Why Do Different Charge Demand Tests Give Different Endpoints?

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Abstract

Have you ever encountered situations where two people, both measuring the same samples taken from a paper machine system, have reported sharply different results for cationic demand tests? Such situations actually are quite common. A lot of needless energy can be spent trying to figure out which of the two sets of data is “correct.” Fortunately, there are some understandable reasons to expect variations in the details of charge titration tests to yield significantly different results. By keeping these issues in mind, it is possible to get beyond questions of the correctness of different procedures. The end goal should be to improve the reproducibility of the results of charge demand titrations and to interpret the results with greater confidence.

Introduction

Technical people who are concerned about the efficiency of papermaking operations have a variety of tools that can be used for monitoring or control of the electrical charge at the surfaces of fibers and other suspended matter [1]. For example, streaming current titrations have become very widely used for determining the cationic demand of process water collected at various points in papermaking processes [2-6]. Alternatively, it is possible to perform similar measurements in a more direct way with a pad-forming streaming potential device [7-10]. Issues related to selecting the most appropriate test equipment and procedure for a given situation were considered in paper presented at a Pira conference in 2000 [1].

Key motivations for carrying out cationic demand determinations in a paper mill often can be summarized by the words “troubleshooting,” “optimization,” and “control.” Just like pH and temperature, cationic demand data sometimes can help in finding the root causes of problems like foam, cycles of poor drainage, and deposit problems. By paying attention to charge, it is often possible to improve the efficiency of, say, retention aids. Since retention aids affect the efficiency of other wet-end additives, e.g. sizing agents, such adjustments are likely to affect the mill’s bottom line.

The scope of the present paper will be mainly limited to answering the question given in the title. In other words, why do different procedures, used for
evaluation of the charge demand characteristics of different filtrate and whitewater samples collected at paper mills, often give conflicting information?

Contrasting Test Methods and Procedures

The first issue to face is the proliferation of various contrasting test methods, all related in some way to the electrical charged nature of papermaking fibers and the aqueous medium in which they are suspended. As explained in more detail elsewhere [1], some test procedures, such as microelectrophoresis [11-16] have mainly been employed for measurement of an intensive property. The zeta potential is an example of an intensive property because its value does not depend on the size of the sample. Rather, zeta potential is something like a voltage, which ought to be independent of sample size, as long as the samples are representative and enough measurements are taken.

While zeta potential and related intensive variables clearly play key roles, governing the interactions between different wet-end additives, fibers, and fillers [1], papermakers often need to answer questions that include the words “how much.” Answers to that type of question usually involve extensive variables. For instance, it is important to know how much of a highly charged additive such as poly-ethylenimine (PEI) or poly-aluminum chloride (PAC) ought to be added to a specified amount of furnish to achieve the most efficient performance of a retention aid and various functional additives. The answers to such questions usually involve some sort of titration. In addition to the work involving streaming current titrations, which already was cited [2-6], papermakers also have used charge titration methods with colorimetric endpoints [17-19] or conductometric endpoints [20]. Micro-electrophoresis has been used occasionally as a means of finding how much of a cationic additive is needed to achieve a zero zeta potential [21]. More recently, fiber-pad streaming potential has been found to be an effective means of evaluating cationic demand, by means of titrations [10, 22-24].

The properties of the titrant also can affect on the results of charge titrations. According to Laine and Lindström [25], the relative charge density of the titrant vs. that of the polyelectrolytes in the sample can become increasingly important as the salt concentration of the sample increases. Other potentially important variables include the molecular mass and structural details of the polyelectrolytes.

Two of the most widely used titrants for charge evaluations are shown in Fig. 1. Both of these titrants are 100% charged, i.e. they have one ionic charge per repeating unit. Such high charge density generally has proven to be advantageous, making it possible to titrate a wide range of different samples under different electrolytic conditions. Poly-DADMAC, which is shown in the left-hand frame of the figure, is noted for its high chemical stability during storage, so it is often used as the primary standard for titrations. The ionic groups of both poly-DADMAC and PVSK are pH-independent. Such pH-independence can help simplify the interpretation of data.
Fig. 1. Titrants often used for charge demand titrations: (a) Poly(diallyldimethylammonium chloride; (b) potassium salt of poly(vinylsulfate)

Reasons why the nature of the titrating polymer can affect titration results can be understood by considering the kinds of interactions illustrated in Fig. 3. As shown, it makes sense to envision two main types of contribution to the cationic demand of an aqueous sample from a paper mill system. Part of the charge can be classed as “soluble,” in the sense that it will pass through a filter paper. That part may include anionic polyelectrolytes, such as breakdown products of hemicellulose and lignin, as well as size-press starch. Colloidal materials, such as wood pitch, also might be able to pass through the filter paper, at least partly. The other main type of contribution to cationic demand can be called “surface charge.” In other words, fiber fines, filler, and other filterable matter in the sample can take up a certain amount of cationic titrant.

