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# Charge-Related Measurements – A Reappraisal.

## Part 2: Fibre-Pad Streaming Potential

This article addresses concerns raised in Paper Technology in 1995 about the use and interpretation of charge-related measurements – it is Part 2 of a reappraisal, and follows the publication of Part 1 in the October issue of Paper Technology.

*The “fibre-pad streaming potential” method is becoming increasingly popular at paper mills and in the research labs of companies involved with papermaking technology. One drawback of the method, as it is commonly practiced, involves a lack of calibration to more fundamental quantities, such as zeta potential.*

*Nevertheless, progress has been achieved with respect to the precision of the method, especially at increased levels of salinity. Also, one can avoid many theoretical difficulties by using the method to determine endpoints of charge titrations.*

*With these considerations in mind, fibre-pad streaming potential tests can reveal important information about the charge-related properties of fibre suspensions.*

As papermakers look for more precise and effective means of optimizing the addition of charged chemical additives, the fibre-pad streaming potential (SP) method stands out as an especially promising option.

A key advantage of the SP method, compared to some related methods, is the fact that measured signals originate directly on the surfaces of the fibres from which the paper will be made. However, the compressible nature of papermaking fibres has led some researchers to seriously question the validity and calibration of results from SP tests.

In 1995 Jaycock noted that results of SP tests are expected to be highly dependent on the density of the fibre pads formed during the tests.<sup>(1)</sup> This fact had been demonstrated repeatedly in earlier studies.<sup>(2-5)</sup> Nevertheless, the most commonly used modern devices for measuring the streaming potential of papermaking fibre surfaces do not even consider this parameter.<sup>(6-21)</sup>

Rather, the SP devices most commonly used for papermaking applications differ in some key ways from those that have been used in fundamental research.<sup>(23-25)</sup> The present paper re-examines such issues in the light of more recent work.

To begin, it is worth quoting from the 1995 article.<sup>(1)</sup> The second conclusion of that article reads, “The commercially available streaming potential devices that rely on pad formation assume that the Helmholtz-Smoluchowski equation is valid. Evidence examined in this paper indicates that this is not the case. If the measured potential in these devices is to remain proportional to the zeta potential, then the pad concentration and the dimensions must remain constant. This would seem unlikely generally, but particularly if the samples studied involve pulps with different drainage characteristics.”

Furthermore, one could add, it can be expected that treatment of papermaking furnish with either highly charged additives or with high-mass flocculating polymers ought to affect the bulk, permeability, and even the uniformity of a fibre mat. As an alternative,

Jaycock advocated increased reliance on microelectrophoresis – a method for which there is a strong foundation of careful theoretical work.

Before addressing the issues raised in the preceding paragraph, it may be useful to describe the main features of the fibre-pad SP method, including the manner in which it has been applied in the case of papermaking slurry samples.

### *The streaming potential method*

Streaming potential (SP) experiments involve flow of a liquid past fixed surfaces and measurement of the flow-induced changes in an electrical potential. As has already been pointed out by Jaycock,<sup>(1)</sup> the physical phenomena giving rise to SP signals are the same as those giving rise to the SC signals discussed in Part 1 of this series.<sup>(26)</sup>

Whereas, in the case of SC tests, the instrument evaluates an alternating current signal (which, in principle, also might be detected as a voltage), the SP test simply measures the electrical potential difference between two probes on either side of a flow cell, which may include a packed bed of particles or fibres. The voltage resulting from the application of a pressure differential across the sample is compared to the baseline potential measured in the absence of applied pressure or vacuum.

In a classical SP, analysis of the material of interest is in the form of (a) a capillary tube or a bundle of capillary tubes, (b) a thin “cell” formed by two flat plates of material, spaced a short distance apart and sealed at the edges, or (c), as shown in *Figure 1 (next page)*, a packed bed that is prepared in advance of the measurement.<sup>(27-32)</sup> In the case of either capillary tubes or thin rectangular cells, the equations needed to relate the SP output voltages to zeta potentials have been solved.<sup>(30,32-35)</sup>

In the case of packed beds the relationship between the observed streaming potential and the zeta potential of the surfaces is difficult to predict, especially if the particles have irregular shapes or unknown orientations.<sup>(2,35)</sup>

Nevertheless, results still often can be fitted to the following form of the Helmholtz-Smoluchowski equation, in which the fitting parameter  $f$  has been added as a calibration constant.

$$\zeta = 4 f \pi \eta \Omega E / (\epsilon P) \quad (1)$$

In Equation (1)  $\zeta$  is the zeta potential (usually expressed in millivolts),  $\eta$  is the viscosity of the solution,  $\Omega$  is the electrical conductivity,  $E$  is the measured change in potential resulting from the application of pressure,  $\epsilon$  is the dielectric constant of the solution, and  $P$  is the differential pressure applied across the sample.

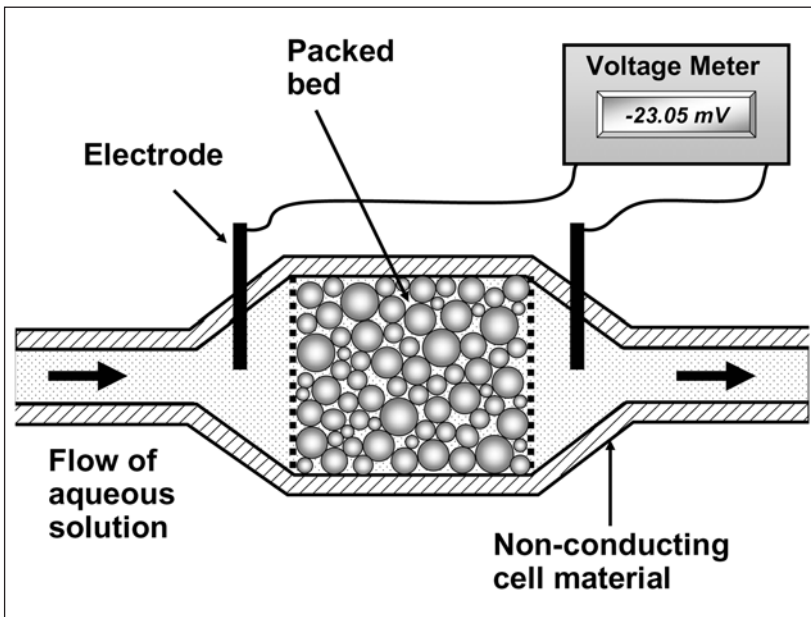


Figure 1 Schematic diagram of packed bed experiment for evaluation of streaming potential

