Effects of zeta potential on flocculation measurement in microparticle systems

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ABSTRACT: The effects of zeta potential on dynamic flocculation behavior was studied. The study focused on microparticle retention systems in neutral papermaking. In wood-containing grade when zeta potential was strongly negative, anionic polyacrylamide (PAM) did not make flocs. The combination of bentonite and anionic PAM created large flocs. When the zeta potential was adjusted to near the isoelectric point, a single addition of anionic PAM or bentonite formed large flocs. In neutral papermaking of wood-free pulp, low charge and high molecular weight cationic PAM effectively made flocs. Flocs of chemical pulp were harder and more resistant to hydrodynamic shear than mechanical pulp. Cationic starch had little effect, or poor effect, on flocculation. Cationic PAM plus bentonite worked well, with zeta potential at the isoelectric point. The bentonite and anionic PAM system formed large flocs across zeta potential ranges.

KEYWORDS: Acrylamide, acrylic compounds, addition polymers, amides, anionic compounds, bentonite, cationic compounds, clay, electrical properties, flocculation, glucans, measurement, minerals, natural polymers, on line measurement, polyacrylics, polymers, polysaccharides, retention aids, starch, synthetic polymers, thermoplastics, vinyl compounds, zeta potential.

Wet-end chemistry plays a leading role in improving first-pass retention without damaging the sheet formation caused from excess flocculation. At the wet end of a paper machine, both the hydrodynamic and colloidal forces determine the degree of flocculation. We *(1)* reported that on a low-speed fourdrinier machine, where microturbulence was mild on the wire, the electrokinetic force, or zeta potential, was the predominant factor affecting first-pass retention. As first-pass retention improved, sheet formation deteriorated. On a high-speed Bel-Baie 2 former, where strong microturbulence was created on the wire, macro flocs were broken down and sheet formation was not affected by the first-pass retention up to 50%. Krogerus *(2)* measured flocculation, drainage, and sheet formation in the laboratory. He elucidated the flocculation behavior of the fines in a supercalendered magazine pulp furnish with different retention polymers alone and with bentonite. But he could not study the dynamic phenomena of flocculation with the off-line instruments he used. Also, in preparing samples, fractionation and dilution of the mechanical pulp lowered the amount of dissolved colloidal substances, and the effect of the anionic trash charge on flocculation was not investigated. Sanders *(3)* found the importance of charge characterization of papermaking furnish colloids. He compared several colloid charge measurement methods and determined each method's sensitivities and precisions to fines, fillers, and solubles. Scott *(4)* observed the surface charge decay by use of an on-line zeta potential sensor and confirmed the polymer reconformation theory of Lindstrom *(5)*. He emphasized the importance of dynamic zeta potential analysis. My previous study *(6)* introduced a new calibration method of an on-line zeta potential instrument and greatly improved a correlation between streaming potential data and electrophoresis data. Furthermore,

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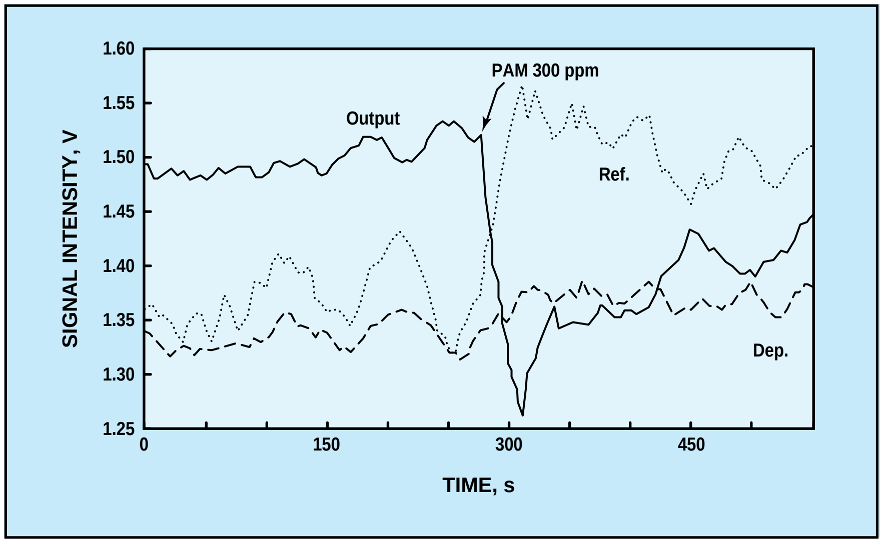
these two data groups showed that a cationic polyelectrolyte first reacted with anionic solubles, next with fines, and finally with fibers. Those experiments determined the optimum zeta potential range for newsprint furnish. This calibrated instrument made it possible to perform on-line zeta potential analysis on a fine paper machine and a newsprint paper machine in paper mills. Computer statistical analysis successfully extracted the critical process disturbances which created zeta potential fluctuations. Penniman *(7)* developed an on-line method to concurrently measure zeta potential and drainage, but the degree of flocculation was not studied in his experiments. So far, the dynamic flocculation behavior when the zeta potential varies has not been well understood, especially in microparticle systems. Research on this issue is necessary for a better understanding and optimization of the wet end of a paper machine.

