Decontamination of Process Streams Through Electrohydraulic Discharge

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Executive Summary

Contaminants present in paper recycling mills can degrade product properties and can also lead to substantial downtime. Of these, adhesive material such as hot melts and pressure sensitive adhesives are especially troublesome. These are known as “stickies” and their handling and removal requires process equipment such as screens and cleaners as well as chemical additives. In the preceding phase of the project we demonstrated that firing an underwater spark in a tank of stock reduces the tack of the stickies and reduces their impact. The present phase was to demonstrate the technology in full-scale trials, address any issues that might arise, and commercialize the process.

Trials were run at the Appleton papers mill in West Carrollton, OH, the Graphics Packaging mill at Kalamazoo, MI, Stora Enso mills at Duluth, MN, and Wisconsin Rapids, WI, and the Jackson Paper mill at Sylva, NC. It was shown that the sparker not only detackified stickies but also increased the efficiency of their removal by centrifugal cleaners, improved the effectiveness of dissolved air flotation, and increased the efficiency of flotation deinking.

It is estimated that the sparker improves the efficiency of hydrocyclone cleaner, deinking cells and dissolved and dispersed air flotation units by 10-15%. This translates to a corresponding energy benefit in operating these units. The technology has been licensed to Eka Chemicals, a division of Akzo Nobel.

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1. Overview

"Stickies" are adhesive materials such as pressure sensitive adhesives and hot melts that enter the mill with the furnish. They cause process-related problems by depositing out on surfaces such as wires and felts and plugging wires and felts. They can also be responsible for degrading product quality by picking or blemishing the paper. Stickies are commonly controlled through screening and cleaning equipment or through chemical additives. Despite these measures, they still cause substantial downtime and represent a cost and energy burden to the mill.

In the preceding phase of the project we demonstrated that firing an underwater spark in a tank of stock reduces the tack of the stickies and reduces their impact. We now demonstrate that sparking can also enhance the removal efficiency of stickies in screening and cleaning and increase the efficiency of flotation deinking. Several full-scale trials were run and these demonstrations provided the basis for commercializing the technology, which has been licensed to Eka Chemicals, a division of Akzo Nobel.

This report is divided into several sections, some of which have been published. A summary of each section is provided here.

Trial at the Appleton Papers West Carrollton, OH, mill

The sparker was placed in the forward cleaner feed chest and a trial was run for two five-hour periods without incident. The sparker was then operated continuously, and copious amounts of a waxy deposit consisting of a mixture of defoamer and EVA hot melt appeared in the gyrocleaner rejects after about 36 hours. Pinholes containing the waxy material were found throughout the product. Defoamer use is high at the mill at 6 lbs/ton and it appeared to deposit when the mixture was sparked. Laboratory work showed that this deposition is promoted in the presence of calcium or aluminum. The process streams at the mill traditionally have a high calcium level of 1,200-2,000 ppm.

In a follow-up trial, the unit was placed in the screw press filtrate which feeds the gyrocleaners so that production would not be affected. After eight hours a frothy white buildup began to form in the Gyrocleaner rejects trough. These proved to be a mixture of hydrocarbon resin (similar to that used on adhesive tapes), PVAc and acrylate. The white particles were $CaCO_3$ and silicate. The build-up was confirmed in a second trial, which was run for twelve hours. These results are important in that in demonstrates that the sparker improves the efficiency of centrifugal cleaners.

Trial at the Graphic Packaging Kalamazoo mill

The sparker was placed in the whitewater return loop and its effectiveness measured by measuring the build up on the foil. The sparker significantly reduced the amount of deposits from 2.4 lbs/week to 1.5 lbs/week. However, there was no relationship between hole counts & foil deposits for either baseline or trial periods. The hole counts are probably not caused by stickies; problems with formation could be responsible. Laboratory work showed that much of the tacky deposits derived from pitch rather than from stickies.

Trial at the Stora Enso, Duluth mill

Several trials were run at this mill. The sparker was first placed in the 24,000 DAF clarifier and the unit improved clarification efficiency from 95 to 98%. It also reduced the average filtrate consistency from 1.4 to 0.63%, which translates to 64 lbs/1,000 gallons. The solids are principally fines and filler and fines are known to have a disproportionately high attraction to stickies. The sparker was then moved to the light cleaner feed chest from which the stock flows to the fine screens. The microstickie counts in the accepts stream decreased by about 15%, indicating that sparking improved cleaning efficiency. The sparker was then moved to the flotation feed tank where it increased the ink content in the rejects stream indicating an improvement in deinking efficiency. Hence, sparking improved the performance of several unit operations, namely clarification, cleaning and deinking.

Trial at the Stora Enso Wisconsin Rapids mill

The sparker also aggregates biological sludge particles much in the way that it does stickie contaminants and a brief trial was run at the Wisconsin Rapids mill. Initial laboratory work showed that the sparker was able to increase both cake solids and the drainage rate. The sparker was positioned at the bottom of the secondary thickener. This tank was estimated to contain 80,000 gallons at the time. The unit was placed just above the outflow pipe, so that the sludge pumped to the blend tank would be sparked. The sparker only works with secondary sludge and the mill was able to accommodate us by running pure secondary sludge for a few hours. However, only a single point could be taken because the sparker stopped working after a short while. Sparking increased pressed solids from 18.2 to 19.1%. The solids returned to 18.2% when the sparker was shut off.

Trial at the Jackson Paper, NC mill

A four-week trial was run at Jackson Paper to determine if the sparker removed microstickies from the water system with the ultimate goal of improving runnability. The sparker was placed just after stock introduction to the Hydrocal unit where he process water was clarified. The hydrocal removal efficiency increased by at least eight points during the trial. In fact, a record efficiency was obtained during the final week. Deposits in the press section also progressively decreased and the sparker increased microstickies removal from the sludge press filtrate by 20%.

Effect of electrohydraulic discharge on flotation deinking efficiency

Discharging a high-energy spark underwater creates a shock wave which 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 zeta potential. This decrease inhibits the tendency of the particles to reattach 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 sparked *during* deinking, possibly because the shock wave changes the bubble size distribution.

Spark-induced agglomeration of aqueous polymeric suspensions

Discharging a high-energy spark underwater creates a shock wave that dissipates through an acoustic field. Colloidal acrylate polymers suspended in water containing dissolved calcium are agglomerated as a result. The degree of agglomeration increases with the number of sparks applied and with increasing calcium content. The calcium decreases the charge on the colloidal particles and thereby increases their propensity to be agglomerated by the acoustic wave. These observations are confirmed in full-scale trials in paper recycling mills where sparking improves the efficiency of centrifugal cleaners by increasing the particle size of the contaminants.

Spark-induced consolidation of biological sludge

Subjecting a suspension of biological sludge to underwater sparks (3kV, 50 kA) leads to its consolidation, decreases the charge density on the solids, and increases its settling rate. The cake solids increase, but by only one percentage point. High-speed video images show that the spark generates a steam bubble. The dynamics of bubble growth could be estimated through the Rayleigh model. The bubble collapses into an acoustic field, which then agglomerates the particles. Sparking does not affect the settling rate of an aqueous slurry of softwood pulp because the fibrous particles are too large to be aggregated by an acoustic pulse.

Properties of the shockwave

The shockwave pressure was measured and the efficiency of free radical production by the resulting wave calculated in order to define the action of the spark.

Other potential sparker applications

The sparker was able to degas water in small laboratory-scale work. Attempts to scale up failed because the liberated bubbles redissolved as they floated to the surface. An effort to collapse foam by the sparker was unsuccessful.

Energy implications

The major benefit of the sparker lies in improving process efficiency through better stickies removal, improved flotation and clarification. On average the improvement obtained is about 10-15%. This translates to a direct energy benefit; the efficiency of hydrocyclone cleaner, deinking cells and dissolved and dispersed air flotation units increase by this amount. A major indirect benefit is also realized through downtime reduction.

2. Trial at the Appleton Papers West Carrollton, OH, mill

Samples from four different locations were obtained from the mill prior to the trial to establish baseline conditions. The tower sample is the final product from the Recycle Plant. The 150-ton sample represents material from the 150-ton per day pulper, which runs unprinted paper only. The 250-ton sample represents stock from the 250-ton per day pulper, which runs about 66% unprinted & 33% printed material. The printed material contains only impact inks (no non-impact inks such as toner).

The samples were coarse-filtered through a Whatman #4 filter and then ultrafiltered through a 3,000 Da membrane. The difference in TOC between the filtrate and the ultrafiltrate corresponds to high-MW carbon which represents microstickies. The results are provided in Table 1. The stickies level in the broke recovery chest is surprisingly low. However, broke pulping is not aggressive, and it appears that the large stickies present are not broken into microstickies during this operation.

The filtered samples were then boiled down from 1 L to 2 ml. One ml of the concentrate was plated on a metal coupon and dried at 25-40^{o}C overnight. The coupon was warmed in warm water, the water shaken loose, and the tack measured with a Polyken tack tester as a function of temperature. The results (Table 2) were normalized to 40^{o}C to enable comparison. The tack is also a measure of stickies and correlates roughly with the high-MW TOC values reported above. The tack-TOC relationship falls on a previously established curve derived from several mills.

In the mill the repulped stock is cleaned and screened and thickened with a screw press. The brownstock is bleached (CEH sequence) and then screened and cleaned with forward and gyrocleaners. The mill trial started in mid-June with the sparker placed in the forward cleaner feed chest. The trial was run for two 5-hour periods without incident. The sparker was then operated continuously, and copious amounts of a waxy deposit appeared in the gyrocleaner rejects after about 36 hours. Pinholes containing the waxy material were found throughout the product. FTIR analysis showed the material to be aliphatic hydrocarbons containing a small amount of EVA hot melt. The hydrocarbons were identical to a defoamer used in the mill. Forty percent of a sample of the gyrocleaner rejects was benzene-extractable. Mass spectra showed the extracts to be predominantly C_{23}-C_{33} hydrocarbons with a small amount of aromatic components. A mass spectrum of the defoamer itself corresponded to C_{20}-C_{32} hydrocarbons. There results confirm the FTIR identification of defoamer as the principal constituent of the rejects. Defoamer use is high at the mill at 6 lbs/ton.

Since the composition of the defoamer in the rejects stream is similar to that of the "pure" defoamer, it is unlikely that the sparker altered the defoamer itself. It is more likely that the defoamer forms aggregates with other hydrophobic components such as stickies and pitch in the system (as seen in the FTIR and mass spectra) and the aggregate is oxidized by the sparker. We know from previous work that stickies are oxidized by the sparker. The zeta potential of the aggregate would decrease and it would be attracted to cations in the system. One possibility is calcium; the process streams traditionally have a high calcium level of 1,200-2,000 ppm. We found calcium to be present in the gyrocleaner rejects at 2,180 ppm (dry weight basis).

Table 1: TOC (ppm) of samples from West Carrollton.

sample	coarse-filtered	ultrafiltered	high-MW TOC (microstickies)
broke recovery			
4/22/02	166	59	108
4/23/02	159	55	104
4/24/02	215	86	129
4/25/02	181	98	83
to tower			
4/22/02	228	63	165
4/23/02	297	81	217
4/24/02	274	70	204
4/25/02	194	59	135
150-ton			
4/22/02	1,900	199	1,700
4/23/02	1,020	120	901
4/24/02	1,210	115	1,100
4/25/02	670	198	473
250-ton			
4/22/02	1,160	146	1,020
4/23/02	1,200	187	1,020
4/24/02	1,340	160	1,180
4/25/02	1,040	197	838

Table 2: Tack results from samples from West Carrollton (04/22/02)

broke		to tower		250 ton		150 ton	
temperature (^{o}C)	**tack (g force)**	**temperature (^{o}C)**	**tack (g force)**	**temperature (^{o}C)**	**tack (g force)**	**temperature (^{o}C)**	**tack (g force)**
35	5	38	24	36	106	35	112
38	3	41	67	39	113	35	117
		46	46	40	134	39	125
		44	49	40	163	39	127
		44	56	42	127	40	116
				42	131	40	119
				43	154		
40 (estimated)	**5**		**46**		**132**		**125**

Table 3: Aggregate formation on the impeller.

OD-fines (%)	clay (%)	pitch (%)	alum (%)	DADMAC (ppm)	brittle
0.07	0.26	1.15	0.26	44	No
0.19	0.25	1.13	0.25	44	No
0.19	0.25	1.13	0.38	43	No
0.30	0.25	1.14	0.25	0	No
0.20	0.25	1.13	0.49	44	No
0.20	0.24	1.12	0.97	45	No
0.19	0.24	1.10	1.92	44	No
0.10	0.25	1.15	2.0	46	partly (extremely brittle after oven-drying

Some support for this position was obtained by subjecting a 2,000 ppm suspension of defoamer in water to 100 sparks and agitating it in a Bioflo reactor fitted with a Rushton impeller at 1,000 rpm for two hours. The process was repeated in the presence of 1,000 ppm of calcium (as chloride). The quantity of deposits increased to about twice the amount obtained without calcium. It is emphasized that this proposed mechanism is only a hypothesis that appears to fit all the observations, and is not a proven finding.

In an earlier trial at Augusta Newsprint we found that sparking generated deposits that consisted of fines, pitch (or stickie) and clay. Several attempts were made to synthesize the aggregates in the laboratory. Pitch obtained from a plywood mill was ground and suspended in water at a pH of 12.7. A mixture of pitch, NSSC fines, clay, DADMAC and alum was sparked 200 times at 4 kV. The pH of the sparked mixture was adjusted to 4.2 and agitated in the BioFlo reactor described above at 1,000 rpm for 2 hours. Aggregates (mostly fiber) deposited on the impeller. The aggregates were air dried at room temperature; the dried material was not brittle. However, a brittle aggregate formed at the highest chemicals:fines ratio; the degree of brittleness increased when the aggregate was oven-dried overnight at 105^{o}C as shown in Table 3.

Since handling large sample volumes in the laboratory-scale sparker is unwieldy, a 0.5% suspension of fines was sparked 200 times, mixed with various additives, and an aliquot of the suspension oven-dried. The results are shown in Table 4. While it is difficult to deconvolute the separate effects of each of the components, brittle aggregates seem to form when the concentration of pitch is at least 0.05% and either alum or a cationic polymer such as DADMAC is present. The presence of clay does not appear to be critical.

Since sparking leads to oxidation and to a decrease in zeta potential, we determined the effect of sparking DADMAC. Solutions of DADMAC were sparked and net charge was measured through PVSK titration. There is a drop in the net charge (Table 5), but only after prolonged sparking. Since free DADMAC will experience very few sparks before it will be bound up with fiber, the effect of sparking should be negligible.

Table 4: Aggregate formation from mixtures of fines and chemicals.

OD-fines (%)	clay (%)	pitch (%)	alum (%)	DADMAC (ppm)	brittle aggregate	aggregate color
0.4	0.5	1.15	0.5	45	++	dark brown
0.4	0.0	1.15	0.5	45	+	dark brown
0.2	0.5	1.15	0.5	160	+++	dark brown
0.4	0.5	1.15	0.25	45	0	dark brown
0.2	1.0	0.25	0.5	200	+++	light brown
0.2	1.0	0.50	0.5	200	+	brown
0.2	2.0	0.25	0.5	200	+++	beige
0.2	2.0	0.10	0.5	200	++	white
0.1	2.0	0.10	0.5	200	++	white
0.4	1.0	0.10	0.25	0	+	light brown
0.4	0.5	0.05	0.25	0	½+	light brown
0.4	0.25	0.05	0.125	0	½+	brown
0.4	0.25	0.05	0.25	0	½+	brown
0.4	0.25	0.026	0.25	0	0	brown
0.4	0.25	0.026	0.125	0	0	brown
0.4	0.125	0.026	0.125	0	0	brown
0.4	0.125	0.026	0.063	0	0	brown
0.4	0.5	1.15	0.5	0	+++	dark brown
0.4	0.0	1.15	0.5	0	½+	dark brown
0.2	0.5	1.15	0.25	0	+	dark brown
0.2	1.0	0.25	0.5	0	++	brown
0.2	1.0	0.5	0.5	0	+++	dark brown
0.2	2.0	0.1	0.5	0	½+	beige
0.1	2.0	0.1	0.5	0	+	beige

Table 5. Effect of sparking on DADMAC.

sparks	pH	zeta potential (mV)	net charge (meq/g polymer)
40 ppm DADMAC			
0	5.62	44.3	5.87
50	4.61	46.8	5.60
100	4.31	45.8	5.66
200	4.14	43.2	5.37
400	3.90	45.5	4.60
100 ppm DADMAC			
0	5.62	52.6	5.70
50	4.55	50.5	5.62
100	4.43	54.6	5.56
200	4.17	54.4	5.50
400	4.05	51.1	5.44

Laboratory work was conducted to determine the effect of sparking on the defoamer used at Appleton. A 200 ppm suspension of the defoamer in water was sparked, and zeta potential and particle size were measured. Charge titrations were also made. A few sparked samples were agitated in our Bioflo mixer at 1,000 rpm for 2 hours in order to induce deposition. Calcium and/or DADMAC was added on occasion prior to agitation. The results are shown in Table 6.