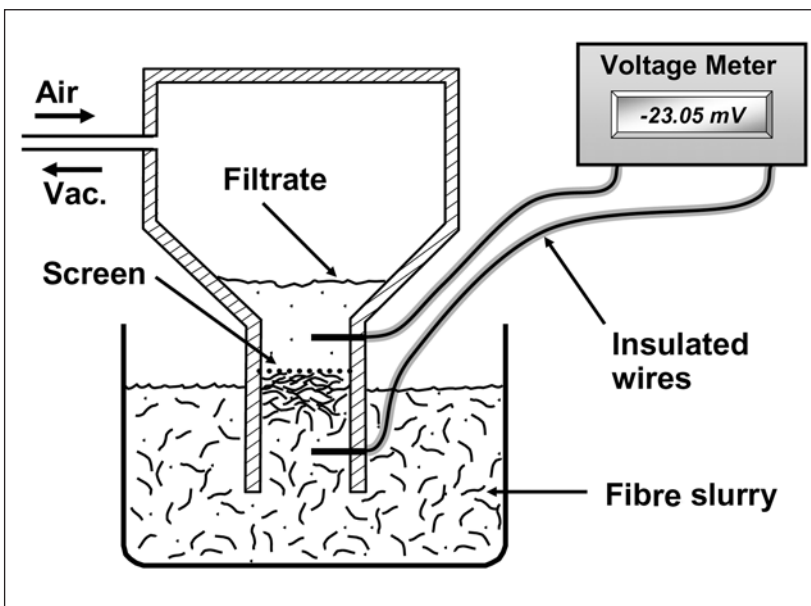


Figure 2 Schematic diagram of pad-forming streaming potential device, as used in modern papermaking applications

The reasons why the fitting parameter  $f$  is required in Equation (1) include:

(a) the fact that the laminar flow does not have a chance to become fully developed,<sup>(30)</sup>

(b) unpredictable, but finite overlap of double-layers on some of the facing surfaces, especially at the limit of low ionic strength,<sup>(33,36)</sup> and

(c) surface conduction, which is an unavoidable consequence of the presence of charged double-layers, even if the solid materials are good insulators.<sup>(27,29,37-38)</sup>

Bieffer and Mason<sup>(4)</sup> concluded that surface conduction was a main contribution to deviations of  $f$  from unity in the case of fibres if the average orientation of pore channels was allowed to vary from test to test. In addition, the presence of polyelectrolyte gel layers at the surfaces can cause some theoretical difficulties in the computation of zeta potentials.<sup>(2,37,39)</sup>

As a consequence of some of these effects, Equation (1) is expected to give increasingly reliable results as the electrical conductivity of the solution increases, reducing the relative importance of surface conductance and also reducing the extent of overlap of ionic double-layers at facing surfaces within the packed bed.

#### Pad-Forming SP Devices

For SP work related to papermaking applications, though fibres sometimes have been packed into plugs before the measurements,<sup>(40-42)</sup> most recent work has involved a new class of apparatus in which a pad of fibres is repeatedly formed on the surface of a screen.<sup>(6-20)</sup> As illustrated in Figure 2, the most popular devices use vacuum to draw a slurry of fibres toward the screen, and subsequently to draw filtrate into an upper chamber of the device.

While some of these devices give output that bears the label “zeta potential,” it is important to note, as also mentioned by Jaycock,<sup>(1)</sup> that the reported values are merely the result of application of Equation (1) with the cell constant  $f$  arbitrarily set equal to one. As already noted,<sup>(1)</sup> one would not expect quantitative agreement with zeta potential value obtained by conventional methods, including either microelectrophoresis<sup>(35)</sup> or by extrapolating SP values to zero density of the fibre pad.<sup>(2-5)</sup>

Only one author was brave enough to attempt using a cell constant with this type of device so that a fibre-pad SP device could give output that agreed, at least approximately, with actual zeta potentials.<sup>(43)</sup> It is worth noting that Ciriacks and Williams<sup>(44)</sup> were apparently successful in calculating zeta potentials that were independent of fibre-pad density, but their approach requires smooth fibres of known dimensions and orientation.

Given the issues mentioned above, why do some authors,<sup>(7-10,12,14-16)</sup> including one of the present authors<sup>(18)</sup> expect the fibre-pad SP method to emerge in the future as one of the most important tools for evaluating paper stock? Some reasons for this optimism, despite an inability to equate SP results with a more fundamental quantity such as zeta potential, can be listed as follows:

(a) The measurements directly sense the electrical condition of a surface that the user is interested in – the surface of cellulosic fibres, including anything that is adsorbed onto those surfaces.

(b) By use of pad-forming SP devices the tests are easily repeatable, either about every minute,<sup>(7-15,19)</sup> or as often as every two seconds.<sup>(17)</sup>

(c) It is possible to observe relative changes, as long as the test conditions make it reasonable to assume that factors such as pad density and solution conductivity have not changed by large amounts.

In addition, as will be described in a later section, SP measurements also can be used to detect titration endpoints.<sup>(17,19-20,45)</sup>

#### *Practical use of streaming potential data*

Paper mill control systems thrive on relative signals. Evidence of this fact can be found in the way papermakers calibrate online signals. The output values usually are adjusted with arbitrary “gains” and “offsets” in order to match offline laboratory measurements.<sup>(46)</sup>

As another example, data from charge titrations in paper mills is often reported without any units, or just as “ml” of an unidentified titrant. The user of such data considers only the relative changes, without ever bothering to express the results in absolute terms.

