Understanding conductivity and soda loss

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ABSTRACT: For more than 40 years, conductivity has been the inline measurement of choice for inferring black liquor/soda losses from brownstock washing. If properly applied, conductivity can provide a benefit in tracking changes in black liquor filtrate concentration. The implied concentration changes in turn can be used to provide feedback for dilution factor or shower flow control on the last stage of a brownstock washing system. A further extrapolation of this application is the correlation (or lack of correlation) of conductivity to soda loss. For each type of conductivity-based application, there are fundamental principles and assumptions that must be understood and managed to achieve the expected outcomes. The fundamentals of conductivity, the application of conductivity to measure black liquor losses during brownstock washing, and laboratory considerations when attempting to correlate inline process conductivity to absolute sodium content are reviewed and investigated. Finally, the operational objectives and measurement alternatives for employing conductivity measurements are discussed.

Application: Mills can gain knowledge about the theory, practice, and limitations associated with conductivity measurements, which can be used as a reliable feedback control mechanism for controlling brownstock washers.

Electrical conductivity (or specific conductance) of an electrolyte solution is a measure of its ability to conduct electricity. Much work has been done over the past 30–40 years to use electrical conductivity (EC) to measure black liquor losses during brownstock washing. There are some advantages to using this electrochemical measurement but there are also many disadvantages and misconceptions. First, EC probes are relatively inexpensive, easy to install, and provide a continuous signal with a quick response to changes in ionic concentration. The probe installation does not require any specialized sampling system. The probe can be placed directly into process lines and, except for periodic cleaning, it is low maintenance.

Unfortunately, EC measurements are not ion specific. Changes in any species within the solution exhibiting ion activity (both anodic and cathodic) will result in changes in the EC measurement. Such measurements are quite sensitive to temperature changes, and, even with temperature compensation, are only functional over a relatively narrow temperature range. In addition, some EC probes are subject to drift, as well as probe saturation; this results in either erroneous or flat-line responses. Finally, EC correlation to absolute concentration changes (e.g., sodium sulfate [Na_2SO_4], sodium hydroxide, sodium carbonate) has significant limitations when applied to black liquor.

FUNDAMENTALS OF CONDUCTIVITY

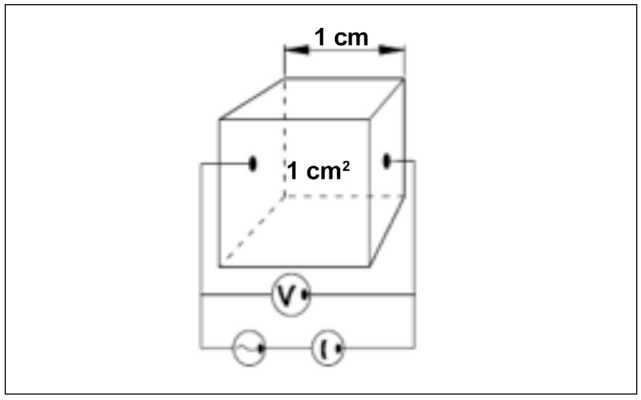
In the context of aqueous solutions, EC is a measure of the ability of the solution to conduct an electric current. Electrical conductivity measurements are affected by the concentration of the ions in solution (i.e., the higher the ion concentrations, the higher the EC values), the temperature of the solution (i.e., the higher the temperature, the higher the EC value), and the specific nature of the ions present (i.e., the higher specific ability and higher valence of the ions, the higher the EC value).

Electrical conductivity is measured as the inverse of resistance (R). From Ohm's Law (V = I * R), EC can be determined by applying a voltage (V) across two electrodes in a solution and measuring the induced current (I). Electrical conductivity is then calculated by dividing the current by the voltage. Using 1/R as the reciprocal of EC, EC= I/V.

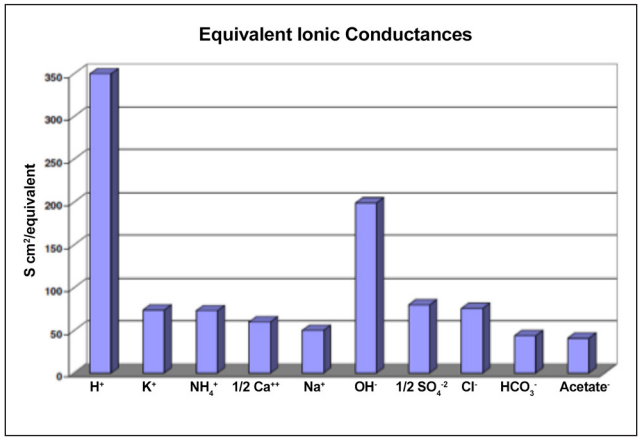
Historically, EC was measured in mhos or mmhos. Currently, the accepted SI unit for EC is Siemens/cm (S/cm) where a Siemen is equivalent to 1/ohms. Thus, the conductance in Siemens is the reciprocal of the resistance in ohms.

The unit conductivity cell

The strict definition of electrical conductivity is the amount of current passing between two standard plates (electrodes) of opposite charge (cathode [+] and anode [-]) of known area and separation distance. To accommodate a range of conductivities and to establish a benchmark standard, a cell constant (a result of the distance between electrodes divided by the cross-sectional area of the electrodes) is provided for each probe, with units of cm^{-1}. A cell constant of 1 is defined for electrodes each with a surface area 1 cm x 1 cm and separated at a distance of 1 cm. In terms of dealing with solutions, consider measuring the ionic activity of 1 cm^3 of solution between the standard plates. **Figure 1** [1] is a representation of the standard EC cell with a cell constant of 1.



1. Cell constant derivation [1].



2. Conductance of selected common ions at 25°C and 1 equivalent [3].

Ion type and pH impact

A large disparity in ion strength exists between different ion species. A conductivity reading of 9.2 S/cm, for instance, indicates a solution of either 18% potassium chloride or 6% potassium hydroxide [2]. **Figure 2** [3] shows the conductance of several ions common to the pulp and paper industry. It also shows that the presence of either the hydroxide ion (OH^-) or hydrogen ion (H^+) will contribute far more than other ions to the overall EC of a solution and even mask the presence of some salts (2). Therefore, the solution pH will have a major impact on the solution conductivity as the pH moves farther from 7.0 in either direction.