The charge titrations show that the defoamer becomes progressively more negative upon sparking. No visible deposits were seen because the amount of defoamer used was too small. Agitating a sparked suspension of 2,000 ppm defoamer in the presence of calcium or DADMAC led to deposits of the type observed at the mill. Hence, it appears that sparking oxidizes the defoamer and promotes its association with cationic material.

Table 6: Effect of sparking on charge concentrations of defoamer.

defoamer (ppm)	sparks		pH	zeta potential (mV)	charge (meq/10L)	net charge (meq/g	film formation
0	0		5.52	-20.7	-0.001		
	50		4.57	-29.4	-0.065		
	100		4.47	-31.3	-0.143		
	200		4.38	-32.4	-0.298		
	400		4.16	-36.1	-0.641		
200	0		6.29	-44.1	0.025	0.013	
	50		5.03	-36.0	-0.085	-0.01	
	100		4.62	-36.8	-0.170	-0.013	
	200		4.59	-38.4	-0.320	-0.011	
	400		4.05	-36.7	-0.620	-0.010	
	400	agitated[1]	4.52	-38.4	-0.658	-0.009	
	400	agitated with DADMAC[1,2]	4.21	+50.2	1.417	1.029	½+
2000	0		8.84	-67.8	-0.50	-0.025	
	50		8.34	-67.7	-0.54	-0.024	
	100		7.70	-58.1	-0.60	-0.023	
	200		5.98	-44.2	-0.93	-0.032	
	400		4.92	-42.0	-1.15	-0.025	+
	400	agitated[1]	5.46	-38.5	-1.20		+
	400	agitated with DADMAC[1,2]	5.00	+9.0	+0.30		+
	400	agitated with $CaCl_2$ & DADMAC[1-3]	4.97	+16.1			++
	400	agitated with $CaCl_2$[3]	4.95	-5.8			++

[1]agitated at 1,000 rpm for 2 hrs; [2]40 ppm DADMAC; [3]2,000 ppm $CaCl_2$

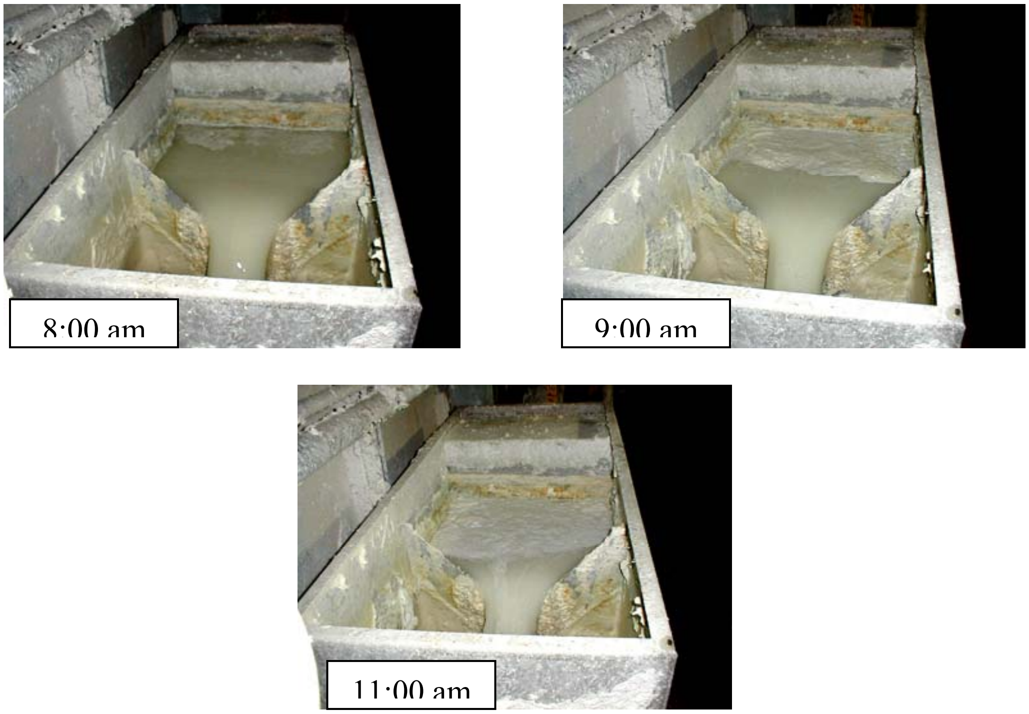

Figure 1: Stickie deposits in the gyrocleaner rejects trough.

In a follow-up trial, the unit was then placed in the screw press filtrate which feeds the gyrocleaners so that production would not be affected. The trial was run for 10.5 hours. After eight hours a frothy white buildup began to form in the Gyrocleaner rejects trough. The rejects were run through the Pulmac Screen and a large amount of white contaminate is collected on the 0.006" inch slot screen. The rejects were analyzed by FTIR and were found to correspond to a mixture of hydrocarbon resin (similar to that used on adhesive tapes), PVAc and acrylate. The white particles were $CaCO_3$ and silicate. These rejects only appeared when the sparker is on.

In a second trial the unit was run for 12 hours on September 20 and the pulp that was produced was segregated into #3 High-Density Tower. No quality problems were encountered. As before, the Gyrocleaner rejects trough had some white material buildup during the trial period, as shown in Figure 1. Note the progressive build-up of the solid rejects. In conclusion, the sparker successfully agglomerated stickies and removed them in the gyrocleaner.

Mechanism of agglomeration

In order to investigate whether sparking enhanced the binding between calcium and stickies, laboratory work was done with Carbotac 26207, a PSA similar to and slightly tackier than the Carboac 261717 that we have used before. A 200 ppm suspension of this material (formulated as 49% solids) and calcium chloride (1, 5, 10, 100 ppm) in DI water was sparked up to 200 times. Samples taken at various intervals were ultrafiltered through a 3,000 MW cut-off membrane to remove the Carbotac and any calcium bound to it. The calcium in the permeate was determined by ICP. Calcium was detected in pure DI water at 0.203 ppm because of a contamination problem.

Calcium binds to Carbotac as shown by the reduction in free calcium upon mixing with the Carbotac (Table 7). Sparking does not induce any major change in free calcium. There appears to be a release of calcium when the 1 ppm $CaCl_2$ solution is sparked, but the opposite effect is seen for the 5 ppm solution, and these differences cannot be taken as significant. The effect of sparking mixtures of calcium and Carbotac as a function of the number of sparks applied is summarized in Table 8. Again, any effect is relatively small.

Table 7: Effect of sparking on the binding of calcium with Carbotac.

	free Ca (ppm)			
pure $CaCl_2$ solution[1]	0.782	1.92	3.67	32.7
plus 200 ppm 49% Carbotac	0.442	1.77	3.59	31.7
20 sparks	0.654	1.72	3.78	32.5
200 sparks	0.614	1.92	4.85	32.1

[1] the amount of $CaCl_2$ added was 1, 5, 10 and 100 ppm, respectively.

Table 8: Effect of sparking on free calcium.

	Ca (ppm)[1]	**Ca (ppm)[1]**
pure $CaCl_2$	1.77	1.63
plus 200 ppm 49% Carbotac	1.52	1.87
no. of sparks		
1	1.27	2.10
2	1.22	2.11
5	1.55	1.57
10	1.52	1.91
20	1.46	1.57
50	1.48	-
200	1.41	-

[1] duplicate runs

Table 9: Amount of unbound calcium (ppm) when only the Carbotac is sparked.

	Ca (#1)	Ca (#2)
5 ppm $CaCl_2$	1.80	1.75
plus 200 ppm 49% solids Carbotac	1.39	1.86
1 spark	-	1.81
5 sparks	1.86	1.97
20 sparks	1.97	2.01
200 sparks	1.78	-

Table 10: Effect of sparking on free aluminum.

	Al (ppm)[1]	
pure Al sulfate[2]	1.24	3.00
Al sulfate + 200 ppm 49% Carbotac	0.724	2.02
5 sparks	0.598	1.99
20 sparks	0.571	2.11
200 sparks	0.658	1.86

[1]duplicate runs; [2]the amount of $Al_2(SO_4)_3 \cdot 18H_2O$ added was 20 and 40 ppm.

Table 11: Average turbidity [NTU] for the first hour after initial mixing of aluminum sulfate/Carbotac mixtures.

	ppm Al sulfate / ppm Carbotac		
sparks	20/400	20/200	40/200
0	86.1	40.6	49.2
5	86.2	42.3	49.3
20	86.3	43.2	48.9
200	87.1	48.4	50.7

Table 12: Effect of sparking on the $CaCl_2$ - PAA equilibrium.

	5 ppm $CaCl_2$	50 ppm $CaCl_2$
	free Ca (mg/L)	
pure $CaCl_2$	1.73	15.5
$CaCl_2$ + 100 ppm PAA	1.53	13.7
5 sparks	1.54	14.0
20 sparks	1.58	14.7
200 sparks	1.64	14.2

Table 13: Effect of sparking on the Al sulfate - PAA equilibrium.

	20 ppm Al sulfate	200 ppm Al sulfate
	free Al (mg/L)	
pure Al sulfate	1.57	17.0
Al sulfate + 100 ppm PAA	0.0690	8.19
5 sparks	0.0690	8.28
20 sparks	0.0690	8.48
200 sparks	0.0590	8.46

Finally, we studied the interaction of calcium with sparked Carbotac. Here, 266 ppm of the Carbotac was sparked 200 times and 30 ml samples were taken periodically. Ten ml of 20 ppm $CaCl_2$ was added to each sample, mutually diluting the samples to 200 ppm Carbotac, and 5 ppm $CaCl_2$. As before, the samples were then filtered to remove the Carbotac, and the permeate analyzed for calcium content. The experiment was then repeated for each sparking level. The results, listed in Table 9, show only minor changes. We conclude that while Carbotac picks up calcium, the interaction is not sensitive to sparking.

Experiments analogous to those reported above for calcium were performed with aluminum sulfate octadecahydrate in place of calcium chloride. As before, 200 ppm of 49% solids Carbotac 26207 was added. Samples taken after 0, 5, 20, and 200 sparks were ultrafiltered as above to remove the Carbotac and any bound aluminum. Aluminum in the permeate was determined by ICP. The results, presented in Table 10, show that sparking does not significantly disturb the aluminum-Carbotac interaction.

During the experiment a white flaky precipitate fell out of solution. A similar precipitation also occurred by merely allowing the mixture to sit overnight. However, sparking the 40 ppm Al sulfate system increased the precipitation rate and reduced the final size of the flakes. For the 20 ppm Al sulfate system, there was no noticeable difference in the size of the precipitate with regards to the sparking. However, sparking accelerated the onset of deposition. To quantify this phenomenon we sparked the Carbotac-aluminum sulfate mixture up to 200 times, and measured turbidity with an Obreco-Hellige 965-10A turbidimeter every minute for at least an hour. The average turbidity over the first hour after initial mixing is listed in Table 11; the turbidity increases, especially for the 20/200 entries. The deposits begin to settle after 50 minutes from the time of initial mixing only for the 40/200 entries.

The Carbotac formulation used is proprietary, and we attempted to reproduce the effects observed above with a well-defined system: water soluble polyacrylic acid MW: 90,000 from Arcos Organics and calcium or aluminum. As with Carbotac, sparking does not significantly disturb the equilibrium between polymer and the metal ions as shown in Tables 12 and 13. However, a white flaky precipitate settled out of the solution for the 200 ppm Al sulfate/100 ppm PAA system. A series of experiments verified that this precipitate forms when the concentration of aluminum sulfate is approximately two or more times that of the PAA. Sparking reduced the size of the deposits and settling usually started earlier.

A mixture of aluminum sulfate octahydrate and PAA was prepared in DI water as follows. One liter each of PAA (600 ppm) and aluminum sulfate octadecahydrate (1,500 ppm) was simultaneously poured into the reactor containing 3 liters of DI water. An additional 3 liters of DI was then poured into the reaction vessel. This diluted the PAA concentration to 75 ppm and the Al sulfate to 187 ppm. The system was then sparked. In the first run the system was sparked a total of 5 times, with a sample collected after the first, second, and fifth sparks. The second run the system was sparked 100 times with a sample collected after the fifth, twentieth and hundredth spark. The turbidity of the samples was measured with an Obreco-Hellige 965-10A turbidimeter every minute. The results, illustrated in Figure 2, show the evolution of turbidity [NTU] relative to the

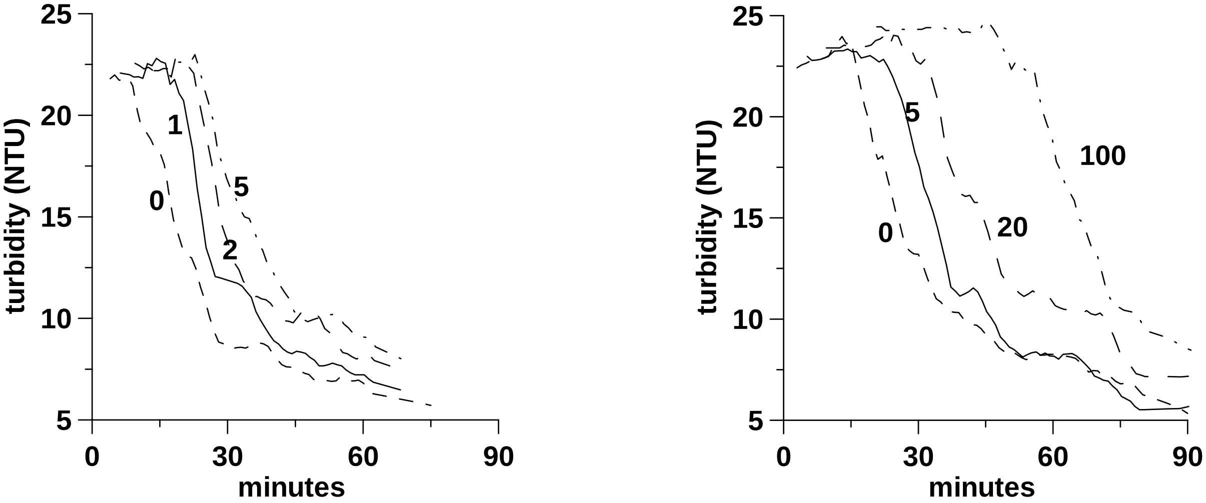

Figure 2: Effect of sparking on turbidity. The number of sparks applied is labeled in the plots.

time of initial mixing and time of sample collection. Sparking retards settling of the particles in both cases. Consistent with these results was the observation that the unsparked samples formed the largest agglomerates. For the sparked samples, the size of the aggregates decreased with the number of sparks.

A point of difference between this and the Carbotac-Al system is that the deposit here is formed via nucleation and growth, whereas a coagulation of suspended particles occurs for the Carbotac-Al suspension. The plasma sparker encourages the formation of nucleation points, which decreases the time it takes for the deposits to form and also reduces particles size. As a result, the sparked systems tend to start settling faster but take longer to settle due to the smaller agglomerate sizes.

These measurements allow us to propose a mechanism for the deposits observed at Appleton Paper and (previously) at Augusta Newsprint. We had previously shown that sparking increased the negative charge on Carbotac, probably because of oxidation, and had suggested that this increased charge would increase its binding to cations. Sparking also progressively reduced the pH of an aqueous 200 ppm PAA solution from 6.11 to 5.68 over 200 sparks, suggesting a similar increase in charge. However, the data provided above are clear in that there is no increase in binding, and our previous postulate is, therefore, incorrect.

The sparker releases energy with each spark in a wide variety of broadband sound and light waves. Past research has shown that the most significant portion is the ultrasonic pulses that are sent through the system. These create cavitation bubbles, which are significantly increased in the presence of multiple ultrasonic frequencies (Feng *et al. Ultrasonic Sonochemistry* 9 (2002) 231). The local region in the vicinity of a collapsing cavitation bubble has a very extreme environment. Measurements made in aqueous systems at an ultrasonic frequency of 20 kHz showed collapsing bubbles generated localized temperatures in the neighborhood of 4000 K and in excess of 1,000 atmospheres (Neppiras, *Ultrasonics* (1984) 22, 25; Henglein, *Ultrasonics* (1987) 25, 6; Suslick, *Science* (1990) 247, 1439). In a homogeneous liquid-phase reaction the collapse of the bubble generates intense microshear. This microshear can cause nucleation of a precipitate.

We presently believe that sparking causes small particles to deposit out of water. These deposits grow as they circulate through the system and eventually form particles large enough to fall out.