Fig. 2. Schematic diagram indicating how cationic demand may involve a summation of effects due to non-filterable and filterable materials.

The hypothesis upon which charge titrations generally rely is that there is a 1-to-1 stoichiometry of charge between ionic groups on the titrant molecule and those on the polyelectrolytes, surfaces, and other entities in the sample. While this
hypothesis is seldom strictly true, it comes close enough to being true in order to achieve useful information. Some issues concerning charge stoichiometry have been considered elsewhere [1,26].

The principle by which several of the commonly used charge titration methods work is illustrated in Fig. 3. Imagine a flat substrate having a net negative charge (indicated in the figure as little minus signs in circles). As shown in the left-hand frame of the figure, counter-ions, such as sodium ions, can be expected to be present in excess adjacent to the surface, since the total charge of the system needs to be zero. Because of the thermal energy of molecules and ions, all of the dissolved ions will continually move in semi-random directions. What results from these effects is a distribution of ions at various distances from the charged surface. The average positions of counter-ions can be predicted based on the sum of the attractive electrostatic forces between the counterions and the surface, plus the random motions due to thermal energy. As shown in the diagram, flow past such a charged surface will tend to move some of the counter-ions, especially those that happen to be relatively far from the charged surface. The resulting current can be measured by various tests, some of which will be illustrated in examples to be considered later in this article.

The right-hand frame of Fig. 3 shows the situation when a sufficient amount of cationic titrant has been added to the system in order to achieve an “endpoint” condition at which the electrokinetic signal is zero. In principle, if the amount of titrant exactly matches the charged groups on the surface, then the net charge will be zero. Under such conditions the net charge in the solution adjacent to the surface also will be zero. It follows that flow past the surface will not give rise to any current or electrical potential. Again, this theory is a simplification, but it appears to be sufficiently true so that the charge evaluation methods can be quite useful and reliable.
It might be said that the foregoing brief introduction to the subject of charge demand titrations provides almost enough information to be dangerous. One of the biggest dangers is overconfidence. For instance, how many people do you know who have gone back and rechecked their charge analysis numbers by using a second, reference method? Probably none. So, with an eye to encouraging caution, let’s continue by considering a series of horror stories. Each of the case studies considered in the subsections that follow is based on a real experience.

Case One: Parallel Streaming Current Tests Get Different Results

The first case study involves a paper machine trial at an alkaline fine paper mill. Various adjustments to wet-end additives were being made during that study in order to meet the specifications of a new paper grade under development. Naturally, representatives of various chemical suppliers were on the scene. For instance, the supplier of cationic starch had made sure that their representative had an assistant assigned to carrying out cationic demand titrations. Let’s just call this assistant “Analyst 1.” As shown in Fig. 1, Analyst 1’s procedure involved simply collecting whitewater samples and running the titrations.

A representative from the supplier of calcium carbonate filler also was on the scene. As shown in Fig. 1, her procedure involved exactly the same kind of whitewater samples, collected at approximately the same times. However she passed the samples through filter paper as soon as they were collected and did subsequent analysis on the filtrates.

Figure 5 illustrates the kind of apparatus used by both analysts to carry out their charge demand titrations. This kind of device is called a streaming current detector. Also, just by chance, both of them used essentially identical solutions of poly-DADMAC as the cationic titrant.
Just to review how streaming current tests work, imagine a plastic piston moving up and down repeatedly by about 0.5 cm with a frequency of approximately four Hertz. The piston fits inside of a plastic cylinder housing, with an annular space of about 0.5 mm. The aqueous sample is placed in a reservoir so that it flows down and fills the annulus. The reciprocating motion of the piston causes liquid to rush back and forth past the plastic walls of the piston and cylinder. Based on the principles shown earlier in Fig. 3, the movement of aqueous solution relative to the plastic surfaces can give rise to a measurable current. However, such a current exists only if there is a net charge on the plastic surfaces. Whenever this kind of device is used for charge titrations, there is an implicit assumption that colloidal matter from the sample can adsorb efficiently onto the plastic.

