to detrimental effects on the ink-bubble attachment process, as well as decreased foam stability, thus negating the positive effects of reducing the zeta potential of the ink particles.
2 LITERATURE REVIEW

The following sections are a review of issues pertinent to this project: paper recycling, flotation deinking of newsprint, electrohydraulic discharge, and shockwave effects. The sections outline key phenomena in these areas, and seek to provide adequate background information for an understanding of the goals and methods of this research project.

2.1 RECYCLING OF PAPER GOODS

Paper products are an important part of everyday life. Worldwide, almost 365 million tons of paper products are produced and consumed each year. The United States holds a disproportionate market share, producing 89 million tons (24%) and consuming 97 million tons (27%) each year, despite having less than 5% of the world's population. This means that the average American uses over 660 pounds of paper products per year[9, 10]. Furthermore, paper goods make up over 38% of the material landfilled in the United States, making them our largest landfill component[11, 12]. Add to this that it would take about 786 million trees to meet the material requirement for the world's annual paper consumption[13] (209 million for the US alone), and it is easy to see the importance of paper recycling, particularly in the United States.

Besides reducing the landfilling and raw material demands of the world's increasing paper consumption, recycling has other advantages. The processing of recycled paper requires 55% less water and 70% less energy than the processing of virgin fiber. It also uses less (and less expensive) chemicals, cutting costs as well as the emission of toxic
pollutants[12]. On top of all this, there is a large and rapidly increasing demand for the export of American recovered paper, particularly from countries with developing paper industries or with limited natural resources[14].

All of these environmental and economic factors are driving a national shift toward mandatory recycling of paper goods. As of 2000, about 40 states had passed mandatory recycling laws or implemented voluntary goals or directives. Most states have set a post-consumer paper recycling goal of 20% to 70%[15]. Of course, setting goals for increasing consumer recycling will do no good unless the recovered paper is actually used in the manufacturing of new products, which then must be purchased by consumers. Unfortunately, many consumers are not interested in buying recycled paper products, due to concerns about quality. However, there are some products, such as newspapers, in which recycled content does not seem to bother consumers.

The use of recycled fiber in newsprint has risen steadily since publishers made it a priority in 1988. From a mill standpoint, there are plenty of good reasons for this increase. Obviously, reducing the amount of virgin fiber in the furnish cuts down on raw material costs quite a bit. But, according to the Federal Environmental Executive's Paper Calculator[16], switching from virgin furnish to 25% recycled furnish also cuts total energy usage by 10%, reduces greenhouse gas, NOX, and particulate emissions by 14%, 10%, and 11%, respectively, and decreases solid waste production by 13%.
In 2002, almost 9.5 million tons of post-consumer newspapers were recycled. This corresponds to a recovery rate of over 71%, up from 45% in 1991. Of this recovered newsprint supply, 38% (3.2 million tons) was used in the domestic production of newsprint. The remainder was exported (22.7%) or used in other recycled products[14]. With this amount of recycled newsprint being utilized in the United States alone, it is easy to see the importance of cleaning and deinking the recovered fiber. If the ink were not properly removed, then recycled newsprint would not be a suitable fiber source for most paper products. Any enhancements to the deinking process could lead to cost savings and/or an increase in the amount of recycled content that could be used in certain papers.

2.2 FLOTATION DEINKING

Wash deinking and flotation deinking are the two most common ways of removing ink from recycled fibers. The two are often used in combination, in order to remove a broad range of particle types and sizes. Wash deinking involves rinsing the pulp, often in the presence of deinking chemicals, and subsequently dewatering it. This method is most efficient at removing very small (below 30 µm) particles, especially if they are hydrophillic. Such particles include fines, fillers, and some inks and stickies.

Flotation deinking involves removing ink and other contaminants by bubbling air through the pulp in the presence of deinking chemicals. This method is best for removing hydrophobic particles, which will preferentially attach themselves to the bubbles.
Flotation removes somewhat larger particles than washing, typically in the size range of 10 \( \mu m \) to 250 \( \mu m \). Some flotation systems can even remove particles up to 500 \( \mu m \) in diameter. Figure 2.1 shows the typical size ranges for removal by wash and flotation deinking[15, 17].

![Diagram showing ink removal efficiency by washing and flotation](image)

*Figure 2.1. Ink removal efficiency by washing and flotation[17].*

A typical laboratory flotation cell is shown in Figure 2.2. The stock is typically introduced at 1% consistency, a pH of 7-9, and a temperature of 40-70°C. Laboratory flotation is a batch operation with recirculation. Air is injected at roughly 3 times the volumetric stock recirculation flow. An impeller breaks up the air into tiny bubbles and mixes the air/pulp suspension. Foam is removed from the surface of the suspension by way of a scraper. Laboratory cells such as this one typically give brightness and solids loss results that are consistent with industrial operations[15].
The four mechanical stages of deinking are detachment, redeposition, suspension, and frothing. Detachment occurs mostly during pulping, when shear forces, caustic swelling, and elevated temperatures cause the bound ink to fragment and separate from the fibers. Redeposition, a highly undesirable effect, can also occur during pulping. Ink may be readsorbed onto the fiber surface, or it may enter the fiber lumens during alkaline swelling. Ink redeposition during pulping is largely irreversible, and tends to increase with increasing pulping time and consistency[15, 18-20].

During flotation, the ink ends up in the aqueous phase, either dispersed or weakly associated to the fibers. This is the suspension stage. The goals at this point are to prevent the ink from redepositing on the fibers, and to permit the ink to be removed from suspension by the rising air bubbles. This is accomplished through a combination of various deinking chemicals, which are usually introduced during pulping or immediately before flotation. The addition of sodium silicate increases the colloidal stability of the
ink particles, preventing redeposition. Collector agents, such as soaps, surfactants, and fatty acids, cause the small ink particles to agglomerate into larger ones, improving the efficiency of their removal. Depending on collector chemistry and water hardness, calcium may be added as well. Figure 2.3 shows how calcium works together with a collector to agglomerate small ink particles and to increase the hydrophobicity of the agglomerates, thus improving the removal efficiency[15, 18, 21-24].

![Figure 2.3. The use of calcium and a collector in flotation deinking[15].](image)

The air bubbles which scour the suspension during flotation preferentially remove the ink agglomerates due to the hydrophobic nature of the agglomerates and the hydrophilic nature of the fibers. The contact angle of water on a fiber surface is low (less than 20°), while that on an ink particle is high, around 120°. Thus, the ink prefers to attach to an air bubble, while the fiber prefers to remain in the water. To put it another way, surface
tension will tend to pull a fiber out of an air bubble and into the water phase, while it will tend to pull ink out of the water phase and into an air bubble[25].

The attachment of particles to bubbles also depends on several other factors, including the number, size, and shape of the particles and bubbles, as well as their relative motion. The effect of the number of particles and bubbles is straightforward: the more particles and bubbles there are in a given volume, the greater the probability of collision. The effect of bubble and particle size is slightly more complicated. Small bubbles can pick up small particles. Large bubbles can pick up large or small particles. However, large bubbles provide a much lower interfacial area for collecting ink than the same total volume of smaller bubbles would. Figure 2.4 shows the collection ability of a large bubble toward various ink particle sizes. It is clear that, while a bubble of this size is required to remove the largest ink particle shown, the smaller particles would be more efficiently removed by smaller bubbles[15].