3. Trial at the Graphic Packaging Kalamazoo mill

Samples collected from several locations were filtered through Whatman 4 filter paper (coarse filter). An aliquot of each filtrate was then ultra-filtered through a 3,000 Da membrane filter. Both filtrates were analyzed for total carbon (TC) and inorganic carbon (IC) from which total organic carbon (TOC) was obtained by difference. The difference in TOC between the coarse filtrate and the ultrafiltrate corresponds to high-MW carbon which represents stickies. The results are shown in Table 1. One liter of each coarse filtrate was boiled down to approximately 5 ml. The concentrate (1 ml) was spread on a metal coupon and dried overnight at 25-40°C. The coupon was warmed in 60°C water for 30 seconds, the water was shaken loose, and the tack measured with a Probe Tack PT-500 tack tester. The results are shown in Table 2. Both the tack and TOC values are quite low, which suggests that the mill may not have a significant stickies problem. We suspect that the tacky materials that they encounter probably derive from pitch.

The sparker does not reduce the total number of microstickies as shown in Table 3. This was expected; the sparker makes the stickies less tacky nut it does not remove them. Deposits from the foil were collected weekly both before and during the trial and these are summarized in Table 4. The sparker significantly reduces the amount of deposits. Results from a trial with a stickies-control enzyme formulation are included in Table 4. Although the enzyme performs better in this regard, it is much more expensive than the sparker. There is no relationship between hole counts & foil deposits for both baseline and trial periods. The hole counts are probably not caused by stickies; problems with formation could be responsible.

Table 1: TOC of samples from Graphics Packaging.

	coarse-filtered TOC	**ultrafiltered TOC**	**high MW TOC**
June 24, 2002			
backliner stuff box	747	583	164
OCC transfer	1236	957	279
news transfer	862	780	82
filler blend chest	801	756	45
July 8, 2002			
filler blend	778	633	145
news transfer	843	611	232
OCC transfer	1235	1032	203
BL stuff box	858	544	314
July 3, 2002			
filler blend	1017	817	200
news transfer	920	798	122
OCC transfer	1671	1454	217
BL stuff box	1043	892	151

Table 2: Tack results of samples from Graphics Packaging.

backliner stuff box		**OCC transfer**		**news transfer**		**filler blend chest**	
tempera-ture (^oC)	**tack (g force)**	**tempera-ture (^oC)**	**tack (g force)**	**tempera-ture (^oC)**	**tack (g force)**	**temperature (^oC)**	**tack (g force)**
June 24, 2002							
32	6	32	4	30	1	36	2
40	3	37	6	34	2	37	2
40	14	40	12	34	1	40	2
45	20	40	25	38	3	43	3
47	20	44	15	41	13	47	5
		44	16	45	21	50	9
40 (avg)	**13**		**14**		**8**		**4**
July 3, 2002							
31	1	37	1	35	1	29	1
39	2	37	1	37	3	32	1
40	1	37	5	38	4	37	1
42	1	40	2	40	10	38	1
42	1	40	4	42	11	40	2
43	1	42	6			43	2
48	3	44	4			45	2
40 (avg)	**1.5**		**3.4**		**6.3**		**1.5**

Table 3: High-MW TOC of samples from Graphics Packaging.

	high MW TOC (ppm)
June 24, 2002 (sparker off)	
backliner stuff box	164
OCC transfer	279
news transfer	82
filler blend chest	45
July 8, 2002 (sparker off)	
filler blend	145
news transfer	232
OCC transfer	203
BL stuff box	314
July 3, 2002 (sparker off)	
filler blend	200
news transfer	122
OCC transfer	217
BL stuff box	151
September 19, 2002 (sparker on preceding week)	
OCC transfer	389
broke chest #1	283
TL transfer	281
box transfer	381

news transfer	165

Table 4: Median dry weight of foil deposits (lbs/week) at Graphics Packaging.	
baseline (6 mos)	2.4
enzyme trial (2 wks)	0.75
sparker trial (5 wks)	1.5

4. Trial at the Stora Enso, Duluth mill

4.1 Installation at the clarifier

The sparker unit was placed in the 24,000 DAF clarifier, which has a flow of 1,300 gpm. Sparking improved clarification efficiency as shown in Figure 1. However, there is considerable scatter in the efficiency data. It is difficult to measure efficiency for low-consistency samples because two small numbers are compared. Hence, the data were screened through a two-sigma filter prior to analysis. The F-test shows the distributions for the sparked and unsparked samples to be different with 99+% confidence for the consistency and 98% efficiency for the efficiency values. Furthermore, the fact that sparking reduces filtrate solids and increases DAF efficiency makes a compelling case that the sparker is responsible. The sparker reduces the average filtrate consistency (Figure 1) from 1.4 to 0.63%, which translates to 64 lbs/1,000 gallons. The solids are principally fines and filler and fines are known to have a disproportionately high attraction to stickies (*Tappi J.,* 80(4), 193, 1997). Fillers are capable of forming neutral buoyancy aggregates with stickies.

The observation that efficiency increases with increasing solids is well-known, but the efficiency is generally higher when the sparker is on. The improvement is small from the clarification point of view; the decrease in solids is of little value. However, we have noted earlier (*Tappi J.,* 80[4], 193, 1997) that stickies associate preferentially with fibrils, which suggests that the fines carry a disproportionately high load of stickies. Hence, the improvement in clarification should reflect a significant removal of stickies.

Atomic Force Microscopy (AFM) scans were also run on several samples, and a typical example is provided in Figure 2. Note that the advancing and retracting curves are very different for the unsparked control because the probe tip picks up some stickie material upon contact with the surface. The two curves are near-identical for the sparked sample, because the surface is harden and non-sticky and the probe is able to cleanly withdraw from the surface.

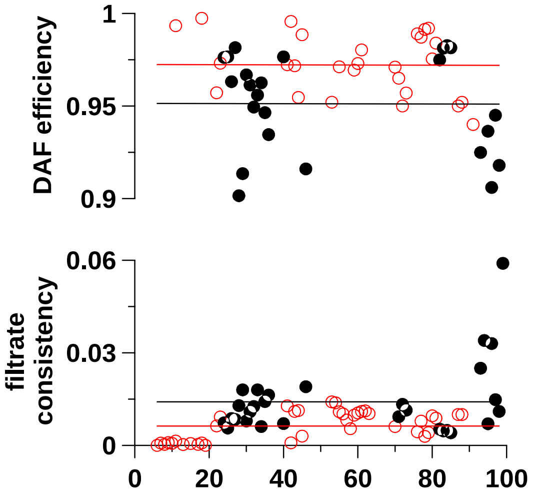

Figure 1: Effect of sparking on DAF performance. The open circles designate a "sparker on" condition. The abscissa is time in days.

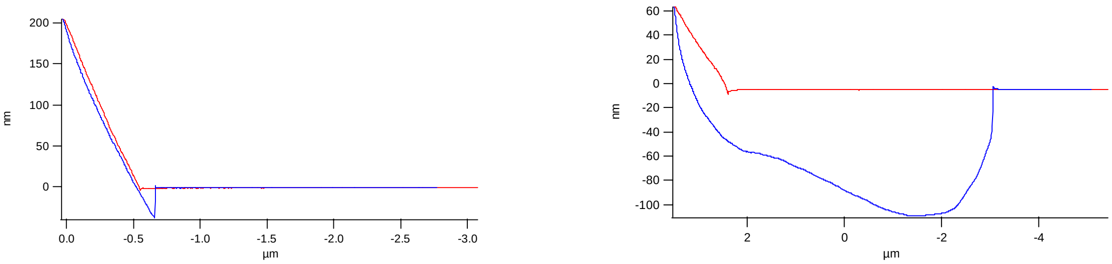

Figure 2: AFM scans of DAF rejects with the sparker on (1/7/03, left panel) and with the sparker off (12/17/02, right panel). The top and bottom curves reflect advancing and retracting measurements, respectively.

The DAF rejects were screened and collected on a sheet. The sheet was compressed between two blotters and sent to IPST. When the blotters were separated, some of the stickies transferred from the sheet to the blotter. The number of stickies transferred decreased when the sparker was on (Table 1), which confirms that the stickies are detackified. Hence, sparking reduces the number of stickies by increasing DAF efficiency and is also able to detackify them.

4.2 Installation at the cleaners

The sparker was then moved to the light cleaner feed chest from which the stock flows to the fine screens. Microstickie levels of related process streams were run with our recently described microstickie sensor (*Tappi J.*, April 2003). The results are presented in Table 2 and show that sparking decreases the microstickie counts from 495 to 409 ppm, indicating (tentatively) that sparking improves cleaning efficiency. We have previously seen this behavior at Appleton Paper. Microstickies at fine screens are unaffected at 452 ppm (sparker on) and 469 ppm (sparker off).

Table 1: Stickies transferred from sheet to blotter.

	stickies count			
sparker:	**off**		**on**	
	sheet	**blotter**	**sheet**	**blotter**
12/22/02	3	0		
1/6/03	11	3		
1/8/03	12	2		
1/27/03	12	3		
1/22/03			7	2
1/28/03			5	1
1/31/03			7	1
2/4/03			8	1
2/5/03			16	0
2/7/03			15	1
2/9/03			17	0

Table 2: Microstickies analysis of various samples.

		TOC (ppm)		
	collection date	**fil-tered**	**ultra-filtered**	**ΔTOC (microstickies)**
sparker on				
#2 prim. fine screen accepts	3/1/03	715	597	118[1]
#2 light cleaner accepts	3/5/02	1177	729	448
#2 prim. fine screen accepts	3/5/03	1189	857	332
#2 light cleaner accepts	3/6/03	744	620	124[1]
#2 fine screen ACC MPR	3/7/03	525	415	110[1]
#2 light cleaner accepts, MPR	3/7/03	548	434	114[1]
#2 fine screen accepts	3/9/03	957	501	456
#2 light cleaner accepts, HQ	3/9/03	925	524	401
#2 prim. fine screen accepts	3/10/03	844	470	374
#2 light cleaner accepts	3/10/03	922	533	389
light cleaner accepts	3/10/03, 10am	957	561	396
#2 prim. fine screen accepts	3/11/03, 10am	971	517	454
#2 prim. fine screen accepts	3/20/03	1090	580	513
#2 prim. fine screen accepts, HQ	3/21/03, 10am	1370	789	581
sparker off				
#2 prim. fine screen accepts	3/14/03, 10am	792	378	414
#2 light cleaner accepts	3/14/03, 10am	1080	564	514
#2 light cleaner accepts	3/14/03, 10am	836	404	432
#2 prim. fine screen accepts	3/14/03, 10pm	1010	564	443
#2 prim. fine screen accepts	3/15/03, 10am	1150	631	517
#2 light cleaner accepts	3/15/03, 10am	1220	744	477
#2 light cleaner accepts	3/16/03, 1am	1080	521	555
#2 prim. fine screen accepts	3/16/03, 1am	1020	519	501

[1]these samples represent furnish that should have fewer microstickies; they are not included in the averages.

A longer-term study was then run at this location. Accepts were analyzed for both micro- and macrostickies (Pulmac). Sparking had no significant effect on the Pulmac data, probably because of high measurement uncertainty. The microstickies results are shown in Figure 3. The "microstickies (ppm)" represents only the organic carbon in the microstickie; the total microstickie weight is twice as much. Sparking reduces the microstickies in the accepts from 640 to 550 ppm. However, because of the variability of the data, the F-test shows the difference data plotted as a ratio of the organic carbon present in the microstickies fraction to that of the total dissolved and colloidal carbon present in the system. This ratio tends to reduce variability by normalizing the stickies load. The difference is now significant at the 95% confidence level.

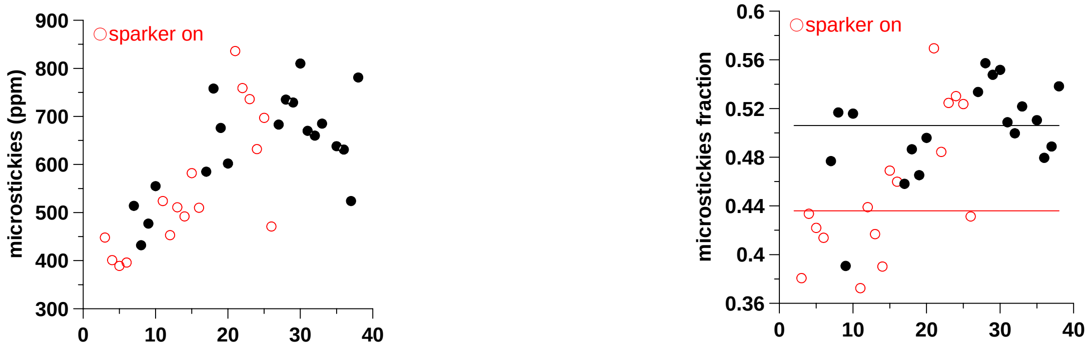

Figure 3: Effect of sparking on cleaner efficiency. Microstickies are shown on the left panel. The microstickies fraction is displayed on the right.

The removal of stickies in cleaners was clearly seen at a previous trial at Appleton Paper and the reduction here is fully consistent with the Appleton results. Figure 3 demonstrates that sparking reduces the microstickies load by 10%. If a baseline stickies value of 1,200 ppm (2 x 600 ppm organic carbon) be assumed, then the sparker removes 450 kg per million gallons of water. The stickies are probably removed through spark-induced aggregation where the larger particles are now more amenable to cleaning. In the absence of sparking these same particles would be more likely to aggregate and deposit out than the others, so sparking removes the subset of stickies that would be most problematic.

The cleaner accepts flow into the screens and the microstickie content of the screen accepts were also determined. No significant differences were observed. In conclusion, sparking improves the efficiency of the DAF and indirectly reduces the stickies in the accepts. It removes a considerable amount of microstickies from the cleaners, and has no effect on screening efficiency.

4.3 Installation at the float cell

The sparker was placed in the flotation feed tank (illustrated in Figure 4) and run at about 0.3 sparks/second. The furnish processed was exclusively MOW. Samples taken at the primary flotation feed and at the secondary flotation rejects were analyzed for consistency and ash. The results are listed in Table 1. The results are present as consistencies of fiber and ash in water, which were calculated from the solids consistency and the ash content data provided by the mill.

Sparking does not change the ash distribution between the feed and reject streams, but it has an effect on the non-ash solids, which should be mainly fiber and ink. The rejects/feed ratio for these organics is 1.04 (σ: 0.19) with sparking and 0.94 (σ: 0.22) for the control. The difference is significant at the 94% level using a one-tailed t-test. If the outliers flagged in Table 3 are dropped, then the sparked and unsparked rejects/feed ratio for the organics change to 1.06 (σ: 0.16) and 0.91 (σ: 0.17), respectively. The difference is now significant at the 99% level as indicated by the above t-test. This indicates that sparking increases organic material in the rejects

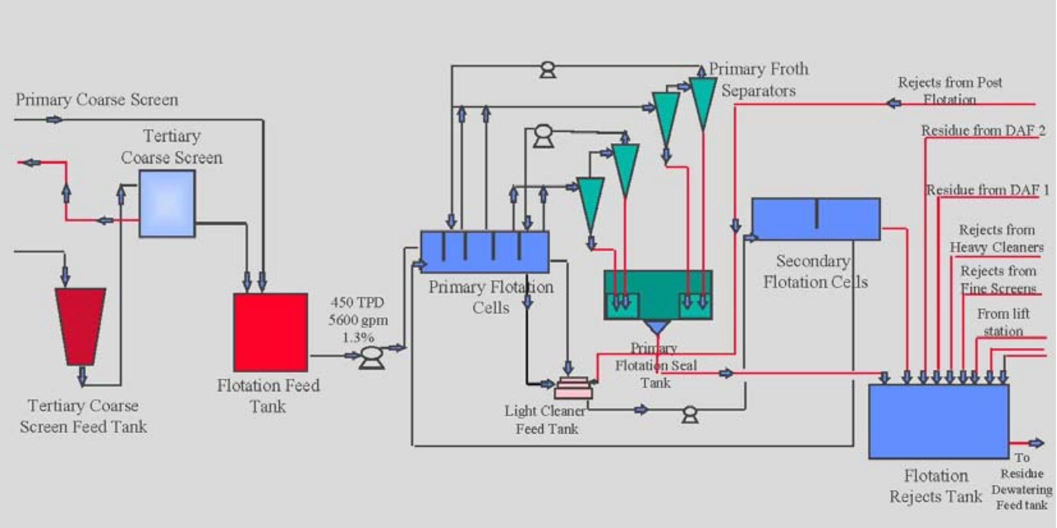

Figure 4: Schematic of the flotation assembly.

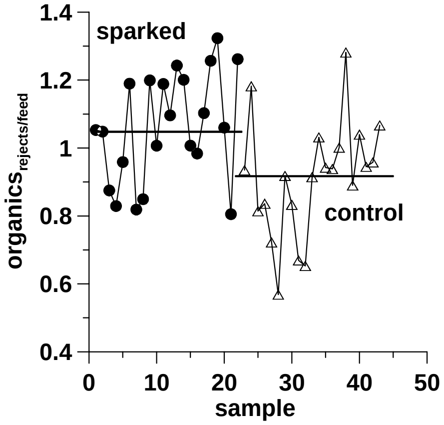

Figure 5: Effect of sparking on the distribution of organics.

stream. A comparison (with the two Table 1 outliers removed) is shown in Figure 5. The "organics" in the ordinate represent the sum of fiber and ink.

