On-line zeta potential analyses of a fine paper machine and a newsprint paper machine

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ABSTRACT: A new method for calibrating an on-line sensor has been developed. The magnitude and trend of properly calibrated on-line streaming potential measurements correlated well with off-line electrophoresis measurements. The slight deviation between two measurements showed the absorptivity difference of cationic chemicals with furnish components. In a fine paper machine trial, zeta potential did not fall immediately, even after the cationic polymer addition was ended. This was attributed to the residual effects of polymers remaining in the recirculating white water system. In a newsprint paper machine trial, zeta potential varied due to unknown disturbances. By multiregressional analysis of the process data base, the pulp freeness and thermomechanical pulp ratio were found to be the most critical process parameters in that system. These phenomena were further elucidated using the on-line sensor in a laboratory.

KEYWORDS: Calibration, electrical properties, electrophoresis, on-line measurement, paper machines, procedures, process control, regression analysis, sensors, statistical analysis, wet ends, zeta potential.

In the past decade, we have made wet-end analyses on more than 10 paper machines to improve paper machine performance and paper quality *(1–4)*. Realizing that the zeta potential is one of the most important process parameters, we have accumulated data using a microelectrophoresis instrument and recommended the optimum zeta potential range to papermakers in our mills when required. The instrument measures the speed of movement of fines under an applied electric field. Although a microelectrophoresis instrument is a very useful tool, its major drawback is that it is an off-line, time consuming manual instrument.

Therefore, on-line charge analyses have been needed over the years. Recently, several evaluation studies of new on-line streaming potential sensors have been published. An on-line zeta potential sensor utilizes the streaming potential principle, which consists in forming a pulp pad, pumping white water through the pad, and measuring the electrical charge of streaming potential across the pad. The zeta potential is calculated from the Helmholtz-Smoluchowski equation.

Crill made a comparison between the data obtained from her on-line sensor, the fiber charge analyzer (FCA), and an off-line mobility meter *(5)*. Both measurements had good correlation but the magnitude of the FCA was 100 times larger than that of the mobility meter. Crill noted that the FCA numbers were relative and could be compared only within a given system.

In Penniman's experiments, a cationic wet-strength resin was added to bleached kraft pulp *(6)*. On-line streaming potential and off-line electrophoresis compared closely and responded in a similar manner. However, the cationic demand observed

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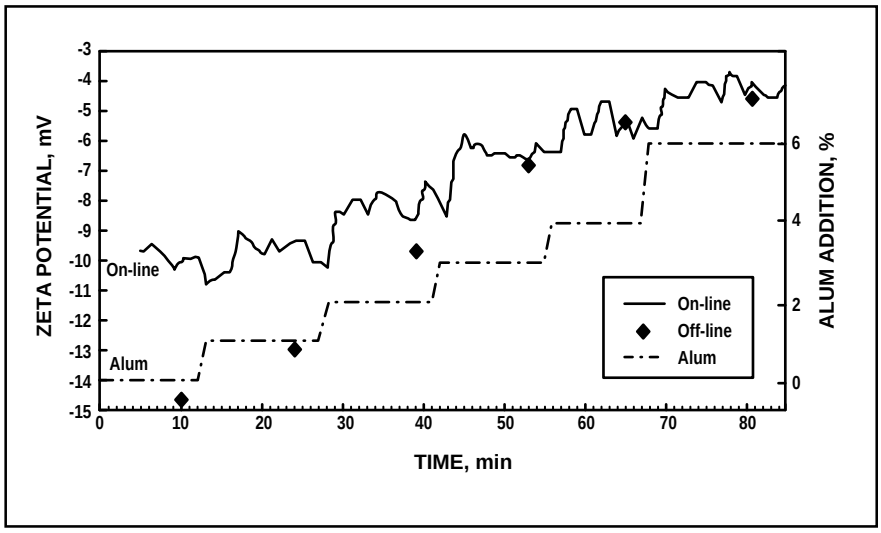
from the chemical addition vs. the zeta potential plot was four times larger in streaming potential data than in microelectrophoresis data.