Figure 6 shows the results of the titrations carried out by the two analysts. Notice that in each case it was possible to determine a clearly identifiable endpoint of the titration, i.e. the point at which the curve crosses zero streaming current meter output. Both analysts were pleased that their titration curves were relatively steep and linear at the point where the meter output changed from negative to positive, since those characteristics tend to be an indication of precision of the method. Also, each of them was able to get approximately the same endpoint when the same procedure was repeated.

But members of the technical team at the paper mill were not so pleased. Why, they wanted to know, were the two sets of results giving different answers by more than a factor of two?

![Titration Results](image)

**Fig. 6.** Hypothetical (but typical) results from streaming current titrations (1) without and (2) with filtration to remove solids before the test.

Now comes the test. Just for fun, before you turn the page, what do you know that might explain the discrepancy between these two titration results? Could it have something to do with the procedures that were used by the two analysts?
Gotcha! You thought that I wasn’t looking, when you turned that page without figuring out the explanation. Congratulations to those who did!

As illustrated in Fig. 7, the explanation almost certainly lies in the fact that one of the samples was filtered, and the other was not. Remember that cationic demand often can be treated as a sum of two terms – a demand due to “soluble” matter such as anionic polyelectrolytes, plus a demand due to the negative surfaces of various filterable solids. If one filters calcium carbonate filler from white water, it is likely that one is filtering out a major part of the charge demand present in the original sample.

![Diagram showing Analyst 1’s Sample and Analyst 2’s Sample](image)

**Fig. 7.** Schematic representation of annular region within a streaming current apparatus either (a) without, or (b) with filtration to remove solids before the titration.

Before leaving this case it is worth mentioning one very important implication. That is, in cases where charge titrations are carried out with unfiltered white water, one can expect to find a high correlation between the charge titration results and first-pass retention. When first-pass retention is low, the amount of solids in the white water are likely to be higher, and vice versa. Paper machines where online charge and consistency tests are both carried out with the same unfiltered whitewater samples may find such a high correlation between the two. In fact, the two kinds of measurements may tend to be redundant. In such cases it can make sense to install an automatic filtering system. For instance headbox stock can be filtered through a screen. Even in the absence of filter paper, the fiber mat on the screen tends to do a very good job of filtering out fine particles, making it possible to attribute charge titration data just to the soluble (or colloidal) portion of overall cationic demand.

**Case Two: Parallel Tests from the Same Beaker**

OK, the previous case made a certain amount of sense, because it was clear that the samples were each obtained by a somewhat different procedure. But what
about a case in which two different types of titration curves were obtained by taking a series of samples from the same beaker, to which incremental amounts of titrant had been added?

As depicted in Fig. 8, one of the methods of determining the titration endpoint involved a pad-forming streaming potential device [7-10]. The figure illustrates one of the ways in which this type of device can work. As shown, the guts of the apparatus involve a screen, toward which a stock suspension is pulled by means of vacuum. Filtrate passes through the screen, and a mat of fibers builds up, creating a resistance to flow. Metal probes on either side of the mat sense the change in electrical potential that results from flow through the fiber pad. The principle by which the signal arises is essentially the same as that shown in Fig. 3, except that the fibers themselves are now substituting for the “wall” surface shown in that figure. Because of various factors affecting the condition of metal probes, the measured signals during the application of flow are always compared to a reference measurement at zero (or other) pressure.

Figure 9 depicts the other type of device that was used in Case Two. Micro-electrophoresis involves the microscopic observation of tiny particles within a capillary tube. A known voltage is applied between two cell chambers at the ends of the capillary tube, and the small particles migrate in response to the applied field. In the case described, the samples for micro-electrophoresis were periodically withdrawn from the filtered side of the streaming potential apparatus, right during the titration. Then, after completing the micro-electrophoresis test, the streaming potential test was continued with the next higher increment of poly-DADMAC titrant addition.

Results of the two tests, both involving exactly the same mixture, are shown in Fig. 10 [23]. The figure shows that adding the cationic titrant tended to make the output of each device less negative or more positive. But the endpoints? Not even close! About five times as much titrant was required to achieve zero streaming potential, compared to the endpoint based on microelectro-phoresis.
To begin to account for the surprising results in Fig. 10, let’s start by considering one of the standard explanations [10]. We will return to this issue after one of the later case studies, where we will learn another part of the mystery, all helping to account for that remarkable factor of five.