The term equivalent ionic conductance is used when referring to the conductance of a single ion species in its single valence state. Thus, divalent ions such as Ca^{+2} and SO_4^{-2} are expressed as ½ Ca^{+2} and ½ SO_4^{-2}, respectively.

Black liquor contains, as a minimum, OH^-, Na^+, CO_3^{-2}, Ca^{+2}, and SO_4^{-2} ions. Four of these ions are listed in Fig. 2. Therefore, it can be inferred that a change in the amount of any one of these species, particularly OH^-, can affect the measured EC of a black liquor solution.

Conductivity-concentration relationship

Frequently, EC measurements have been used as a surrogate measurement of black liquor or saltcake losses in pulp washing systems. As such, it is necessary to convert EC measurements of S/cm to concentration-based units of mass per unit volume such as g/L or lb/gal. As stated previously, EC is affected by a change in the ion species whether they be positively (cation) or negatively (anion) charged. The EC of a solution in theory is a function of the sum of the individual active ion equivalent conductivities multiplied by their individual concentrations. A mathematical model of this is represented in Eq. (1):

$$k = \sum_{i=1}^{n} \alpha_i l_i C_i \qquad (1)$$

where:
k = conductivity of the solution
α_i = fraction of the i^{th} constituent (of n ions) present as a free ion
λ_i = equivalent conductivity of the i^{th} ion
C_i = concentration of the i^{th} ion specie.

The equivalent conductivity, λ, of several ion species can be found in publically available tables; examples of these are shown in **Table I** [4]. There are also published conductivity factors of λ_i/C_i or EC per some standard concentration expressed as µS/cm per mg/L [4]. **Table II** [4] lists conductiv-

Cation	Equivalent Conductivity, $cm^2\ equiv^{-1}\ ohm^{-1}$	Anion	Equivalent Conductivity, $cm^2\ equiv^{-1}\ ohm^{-1}$
H^+	349.7	OH^-	198.0
Li^+	38.7	Cl^-	76.3
Na^+	50.1	HSO_3^-	50.0
K^+	73.5	HCO_3^-	44.5
NH_4^+	73.7	CO_3^{-2}	72.0
Mg^{+2}	53.1	SO_4^{-2}	79.8
Ca^{+2}	59.5	$HCOO^-$	56.0
Ba^{+2}	63.7	CH_3COO^-	40.9

I. Equivalent conductivities of aqueous ions at 25°C [4]. Note that 1 equivalent equals 1 mol for monovalent ions and ½ mol for divalent ions.

Ion	Conductivity Factor, mS/cm per mg/L
Cations	
Ca^{+2}	2.60
Mg^{+2}	3.82
K^{+}	1.84
Na^{+}	2.13
Anions	
HCO_3^{-}	0.715
Cl^{-}	2.14
SO_4^{-2}	1.54
NO_3^{-}	1.15

II. Examples of conductivity factors [4].

ity factors for several ion species of interest in brownstock washing. While both anions and cations carry current, they do so to different degrees. In general, divalent cations have higher specific conductivity than monovalent ones. This is not true of anions. **Table III** shows a simple example of how to use Eq. (1) to determine the theoretical conductivity of a sodium sulfate solution of a known concentration.

One simply multiplies the known concentration of each ion by its conductivity factor to determine the conductivity contribution of the ion. Then, one sums the conductivity contribution of each ion, in this case just two, to obtain the conductivity of the solution, in this case 880 µS/cm. From this information, it is possible to determine the dissolved inorganic solids to be 427.5 mg/L. In black liquor, organic dissolved solids also contribute to total dissolved solids (TDS); therefore, the amount of dissolved organics must also be known to determine the TDS of any black liquor sample. It has been shown that the inorganic components contribute significantly more to the total conductivity of black liquor than do the organic components [5].

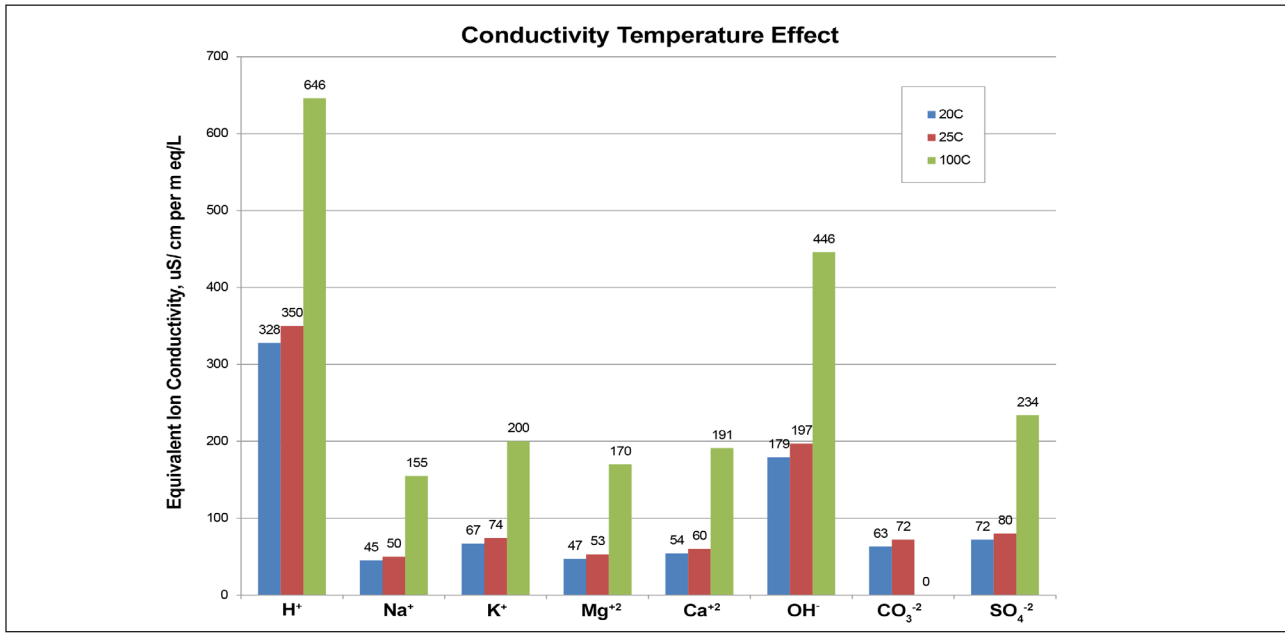
In general, for washer control, the inverse of this process is employed. The practical implication is that if the conductivity, the conductivity factor, and the species molar distribution are all known, then the concentration can be calculated. This approach could work if it can be assumed that the relative ratios among the species were constant and those ratios were known. For the example case shown in Table III, the $Na+:SO_4^{-2}$ ratio is 346.2:51.9 or 7.237:1. Unfortunately, in practice, these ratios do not stay constant.

