The Importance of Electrochemical Control during Moulded Pulp Production

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Introduction

Pulp moulders continually face economic and social pressure to make use of alternative sources of raw materials in place of the more traditional tree-based sources of cellulose fibres. The reasons for the shift are straightforward enough. Alternative raw materials are much lower in cost relative to virgin market pulps. Processes used to produce the alternative materials are more energy-efficient and have higher yields for mouldable fibres produced. The alternatives are often by-products of other industries (agricultural, mining or forestry waste) or are recycled after use by consumers or industry. Unfortunately, these alternative raw materials carry a significant amount of baggage – in the form of excess levels of dissolved solids and fine particulate materials (popularly known as anionic trash). Moulders are often surprised when switching to the alternatives because runnability and processability suffer. Whenever using alternative raw materials, pulp moulders must take special precautions to compensate for the greater amounts of dissolved solids present and for the higher level of negative charge potential in solution.

Comparison of traditional cellulosic sources with alternative raw materials

Tree-based cellulose fibres were once the main raw material used in production of parts in the moulding process. There were several good reasons for this. The raw materials were usually easily obtained from local forests, which had consistent numbers of hardwood (poplar, aspen, maple, cottonwood) or softwood (pine, spruce, fir) species to draw from. Virgin bleached fibre was easy to produce in pulp mills, and also easily and economically transported to moulders in dry sheet or lap (wet) pulp form. The resultant pulps were very clean, with low levels of silica and dissolved materials to affect the moulding process. As a result, moulders were able to easily produce parts from the virgin-fibre raw materials, with minimal losses of raw materials and maximum "first pass" fibre retention on wire moulds. Deposits on equipment were low, and the parts themselves were able to dewater rapidly, without excessive heat applied to the platens of the moulding machine.

The moulding industry has changed substantially over the past several decades, mainly due to pressures from advocacy groups and government agencies to comply with regulations and to be better stewards of the environment. Paper mills now have to factor in the cost of abatement of process by-products, so the approach taken is a shift to higher-yield semi-mechanical processes (versus 100% chemical processes used in years past). Energy costs are also substantially higher, which means that pulp moulders have to pay more for virgin fibre sources. Subsequently, there is a large push to employ raw materials with lower environmental footprint or greater renewable/recycled content.

The alternative materials can be broken down into four distinct subgroups, as follows:

1. Non-tree cellulose fibre (bagasse, sawgrass, bamboo, hemp, corn husk and wheat straw pulps; often by-products from agriculture and/or forestry)
2. High-yield tree-based cellulose fibre (thermomechanical or semi-chemical/mechanical processes; tree "flour" fillers)
3. 100% recycled cellulose fibre (old corrugated cardboard; old office mixed waste; white blank news; old newsprint; old envelope stock; off-specification industrial paper; paper mill "broke")
4. 100% mineral fillers (clays; silicas; pigments; precipitated or ground calcium carbonates).

As mentioned previously, the alternative raw materials are more problematic to use due to increased amounts of dissolved and charged materials in the paper solution (relative to bleached virgin tree-based fibres) after rehydration. Recycled materials have an additional disadvantage of containing old processing chemicals, inks, coatings, waxes and adhesives, along with the usual dirt and contaminants from the collection process. High-yield pulps tend to be much more consistent than recycled materials, but they also contain fine cellulose particulates, hemicellulose, sugars and other dissolved materials. The mineral fillers often have a fraction of materials that are easily dissolved and dispersed in water solution. It is for this reason that processing chemicals from the continuous papermaking industry are becoming more prominent in the pulp moulding industry for use in improving processability and runnability.

Ancillary chemicals used for abatement of anionic trash are often known as retention chemicals, for they actually permit the dissolved substances to drop out of solution, retaining the bulk of the cellulose fibres themselves. For example, coagulant, proflocculent and colloidal silica packages help to manage anionic trash, ensure fines retention, optimise formation and improve energy efficiency. However, manufacturers need to consider the compatibility of chemicals in use. Variations in pH can cause "kick-out" of components, which can result in foam and precipitates. This leads to costly machine shutdowns, time-consuming cleanings, premature tooling changes and lost production time. In addition, some chemicals are shear-sensitive and prone to scale formation or deposits on machinery. These are important considerations, especially when using fluorochemicals, which are often the most expensive component.

Measuring and managing charge balance

In discussing the issue of charge balance management, it is often helpful to understand how the colloidal character (i.e. predisposition of the raw materials to be dissolved in water) is measured in papermaking solutions.