Scott added various cationic chemicals to anionic pulp furnishes and compared the responses of two on-line sensors (labeled Sensor 1 and Sensor 2) with standard off-line microelectrophoresis measurements *(7–8)*. All sensors showed similar changes to chemical treatments, but the magnitude of charge was quite different among them. The absolute value of electrophoresis data was about 20 percentage points lower than that of on-line Sensor 1. He attributed the lower magnitude of the off-line data to the time elapsed in preparing samples. But his theory did not explain why the zeta potential magnitude measured by streaming potential Sensor 2 was 10 times larger than that measured by Sensor 1.

We also had similar experiences a few years ago in our laboratory and had concluded at that time that on-line streaming potential data were only relative and of a limited value in a given system. Even so, we had expected that an on-line sensor could monitor variations in the furnish charge and hence predict a wet-end upset. As a test, we installed an on-line zeta potential meter on a commercial paper machine. But the large difference in magnitude of on-line data from the previously accumulated microelectrophoresis data was very confusing to papermakers in a mill and was difficult to interpret.

Generally, any instrument must be calibrated with standard material before it is to be used. A microelectrophoresis instrument, for example, is usually calibrated with a titanium dioxide suspension of known zeta potential. On the other hand, there is no standard sample for adjusting a streaming potential instrument. As the instrument measures the subtle changes of streaming potential in the range of a few millivolts, it is very sensitive to environmental conditions. However, it is installed on a paper machine wet-end, where conditions are the most severe in a mill. When zeta potential fluctuations are observed, it is difficult to tell whether these are caused by a process upset or because of instrument failure, as there is no suitable method to calibrate and confirm the validity of the on-line instrument.

1. Effect of alum addition on the charge of model newsprint furnish (pH 6)



Even if the data are validated, a paper machine wet-end is a very complicated process, and the process disturbances that give rise to the zeta potential fluctuations are not well understood. Therefore a numerical method needs to be developed to elucidate the effects of process parameters on furnish charges.

Objectives

The purposes of this study are as follows:

1. To develop a method to calibrate an on-line streaming potential sensor
2. To analyze the charge of various furnish components in a laboratory
3. To determine the effects of process parameters on zeta potential variation on a commercial paper machine by statistical analysis.

Calibration of streaming potential sensor

Streaming potential principle

The streaming potential is converted to zeta potential by the Helmholtz-Smoluchowski equation, given the specific conductance and the temperature of the sample. The viscosity and dielectric constant is calculated as a function of the temperature. The Helmholtz-Smoluchowski equation is given below:

$$\zeta = 4\pi\eta\lambda E/\varepsilon P \qquad (1)$$

where

ζ = zeta potential

η = viscosity

λ = conductivity

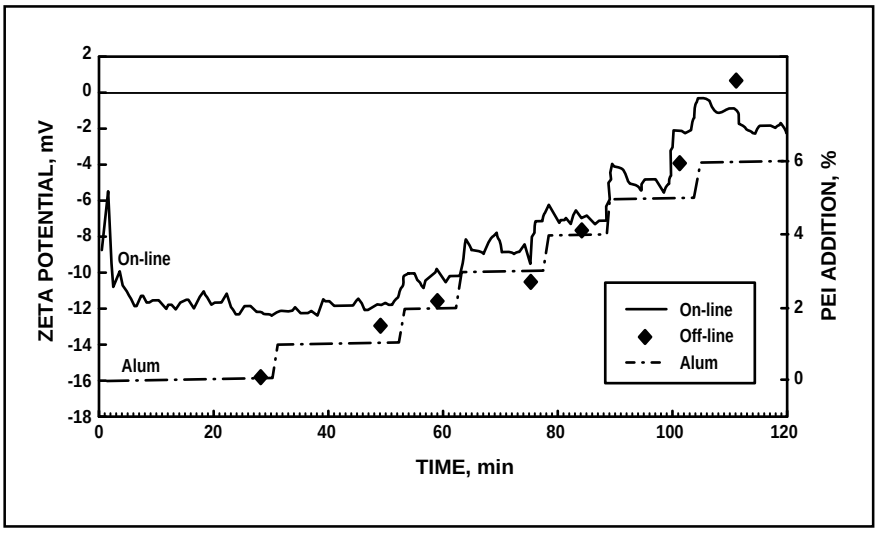
E = streaming potential

ε = dielectric constant

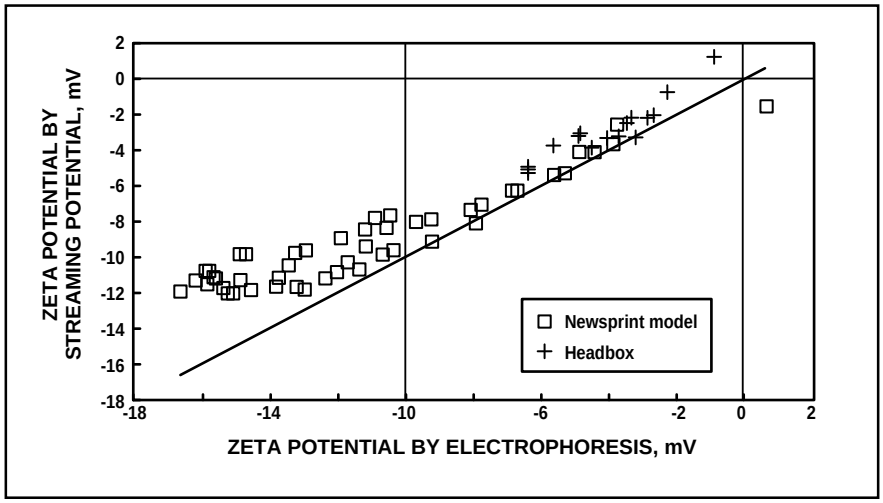
P = hydrodynamic pressure.

In conductivity measurements, an electric pressure is applied to electrodes and the electric current flowing between two electrodes immersed in a electrolyte solution is measured. In streaming potential measurements, the white water flows through the formed pulp pad under the applied hydraulic pressure, and the electric pressure generated between two electrodes positioned on

2. Effect of PEI addition on the charge of newsprint model furnish (pH 6)



3. Comparison of streaming potential with electrophoresis



both sides of the pulp pad is detected. Conductivity and streaming potential are completely different properties yet they are similar in the way that each uses two electrodes.

There are many factors that affect the sensitivity of the streaming potential instrument. Among them, the surface conditions of electrodes and the electrical circuit efficiency to amplify the generated streaming potential are considered to be the main factors. It was assumed that if we measure conductivity and streaming potential with the same electrodes and amplifier, both conductivity and streaming potential would be affected to the same extent by the conditions of electrodes and circuit. Then the streaming potential would be calibrated by measuring conductivity with streaming potential electrodes.

Calibration procedure

The calibration procedure is as follows.

1. Sodium chloride solutions of different concentrations were prepared.
2. The conductivity of the sodium chloride solutions was measured with the standard laboratory conductivity meter.
3. The same solutions were measured with the standard on-line conductivity meter. The meter consisted of electrodes and an amplifier, and was calibrated by adjusting the amplifying gauge. The number of the gauge was defined as F1 and was called the amplifying factor.
4. The on-line conductivity meter was separated into electrodes and the amplifier. The amplifier was connected to the streaming potential electrodes. The streaming potential electrodes were immersed in the sodium chloride solutions and conductivity was measured. This "hybrid conductivity meter" was calibrated by adjusting the amplifier gauge. The amplifying factor was defined as F2. The components of the "hybrid conductivity sensor" were as follows: [Electrodes of streaming potential] →[Amplifier of conductivity meter].
5. When F2 > F1, the streaming potential electrodes were evaluated as not sensitive enough and should be amplified further. When F2 < F1, the electrodes were regarded too sensitive and the amplifying factor should be reduced. When F2 = F1, the electrodes had a suitable sensitivity and there was no need for compensation. In either case, the streaming potential adjustment factor (A) was calculated as $A = F1/F2$.