Temperature impact

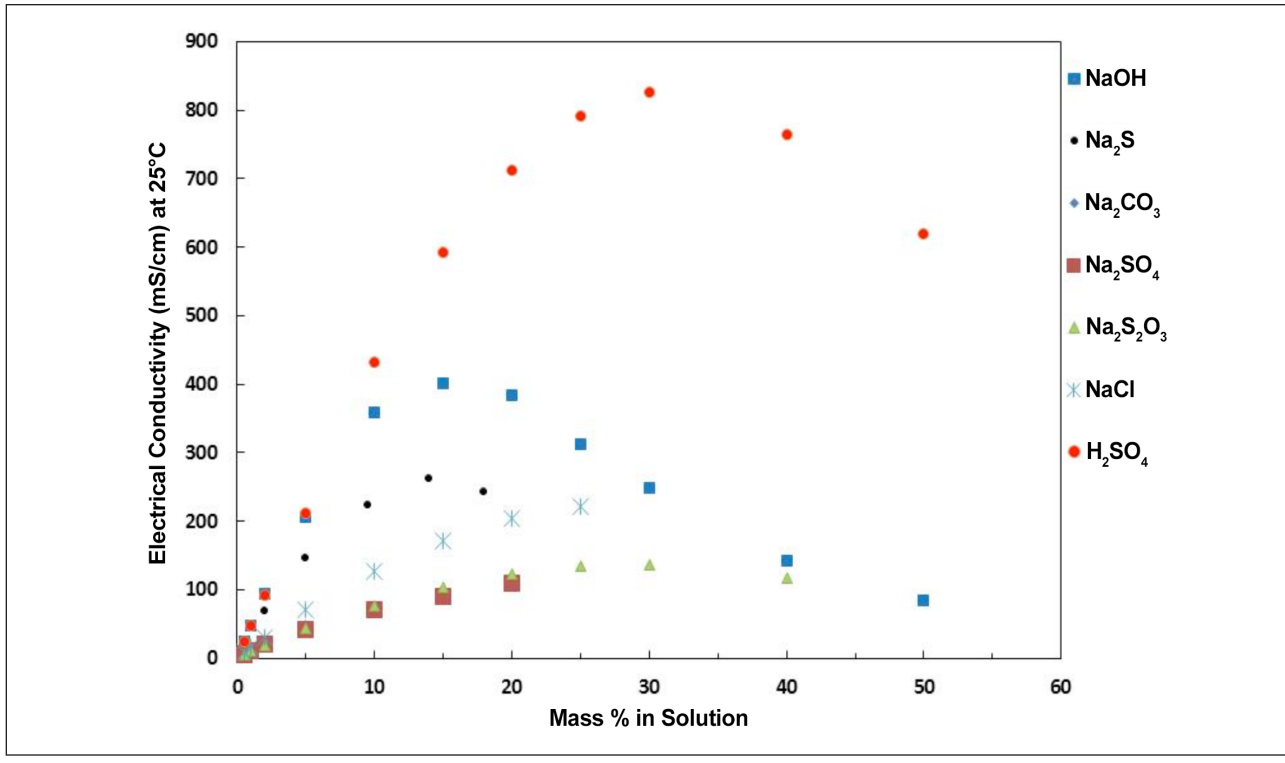
The activity of each ionic species behaves differently to changes in temperature. **Figure 3** [6] is a graph of a select

Ion	From Table II Conductivity Factor, µS/cm per mg/L	Example Concentration, mg/L	Calculate Conductivity, µS/cm
Na^{+}	2.13	375.6	800
SO_4^{-2}	1.54	51.9	80
	Total	427.5	880

III. Conductivity calculated from concentration.



3. Temperature effect on conductivity for select ions [6]. Note that 1 equivalent = 1 mol for monovalent ions and ½ mol for divalent ions.



4. Change of the conductivity with increasing concentration [7–9].

group of ions. The y-axis is the equivalent ion conductivity and the blue, red, and green bars display the equivalent ion conductivity for each of these ions at 20°C, 25°C, and 100°C, respectively. With the exception of the H^+ ion, all of the other inorganic ions are expected to be present to some degree in black liquor. From these results, it might be concluded that the presence of OH^- in any appreciable amount will skew the reading. In addition, the carbonate ion behaves differently than the other ions, reversing its EC value once a certain temperature is reached. As sodium carbonate can account for as much as 20% of the sodium present in a black liquor solution because of inherent inefficiencies in the causticizing process, its inverse behavior with temperature makes it difficult to develop universal temperature compensation. Finally, as typical operating temperatures for the last-stage shower water of brownstock washers are about 65°C–75°C, the temperature compensation is important for high-quality EC measurements to predict black liquor concentrations.

Common ion effect, nonlinearity, and dissociation of ions

A theoretical EC limit is reached as the compounds of interest dissociate into ions and move about the diluted solution. As the general ion concentration increases, more ions dissociate into the solution, increasing the EC. This continues until the space between the free-moving ions decreases and their potential to reunite with oppositely charged ions increases to the point that they begin to reform back into salts. Thus, it is not practical to correlate conductivity to black liquor solids above a certain concentration. That concentration limit is beyond the scope of this paper.