Though such practices can be criticized as “sloppy,” it is hard to argue that the mill would run better if someone took the time to calculate the results in microequivalents per unit volume of filtrate.

While it is well known that the magnitudes of zeta potential tend to decrease with increasing electrical conductivity of solution, raw SP data is even more sensitive to conductivity.<sup>(19)</sup> For instance, if trends in the ratio  $\Delta E/\Delta P$  in Equation 1 are used in place of trends in conventional zeta potential data,<sup>(31)</sup> the results would not be very useful for predicting effects on coagulation phenomena.

Fortunately, by applying Equation 1, one obtains a relative (or calibrated) value that has almost the same conductivity-dependence as zeta potential data derived from other methods.

To be able to use fibre-pad SP data as a relative measure of zeta potential, it is necessary to avoid practices likely to change the cell

constant  $f$  in Equation 1. Depending on the goals of the study, the factors to maintain as constant as practical from one test to the next include:

- The geometry of the apparatus.
- The amount, solids content, freeness of the fibre slurry sample.
- Procedural factors, such as stirring, the magnitude of applied pressure, and the amount of time over which the pressure difference is applied.

Despite such measures, it still may not be possible to know whether observed changes in SP data resulting from chemical addition represent real changes in zeta potential. In particular, chemical coagulants or flocculants can be expected to affect the packing density of the fibre pad.<sup>(47-48)</sup>

The user has to judge whether a given change of streaming potential is larger than might reasonably be expected to result from changes in pad structure. Further study, possibly by means of nonionic flocculants, is recommended to provide more justification for such approaches.

#### *Use of higher pressure to overcome salt effects*

In addition to the concerns already mentioned, SP tests suffer from a loss in amplitude of the streaming potential value as the level of salt increases.<sup>(20,23,32)</sup> The problem is especially important to deal with, since there are two different mechanisms by which salt acts to reduce the voltage response of SP instruments.

i) On the one hand, it is well known that the effective thickness of the ionic double-layer at a charged surface exposed to aqueous solution is reduced by the addition of salt.<sup>(31)</sup> According to the Debye-Hückel equation,<sup>(31)</sup> the effective double-layer thickness is inversely proportional to the square-root of the solution's ionic strength. A thinner double-layer means that the counter-ions, which balance the net charge of the charged surface, will remain closer on average to that surface.

If one assumes a linear gradient of flow velocity with distance from the surface, then it follows that the measured streaming potential (or zeta potential, in the case of other methods) ought to decrease by roughly the same factor.

Some authors have dealt with this situation by envisioning a “hydrodynamic slip plane” and assuming that flow past a charged surface is able to affect the motion only of those counter-ions that lie farther away from the surface, compared to the slip plane.<sup>(24,35)</sup>

ii) The other main contribution to loss of absolute value of streaming potential results from conductive dissipation of the very signal that one is attempting to measure. The situa-

tion can be compared to what happens when one starts a car; the draw of current will momentarily depress the difference in voltage at the two terminals of the battery, causing the headlights to dim.

Likewise, during an SP experiment, the conductivity of the solution itself provides a path by which a current can flow in response to the difference in electrical potential caused by the fluid motion past the charged surface. Current that flows through the solution phase reduces the potential evaluated between the electrical contacts.

In order to address these concerns, and also to overcome some signal problems resulting from the generation of bubbles by the use of vacuum during SP measurements,<sup>(18)</sup> a modified type of test unit was designed and tested.<sup>(19)</sup>

The "SPJ" device uses pressurized air, rather than vacuum, to form the pad. The sample of fibre slurry is first placed inside a sealed jar, where it is stirred continuously throughout the experiment. Application of a known pressure of air causes the slurry to flow towards the lower surface of a screen, and a pad of fibres begins to form on that screen.

Highly reproducible results were achieved with pulp slurry samples having a range of electrical conductivity between about 20  $\mu\text{S}/\text{cm}$  and 20  $\text{mS}/\text{cm}$ .<sup>(19-20)</sup> Within this range the relative standard deviation of repeat tests was 0.5% to 20%.

It is worth noting that higher applied pressure also can be expected to reduce the relative importance of chemically-induced changes in fibre pad density, thus helping to

justify application of Equation (1). The idea is that higher compressive forces acting on the fibre pad will increasingly be able to overwhelm the chemical factors affecting how tightly the fibres are packed.

#### Use of the SP method for charge titrations

Many of the theoretical difficulties associated with the fibre-pad SP method disappear in cases when the method is being used to determine the endpoint of a charge titration. This type of titration is also part of a patented system for online evaluation of furnish charge in papermaking applications.<sup>(45)</sup>

The device used in those applications was designed to carry out an independent measurement cycle each two seconds, making it possible to complete a titration within about a minute. In cases where the initial value of SP was negative, a dilute solution of poly-diallyldimethylammonium chloride (poly-DADMAC) was added gradually by means of a positive displacement pump. The endpoint was taken as the amount of added titrant at the point where the SP value, determined by interpolation of the data, was equal to zero.

Figure 3 shows some typical results for charge titrations carried out with the SPJ device, comparing a bleached hardwood kraft furnish with a mixed-office-waste (MOW) furnish. Though the titrations are in many respects similar to those discussed in Part 1 of this series, some characteristic differences are worth noting.

i) First, the fibre-pad SP method yielded more reproducible "initial" data, in the absence of titrant. The reproducibility of such tests was excellent, as long as the stock sample was highly uniform.

ii) Second, the full impact of titrant addition on the output values could be sensed much more quickly, compared to streaming current (SC) experiments.

iii) Third, essentially all titrations can be carried out to an endpoint where the streaming potential becomes equal to zero. In other words, even at high levels of salt there were no cases where the system failed to respond in a sensible way to the addition of titrant.