In previous work we showed that sparking reduced yield loss and increased brightness, which means that it decreased fiber and increased ink in the rejects. The present experiment suggests an increase in organic solids (ink plus fiber) in the rejects. Since sparking is not known to decrease yield, the most likely cause is that the yield does not change much, but that the ink content in the rejects increase; *i.e.* sparking increases deinking efficiency. This will need to be confirmed by ERIC measurements. Sparking has been shown to increase microstickies removal across the reverse cleaners at Duluth, so this benefit can also be taken.

Table 3: Ash and fiber levels across the float cells.

	primary flotation feed consistency		**secondary flotation rejects consistency**	
	percent ash	percent organics	percent ash	percent organics
sparker on				
3/3/2004	0.148	1.012	1.32	1.07
3/4/2004	0.133	1.017	1.18	1.07
4/28/2004	0.150	1.050	0.99	0.92
4/28/2004	0.177	1.103	1.07	0.91
4/29/2004	0.169	1.111	0.99	1.07
4/29/2004	0.101	1.019	1.09	1.21
4/30/2004	0.169	1.291	1.14	1.06
4/30/2004	0.180	1.220	1.07	1.04
8/2/2004	0.125	1.225	1.50	1.47
8/2/2004	0.120	1.260	1.13	1.27
8/3/2004	0.129	1.251	1.72	1.49
8/3/2004	0.135	1.225	1.35	1.34
8/4/2004	0.132	1.158	1.56	1.44
8/4/2004	0.135	1.205	1.49	1.45
8/5/2004	0.123	1.037	0.96	1.04
8/5/2004	0.173	1.177	1.18	1.16
8/62004	0.149	1.141	1.24	1.26
8/6/2004	0.180	1.360	1.80	1.71
8/7/2004	0.124	1.026	1.36	1.36
8/8/2004	0.135	1.085	1.24	1.15
8/9/2004	0.154	1.206	0.58	0.64[1]
8/9/2004	0.166	1.214	1.07	0.98
8/12/2004	0.126	1.244	0.53	1.57
sparker off				
3/8/2004	0.146	1.214	1.31	1.13
3/8/2004	0.138	1.062	1.46	1.26
5/1/2004	0.114	1.206	0.88	0.98
5/1/2004	0.140	1.210	0.92	1.01
5/2/2004	0.159	1.341	0.97	0.97
5/2/2004	0.227	1.873	0.98	1.06
5/3/2004	0.135	1.185	1.02	1.09
5/3/2004	0.144	1.176	0.97	0.98
5/4/2004	0.087	1.053	0.70	0.70
5/4/2004	0.109	1.191	0.79	0.78
5/5/2004	0.071	1.179	1.13	1.08
5/6/2004	0.187	0.953	1.54	0.98
5/6/2004	0.208	1.022	1.47	0.96
7/27/2004	0.078	0.992	0.86	0.93
7/28/2004	0.126	1.034	0.96	1.04
7/28/2004	0.127	1.093	1.48	1.40
7/29/2004	0.154	1.156	0.95	1.03
7/29/2004	0.141	1.109	1.90	1.73[1]
7/31/2004	0.119	1.241	1.04	1.29
7/31/2004	0.131	1.329	0.96	1.26
8/1/2004	0.129	1.251	1.24	1.20
8/1/2004	0.144	1.236	1.35	1.32

[1] outlier

5. Trial at the Stora Enso Wisconsin Rapids mill

Sparking consolidates small particles, which is useful in various recycle operations such as centrifugal cleaning and dissolved air flotation. We were running a chemical trial at the Stora Enso Wisconsin Rapids mill, and we took advantage of this opportunity to determine if the sparker would consolidate biological sludge particles in a full-scale system. This is useful in and of itself, but is also valuable in generalizing the effect of sparking in particle agglomeration.

Lab work was conducted prior to the trial. Secondary sludge and flocculating chemicals were obtained from the Stora Enso Water Quality Center in Wisconsin Rapids, WI. The chemicals used were ferric chloride, a coagulating and anti-odor agent, Praestol 186KH, a coagulating agent, and Praestol K133L, a flocculating agent. The sludge had a solids content of roughly 1.3%. Sparking was performed before adding the chemicals. Then the ferric chloride was added, at a dosage of 0.632 ml/gal. Subsequently, the Praestol 186KH (0.89 ml/gal) and the Praestol K133L (147 ml/gal) were added. Samples (150 ml) of treated sludge were allowed to drain freely for 2 minutes, and then the solids were put into a benchtop Crown press. Final solids were determined by drying the resulting cakes overnight in an oven. The results, listed in Table 1, showed 50 sparks gave the best results. Hence, more data were collected in the 0-60 spark region. These results (Table 2) confirm that sparking provides a 0.6% increase in cake solids.

A t-test was run for all the unsparked samples in Table 2 gathered into one group, and all the sparked samples (60 sparks and less) collected into another. The result was a 96% probability of higher final solids attributed to sparking.

Next, the effects of sparking on sludge drainage were investigated. The chemicals were added after sparking again, at the same dosage as before. A specific resistance test was performed, where 40 ml samples of treated sludge were filtered through a Whatman 4 filter under a vacuum pressure. The specific resistance to drainage was found to vary with the number of sparks as shown in Table 3. Sparked and unsparked secondary sludge samples were then examined under a light microscope at 40X magnification. It appears that sparking enhances the agglomeration of sludge solids. Representative images are illustrated in Figure 1.

Table 1: Effect of sparking on cake solids.

sparks	percent cake solids (avg.)
0	16.0, 15.5, 14.6 (**15.4**)
50	15.7, 16.1, 16.2 (**16.0**)
100	15.9, 15.1, 16.0 (**15.7**)
150	16.4, 15.3, 15.4 (**15.7**)

Table 2: Effect of sparking on cake solids.

sparks	percent cake solids (avg.)
0	16.4, 15.7 15.3 (**15.8**)
20	17.0, 16.0, 16.1 (**16.4**)
40	17.2, 16.1, 16.0 (**16.4**)
60	16.5, 16.1, 15.3 (**16.0**)

Table 3: Specific resistance to filtration of sludge

sparks	specific resistance (m/kg / 10^12)
0	87.3, 157.8 (**123**)
25	6.0, 15.1 (**11**)
50	42.5, 45.1 (**44**)
75	8.9, 57.3 (**33**)

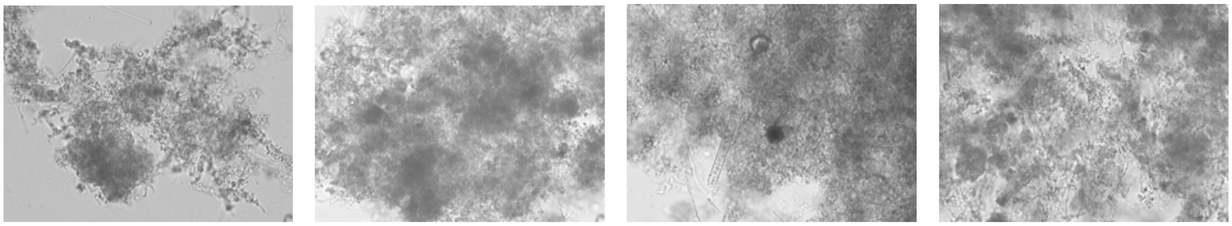

Figure 1: Images of biological sludge after 0, 25, 50 and 100 sparks.

The Stora wastewater center collects effluent from three facilities. The effluent is routed through a primary clarifier and the overflow treated in an AST. The primary and secondary sludge is mixed in an 18,000 gallon blend tank from which 800 gpm is pumped to four belt presses. Flow from the primary and secondary thickeners is 280 and 500 gpm, respectively. Ferric chloride (38% active) was added to the blend tank at 600 ml/min. Polymers, (Stockhausen 187 KH) at 15 lbs/ton) and flocculant (Stockhausen K133L) at 7.5 lbs/ton were added to each individual press. Press #1 is an Andritz machine equipped with a gravity belt, press # 2 is from Ashbrook and has an extended gravity table. Press #3 is an old Andritz press, and press #4 is a very old machine that was not considered in our work. The sparker was positioned at the bottom of the secondary thickener. This tank was estimated to contain 80,000 gallons at the time. The unit was placed just above the outflow pipe, so that the sludge pumped to the blend tank would be sparked. The sparker was run at 4-5 kV, with a spark generated every 2.5 seconds.

The sparker only works with secondary sludge and the mill was able to accommodate us by running pure secondary sludge for a few hours. However, only a single point could be taken because the sparker stopped working after a short while. Sparking increased pressed solids from 18.2 to 19.1%. The solids returned to 18.2% when the sparker was shut off. Importantly, the pressed sludge felt different when the sparker was on. It was much more difficult to manually squeeze water out of it, which indicates a drier cake.

6. Trial at the Jackson Paper, NC mill

The objective of the four-week sparker trial at Jackson Paper was to increase the removal of microstickies from the water system. The ultimate goal was to improve machine runnability by purging the system of microstickies. The mill indicated that a 10-point gain in hydrocal (clarifier) efficiency would indicate that the sparker had a very significant effect on water clarification. Definitions of improved paper machine runnability included reducing deposition of stickies and fiber in the press section and reducing the number of breaks per day. Currently, enough stickie/fiber deposits are doctored from the press section to fill about one-half of a 55-gallon barrel each shift. Jackson experiences about 3 breaks per day when producing their 23# grade. The mill indicated that reducing the number of breaks per day from three to two would be highly desirable.

Key results included an increase in hydrocal efficiency of 8+ points, a 20% reduction in sludge press filtrate microstickies, a reduction in 1st press section deposits, and an initial indication of reduced breaks during lightweight grade runs.

Our previous work indicates that the sparker can remove stickies from flotation units and reverse cleaners under certain conditions. Specifically, the application point should be of low consistency and have high enough residence time so that the volume is exposed to at least 20 sparks. Three potential sparker application points were analyzed: hydrocal dispersed air clarifier; the cloudy water chest; and the primary screen rejects chest. Table 1 summarizes the operating parameters for the three application points.

The hydrocal was the best-suited application point based on unit operational stability and low solids consistency. Also, microstickies change across the hydrocal, accessibility to service the unit, and access to historic and microstickies baseline data. The point of application was agreed upon to be just after the stock introduction to the unit and centered, roughly 3.5 feet from the head wall. This was in the area of highest mixing and should improve the spark exposure rate and uniformity of the treatment.

The major expected trial outcome was the demonstration of a statistically quantifiable improvement in operating efficiency and microstickies reduction across the hydrocal. IPST performed microstickies analysis on the inlet and outlet of the hydrocal for the duration of the trial. Aside from deposits and stickies in the final product, the single purge point for microstickies was with the sludge sent to an incinerator. Therefore, microstickies analyses were also performed on the sludge belt feed and filtrate.

The chemistry and dosage to the hydrocal was kept constant during the trial. However, it should be noted that a felt-life optimization trial evaluating vacuum, shower temperature and water, was running concurrently with the sparker trial. The trial began on February 18, 2004 at 7:30 a.m. and concluded March 19 at 1:45 p.m. The sparker was set to discharge at 4.5 kv. The mill tracked the discharge range between three and five times per day, beginning one week into the trial. Voltage variation was on the order of ± 10%.

Table 1: Potential application points for the sparker.

	Hydrocal	**cloudy water chest**	primary screen rejects
volume, ft^3	800	4,500 (run volume)	**2,500 (run volume)**
volume, gallons	6,240	35,000 (run volume)	**20,000 (run volume)**
flow, gpm	280	1,500	**725**
residence time, min	22.3	23.3	**27.6**
spark rate, #/min	15	15	**15**
sparks/turn	334	350	**414**
sparks/ft^3	0.42	0.003	**0.006**
solids in, ppm	920	350	**4,200**
solids out, ppm	**260**	--	**--**

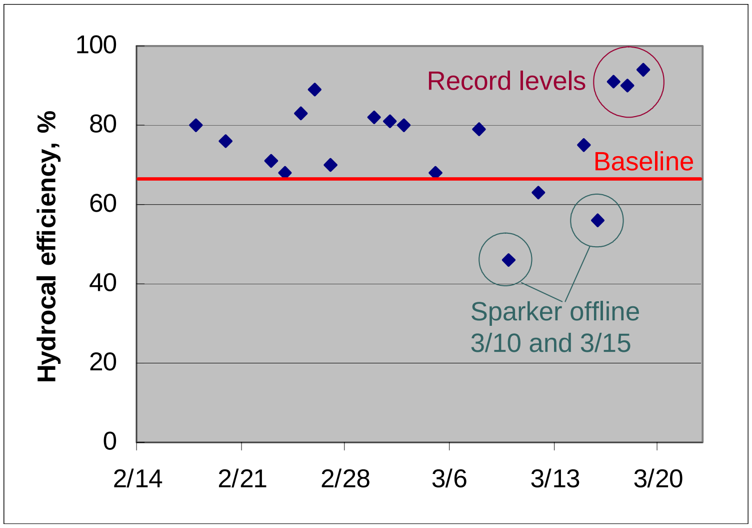

Figure 1. Hydrocal clarifier efficiency during sparker trial.

The hydrocal removal efficiency demonstrated an increase of at least eight points over the course of the trial. Measurements below the historical baseline of 66% only occurred on days of or following sparker shutdowns. Record efficiencies (greater than 92%) were consistently observed during final week of trial. Figure 1 illustrates the effect of sparking on clarifier efficiency. The sparker demonstrated a statistical improvement in clarifier efficiency (raw data presented in Appendix 1). Prior research at IPST has shown that increased solids removal correlates with stickies removal from water loop. Less stickies in water loop leads to fewer deposits and ultimately fewer machine breaks.

In contrast to the improved hydrocal efficiency, microstickies were observed to *increase* during the course of the trial, as shown in Table 2. This is an artifact and has been observed in other studies, usually reflecting the polymer load being added to the clarifier. It should be noted

Table 2: Microstickies levels across the Hydrocal.

date	time	Hydrocal in	Hydrocal out	% change
2/19	8:30 AM	680	835	+23%
2/20	3:00 PM	675	880	+30%
2/23	7:30 AM	720	775	+8%
2/23	4:00 PM	720	660	-8%
2/24	10:40 AM	720	920	+28%
2/25	7:30 AM	750	860	+15%
2/25	10:00AM	475	430	-9%
2/26	10:00AM	630	880	+40%
3/3	6:10AM	660	860	+30%
3/5	7:00AM	625	850	+36%

Table 3: Microstickies levels across the belt press.

date	time	sludge feed	belt press filtrate	% change
2/19	8:30 AM	530	405	-24%
2/20	3:00 PM	515	470	-9%
2/23	7:30 AM	500	405	-19%
2/23	4:00 PM	525	470	-10%
2/24	10:40 AM	580	385	-34%
2/25	7:30 AM	530	385	-27%

that the microstickies measure is based on molecular weight. Therefore, high molecular weight polymers, such as agglomeration aids, will be measured as microstickies. Microstickies at the sludge press were reduced by roughly 20%, as shown in Table 3. This represents the largest process water purge point for microstickies in the system. Post-trial baseline data is being collected to determine whether the sparker improved microstickies removal from the sludge filtrate.

It should be noted that no removal is observed during operations before 7:30 a.m. This is due to the transience associated with the sludge press process. Sludge is dewatered only during the first shift. The sludge accumulated overnight in the feed tank separates, with solids rising to the top. As sludge feeds from the bottom of the tank, poor dewatering performance is observed during initial operations in the morning. This may cause the noted poor microstickies removal prior to 7:30 a.m.

The mill was also concerned about deposits in the first press section. This is a key runnability parameter, as increased sticky deposits generally lead to increased sheet breaks. Jackson has a qualitative metric to assess press section deposits, which we made more quantitative. Deposits are doctored off the press roll and accumulate in a 55-gallon garbage can. Though previously unmeasured, the mill felt that about 12 inches accumulated each shift in the bucket. The bucket is emptied once each shift. We asked the mill to measure the depth of the stickies in the bucket with a yard stick once per shift. The results are summarized in Figure 2. It is clear that the

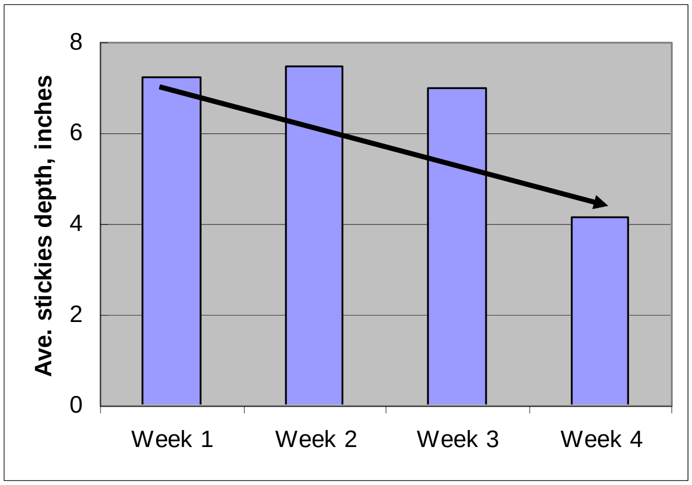

Figure 2: Stickies deposits on first press section during trial.