As shown in Fig. 11, you can think of a kraft fibers as being something like a sponge. The nanoporosity of kraft and sulfite fibers have been characterized in a variety of ways [27-30]. In principle, a polyelectrolyte molecule ought to be able to fit into such pores. Even if the average randomly coiled size of the macromolecule is larger than the pore, it is still possible that the molecule could enter the pore like a worm; the technical term of this kind of polymer movement is “reptation” [31]. Alternatively, a polyelectrolyte ought to be able to gradually work itself into the tiny spaces underneath cellulosic microfibrils and nanofibrils at the fiber surface [32-33]. Either one of these mechanisms could account for the charge decay phenomena reported by various investigators [24,34-36].

But what about those semi-simultaneous measurements involving micro-electrophoresis? Since those measurements involved samples taken at the same stages of titrant addition, and at the same times, how does the charge decay mechanism help to account for these results? The key to the explanation is that micro-electrophoresis always involves tiny particles, such as fiber fines and filler particles. It does not involve full-length fibers.

To explain Fig. 10, we would make the hypothesis that such fine particulates tend to become saturated with titrant much more quickly than the fibers. In other
words, as illustrated in Fig. 12, the adsorption of titrant molecules onto the fines reaches a steady state almost immediately, as soon as the mixing is done. Such an explanation is consistent with various facts that we know:

- The surface area per unit mass of fine particulate matter tends to be much higher than that of the fibers [37-38]; it follows that the initial amount of titrant adsorbing onto the fine material, per unit mass, will be higher by about the same ratio.
- Filler particles, which often make up a big fraction of the surface area of fine matter are generally non-porous.
- Porosity also is not an issue in the case of any dissolved polyelectrolytes that happen to be part of the cationic demand of a papermaking furnish. Such material ought to form relatively stable polyelectrolyte complexes with the added titrant within a second or so after mixing.
- Finally, we know that fine particles, by definition, are not as big as fibers. That means that added titrant molecules do not have as far to travel in order to penetrate into all of the accessible pore spaces.

“Sponge-like” Nature of Fibers

<table>
<thead>
<tr>
<th>Time = 5 seconds</th>
<th>Time = 5 minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fiber</td>
<td>Fiber</td>
</tr>
</tbody>
</table>

Fig. 11. Schematic representation of a porous fiber surface to rationalize the decay of electrokinetic data after addition of cationic polyelectrolyte

Rapid Saturation of “Fines”

<table>
<thead>
<tr>
<th>Time = 5 seconds</th>
<th>Time = 5 minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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</tbody>
</table>

Fig. 12. Schematic representation of the interaction of cationic polymers with fine materials, which quickly become saturated

Case Three: Today’s Re-measurement of Yesterday’s Sample

Sometimes the most well intended attempts to do things carefully can have unintended consequences. Those words start to describe the situation of Case Three. The issue involved zeta potential measurements of headbox stock. The work was done in a mill making brown kraft paper for bags. In order to meet customer requirements the furnish was being treated with a wet-strength agent, polyamidoamine epi-chlorohydrin. Other additives included alum and alkylketene dimer (AKD) size.
The method used to obtain the measurements, once again, was fiber-pad streaming potential, as was illustrated in Fig. 8. A summer intern doing the work obtained some headbox stock and obtained the data shown on the right side of Fig. 13. These positive numbers at first seemed surprising, given the generally negative nature of papermaking fibers, so the boss was skeptical. Just to be sure, the intern was asked to make additional measurements the next day. The sample was still sitting on the bench, so it was easy to obtain an additional four measurements, as shown in Fig. 13. As you can see, the results came out quite differently.