Figure 4 shows the data taken from three literature sources [7–9] for the most prevalent inorganic sodium compounds found in black liquor, plus sulfuric acid for comparison. Each of the species shown, except for sodium chloride, reaches a maximum electrical conductance. As the concentration of the species increases beyond its maximum conductance point, the specie's conductance will steadily decrease as its concentration further increases. The problem is that for any given EC for each ion species, only two different concentrations are possible. It is further compounded by the fact that many ion species are present and concentrations of these species change as process conditions change (e.g., causticizing efficiency, residual effective alkali). On the positive side, the concentrations of washed pulp filtrate should be low enough (<1%) to avoid this effect. However, weak electrolytes, such as the organic salts formed from the lignin, increase in conductivity as the solution becomes more dilute.

BROWNSTOCK WASHING APPLICATION

It is prudent to discuss the larger objectives and key process indicators (KPIs) of brownstock washing before covering field measurement applications, probe locations, and laboratory methods used to correlate EC values to soda losses and washer efficiencies.

Parameters of interest in brownstock washing

Brownstock washing is uniquely positioned at the crossroads of

the fiber line and the recovery processes, and its performance affects both areas. Both areas have parameters of interest, and brownstock washing also has environmental implications. When establishing a washing control program, it is important to define the operational parameters of interest, to be able to measure those parameters, and to be able to control the process to maintain those parameters within acceptable limits.

There are a myriad of ways to expresses washer losses, such as soda losses, inorganic solids, organic solids, total black liquor solids, chemical oxygen demand (COD), bound soda, and total soda in either metric or English units of mass. The denominator fiber mass can be equally diverse, employing such units as o.d. tons, a.d. tons, machine dried (m.d.) tons, brown tons, bleach tons, metric tons, and short tons. The issues to be addressed before any work is done are to define what will be measured and why, how it will be measured (often the only issue defined in practice), how the information will be used, what measurement frequency is required, and what degree of accuracy and precision/repeatability is demanded. A few of these will be explored.

Soda loss

Historically, brownstock washer soda loss has been defined as the pounds of equivalent saltcake (Na_2SO_4) lost per ton of air-dried pulp washed. The reality is, of course, that a minimal amount of sodium sulfate is present in the washer filtrate; rather, all of the sodium-based compounds are converted to their stoichiometric equivalent Na_2SO_4. Much like sodium oxide has been the standard expression of equivalent sodium compounds present in white, green, and black liquors (to a lesser degree), saltcake has been used for decades as the equivalent sodium compound of choice for washer losses. Historically, it has been the predominant makeup chemical in the recovery furnace before the environmental push to low-odor recovery boilers in the 1970s. Despite few mills still using saltcake as a makeup chemical, old habits are hard to break and it remains the reference expression for many unbleached mills today.

COD

During the Cluster Rule years of the early 1990s, organic loading on the bleach plant became a priority. For mills with bleach plants, the logical new washer loss parameter of choice has become the COD test. COD more closely correlates to first-stage bleaching chemical usage and the organic chemistry involved. As an environmental parameter, COD also became more popular because results can be achieved in an hour or so, whereas BOD_5 by design is a 5-day test. Unfortunately, COD does not reliably correlate well with biological oxygen demand (BOD) for reasons beyond the scope of this paper.

Total dissolved solids

Strictly in terms of the washing operation, total dissolved solids (TDS) is the parameter of interest for several reasons. First, displacement ratio (reduction of dissolved solids/maximum reduction of dissolved solids possible), wash yield (dissolved solids removed/dissolved solids entering), Norden's modified efficiency factor, and equivalent displacement ratio number all use dissolved solids in their determination. Second, all washer material balance calculations must use dissolved solids mass. Third, it is a relatively easy test to run and new laboratory devices can complete the task in less than 15 min. This would apply to not only the last-stage filtrate squeezing, but to all shower streams, vat liquors, and previous-stage mat squeezings. Fourth, knowing dissolved solids losses at the washers can help account for changes in daily solids burned in the recovery boiler and even the steam used to evaporate the water associated with those solids. Neither conductivity nor COD can contribute toward the understanding of any of these parameters.

Balancing pulp cleanliness and first-stage black liquor solids

The most basic parameter of interest is pulp cleanliness. Black liquor-laden pulp can cause a number of downstream issues, including increased first-stage bleaching chemical usage and wet-end chemistry problems on the paper machine. Both the machine and bleach plants run at a significantly lower pH than the brownstock washers, so downstream acid usage is directly affected by the amount of high-pH black liquor carried over with the pulp.

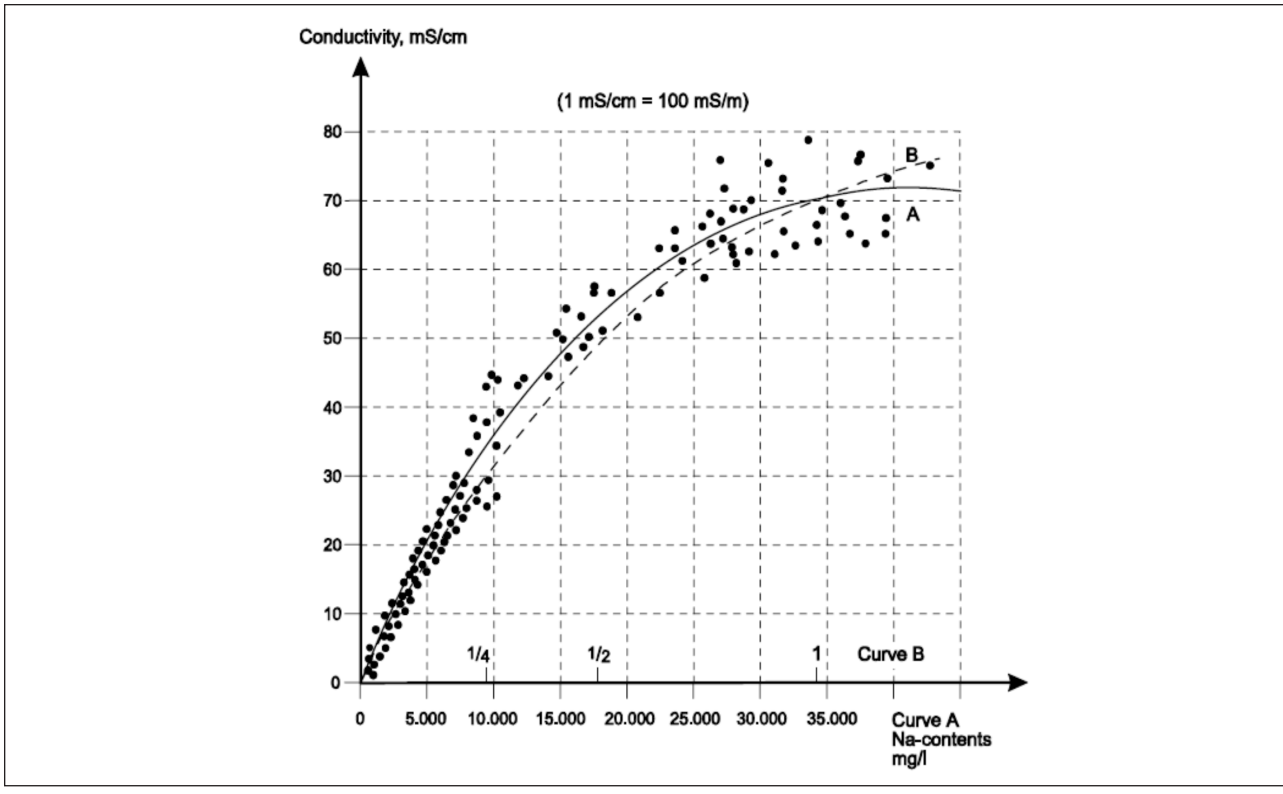
The amount of sodium in the black liquor leaving with the pulp has obvious direct cost implications. In most washing systems, it is the only parameter tested or measured. There is no direct online/inline measurement of sodium losses. Several inferential measurement technologies are available, each with their advantages and disadvantages. Conductivity is one of these methods.

