

# MEASUREMENT AND IMPACT OF CHARGE: A PRACTICAL GUIDE

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**Electrical charges on the surfaces of fibers and other materials in a papermaking furnish have profound but subtle effects on both the process and the product.** Because “charges” are invisible, they are sometimes overlooked as a source of operational problems and variability. However, the balance of surface charges within a paper machine system can directly affect the performance of retention aid chemicals.

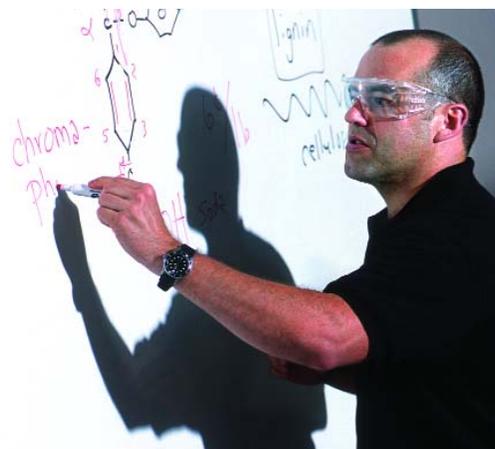
Low or variable retention of fine materials during paper formation can lead to other problems. Charge also can impact such things as dewatering rates, sizing efficiency, and deposit control.

About three years ago at North Carolina State University, Durham, North Carolina, USA, we began a detailed study of one of the most widely used methods for charge determination—the streaming current titration method. One of us (Chen) earned a PhD degree in the process. Details of our research results have appeared or will appear elsewhere (see, for instance *Colloids and Surfaces*

223: 215, 2003). During this work, and also while putting together and checking the literature review section of the thesis, we have had occasion to think about practical implications of charge measurements. Though the opinions expressed below are our own, we need to acknowledge the substantial research progress by others that helped lead us to the following general conclusions.

## WHAT IS CHARGE?

Charge effects in a papermaking furnish system are due to a form of static electricity. Most readers will be familiar with effects that can occur when the air is very dry—including hair that will not behave. The “hair standing on end” effect results from mutual repulsion of like charges on the neighboring strands of hair. Though sys-



**Dr. Med Byrd, professor, NC State University, Wood and Paper Science department, makes a point about wood chemistry. All photos by Roger W. Winstead, NC State Creative Services.**

tems immersed in water behave very differently from hair on a dry day, the basic rule still holds—like charges repel, but opposite charges attract.

There are three ways in which a solid surface immersed in a water solution can become charged. First, the surface may contain some acidic or basic groups. For example, fiber surfaces often contain between 20 and 100 millimoles of carboxylic acid groups per kg of fiber. These groups can dissociate, meaning that a positively charged hydrogen ion leaves the fiber surface and becomes dissolved in the adjacent water. This explains why most papermaking fibers have a negative surface charge, and why their charge becomes more negative when the conditions are changed from acidic to alkaline.

The second way that surfaces can become charged is related to crystal structure. Pure crystals, such as quartz ( $\text{SiO}_2$ ), have a fixed ratio between the numbers of each type of atom. A marked change in the surface charge is expected if some of the atoms in the crystal, for instance the silicon atoms, are replaced by another element, such as aluminum. Finally, and most importantly, immersed surfaces become charged by adsorption—meaning that other charged things come out of the water phase and get

## WHAT YOU WILL LEARN

- Some of the practical implications of charge measurement.
- How charge develops in the papermaking process.
- Key methods of charge measurement and how they can be used in the papermaking process.

## ADDITIONAL RESOURCES

- “A marriage for performance sake,” by Kasy King *Solutions!*, April 2003. To access this article, enter the following Product Code in the search engine on [www.tappi.org](http://www.tappi.org) :03APRS029.
- “Synergistic effects from performance chemicals,” by Kasy King, *Solutions!*, April 2004. Product Code: 04APRS045.

attached to the surface. These “charged things” can include salt ions, long-chain molecules (polyelectrolytes), as well as colloidal materials. The word “colloidal” can be taken as a synonym for “extremely small, but bigger than a molecule.”