1. Effects of retention aid on focculation measurement. LBKP 100%, $CaCO_3$ 20%, A-PAM 300 ppm



I. Polymer properties

	Charge density, meq/g	Molecular weight, millions
A-PAM low charge, high MW	1.1	12
C-PAM		
0 low charge, low MW	0.2	0.2
1 med. charge, med. MW	2.6	1.5
2 low charge, high MW	1.4	3
3 med. charge, high MW	3.3	10

Objectives

The purposes of this study are:

1. To measure the flocculation by an on-line method
2. To study the effects of zeta potential on flocculation
3. To find the optimum wet end conditions for the effective chemical usage, especially microparticle systems.

Measurement procedure

Optical Activity

Kaunonen *(8)* tested several commercial consistency transmitters for retention measurement. One method was to use the optical activity. When a plane-polarized light enters a crystalline material, such as quartz, the plane of polarization changes to some other plane from the one it entered. This phenomenon is called optical activity and is exhibited in many substances, such as sugar solutions and cellulose fiber. The instrument measures both the depolarized light and the non-rotated light, which are transmitted through the pulp suspension. The output is a ratio of those signals where the reference light is non-polarized light.

Output = 10 x depolarized light/reference light (1)

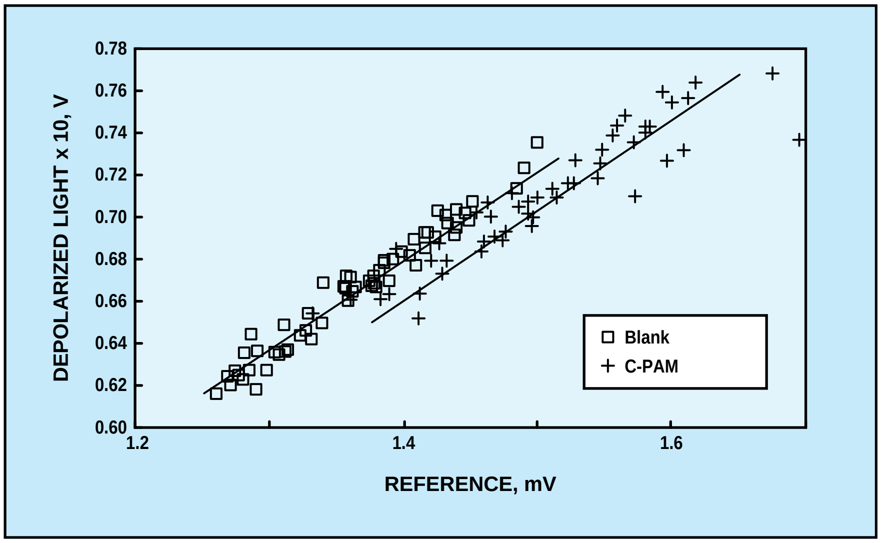
Chemical pulp contains relatively less optically non-active lignin and more optically active carbohydrates than mechanical pulp. In Kaunonen's experiments, shifting from mechanical pulp to chemical pulp increased the output of the instrument. He also found that retention aids in normal additions did not affect the consistency measurement, but they were found to affect the measurement at an impractically high addition.