Of note, EC measurements respond almost exclusively to changes in inorganic chemistry; therefore, EC is not a direct predictor of organic black liquor solids losses during washing. Rather, EC measurements infer that changes in the inorganic losses during brownstock washing correlate with changes in organic solids losses as well.

As brownstock washing is a balancing act between obtaining well-washed pulp with a minimal amount of shower water and obtaining a high TDS concentration in the black liquor being sent to recovery, it is important to establish good and reasonable control boundaries for each end. A maximum soda loss limit on the washed pulp leaving the last washer is typically specified to control the negative impact on bleaching chemical demand, cost of sodium makeup chemicals, or wet-end chemistry on the paper machine. A minimum TDS concentration on the liquor being sent to recovery from the first-stage washer is typically defined by the mill evaporator capacities. These two operating parameters are typical process boundaries employed in industrial brownstock washing.

Relating field measurements to laboratory tests and operational KPIs

For at least 40 years, inline conductivity probes have been used



5. Change of the conductivity with increasing concentration [1].

in brownstock filtrate lines to infer soda losses (i.e., pounds Na_2SO_4 per ton of pulp.) Some mills report excellent correlation while others are unsuccessful. Mills that are successful tend to have more stable process conditions. Successful conductivity measurement must start with relatively stable brownstock washer operating temperatures with consistent wash water cleanliness and well-performing temperature compensation algorithms. When the washer filtrate or wash water temperature varies, the conductivity measurements can become unpredictable. Stable cooking conditions and consistent wash water quality also improve conductivity reliability for control purposes.

Sampling and testing

Sampling and testing, whether applied to a measurement calibration-correlation or to routine laboratory testing (e.g., of liquor, effluent, or water), should all be conducted with thoroughly defined, followed, and understood procedures using laboratory-grade diligence. For the soda loss discussion alone, these will be covered in more depth to appreciate where erroneous results might occur.

Accuracy, repeatability, and reproducibility

Numerous statistical terms and applications are applied to liquor and pulp laboratory testing and correlation. The two most often mentioned are accuracy and repeatability. Joint ANSI/TAPPI Test Method T 1200 sp-14 "Interlaboratory evaluation of test methods to determine TAPPI repeatability and reproducibility" defines repeatability as an estimated limit below which the difference between two test results is expected to fall 95% of the time, when the results are obtained at a single laboratory. Repeatability reflects the variability inherent in the experimental system used to determine its value. Unlike repeatability, the term accuracy compares test results against a stable standard with sheet grammage (Mylar plastic sheet) and brightness (MgO disk) being examples. Although used frequently, the term accuracy has no relevance to parameters such as kappa number, for which there is no stable standard to calibrate.

The accuracy of a conductivity probe may be measured against a standard solution of known concentration in the laboratory, but when EC values are used to infer black liquor losses, accuracy is no longer relevant. There is no black liquor calibration standard; therefore, the best that can be done is to rely on repeatability and the correlation coefficient between the filtrate and the conductivity readings. Certainly the operating temperature in the field is higher than the laboratory-tested temperature. So, with lab conductivity, we cannot totally rely on a sample collected in the field, even when carefully sealed and tested in the lab, because the two probes will likely have different cell constants and temperature compensation algorithms.

Analytical determination of soda loss

How samples are taken and tested are important considerations in accurately determining the mass-ratio of saltcake pounds per pulp tons. First, the last-stage pulp mat filtrate

must be properly sampled. Variations in procedures exist. The sample may be an individual hand-squeezed sample or a composite taken over several hours. Samples are often taken at a single location across the width of the washer. It is well known that mat filtrates vary in soda content and mat consistency both across the mat and over time at a single location on the drum. As a result of this variation, an often underappreciated element of any sampling procedure is how well the sample represents the larger process. If a sample is taken, for instance, at a point across the washer where the mat is noticeably thinner and dryer, that filtrate will likely be cleaner than the rest of the pulp and render a nonrepresentative result.

The next consideration is how sodium content of the sample is determined. While a few mills might still go no further than to use an in-house table developed decades earlier relating laboratory conductivity to saltcake loss, most mills likely have advanced to the point where a central laboratory mass spectrometer or atomic absorption laboratory unit is employed to measure soda losses. Here, it is important to understand whether the sodium concentration is expressed in units of mass/unit filtrate volume (e.g., g/L) or in sodium mass/mass of filtrate (e.g., ppm.) If sample dilution (using deionized water) is part of the procedure, then that must be taken into account as well. It will be assumed that the sampling and testing procedures were properly prepared and carefully followed to obtain an accurate concentration. The result must still be expressed on the same mass basis as the pulp.