In interpreting the results shown in Figure 3, it is worth noting that the point at which the SP value equals zero is not expected to coincide with the adsorption capacity of the surface for oppositely charged polymer. The reason is that the titrant molecules, if present in excess in the solution, will tend to overcompensate for the amount of charge at the surface of cellulose, which usually can be described as having only a low to moderate density of negative ionic groups.<sup>(49-50)</sup>

Past studies have shown that exposure of surfaces to an excess of polyelectrolyte, opposite in charge to the surface, can easily result in reversal of the zeta potential.<sup>(51)</sup> Many

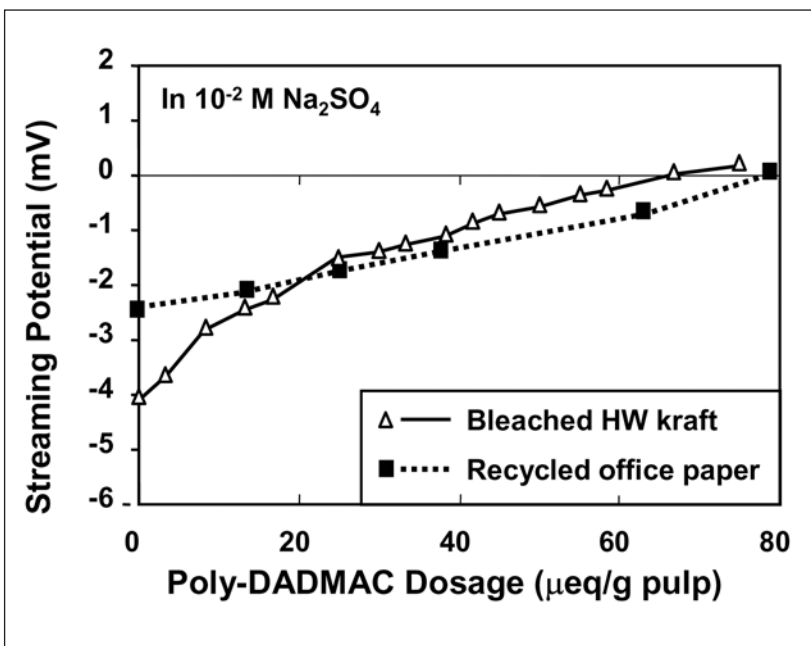


Figure 3 Results of titrations in which a highly charged cationic polymer solution was added to suspensions of papermaking fibres at an intermediate level of salt.



studies have demonstrated multiple reversals of charge when a surface is exposed to successive treatments with oppositely charged polyelectrolytes, especially if rinsing and drying steps are interposed.<sup>(52-54)</sup>

Such results are consistent with a somewhat three-dimensional conformation of adsorbed polymer, in which an excess of loops and tails of the latest-added polymer extend outwards into the surrounding solution, thus dominating the electrokinetic signal.<sup>(51-52)</sup>

*Observations concerning charge decay*

Some of the most intriguing results obtained by fibre-pad SP methods have been those that involve charge-decay phenomena.<sup>(8,20)</sup> Some new results of this type are shown in *Figures 4 and 5*, contrasting the

effects of two different types of cationic additives.

The furnish used in these tests was bleached hardwood kraft, having a Canadian Standard Freeness of 270 ml. The pH was approximately 6, and sufficient sodium sulfate was added in order to achieve an electrical conductivity of 1.05 mS/cm. This is a typical level of conductivity for a paper mill with only a low to moderate level of water-system closure.<sup>(55)</sup>

As shown in *Figure 4*, the addition of a cationic acrylamide copolymer - a retention aid - to a bleached hardwood kraft pulp suspension caused an immediate "spike" in the measured streaming potential. Remarkably, the peaks tended to be even sharper, compared to similar results shown earlier when the same kind of pulp was treated with poly-DADMAC.<sup>(20)</sup>

Because the acrylamide copolymer has a mean molecular mass of several million grams per mole, such results cannot easily be explained in terms of gradual penetration of the polymers into the pore structure of the fibres. Rather, as in an analogous case discussed elsewhere,<sup>(21)</sup> the effect is probably related to changes in the adsorbed conformation of the adsorbed molecules. Further work is needed to test such a hypothesis.

*Figure 5* shows results of similar tests, except that papermaker's alum, a solution of  $Al_2(SO_4)_3$ , was used as the titrant. Two aspects of these results are worth noting.

i) First, there is only slight evidence of charge decay, following the initial response of the system to each addition of cationic additive. Such results suggest that the system achieves a stable condition, with respect to adsorption of aluminum species, within seconds of addition of the alum to the stirred suspension.

The stability of the streaming potential signal, subsequent to alum addition, also suggests a pervasive effect of the additive, permanently neutralizing at least part of the anionic charge of dissolved and colloidal materials in the system. The ability of alum to neutralize anionic charges, even when it is added to weakly alkaline furnish, has been shown by others.<sup>(56-57)</sup>

ii) A second point worth noting is fact that, under the conditions of testing, practical addition levels of alum failed to achieve a streaming potential of zero.

Such results are consistent with the work of Strazdins,<sup>(58)</sup> who showed that although alum can be effective for reduction of excess anionic charges in a paper mill furnish, it is not usually very effective for developing high positive values of zeta potential. In addition, near to a pH of 6, cationic aluminum species will tend to precipitate as neutral products, such as  $Al(OH)_3$ .<sup>(59-60)</sup>

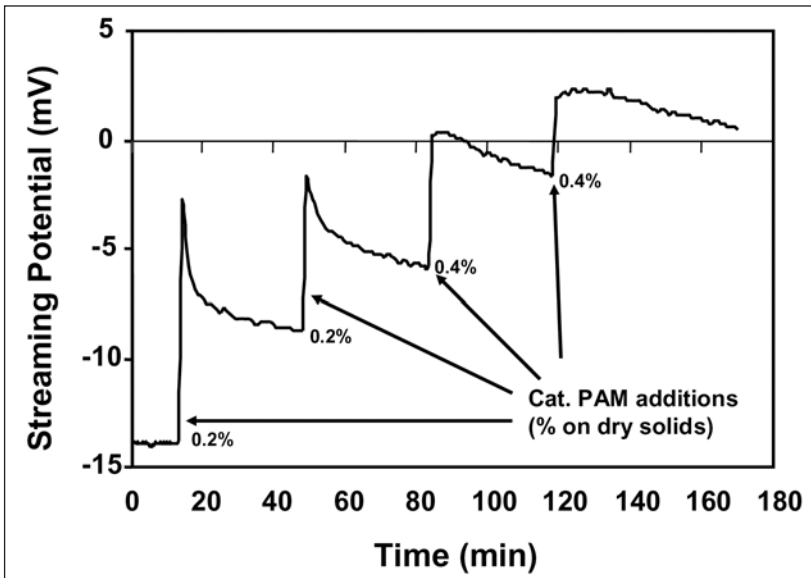


Figure 4 Example of streaming potential decay following each addition of cationic retention aid to a suspension of bleached hardwood kraft fibres.