The adjustment factor (A) was introduced into the original equation as:

$$z = 4\text{phl}E/\text{e}P \times 1/A \qquad (2)$$

where

ζ = zeta potential

η = viscosity

λ = conductivity

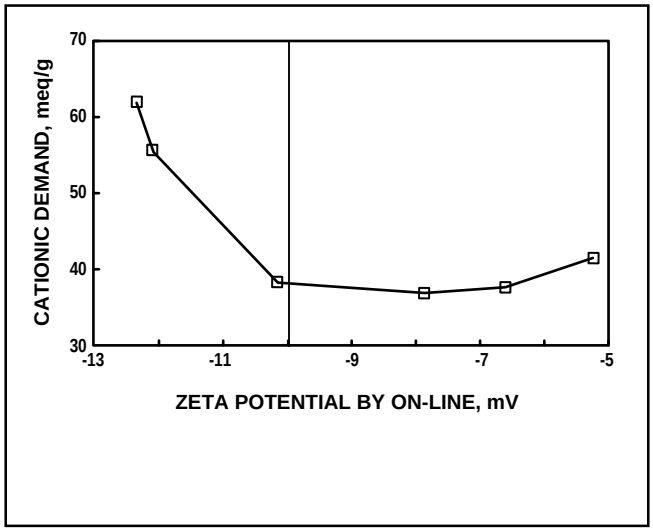
E = streaming potential

ε = dielectric constant

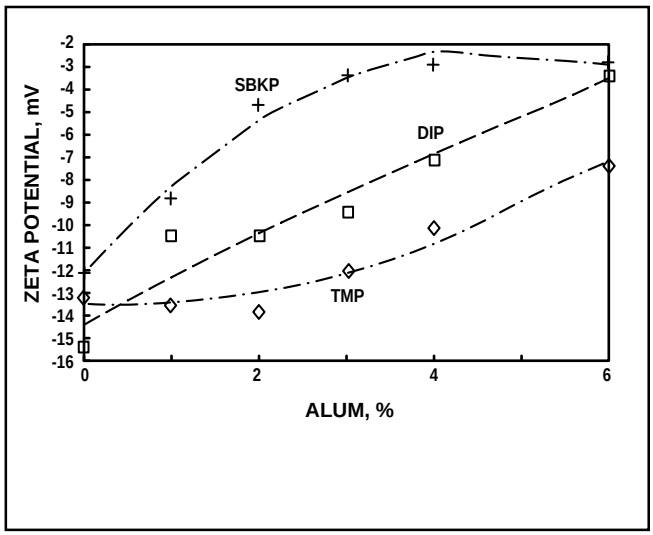
P = hydrodynamic pressure

A = adjustment factor.

4. Effect of alum on cationic demand of newsprint model furnish (pH 6)



5. Effect of alum on the zeta potential of TMP, SBKP and DIP



Charge analysis of pulp furnish in the laboratory – I

Comparison of on-line and off-line measurements

The pulps were sampled from the stuff box of the paper machine and were used in this experiment. Each pulp consistency was 3% and the pulp was not washed before use because anion trash contained in the white water of the pulp was known to affect wet-end performance and we wanted to simulate the wet-end phenomena of a commercial paper machine. Model newsprint furnishes were prepared by blending 15% chemical pulp, 35% mechanical pulp and 50% deinked pulp and were diluted to 0.5% consistency with mill water.

Sulfuric acid and sodium hydroxide solution were used for adjusting the initial pH to 4.5 and 6.0, respectively. Various cationic chemicals such as alum, dry-strength resin PAM (low molecular weight polyacrylamide), retention aid (high molecular weight PAM), and PEI (polyethyleneimine, a low molecular weight and highly charged polymer) were added to the pulp suspension in each experiment. The streaming potential was measured every 1 min by an on-line sensor. A sample was taken, filtered to remove fibers by 100-mesh wire, and measured for zeta potential by an off-line electrophoresis meter. The same experiments were performed using a paper machine headbox furnish.