Table 4: Effect of sparking on sheet breaks.		
	Baseline	**Sparker Trial**
Breaks per 100 tons production	2.7	1.5
Production tons with zero breaks*	4	189
* Based on 6,400 baseline tons and 4,800 sparker tons for 23# basis weight		

weekly average for stickies was well below 12 inches. In fact, if the mill estimate for their baseline is accurate, then by the end of the trial Jackson was realizing a 75% reduction in press section deposits.

The data for paper machine breaks are more difficult to analyze. The mill switches grades on the machine normally once a day on average. During this trial, however, grade changes were made much more frequently, averaging more than three per day. Due to their transient nature, increasing grade changes typically leads to increasing breaks. The mill was also shifting their product mix to more lighter-weight grades. These grades are more challenging to run and are associated with higher breaks. For example, a typical day running 34-pound encounters two breaks, while a day on 23-pound experiences three breaks.

During the month preceding the trial, 23# represented 47% of production. This increased to 61% during the sparker trial. The result was that overall differences in sheet breaks between the trial and preceding month were not statistically different. However, there were some observations that should be followed-up during any upcoming trials.

The following considers only 23# production, which is the mill's most important and difficult to produce grade. The raw data can be found in Appendix 2. This product is expected to represent more and more of the mill's production as demand for lightweight medium increases. One metric that exhibit a quantitative improvement was breaks per 100 tons of production, as shown in the following table. This was computed by dividing the total number of breaks during 23# runs by the total tons of 23# produced. The other metric was total tons of 23# without a break. This indicates the total tons made during runs without a break between grade changes. Both metrics were markedly improved during the sparker trial. These results potentially indicate that machine runnability improved during the sparker trial.

The mill experienced two instances of equipment breakdown. One was during the trial and one occurrence was during operation following the trial. The first breakdown was due to some connections becoming loose during operation. The unit was sparking poorly and was pulled out to examine the submersible components. There was noticeable coning on the electrodes and “erosion” on the insulator blocks protecting the high voltage wires located in the vicinity of the electrode gap. There was also evidence of arcing about 1/3 of the way from bottom of the submersible on the middle support where electrodes go through the frame. Photos taken by the mill may be found in Appendix 3. IPST had supplied a second submersible, which the mill installed and continued the trial. The mill was also able to rebuild the original submersible completely with a few basic and readily available parts. The mill turned the sparker back on after the initial trial. However, one of the electrical connections had come loose and the wire was pulsating in the hydrocal. The voltage level rose to 9 kV before the system was shutoff.

In summary, the results from the month-long, full-scale sparker trial at Jackson Paper are extremely promising. The mill realized a significant, 8-point improvement in clarifier efficiency. This has previously been observed at Stora Enso’s Duluth Recycle Pulp Mill in Duluth, Minnesota. The sparker clearly produced superior results and provided much cleaner process water. The mill is currently considering the economic impact of cleaner process water. Initial findings also indicate the sparker may increase microstickies removal by 20% from the sludge press filtrate. Additional data is required to confirm these results. Paper machine runnability improved, as measured by a reduction in 1st press section deposits, and an initial indication of reduced breaks during lightweight grade runs.

The mill appears to be convinced that sparking improves the efficiency of the hydrocal. However, the mill has concerns about the reliability of the sparker unit, and has an interest in moving forward once this is improved.

Appendix 1. Hydrocal clarifier daily influent and effluent solids concentration and removal efficiency. The trial data were collected during Feb 18 and Mar 19.

Date	Hydrocal In	Hydrocal Out	Efficiency
2-Jan	1507	580	**62%**
5-Jan	1393	327	**77%**
6-Jan	1407	433	**69%**
7-Jan	850	290	**66%**
8-Jan	860	347	**60%**
9-Jan	927	327	**65%**
12-Jan	1167	360	**69%**
13-Jan	1300	367	**72%**
14-Jan	1000	333	**67%**
15-Jan	1420	340	**76%**
16-Jan	1190	493	**59%**
19-Jan	900	340	**62%**
20-Jan	660	510	**23%**
21-Jan	710	270	**62%**
22-Jan	680	400	**41%**
23-Jan	720	460	**36%**
26-Jan	830	260	**69%**
27-Jan	1210	270	**78%**
28-Jan	920	140	**85%**
29-Jan	1020	180	**82%**
30-Jan	1000	340	**66%**
1-Feb	950	270	**72%**
3-Feb	1120	330	**71%**
5-Feb	950	230	**76%**
9-Feb	1460	320	**78%**
10-Feb	1180	340	**71%**
11-Feb	670	230	**66%**
12-Feb	880	280	**68%**
13-Feb	1260	300	**76%**
16-Feb	930	290	**69%**
17-Feb	920	260	**72%**
18-Feb	1160	230	**80%**
19-Feb	850	320	**62%**
20-Feb	620	150	**76%**
23-Feb	1073	307	**71%**
24-Feb	653	207	**68%**
25-Feb	927	307	**67%**
26-Feb	1280	140	**89%**
27-Feb	1340	400	**70%**
1-Mar	980	180	**82%**
2-Mar	1120	210	**81%**
3-Mar	1046	213	**80%**
4-Mar	730	210	**71%**
5-Mar	1020	330	**68%**
8-Mar	1250	260	**79%**
10-Mar	540	290	**46%**
12-Mar	1030	380	**63%**
15-Mar	790	200	**75%**
16-Mar	970	430	**56%**
17-Mar	790	70	**91%**
18-Mar	1020	100	**90%**
19-Mar			**94%**

Appendix 2. Number of breaks during production runs for 23# grade before and during the sparker trial.

Baseline – Month prior to trial				30-day sparker trial			
Basis Wt	**Breaks**	**Tons**	**Breaks/100 tons**	**Basis Wt**	**Breaks**	**Tons**	**Breaks/100 tons**
23.63	7	263.16	2.7	23.45	9	199.55	4.5
23.68	6	272.4	2.2	23.54	3	271.62	1.1
23.82	4	276.01	1.4	23.54	4	278.84	1.4
23.89	3	7.58	39.6	23.58	8	262.65	3.0
23.91	2	233.55	0.9	23.59	2	270.83	0.7
23.94	5	264.13	1.9	23.61	2	127.22	1.6
23.95	2	209.89	1.0	23.61	3	268.39	1.1
23.98	3	269.77	1.1	23.62	3	264.22	1.1
23.99	1	259.97	0.4	23.62	2	282.43	0.7
23.99	4	278.1	1.4	23.63	5	261.67	1.9
23.99	7	264.01	2.7	23.64	2	274.19	0.7
24	1	160.28	0.6	23.64	1	275.14	0.4
24	3	284.05	1.1	23.64	2	276.79	0.7
24.01	3	262	1.1	23.64	2	277.26	0.7
24.03	4	287.66	1.4	23.66	5	262.24	1.9
24.03	0	3.9	0.0	23.72	1	146.89	0.7
24.05	3	286.41	1.0	23.72	3	281.45	1.1
24.05	4	279.66	1.4	23.72	5	271.22	1.8
24.07	10	221.82	4.5	23.73	0	7.97	0.0
24.07	4	231.89	1.7	23.73	0	55.46	0.0
24.07	2	282.73	0.7	23.77	2	35.02	5.7
24.08	2	97.34	2.1	23.81	0	12.02	0.0
24.09	1	237.49	0.4	23.82	0	105.9	0.0
24.09	6	269.73	2.2	23.9	0	7.43	0.0
24.1	1	164.95	0.6	23.96	1	15.45	6.5
24.12	3	212.78	1.4				
24.13	4	230.67	1.7				
24.15	2	169.4	1.2				
24.28	1	105.92	0.9				
Total	**98**	**6387.25**	**Ave = 2.74**	**Total**	**65**	**4791.85**	**Ave = 1.50**

Appendix 3. Photos of the damage to the submersible encountered during the sparker trial.

Pitting wear around the black insulators protecting the high voltage wire from the discharge

Electrode coning

Appendix 4. Raw data taken during the trial.

Date	Day	Basis wt.	Breaks	Tons	Stickies bucket
2/19/2004	1	23.66	5	262.24	4
2/20/2004	2	23.62	3	264.22	17
2/21/2004	3	23.73	0	7.97	
2/21/2004		26	3	281.68	
2/22/2004	4	26.08	2	295.47	
2/23/2004	5	26.2	2	68.16	4
2/23/2004		32.7	1	232.36	
2/24/2004	6	32.6	5	300.23	4
2/25/2004	7	32.46	1	97.59	
2/25/2004		26.33	0	43	
2/25/2004		23.72	1	146.89	
2/26/2004	8	23.64	2	274.19	
2/27/2004	9	23.59	2	270.83	7
2/28/2004	10	23.64	1	275.14	
2/29/2004	11	23.64	2	276.79	
3/1/2004	12	23.54	3	271.62	8
3/2/2004	13	23.61	2	127.22	
3/2/2004		25.94	2	132.73	
3/3/2004	14	23.77	2	35.02	
3/3/2004		25.93	1	253.84	
3/4/2004	15	32.57	3	164.14	12
3/4/2004		37.87	0	4.73	
3/4/2004		26.36	1	11.65	
3/4/2004		23.82	0	105.9	
3/5/2004	16	23.64	2	277.26	
3/6/2004	17	23.61	3	268.39	
3/7/2004	18	23.63	5	261.67	
3/8/2004	19	23.96	1	15.45	
3/8/2004	20	25.86	2	273.81	
3/9/2004		23.73	0	55.46	
3/9/2004		25.94	0	95.63	
3/9/2004		26.99	0	4.27	
3/9/2004		32.58	0	148.87	
3/10/2004	21	33.07	0	66.88	
3/11/2004	22	32.67	0	208.81	2
3/11/2004		35.96	0	41.53	
3/11/2004		26.17	0	35.19	
3/11/2004		23.81	0	12.02	
3/12/2004	23	23.72	3	281.45	
3/13/2004		23.72	5	271.22	
3/14/2004		23.62	2	282.43	
3/15/2004	26	23.58	8	262.65	4
3/16/2004	27	23.54	4	278.84	
3/17/2004	28	23.45	9	199.55	
3/18/2004	29	23.9	0	7.43	8
3/18/2004		26.01	5	267.57	
3/19/2004					
3/19/2004					0.5
3/19/2004					

Samples from Jackson paper were filtered through with Whatman 4 and then ultrafiltered through a YM3 membrane. The TOC of both samples was measured; the results are as follows.

Day	**time**	**Sample**	**Filtered**			**Ultra-filtered**			**Stickies**
			TC	**IC**	**OC**	**TC**	**IC**	**OC**	**OC-OC**
3/23/2004	12:00pm	Belt press filter	2030	250	1780	1630	230	1400	380
3/23/2004	12:00pm	Hydrocal In	2450	200	2250	1690	180	1510	740
3/23/2004	12:00pm	Hydrocal out	2430	210	2220	1680	170	1510	710
3/23/2004	12:00pm	Sludge Feed	2720	200	2520	2280	170	2110	410

Day	**time**	**Sample**	**Filtered**			**Ultra-filtered**			**Stickies**
			TC	**IC**	**OC**	**TC**	**IC**	**OC**	**OC-OC**
3/26/2004	7:30am	Belt press filter	2140	260	1880	1635	230	1405	475
3/26/2004	7:30am	Hydrocal In	2590	190	2400	1725	170	1555	845
3/26/2004	7:30am	Hydrocal out	2610	190	2420	1680	170	1510	910
3/26/2004	7:30am	Sludge Feed	2840	200	2640	2280	180	2100	540

Day	**time**	**Sample**		**Filtered**		**Ultra-filtered**			**Stickies**
			TC	**IC**	**OC**	**TC**	**IC**	**OC**	**OC-OC**
4/26/2004	12:00	Belt press filter	1750	310	1440	1200	280	920	520
4/26/2004	12:00	Hydrocal In	1980	280	1700	1255	250	1005	695
4/26/2004	12:00	Hydrocal out	1950	280	1670	1260	260	1000	670
4/26/2004	12:00	Sludge Feed	2330	380	1950	1665	310	1355	595

Day	**time**	**Sample**	**Filtered**			**Ultra-filtered**			**Stickies**
			TC	**IC**	**OC**	**TC**	**IC**	**OC**	**OC-OC**
4/27/2004	9:00	Belt press filter	1750	400	1350	1240	320	920	430
4/27/2004	9:00	Hydrocal In	1900	270	1630	1240	240	1000	630
4/27/2004	9:00	Hydrocal out	1870	280	1590	1225	250	975	615
4/27/2004	9:00	Sludge Feed	1910	440	1470	1460	350	1110	360

Day	**time**	**Sample**	**Filtered**			**Ultra-filtered**			**Stickies**
			TC	**IC**	**OC**	**TC**	**IC**	**OC**	**OC-OC**
4/28/2004	3:30am	Belt press filter	1580	400	1180	1120	350	770	410
4/28/2004	3:30am	Hydrocal In	1810	270	1540	1270	250	1020	520
4/28/2004	3:30am	Hydrocal out	1880	280	1600	1195	260	935	665
4/28/2004	3:30am	Sludge Feed	2300	340	1960	1770	320	1450	510

7. Effect of Electrohydraulic Discharge on Flotation Deinking Efficiency

This section is excerpted from Effect of electrohydraulic discharge on flotation deinking efficiency, *Ind. Eng. Chem. Res.*, 43, 7552 (2004).

Abstract

Discharging a high-energy spark underwater creates a shock wave which 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 zeta potential. This decrease inhibits the tendency of the particles to reattach 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 sparked *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 (1-4). 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 (5), 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 (6). The surfaces of acrylate particles suspended in water are mildly oxidized upon exposure, and their zeta potential and tack drops. These contaminants are commonly found in recycle paper process streams, and a reduction in tack minimizes deposits and other operational problems (7, 8). In this paper we demonstrate that the zeta 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

The sparking unit used was obtained from Pulse Power Inc., Stoney 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 msec 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% H_2SO_4, 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 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.

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.

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 float 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 airflow rate of 57 liters per minute 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 pulp pads were made for each of the treated and control samples for a total of nine pads. Filler content was measured by igniting the filtered solids at 525 °C. Brightness and ERIC testing (9) was 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 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 3 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 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 zeta potentials. In all cases, sparking decreases pH and zeta potential, suggesting that the particles are oxidized. Very similar behavior was reported in our earlier 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.

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. In a mill application, the sparker would be placed in a feed chest and not in the float cell itself. Brightness and ERIC measurements are presented in Figure 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 correlate quite well (r^2=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. Flotation efficiency is optimal when the bubble size and particle size distributions overlap (10). 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 shockwave. 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 shockwave on each individual bubble depends largely on the size of the bubble, but also on factors as the bubble's proximity to other bubbles.

Figure 5 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 videos. 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 (11) 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 (12). This also appears to be true in our case where we have short acoustic pulses. The peak frequency of the sound wave emitted by the sparker has been estimated at about 5 kHz (12), which is the resonance frequency of a bubble with a radius of about 0.6 mm. Figure 5 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 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 shockwave. This is, perhaps, 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. 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 would appear that the changes in bubble distribution adversely affect the overlap between 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 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 the 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.

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 t-test showed that the probability that the means between the control and the sparked values were different at a confidence level of over 99.9%. The one-percentage point 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 improve increase both 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 reagglomeration, 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 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, 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 zeta potential. Others (13-15) have studied the effect of ultrasound on toner particles and have found that large particles break up into smaller ones. One study (16) 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 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. 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. There is also a 50% reduction in filler loss across flotation following sparking. These improvements appear to derive from the decrease in zeta potential of the ink and toner particles upon sparking.