![Figure 2.4. A 1-mm air bubble collecting various ink particles][15].
A flotation cell in operation contains a certain distribution of ink particle sizes. Generally, there will be a large number of very small particles, and larger particles will be present in smaller numbers. A typical particle size histogram, determined after pulping, is shown in Figure 2.5 (note that the y-axis is logarithmic).

![Particle Size Distribution](image)

**Figure 2.5.** A typical ink particle size distribution, prior to flotation [15].

It is clear from the above two figures that a large number of small bubbles, along with a relatively minute number of larger bubbles, would remove the ink particles most efficiently. The smaller bubbles, having a large specific surface area, would remove the small particles, while the larger bubbles would collect the particles too large to be removed by the smaller bubbles.

Of course, for any bubble to collect a particle, the two must first collide. There must be a relative motion between the bubble and the particle for them to get close enough for collision. As can be seen from Figure 2.6 below, collision will occur for all particles that approach the bubble within a critical radius ($r_{\text{capture}}$). The collision may be an impact...
collision, a sliding collision, or some combination of the two. The critical radius depends on the size of the bubble, the size of the particle, and the relative velocity between the two, as well as other factors[15].

Figure 2.6. Bubble-particle collision requirements[15].

The shape of an ink particle also has an effect on whether it will collide with a bubble. Disk-shaped particles are less likely to come into contact with an air bubble than spherical particles of the same diameter, since they are two-dimensional and particle alignment comes into play. However, if a disk-shaped particle and a spherical particle have the same mass, the disk will probably be more likely to collide with a bubble, since its diameter would be much larger.

Collision, of course, does not necessarily lead to attachment. Upon collision with a bubble, a particle may indeed attach firmly to the bubble, but it may rebound instead. Whether the particle rebounds from or attaches to the bubble is a statistical issue, and depends upon the area of contact, the duration of contact, and the local flow forces that
are present. If the particle remains adjacent to the bubble long enough to displace the liquid film between them and allow the system to reach a three-phase state of equilibrium (Figure 2.7), then it is likely to become firmly attached. If the three-phase equilibrium is not reached, then the ink particle can easily be swept away by flow forces. Incidentally, particles which are smaller than about 10 µm do not seem able to approach close enough to a bubble to completely attach to it. This is the reason that flotation does not efficiently remove these small particles; flow forces can easily separate them from the bubbles[15, 26].

![Figure 2.7. Mechanism of particle-bubble attachment[15].](image)

Due to the buoyancy of the bubbles, the ink is carried upward from the suspension to the froth at the surface, where it is removed from the flotation cell. Figure 2.8 below shows the ascent velocity of air bubbles in water with respect to their size. The ink is transported either by attachment to a single rising bubble or by entrapment in a rising cluster of bubbles. The former process is preferred, since fibers, fines, and fillers can be
trapped along with the ink in a bubble cluster, only to be removed with the foam. This adversely impacts the yield of the flotation process. Further, rising bubble clusters can cause excessive flow recirculation and channeling, and they may also coagulate into larger bubbles, greatly reducing their ink-collecting efficiency[15, 27].

Figure 2.8. *The ascent velocity of air bubbles in water*[15].

Once the ink reaches the foam at the surface, it must remain there until the rejects are scraped away. If the foam is not stable, some of the ink will drop back into the suspension and need to be collected again. This is a distinct negative, since more ink needing to be collected means that a longer flotation time is required to reach the target pulp brightness. Furthermore, longer flotation times can lead to lower yield. Figures 2.9 and 2.10 illustrate the trends among brightness, flotation time, and yield. As can be seen from Figure 2.10, it is possible that, once the removable ink has been collected, the pulp brightness may actually decrease somewhat with further flotation. This is due to the removal of bright fillers and pigments. The brightness may later rebound due to removal of dark mechanical fibers[15, 18].
Figure 2.9. The relationship between pulp brightness and yield[15].

Figure 2.10. The relationship between pulp brightness and flotation time[15].

It should be noted that each pulp suspension in a flotation operation has a unique ink particle size distribution, due to differences in ink type, pulping conditions, chemical addition, water hardness, flow patterns, and a host of other variables. For each particle size distribution, there is a bubble size distribution which would remove the ink most
efficiently. Further, as a flotation operation progresses and the ink particles are removed, the remaining particle size distribution, and thus the optimal bubble size distribution, changes. However, it is impossible to generate the perfect bubble size distribution for all possible ink distributions. One must settle for a flotation cell and operating conditions which produce acceptable results across the range of typical feed conditions. There is always room for improvement in a flotation operation.

### 2.3 DEINKING OF NEWSPRINT

The two most common printing methods used in newspaper production are web-fed rotary offset and water-based flexographic. Both techniques use carbon black as the pigment, but that is where the similarities end. Offset printing ink uses hydrocarbon resin as the binder (the chemical that envelops the pigment and binds it to the paper after drying) and mineral oil as the carrier (the chemical that dissolves the binder and keeps the ink as a fluid until the printing process is finished). Offset printing, the most common technique for printing newsprint, is a lithographic method involving the indirect transfer of the printing image from the printing plate to the paper via a rubber blanket or cylinder. Flexographic printing uses acrylic or maleic resin as the binder, and water as the carrier. This technique, with only about 10% of the US daily newspaper market share, involves direct printing from flexible rubber or photopolymer relief plates, wrapped around a cylinder on the press[15, 28].
Web offset printing inks are typically formulated for absorptive rather than evaporative drying. Thus, they do not completely dry, leading to newspaper readers finding their fingers have turned black after turning a few pages. Fresh newspapers printed by this method are therefore easy to deink using a conventional flotation process. Newspapers printed by the flexographic process, on the other hand, are not easy to deink. This is largely due to the hydrophilic nature of flexographic inks, which makes it difficult to separate the ink particles from the fibers and fines using the selective flotation process. Another reason that flexographic ink is hard to remove in this manner is that the dispersed particle size is very small. After pulping, the particle size of flexographic ink particles is typically between 0.3 and 2 µm, compared with 2 to 100 µm for offset ink aggregates.

Figure 2.11 shows the deinkability of offset-printed and flexography-printed newspapers by flotation, using several different surfactant collectors. The lower initial brightness of the flexographic pulp is due to the finer particle size. Because of the hydrophilicity and the small size of flexographic ink particles, wash deinking is a more efficient method for removal of this type of ink than flotation deinking[15, 19].
It is commonly known that efficient newsprint deinking requires that up to 20% of the furnish be coated magazine. The improvement, seen in terms of fiber loss as well as ink removal, is commonly credited to the high clay loading in the magazine coating.

Magazine papers are typically printed by rotogravure and offset processes. Figure 2.12 shows the deinkability of uncoated and coated magazine papers printed by each process. Rotogravure printing seems to yield better deinking results than offset printing. Coated papers are easier to deink than uncoated papers, since the coating, which detaches easily, can carry the ink with it[15, 29].
Figure 2.12. Deinkability of coated and uncoated magazine papers[15].

2.4 THE PLASMA SPARKER

The plasma sparker (shown in Figure 2.13 below) is an electrohydraulic discharge (EHD) device which was manufactured by Pulsed Power, Inc., Ontario, Canada.

Electrohydraulic discharge is a rapid, underwater electrical spark event. The high voltage spark is discharged through a plasma which is generated when a strong electric field is applied between two electrodes (see Figure 2.14). This causes a powerful acoustic shockwave which exerts pressure on the surrounding water.
Figure 2.13. The plasma sparker unit[30].

