Sacrificial Protective Coating Materials that can be Regenerated In-Situ to Enable High Performance and Low Cost Membranes

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Agenda 2020, WestRock Company

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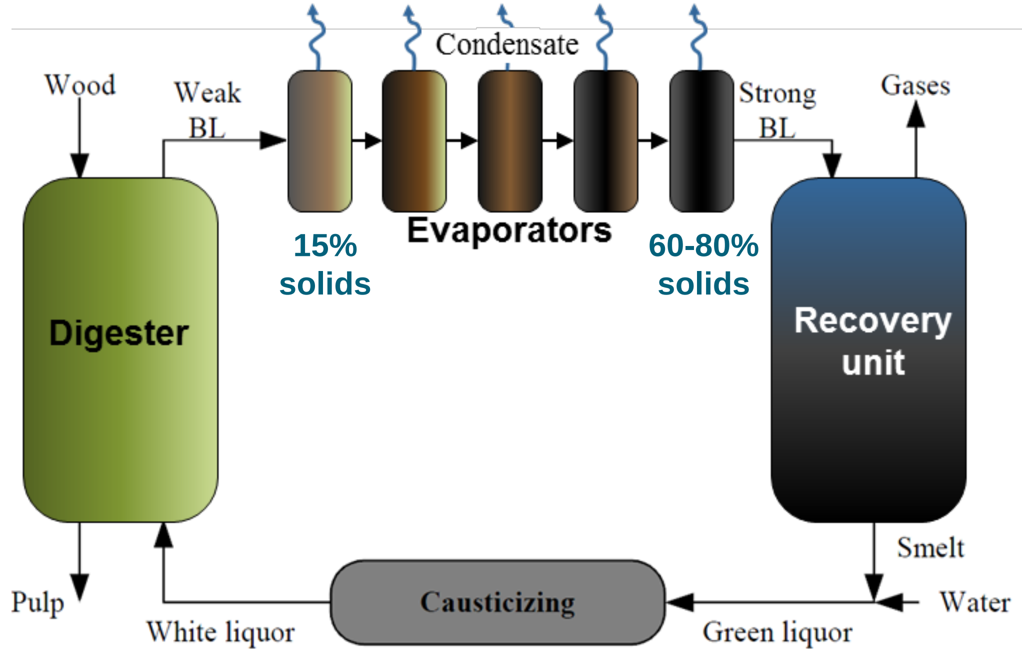
Project Objective

Problem

- Pulp & Paper Industry weak black liquor (WBL) byproduct must be concentrated for reuse
- Concentration is carried out using energy intensive evaporators



Goal

- Reduce energy consumption during WBL concentration via membrane-based separation of water from WBL
  - ➢ pressure-driven separation of water saves energy over heat-driven

Challenges

- Membrane clogging and fouling from organics and ions is a major problem
- Fouling increases operational maintenance and capital costs
- Must retain sulfate (recycled by reducing to sulfide) and organics (burned in recovery boiler to generate energy and reduce sulfate)
- Membrane must sustain hot (>85°C) WBL at pH of 13-14

Innovation: Black Liquor Concentration

Current technologies

- **400 TBtu/year** required by pulp & paper industry to concentrate weak black liquor using multi-effect **evaporators**

Approximation assuming 1 ton H_2O @ 85 °C

Evaporation, 2107 MJ

- Heating: 85 °C → 100 °C = 57.0 MJ
  - $Q = c_p \cdot m \cdot \Delta T = (4.187\ kJ\ kg^{-1}\ °C^{-1})\ (907.2\ kg)\ (15\ °C)$
- Latent heat: @ 100 °C = 2,050 MJ
  - $Q = m \cdot L = (2260\ kJ\ kg^{-1})\ (907.2\ kg)$

Pressure-driven separation, 86 MJ

- Heat loss: 85 °C → 80 °C = -19.0 MJ
  - $Q = c_p \cdot m \cdot \Delta T = (4.187\ kJ\ kg^{-1}\ °C^{-1})\ (907.2\ kg)\ (-5\ °C)$
- Pumping: 400 psi, 30 gpm, 40 LMH = 67.0 MJ
  - $E = P \cdot F \cdot t = (2{,}760\ kN\ m^{-2})\ (0.114\ m^3\ min^{-3})\ (213\ min)$