Acknowledgment

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Table 1: Target pulping conditions.

consistency, %	1
temperature, °C	40
pH	9
hardness, ppm	150
NaOH, % dry fiber	0.7
H_2O_2, % dry fiber	0.7
sodium silicate, % dry fiber	1.2
surfactant, % dry fiber	0.6
soap, % dry fiber	0.05

Table 2: Average brightness gain (points) with flotation time for sparking during flotation.

time (min)	control average (std dev)[1]	sparker average (std dev)[2]
sparked during flotation		
0-4	5 (1)[1]	5 (2)[2]
0-7	7 (1)	7 (1)
0-10	10.1 (0.4)	10 (2)
avg. initial brightness: [1]47.5% (n=6); [2]46.0% (n=6)		

Table 3: Average fiber and filler loss after flotation.

	control average (std. dev.)	sparker average (std. dev.)
sparked before flotation		
reject (g)	200 (20)	125 (6)
inorganic (g)	100 (10)	50 (3)
fiber loss (g)	101 (5)	75 (4)
percent fiber loss	4.0	3.0
sparked during flotation		
reject (g)	190 (20)	180 (20)
inorganic (g)	87 (5)	80 (10)
fiber loss (g)	100 (10)	96 (6)
percent fiber loss	4.0	3.8

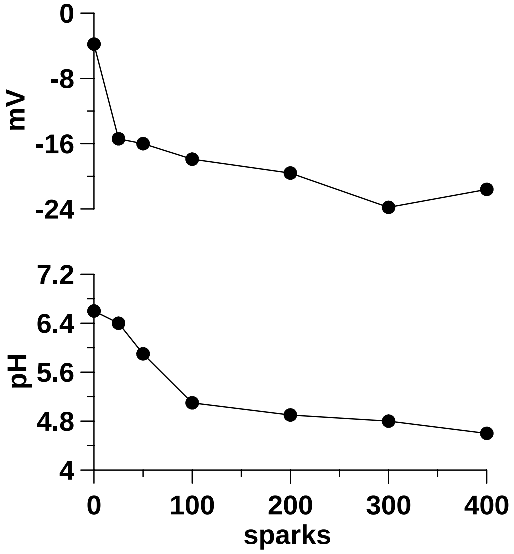

Figure 1: Effect of sparking on pH and zeta potential (top) of toner.

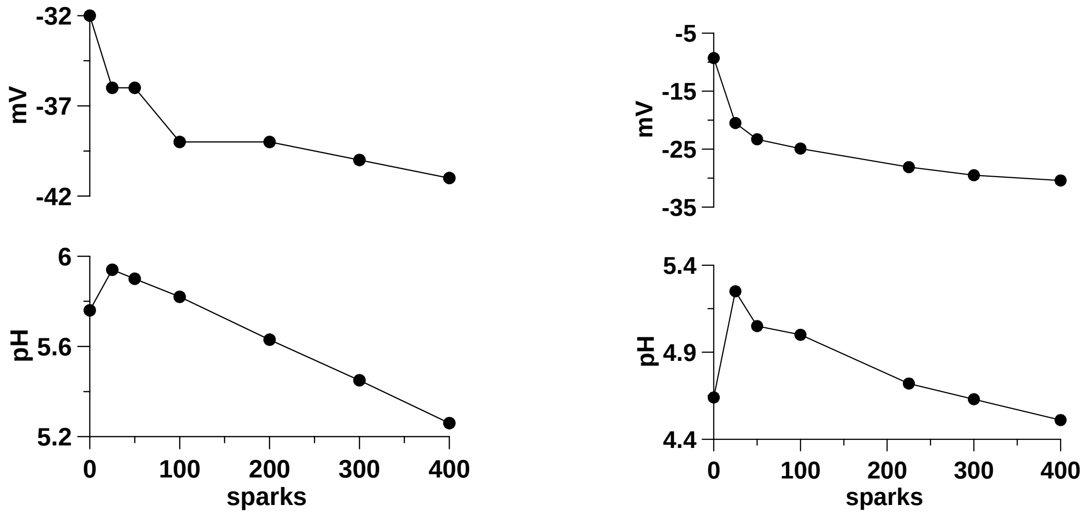

Figure 2: Effect of sparking on pH and zeta potential (top) of flexographic ink. The two plots reflect different starting pH.

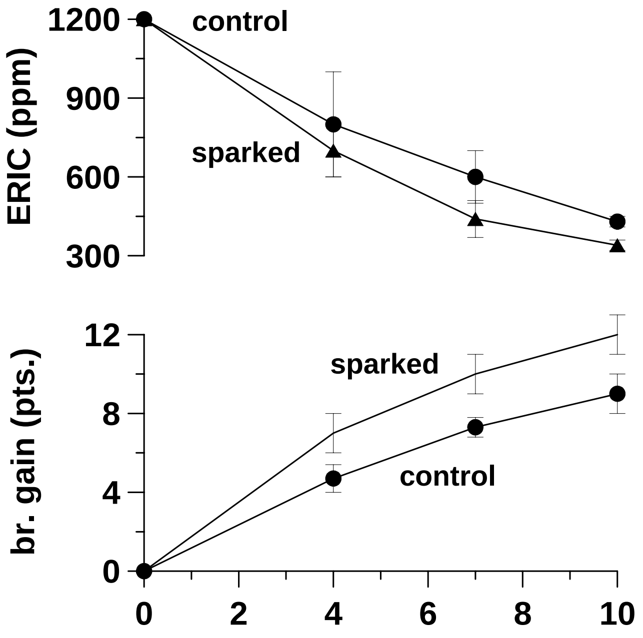

Figure 3: Changes in brightness (points) and average ERIC (ppm) with flotation time in pulp sparked before flotation. The average initial brightness was 48.1% for the control and 46.3% for the sparked sample.

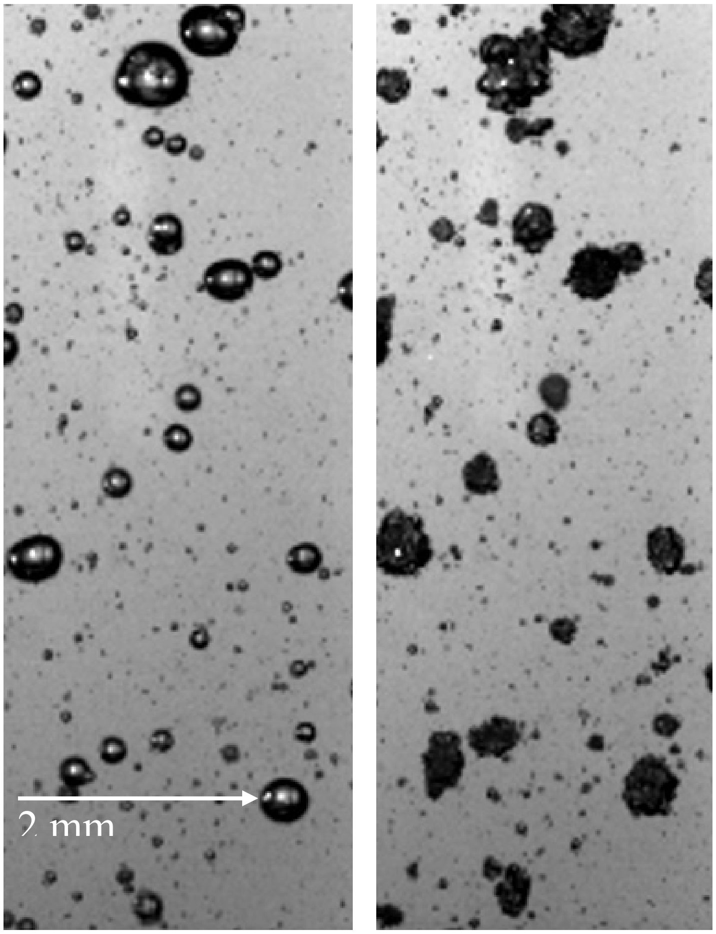

Figure 4**:** Effect of the shock wave on bubbles. The left and right frames are before and after sparking. The bubbles were about 500-cm from the spark source.

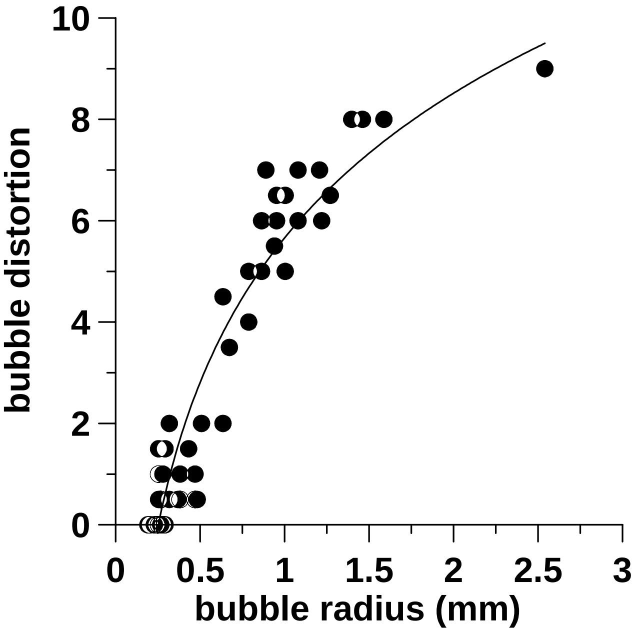

Figure 5: Bubble distortion vs. equilibrium radius.

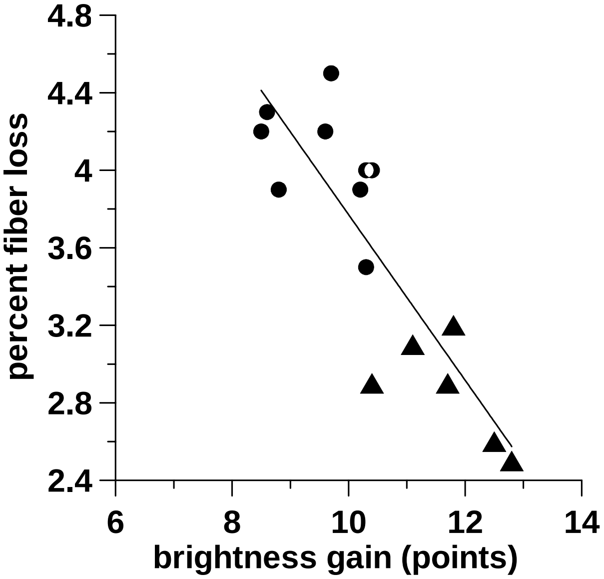

Figure 6: Relationship ($r^2 = 0.74$) between fiber loss and brightness gain with (triangles) and without (circles) sparking.

8. Spark-Induced Agglomeration of Aqueous Polymeric Suspensions

This section is excerpted from S.Banerjee, *J. Colloid Interface Sci.* **292**, 595 (2005).

Abstract

Discharging a high-energy spark underwater creates a shock wave that dissipates through an acoustic field. Colloidal acrylate polymers suspended in water containing dissolved calcium are agglomerated as a result. The degree of agglomeration increases with the number of sparks applied and with increasing calcium content. The calcium decreases the charge on the colloidal particles and thereby increases their propensity to be agglomerated by the acoustic wave. These observations are confirmed in full-scale trials in paper recycling mills where sparking improves the efficiency of centrifugal cleaners by increasing the particle size of the contaminants.

Introduction

Discharging a high-intensity spark underwater creates a shock wave that decays through an acoustic field and generates hydroxyl radicals from water. These radicals are able to detackify adhesives (1), oxidize pollutants (2), disinfect water (3), and alter the surface properties of ink particles suspended in water (4). The acoustic pulse has been used to aggregate small particles; *e.g.* sparking consolidates biological sludge and increases its settling rate (5). This paper shows that sparking agglomerates colloidal polymers if calcium is present in the system. This is a desirable outcome if the particles are present as contaminants in process streams. For example, acrylates and polyvinyl acetate particles are usually present in paper recycling operations and are purged by centrifugal cleaners and other means. However, the removal efficiency decreases for sub-millimeter particles (6, 7), and micron-sized particles are transparent to cleaners. Sparking in the presence of calcium increases the size of the particles and facilitates their removal through centrifugal cleaning, as demonstrated in full-scale mill trials.

Materials and Methods

The sparker used was obtained from Pulse Power Inc., Stoney 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. The approximately 0.1 msec discharge was of 15 kA and 4 kV. The commercial acrylate adhesive formulation (Carbotac 26171), a water-based PSA latex emulsion, contained 49% polymer and was obtained from Noveon, Cleveland, OH). The acrylate suspensions were sparked in the presence of varying amounts of calcium chloride. Particle size and zeta potential were measured with a Zetasizer (Malvern Instruments Ltd., UK). Colloidal organic contaminants in process streams were determined as described earlier (8). Full-scale work was done with the submersible electrode unit described by Welch *et al.* (9). Installation consisted of tying a nylon line to the electrode assembly and lowering it into the tank of interest so that it remained submerged throughout the trial. A level controller was used to ensure safe operation by shutting down the unit if the water level dropped; sparking in air could dislodge the wires.

Results and Discussion

Sparking the acrylate polymer in the absence of calcium does not significantly change the average particle size of about 200 nm as shown in Table 1. The zeta potential (the charge that develops at the interface between a solid surface and the liquid medium) also remains substantially unchanged indicating that the charge on the particles is relatively unaffected. This is broadly consistent with the small change of about 7 mV measured earlier (1) at neutral pH using a different formulation. Adding calcium (without sparking) increases the zeta potential as expected, but the particle size increases only marginally. On the other hand, sparking increases the particle size for each mixture of polymer and calcium as shown in Table 1, but does not alter the zeta potential. These results are interpreted quite easily. Adding calcium without sparking tends to neutralize the charge on the polymer particles, but this, in and of itself, does not destabilize the polymeric suspension, since the charge remaining on the particle is high enough to stabilize the suspension. Sparking in the absence of calcium is similarly unable to agglomerate the particles because of charge repulsion among the particles. The addition of calcium neutralizes the charge to the point that acoustic agglomeration can occur, which explains why the degree of agglomeration increases with increasing calcium concentration. Cations other than calcium are also able to reduce the charge on the particle and promote agglomeration; *e.g.* aluminum is also effective in this regard (10). The Table 1 results are for sub-micron particles; however, surface effects will be less dominant for larger particles, which should agglomerate more readily upon sparking.

The results in Table 1 suggest that colloidal contaminants contained in a process stream of a paper mill using secondary (recycled) fiber could be agglomerated if the hardness of the water is high enough. This would increase the efficiency of the centrifugal cleaners that are used to remove low-density contaminants from process streams. Sub-millimeter sized particles are not easily removed, and increasing the particle size through sparking should improve contaminant removal. This was evident in our first full-scale trial in a specialty paper mill (10). The rejects stream from the centrifugal cleaners (configured to remove low-density contaminants) was visibly clean prior to sparking. A white contaminant consisting of a mixture of ethylvinylacetate, wax, and calcium carbonate appeared in the rejects upon sparking. It disappeared when sparking was discontinued. The feed stream had a hardness of 1,200 ppm, so it is likely that sparking agglomerated the contaminants, which were then removed by the cleaners.

More quantitative results were obtained in a newsprint mill where the sparker was placed in the feed tank of the centrifugal cleaners (10). The colloidal organic material in the accepts stream is profiled in Figure 1. These colloids are known to mostly represent adhesive contaminants (8, 11) and are expressed as a fraction of total dissolved and colloidal organic material present in the stream. Sparking reduced the colloidal material in the accepts; a t-test showed that the mean values of the sparked and unsparked groups in Figure 1 were different at the 99% confidence level. Again, the likely reason for the improved cleaning efficiency is that sparking increased the particle size of the contaminants and facilitated their centrifugal separation from water. It is important to note that sparking causes very little shear outside the electrode region. The amount of energy expended is far too small to generate significant shear in the large water volumes processed in the mill. Hence, although agglomeration of polymeric adhesives can also be induced through shear (12), the mechanism involved here is very different and involves interparticle collision induced by ultrasound (13).

In summary, laboratory work demonstrates that acrylates and adhesive contaminants present in paper recycle streams can be agglomerated upon exposure to underwater sparks. These streams usually contain calcium, which neutralizes the charge on the polymeric contaminants to the point where they can be acoustically agglomerated. Full-scale mill trials demonstrate that sparking can increase the particle size of contaminants to the point where they can be centrifugally rejected. This application is of economic importance because additives are frequently added (at appreciable cost) to counter the effect of these contaminants. The capital cost of the sparker and its power requirements are quite modest by comparison.

Acknowledgment

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Table 1: Effect of sparking on size and zeta potential.

sparks	size (nm)[1]	zeta potential, (mV)[1]
1,000 ppm polymer[2]		
0	198 (2)	-38.1 (0.3)
20	202 (3)	-38.6 (0.3)
80	202 (1)	-36.2 (0.3)
200	203 (3)	-34.4 (0)
1,000 ppm polymer[2] + 500 ppm Ca		
0	197 (1)	-19.6 (0.1)
20	200 (2)	-19.5 (0.1)
80	217 (2)	-18.0 (0.3)
200	275 (4)	-19.1 (0.1)
1,000 ppm polymer[2] + 1,000 ppm Ca		
0	205 (3)	-16.0 (0.6)
20	211 (4)	-16.6 (0.2)
80	234 (2)	-18.0 (0.2)
120	255 (3)	-17.0 (0.2)
200	370 (10)	-16.5 (0.8)

[1]average of 3 determinations, average deviation in brackets; [2]as the Carbotac formulation.

