ADVANCES IN CNC PRODUCTION AND PURIFICATION PROCESSES

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SUMMARY

Applications for Cellulose Nano Crystals (CNC) are being developed, resulting in greater demand for high-quality CNC. NORAM Engineering & Constructors Ltd. and its partners have developed two improvements to the well-known acid hydrolysis pathway: a continuous reactor using compressed pulp to improve reaction uniformity and reduce the acid:pulp ratio required to achieve adequate wetting, and the use of electrodialysis and ion exchange for sulfate removal from CNC suspensions.

Pulp is compressed, resulting in a higher pulp density. The compressed pulp exhibits rapid wicking of the acid, resulting in a uniformly wetted reaction mixture with ~3x less total acid usage and far less mixing energy required. The mixture is pumped continuously through a reactor where the required residence time at temperature is maintained until the reaction of the pulp fibers into CNC is complete. By completing the reaction with less acid, the downstream washing and neutralizing steps are greatly reduced.

In order to purify CNC, dialysis is often used to wash out the remaining sulfuric acid and other soluble impurities. However, the dialysis process requires very large quantities of water to adequately remove the acid. NORAM and Electrosynthesis have demonstrated the use of bi-polar electrodialysis combined with ion-exchange resins to selectively remove sulfuric acid from the CNC solution, even at very low residual levels of acid. The power requirements for this process are linear with the acid to be removed, unlike dialysis which experiences logarithmic drops in washing effectiveness as the acid concentration decreases.

These process improvements have the potential to decrease the capital and operating costs of a CNC production facility, making it easier for pulp producers to pivot into this new and exciting industry.

Keywords: Cellulose Nano-Crystal, Acid Hydrolysis, Continuous Reactor, Electrodialysis, Pilot Plant

INTRODUCTION

Cellulose Nano-Crystals (CNC) are an exciting material with unique properties which give it the potential to revolutionize various industries. CNC has a very high surface area, stiffness, aspect ratio and the ability for the individual cellulose monomers to be functionalized[1]. These characteristics allow CNC to act as a unique rheology modifier which changes the activity of other fluids and mixtures. Research in numerous fields is ongoing, with potential for applications in industrial fields such as drilling & fracking fluids[1], concrete-mixing[2], and anti-fog coatings[1]. Other applications exist in Biomedical fields such as delivery of viral inhibitors[3], enhanced delivery of anti-cancer drugs[4], tissue scaffolding[5], injectable biomedical systems with temperature-adjustable rheology[6], anti-microbial films for improved food preservation[7], organic encapsulation for improved probiotic viability[8], and cosmetic product adjuncts[9]. Possible high-tech applications include production of supercapacitors[10], and pressure sensitive adhesives[11]

Toxicological experiments have also shown CNC to be more environmentally benign than other nanomaterials[12], and testing is ongoing into the oral, dermal, and pulmonary toxicity of CNC with encouraging results[13], indicating that aqueous CNC may be eligible for GRAS status.

CNC is produced from cellulose, one of the most abundant organic compounds on earth. This allows CNC to potentially be one of the most sustainable nano-materials available. CNC production facilities can be co-located alongside existing kraft pulp mills which provide a high-quality, reliable and consistent feedstock as well as the co-reactants and utilities required for the CNC acid hydrolysis process. This also provides pulp producers with a high-value co-product to supplement their regular product streams. As demand for CNC increases with greater knowledge and acceptance of its use in its various applications, larger
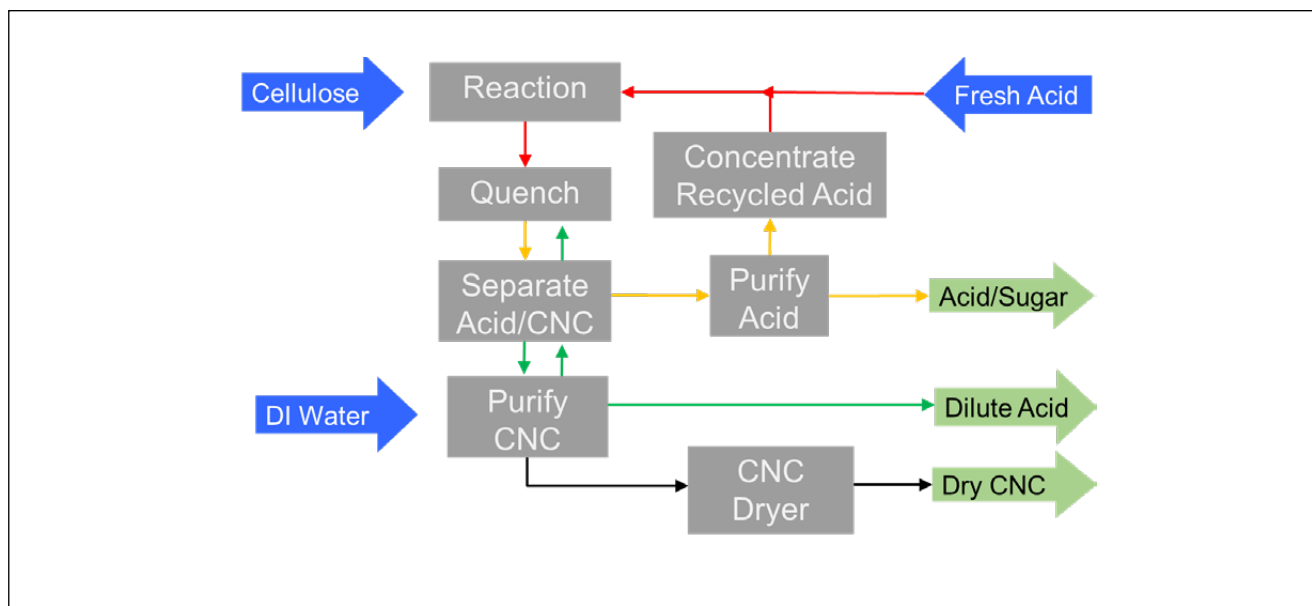
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Figure 1. Block-Flow Diagram for production of CNC via Acid Hydrolysis