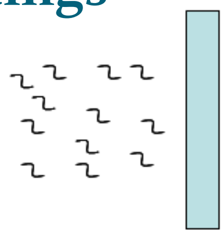
- Membrane-based systems limited to separating lignin from weak black liquor
  - Feed is destructive (pH 12-14, 85 °C)
  - Membrane fouling (small organics, high dissolved solids)

Teledyne technology

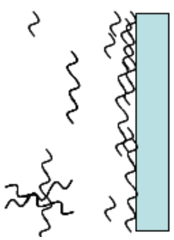
- Coat commercial membranes with anti-fouling coating that can be regenerated *in-situ* to save energy of weak black liquor concentration
  - Protects underlying membrane from destructive feed (makes membranes feasible)
  - Mitigates membrane fouling (decreases maintenance and capital cost)
  - Tunes permeability of salts using charged coatings

Innovation: Coating Technologies

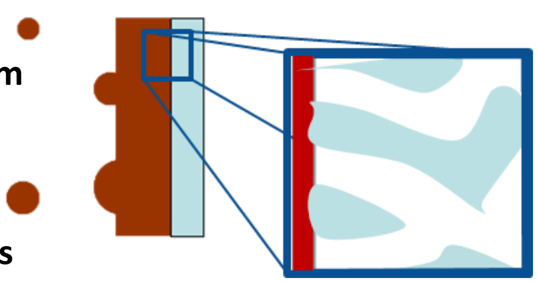
Conventional Coatings



Hydrophilic monomer polymerizes

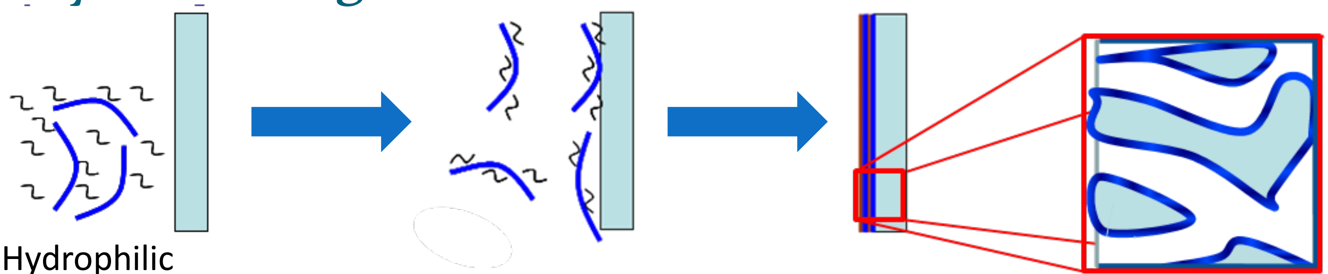


Polymer deposits on surface and creates particles



20-100 nm coating with uneven thickness

Teledyne Coatings

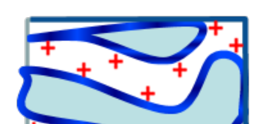


Hydrophilic monomer associates with compound A, slows down diffusion to surface

Exposure to compound B induces layered nanostructure

5 nm thick coating with smooth topography and layered nanostructure

- Conventional technologies result in coatings on membrane surface due to monomer polymerization in solution
- Teledyne technology controls reaction kinetics
  - Monomer deposits on membrane surface and pore walls
  - Polymerization occurs after monomer deposition
  - **Membrane surface and pore walls are coated**
  - Can control surface charge to tune ion rejection