Determination of the reference pulp mass

The sodium concentration in the pulp mat sample must be proportioned to the o.d. pulp mass. The most direct approach is to take a large stock sample (>100 g) off the washer just before it enters the repulper while being careful not to lose any filtrate in the sampling process. The collected sample is bagged and taken to the laboratory, where it is weighed as received, dried, and then weighed again for o.d. mass. The sample's consistency is determined from these two mass measurements. The squeezed sample should ideally be taken from the same sample. By knowing the consistency and the soda content of the squeezed sample, it is now possible to calculate the soda loss.

Successful correlation between conductivity and soda loss

The fact is that some mills have (or claim to have) successfully correlated field conductivity to soda loss. While this seemingly contradicts the previous arguments, there is at least one explanation. Most correlations between conductivity and soda loss are done in a short-term period. In this context, the production rate, operating conditions, and white liquor chemistry are relatively stable and result in a reasonable short-term correlation. Causticizing efficiency, which defines the carbonate content in the black liquor even if highly variable, would likely not affect the residual liquor chemistry within a period of 8–12 h when considering the residence time and mixing within a typical white liquor storage system. Thus, stable conditions might render favorable correlation, assuming laboratory procedures are also carefully followed.

Figure 5 [1] illustrates a characteristic correlation between black liquor sodium content and conductivity from an equipment supplier using EC probes to monitor and control brownstock washing. This figure includes two different curves. Curve A shows conductivity versus sodium content from an entire continuous diffuser washing plant, while curve B represents the black liquor obtained from the digester at the blow line diluted to various dilution levels (i.e., ¼, ½, and undiluted) [1]. Figure 5 confirms that at low sodium concentrations (<10 mg Na^+/L) a near linear correlation to conductivity can be achieved; however, above 10 mg Na^+/L concentration, more statistical scatter is evident.

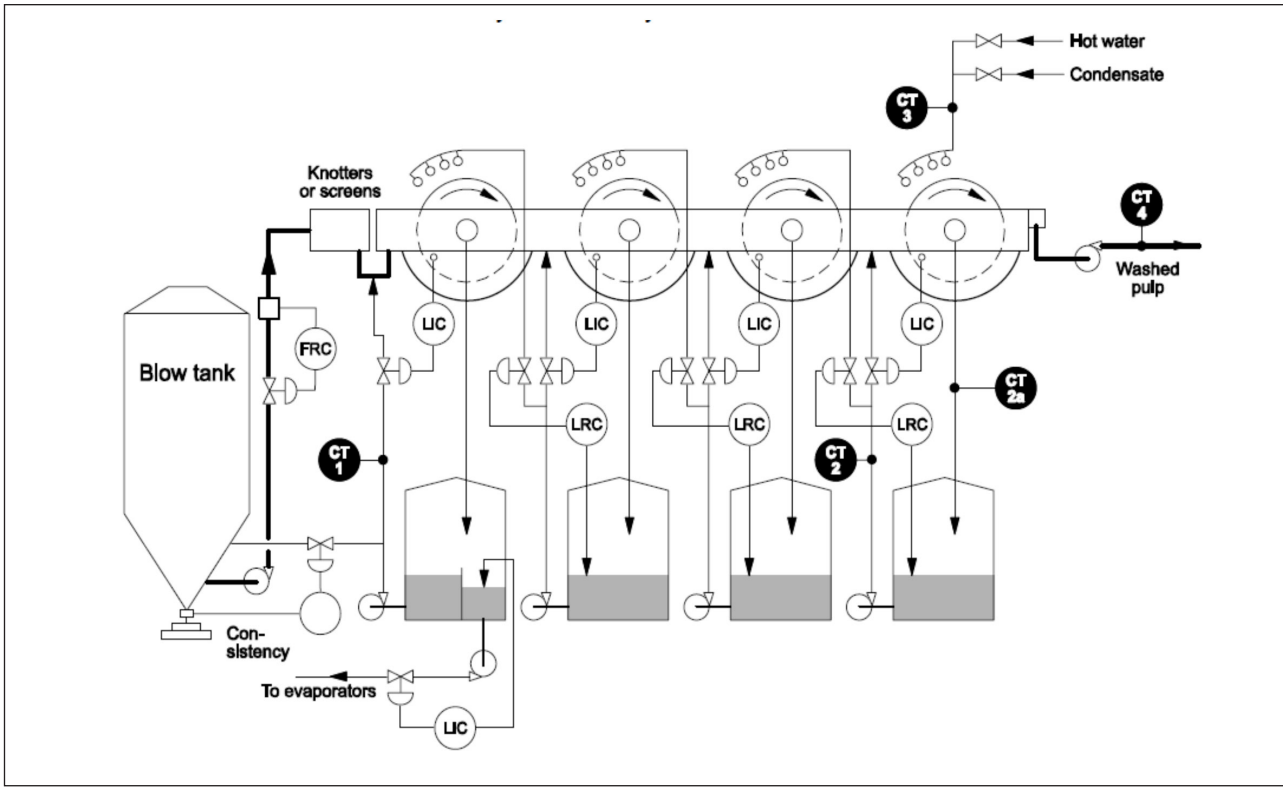
Investigators at a university [10] reported a linear correlation between the measured EC values and inorganic levels found in black liquor filtrates of a brownstock washing system. Sodium, the most prevalent inorganic component of black liquor, usually represents all the inorganics. This implies that conductivity can be correlated to sodium content.

Measurement location

For EC measurements to work as a pulp washing control method, the locations of probes and an understanding of the actual measurement being employed are essential. The probe needs to be located in a weak liquor stream with a reasonably stable operating temperature. Relative changes in the EC measurement can be used as a surrogate to monitor changes that arise during the brownstock washing process with technical success. Employing the EC probe as a method of closing the last-stage shower water flow control loop with direct EC feedback has proven valuable in several of our mills. **Figure 6** [1] represents a recommendation from an equipment supplier on the location of conductivity probes for a vacuum washer. These recommendations are not necessarily endorsed by us.