installations can be installed with a lower unit cost for CNC. While some applications such as those in the biomedical field would require a highly purified CNC product, other industrial uses such as concrete adjuncts may be tolerant of a lower-cost, more crudely processed CNC.

The production of CNC by acid hydrolysis (Figure 1) is performed by mixing cellulose fibers, such as wood pulp, with ~60wt% sulfuric acid at ~60ºC for some amount of time, typically 45~60 minutes. The cellulose's amorphous regions are hydrolyzed into short-chain soluble sugar oligomers, while the cellulose's highly-ordered crystalline regions are liberated into Cellulose Nano-Crystals (CNC). The reaction product is quenched to avoid over-hydrolyzing of the crystalline cellulose, and the resulting mixture is separated into an acid/sugar solution and a concentrated CNC product. The CNC is further washed and purified, often by dialysis. The resulting solution can be used directly for aqueous applications, or dried, whereupon the nano-particles agglomerate into larger (micron-ranged) particles.

NORAM worked with FP Innovations and Domtar (which later formed the joint venture Celluforce) on the process development/optimization, scale-up, costing and design of the first large scale (1TPD) CNC demonstration plant built in Windsor, Quebec, Canada. NORAM also supplied the sulfuric acid reconcentration system.

Since then, NORAM has remained active in the area and has developed and patented several improvements to the process. Notably, this includes a continuous CNC reactor which uses compressed cellulose that enables a ~3x reduction in the acid ratio required for the hydrolysis step compared to the traditional

batch design as demonstrated last year at Innotech's CNC pilot plant in Alberta with support from Alberta Innovates and Alberta Pacific (Al-Pac).

NORAM have also collaborated with Electrosynthesis to incorporate the use of electrodialysis and ion-exchange resins to accelerate the final purification of CNC, which can reduce water usage by more than 80%, resulting in decreased capital and operating costs.

MATERIALS AND METHODS

Hydrolysis of Uncompressed and Compressed Cellulose

Dry bleached softwood Kraft pulp was milled to a fineness of 20 – 100 mesh (150-840 microns) with a knife mill. Following this procedure, the loose, fluffy pulp had a density of between 50 and 100 kg/m³.

This milled dry pulp was reacted with sulfuric acid while the temperature of the reactants was maintained using a water bath. Typical duration was 45 minutes at a temperature of 60 Celsius, and typical acid solution concentration was 60% H_2SO_4, by weight.

Uncompressed, milled pulp at a density of 50-100 kg/m³ was mixed manually in a beaker with the acid solution. Typically, 10 g was mixed with 90 g of acid, which was the lowest acid ratio found to be feasible for uncompressed pulp.

Compressed pulp was prepared by compression within a 24.5 cm inside-diameter glass cylinder using a hydraulic press at various compression ratios to produce compressed plugs of varying density. The compressed pulp re-expanded only slightly once the pressure was removed, such that the compressed

material maintained nearly the same increased density. The compressed plugs, approximately 1 cm in height, were removed from the cylinder and placed in a beaker containing acid solution, whereupon the acid solution transfused through the sample via wicking action. After initial transfusion, gentle mixing was conducted to help maintain constant temperature to counteract the cooling action of the air above the beaker.

Following the reaction time, the cellulose/acid mixtures prepared from either compressed or uncompressed cellulose were subjected to the following steps:

1. The mixtures were first quenched with 1000 mL of de-ionized water and allowed to settle overnight.
2. In the morning, the clear supernatant layer was decanted off and the approximately 300 g remaining suspension was divided into 10 - 30mL aliquots, which were treated in a lab-scale batch centrifuge for 10 minutes at 1,100 rpm.
   a. The aliquots were then decanted, refilled with de-ionized water, and treated again in the centrifuge two more times until the suspension no longer separated. This corresponded to a pH of about 1.2.
3. The 10 individual aliquots were then placed in dialysis bags and dialyzed with de-ionized water until reaching a pH of at least 3.3.
4. The colloidal partly-hydrolyzed cellulose was then decanted, sonicated for 90 minutes, filtered through a 0.3 micron filter and dried overnight at 40C into a thin film.

Electrodialysis of Nano-Cellulose Suspensions

The electrodialysis experiments on the nano-cellulose suspension were performed in a modified Microcell electrochemical cell (Electrocell AB) with five pairs of membranes. Each membrane has a surface area of 10 cm². Experiments were run with 0.1 M sulfuric acid in the receiving compartment and 50 mM sulfuric acid in the rinse compartment. Solutions in each of the compartments were recirculated through the cell by peristaltic pumps and samples taken periodically throughout the batch-separation process. Samples were analyzed for sulfate by ion chromatography and titrated for acid content. All experiments were performed at 40ºC. The feed solution used for these experiments was prepared in the course of CNC preparation described above and contained ~ 0.4 % suspended CNC particles and 75-95 mM sulfuric acid.