Figure 2.14. The electrohydraulic discharge event[30].

The electrical circuit which makes up the plasma sparker consists of a high voltage source, a bank of three capacitors, a power resistor, an air gap switch, an underwater electrode gap, and a voltage meter, wired as shown in Figure 2.15:
Figure 2.15. Circuit representation of the plasma sparker.

The high voltage source is a transformer which takes AC power at 115 V and 15 A, and converts it to DC power at 10,000 V and 0.25 A. The three 66 $\mu$F capacitors are connected in parallel, giving them a total capacitance of 198 $\mu$F. The power resistor has a resistance of 0.2 ohms. The air gap switch, labeled A in Figure 2.15, consists of two 1/4" diameter steel electrodes, separated by an adjustable gap. The water gap, labeled W, consists of two 1/2" diameter steel electrodes, separated by a set 1/8" gap. The voltage meter, labeled V, reads the potential across the capacitor bank, stepped down by a factor of 1000 through the use of an attenuating probe.

The water gap can be modeled as a high-valued resistor in parallel with a small capacitor[31]. The resistance is inversely related to the conductivity $k$ of the water, according to the following relation:

$$R(\text{ohms}) = \frac{L(cm)}{k\left(\frac{L}{cm}\right)A(cm^2)}$$

(2.1)

where $L$ is the gap length and $A$ is the area of the electrode face. The capacitance of the water gap is related to the dielectric constant $K$ of the water as follows:
where $\varepsilon_0$ is the permittivity of free space. The dielectric constant of tap water is roughly 50, which means that the capacitance is about 0.018 nF. The conductivity of tap water is typically between 100 and 200 $\mu$S/cm$^{-3}$, so the resistance of the water gap is about 1700 ohms.

To be precise, equations (2.1) and (2.2) can also be applied to the air gap, but the capacitance is several orders of magnitude lower than that of the water gap, and the resistance is so high that it can be considered infinite. Thus, at least initially, the air gap acts as a break in the circuit. This break allows the capacitors to charge when the high voltage source is turned on, and prevents discharge from taking place until the capacitor voltage reaches a predetermined set point.

The charging of the capacitors is governed by the equation[33]:

$$ V_C = V_S \left( 1 - e^{\frac{t}{RC}} \right) $$  \hspace{1cm} (2.3)

where $V_C$ is the capacitor voltage, $V_S$ is the source voltage (10,000 V) and $RC$ is the time constant of the charging circuit. It must be noted that $R$ in this case is not the 0.2 ohm power resistor in the discharge circuit. The charging current does not pass through this
resistor. Rather, the resistance in this case is internal to the transformer, and can be calculated from Ohm's law:

\[ V = IR \]  

(2.4)

Thus, \( R \) is the ratio of 10,000 V to 0.25 A, or 40,000 ohms. Therefore, from equation (2.3), the capacitors will reach a potential of 4,000 V roughly 4 seconds after the transformer is turned on. This is confirmed by observation.

As long as the air gap remains nonconductive, no current will flow through the discharge circuit, and the potential drop across the 0.2 ohm resistor will be zero volts. The cathode of the air gap will be at ground potential, despite the presence of the water gap separating it from ground, and the air gap will be standing off the full capacitor voltage. This is because the water gap does not act as a break in the circuit. Water, particularly tap water with its high conductivity, is a "leaky" dielectric, allowing some current flow even when it has not broken down. Therefore, the air gap is the only break in the circuit. Until it breaks down and becomes conductive, the water gap cannot break down, and the capacitors cannot discharge[31].

The breakdown voltage of the air gap is set manually by adjusting the distance between the electrodes. Increasing the electrode gap reduces the strength of the electric field at a given voltage, necessitating a higher voltage to initiate breakdown. Let us assume for this analysis that the gap is set such that breakdown occurs at 4,000 V. As the voltage
across the capacitor bank (and thus across the air gap) increases, free electrons in the gap are accelerated toward the anode by the growing electric field. Electrons may also be emitted from asperities in the cathode, where the field is high enough to overcome the resistance of the gap[34-37].

These electrons collide with gas molecules in the gap. The rate of collisions depends on the number of free electrons traveling through the gap, their rate of movement, and their mean free path in air at ambient conditions. If the kinetic energy of the electrons is high enough, they will knock off more electrons from the gas molecules they collide with. These electrons are then accelerated by the electric field, colliding with further gas molecules. As this process is occurring, the capacitor voltage is still increasing, thus increasing the electric field and increasing the kinetic energy of the free electrons[34].

During this time, a faint glow may be seen near the electrodes, where the concentration of traveling electrons is highest. This corona discharge is caused by the recombination of low-energy electrons and ions, and it removes energy from the ionized gas at a high enough rate to prevent breakdown. However, when the capacitor voltage reaches the set point of 4,000 V, breakdown begins to occur. The number of free electrons in the gap grows exponentially, leading to an "electron avalanche". The kinetic energy of the electrons exceeds the dissipative ability of the corona discharge at this point[34-36, 38-40].
As current begins to flow in the air gap, the gas is ionized by the electrons to the point where it becomes a plasma. Plasma is a dynamic, highly conductive, subatomic state of matter, consisting of ions, radicals, and free electrons. The resistance of the air gap drops dramatically, causing the voltage across it to fall to 100 - 200 V. This is a relatively constant figure for firing spark gaps, and we can assume an average value of 150 V for both the air gap and the water gap after they break down[31].

The plasma channel between the electrodes expands as the current increases, reaching very high local temperatures and pressures, and giving off visible and UV light. Electrons flow toward the anode, and cations flow toward the cathode. The cathode surface is damaged over time by the impacting cations. The anode is not damaged as much by the electrons, since they are much lighter and have less kinetic energy than the cations[34].

Once the air gap has broken down, the remaining capacitor voltage (roughly 3850 V) is placed across the water gap, since it has not broken down yet and isn't very conductive[31]. The capacitor still hasn't discharged at this point. The water gap, now under a high voltage stress, begins to break down. A low-density region forms at the surface of the cathode, as small amounts of current are injected into the water. Local heating by electron injection causes the low-density region to grow and propagate toward the anode. Eventually, the electric field in the gap is distorted enough to allow breakdown of the water[38-41].
J.C. Martin developed the empirical relationship [42]:

\[ F_{mb} \left( \frac{MV}{cm} \right) \left( \mu s \right)^{1/2} A \left( cm^{-2} \right)^{1/3} = \kappa \]  \hspace{1cm} (2.5)

which applies to microsecond pulse durations. In this equation, \( F_{mb} \) is the maximum breakdown field, \( t \) is the pulse duration, \( A \) is the area of the electrode face, and \( \kappa \) is a constant equal to 0.3 for pure water. The equation tells us how long an electric field must be applied across an underwater gap before breakdown will occur. Using \( F = 0.0121 \) MV/cm (corresponding to a peak voltage of 3850 V and a gap length of 1/8"), the required pulse duration is calculated to be roughly 14 ms. This is several orders of magnitude greater than the upper limit of the data range that equation (2.5) is valid for. However, this figure agrees reasonably well with observation. High-speed video of the spark event in tap water shows a period of roughly 3 ms between when bubbles first start to appear at the cathode and when breakdown actually occurs. This is shorter than the predicted 14 ms lag, but that was to be expected since tap water has a much higher conductivity than pure water. Thus, Martin's equation seems to apply fairly well to millisecond as well as microsecond pulse durations.