Zeta potential is defined as the difference in charge potential between the dispersion medium (water) and the stationary layer of fluid attached to the dispersed particle. For paper furnishes, dispersed particles can be cellulose fines, hemicelluloses, sugars, pigments and granules of minerals (such as carbonates, talcs, etc.).

Figure 1 shows the ionic concentration and potential difference as a function of distance from the charged surface of a particle suspended in a dispersion medium.
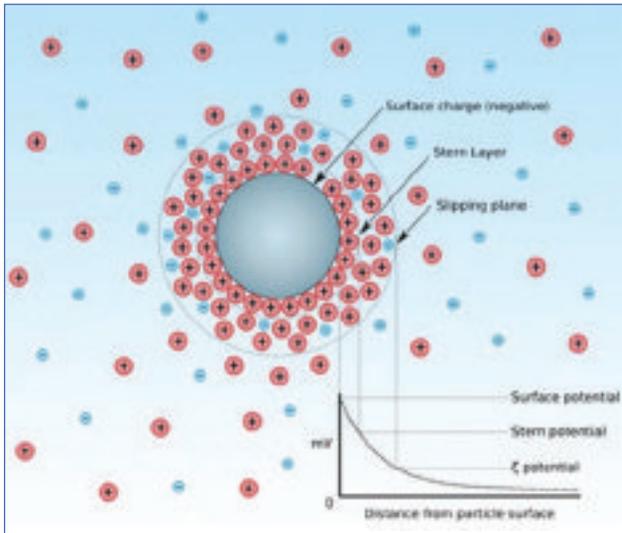

Figure 1

When heavy charge density resides at the particle surface layer, there is a vast difference in electrical potential between the particles and the bulk items in solution (water and the mass of cellulose forming the part). The particles are thus strongly inhibited from joining with the bulk cellulose or joining together with other similarly charged particles in solution (similar charges repel each other). This is the exact opposite of what any pulp moulder wants to occur in their process. The moulder prefers that all of the dissolved materials drop out of solution and become one with the part itself.

When the zeta potential of a paper mixture falls between 0 to ±5mV, conditions are most ideal for paper moulding. Dissolved substances and fines are forced out of the water solution and into the bulk mass of the cellulose as it is being moulded into parts.

By contrast, zeta potentials above +5mV or below -5mV are not desirable, as these conditions indicate that dissolved and suspended particulates are still present in the paper mixture. As such, the dissolved species are not sequestered in the bulk mass of cellulose and can be drawn into the recycled water supply. Evaporation of the resultant high-solids recycled water often results in deposition of those materials on processing equipment.

In addition to high dissolved solids, excessively high or low zeta potential has other drawbacks. Parts often take much longer to de-water, due to inconsistency of the pulp. The paper can exhibit coarse grain structure and a "clumpy" appearance, which is a hallmark of poor paper formation (*Figure 2*).
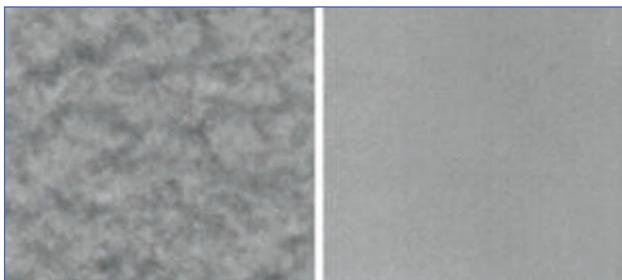

Figure 2

Analytical gauges are available for measurement of zeta potential in paper solutions. However, these gauges tend to be ori-

ented towards laboratory use, limiting their utility/efficacy in the pulp moulding operation. This author has visited a number of different moulding operations in the past, none of which has had a zeta potential gauge. Measurement of zeta potential is performed on the total pulp mixture, which allows moulders to develop a more holistic picture of the charge effects present in the system.

A more traditional and more common method for measuring charge differential is the measurement of streaming current and/or titration for charge demand. This is typically performed on a filtrate of the paper mixture, absent any of the bulk cellulose (due to the bulk's propensity to adversely affect measurement efficacy). Gauges used for measuring these attributes tend to be much more common in the paper industry mainly due to their enhanced portability and their good correlation to zeta potential in clean pulp systems. Unfortunately, the advent of alternative raw materials has meant that paper pulp is not as clean and straightforward as in the past, making the zeta potential measurement more important than before.