**Case 3: Today’s Re-Measurement of Sample Collected Yesterday**

<table>
<thead>
<tr>
<th>Today:</th>
<th>Yesterday:</th>
</tr>
</thead>
<tbody>
<tr>
<td>- 4.2 mV</td>
<td>+ 8.1 mV</td>
</tr>
<tr>
<td>- 6.3 mV</td>
<td>+ 6.4 mV</td>
</tr>
<tr>
<td>- 5.3 MV</td>
<td>+ 5.7 MV</td>
</tr>
</tbody>
</table>

Fig. 13. Hypothetical (but typical) data for electrokinetic data from fresh vs. day-old headbox stock

![Fig. 13](image)

Fig. 14. Effect of time on the streaming potential of bleached kraft fibers, as affected by cationic polymer addition

![Fig. 14](image)

One of the ways to account for the observations shown in Fig. 13 is to assume that the highly cationic wet-strength agent, the positive multi-valent aluminum ions, and cationic polymers used in formulating the AKD size were sufficient to reverse the charge of the fibers, when the sample was freshly obtained from the paper machine. Then, over time, it is reasonable to expect the cationic materials to absorb into the fiber, as in the previous case study. In addition, the distribution of different types of aluminum species often changes with time, resulting in formation of a lot of uncharged Al(OH)₃.

Figure 14 shows some laboratory work illustrating related effects in the case of bleached kraft fibers. Note that addition of a highly charged cationic polymer was able to abruptly change the observed streaming potential, or even reverse it to a positive number if enough of the cationic polymer was added. The charge-decay effects shown in Fig. 14 have been attributed to the same factors mentioned earlier, i.e. gradual migration of charged materials into the pores spaces of the fibers, including the spaces underneath the microfibrillar fuzz at the fiber surfaces.

In order to check this kind of explanation, some further tests were carried out with different types of fibers known to have different pore-size distributions [28]. Results are shown in Table 1. What is particularly striking about these data is that lower rates of charge decay were observed in the case of the chemithermo-
mechanical pulp (CTMP) fibers. Such fibers still have most of their lignin. By contrast, bleached kraft pulps have had the lignin taken out, so it makes sense that polymers could occupy sites vacated by that lignin during pulping and bleaching.

<table>
<thead>
<tr>
<th>Fiber Type</th>
<th>Initial Relative Rate of Charge Decay (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>At 60 µS/cm conductivity</td>
</tr>
<tr>
<td>Chemithermomechanical Pulp (CTMP)</td>
<td>0.05</td>
</tr>
<tr>
<td>Refined Bleached Hardwood Kraft, Fines Removed</td>
<td>0.16</td>
</tr>
<tr>
<td>Unrefined Bleached Hardwood Kraft, Whole Pulp</td>
<td>0.17</td>
</tr>
</tbody>
</table>

* Taking initial slope of streaming potential value over time, immediately after polymer addition, and dividing it by minus the initial streaming potential value before polymer addition. In each case just enough poly-DADMAC was added to achieve a streaming potential of about zero at time equal to zero.

The rapid rates of decay observed in the absence of added salt (60 µS/cm conductivity) are tentatively attributed to a longer range of the electrostatic interactions. At a conductivity of 60 µS/cm conductivity the Debye length (which is related to the range of electrostatic forces in aqueous solution) is about 200 nm. By contrast, at a conductivity of 1000 µS/cm the Debye length is about 1 nm. That implies that the electrostatic forces will tend to be more effective in the absence of salt, more quickly attracting the polyelectrolyte into positions that maximize the charge interactions. This new hypothesis needs to be evaluated in the future by other kinds of experiments.

**Case Four: Parallel Tests by Streaming Potential With or Without Salt**

The next case involves a situation where the research facility was located in a different state from the paper mill. It just seemed to make sense to carry out the tests in a location where a full range of scientific equipment, in addition to technical staff, were available. However, it didn’t seem to make sense to carry at lot of buckets of headbox furnish. So instead, portions of headbox furnish were poured into a handsheet device. The resulting pulp pads had a consistency of about 10%.

Once the samples arrived back at the research center, the question arose as to whether it would be better to carry out charge-demand titrations at the same electrical conductivity of about 1000 µS/cm, as found in the mill, or whether it would make more sense to used distilled water as the suspending medium. The
argument in favor of adding salt was basically to keep the system as similar as possible to the mill conditions. The argument in favor of using distilled water was mainly based on the fact that polyelectrolyte complexes tend to form more strongly under those conditions, and it is also more likely that a 1-to-1 stoichiometry of interaction will be achieved. In the interest of being thorough, it was decided to measure the cationic demand of the pulp under three conditions, including a much higher electric conductivity.

Results of the tests are shown in Fig. 15. The endpoints of streaming potential titrations are shown for three different electrical conductivities, achieved by the addition of sodium sulfate. Results are plotted with a logarithmic axis. Remarkably, there was a factor-of-ten difference, depending on the salt concentration. In other words, much more cationic polymer was required to achieve a neutral streaming potential value in the presence of added salt.