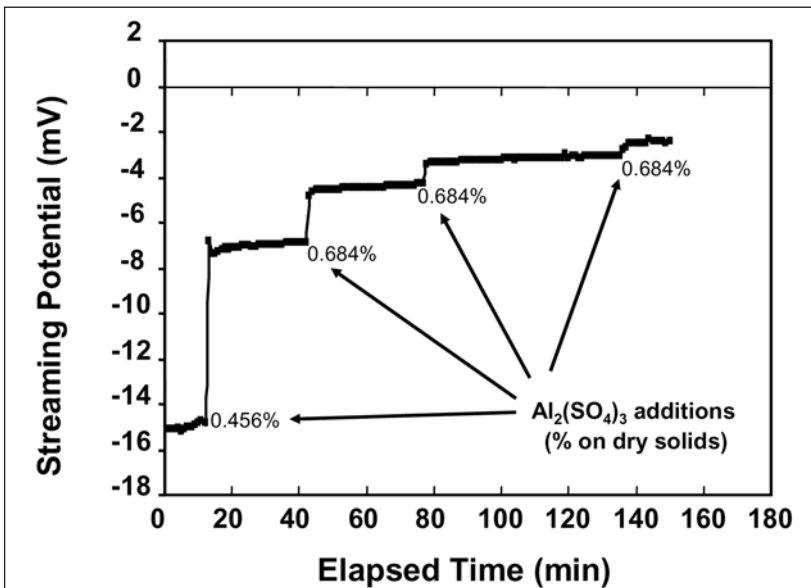


Figure 5 Results showing little evidence of streaming potential decay following addition of aluminium sulphate (papermaker's alum)

#### Comparison with micro-electrophoresis

Some early results reported by Jaycock and Pearson<sup>(61)</sup> have sometimes been cited to justify a claim that fine particles in a paper machine system are representative of the charge condition of the furnish as a whole.

A classical micro-electrophoresis (ME) test is conducted by placing a very dilute suspension of fine particles in a capillary cell, applying a known voltage gradient, and then noting the velocities of the particles. The cited article showed remarkable agreement between such ME tests, compared with SP results. The latter tests, as we have seen, sense the charged condition of the fibre surfaces, including some contribution of fine particles that happen to be attached to those fibres caught in the fibre mat.

It is worth noting that the cited study<sup>(61)</sup> involved an extrapolation procedure, varying the fibre pad density in a systematic way, as recommended by previous workers.<sup>(5)</sup>

Such an agreement cannot normally be expected when using modern pad-forming SP devices.<sup>(6-20)</sup> As noted in Jaycock's 1995 article,<sup>(1)</sup> the ME method is probably the most reliable and best understood of the various electrokinetic tests that have been applied to samples from paper mills.

Recent work in our lab showed cases where ME results and SP results differed sharply.<sup>(19)</sup> Experiments were carried out in which two types of titration were carried out simultaneously.

On the one hand, the SPJ device was used to evaluate the streaming potential of the fibre surfaces as a function of added poly-DADMAC. After each aliquot of titrant, the operation of the device was momentarily paused, allowing some of the filtrate to be tested by the ME method. Thereafter, the "bor-

rowed" filtrate was returned to the SPJ device, and the procedure was repeated for the next aliquot of titrant.

As reported earlier,<sup>(19)</sup> the amount of cationic titrant needed to neutralize the surfaces of fibres in a mixed slurry was about three times larger than the amount of titrant needed to neutralize the surfaces of fibre fines in the same mixture.

To interpret these findings, it is useful to consider the sponge-like nature of papermaking fibres.<sup>(39,62)</sup> As was demonstrated earlier in *Figure 4*, the measured charge properties immediately begin to revert, following the addition of cationic polymer.<sup>(19)</sup>

Depending on the molecular mass of the titrant, it is reasonable to expect progressive diffusion to the bulk of a fibre. In this way, the surface of the fibre can revert towards its initial state of charge. By contrast, fibre fines and other fine particles in the furnish can be expected to become more quickly saturated with the cationic polymer.

It is worth noting that the explanation given in the preceding paragraph is different from that given elsewhere to explain similar cases.<sup>(63-64)</sup> For instance, it has been argued that smaller particles can interact "more rapidly" with titrant, compared to larger fibres. However, given the slow diffusion rates of these solid particles, compared to molecular diffusion rates,<sup>(65)</sup> it is difficult to place much confidence in such a mechanism.

In addition, it has been shown that hydrodynamic factors often favour more rapid interactions between fibres and various adsorbing species by convection, compared to diffusion-controlled mechanisms of collision.<sup>(65)</sup>

#### Salt and molecular mass affect titration endpoints

The ability of the SPJ device to carry out titrations over a wide range of salt concentration made it possible to obtain the results shown in *Figure 6*. A series of moderate-mass, highly cationic poly-DADMAC solutions were used as the titrants.

As reported earlier<sup>(20)</sup> higher amounts of the cationic polymer were required to reach the neutral endpoint as the salt was increased. In addition, the amount of poly-DADMAC required to reach zero streaming potential also increased with decreasing molecular mass.