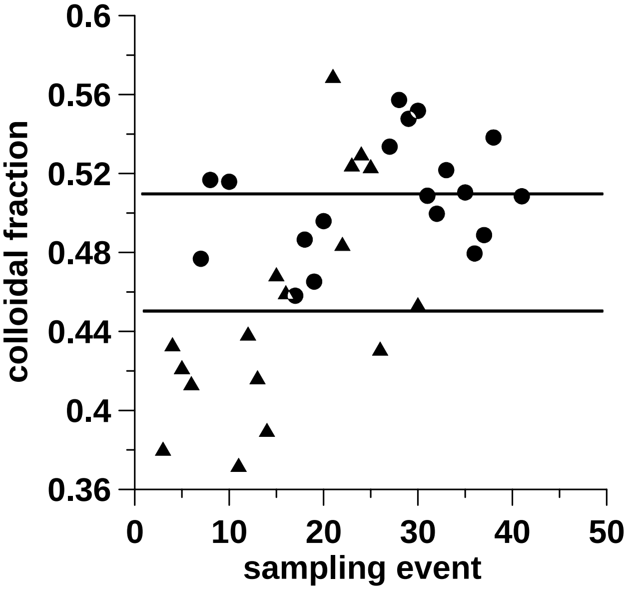

Figure 1: Effect of sparking on colloidal contaminants in the accepts stream. The ordinate represents daily samples. The circles and triangles represent results for control and "sparker on" situations, respectively. The two bars represent averages of 0.45 (sparked) and 0.51 (control).

9. Spark-Induced Consolidation of Biological Sludge

This section is excerpted from J.Yang, B.Hartong, J.Carleton, S.Banerjee, *Water Res., 39 (7), 1374 (2005).*

Abstract

Subjecting a suspension of biological sludge to underwater sparks (3kV, 50 kA) leads to its consolidation, decreases the charge density on the solids, and increases its settling rate. The cake solids increase, but by only one percentage point. High-speed video images show that the spark generates a steam bubble. The dynamics of bubble growth could be estimated through the Rayleigh model. The bubble collapses into an acoustic field, which then agglomerates the particles. Sparking does not affect the settling rate of an aqueous slurry of softwood pulp because the fibrous particles are too large to be aggregated by an acoustic pulse.

Introduction

Biological sludge is usually consolidated through use of thickeners such as polymers or lime (Watanabe and Tanaka, 1999). Mechanical thickening has also been reported, although the process has not been commercialized. For example, Golla *et al.* (1992) have described an electro-acoustic process where the application of electric and acoustic fields consolidates the cake and increases final solids. Riera *et al.* (2000) showed that ultrasonic energy can dewater fine-particle high-concentration suspensions such as slurries and sludges. Discharging a high-intensity spark underwater generates a sound wave, and we have recently demonstrated that some applications that rely on acoustics can also be conducted with the underwater sparker. For example, trace levels of adhesives in process streams of mills that recycle paper can be oxidized by either ultrasonic radiation or sparking (Corcoran *et al.,* 2000*,* 2001; Banerjee, 2003). However, the spark application can be more economical in terms of both capital and operating costs (Corcoran *et al.,* 2001).

Underwater sparking has been applied to anerobically digested sludge in an effort to reduce polymer use (Soszynski *et al.* 1999). Limited pilot-scale success was achieved with low-conductivity sludge, but the spark source was of low power (0.25 joules) and the application did not successfully scale up. In this paper we demonstrate that exposing biological sludge to underwater sparks of much higher energy (~10 kJ) leads to acoustic agglomeration of the particles, which results in faster settling.

Methods and Materials

The sparker was obtained from Pulse Power Technologies, Dundas, Ontario, Canada. The sludge was sparked in a 10-L tank constructed from a section of pipe with integrated 1.3-cm diameter stainless steel electrodes. A discharge of 50 kA and 3 kV was made at 12-second intervals. High-speed video images were taken with a Kodak EktaPro HR-1000 camera capable of 1-msec resolution. Specific charge quantity was measured at a pH of 7.6-7.8 with a Mutek 03m Particle Charge Detector from Mutek Analytic Inc., Marietta, GA. Floc diameter was determined with a microscope; the values cited were averaged over fifty readings, with an average standard deviation of 20%. Fiber length was measured with an LDA96 Fiber Quality Analyzer

(FQA) from OpTest, Hawkesbury, Canada. The results reported were averaged over 5,000 readings. The Crown Press was purchased from Neogen Corporation, Lansing, MI.

Two types of biological sludge were obtained from a municipal treatment plant. Sludge (0.46% solids) collected from the surface of the aeration basin was thickened to 1.29% solids by allowing it to settle and pouring off the supernatant. This material is referred to as *surface sludge*. Lime was added at 0.65% of dry solids. *Bottom sludge* was collected from the bottom of the aeration basin at 3.41% solids; lime addition increased the solids to 3.53%. Sludge settling rate was determined by placing 250 ml of it in a 3.7-cm diameter cylinder and measuring the clarified volume.

Paper mill primary sludge was simulated using southern pine fiber. Different size fractions of the fiber were obtained by first drying the fiber overnight at 105^{0}C. The dry material was then shaken to break up the fibers and sieved through 40, 60, and 200 mesh screens. These correspond to 250, 125 and 75µ holes, respectively. The average fiber lengths accepted by these screens were 454, 326 and 212 µ, respectively as measured by the FQA. The length of the unscreened fiber was 2.8 mm. The fibers were suspended in water at a consistency of 0.10% and sparked.

The solids in the supernatant were measured in two different ways. First, the samples were centrifuged at 400 g for ten minutes, and the supernatant solids determined by filtering and drying the residue. Second, the sample was poured into a funnel and allowed to settle for ten minutes. The supernatant solids were then measured.

Results and Discussion

Bottom sludge

Sparking the bottom sludge greatly increased the settling rate as shown by the results illustrated in Figure 1. The supernatant solids after settling or centrifuging the suspension decreased substantially upon sparking (as shown in Table 1), which is in keeping with solids agglomeration. Corresponding measurements made with lime-treated sludge are included in Figure 1 and Table 1. The Figure 1 comparison reveals that lime-treatment increases the settling rate of the control as expected, but has a smaller effect on the sparked samples. The proportional decrease in supernatant solids upon sparking is roughly the same for both the lime-treated and untreated sludge as shown in Table 1. Microscopic inspection of the settled sludge confirms that sparking consolidates the solids. Aggregates were commonly found in the treated material, but not in the unsparked control as shown in the typical micrographs illustrated in Figure 2. The lime-treated sample was sparked and dewatered in a Crown Press (a belt press simulator) at an applied force of 1,655 kPa for three minutes. The resulting solids in the sparked sludge were (at best) only one percentage point higher than that of the control as shown in Figure 3, suggesting that the binding of water to sludge solids is only minimally affected by sparking.

Surface sludge

Sparking the lime-treated surface sludge increased the 30-minute clarification volume to 70 ml, which is comparable to the results shown in Figure 1 for bottom sludge. The magnitude of the specific charge quantity (the surface charge of all particulate and colloidal material present) decreased linearly with the number of sparks as shown in Figure 4. This would be the expected outcome if the particles agglomerated; the magnitude of the surface charge would drop because agglomeration would decrease the total surface area. The floc size increased with sparking as also shown in Figure 4, leveling off at a value approximately twice that of its initial size. These data confirm and complement the size increase noted in the micrographs of Figure 2.

Sparking the untreated surface sludge did not increase the settling rate and no changes in floc size were seen, in contrast to the effect observed with the lime-treated material. The acoustic pulse resulting from a single spark is short-lived, and particles can only be acoustically agglomerated if they are in close proximity to one another. Sludge that is compacted (as in the case of bottom sludge) or flocculated through lime-treatment would, therefore, be more amenable to aggregation through sparking than would a dilute slurry.

Mechanism of agglomeration

The agglomeration of particles in an acoustic field is well-known. Two mechanisms have been proposed. First, the particles can move to the nodes or antinodes of a standing acoustic wave where they can concentrate and then aggregate (Spengler and Jekel, 2000). This situation cannot apply to our case since there are no standing waves. In the second mechanism, an acoustic pulse can make small particles in close proximity to each other move with different velocities and agglomerate. Doktycz and Suslick (1990) showed that 5-50 μ metal particles suspended in a hydrocarbon liquid collide and fuse when irradiated with ultrasound. The particle size of activated sludge is in the same range. Its size distribution is bimodal, comprising 25-100 μ flocs and 0.5-5 μ free colloids (Mikkelsen, 2002).

The interparticle velocities depend on particle size, and large particles are minimally accelerated (Doktycz and Suslick 1990). Sludge particles are neither spherical nor uniform and it is difficult to define an optimal size for aggregation. However, sparking should have a smaller effect on larger particles, such as those that comprise paper mill primary sludge. This sludge was simulated by 0.1% suspensions of softwood fiber in water. Slurries containing fibers of various lengths were exposed to twenty, fifty and one hundred sparks, and the settling rate measured over thirty minutes in each case. The rates were similar for all the sparked samples; results for those sparked twenty times are illustrated in Figure 5. The settling rate for the unfractionated sample is insensitive to sparking because the particles are too large to be agglomerated by the acoustic pulse; the clarified volumes for the sparked and unsparked samples were identical. The fractionated unsparked samples settle more slowly (as shown by the black bars in Figure 5) because of their smaller particle size. However, the settling rates of these particles double upon sparking because they are acoustically agglomerated.

An estimate of the acoustic energy delivered to the system was obtained by capturing high-speed images of the electrode region during sparking. As voltage was applied to the electrodes, a stream of microbubbles flowed from the cathode to the anode. The spark discharge that followed was very rapid at less than 1 msec. A steam bubble of roughly 6.5-cm radius formed around the electrode gap by the water vaporized by the discharge as shown in Figure 6.

According to the Rayleigh model, the time for an expanding bubble to reach its maximum radius (R_{max}) is given by

$$\Delta t = R_{\max}\sqrt{\frac{\rho}{6P_a}}\frac{\Gamma\left(\frac{5}{6}\right)\Gamma\left(\frac{1}{2}\right)}{\Gamma\left(\frac{4}{3}\right)} \tag{1}$$

where Γ is the gamma function, ρ is the density of water and P_a is the ambient pressure (Larsson *et al* 2001). The Lanczos approximation simplifies eq (1) to eq (2)

$$\Delta t = 0.915R_{\max}\sqrt{\frac{\rho}{P_a}} \tag{2}$$

Substitution of ρ=1,000 kg/m^3, P_a=101,325 Pa and R_{max}=5.7 cm yields a Δt value of 5.2 ms, which is in good agreement with observations from the video, which shows the bubble growing for about 5 frames before reaching its full size.

The bubble wall velocity (U) and initial kinetic energy (W_0) are given by eq 3 and 4, respectively,

$$U(R) = \sqrt{\frac{2P_a}{3\rho}\left(\frac{R_{\max}^3}{R^3} - 1\right)} \tag{3}$$

$$W_0 = \frac{4\pi}{3}P_a R_{\max}^3 \tag{4}$$

from which W_0=78.6 J. This is much higher than that delivered by most ultrasonic devices, and there is, therefore, clearly enough energy input to generate the necessary acoustic field. Despite its higher power output the overall energy cost of sparking is quite low, because sparking is not continuous; a spark was fired only once every twelve seconds in our work.

Conclusions

In conclusion, sparking appears to consolidate biological sludge through acoustic agglomeration. The improvement in cake solids is relatively small. However, the increase in settling rate is appreciable, which should translate to an increase in throughput across the gravity table. Primary (fibrous) sludge, which is composed of larger particles is unaffected by sparking. High-speed images demonstrate that the spark generates a steam bubble, whose implosive collapse gives rise to the acoustic field.

Acknowledgment

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Table 1: Effect of sparking on supernatant solids (mg/l).

sparks:	**0**	**20**	**50**	**100**
untreated				
solids after centrifuging	15.5	8.81	6.60	8.46
solids after settling	26.0	24.9	8.27	11.0
lime-treated				
solids (after centrifuging)	67.1	45.6	31.0	28.7
solids (after settling)	102	55.9	35.1	30.9

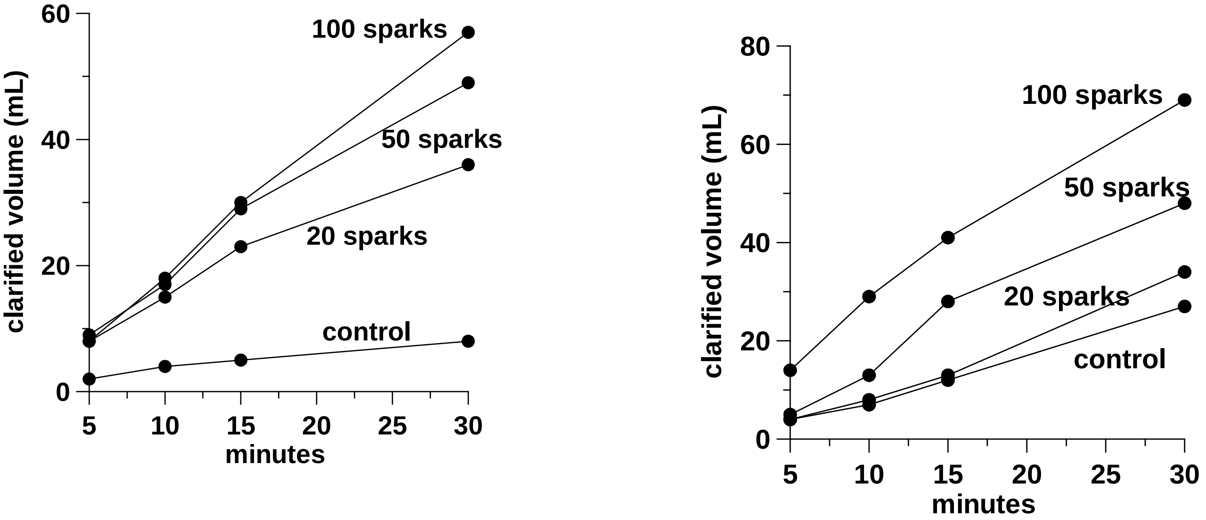

Figure 1: Settling of untreated (left) and lime-treated sludge (right).

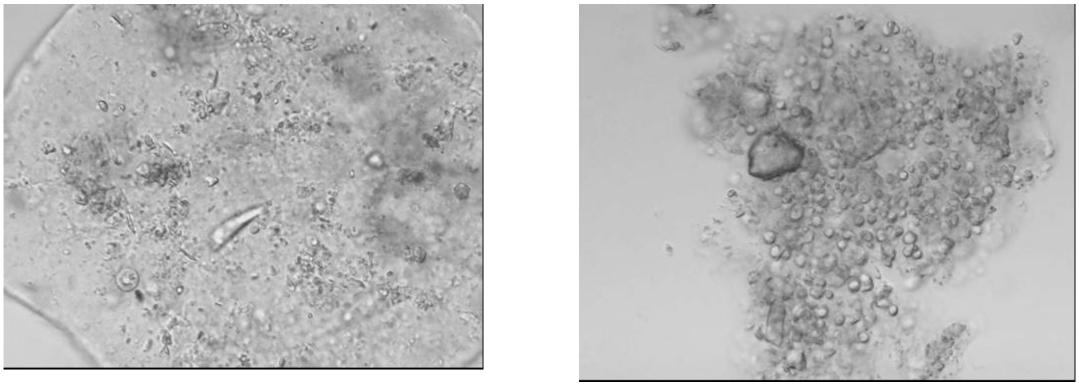

Figure 2: Typical photomicrographs (differential interference contrast, 400 magnification) of sludge before (left) and after exposure to 200 sparks.

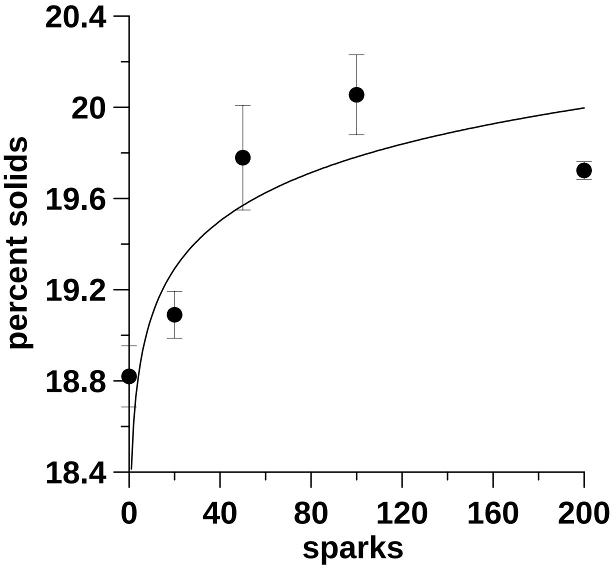

Figure 3: Effect of sparking on final solids. Each point is the average of three values; the uncertainties displayed are average deviations.