Flocculation measurement

When I measured the colloidal surface charge and pulp consistency simultaneously by new on-line methods in a laboratory, contradictory to Kaunonen's work, dynamic flocculation was observed even at normal retention aid levels.

Experimental procedures. Hardwood bleached kraft pulp, which was beaten to a freeness of 400 ml CSF, was mixed with 20% precipitated calcium carbonate, and diluted with tap water to a 0.5% consistency. The prepared sample was recirculated with a pump through a sampling tank to the measurement cell. 300 ppm cationic polyacrylamide (PAM) retention aid (molecular weight = 3 million, charge density = 1.4 meq/g) was added in the sampling tank to form flocs (300 ppm is the normal addition level). The depolarized light,

2. Depolarized light vs. reference light



the reference light and the output signal were monitored and stored in a computer data base. When cationic PAM was added, the output signal decreased markedly (**Fig. 1**). This did not derive from the consistency variation, because the mass of cationic PAM was negligible in comparison with the mass of pulp and filler in the sampling tank. The recirculating line was a closed loop and the total mass and volume of the suspension was constant. The depolarized light intensity changed little and remained almost constant, which meant that the changes of optical activity of the pulp suspension were small. On the other hand, the reference light intensity, the denominator in Eq. 1, increased greatly.

Figure 2 plots depolarized light and reference light on an X-Y graph. Flocculation shifted the relationship of these two light intensities. At the same depolarized light intensity, the reference light intensity increased with flocculation. Before the retention aid addition, large quantities of filler were suspended, and scattered the reference light. Flocculation caused some suspended fillers to be reduced and be retained on the fibers. The mass distribution of the pulp suspension also became nonuniform because of flocculation, and the incident light could easily pass through the thin local areas between flocs and decay to a lesser degree then was the case before flocculation.

Effects of zeta potential on flocculation

Polymer properties are listed in **Table I**, and experimental conditions are summarized in **Tables II and III**.

Wood-containing grade

Bleached hardwood kraft pulp and groundwood pulp were mixed at a 60:40 ratio, and 20% talc was added. The sample was diluted with tap water to 0.5% consistency. The pH range was 6.9–7.3 except in Case 4, No. 8, where the pH was reduced to 5.5 by alum. Chemicals were added sequentially to the sampling tank, and the consistency output signal, given by Eq. 1, and zeta potential were monitored. Zeta potential was based on the streaming potential principle and was calibrated following the method of my previous study *(6)*.

Case 1: p-DADMAC (polydiaryldimethylammonium chloride) + anionic PAM (**Figs. 3 and 4**)

1. When low charge, high molecular weight anionic polyacrylamide (charge density = 1.1 meq/g, MW = 12 million) was added, the zeta potential of the sample remained at –14 mV. Flocs were not formed.
2. p-DADMAC, the highly charged cationic polyelectrolyte, was added at 400 ppm to 700 ppm to adjust the zeta potential just above the isoelectric point. p-DADMAC did not cause flocculation. Anionic PAM, which was added after p-DADMAC, caused flocculation.

Case 2: p-DADMAC + bentonite + anionic PAM (**Figs. 5 and 6**)

3. Bentonite and anionic PAM were added sequentially at 0.5% and 300 ppm, respectively. These additives did not cause large zeta potential changes. Bentonite alone had no flocculation capability. When anionic PAM was added, strong flocculation was observed.
4. Zeta potential was increased to +1 mV at 500 ppm addition of p-DADMAC. Flocculation occurred twice, at the addition of bentonite and anionic PAM. It was interesting to note that bentonite created flocs when the zeta potential was near the isoelectric point. This was in contrast to experiment No. 3. The decrease in zeta potential by bentonite was much larger than in experiment No. 3.

Case 3: p-DADMAC + cationic PAM + bentonite (**Figs. 7 and 8**)

5. Low charge, high molecular weight cationic PAM (charge density = 1.4 meq/g, MW = 3 million) was used in this case. Cationic PAM (300 ppm) and bentonite (0.5%) did not cause flocs. Zeta potential was –14 mV to –12 mV.
6. Zeta potential was increased to –4 mV by p-DADMAC (400 ppm) and was further increased to 0 mV by cationic PAM (300 ppm) and then decreased to –10 mV by bentonite (0.5%). Strong flocculation occurred by bentonite.