Teledyne (+) coating

Teledyne (–) coating

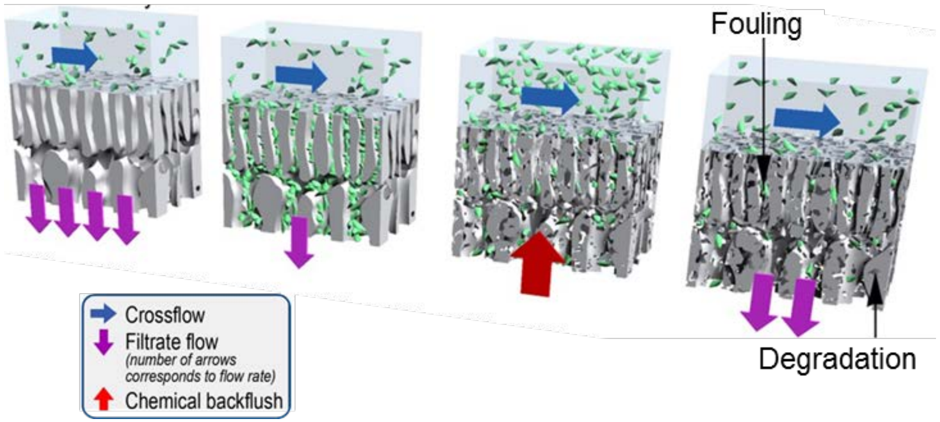
Approach: Anti-fouling Coatings

Sacrificial anti-fouling coatings

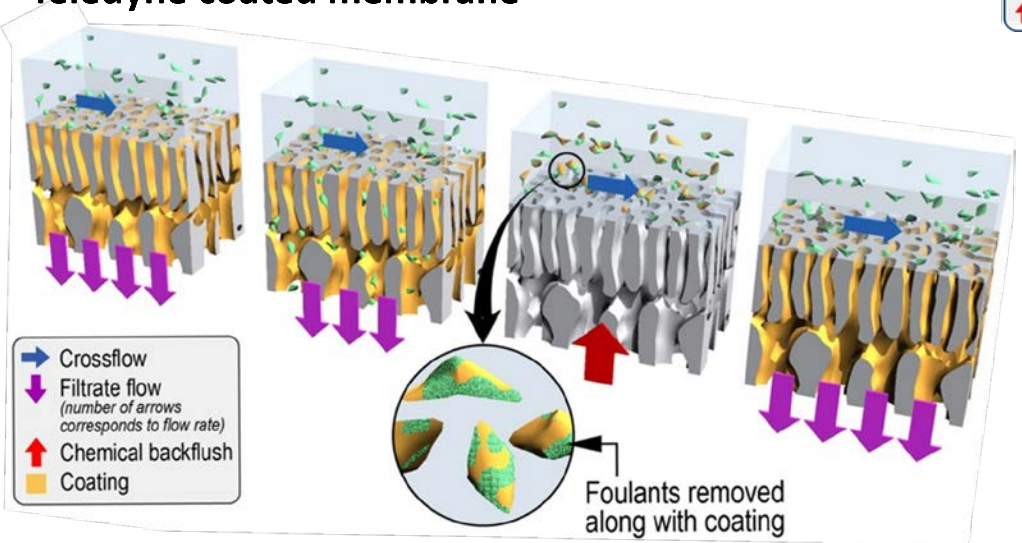
- Although widespread adoption of membranes has lowered cost, no known long-term methods to alleviate fouling