Once the water gap begins firing, the resistance drops, and the voltage across it falls to about 150 V, as was the case with the air gap. Now the remaining voltage (3700 V) appears across the 0.2 ohm resistor [31]. The capacitors discharge according to the equation [33]:
\[ V_c = V_0 e^{-\frac{t}{RC}} \]  \hspace{1cm} (2.6)

where \( V_0 \) is the initial capacitor voltage, and \( R \) is actually closer to 0.24 ohms than 0.2 ohms, due to the additional resistance of the 100 ft. of #6 AWG wire running from the capacitor unit to the submersible unit and back[31].

The time constant of the discharge is 47.5 µs. If we assume the gaps stop firing when the capacitor voltage falls below 300 V, we can calculate from equation (2.6) that the discharge will last for about 120 µs, or 2.6 time constants[31]. Figure 2.16 shows a graphical representation of the capacitor voltage during one charging and discharging cycle.

![Graph of capacitor voltage](image)

**Figure 2.16.** Capacitor voltage during charging and discharging.

Once both gaps are firing and the capacitors begin to discharge, the current will be uniform with respect to position throughout the discharge circuit, and it will vary with respect to time according to the equation[33]:

26
\[ I = \frac{V_0}{R} e^{-\frac{t}{RC}} \]  

where \( V_0/R \) is the maximum current through the circuit, calculated to be 15.4 kA.

As the current flows through the plasma channel in the water gap, energy is dissipated as heat. This causes thermal ionization of the water immediately surrounding the gap, effectively increasing the diameter of the plasma channel. Further thermal breakdown occurs at the new boundary, and so on, with the result being that the plasma channel expands very rapidly and violently during the initial part of the discharge, when the current is the highest. This expansion causes a shockwave to propagate through the surrounding water[30, 31, 41, 43-46]. Since the gap discharges will cease when the capacitor voltage falls below the total potential across them, roughly 300 V will be left on the capacitor bank after the current stops flowing[31].

Following the discharge, a bubble of entrained air, vaporized water, and the gaseous products of electrolysis forms around the plasma channel[47, 48]. It expands rapidly until its internal pressure is roughly 1/10 of the ambient pressure. At this point, the kinetic energy of the bubble surface is overcome by the outer hydrostatic pressure, and the bubble collapses violently[49]. The bubble growth occurs on the order of milliseconds, and the collapse takes place even more rapidly. The expansion of this bubble gives rise to a secondary pressure pulse of much lower magnitude than the shockwave. This bubble would, under normal circumstances, continue to expand and
collapse in a damped oscillatory manner, causing a weakening succession of pressure pulses[50, 51]. However, the presence of the electrodes at the point of collapse causes it to explode into thousands of tiny bubbles.

Before discharge, the capacitor stores energy according to the equation:

\[ E_c = \frac{1}{2} C V_c^2 \]  

which corresponds to a maximum stored energy of 1584 J. After the discharge, there is a residual energy of 9 J left on the capacitor bank due to the leftover 300 V. Thus, 1575 J are released in each capacitor discharge. This energy is dissipated in the resistor and in the two plasma channels during the discharge.

The energy spent in each spark gap can be calculated from the equation:

\[ E_g = I V_g t \]  

where \( V_g \) is roughly 150 V. This can be integrated with respect to time over the discharge interval to find the total energy spent in each gap:

\[ \Delta E_g = V_g I_{max} \int_0^{120 \mu s} e^{-\frac{t}{RC}} dt \]  

(2.10)
This amounts to approximately 102 J of energy dissipated in each spark gap. Subtracting twice this number from the total energy released in the discharge leaves 1371 J dissipated in the resistor. Thus, only about 6.5% of the released energy was spent in the water gap during the discharge[31].

2.5 EFFECTS OF THE PRESSURE WAVE

There are two subsets of effects that the EHD pressure wave can have on the surrounding medium: mechanical and sonochemical. The use of lithotripsy to break up kidney stones in a patient[30] and the use of EHD to crack the shells of zebra mussels in water pipes[52] are clear examples of the mechanical effects of EHD. Another mechanical effect occurs when bubbles are present in the water. A photographic study has revealed that the pressure wave released during EHD causes preexisting bubbles to undergo rapid changes. The bubbles either shatter into many smaller bubbles, oscillate in size and shape, or move rapidly toward or away from each other. The effect of the shockwave on each individual bubble depends largely on the size of the bubble, but also on such factors as the bubble's shape, or its proximity to other bubbles. Figure 2.17 shows a group of bubbles, located about 1.5 feet from the electrode gap, before and after a spark discharge.
Figure 2.17. The EHD-induced breakup of bubbles.

Figure 2.18 shows how the degree of bubble distortion and breakup depends on bubble size. The distortion was rated visually on a scale from 0 to 10; a rating from 0 to 2 signifies very little or no shape distortion, 2 to 4 reflects moderate, 4 to 7 stands for moderate breakup, and 7 to 10 represents violent breakup. The data were assembled from three separate experiments.
It is suspected that the shockwave-induced bubble breakup is a resonance effect. Bubbles have a certain resonance frequency that depends upon their equilibrium size; Prosperetti[51] has hypothesized that a bubble driven by a continuous acoustic wave near its resonance frequency will break up if the sound amplitude is high enough. This also appears to be true in the case of short acoustic pulses. The peak frequency of the sound wave emitted by the sparker has been estimated at about 5 kHz[45], which is the resonance frequency of a bubble with a radius of about 0.6 mm. Figure 2.18 shows that moderate bubble distortion occurs when bubbles are of this size or larger, confirming the importance of resonance effects.

Smaller bubbles that do not break up are affected by the shockwave in other ways. In some cases, they may undergo rapid size oscillations before returning to their equilibrium size. Often, the smaller bubbles move rapidly toward or away from each other under the influence of the shockwave. This is due in part to two effects: the interactions of the
oscillation patterns of the bubbles, and the eddy currents caused by the breakup of other bubbles.

Sonochemical effects of EHD are attributed to cavitation. Cavitation bubbles are generated during the rarefaction or negative pressure phase of an acoustical wave, if the amplitude is high enough. These bubbles, which originate from microscopic gas pockets in water or at asperities on submerged solid surfaces, implode rapidly after formation. Figure 2.19 shows evidence of cavitation bubble formation on the surface of aluminum foil due to EHD. Upon collapse, the gas and vapor in the bubble are compressed, resulting in very high local temperatures and pressures. Water molecules inside and immediately around the bubble may undergo homolysis, releasing hydroxyl radicals. These radicals are highly reactive, and go on to initiate various sonochemical oxidation reactions with whatever species they might encounter[30, 53].

![Figure 2.19. Unsparked and sparked samples of aluminum foil.](image)

Previous work[6, 30] has shown that the surfaces of acrylate particles suspended in water are mildly oxidized upon sparking. This is due to hydroxyl radicals, which were released
from cavitation bubbles that formed on the particle surfaces. The zeta potential of the particles was shown to decrease with sparking, as was their tack.
3 EXPERIMENTAL RESULTS AND DISCUSSION

The discussion below demonstrates that the zeta potential of ink particles can be reduced upon sparking, and that this reduction can serve as the basis of a new technique that promotes ink removal, while simultaneously decreasing fiber loss during flotation deinking.