Measuring the pulp as it leaves the washer before further dilution results in an ideal location to represent washer effectiveness; however, this location is an extremely difficult application for a conductivity probe. If the EC is measured in the pulp stream after repulper dilution, what is being measured is the combination of soda loss in the pulp along with the dilution water EC. When the combined measurement is used for control, changes in repulper dilution water will be interpreted by the EC measurement as changes in brownstock washing efficiency. Electrical conductivity measurements from the combined streams cannot be used for displacement ratio calculations. However, if the mill is only interested in the relative changes in the amount of black liquor leaving the system and reasonably maintains constant repulper dilution flows, then this application is appropriate.

Another common probe location is in the last-stage filtrate line. If the EC measurement is located in the last-stage filtrate line, it should track final filtrate concentration changes; how-



6. Suggested conductivity probe (CT) locations [1].

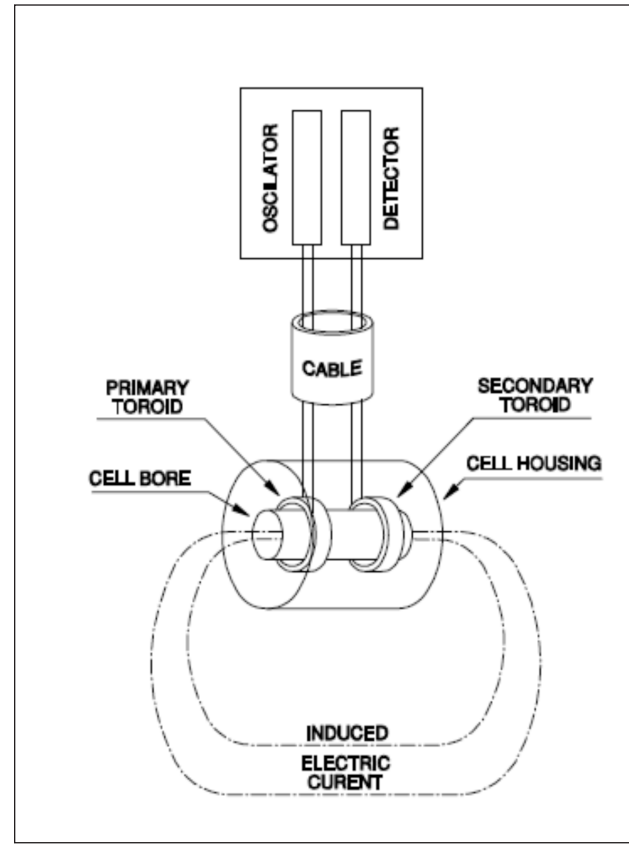
ever, it will not be representative of the liquor that leaves with the pulp [11]. Locating the probe on the outlet of the filtrate dilution pump of the last washing stage is of limited value because of the large capacity turnover time in the filtrate tank and the mixing effects that preclude the system ever reaching equilibrium. The resulting time constant of the filtrate tank system is too large when compared with the changes occurring on the washer for adequate control. Locating an EC probe in the first stage of brownstock washing will result in probe saturation. A saturated probe does not respond to changes in the black liquor concentration, which results in poor process control.

Conductivity probe selection

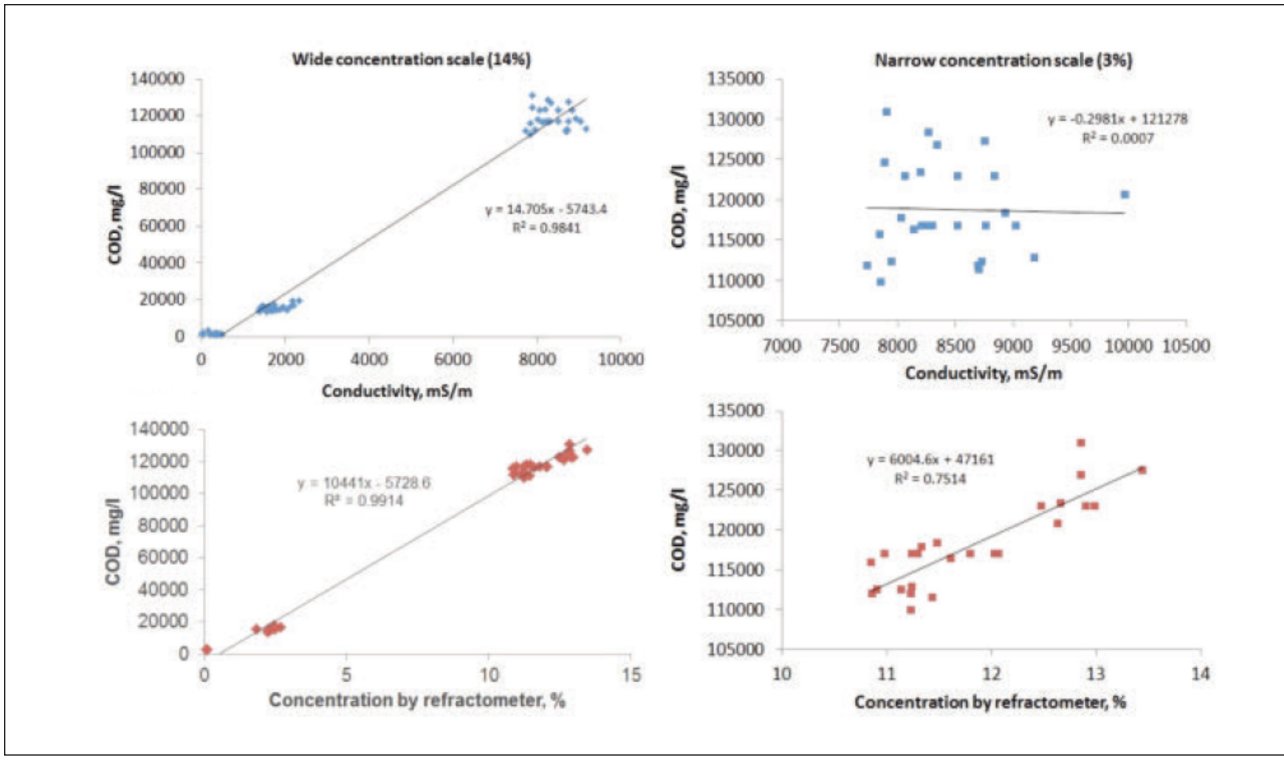
There are many conductivity probe configurations representing differing probe types, metallurgy, and cell constants. If conductivity is going to be employed, then the equipment manufacturer should be directly involved in the probe selection process.