To measure and control effective cell voltage, platinum probes were installed inside each of the feed compartments nearest the electrodes such that there were 4 complete working cells between the two probes. The membranes tested were Neosepta CMX cation membranes, Asahi AAV anion membranes and Neosepta BP-1E bipolar membranes.

In order to achieve lower sulfate concentrations and improve efficiency, experiments were also conducted with the feed compartments filled with an anion exchange resin (Supelco Amberlite IRA400) which has the effect of raising the total conducting anion concentration. The resin was initially in hydroxide form. The active area of the feed flow frames was filled with the resin and the inlet and outlet channels of the frames were filled with glass wool.
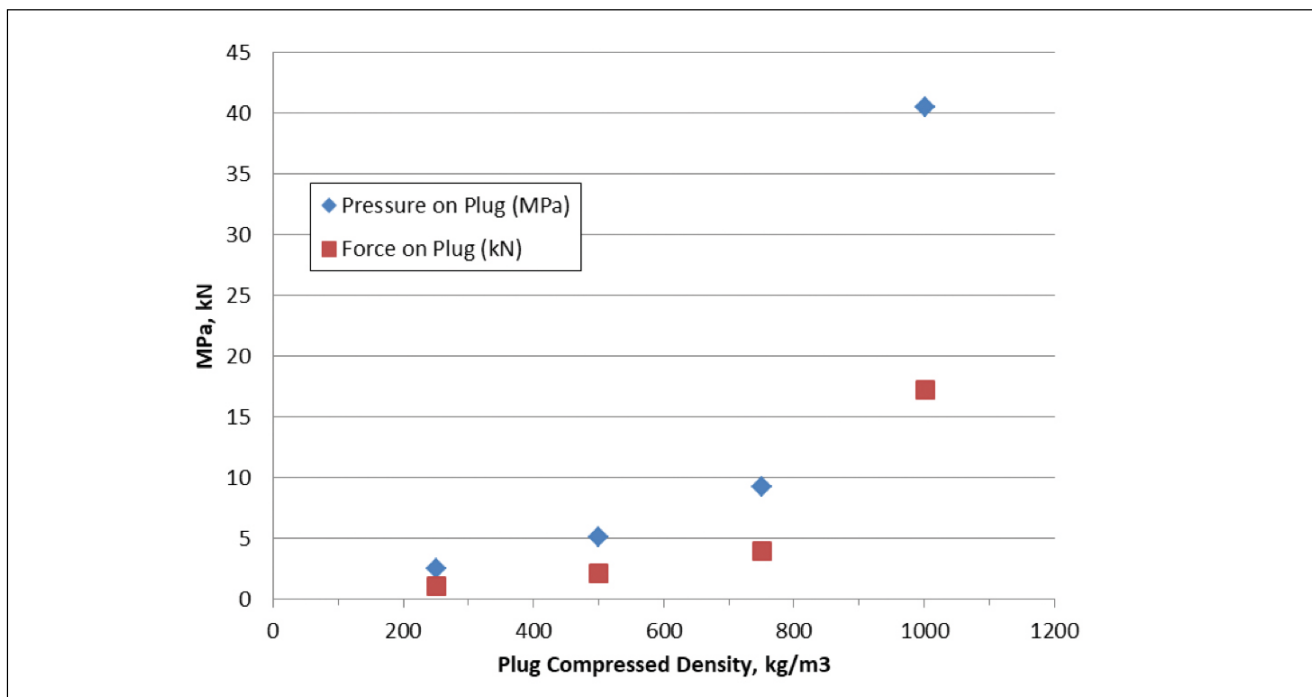

Figure 2. Density of compressed cellulose vs applied pressure

RESULTS AND DISCUSSION

Hydrolysis of Uncompressed and Compressed Cellulose

The density of compressed pulp is shown in Figure 1 as a function of applied pressure. A density of 500 kg/m³ was achieved with a compression pressure of about 5.5 MPa; 750kg/m3 with about 10 Mpa. Above this density, the required compression pressure increased rapidly.

Initial experiments comparing CNC preparation using compressed vs uncompressed cellulose were conducted using a temperature of 65°C and a reaction duration of 45 minutes. Acid ratio was 9 parts acid solution to 1 part uncompressed cellulose and 4.5 parts acid solution to 1 part compressed cellulose. Both experiments produced films showing iridescence indicative of self-ordering chiral nematic cellulose nano crystals[14]. CNC yield under these conditions was 8.0% for uncompressed and 7.8% for compressed cellulose.

Conditions were varied to determine impact on yield. When acid strength was varied, a narrow zone of concentration was found which created an impermeable gel that prevented wicking. This range was 63-64% acid, by weight, independent of temperature. Above and below this zone, wicking proceeded at similar speed[15].

The effect of reaction time for compressed cellulose at lower acid strength and temperature (58% H_2SO_4 and 56°Celsius) is shown in Figure 3. The reject material is that which is retained by 0.3 micron filtration, following dilution washing and dialysis. As the reaction proceeds the reject portion declines while additional CNC is liberated from the milled cellulose particles. Based on the physical observation of thorough penetration by the acid solution, it is concluded that distribution of the acid to the particle surface is not rate limiting. Nonetheless, significant reaction time must be allowed in reactor design, depending on acid strength and temperature chosen.