If fiber surfaces were the only contribution to the overall charge of a paper machine system, then there would be little need to write this article. However, most papermaking furnish can be expected to have charged contributions from various other sources, some of which are included in the following list:

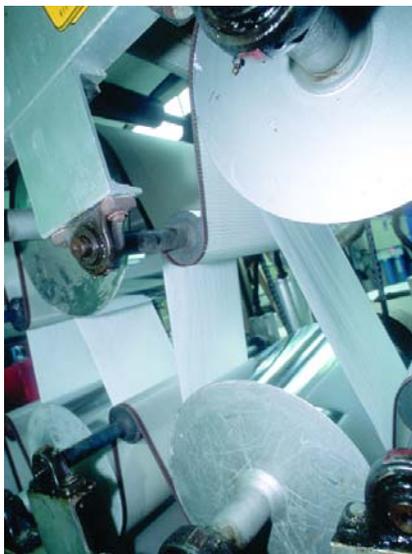
- Wood resins
- Black liquor carry-over
- Dissolved products of bleaching
- Dispersants from coated broke
- Soaps used in deinking
- Various papermaking additives

These materials generally contribute a negative charge to the paper machine system. The amount of negative charge entering the system from any of these sources is likely to vary over time.

### MEASUREMENT OF CATIONIC DEMAND

Of the two main types of charge measurement carried out at paper mills, usually the more important involve titrations to determine the “cationic demand” or “anionic demand”. The usual objective of such titrations is to estimate the surface and colloidal charge amount, per unit volume, of a sample of process water or fiber slurry. Let’s suppose, for instance, that the sample consists of whitewater from a paper machine, and that the sample has an excess of negatively charged colloidal materials suspended in it. In that case, the cationic demand equals the amount of a highly charged cationic (positively charged) polymer needed to exactly neutralize the charge.

Though it’s not our purpose to give detailed instructions, it is worth noting that scientists have devised several ways of determining the endpoint of charge titrations—that is, when the system has been ren-



**A Sheet of newly-formed paper being dried in the pilot paper machine system.**

dered “neutral” by the addition of an oppositely charged titrant polymer. These methods include the use of a color indicator, the observation of tiny particles migrating in an electric field, and the observation of electrical signals when water is forced through a plug of fibers. However, the most popular method for detecting the endpoint of a charge titration is called streaming current, or “the SC method.” The wetted parts of an SC instrument are very simple—just a plastic piston moving back and forth in a plastic cylinder, with the annular space filled with the sample of interest. Two metal probes provide a way to collect electrical signals, which are then converted into numbers that are easily read by the user. The SC device usually can detect the endpoint because colloidal materials from the sample come out of solution and coat the plastic surfaces. Equipment for running this type of test is well known and available from various sources.

### MEASUREMENT OF ZETA POTENTIAL

The term zeta potential refers to a voltage quantity, similar to the voltage of a flashlight battery. Zeta potential can be defined as the electrical potential very close to the surface

of a solid material immersed in a water solution. By knowing the magnitude of zeta potential, it is possible to estimate whether a suspension of particles will have enough mutual, electrostatic repulsion to prevent the particles from coming together. This can be a critically important question, for instance, if one needs to disperse or store a slurry of mineral particles. Zeta potential information also can be used in troubleshooting (see later), and when one is trying to figure out the most logical or the most effective sequence of additives to a process.

As mentioned in passing earlier in this article, there are two main ways to evaluate zeta potential. If one is interested in the zeta potential of very small particles, such as fiber fines or filler particles, it is recommended to use microelectrophoresis (ME). ME involves microscopic observation of particles migrating in an electric field. The zeta potential can be calculated from the velocity of migration, divided by the strength of the electrical field. Such measurements can be highly reliable and easy to interpret, though the equipment tends to be delicate, requiring a certain amount of training and skill.

If, on the other hand, one is interested in the electrical potential near to the surfaces of fibers, it is recommended to use a method called “fiber-pad streaming potential” (SP). SP measurements involve detection of a voltage signal when aqueous solution is forced through a pad of fibers.