Figure 3 provides an example of a typical cationic demand versus zeta potential curve for a "clean" 70/30 bleached kraft mixture at different levels of PAAE fix agent treatment (dry/OD).
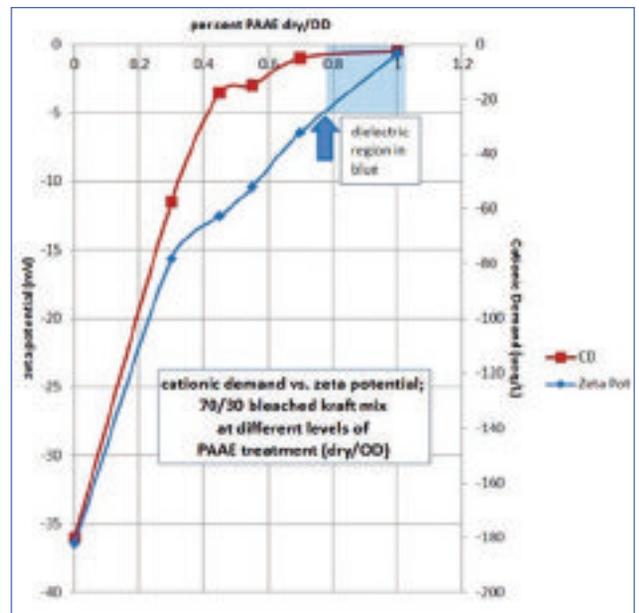

Figure 3

Also worth noting in *Figure 3* is that the cationic charge demand curve and zeta potential curves mirror each other roughly, such that both are close to zero demand/zero charge. When solution charge potential is near zero, the pulp mixture is said to be close to the dielectric point, i.e., where the charge demand and zeta potential are both equal to zero. Papermakers traditionally define a dielectric region, in which zeta potential falls between -5mV and +5mV and charge demand is between -10µeq/L and +10µeq/L.

Figure 4 shows what happens to the charge demand versus zeta potential curve when the pulp becomes more problematic due to 100% recycled content and large amounts of dissolved materials present.

The pulp in this case is 100% old corrugated cardboard, which in and of itself is a mixture of hardwood and softwood kraft linerboards glued to a centre flute of 100% mechanical pulp. Worth noting in the charge demand versus zeta potential curve is the steady plateau attained for charge demand (at -6µeq/L) at EPIDMA fix agent dosages above 0.30% dry/OD. The zeta potential curve shows the system entering the dielectric region and
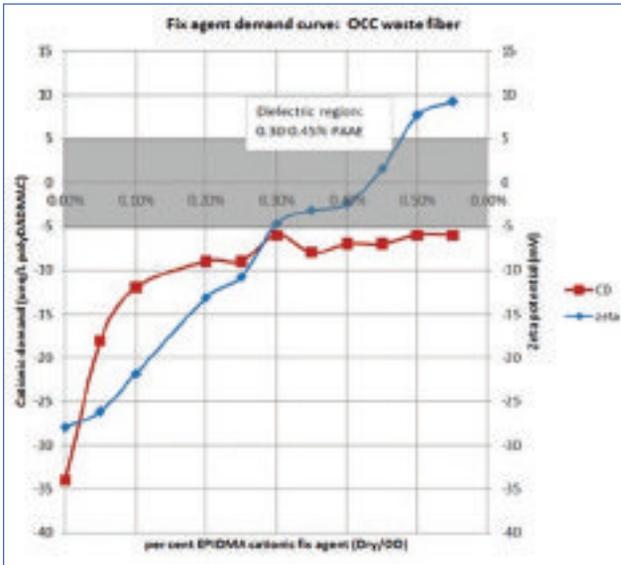
Figure 4

eventually attaining positive potential value; however, charge demand does not change. What this means is that, for a difficult and "dirty" mixed-pulp system, charge demand does not ultimately provide an accurate assessment of where the dielectric region occurs. Moulders run the risk of over-dosing with the EPIDMA cationic fix agent and heading past the dielectric entirely.

The charge demand and zeta potential curve become even more bizarre for a blended pulp with extremely high levels of thermo/chemical pulp (*Figure 5*).
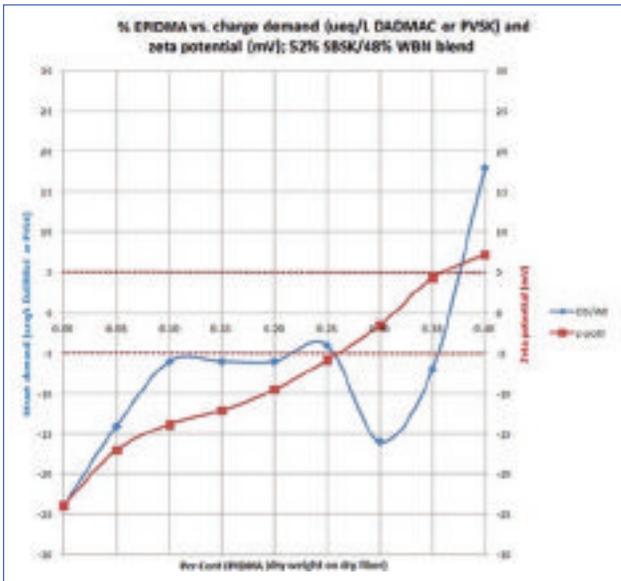