A pilot-scale apparatus was designed (Figure 4) to verify continuous CNC production employing compression followed by acid contact via wicking mechanism.
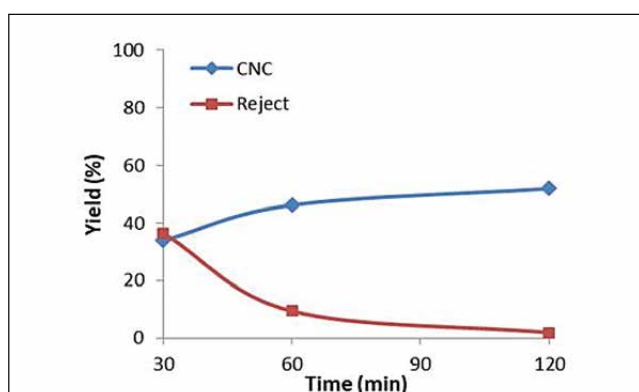

Figure 4: Design of pilot-scale continuous CNC reactor

The apparatus consisted of compression auger producing a 6.5 cm diameter compressed plug, exit nozzle, acid distributor / wetting ring, standpipe, transfer pump and up flow plug-flow retention vessel with external jacket for temperature control. At a production rate of one ton CNC/day the retention vessel provides 60 minutes of retention time. Initial short-term tests were conducted at BC Research facilities with the objective of validating the concept and testing of component design.

Figure 5 depicts the still-reacting mixture as sampled at the exit of the pump located between the wetting ring and retention vessel. The viscosity of the paste-like mixture increases as the acid ratio is reduced with consequent increase in pump power consumption and pressure drop.
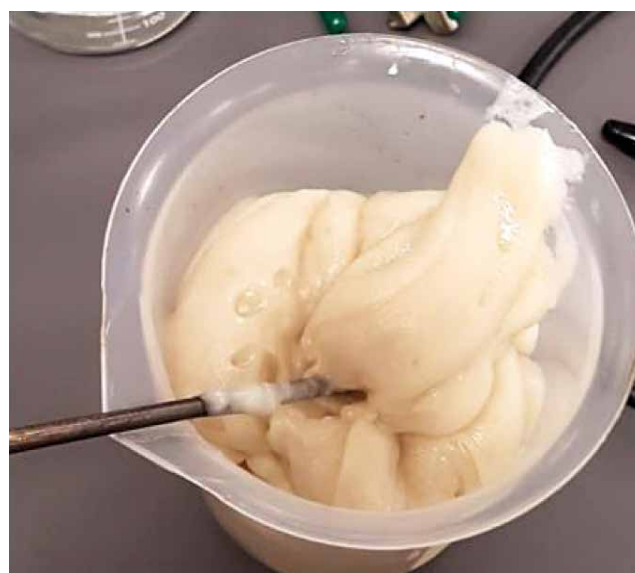

Figure 3. Yield of CNC and reject vs reaction duration, 58% acid strength & 56°C

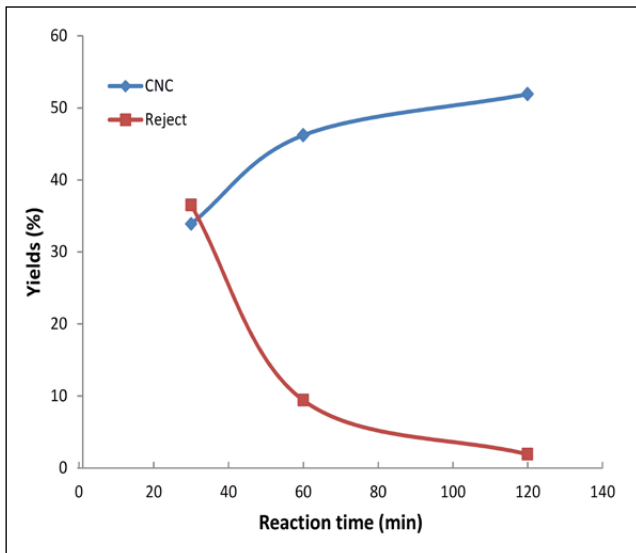**Figure 5. Reaction mixture at pump**

Figure 6. Yield of CNC and reject vs reaction duration for pilot-scale mixing system

Figure 6 shows the proportion of CNC and reject material as a function of time for a sample from the same location held at constant temperature, without mixing. Conditions were 4:1 acid:pulp (wt basis), using 61 wt% acid in solution and 50ºC.

Some components were redesigned as a result of testing experience. Improvements in compression and mixing design allowed the acid ratio to be reduced to as low as 3:1. Control of the pilot system remained largely manual.

For longer-term testing, incorporating product purification and drying, the pilot equipment was re-located to Innotech Alberta, Edmonton, Canada, and integrated with the complete CNC pilot production system located there. Figure 7 depicts the installation.

The integrated plant affords opportunities to produce large quantities of CNC using different cellulose sources and operating conditions, and numerous runs have been conducted to date. The run of longest duration to date has been 5 hours, processing dry-milled dissolving pulp. The CNC yield and quality produced is shown in Table 1 and SEM imaging of the product is shown in Figure 8.