II. Wood-containing grade

LBKP/GP[a] = 60/40, talc = 20%, pH = 6.9 - 7.3 (Case 4, No. 8, pH = 5.5)
Original zeta potential was from - 14 mV to -15 mV
( ) = zeta potential in millivolt after chemical addition
Underline = flocculation

Case	No.	p-DADMAC, ppm	Alum, %	C-PAM-2, ppm	Bentonite, %	A-PAM, ppm
1	1					300 (-12)
	2	700 (+5)				300 (+ 1)
2	3				0.5 (-15)	300 (-15)
	4	500 (+1)			0.5 (-6)	300 (- 7)
3	5			300 (-12)	0.5 (-14)	
	6	400 (-4)		300 (0)	0.5 (-8)	
4	7			300 (-14)		
	8		3 (-4)	300 (+ 8)		

[a] Bleached hardwood kraft pulp/groundwood pulp

III. Wood-free grade

LBKP[a] = 100%, PCC = 15%, pH = 7.7 - 7.9
Original zeta potential was from -12 mV to -13 mV
( ) = zeta potential in millivolt after chemical addition
Underline = flocculation

Case	No.	C-starch, %	C-PAM-1, ppm	C-PAM-2, ppm	C-PAM-3, ppm	Bentonite, %	A-PAM, ppm
5	9			300(-8)			
	10	1.2(-3)		300(-2)			
6	11		300(-7)				
	12	1.2(-4)	300(-1)				
7	13				300(-8)	0.5(-12)	
	14	1.2(-3)			300(0)	0.5(-5)	
8	15					0.5(-12)	300(-12)
	16	1.2(-3)				0.5(-5)	300(-8)

[a] Bleached hardwood kraft pulp

Case 4: Alum + cationic PAM

7. Addition of cationic PAM (300 ppm) produced small flocs. The zeta potential did not change.

8. Prior to adding cationic PAM, the zeta potential was adjusted to –2 mV by alum (3%). The zeta potential was further increased by cationic PAM (300 ppm) to +8 mV. Considerable flocculation was observed with cationic PAM addition. The zeta potential changes caused by cationic PAM and bentonite in No. 6 were greater than No. 7. This difference was more pronounced in Case 4.

Wood-free grade

Fifteen percent precipitated calcium carbonate was blended with hardwood bleached kraft pulp and diluted with tap water to 0.5% consistency.

Case 5: Cationic starch + cationic PAM

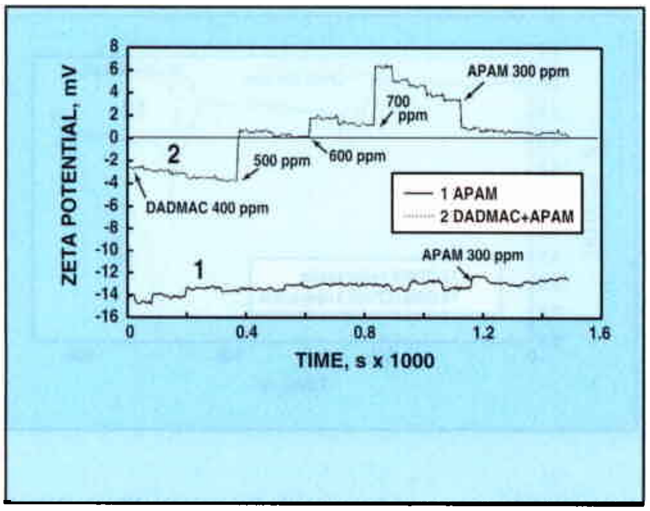
9. Low charge, high molecular weight cationic PAM (charge density = 1.4 meq/g, MW = 3 million) was added in amounts of 150 ppm and 300 ppm. Flocculation occurred at each addition.

10. Cationic starch was added (1.2%) and the zeta potential increased from –13 mV to –3 mV. Flocs were created by cationic PAM. The shift in zeta potential by cationic PAM addition was smaller when the cationic starch was added first.