### CHARGE MEASUREMENT BENEFITS

There are four main ways to benefit from charge measurements:

**Troubleshooting:** Being in trouble in the mill often means that you want a lot of information fast; you want to find out what is wrong. You’re in luck if routine charge data was obtained during a period when the process was behaving well. Then, at least, one can find out whether something concerning charge is “different” compared to the usual. Otherwise, in troubleshooting it is hard to generalize. In some paper machine sys-

tems, episodes of poor drainage and foam can be traced to an overdose of positively charged additives—and the diagnosis can be confirmed by measuring the zeta potential. Unfortunately, positive zeta potential numbers may be “normal” in a different paper mill, especially if a wet-strength paper grade is being made. It is a good idea to occasionally measure both the cationic demand and the zeta potential of each major stock stream and the whitewater; that way, when trouble strikes you will have some idea what “normal” is.

**Optimization:** Charge information can be valuable when one is trying to figure out the best addition level of a highly charged cationic additive, such as polyaluminum chloride (PAC), polyamine, or polyethyleneimine (PEI). These additives are often the key to optimizing the performance of retention aids and microparticle systems. In this regard, the charge demand measurements (tests that involve titrations) are especially useful *after* a dosage level has been found that provides a good combination of paper machine operation and product quality. Quite often there is a certain level of cationic demand in the system that provides the best combination of retention aid effectiveness and other desirable results.

**Control:** Charge demand titrations, such as those carried out with the SC method, have been found especially useful in paper mills where there are significant sources of variability, as in the list given earlier. The idea is to vary the quantity of a high-charge cationic additive, such as polyamine, so that the variations in cationic demand of the system are reduced or eliminated. In theory, this could be done with manual, lab-based measurements. But the most successful results have been obtained by online measurement of charge demand, with automatic adjustment of the charge-control additive.

There are two main schools of thought regarding where in the process to measure and control charge. The traditional approach has been to measure the charge of either whitewater or of filtrate collected from thin-

stock in the approach flow to the headbox. Such measurements allow the paper machine operators to compensate for the total of all contributions to charge variation. A more innovative approach has been to monitor and control the charge of thick stock. It makes sense to monitor the charge of whatever type of fiber stock makes the largest contribution to overall charge variation in the system. Thick-stock samplers make it possible to collect the filtrate samples needed to carry out such SC measurements automatically.

**Development:** Product development offers opportunities to use both charge demand and zeta potential measurements. The only limitations are the time requirements and the imagination of the technologist. Zeta potential tests can be especially useful in determining the best addition point for a critical additive, especially if something expensive needs to be retained with high efficiency.

#### SOME CAUTIONS

There are several “yellow flags” in charge measurement, including the following:

**Interferences, salts:** One of the biggest enemies of conventional charge-measurement methods is “salt,” in the sense of ionic materials in the water. The salt content can be roughly estimated based on electrical conductivity measurements, which are quick and easy to make. Our recent research showed that SC tests can become more difficult to interpret at conductivity levels above about 1000  $\mu\text{S}/\text{cm}$ . When in doubt, it is recommended to dilute the samples at a fixed ratio with distilled or deionized water (often at a

ratio of 10:1), and repeat the titration, multiplying the final result by the same factor.

Though aluminum ions are often considered to “interfere” with SC measurements, our most recent research has shown that under certain conditions of pH the aluminum ions can have a predictable interaction with an anionic titrant.

**Manual tests needed:** Before making changes involving online control of highly charged additives, it makes sense to first run manual trials. One goal of such tests is to estimate the cost of chemicals needed to achieve the best wet-end operations. Usually, a mill must make a cost-benefit decision. The next step in implementing online control is to verify that the additive selected for control has a sufficiently large effect on the measured charge. This can be verified by a “bump test,” in which the dosage of the selected additive is varied up and down, or down and up, within the proposed range of addition.

**Zero is not necessarily “best”:** Finally, “good charge is steady charge,” but there is nothing magic about the number zero. If one looks at publications from the 1970s, there was once a belief that paper machine systems “should” give the best retention and dewatering when the zeta potential at the headbox was near zero. But the studies from which such statements were drawn generally did not involve the use of retention aids. In addition, papermakers have generally learned that charge demand titrations provide a better basis for process control, compared to zeta potential (EM) or streaming potential (SP) measurements. **SI**

#### ABOUT THE AUTHORS:

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