Table 1: CNC Product Characterization

CNC Yield	**56.80%**
Reject Yield	**2.60%**
Crystallinity (Siegel method)	**74.4-81.4%**
Sulfur Content	**0.47-0.82%**
Thermal Resistance	**240-250 C**
Average Particle Size	**120 nm +/- 5.9 nm**
Zeta potential	**-44.9 mV +/- 0.05 mV**

Electrodialysis of Nano-Cellulose Suspensions

The initial configuration tested incorporated cation and anion membranes (Figure 9 showing 2 cells). In this configuration, the sulfate travels across the anion membrane.
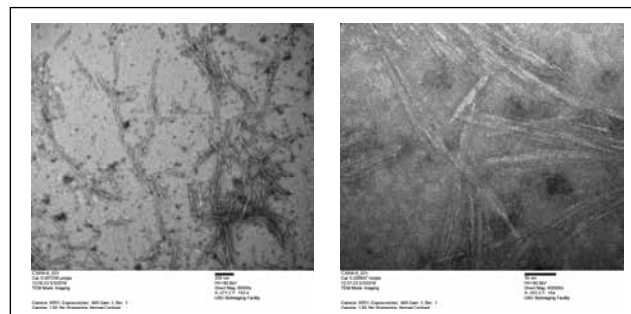

Figure 8. Transmission Electron Microscope (TEM) images from first demo run

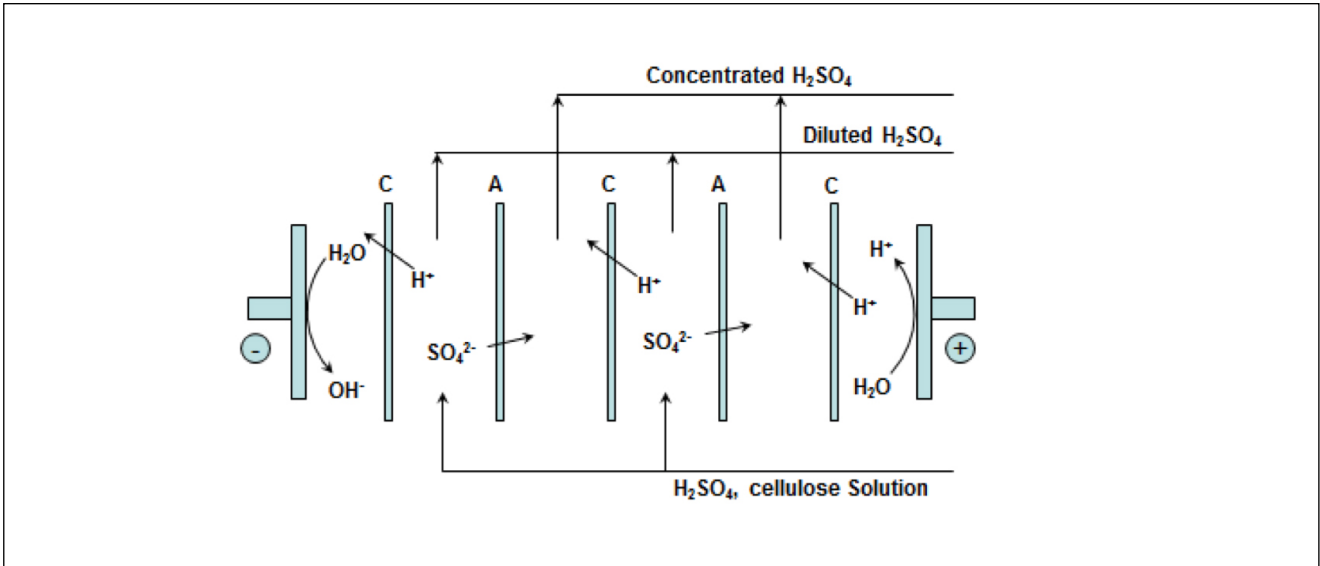**Figure 7. Integration of reactor (center) at the Innotech Alberta Inc. CNC Pilot Plant**

Figure 9. Cell configuration for Sulfuric Acid Removal using Cation (C) and Anion (A) Membranes

This removes the sulfate from the feed solution, which then combines with the protons crossing the cation membrane to increase the acid strength in the receiving compartment.

The cell was charged at a constant 3.2 V across the platinum electrodes. Figure 10 shows the voltage and current density throughout the run. Although a relatively high current density of 25 mA/cm² was first obtained, it decreased considerably to about 2 mA/cm² by the end of the experiment. Overall, an average current density 5.9 mA/cm² was obtained.

Figure 11 shows the feed and receiving sulfate concentrations and the calculated current efficiencies. The sulfate concentration in the feed decreased steadily over the whole run with a final sulfate concentration for the cation/anion cell configuration of

3.5 mM. The overall current efficiency was 79%; with very good correlation between feed and receiving current efficiencies. The current density and efficiency dropped throughout the run as the feed was depleted and the acid concentration increased in the receiving compartment. Back migration of protons plays a dominant role in reduced current efficiency at lower feed concentrations.