Toroidal conductivity probe

For harsh inline applications or applications under pressure (e.g., pulp washing) and for applications in solutions (e.g., white liquor) that tend to form hard scales, traditional conductivity probes are not reliable. Instead of using two electrodes, a toroidal-shaped electrode may be employed for fiber-free, filtrate applications. The kinetic energy of the ionic solution flowing through the hole in the toroidal electrode induces a



7. An inductive toroidal sensor [1].



8. Correlation of chemical oxygen demand (COD) and black liquor solids measured by refractometer and conductivity probes [12].

current in the inductive coil magnet housed in the probe. The current may then be measured to determine the EC of the solution. In addition to withstanding pressurized, higher temperature conditions, all of the wetted parts of the probe are typically constructed of inert PEEK polymer (polyetheretherketone). **Figure 7** [1] illustrates an inductive toroidal sensor.

Alternative measurements

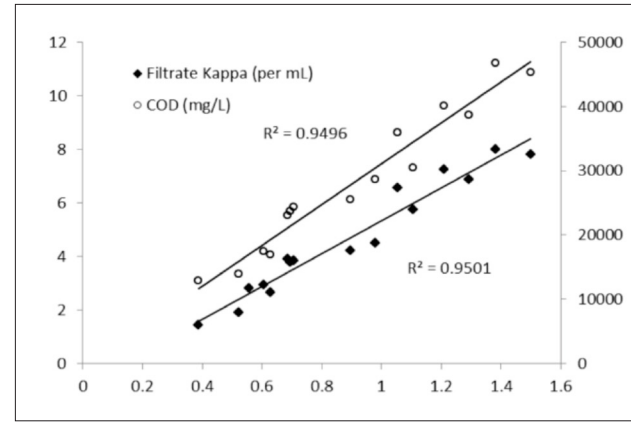
Several new technologies have been introduced in the past few years that offer promise to more accurately measure washer losses.

Refractive index

One equipment supplier [12] has developed a refractometer probe that has had success in correlating to brownstock washer losses in general. It has the advantage of being inserted into either a filtrate or stock stream and can be removed without shutting down the process. In addition, on a drum displacement washer system, refractive index measurements have been shown to correlate well to COD [12]. Recent work has shown that while conductivity may have success over a wide measurement span, it displays significant scattering relative to the refractometer when applied over a narrow range as shown in **Fig. 8** [12].

Dissolved lignin transmitter

A new technology using an advanced optical measurement probe has successfully measured dissolved lignin in a brownstock washer pulp slurry. The equipment supplier of this technology [13] has shown linear correlations obtained from the probe's sensor signal values to laboratory measurements of the filtrates' kappa numbers and COD values (**Fig. 9**).



9. Filtrate kappa (per mL filtrate; left y-axis) and COD (mg/L filtrate; right y-axis) versus sensor signal (x-axis) [13].

CONCLUSIONS

Electrical conductivity has been successfully employed in feedback control of brownstock washer systems for several decades. Some mills have reported good success with conductivity-based control systems while others have experienced extreme difficulties.

It is important to understand that EC measurements only measure ion species within an aqueous solution. Electrical conductivity measurements have been correlated to black li-

quor concentrations, but those correlations change when the temperature of the solution changes and when the relative concentrations of the different ionic species changes. For example, small increases in the residual alkali (OH^- concentration) result in significant increases in the reported EC measurement. Process temperatures >25°C can result in decreases in the EC measurement, particularly with the CO_3^{-2} ion contribution as seen in Fig. 3.

Placement of EC probes is also important to successful control loop operation. Conductivity probes should only be employed in relatively low concentration solutions. Placing an EC probe toward the front end of the washing system will result in probe saturation and poor process control. Placing an EC probe in the discharged pulp stream after the last repulper will result in a combined measurement of the true pulp cleanliness (from an inorganic viewpoint) and the EC measurement of the repulper dilution water. Therefore, changes in repulper dilution flow (or concentration) will erroneously infer changes in washer performance. The ideal location for an EC probe is in the pulp being discharged from the last stage of washing before the addition of dilution water. In practice, this location is extremely difficult to locate and maintain a working EC probe that will reliably provide measurements. Placing a probe in the intermediate shower water lines fed from any of the liquor filtrate tanks will result in significantly long process time constants for the washer controls because of the long residence times in the filtrate tanks. In addition, the filtrate in these tanks rarely comes to process equilibrium with the washed pulp so the EC measurements obtained from these locations are not truly representative of the washer performance. **TJ**

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ABOUT THE AUTHORS

We chose this topic because the application of conductivity measurements seems to be a misunderstood and sparsely researched subject. Conductivity measurements apply to virtually every brownstock washer mill, so it is something that is important to understand.

Our research complements previous work that has discussed conductivity in general and washer losses in particular. What is different here is that we cover the application of this measurement to the brownstock soda losses. The difficulty was in finding papers that would bridge the gap between theory and application as it relates to using conductivity as a surrogate measurement of soda loss. This paper finally does that. Publicly available papers, some mill washer testing work, as well as personal experience covering more than 40 years were required to complete this work.

This work expanded our understanding of the importance of temperature on conductivity measurements, the reformation of salts in an electrolytic solution at higher concentrations, and the resulting erroneous conductivity readings associated with them. The inverse conductivity of the CO_3^{-2} ion at elevated temperatures and the process implications associated with the causticizing efficiency upstream from the washers and digesters were all interesting and important realizations.

Brown

Hart

This paper offers insights into the measurement of soda losses for every brownstock washer operation at every kraft mill, as well as the benefits and limitations of using conductivity measurements generally and applied to washer losses specifically. The next step is to apply these learnings to our fleet of more than 40 brownstock washer lines.

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