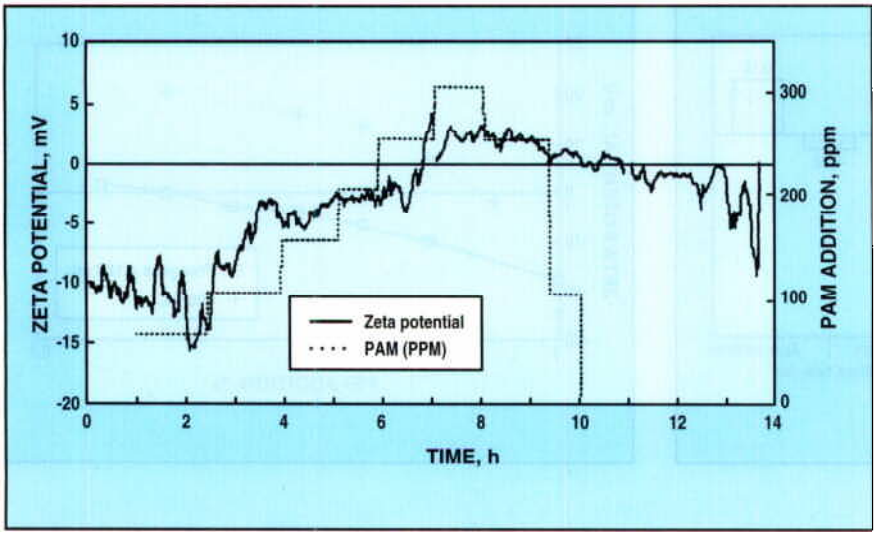
Figure 1 shows the change in zeta potential when alum was added to the model furnish with initial pH 6.0. The on-line and off-line data correlated well. When observed carefully, the magnitude of on-line data was slightly smaller than off-line data when the alum addition level was less than 2%. This result is the opposite of that found by Scott *(7–8)*. In his study, the magnitude of on-line data was always larger than off-line data.

The PEI addition experiment to the newsprint model furnish gave similar results (**Fig. 2**). We performed a total of 11 experiments by the same method. To determine the general relationship, all of the experimental data were plotted in **Fig. 3**. In the zeta potential range of less than –10 mV, the magnitude of on-line data was smaller than off-line, and the on-line data were virtually constant. In the zeta potential range of –10 mV to the isoelectric point, the on-line data and off-line data were almost the same and had a linear relationship.

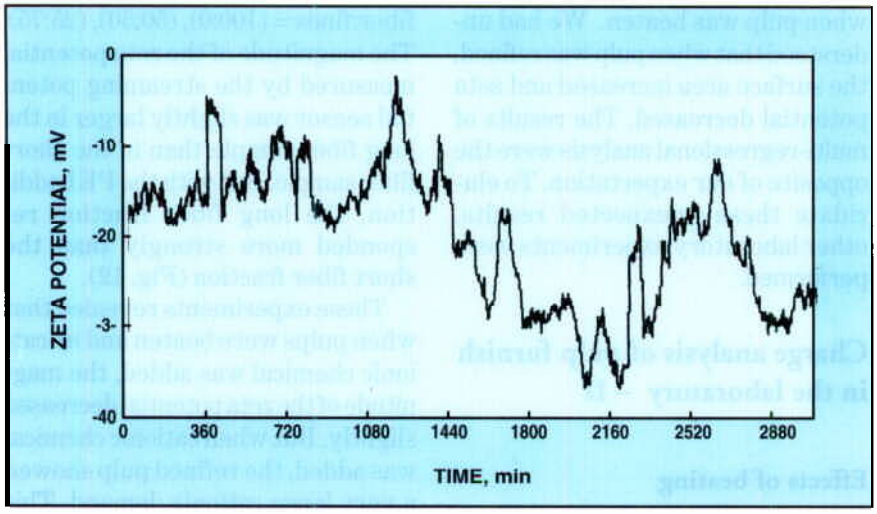
The electrophoresis instrument measured only the fines fraction that was separated with a 100-mesh screen. Cationic chemicals added to papermaking furnish first react with the soluble anionics. They then react with fines and fillers because they have a large specific surface area. Off-line data responded from the beginning to chemical addition because they measured only the fines charge. On the other hand, the streaming potential instrument measured the whole-pulp charge including fibers and fines. The contribution of the fines' charge to the total charge in the on-line measurement was smaller than found by the electrophoresis method. Until the cationic chemical reaction with the fines was completed, the total charge did not change markedly. When more chemical was added to the furnish, it became adsorbed on the long fiber surface and the whole-pulp charge increased. Figure 3 shows that the alum reaction with solubles and fines was completed at a zeta potential of –10 mV.