3.1 EXPERIMENTAL SETUP

The EHD units used were obtained from Pulsed Power, Inc., Ontario, Canada. Laboratory experiments were conducted in a 10-L tank constructed from a section of pipe with integrated 1.5-cm diameter steel electrodes with a 4-mm gap. Pilot work was done with a submersible electrode unit (as described earlier), which was placed inside the flotation cell. The approximately 0.1 ms discharge was of 15 kA and 4 kV.

Zeta potential was measured with a Zetasizer (Malvern Instruments Ltd., UK). These measurements were made on laser printer toner, type PX Black (containing styreneacrylate copolymer, carbon black, polypropylene, and charge control agents), supplied by Southern Cross Systems Corporation. The toner was cured at 400°C for 30 seconds; it fuses in less than one second at 400°C in a printer. The fused toner (0.63 g) was ground to a fine powder and suspended in 7.2 L of DI water. The pH was adjusted to 6.6 with 50% NaOH. The suspension was subjected to sparking and samples were collected periodically. A similar experiment was done on flexographic ink obtained from
the *Atlanta Journal and Constitution*. A small quantity (0.34 g) of the ink paste was dispersed in 1% NaOH for 3 hours at 60°C. The dispersed ink was added to 7 L of deionized water, the pH was adjusted with 20% H₂SO₄, and the suspension was sparked.

The effect of sparking on bubble size and geometry was imaged with a Kodak EktaPro 1000HR camera, which is capable of capturing a frame every millisecond. The camera captures images of bubbles that are greater than 0.3 mm in diameter. The bubbles were created by dropping an Alka Seltzer tablet into water.

Pilot-scale flotation deinking runs were made with 20% magazine (Time) and 80% newspaper (*Atlanta Journal Constitution*). Such a mixture of newspaper and magazine is typically used in the industry. Two 2.5 kg sets were torn up, soaked in 40°C water for one hour, and pulped in a 25 L Lamort laboratory pulper with a high-consistency Helico rotor. Pulping was done at low rpm (730 rpm, 2-3 kW) under the conditions specified in Table 3.1. The surfactant (Resolution 4283) and soap (Eka 4030) used were supplied by Eka Chemical. The final pulp was held at temperature for an additional 20 minutes prior to flotation to enhance deinking efficiency. Sufficient pulp was made in each batch to perform one control and one sparker-treated experiment.
Table 3.1: Target flotation conditions.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>consistency, %</td>
<td>1</td>
</tr>
<tr>
<td>temperature, °C</td>
<td>40</td>
</tr>
<tr>
<td>pH</td>
<td>9</td>
</tr>
<tr>
<td>hardness, ppm</td>
<td>150</td>
</tr>
<tr>
<td>NaOH, % dry fiber</td>
<td>0.7</td>
</tr>
<tr>
<td>H₂O₂, % dry fiber</td>
<td>0.7</td>
</tr>
<tr>
<td>sodium silicate, % dry fiber</td>
<td>1.2</td>
</tr>
<tr>
<td>surfactant, % dry fiber</td>
<td>0.6</td>
</tr>
<tr>
<td>soap, % dry fiber</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Flotation was conducted in a 250 L Voith Sulzer atmospheric flotation cell. During flotation, pulp is pumped from the bottom of the cell into a circulation loop. Air is added to the pulp, and the resulting mixture is pumped back into the cell, where it is sprayed radially out of a horizontal, circular nozzle near the bottom of the unit. This spraying action disperses the bubbles and keeps the cell fully mixed. The dispersed bubbles then rise to the top, picking up ink and some fiber, and form a foam at the top, which is removed.
3.2 EXPERIMENTAL PROCEDURE

The baseline pulp was added at 2.5 kg bone-dry fiber and made up to 1% consistency with 40°C tap water. The temperature was maintained within 5°C for both pulping and flotation. Calcium chloride was added to raise the hardness in the flotation cell to 150 ppm. The system was mixed through recirculation for about one minute prior to introducing air. Semi-batch flotation was carried out for 10 minutes. A 2 L sample was collected from a sample port in the circulation loop at 0, 4, 7 and 10 minutes. A baseline ISO brightness gain of 10 percentage points was targeted. Trial and error determined that an air flow rate of 57 L/min led to a ten-point gain in brightness with the chosen chemistry. The reject rate was monitored and targeted at less than 10% total fiber loss, as measured by solids content, ash values, and material balance. Pulp pads (3 g) were prepared for the measurement of brightness and of the effective residual ink content (ERIC) by using a Buchner funnel and Whatman #40 filter paper. Three pads were prepared from each sample. Brightness and ERIC testing[54] was performed at Eka Chemicals in Marietta, GA, using a Technidyne ColorTouch Model ISO and the accompanying Free Ink software routine. Measurements were made at six locations per side and averaged.

Two different sparking procedures were used for the pilot work. In the first, the electrode assembly (referred to hereafter as the “sparker”) was submerged in the flotation cell during flotation, and the unit was discharged once every three seconds for 10 minutes at 4 kV. The results from these experiments are tagged as “sparking during flotation”. In the
second procedure, the pulp was treated before flotation. The furnish was placed in the flotation cell, recirculated, and sparked once every three seconds for five minutes without air flow. The sparker was then removed from the flotation cell and air was introduced to initiate flotation. The control samples were treated identically but without sparking. The results from these experiments are designated “sparking before flotation”. It should be noted that the additional five minutes of mixing that occurs in the latter procedure does not affect the results; air is not introduced to the system during this time. The recirculation serves only to ensure that the pulp, water, and chemicals are mixed thoroughly during sparking.

Fiber and filler loss was determined by collecting the rejected foam, washing and draining it, and firing it at 525°C. The fiber content of the foam was assumed to be equal to the organic material that was burned away. Other contributions to the organic portion, such as polymeric ink components, were negligible. The inorganic material was assumed to be mostly filler.

### 3.3 EXPERIMENTAL RESULTS

Laboratory results from sparking laser printer toner and flexographic ink are presented in Figures 3.1 and 3.2, respectively. The ink was run at two different starting pH values, which gave rise to different initial zeta potentials. In all cases, sparking decreases pH and zeta potential, suggesting that the particles are oxidized. Very similar behavior was reported in previous work with adhesives[6] where a zeta potential drop of up to 20 mV
was accompanied by increased wettability and reduced tack. Tack is not an issue here, but the increased negative charge on the ink/toner particles should inhibit redeposition on the negatively charged fiber. If so, then sparking should decrease the ink content of pulp after flotation deinking, and thereby increase its brightness.

Figure 3.1. Effect of sparking on zeta potential (top) and pH of toner.

Figure 3.2. Effect of sparking on zeta potential (top) and pH of flexographic ink. The two plots reflect different starting pH.
ISO Brightness and ERIC measurements are presented in Figure 3.3. A t-test shows that sparking before flotation increases brightness over that of the control at a confidence level of over 95%. As expected, ERIC and brightness are inversely related; the two sets of data in Figure 3.3 correlate quite well ($r^2=0.96$). Hence, both the brightness and ERIC data support the suggestion that sparking before flotation inhibits ink redeposition.