An alternative cell configuration was tested replacing the cation membranes with bipolar membranes (Figure 12). The bipolar membrane splits water at low voltage to produce protons on the cathode facing side of the membrane and hydroxide on the anode facing side. In this case, the proton in the cellulose solution does not need to be free, but is neutralized
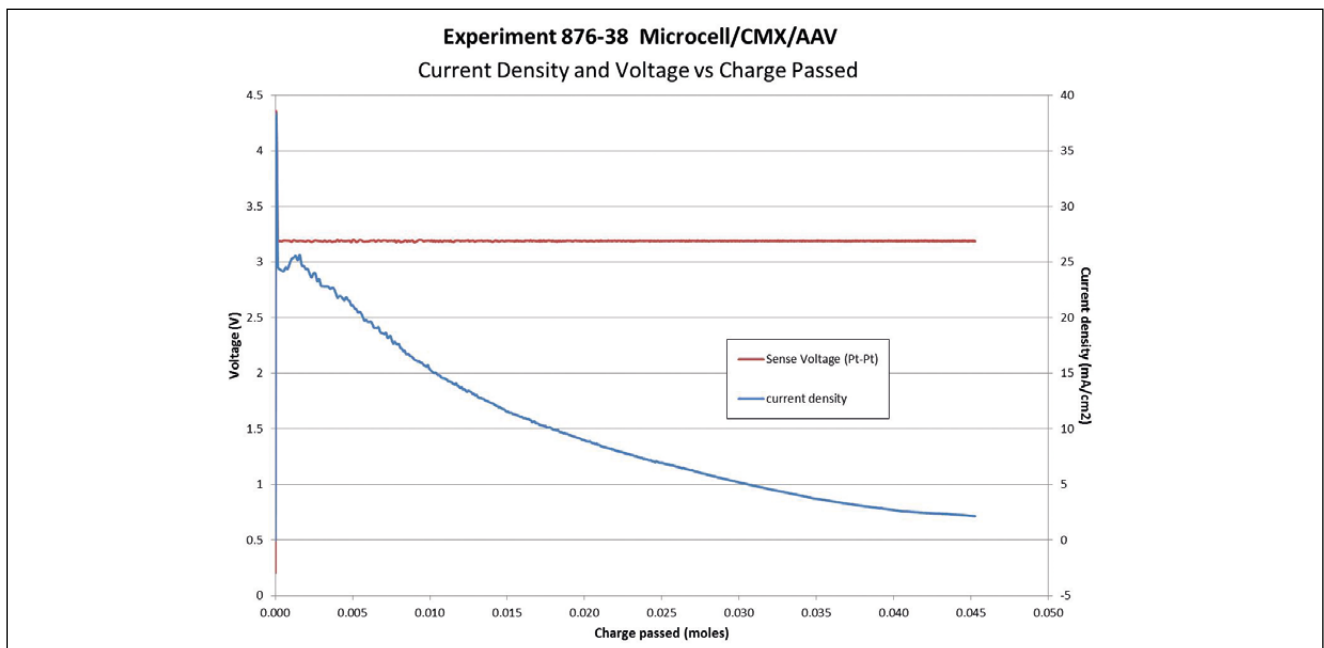

Figure 10. Pt-Pt Voltage and Resulting Current Density for Cation/Anion Configuration
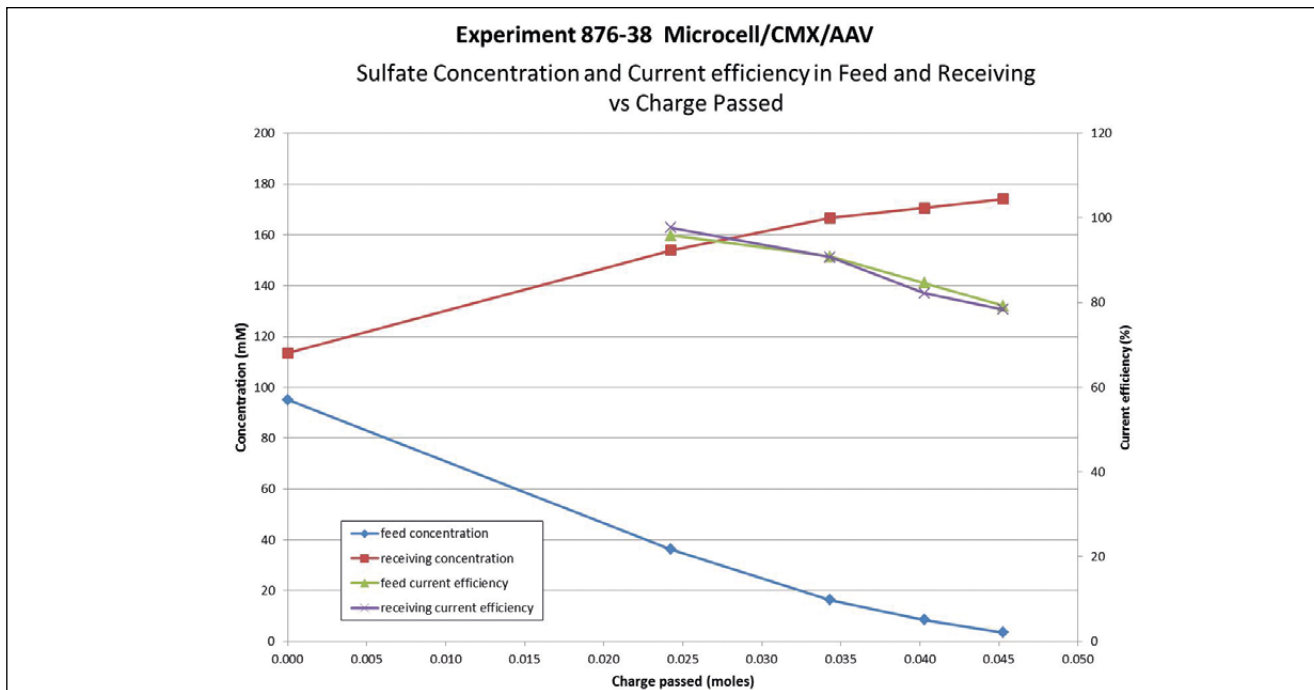
Figure 11. Sulfate Concentration and Current Efficiency in Feed and Receiving Solutions

by hydroxide produced at the membrane surface, which allows for a greater degree of acid removal. The sulfate is transported similarly to the previous configuration. Applied voltage over the four bipolar and four anion membranes varied from 4.5 to 5.6 V due to power supply limitations and high electrode voltage drops, possibly due to some protons being associated with the CNC and not free in solution, and therefore not available for transport across the membrane. The bipolar membrane removes this limitation by producing hydroxide which can react with any adsorbed proton on the CNC.