One of the important tasks of wet-end chemistry is to improve the first-pass retention. Almost all long fibers are retained on the paper machine wire, and part of the fines can pass through the wire in the sheet forming process. Thus more fines should

6. Effects of cationic PAM on the zeta potential of a fine paper machine



7. Zeta potential of a newsprint paper machine for regression analysis



be retained in the sheet to improve the first pass retention. In this procedure, cationic chemical serves as an anionic trash scavenger and neutralizes the anionic charges of solubles and fines. The amount of anionic trash is measured as the cationic demand. The variation of cationic demand with addition of alum is illustrated in Fig. 4. The cationic demand decreased with the addition of alum. At a zeta potential of –10 mV, it became constant. This cationic demand plateau coincided well with Fig. 3. Thus, the optimum range of zeta potential in this newsprint furnish was considered to be from –10 mV to the isoelectric point.

Before we used an on-line sensor, the optimum range of zeta potential was determined on this newsprint paper machine by means of electrophoretic data accumulated from a number of mill trials. The optimum range was from –10 mV to zero mV. It was concluded that the calibrated on-line sensor had a good correlation with the off-line sensor, and that the slight deviation between the two measurements gave useful information on the surface charge of furnish components.

Charge response of various pulps

In Japan we use various kinds of pulp furnish for newsprint stock. In order to study the contribution of each pulp furnish, three pulps were prepared: semibleached softwood kraft pulp, thermomechanical pulp and deinked pulp. Alum was added to each pulp and the zeta potential was measured with the on-line sensor (Fig. 5). Thermomechanical (TMP) pulp responded least to alum addition, kraft (SBKP) pulp gave the highest response, and deinked (DIP) pulp responded to an intermediate degree to alum addition. Hence TMP had the largest cationic demand. It is known that TMP contains various kinds of anionic trash in white water, such as lignin, hemicellulose, humic acid, wood resin, fatty acid, sodium silicate derived from hydrogen peroxide bleaching and so forth *(9)*. TMP also contains large quantities of pulp fines. In addition, carboxyl groups of cellulose and hemicellulose are retained on TMP pulps. These components consume cationic chemicals. Thus TMP is the most important pulp in the wet-end control of a newsprint paper machine.

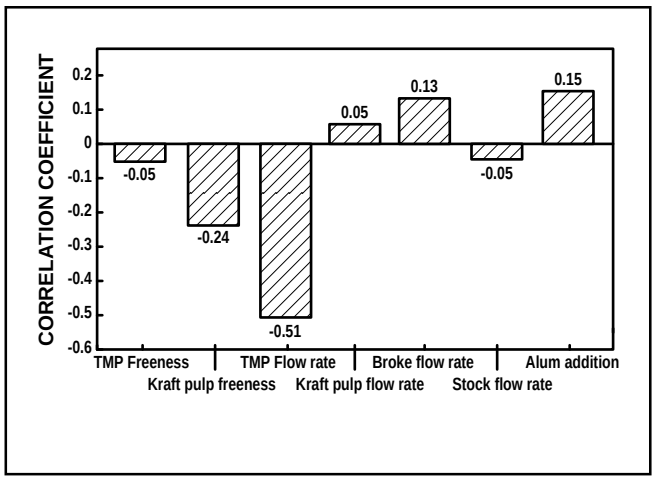
Zeta potential analyses of commercial paper machines

After the calibration and laboratory studies, we installed an on-line zeta potential sensor on high-speed commercial paper machines: first on a fine paper machine as a preliminary trial and next on a newsprint paper machine.

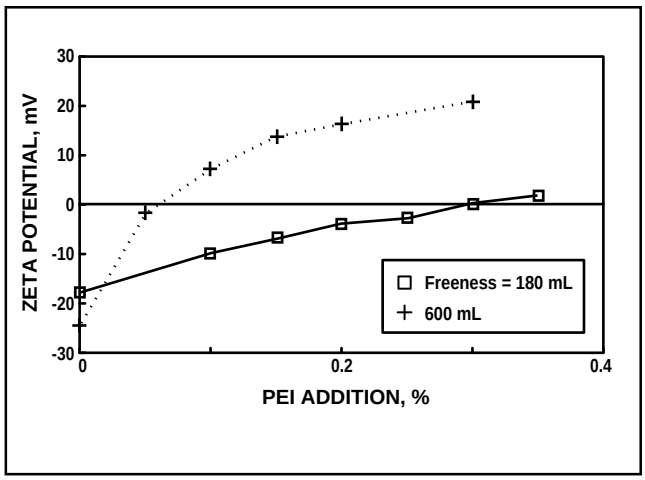
Fine paper machine trial

The fine paper machine was using 100% bleached hardwood kraft pulp. As that kraft pulp mill was a modern facility with a good washing capacity, the pulp was well washed and clean. When the addition of cationic retention aid (high molecular weight, low-charge PAM) was increased, the zeta potential increased from minus to plus over the isoelectric point (Fig.