![Figure 3.3. Changes in ISO brightness and average ERIC with flotation time in pulp sparked before flotation. The average initial brightness was 48.1% for the control and 46.3% for the sparked sample.](image)

In contrast, sparking during flotation does not improve the brightness, as shown by the results in Table 3.2. Flotation efficiency is optimal when the bubble size and particle size distributions overlap[55-57]. We expect the shock wave to change the bubble size distribution, which could be either beneficial or detrimental depending on how the overlap changes. Given that no brightness gain develops during deinking under these conditions it would appear that the changes in bubble distribution adversely affect the overlap between bubble and particle size. Another possibility is that the shockwave
causes the ink particles to detach from the bubbles before they have a chance to firmly attach. A third possibility is that the shockwave breaks up the foam at the surface somewhat (this was in fact observed), and causes some of the ink to fall back into the suspension. In any case, any gains in brightness and yield caused by decreased ink redeposition are offset by the reduced flotation efficiency caused by bubble distortion.

\[\text{Table 3.2: Average brightness gain (points) for sparking during flotation.}\]

<table>
<thead>
<tr>
<th>time (min)</th>
<th>control average (std dev)(^1)</th>
<th>sparker average (std dev)(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-4</td>
<td>5 (1)(^1)</td>
<td>5 (2)(^2)</td>
</tr>
<tr>
<td>0-7</td>
<td>7 (1)</td>
<td>7 (1)</td>
</tr>
<tr>
<td>0-10</td>
<td>10.1 (0.4)</td>
<td>10 (2)</td>
</tr>
</tbody>
</table>

avg. initial brightness: \(^1\)47.5\% (n=6); \(^2\)46.0\% (n=6)

Fiber and filler loss data from the pilot runs are presented in Table 3.3. Again, sparking during flotation provides no benefit over the control, whereas fiber and filler loss is significantly reduced for the runs where the pulp was sparked prior to flotation. A t-test showed that the means between the control and the sparked values were different at a confidence level of over 99.9%.
Table 3.3: Average fiber and filler loss after flotation.

<table>
<thead>
<tr>
<th></th>
<th>control average (std. dev.)</th>
<th>sparker average (std. dev.)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>sparked before flotation</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>reject (g)</td>
<td>200 (20)</td>
<td>125 (6)</td>
</tr>
<tr>
<td>inorganic (g)</td>
<td>100 (10)</td>
<td>50 (3)</td>
</tr>
<tr>
<td>fiber loss (g)</td>
<td>101 (5)</td>
<td>75 (4)</td>
</tr>
<tr>
<td>percent fiber loss</td>
<td>4.0</td>
<td>3.0</td>
</tr>
<tr>
<td><strong>sparked during flotation</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>reject (g)</td>
<td>190 (20)</td>
<td>180 (20)</td>
</tr>
<tr>
<td>inorganic (g)</td>
<td>87 (5)</td>
<td>80 (10)</td>
</tr>
<tr>
<td>fiber loss (g)</td>
<td>100 (10)</td>
<td>96 (6)</td>
</tr>
<tr>
<td>percent fiber loss</td>
<td>4.0</td>
<td>3.8</td>
</tr>
</tbody>
</table>

3.4 DISCUSSION

For the pilot work, the furnish was sparked either during flotation or prior to it by placing the sparker in the float cell and introducing air only after sparking was complete. It should be noted that in a mill application, the sparker would be placed in a feed chest and not in the float cell itself.

One should also consider the question of attenuation. Sound wave attenuation in solid-liquid suspensions depends largely on the solids concentration, as well as on the frequency of the sound. The peak frequency of the sparker output is less than 10 kHz. The wavelength of a 10 kHz sound wave is about 15 cm, which is about 100 times longer
than a wood fiber. Thus a suspension of wood fibers will not attenuate the sound waves in question to any great extent, particularly at 1% consistency. There is some attenuation, especially of higher frequencies, but the sound waves will still travel several meters through the suspension. Thus, the bubbles throughout the entire flotation cell should be affected by the sparker.

The rationale for the increase in yield is as follows. When ink particles attach to fiber, they increase its hydrophobicity and add to the likelihood that the fiber will associate with a bubble and be removed through flotation. This work suggests that decreasing the zeta potential of the ink through sparking inhibits ink redeposition, increasing the proportion of ink-free fiber. The free ink particles would be more easily removed, leading to increased brightness, and the hydrophilic ink-free fiber would tend to remain in the water, which would give rise to the increased yield. Sparking during flotation does not change the yield significantly, as shown by the results in Table 3.3. This is consistent with the finding that the brightness also remains unchanged under these conditions. One unexpected outcome of sparking during flotation was that the total reject volume was about one-quarter less than that from the control because of disruption of the foam structure by the shockwaves.

In summary, the benefit of sparking is attributed to the oxidation of the ink particles by hydroxyl radicals generated by the acoustic field, which is supported through the zeta potential measurements. Others[58-60] have studied the effect of ultrasound on toner particles and have found that large particles break up into smaller ones. One study[61]
suggested that microcavitation at the ink-paper interface might separate the ink from the paper. A yield increase was not noted in any of these reports. An acoustic field, whether continuous or pulsed (as in this case), will have both mechanical and oxidative effects, and both probably contribute to the benefits observed. However, it appears that the oxidative effects are principally responsible for the gains in brightness and yield during sparking, primarily because of the decrease in ERIC, which is an estimate of the amount of ink particles below 8 µm attached to the fiber. The reduced ERIC must reflect removal of the small ink particles; this subset would have increased if the larger particles were comminuted. Also, the zeta potential reduction is of the same order as that measured earlier for adhesive particles suspended in water[6], where the effects were related to changes in surface properties rather than in particle size.

Sparking before flotation can reduce fiber loss by about 25% in a single flotation stage. This benefit in yield is economically very significant, especially when coupled with a parallel increase in brightness, and is easily the most important benefit of sparking. The total benefit realized from multi-stage cells may be correspondingly greater. The economics are attractive; payback is of the order of three months based on fiber savings alone. Also, at about 1.5 kJ per spark, the power requirements are minimal with respect to the benefit derived.
4 CONCLUSIONS AND RECOMMENDATIONS

The significance of this work is that it introduces a method for improving both brightness and fiber yield in flotation deinking. It is not conventionally possible to do this, as the two are usually inversely related. Following are a list of conclusions drawn from this work and a list of recommendations for future work in this area.

4.1 SUMMARY OF CONCLUSIONS

- The spark discharge generates a spherical pressure pulse which causes cavitation at the surface of the ink particles.
- The ink particles are oxidized by the resultant hydroxyl radicals, as evidenced by a drop in zeta potential after sparking.
- The more negatively-charged ink particles are then less likely to redeposit on fibers in the suspension.
- The oxidized particles also agglomerate more readily in the presence of a collector, making them easier to remove and resulting in almost three more points of brightness gain in this study.
- The ink-free fibers are less likely to be floated out of the suspension by air bubbles, resulting in a 1% higher yield in this study.
- This technology can easily be scaled up and implemented by placing the submersible unit in a feed chest before the flotation cell.
• Finally, at about 1.5 kJ per spark, the power requirements of this system are minimal with respect to the benefit derived.

4.2 RECOMMENDATIONS FOR FUTURE WORK

In any future research in this area, more work should be done to verify the mechanisms of brightness and yield improvement. For example, fibers could be examined to see if there are less ink particles attached to them after spark pretreatment and flotation than there are after flotation only. Also, perhaps a photographic study could be done to see if the pressure pulse does shear ink particles off of the bubbles when sparking is performed during flotation. Finally, the effects of feed chest size and stock flow rate could be investigated in a scale-up study.