More charge was passed than with the cation membrane and the final feed sulfate concentration was lower as well at 1.9 mM. The overall current efficiency for this run was also lower at 61%. The lower current efficiency is due to a longer run time with part of the run occurring with lower sulfate concentrations, than

achieved in the cation/anion configuration. The lower current efficiency for these last samples again shows that proton back migration increases as the sulfate level reaches low levels. The cell ran at an average current density of 6.0 mA/cm², similar to the cation/anion configuration, despite achieving lower final feed concentration.

In order to achieve lower sulfate concentrations in the product CNC solution and to help with efficiency of the process, the feed compartment was filled with an anion exchange resin. The use of ion exchange resin in a compartment can help facilitate the transfer of free ions at low concentrations by increasing the total concentration of ions. The cell was built with bipolar and anion
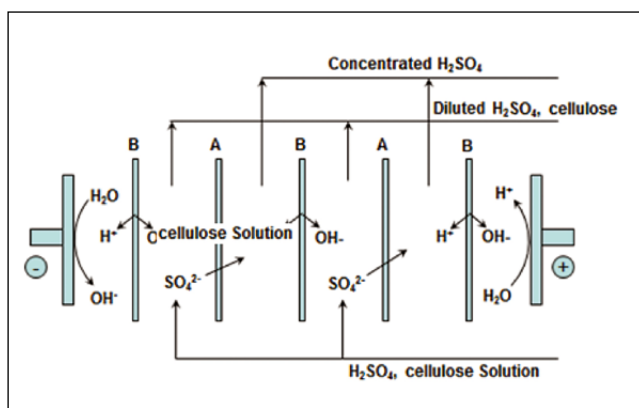

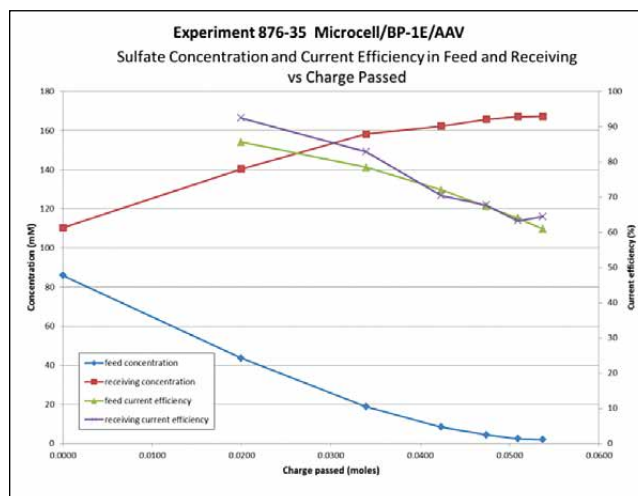**Figure 12. Schematic of Cell with Bipolar and AAV Membranes**

Figure 13. Sulfate Concentration and Current Efficiency in Feed and Receiving Solutions
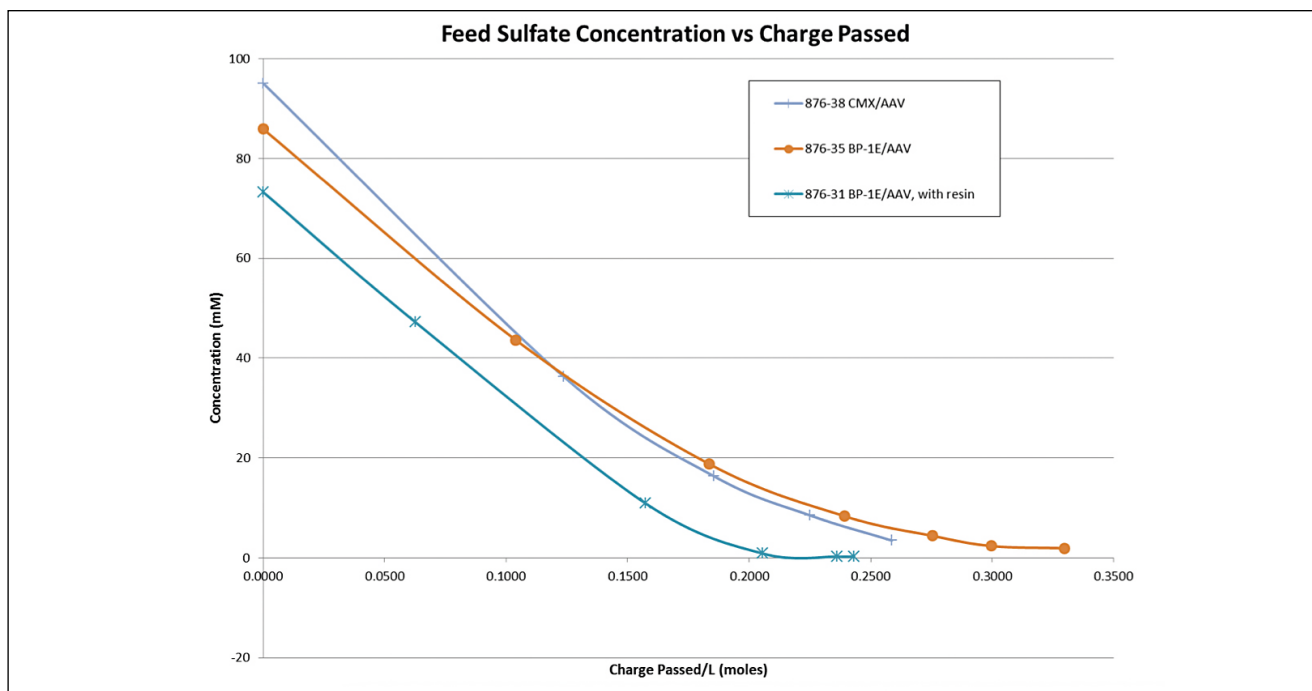
Figure 14. Comparison of the Sulfate Concentration for Feed in the Three Reported Runs