Figure 5

In the case above (*Figure 5*), charge demand (blue curve) rises to -0.6µeq/L after the EPIDMA dosage reaches 0.10% dry loading on dry fibre. This suggests proximity to the dielectric region (between the dashed red lines); however, the zeta potential curve tells the real story. In actuality, charge demand has reached another plateau. The dielectric region is not actually attained until EPIDMA dosage reaches 0.26% dry/OD. What is even more confusing is that charge demand appears to drop (to -1µeq/L) once the pulp is fully dielectric. The risk here is that the moulder may select an inappropriate fix agent dosage for the system based on an erroneous assumption of where the system is relative to

the dielectric region. This can only result in poor formation, inadequate drainage and higher energy use rates.

Cationic fix agent – core component of retention chemistry

The most important component of any charge balance management system is the cationic fix agent (or fix agents) in use. These chemical agents possess tertiary or quaternary amine functionality and as a result have a high level of stable cationic charge in solution. The cationic charge is extremely useful for sequestration of fines, hemicelluloses, sugars and other anionically charged species present in the paper mixture. Aforementioned sequestration has two primary functions. The first of these is to cause the fine particulates and dissolved materials to cascade out of solution, thus allowing these components to bind to the bulk of the cellulose mass. The second function is to prepare the pulp system for addition of ancillary chemicals (such as pro-flocculents, fluorochemicals, reactive size agents and drainage aids).

Table 1 provides a summary of cationic fix agents typically encountered in the papermaking industry.

Table 1

The utility of cationic fix agents is particularly evident when using cationic fluorochemicals for oil and grease resistance (OGR) enhancement. The best practice is to use a cationic fix agent prophylactically to ensure that the negatively charged fines and colloidal substances do not sequester against expensive fluorochemicals.

Figure 6 shows effects on an OGR-inclusive paper system when cationic fix agents are not used. The fines and colloidal substances present in the pulp mixture (negatively charged) attract and sequester some of the cationically charged fluorochemical. As a result, the fluorochemical efficiency drops, and oil and grease resistance suffers.
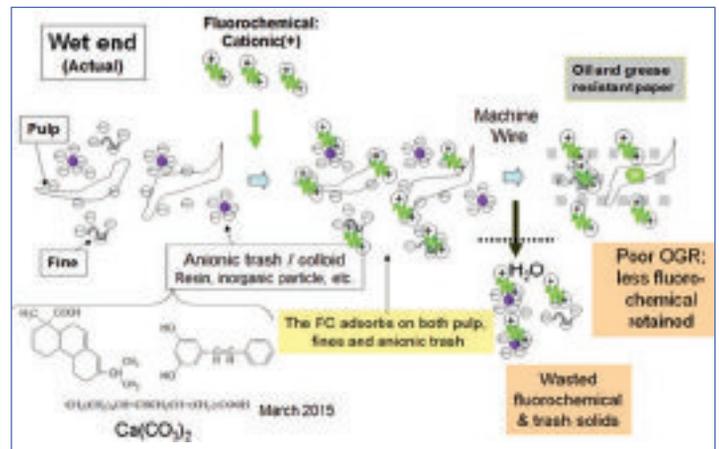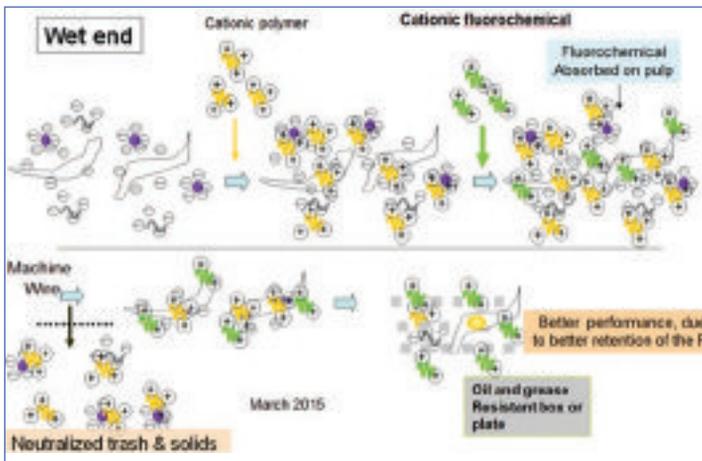