Both of these findings are consistent with migration of some of the polymer into the interior porosity of kraft fibres. As shown by others,<sup>(66-67)</sup> some of the pores are so small that polymers above a certain molecular mass are effectively excluded. The effect of salt is consistent with a tendency of charged polymers to adopt less extended molecular conformations as the ionic strength increases.<sup>(68)</sup> These

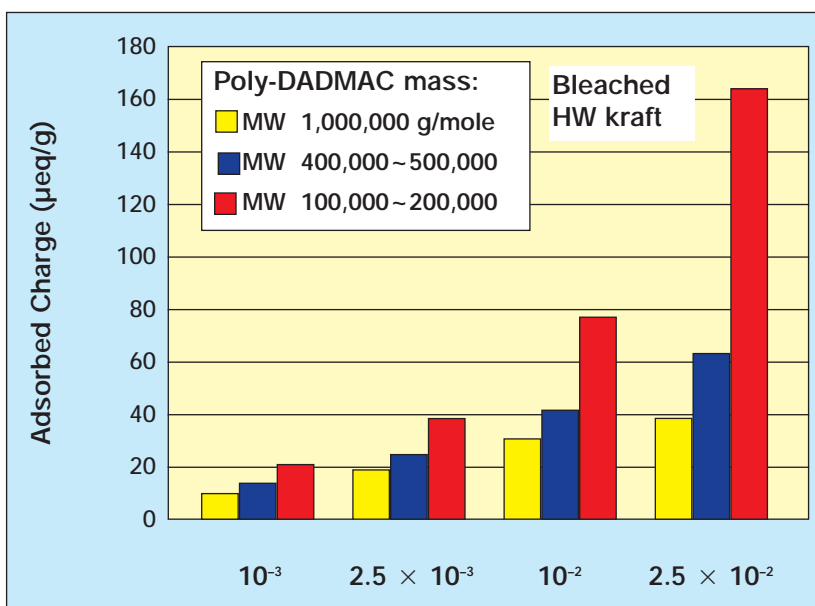


Figure 6 Effect of salt concentration and the molecular mass on the amount of poly-DADMAC adsorbed at the point of zero streaming potential.

factors need to be taken into consideration when interpreting results of SP titrations.

### Conclusions

1. The streaming potential method provides a sensitive way to detect changes in the charge condition of fibre surfaces in paper-making furnish.

2. Relative changes in observed streaming potentials can provide useful information about zeta potentials, especially if factors likely to affect a calibration constant are held constant. Results should be corrected for electrical conductivity of the solution by applying Equation (1), even if the constant  $f$  remains undetermined.

3. Carrying out SP tests under increased differential pressure has the potential to increase the precision of the results, especially at increasing concentrations of salt ions. In addition, higher pressure is expected to overcome some chemical-induced differences in the density of fibre-pads collected on a screen surface in successive experiments with the same batch of fibre slurry.

4. Theoretical problems related to the absolute value of the results, in terms of zeta potential, can be largely ignored when the method is used as a means of detecting the endpoints of charge titrations.