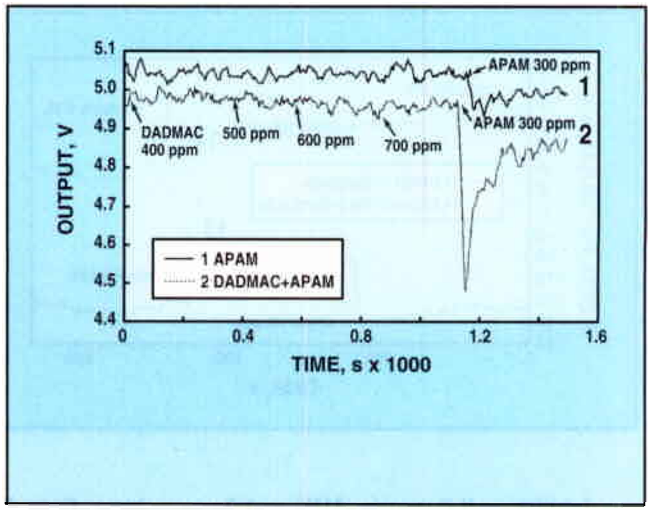
In all cases of wood-containing grade, the flocculation peaks were sharp and decayed rapidly with time. In Case 5 of the wood-free grade, the flocculation peaks decreased slowly. Flocs of chemical pulp were resistant to hydrodynamic shear.

Case 6: Cationic starch + cationic PAM

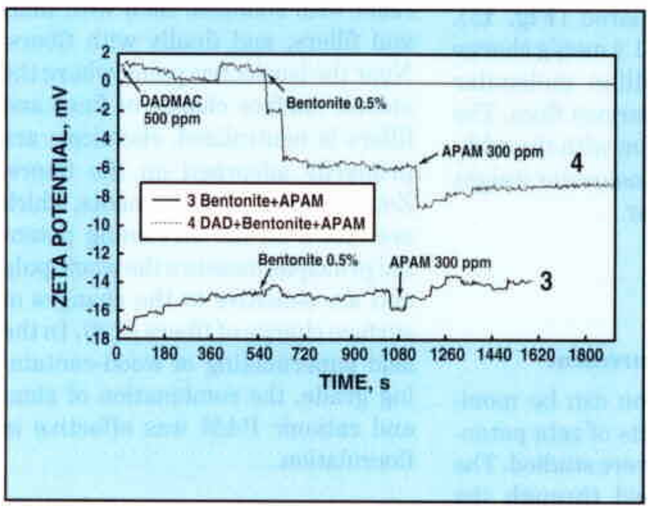
11. Medium charge, medium molecular weight cationic PAM (charge



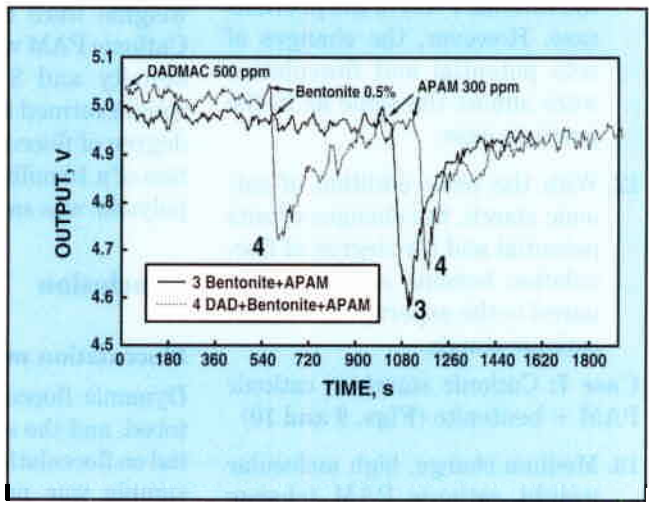
3. Zeta potential (A-PAM). LBKP/GP 60/40, talc 20%. Case 1, see Table II.