membranes in the same configuration as Figure 12. As with the previous test with bipolar membrane, the total cell voltage again was limited, and the run did not reach 5.6 V between the platinum probes until 0.055 moles of charge had passed. The feed solution was reduced to 0.3 mM in sulfate; an order of magnitude lower than the experiments without ion exchange resin. An average current density of 8.2 mA/cm^2 was obtained, which was the highest current density obtained in this work.

Figure 14 compares the three experiments discussed thus far. Overall, the electrodialysis was very effective in removing the sulfate from the cellulose solution. By adding the resin in the feed compartment, virtually the entire amount of sulfate was removed.

In order to counter the effects of proton back-migration on current efficiency, experiments were run with sodium hydroxide added to the receiving side to keep the pH above 2.5. A cation/anion cell configuration ran at a lower average current density (6.1 mA/cm^2) than the same cell with sulfuric acid receiving

solution (7.9 mA/cm^2), which is likely due to the lower conductivity of sodium sulfate. However, it had an average current efficiency of 102%, compared to about 60% for the sulfuric acid run. This run indicates that the low current efficiency is indeed due to proton back-migration across the AAV membrane.

A comparison of the reported runs is shown in Table 2, which indicates that it was possible to decrease the sulfate concentration to 0.3 mM in an electrodialysis cell with anion exchange resin located in the feed compartment chamber. It was also possible to decrease the sulfate concentration to below 2 mM using a more conventional cell arrangement.

After each experiment, the cell was disassembled and examined for signs of solids pluggage and membrane fouling, which is a common issue with electrodialytic treatment of particulate bearing streams. Surprisingly, no visible signs of solids deposition were observed in any experiments.

A dilution based dialysis system's capacity, flows and cost are roughly proportional to the log of the percentage removal rate

Table 2. Summary Table for Electrodialysis Runs

Run time (hr)	Cell Configuration	Average Current Density (mA/cm²)	Moles of charge passed	End Feed			
				Sulfate conc. (mM)	Conductivity (mS/cm)	pH	Feed Current Efficiency (%)
4.2	cation/anion	5.9	0.045	3.5	2	2.45	79
4.8	bipolar/anion	6.0	0.054	1.9	2	2.29	61
3.8	bipolar/anion/resin	8.2	0.058	0.3	0	3.31	63
3.5	cation/anion	6.1	0.039	20.5	6	3.18	102

required regardless of the absolute concentration or removal. Each 10-fold reduction requires an equivalent equipment size and operating cost. In contrast, the sizing and membrane area requirements and cost of an electrodialysis purification based system have been shown to be dictated much more closely by the actual quantity of ions removed. Electrodialysis, however, becomes less efficient as feed concentration drops, resulting in lower conductivity, current density and current efficiency. Therefore, electrodialysis has been found to be particularly well suited to the intermediate and final stages of purification of partly-hydrolyzed cellulose where free ion concentrations are fairly low in absolute terms, but still high enough to result in efficient transfer via electro-motivation. Significant capital, water usage and operating cost reductions may be realized through the appropriate and optimized use of electrodialysis in CNC purification.

CONCLUSIONS

Hydrolysis of Uncompressed and Compressed Cellulose

Pulp fiber from milled NBSK was compressed, allowing it to readily wick 60% sulfuric acid. This wicking action allows for improved dispersion of acid into the pulp fibers at ~3x lower acid use and greatly reduced mixing requirements. A pilot plant including pulp compression, acid contacting, reaction, and quench was designed and installed at Innotech Alberta, where the system ran continuously for a 5-hour campaign. The resulting CNC was analyzed for quality and yield, obtaining results consistent with the more conventional batch reaction at ~10:1 acid ratio.

Electrodialysis of Nano-Cellulose Suspensions

A selection of cation, anion and bipolar membranes were tested in an electrodialysis (ED) cell for the removal of sulfate from CNC solution. A cell using alternating cation & anion membranes achieved an average current density of 5.9mA/cm^2 and reduced sulfate concentration to 3.5mM. A cell using bipolar membranes achieved a similar current density and reduced the sulfate concentration in the CNC solution to 1.9mM. A challenge for the electrodialysis process is the reduction in current efficiency due to proton back migration. Combining Bipolar ED with ion exchange resin in the feed compartment allowed for a lower final sulfate concentration of 0.3mM. Combining cation/anion ED with hydroxide addition allowed for increased current efficiency by stopping proton back-migration.

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