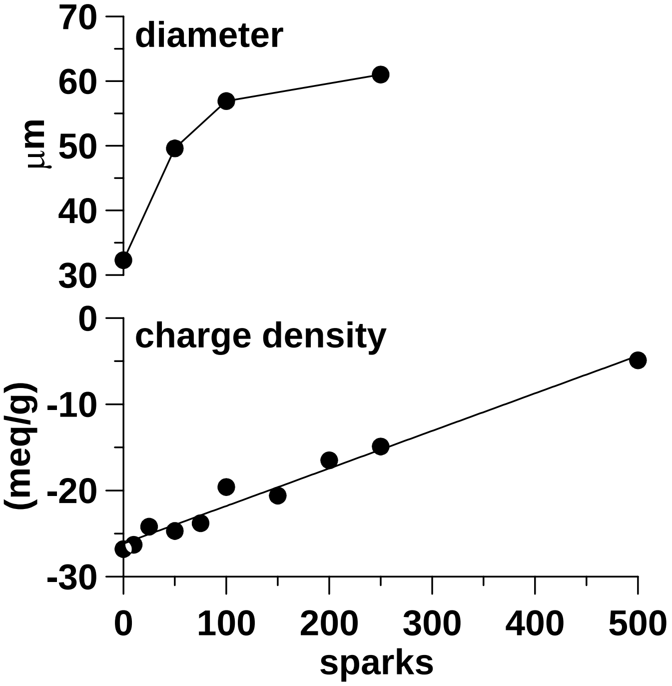

Figure 4: Effect of sparking on charge density and floc diameter.

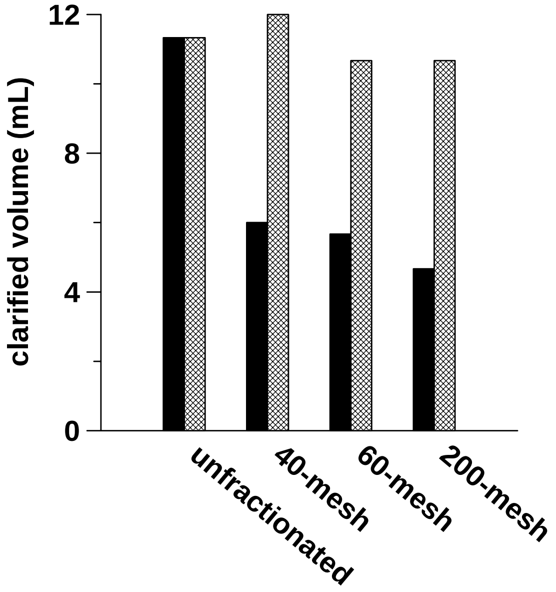

Figure 5: Effect of sparking (20 sparks) on fiber settling. The dark and hatched bars represent unsparked and sparked samples, respectively.

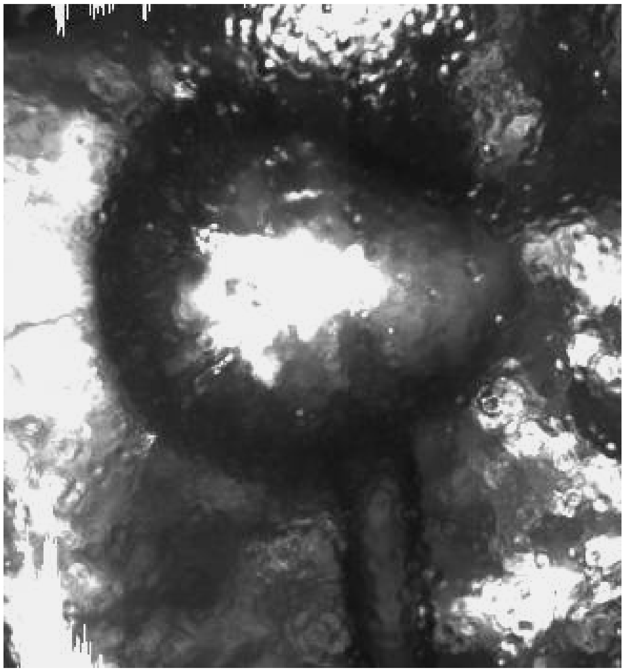

Figure 6: Image of a steam bubble. One of the electrodes is visible in the lower part of the frame.

10. Properties of the shockwave

Measurement of shockwave pressure

To accomplish our goal of understanding the dependence of shockwave magnitude on discharge voltage, we set up a data acquisition system consisting of an underwater blast pressure sensor (PCB Piezotronics Model W138A02) and a digital oscilloscope (LeCroy Model 9424E). With the sparker immersed in a 90 gallon water tank, we placed the pressure sensor at a set distance from the electrode gap and recorded the pressure pulse during sparking at four different discharge voltages. This was performed with the sensor at four different distances from the gap, giving us 16 pressure data points (each recorded in triplicate to reduce random error) and a good idea of how the pressure waveform changes with increasing discharge voltage and with increasing distance from the source. Figure 1 illustrates a typical waveform.

The peak pressure (taken as the pressure at the plateau before the high frequency noise) was found to vary with distance roughly according to the following power law relationship:

$$P = 30d^{-0.3}$$

where P is in psi and d is in feet. The measured constants in this equation vary somewhat with discharge voltage. The peak pressure was found to be linear with respect to voltage, as expected. The slope tends to decrease with increasing distance from the source. At five inches from the source, the equation is as follows:

$$P = 5v + 2.4$$

where v is in kV.

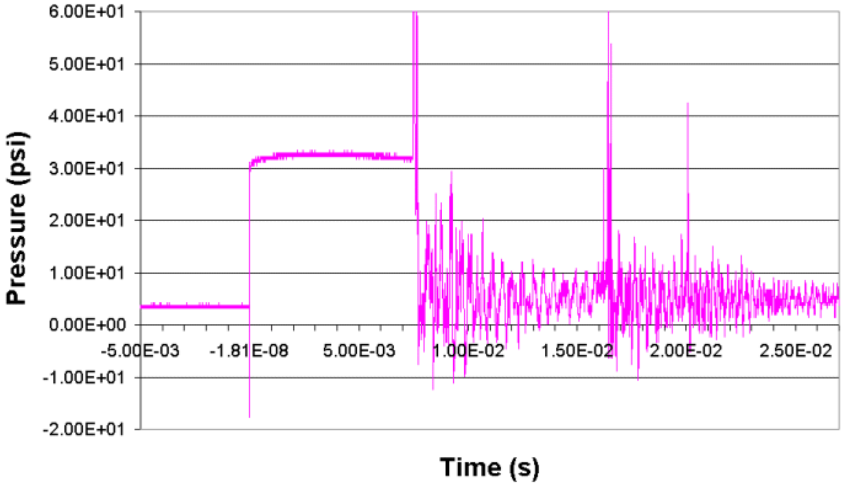

Figure 1: Pressure profile at 5 kv at a distance of 7".

An interesting feature of the pressure waveforms is the presence of high frequency noise, which occurs some time after the initial pulse. It was originally thought that this was due to reflections of the pulse coming back to the sensor from the surface and the walls of the tank. However, it was found that the time between the initial pulse and the HF noise does not depend on the distance, as one might expect in that case, but rather depends on the discharge voltage. Thus, it has been concluded that the HF noise must be due to the collapse of the gas/vapor bubble formed at the electrode gap immediately after the discharge. The collapse of this bubble causes the electrodes to vibrate, and also results in the formation of many tiny bubbles which radiate outward from the collapse site. Either or both of these phenomena may be the cause of the HF noise. This is supported by three observations:

1. There is a pressure pulse but no HF noise when the discharge voltage is set so low that the water does not break down (i.e. when the capacitors discharge but there is no "spark".) This is interesting and will be explored further.
2. It was noticed that the amplitude of the noise depends not on the amplitude of the pressure pulse, but rather on the discharge voltage. Higher-voltage discharges are louder and more violent.
3. According to high-speed video observations, the time between the initial pulse and the noise is close to the time from the discharge to the collapse of the bubble.

A higher discharge voltage means there is more current flowing through the gap during the discharge. Thus, the plasma gets hotter, and the water surrounding the gap vaporizes faster. This results in a faster bubble growth and collapse. This explains why the pressure waveforms show less time between the initial pulse and the HF noise at higher discharge voltages.

Discharge Voltage

A LabView program was written to sample the capacitor voltage via a PC-based data acquisition card (National Instruments Model PCI-6034E), thus giving us a profile of the voltage during charging and discharging. Having an exact value of the discharge voltage is useful because, for a given set voltage, the actual discharge voltage can vary up to 500 V either way. The time-dependent changes in voltage are illustrated in Figure 2.

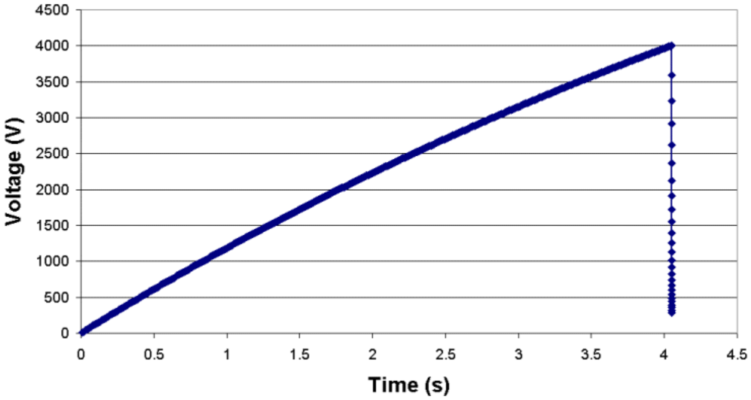

Figure 2: Capacitor voltage during charging and discharging.

Radical production with the sparker

A fundamental study on how radicals are formed from the sparking event was initiated. Corcoran (Ph.D. thesis, IPST, 2000) performed Fricke dosimetry experiments with the Sparktec Sparker to determine its oxidative potential. He found that, for 60 sparks, the ferrous ion concentration decreases by 0.0007 mM at 2000V, and decreases by 0.0011 mM at 6500V. As Jana and Chatterjee (Ultrasonics Sonochemistry, 1995, vol. 2, no. 2, pp. S87-S91) have shown, the number of hydroxyl radicals formed during sonication is approximately equal to one-fourth the number of ferrous ions consumed. Therefore, at 2000V, roughly 1×10^{17} radicals per liter are produced, while at 6500V, about twice that number are produced. Thus, over the operating range of the Sparker, the production of hydroxyl radicals is on the order of 10^{17} radicals per liter.

An equation has been developed to model hydroxyl radical production by the sparker. This equation treats the sparker theoretically as a pulsed ultrasonic source.

$$Q = \sum_r SLF_c B_r R_r \varepsilon_r \tag{1}$$

Here, Q is the total number of radicals produced per liter, r is bubble radius, S is the number of pulses, L is the pulse duration, F_c is the center frequency of the pulse, B_r is the number of bubbles of radius r ideally present at steady state during the pulse, R_r is the number of radicals produced ideally per bubble per acoustic cycle, and ε_r is the efficiency of radical production for bubbles of radius r.

In order for this equation to be useful, a number of simplifying assumptions had to be made. First, it was assumed that the bubbles formed by the spark are of uniform size. Thus, the summation is eliminated, and ε_r becomes an overall efficiency, taking into account bubble size deviations. A diameter of 30 μm was chosen as representative of bubbles produced by low-frequency ultrasound (Gong, Ph.D. thesis, MIT, 1999). This model for radical production was used to predict that approximately 5×10^8 radicals are produced per bubble per acoustic cycle. In addition, Shah *et al's* estimate (Cavitation Reaction Engineering. Kluwer Academic/Plenum Publishers. New York, 1999) of a steady-state concentration of 5×10^{10} bubbles per liter was used. Finally, a pulse length of 150 μs and a center frequency of 5 kHz were assumed, according to data from Sparktec.

Before evaluating ε_r, the above equation, subject to the above assumptions, yields a figure of $10^{21}\varepsilon_r$ radicals per liter. For this theoretical value to match with Corcoran's experimental value, the efficiency must be on the order of 0.0001. As will be shown, this is in fact quite reasonable.

Why is the radical-producing efficiency of the sparker so low compared to ideal ultrasonic production? First of all, the system is not at steady state during sparking. The shockwave nucleates bubbles which then grow, oscillate, and collapse, but between sparks the system returns to a noncavitating state. The energy loss associated with renucleation is estimated to reduce the efficiency to ¼ of the ideal production. In addition, the bubbles do not behave ideally. A broad size distribution, interactions between bubbles, and shielding by bubble clouds all mean decreased collapse efficiency. Add to this the effects of intensity attenuation with distance from the spark, as well as the spatial inhomogeneity of the system, and this could reduce the efficiency to 1/20 of the ideal production. Also, the ferrous ion must migrate to the bubble interior in order to react with the hydroxyl radical. Inefficiencies associated with this transport are estimated to reduce the apparent radical reactions to ¾ of ideality.

Aspherical bubble collapse represents possibly the largest source of efficiency loss. The action of the shock wave and the presence of container walls and bubble clouds cause parts of the bubble wall to accelerate faster than other parts. This results in an aspherical collapse. The resultant microjet from the bubble can reduce the interior temperature and pressure by an order of magnitude or more, meaning that the radical production may be reduced to less than 1/100 of the ideal production. All of these loss sources taken together will reduce the overall efficiency, and a radical production efficiency of 0.0001 is not unreasonable. Hence, despite the large number of assumptions and estimations made in this analysis, it has at least been shown theoretically that radical production on the order of 10^{17} radicals per liter is possible with the sparker, thus giving support to Corcoran's experimental results.

11. **Other potential sparker applications**

11.1 Attempts to degas water through sparking

We had previously shown that sparking water in a 8L led to its degassing as indicated by a drop in dissolved oxygen (DO) levels. Scaled-up experiments were run in a 50 gallon tank. Water at room temperature (21°C) was sparked with continuous DO monitoring at distances of 1 and 20 inched from the electrode. The results, shown in Table 1 demonstrate no significant reduction of DO. It seemed possible that the water could be rapidly reaerating between sparks, and the experiment was repeated with oxygen-saturated water, which would allow the rate of reaeration to be measured. The results, shown in Table 2, demonstrate that sparking does not induce deaeration under scaled-up conditions. These results contrast with our previous results where sparking in an 8-liter vessel led to significant deaeration. The discrepancy is tentatively attributed to the difference in the surface area:volume ratio. It is possible that the bubbles generated in the larger vessel redissolve on their passage to the surface.

Table 1: Effect of sparking on DO.

sparks	**DO (ppm)**	
	distance from electrode (in)	
	1	**20**
0	5.8	5.8
25	5.4	4.9
50	5.6	5.27
100	5.4	5.5
200	5.9	5.6
300	5.4	5.1
400	5.3	5.5

Table 2: Effect of sparking on oxygenated water.

sparks	**time (min)**	**DO (ppm)**		**control**
		distance from electrode (in)		
		1	**20**	
0	0	19.0	19.0	19.0
25	5	15.0	16.6	15.8
50	15	14.0	14.0	14.6
100	25	15.4	14.8	13.0
200	43	14.4	15.7	15.0
300	58	14.7	14.6	14.0
400	75	15.4	15.0	14.2

11.2 Effect of sparking on foam

In order to determine whether sparking might be able to collapse foam, an 8 L aliquot of 1,000 ppm Liquid-Nox was prepared in the 10-liter reactor. Liquid-Nox is a critical component cleaner and has the capability to form a large head. In the first experiment, the surface was clear of foam prior to sparking. With small amounts of sparking a small amount of bubbles were found on the surface, with increasing amounts of sparking the system became cloudy, but there was no significant foaming; just a cloudy surface of small bubbles. In the second experiment, the system was stirred until a significant head was formed. Sparking the system, did not significantly reduce the amount of foam, and after 200 sparks some foam still remained, although the surface did appear cloudy as in the first experiment. Since there were no significant results from sparking the foam, this set of trials was abandoned.

12. Publications, Presentations and Technology Transfer

Publications

1. S.P.Makris, T.Le, J.Carleton, F.K.Kazi, S.Banerjee, Effect of electrohydraulic discharge on flotation deinking efficiency, *Ind. Eng. Chem. Res.*, 43, 7552 (2004).
2. J.Yang, B.Hartong, J.Carleton, S.Banerjee, Spark-induced consolidation of biological sludge, *Water Res.*, 39 (7), 1374 (2005).
3. S.Banerjee, Spark-induced agglomeration of aqueous polymeric suspensions, *J. Colloid Interface Sci.*, 292, 595 (2005).

Presentations

1. S.Banerjee, S.P.Makris, T.Le, J.Carleton, Applications of underwater spark technology to recycle paper processing, 7th Research Forum on Recycling, Quebec, September 2004.
2. S.Banerjee, S.Makris, J.Carleton, T.Le, F.Kazi, Spark technology: mill trials, Tappi Summit, Atlanta, GA 2004.
3. S.Banerjee, Sludge reduction, compaction, and reuse, Paperex, New Delhi, India, 2003.
4. S.Banerjee, Spark technology, Recycled Paperboard Technical Association Meeting, Minneapolis, 2003.

Presentations were also made to Stora Enso, Eka Chemicals, and Buckman Labs.

Patents

1. S.Banerjee, System and method for altering characteristics of materials using an electrohydraulic discharge, US patent 6,572,733 (2003).
2. H.Corcoran, S.Banerjee, System and method for altering the tack of materials using an electrohydraulic discharge, US patent 6,521,134 (2003).

Technology Transfer

The technology has been licensed to Eka Chemicals, a division of Akzo Nobel.