Figure 16 illustrates the conventional way in which the effect of salt could be explained in such a situation. It is well known that polyelectrolytes tend to have an expanded conformation of their semi-random coils, compared to uncharged soluble polymers [39-40]. The expanded conformation is often explained in terms of charge repulsion between like-charged groups. However, salt ions tend to screen those repulsive forces, so the amount of expansion tends to decrease with increasing salt. In principle, a reduced effective size of the polyelectrolyte ought to allow it is fit more easily into a small pore. In addition, as mentioned by Farley [36], salt will tend to reduce the strength of interactions between polymer segments and cellulosic surfaces; the reduced strength of interaction ought to help prevent the polyelectrolyte from getting “stuck” near the entrance to a pore, for instance.

The explanations just given might be considered adequate to explain the results Fig. 15, except for one disturbing fact. That is, it was possible to change the sign
of the measured streaming potential back and forth just by changing the concentration of salt in the water being used for testing. The experiment was carried out by first exposing the fibers to cationic polymer in the absence of salt. The cationic polymer was added until the streaming potential changed from negative to positive. Immediately, the charge started to decay back toward the negative side, so more cationic polymer was added. This was repeated until the fibers gave a strongly positive streaming potential indication in the absence of salt. Then salt was added to the system. Then the solution was replaced by salt-free solution, etc.

Results of the tests described are shown in Fig. 17. Note that it was only after adding the second dose of 0.3% poly-DADMAC, on a solids basis, that the streaming potential first became positive. A net addition of 0.9% poly-DADMAC yielded a strongly positive signal of ca. 70 mV. As shown, addition of salt changed the sign of streaming potential from positive to negative. The situation was reversed by filtering out the fibers and redispersing them in salt-free solution having the same pH (indicated by “60 µS/cm”). As shown, the gradual addition of salt made the signal go back to negative. Then the same cycle was repeated for a third time at the right-most section of the plot.

It should be admitted that the simultaneous occurrence of the charge-decay phenomenon can make it complicated to observe the effect of switching salt back and forth in Fig. 17. We probably would never have discovered the effect in the first place if we had restricted our research to cellulosic fibers. Fortunately, we have been carrying out parallel experiments with silica gel, a substance with known, relatively uniform pore sizes. A further advantage of silica gel, in terms of fundamental studies, is that these pore sizes are not expected to swell or shrink depending on such factors as salt concentration and pH. When silica gel was used in experiments similar to that shown in Fig. 17, the salt effects were even more dramatic relative to the simultaneous effects of charge decay. Those results will be presented in detail in a future publication.
Our current hypothesis to explain the effect of salt on the sign of streaming potential, following addition of cationic titrant to fibers, is shown in Fig. 18. First, we assume that the cationic polymer adsorbs mainly on the outside of a porous layer of microfibrils and nanofibrils at a fiber surface. At very low salt concentration we assume that the streaming potential signal is almost completely due to the charged nature of the outer-most layers of the fibers. Because those outer-most layers have a high concentration of cationic polymer, a positive streaming potential is observed. Then, after addition of salt, the observed streaming potential appears to involve a summation of two component signals – one originating at the fiber surface, and another component involving flow among and through pore spaces near to the fiber surface. Since the accessible surfaces between and under cellulosic fibrils and nanofibrils at the fiber surface are expected to have less of the cationic polymer adsorbed on their surface, this mechanism can explain why the second component signal will tend to be negative, and why the observed streaming potential switched back and forth in sign with changes in salt concentration.

Due to the surprising and subtle nature of the effects just described, a study has been initiated to discover its implications for the papermaking process. For instance, preliminary tests suggest that dewatering rates of fiber pads are highly correlated to the streaming potential, but only when those measurements are made in salt-free solution. Does that observation imply that drainage characteristics are most directly affected by the charge characteristics on the outermost surfaces of the fibers, as would be measured in salt-free solution? Some of our ongoing research efforts are aimed at finding answers to questions of that nature.

**Case Five: Some Samples that Give Poor Endpoints**

The next case to be considered involves the kind of samples that often seem to be particularly challenging for streaming current titrations, the method that was considered in Case One. Streaming current titrations were carried out with aliquots from a dilute solution of touch-oxidized size-press starch [41]. Titrations were repeated at various levels of NaCl addition. Results are given in Fig. 19.