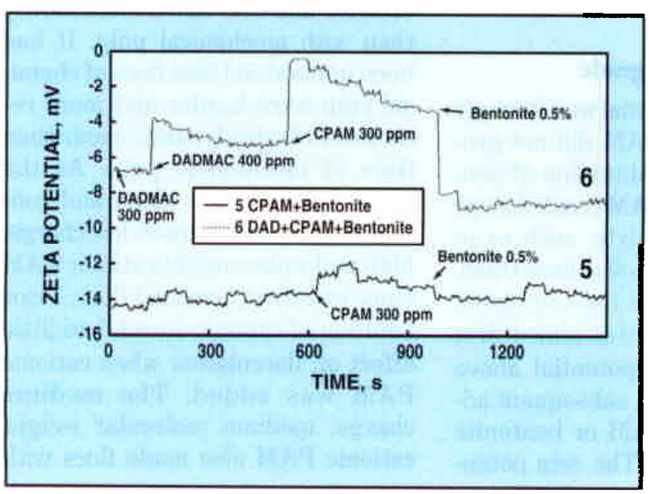
4. Output charge (A-PAM). LBKP/GP 60/40, talc 20%. Case 1



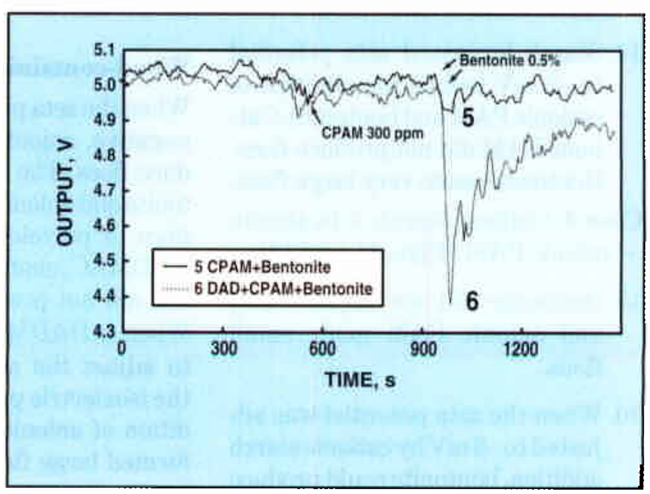
5. *Zeta potential (bentonite + A-PAM). LBKP/GP 60/40, talc 20%.* Case 2, see Table II.



6. Output (bentonite + A-PAM). LBKP/GP 60%, talc 20%. Case 2

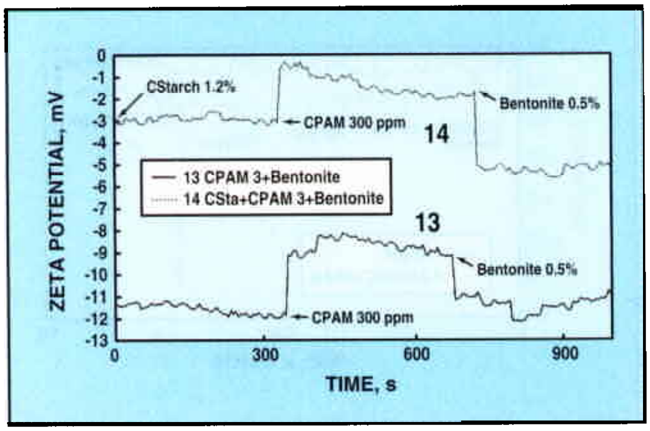


7. Zeta potential (C-PAM+bentonite). LBKP/GP 60/40, talc 20%. Case 3, see Table II.

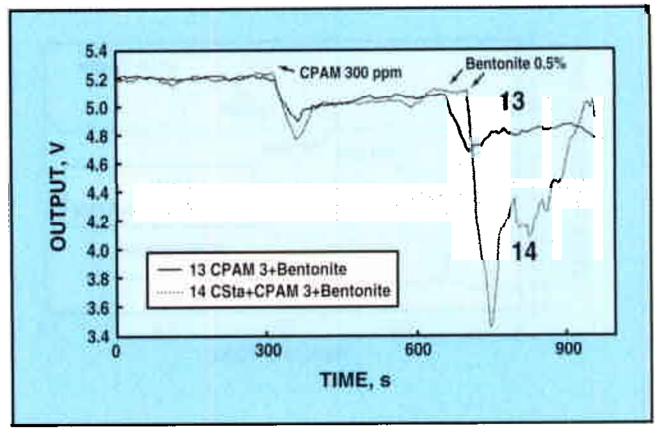


8. Output (C-PAM+bentonite). LBKP/GP 60/40, talc 20%. Case 3

9. Zeta potential (C-PAM 3 + bentonite). LBKP 100%, PCC 15%. Case 7, see Table III.



10. Output (C-PAM 3 + bentonite). LBKP 100%, PCC 15%. Case 7



density = 2.6 meq/g, MW = 1.5 million) was used. Its charge density was higher, and molecular weight was lower than that of the cationic PAM of the previous case. However, the changes of zeta potential and flocculation were almost the same as in the previous case.