For my own future research, I plan to further investigate the effects of the pressure pulse on bubbles. This will involve generating single bubbles of variable size in a water tank, running the sparker, and recording the bubble dynamics with a high-speed camera. I will then complicate the system by adding particles that can attach to the bubbles, and investigate the effects of the pressure pulse on the particle-bubble equilibrium. Experimental results will then be compared to theory, which will be derived from other works as well as my own.
APPENDIX - Paper Published in Industrial Engineering and Chemistry Research

SEPARATIONS

Effect of Electrohydrodynamic Discharge on the Flotation Deinking Efficiency

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Discharging a high-energy spark underwater creates a shock wave that dissipates through an acoustic field. The hydroxyl radicals created by the field are able to mildly oxidize the surfaces of ink and toner particles suspended in water, thereby decreasing their ζ potential. This decrease inhibits the tendency of the particles to restack to fiber, which is negatively charged. Pilot studies showed that sparking a slurry of recycled newspaper and magazine furnish decreased residual ink on fiber by 21%, increased brightness by 1%, and reduced fiber loss by 1% when the treated furnish was subsequently subjected to flotation deinking. No benefit was realized if the furnish was spark-deinked during deinking, possibly because the shock wave changes the bubble-size distribution.

Introduction

Flotation deinking is commonly used in paper recycling to remove ink from fiber. Atmospheric pressure cells are most effective in removing particles in the 15–50-μm range. Pressurized deinking modules generate bubbles of smaller size and are able to remove smaller particles. Ink removal is inevitably accompanied by fiber loss, and a compromise is usually struck based on product specifications.

We have previously shown that firing a high-intensity spark underwater creates a spherical shock wave that generates an acoustic field, which, in turn, breaks water into hydroxyl radicals. The surfaces of acrylate particles suspended in water are mildly oxidized upon exposure, and their ζ potential and tack drop. These contaminants are commonly found in recycle paper process streams, and a reduction in tack minimizes deposits and other operational problems. In this paper, we demonstrate that the ζ potentials of ink particles can be similarly reduced upon sparking, and that this reduction can serve as the basis of a new technique that promotes ink removal, while simultaneously decreasing fiber loss during flotation deinking.

Experimental Section

The sparking unit used was obtained from Pulse Power Inc., Stony Creek, Ontario, Canada. Laboratory experiments were conducted in a 10-L tank constructed from a section of pipe with integrated 1.5-cm-diameter steel electrodes with a 4-mm gap. Pilot work was done with a submersible electrode unit, which was placed inside the flotation cell. The approximately 0.1-ms discharge was 15 kA and 4 kV.

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ζ potential was measured with a Zetasizer (Malvern Instruments Ltd., Malvern, U.K.). These measurements were made on laser printer toner, type FX Black (containing styrene-acrylate copolymer, carbon black, polypropylene, and charge control agent), supplied by Southern Cross System Corp. The toner was cured at 400°C for 30 s; it was less than 3 s at 400°C in a printer. The fused toner (0.62 g) was ground to a fine powder and suspended in 7.2 L of deionized water. The pH was adjusted to 6.8 with 50% NaOH. The suspension was subjected to sparking, and samples were collected periodically. A similar experiment was done on flexographic ink obtained from the Atlanta Journal and Constitution. A small quantity (0.34 g) of the ink paste was dispersed in 1% NaOH for 3 h at 90°C. The dispersed ink was added to 7.1 L of deionized water, the pH was adjusted with 20% H2SO4, and the suspension was sparked.

The effect of sparking on the bubble size and geometry was imaged with a Kodak Ektapro 1000HR camera, which is capable of capturing a frame every 1 ms. The camera captures images of bubbles that are greater than 0.3 mm in diameter. The bubbles were created by dropping an Alka Seltzer tablet into water.

Pilot-scale flotation deinking runs were made with 20% magazine (Time) and 80% newspaper (Atlanta Journal and Constitution). Such a mixture of newspaper and magazine is typically used in the industry. Two 2.5-kW sets were used up, soaked in 40°C water for 1 h, and pulped in a 25-L Losorri laboratory pulper with a high-consistency Helico rotor. Pulping was done at low rpm (750 rpm, 2–3 kW) under the conditions specified in Table 1. The surfactant (Resolution 4282) and soap (Eka 4520) used were supplied by Eka Chemicals (Solna, Sweden). The final pulp was held at temperature for an additional 20 min prior to flotation to enhance the deinking efficiency. Sufficient pulp was
made in each batch to perform one control and one sparker-treated experiment.

Flotation was conducted in a 250-L Voith Sulzer atmospheric flotation cell. During flotation, pulp is pumped from the bottom of the cell into a circulation loop. Air is added to the pulp, and the resulting mixture is pumped back into the cell, where it is sprayed radially out of a horizontal, circular nozzle near the bottom of the unit. This sprying action disperses the bubbles and keeps the cell fully mixed. The dispersed bubbles then rise to the top, picking up ink and some fiber, and form a foam at the top, which is removed.

The baseline pulp was added to 2.5 kg of bone-dry fiber and made up to 1% consistency with 40 °C tap water. The temperature was maintained within ± 0.5 °C for both pulping and flotation. Calcium chloride was added to raise the hardness in the flotation cell to 150 ppm. The system was mixed through recirculation for about 1 min prior to the introduction of air. Semicontinuous flotation was carried out for 10 min. A 2-L sample was collected from a sample port in the circulation loop at 0, 4, 7, and 10 min. A baseline ISO brightness gain of 10% was targeted. Trial and error determined that an air flow rate of 0.7 L/min led to a 10% gain in brightness with the chosen chemistry. The reject rate was monitored and targeted at less than 10% total fiber loss, as measured by solids content, ash values, and material balance. Pulp pads (8 g) were prepared for the measurement of the brightness of the effective residual ink content (ERIC) by using a Bittnner funnel and Whatman No. 40 filter paper. Three pulp pads were made for each of the treated control samples for a total of nine pads. The fiber content was measured by igniting the filtered solids at 625 °C. Brightness and ERIC testing were performed at Eka Chemicals using a Technidyne ColorTouch model ISO and the accompanying Free Ink software routine. Measurements were made at six locations per side and averaged.

Two sparker procedures were used for the pilot work. In the first procedure, the electrode assembly (referred to hereafter as the “sparker”) was submerged in the flotation cell during flotation, and the unit was charged once every 3 s for 10 min at 3 kV. The results from these experiments are tagged as “sparking during flotation”. In the second procedure, the pulp was treated before flotation. The furnace was placed in the flotation cell, recirculated, and sparked once every 3 s for 5 min without air flow. The sparker was then removed from the flotation cell, and air was introduced to initiate flotation. The control sample was treated identically but without sparking. The results from these experiments are designated as “sparking before flotation”. It should be noted that the additional 5 min of mixing that occurs in the latter procedure does not affect the results; air is not introduced to the system during this time. The recirculation serves only to ensure that the pulp, water, and chemicals are mixed thorough during sparking. Fiber loss was determined by collecting the rejected foam, washing and draining it, and firing it at 525 °C. The fiber content of the foam was assumed to be equal to the organic material that was burned away. Other contributions to the organic portion, such as polymeric ink components, were negligible.