### References cited

- Jaycock, M. J., "Assumptions Made in the Measurement of Zeta-Potential by Streaming Current/Potential Detectors," *Paper Technol.* 36 (3): 35-38 (1995).
- Goring, D. A. I., and Mason, S. G., "Electrokinetic Properties of Cellulose Fibres. 1. Stream Potential and Electro-Osmosis," *Can. J. Res. B28* (6): 307-322 (1950).
- Goring, D. A. I., and Mason, S. G., "Electrokinetic Properties of Cellulose Fibres. 2. Zeta-Potential Measurements by the Stream-Compression Method," *Can. J. Res. B28* (6): 323-338 (1950).
- Biefer, G. J., and Mason, S. G., "Electrokinetic Streaming, Viscous Flow and Electrical Conduction in Inter-Fibre Networks – The Pore Orientation Factor," *Trans. Faraday Soc.* 55: 1239-1245 (1959).
- Chang, M. Y., and Robertson, A. A., "Zeta Potential Measurements of Fibres. D-C. Streaming Current Method," *Can. J. Chem. Eng.* 45 (2): 66-1967).
- Sack, W., "Continuous Measurement of Streaming Potential on a Paper Machine," *Papier* 30 (10A): V42-V46 (1976).
- Richter, R., Rohloff, E., Tretter, H., Müller, F., and Penniman, J. G., "A New Instrument for Automatic Streaming Potential Measurements on the Paper Machine," *Wochbl. Papierfabr.* 117 (15): 682-686 (1989).
- Penniman, J. G., "Comparison of Pulp Pad Streaming Potential Measurement and Mobility Measurement," *Tappi J.* 75 (8): 111-115 (1992).
- Sack, W., Storbeck, W., and Winiker, R., "Ten Years of Research Experience with Continuous Zeta Potential Measurements for Paper Machine Process Control," *Wochbl. Papierfabr.* 121 (19): 803-805 (1993).
- Rohloff, E., and Höschle, O., "Zeta Potential Experiences with Laboratory and On-line Measurements," *Wochenbl. Papierfabr.* 121 (23-24): 990-994 (1993).
- Hand, V., Koethe, J., Kuchibhotla, S., and Scott, W., "An Evaluation of Two Pad-Forming Paper Stock Charge Analyzers," *Papermakers Conf. Proc.*, TAPPI Press, Atlanta, 1993, 591-598.
- Nazir, B. A., "An On-line Streaming Potential Meter (SPM) – Wet-End Applications," *Paper Technol. Ind.* 35 (3): 28-35 (1994).
- Sanders, N. D., and Schaeffer, J. H., "Comparing Papermaking Wet-End Charge-Measuring Techniques in Kraft and Groundwood Systems," *TAPPI J.* 78(11): 142-150 (1995).
- Padovani, E., and Colasurdo, A. R., "Online Real-Time Measurement Reduces Wet-End Variability," *Pulp Paper* 69 (4): 57-62 (1995).
- Miyaniishi, T., and Shigeru, M., "Optimizing Flocculation and Drainage for Microparticle Systems by Controlling Zeta Potential," *Tappi J.* 80 (1): 262-270 (1997).
- Thiele, B., and Kopp, J. W., "Charge Balances of Paper Machine Systems – A Method of Process Optimization," *Wochenbl. Papierfabr.* 125 (11/12): 542-556 (1997).
- Hubbe, M. A., "Method and Apparatus for Measuring an Electrical Property of Papermaking Furnish," U.S. Patent 5,936,151, Aug. 10, 1999.
- Hubbe, M. A., "Selecting and Interpreting Colloidal Charge Measurements," in "Proc. Scientific & Technical Advances in Wet End Chemistry," Barcelona, Spain, PIRA Intl., Leatherhead (2000).
- Wang, F., and Hubbe, M. A., "Development and Evaluation of an Automated Streaming Potential Measurement Device," *Colloids and Surfaces A*, 194: 221-232 (2001).
- Wang, F., and Hubbe, M. A., "Charge Properties of Fibres in the Paper Mill Environment. 1. Effect of Electrical Conductivity," *J. Pulp Paper Science* 28 (10) 347-353 (2002).
- Hubbe, M. A., and Wang, F., "Where to Add Retention Aid: Issues of Time and Shear," *TAPPI J.* 1 (1): 28-33 (2002).
- Ball, B., and Fuerstenau, D. W., "A Review of the Measurement of Streaming Potentials," *Miner. Sci. Eng.* 5 (4): 267-277 (1973).
- Horn, J. M., Jr., and Onoda, G. Y., Jr., "Streaming Potential and Noncreeping Flow in Porous Beds," *J. Colloid Interface Sci.* 61 (2): 272-278 (1977).
- Vernhet, A., Bellon-Fontaine, M. N., and Doren, A., "Comparison of Three Electrokinetic Methods to Determine the Zeta Potential of Solid Surfaces," *J. Chim. Phys.* 91 ( ): 1728-1747 (1994).
- Revil, A., Pezard, P. A., and Glover, P. W. J., "Streaming Potential in Porous Media. 1. Theory of the Zeta Potential," *J. Geophys. Res.* 104 (B9): 20021-20031 (1999).
- Hubbe, M. A., and Chen, J., "Charge-Related Measurements – A Reappraisal. Part 1. Streaming Current," *Paper Technol.* ( Vol 45 \_ No 7 ) Oct, 2004\_).
- Li, H. C., and De Bruyn, P. L., "Electrokinetic and Adsorption Studies on Quartz," *Surf. Sci.* 5 (2): 203-220 (1966).
- Wiese, G. R., James, R. O., and Healy, T. W., "Discreteness of Charge and Solvation Effects in Cation Adsorption at Oxide-Water Interface," *Disc. Faraday Soc.* 52: 302 (1972).
- Van Wagenen, R. A., Andrade J. D., and Hibbs, J. B., "Streaming Potential Measurements of Biosurfaces," *J. Electrochem Soc.* 123 (10): 1438-1444 (1976).
- Van Wagenen, R. A., and Andrade, J. D., "Flat-Plate Streaming Potential Investigations - Hydrodynamics and Electrokinetic Equivalency," *J. Colloid Interface Sci.* 76 (2): 305-314 (1980).
- Hunter, R. J., *Zeta Potential in Colloid Science*, Academic Press, London, 1981.