12. With the prior addition of cationic starch, the changes of zeta potential and the degree of flocculation became smaller, compared to the experiment without cationic starch.

Case 7: Cationic starch + cationic PAM + bentonite **(Figs. 9 and 10)**

13. Medium charge, high molecular weight cationic PAM (charge density = 3.3 meq/g, MW = 10 million) was selected. Cationic PAM did not produce flocs. Bentonite formed small flocs.

14. Starch increased zeta potential to –3 mV before the addition of cationic PAM and bentonite. Cationic PAM did not produce flocs. Bentonite made very large flocs.

Case 8: Cationic starch + bentonite + anionic PAM **(Figs. 11 and 12)**

15. Bentonite did not create flocs, and anionic PAM made small flocs.

16. When the zeta potential was adjusted to –3 mV by cationic starch addition, bentonite could produce large flocs. The degree of flocculation by anionic PAM was small.

Cationic PAMs with different charge densities and molecular weights were compared **(Fig. 13).** Cationic PAM with 1.4 meq/g charge density and 3 million molecular weight formed the largest flocs. The degree of flocculation with the addition of a 10 million molecular weight polymer was smaller.

Conclusion

Flocculation measurement

Dynamic flocculation can be monitored, and the effects of zeta potential on flocculation were studied. The sample was pumped through the measuring line, and hydrodynamic forces were constantly applied to the pulp suspension during measurement.

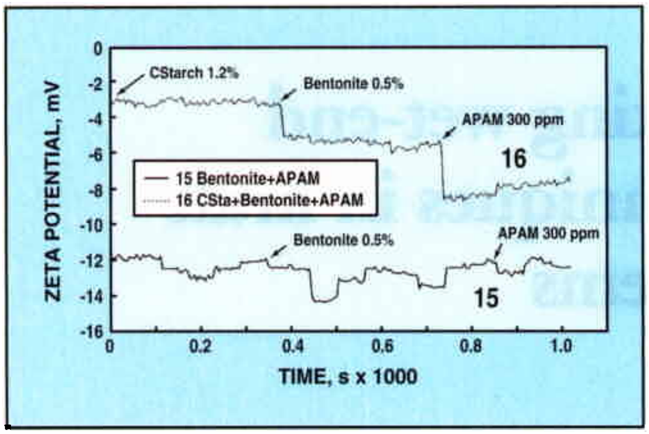
Wood-containing grade

When the zeta potential was strongly negative, anionic PAM did not produce flocs. The combination of bentonite and anionic PAM created large flocs. A polyelectrolyte, such as p-DADMAC, neutralized anionic trash, but did not produce flocs by itself. When p-DADMAC was added first to adjust the zeta potential above the isoelectric point, subsequent addition of anionic PAM or bentonite formed large flocs. The zeta potential responded more readily to chemical addition near the isoelectric point than in the highly negative area. This is because wet end chemicals first react with solubles, then with fines and fillers, and finally with fibers. Near the isoelectric point, where the anionic surface charge of fines and fillers is neutralized, chemicals are primarily adsorbed on the fibers. Zeta potential measurements, which are based on the streaming potential principle, measure the whole pulp and are sensitive to the changes of surface charge of fibers *(3, 6)*. In the acid papermaking of wood-containing grade, the combination of alum and cationic PAM was effective in flocculation.