Results and Discussion

Laboratory results from sparking laser printer toner and flexographic ink are presented in Figures 1 and 2, respectively. The ink was run at two different starting pH values, which gave rise to different initial ζ potentials. In all cases, sparking decreases the pH and ζ potential, suggesting that the particles are stabilize. Very similar behavior was reported in our earlier work with adhesives, where a ζ potential drop of up to 20 mV was accompanied by increased wettability and reduced tack. Tack is not an issue here, but the increased negative charge on the ink to particles should inhibit redeposition on the negatively charged fiber. If so, then sparking should decrease the ink content of pulp after flotation deinking and thereby increase its brightness.

For the pilot work, the furnace was sparked either during flotation or prior to it by placing the sparker in the flotation cell and introducing air only after sparking was complete. In a mill application, the sparker would be placed in a feed chest and not in the flotation cell itself. Brightness and ERIC measurements are presented in Figure 3. A Student’s t test shows that sparking before flotation increases the brightness over that of the control at a confidence level of over 95%. As expected, ERIC and brightness are inversely related; the two sets of data in Figure 3 correlate quite well (r2 = 0.96). Hence, both the brightness and ERIC data support our suggestion that sparking before flotation inhibits ink reattachment.

In contrast, sparking during flotation does not improve the brightness, as shown by the results in Table 2. The flotation efficiency is optimal when the bubble-size and particle-size distributions overlap. We expect the shock wave to change the bubble-size distribution, which could be either beneficial or detrimental depending on how the overlap changes. High-speed images of bubbles taken before and after sparking showed the bubbles to be dramatically affected by the shock wave. Over the course of about 15 ms, the bubbles shattered into many smaller bubbles (Figure 4) and oscillated in size and shape. The effect of the shock wave on each individual bubble depends largely on the size of the bubble but also on factors such as the bubble’s proximity to other bubbles.
Figure 2. Effect of sparking of flongraphic ink on the pH and z potential (top). The two plots reflect different starting pHs.

Table 2. Average Brightness Gain (points) with Flotation Time for Sparking during Flotation

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Control average (std dev)</th>
<th>Sparked average (std dev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0—4</td>
<td>5 (1)</td>
<td>5 (2)</td>
</tr>
<tr>
<td>0—7</td>
<td>7 (1)</td>
<td>7 (1)</td>
</tr>
<tr>
<td>0—10</td>
<td>10 (1) (2)</td>
<td>10 (1) (2)</td>
</tr>
</tbody>
</table>

*Average initial brightness: 45% (n = 76).

Figure 3. Changes in brightness (points) and average EPR ppm with flotation time in ppm-sparked before flotation. The average initial brightness was 48.1% for the control and 45.9% for the sparked sample.

Figure 4. Effect of the shock wave on bubbles. The left and right frames are before and after sparking. The bubbles are about 500 cm from the spark source.

Figure 5. Bubble distortion vs. equilibrium radius.

Small bubbles that do not break up are affected by the shock wave in other ways. In some cases, they may undergo size oscillations, although our camera does not have a fast enough frame rate to capture this clearly. Often, the smaller bubbles move rapidly toward or away from each other under the influence of the shock wave. This is, perhaps, due in part to two effects: the inter-
actions of the oscillation patterns of the bubbles and the eddy currents caused by the breakup of other bubbles. In any case, it is clear that sparking distorts both bubble size and geometry. Given that no brightness gain develops during deinking under these conditions, it appears that the changes in the bubble-size distribution adversely affect the overlap between the bubble and particle size. We conclude that any gains in brightness and yield caused by decreased ink reattachment are offset by the reduced flotation efficiency caused by bubble distortion.

Sound wave attenuation in solid–liquid suspensions depends largely on the solids concentration, as well as on the frequency of the sound. The peak frequency of the sparker output is less than 10 kHz. The wavelength of a 10-kHz sound wave is about 15 cm, which is about 100 times longer than that of wood fiber. Thus, a suspension of wood fibers will not attenuate the sound waves in question to any great extent, particularly at 1% consistency. There is some attenuation, especially of the higher frequencies, but the sound waves will still travel several meters through the suspension. Thus, the bubbles throughout the entire flotation cell are not affected by the sparker.

Fiber loss data from the pilot runs are presented in Table 3. Again, sparking during flotation provides no benefit over the control, whereas fiber loss is significantly reduced for the runs where the pulp was sparked prior to flotation. A Student’s t-test showed that the probability that the means between the control and the sparking values were different at a confidence level of over 99.9%. The 1% benefit in yield is economically very significant, especially when coupled with a parallel increase in brightness, and is easily the most important benefit of sparking. It is not conventionally possible to simultaneously increase both the brightness and fiber yield; they are usually inversely related. The brightness gain over the various flotation intervals shown in Figure 3 (taken from the individual runs) is approximately linearly related to fiber loss (also taken from the individual runs in Table 3), as shown in Figure 6. The results for sparking during flotation were excluded because of high scatter. As discussed above, sparking breaks up some of the bubbles, which introduces additional complexity. The correlation coefficient is relatively low at 0.74, but this is not surprising because only small changes in brightness and yield are being measured. Figure 6 could also represent two clusters of points, and the apparent linearity could simply reflect the gap between the two sets. However, if even a rough relationship between brightness and yield is assumed, then a possible mechanism for the process unfolds.

Our rationale for the increase in yield is as follows. When ink particles attach to fiber, they increase its hydrophobicity and add to the likelihood that the fiber will associate with a bubble and be removed through flotation. Our work suggests that sparking inhibits ink reattachment, which would increase the proportion of ink-free fiber. The free ink particles would be more easily removed, leading to increased brightness, and the hydrophilic ink-free fiber would tend to remain in the water column, which would give rise to the increased yield. Sparking during flotation does not change the yield significantly, as shown by the results in Table 3. This is consistent with the finding that the brightness also remains unchanged under these conditions. One unexpected outcome of sparking during flotation was that the total reject volume was about one-quarter less than that from the control because of disruption of the foam structure by the shock waves.

In summary, we attribute the benefit of sparking to the oxidation of the ink particles by hydroxyl radicals generated by the acoustic field, which we support through our measurements on the ξ potential. Others have studied the effect of ultrasound on toner particles and have found that large particles break up into smaller ones. One study suggested that microcavitation at the ink–paper interface might separate the ink from the paper. A yield increase was not noted in any of these reports. An acoustic field, whether continuous or pulsed (as in our case), will have both mechanical and oxidative effects, and both probably contribute to the benefits observed. However, it appears that the oxidative effects are principally responsible for the gains in brightness and yield during sparking, primarily because of the decrease in ERIC, which is an estimate of the amount of ink particles below 10 μm attached to the fiber. The reduced ERIC must reflect removal of the small ink particles; this effect would have increased if the larger particles were comminuted. Also, the ξ potential reduction is of the same order as that measured earlier for adhesive particles suspended in water, where the effects were related to changes in surface properties rather than in particle size.

Sparking before flotation can reduce fiber loss by about 25% in a single flotation stage. The total benefit realized from multistage cells may be correspondingly greater. The economics are attractive; payback is on the order of 3 months based on fiber savings alone. Also, at about 1.5 kwhr per ton, the power requirements are minimal with respect to the benefit derived. There is also a 5% reduction in fiber loss across flotation following sparking. These improvements appear to derive from the decrease in the ξ potential of the ink and toner particles upon sparking.
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