32. Scales, P. J., Grieser, F., Healy, T. W., White, L. R., and Chan, D. Y. C., "Electrokinetics of the Silica-Solution Interface: A Flat Plate Streaming Potential Study," *Langmuir* 8 (3): 965-974 (1992).
33. Levine, S., Mariott, J. R., Neale, G., and Epstein, N., "Theory of Electrokinetic Flow in Fine Cylindrical Capillaries at High Zeta Potentials," *J. Colloid Interface Sci.* 52 (1): 136-149 (1975).
34. Anderson, J. L., and Koh, W., "Electrokinetic Parameters for Capillaries of Different Geometries," *J. Colloid Interface Sci.* 59 (1): 149-158 (1979).
35. Hidalgo-Alvarez, R., "On the Conversion of Experimental Electrokinetic Data into Double-Layer Characteristics in Solid-Liquid Interfaces," *Adv. Colloid Interface Sci.* 34: 217-341 (1991).
36. El-Gholabzouri, O., Cabrerizo, M. A., and Hidalgo-Alvarez, R., "Comparative Electrophoretic Mobility and Streaming Current Study for z-Potential Determination," *Colloids Surf. A* 159 ( ): 449-457 (1999).
37. van de Ven, T. G. M., "Effect of Fibre Conductivity on Zeta Potential Measurements of Pulp Fibres," *J. Pulp Paper Sci.* 25(7):243-245 (1999).
38. Revil, A., Schwaeger, H., Cathles, L. M., and Manhardt, P. D., "Streaming Potential in Porous Media. 2. Theory and Application to Geothermal Systems," *J. Geophys. Res.* 104 (B9): 20033-20048 (1999).
39. Pelton, R., "A Model of the External Surface of Wood Pulp Fibres," *Nordic Pulp Paper Res. J.* 8 (1): 113-199 (1993).
40. Hoffman, F., Müller, F., Rohloff, E., and Tretter, H., "Experiences with the Streaming Potential Method for Retention and Wet Strength Problems," *Papier* 29 (12): 529-534 (1975).
41. Horn, D., and Melzer, J., "The Effect of High Molecular Cationic Dewatering Aids on the Electrokinetic Properties of Pulp," *Papier* 29 (12): 534-541 (1975).
42. Jain, L., Kumar, V., Bharati, R., Bharati, S., and Aggarwal, S. K., "Zeta Potential Determination of Pulp Suspensions Using Streaming Potential Measurements," *IPPTA* 4 (2): 101-105 (1992).
43. Miyanishi, T., "On-line Zeta Potential Analyses of a Fine Paper Machine and a Newsprint Paper Machine," *Tappi J.* 78 (3): 85-91 (1995).
44. Ciriacks, J. A., and Williams, D. G., "A Happel Flow Model - Streaming Current Relationship for Determining the Zeta Potential of Cylindrical Fibres," *J. Colloid Interface Sci.* 26 (4): 446-456 (1968).
45. Hubbe, M. A., "Method for Determining Electrokinetic Properties of Papermaking Furnish," U.S. Patent 6,176,974, Jan. 23, 2001.
46. Berger, R., Renaud, S., and Waters, K., "Applying Automatic Chemical Control from Stock Prep to the Machine," *Appita J.* 55 (3): 197-201 (2002).
47. Britt, K. W., and Unbehend, J. E., "Water Removal during Paper Formation," *Tappi J.* 68 (4): 104-107 (1985).
48. Maunier, C. O., and Ramarao, B. V., "Effect of Flocculation on Pulp Drainage Characteristics," *TAPPI 1996 Engineering Conf. Proc.*, 221-238, TAPPI Press, Atlanta, 1996.
49. Herrington, T. M., and Petzold, J. C., "An Investigation into the Nature of Charge on the Surface of Papermaking Woodpulp. 1. Charge/pH Isotherms," *Colloids Surf.* 64 (2): 97-108 (1992).
50. Lloyd, J. A., and Horne, C. W., "The Determination of Fibre Charge and Acidic Groups of Radiata Pine Pulps," *Nordic Pulp Paper Res. J.* 8 (1): 48-67 (1993).
51. Wågberg, L., and Ödberg, L., "Polymer Adsorption onto Cellulose Fibres - A Review," *Nordic Pulp Paper Res. J.* 15 (5): 5860597 (2000).
52. Sukhorukov, G., Donath, E., Lichtenfeld, H., Knippel, E., Knippel, M., and Möhwald, H., "Layer-by-layer self assembly of polyelectrolytes on colloidal particles," *Colloids And Surfaces A-Physicochemical And Engineering Aspects* 137 (1-3): 253-266 (1998).
53. Caruso, F., Lichtenfeld, H., Donath, E., and Möhwald, H., "Investigation of Electrostatic Interactions in Polyelectrolyte Multilayer Films: Binding of Anionic Fluorescent Probes to Layers Assembled onto Colloids," *Macromolecules* 32 ( ): 2317-2328 (1999).
54. Wågberg, L., Forsberg, S., Johansson, A., and Juntti, P., "Engineering of Fibre Surface Properties by Application of the Polyelectrolyte Multilayer Concept. Part 1: Modification of Paper Strength," *J. Pulp Paper Sci.* 28 (7): 222-228 (2002).
52. Schwarz, S., Buschhammer, H.-M., Lunkwitz, K., and Jacobasch, H.-J., "Polyelectrolyte Adsorption on Charged Surfaces: Study by Electrokinetic Measurements," *Colloids Surf. A* 140: 377-384 (1998).
55. Huhtamäki, M., "Closing the Water Cycles - How Far Can We Go?" *Paper Technol.* 44 (10): 27-32 (2003).
56. Trksak, R. M., "Aluminum Compounds as Cationic Donors in Alkaline Papermaking Systems," *Proc. TAPPI 1990 Papermakers Conf.*, 229-237 (1990).
57. Farley, C. E., "Influence of Dissolved Ions on Alum Cationicity under Alkaline Papermaking Conditions," *Proc. TAPPI 1992 Papermakers Conf.*, 267-273 (1992).
58. Strazdins, E., "Theoretical and Practical Aspects of Alum Use in Papermaking," *Nordic Pulp Paper Res. J.* 4 (2): 128-134 (1989).
59. Öhman, L.-O., Wågberg, L., Malmgren, K., and Tjernström, Å., "Adsorption of Aluminum (III) on Cellulosic Fibres in Neutral to Alkaline Solutions - Influence of Charge and the Size of the Particles Formed," *J. Pulp Paper Sci.* 23 (10): J467-J474 (1997).
60. Bottéro, J. Y., Cases, J. M., Fiessinger, F., and Poirier, J. E., "Studies of Hydrolyzed Aluminum Chloride Solutions. 1. Nature of Aluminum Species and Composition of Aqueous Solutions," *J. Phys. Chem.* 84 (22): 2933-2939 (1980).
61. Jaycock, M. J., and Pearson, J. L., "Colloidal Aspects of Paper Formation. 1. Factors Affecting Electrokinetic Properties of Cellulose Fibres," *Svensk Papperstidn.* 78 (5): 167-171 (1975).
62. Alinec, B., and van de Ven, T. G. M., "Porosity of Swollen Pulp Fibres Evaluated by Polymer Adsorption," in Barker, C. F., ed., *The Fundamentals of Papermaking Materials*, 771-788, Pira Intl., Leatherhead, Surrey, UK, 1997.
63. Koethe, J. L., and Scott, W. E., "Polyelectrolyte Interactions with Papermaking Fibres: the Mechanism of Surface-Charge Decay," *Tappi J.* 76 (12): 123-133 (1993).
64. Farley, C. E., "Factors Influencing the Rate of Charge Decay," *Tappi J.* 80 (10): 177-183 (1997).
65. Swerin, A., and Ödberg, L., "Some Aspects of Retention Aids," in Baker, C. F., Ed., *The Fundamentals of Papermaking Materials*, Vol. 1, 265-350, Pira Intl., Leatherhead, Surrey, UK, 1997.
66. Stone, J. E., and Scallan, A. M., "A Structural Model for the Cell Wall of Water-Swollen Wood Pulp Fibres based on their Accessibility to Macromolecules," *Cellulose Chem. Technol.* 2 (3): 343-358 (1968).
67. Berthold, J., and Salmén, L., "Effects of Mechanical and Chemical Treatments on the Pore-Size Distribution in Wood Pulps Examined by Inverse Size-Exclusion Chromatography (ISEC)," *J. Pulp Paper Sci.* 23 (6): J245-253 (1997).
68. Lin, K.-F., and Cheng, H.-L., "A Simple Method to Estimate Chain Conformations of Polyelectrolytes in the Semidilute Regime," *Macromolecules* 33 (13): 4961-4965 (2000).