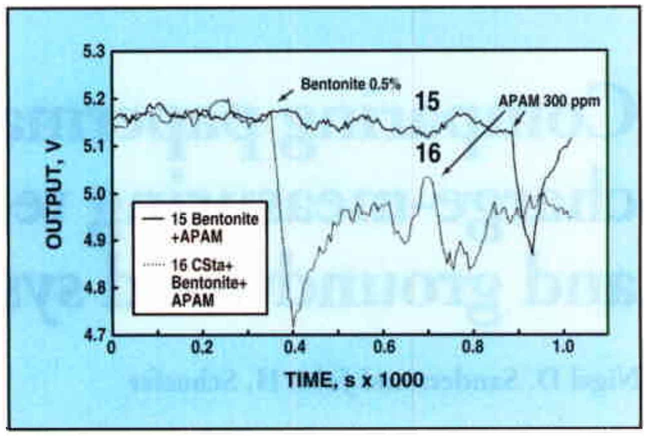
Wood-free grade

In the neutral papermaking of wood-free pulp, the flocculation peaks were broader and decreased more slowly than with mechanical pulp. It had been understood that flocs of chemical pulp were harder and more resistant to hydrodynamic shear than flocs of mechanical pulp. As the wood-free pulp was clean and contained little anionic trash, low charge, high molecular weight cationic PAM alone effectively created flocs. Prior addition of cationic starch had little effect on flocculation when cationic PAM was added. The medium charge, medium molecular weight cationic PAM also made flocs with

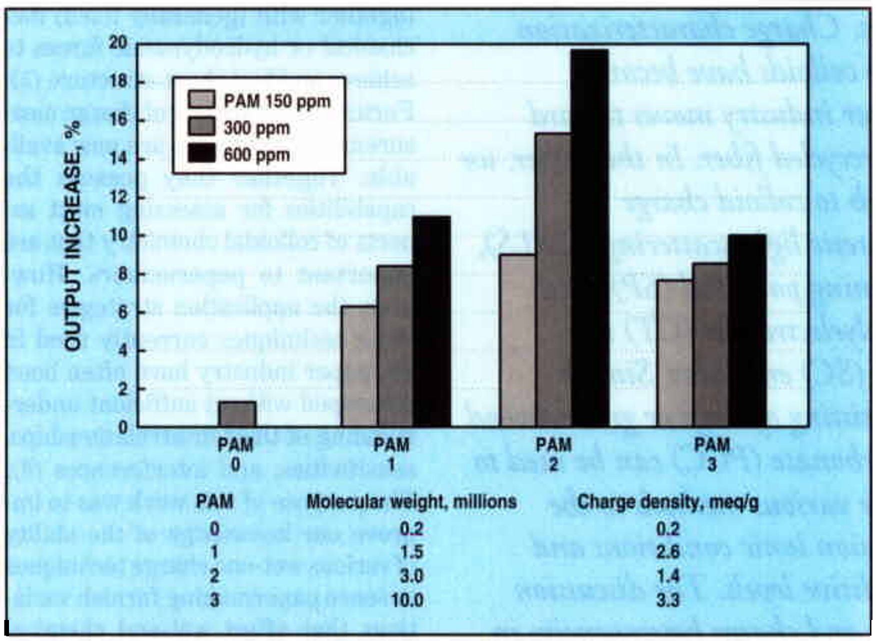
11. Zeta potential (bentonite + A-PAM). LBKP 100%, PCC 15%. Case 8, see Table III.



12. Output (bentonite + A-PAM). LBKP 100%, PCC 15%. Case 8



13. *Effect of MW on flocculation. LBKP 100%, PCC 15%, pH 7.7–7.9.*



the same intensity. But when cationic starch was added before the cationic PAM, the degree of flocculation decreased greatly. The combination of cationic PAM and bentonite worked well when the zeta potential had been adjusted first to the isoelectric point by cationic starch. At the strongly negative zeta potential, the combination of bentonite and anionic PAM was effective in flocculation. The suitable retention aid for the single component usage was selected from several cationic PAMs with various molecular weights and charge densities. Low charge, high molecular weight cationic PAM had the best function of flocculation. Other PAMs whose molecular weights were either lower or higher than the selected PAM did not form large flocs.

Recommendation

It was found that zeta potential affects the degree of flocculation in various retention systems, including bentonite microparticle retention systems. Hence there is a possibility that first pass retention decreases unexpectedly when the zeta potential changes from the isoelectric point to negative or, in another case, when large flocs form suddenly and damage sheet formation as the zeta potential changes in the opposite direction. In order to maintain stable papermaking performance and produce paper of good quality, the zeta potential must be controlled properly. TJ

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