8. Correlation coefficient of the zeta potential of a paper machine



9. Effect of beating on the zeta potential of hardwood bleached kraft pulp



6). It was interesting to note that even after the polymer addition was decreased, the zeta potential remained high and did not drop immediately. This was due to the residual effects of polymers remaining in the recirculating white water system.

Newsprint paper machine trial

Next, we moved the sensor to the newsprint paper machine. In addition to the zeta potential, every minute we monitored other process parameters such as pH, conductivity, chemical addition, pulp flow rate, pulp freeness, basis weight, moisture, and so forth and made a computer database.

During two days trial, zeta potential changed between –40 mV and –5 mV **(Fig. 7**). Pulp freeness, pulp flow rate, and alum addition also varied. Important process variables were extracted by multi-regressional analysis from the accumulated data base.

The most critical process variable was found to be the flow rate of TMP (**Fig. 8**). Its correlation coefficient was negative, which meant that the increase of TMP decreased the zeta potential. The coefficient of alum addition was positive, which was interpreted to mean that alum addition increased the zeta potential. These results fitted well with our previous laboratory studies.

However, coefficients of TMP freeness and kraft woodpulp freeness were negative. This suggested that the zeta potential increased when pulp was beaten. We had understood that when pulp was refined, the surface area increased and zeta potential decreased. The results of multi-regressional analysis were the opposite of our expectation. To elucidate these unexpected results, other laboratory experiments were performed.

Charge analysis of pulp furnish in the laboratory – II

Effects of beating

Bleached softwood kraft pulp and hardwood kraft pulp were beaten and were diluted at 0.5% consistency. To these pulp samples PEI was added and the zeta potential was measured by the on-line sensor in the laboratory (**Fig. 9 and 10**). Before PEI was added, the magnitude of the zeta potential was slightly smaller in beaten pulp than in unbeaten pulp. This was the same result as that obtained with the newsprint paper machine trial. However, when PEI was added, unbeaten pulp responded to a greater extent that beaten pulp. Beaten pulp showed larger cationic demand than unbeaten pulp (**Fig. 11**).

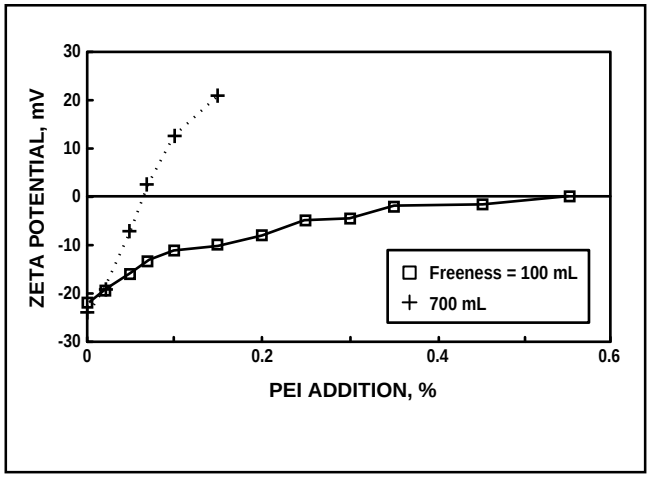
Next, TMP was fractionated into a long fiber fraction and a fines fraction. These two fractions were blended again to prepare samples as fiber:fines = (100:0), (50:50), (25:75). The magnitude of the zeta potential measured by the streaming potential sensor was slightly larger in the long fiber sample than in the short fiber sample. But with the PEI addition, the long fiber fraction responded more strongly than the short fiber fraction (**Fig. 12**).

These experiments revealed that when pulps were beaten and no cationic chemical was added, the magnitude of the zeta potential decreased slightly. But when cationic chemical was added, the refined pulp showed a very large cationic demand. This was attributed to the specific surface area of the pulp components. A streaming potential sensor is a very suitable tool to perform these experiments because it can measure the zeta potential of whole pulp.