Several different effects are shown in Fig. 19. First, the addition of salt tended to suppress the magnitude of the initial signal, before addition of any titrant. Second, the addition of salt tended to push the endpoint of titration toward the right, and effect which was later studied in greater detail [26]. Finally, once the salt level was above about 0.1%, it was not possible to reach any endpoint, even at addition levels way to the right of the plotted values.
Without going into all of the mechanisms that can lead to the problems of streaming current measurements at increasing salt levels [26,41], there are two practical questions that every user of this type of test needs to consider. The first question is whether the tests that are being carried out in a given mill by the streaming current method are inside or outside of the range of conditions where reliable results can be expected [41]. The second question involves whether more reliable results can be achieved by diluting every sample with distilled or deionized water.

Fortunately, there is a way to answer both questions mentioned in the previous paragraph. The test involves a comparison of the regular streaming current titration results with a reference test. The recommended reference test involves diluting the sample by a factor of ten with the distilled water, and then multiply the end result of the titration by ten.

Results of the kind of tests just described are shown in Fig. 20. The samples in question were obtained from a mill using thermomechanical pulp (TMP) with a high level of closure of the white water system. The pH was acidic, due to wood acids, in addition to the effects of aluminum sulfate. The electrical conductivity was approximately 3000 $\mu$S/cm. As shown, the tests were repeated with two different devices. In all cases, both with the "as-is" samples and after dilution with deionized water, the calculated cationic demand of the original samples was approximately the same. Also, each of the four curves was sufficiently linear so that the endpoints of the titration were relatively easy to determine. Though there was a moderate scatter in the endpoints observed in the case of device "A," at least the results were close enough to support the overall validity of the method.
The mill samples represented in Fig. 20 gave generally good titration results, even without dilution, in contrast to the situation shown in Fig. 19. The good results, despite the high conductivity, were tentatively attributed to a relatively high anionic charge density and pitchy nature of the samples. By contrast, the touch-oxidized starch had a very low density of anionic charge, and those titrations were carried out in the absence of wood pitch.

**Things to Keep in Mind**

Obviously the present discussion does not give a complete review of cationic demand titration methods. For example, procedures related to colorimetric and conductometric methods of endpoint determination were merely mentioned, with no consideration of possible interferences or challenges related to interpretation of results. However, it still can be useful to summarize some key points that ought to improve the reliability of charge demand data in general:

The first key point is to **select a test device and procedure** based on what kind of information you want from the test. If you want cationic demand information, then it makes best sense to use a streaming current or colorimetric titration procedure. Other types of detection schemes can be used, including streaming potential, microelectrophoresis, and conductometric titrations, also can be used as reference methods, to check your results. But the latter methods are usually considered to be more tedious, in terms of routine testing, compared to streaming current and colorimetric charge demand tests. By contrast, if you want to monitor changes in the electrokinetic potential of fibers, then streaming potential measurements are highly recommended. Likewise, micro-electrophoresis is the recommended way to determine the zeta potential of fine particulate matter.

The second point is to **pay attention to procedural details**. For example, time delays between collecting samples and running charge-demand tests usually
should be minimized. At the very least, any filtrations of the samples ought to be done immediately when samples are collected, since charge decay phenomena tend to be much less pronounced in the absence of fibers. Another way to minimize delays is by implementation of an online titration system.

Other procedures that need to be considered with care include whether or not samples are diluted by a factor of ten with distilled water, whether the pH is adjusted, whether the titrations are carried out in a forward or reverse direction (after adding an excess of polymer of one sign of charge), and whether there are certain ingredients in a typical sample that tend to interfere with a certain type of charge demand procedure.

The third point is to verify that the tests are giving reliable results. Ideally, such verification tests need to be done only once or twice, as long as there are no major changes in the chemical nature of the system. Microelectrophoresis tests have long been recommended as possibly the best kind of reference measurement, having the best reliability and the fewest problems related to theory [16,42]. Finally, when testing a new kind of sample, especially if the conductivity is higher than 1000 µS/cm, it is recommended to follow the “10X dilution” rule: After carrying out one titration on as-received filtrate from the system, the next sample is diluted 10X with distilled water, and the results are multiplied by the same factor. If your calculated cationic demand for the diluted sample changes dramatically compared to tests of an “as-is” sample, then it is recommended to always use ten-fold dilution with distilled water when testing that type of sample.

Literature Cited