Figure 6

Figure 7

Figure 8

For contrast, a better approach is shown in *Figure 7*. The cationic fix agent added to the pulp system binds up the anionic substances that otherwise would have sequestered against the flurochemical. As a result, the fluorochemical anchors to bulk cellulose – which is the objective of fluorochemical OGR treatments.

Pro-Flocculents and Drainage Aids

Pro-flocculent and drainage chemicals are important to papermaking chemistry, and each is a vital component within a chemical retention package.

Pro-flocculent chemicals tend to be acrylamide polymers and can possess anionic or cationic charge in solution. When used in papermaking, these chemicals ensure coalescence of fine particulates, mineral fillers and colloidal solids present in solution into the bulk cellulose. In doing so, pro-flocculents maximise the "first-pass" retention of these anionic trash items, ensuring that the moulder can sell as many parts as possible. Side benefits include cleaner water supplies (due to lower fines content) and fewer deposits on mould tooling.

One disadvantage of using a pro-flocculent chemical is the decreased drainage rate of water from moulded parts. This has a negative effect on process economics as the pulp moulder is often forced to use more heat on moulding platens to dewater parts. One means for compensation is to add drainage aid chemicals to the pulp mixture. Drainage aids tend to be colloidal silica with anionic charge properties (mainly due to the dispersing aids they employ as an anti-clumping treatment). Drainage aids serve to increase paper sheet porosity, allowing for facile drainage of water from the parts.

Chemical challenges

Whenever process chemicals are used, dosages must be appropriate within the papermaking system. The chemicals must be added to the pulp at specific points in the papermaking process to achieve maximum desired effects. Some process chemicals have limited to no compatibility with each other, so the best approach is often to sequence addition of the incompatible materials in order to avoid those interactive effects.

Benefits to managed retention

Managing retention chemistry is important for mineral-filled systems, particularly when lignin levels remain high in the pulp. In *Figure 8*, two different forms of thermomechanical pulp (TMP) are examined for their ability to retain 20% clay filler in handsheets.

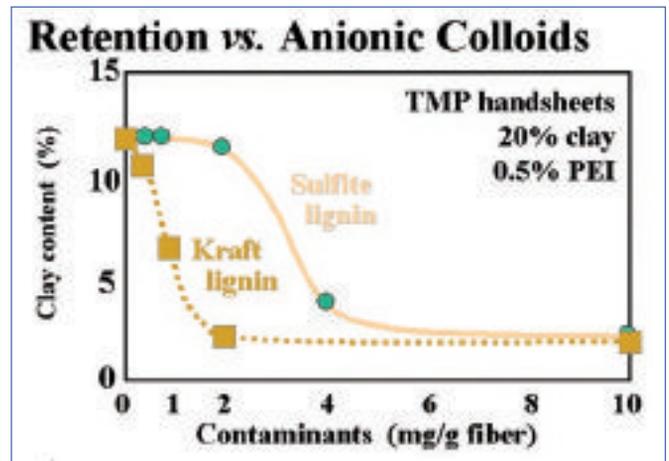For these two pulps, the retention of the clay filler drops dra-

matically as the amount of colloidal contaminants (anionic trash) increases. Results are especially pronounced for the kraft version of the pulp, where only a few milligrams per gram fibre are enough to cause retention to drop from a nominal 12% to an unacceptable 3%. The sulphite version of the pulp (which is much cleaner and has less lignin overall) has a much greater threshold for contaminants.

Management of anionic trash is important in filled systems, as it allows the moulder to operate in the processing window where retention of fillers is the greatest (the left side of the graph, *Figure 8*).

Conclusion

The moulded fibre products industry remains a competitive industry, as always. In recent years, moulders have faced additional challenges. Customers demand high levels of performance from moulded parts as usual, but also insist on proper environmental stewardship through use of renewable raw materials and minimisation of waste. The new renewable materials are not always as good in performance as the traditional raw cellulose fibre sources they replace, so optimisation during the manufacturing process is more important than ever. A full understanding of solution charge balance and its relationship to paper chemistry can improve productivity and reduce downtime and waste, which is a "win-win" proposition for moulders and their customers alike.