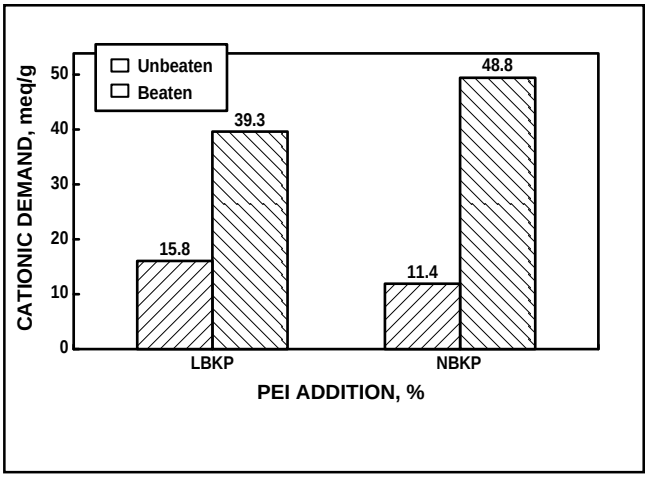
Conclusion

1. A new calibration method for an on-line zeta potential instrument was developed. The magnitude of on-line data correlated well with off-line electrophoretic data. The slight deviation observed between the two measurements in the specific range showed the absorptiv-

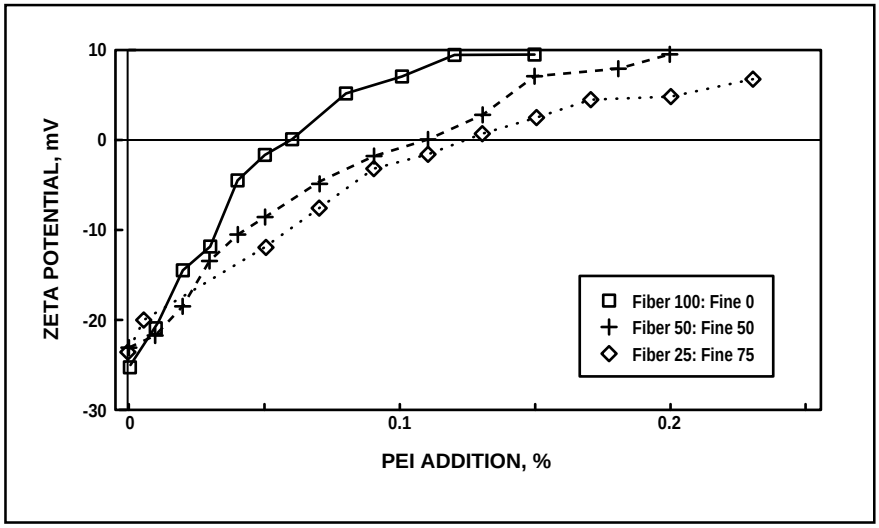
10. Effect of beating on the zeta potential of softwood bleached kraft pulp



11. Effect of beating on the cationic demand of hardwood (LBKP) and softwood (NBKP) bleached kraft pulp



12. Effect of fiber length on the zeta potential of TMP



ity difference of cationic chemicals in furnish components.

2. The properly calibrated on-line instrument was first installed on a fine paper machine, and next on a newsprint paper machine. When cationic retention aid was added to the fine paper machine, the zeta potential increased from minus to plus, as expected. However, even after the polymer addition was decreased, zeta potential did not drop immediately. This was due to the residual effects of polymers remaining in the recirculating white water system.
3. In newsprint paper machine monitoring, the zeta potential varied between –40 mV and –5 mV. Other process variables also fluctuated during that time. By computer multi-regressional analysis of accumulated data, pulp freeness and TMP furnish ratio were found to be the most critical process variable.
4. This was further elucidated in laboratory studies. When pulps were beaten and no cationic chemical was added, the magnitude of the zeta potential decreased slightly. But when cationic chemical was added, refined pulp showed a very large cationic demand. This was attributed to the specific surface area of pulp components.

These findings should contribute to improved zeta potential control in the near future. TJ

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