$$J = \frac{\Delta P}{\mu(R_m + R_F)}$$

Existing low cost polymeric membranes



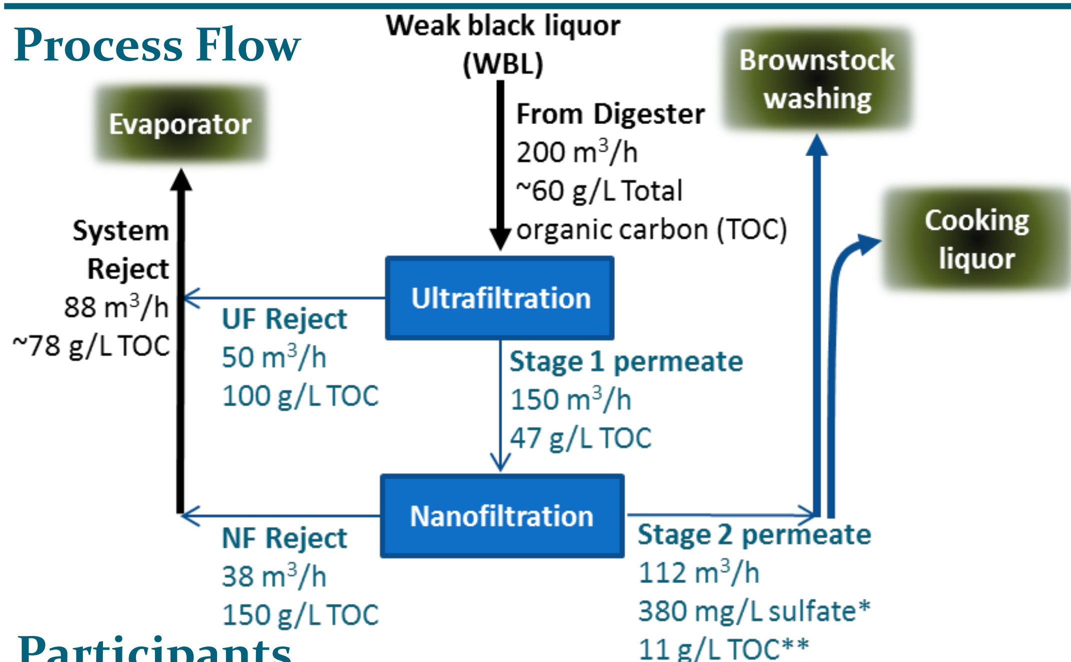
Teledyne coated membrane



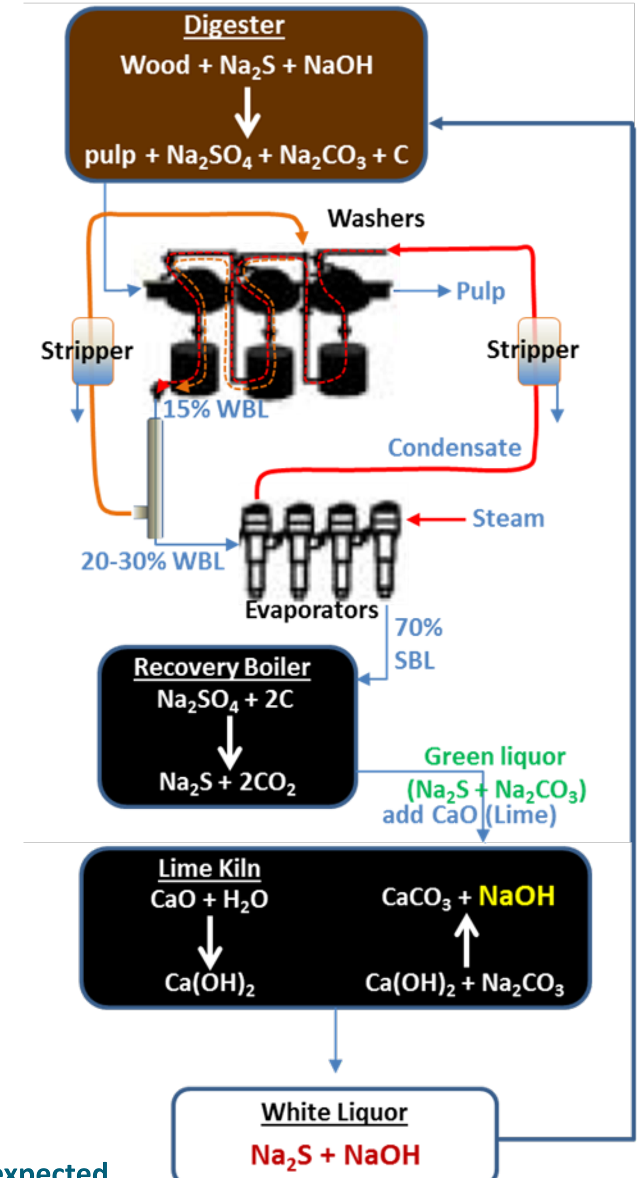
- Teledyne coating coats membrane surface and inner pore walls
- Resists fouling under WBL conditions (foulants adhere weakly to coating)
- Coating is occasionally re-applied in the field
- Result is higher flux, recovery, and lower maintenance

Approach: Membrane-based Concentration

Process Flow



Membrane-based concentration



Participants

- Agenda 2020 (paper industry consortium)
  - Economic models, business plans
- WestRock Company (major paper manufacturer)
  - Provide WBL, process/manufacturing insight

Risk/Mitigation

- Sulfate buildup from brownstock washing
  - Pre-treat permeate before washing
  - Vary dilution factors during washing
- TOC buildup during cooking
  - Scrub organics from permeate

* 100 mg/L sulfate expected

** 1 g/L total organic carbon expected

Transition and Deployment

Who cares?

- Pulp & paper mills are 3rd largest energy-using manufacturing sub-sector in U.S.
  - Accounted for 7% of total U.S. industrial energy
  - Produced 78 million metric tons of paper and paperboard (19% of global production)
- WBL concentrated from ~15% solids to ~65-80% solids by multi-stage evaporators consuming ~400 TBtu/yr
- If first two stages of evaporators are replaced with membrane separation
  - ~**55 TBtu/yr reduction in energy**
- Estimated payback period for membrane-based WBL concentration: 3–4 years

Commercialization approach

- Technology development in close collaboration with paper industry for rapid adoption
- TRL 5 validation at a pulp and paper facility begins October 2016
- Demonstrate performance improvement at customer site
  - Enables continued development beyond TRL 5
- Teledyne pursuing other adjacent areas, e.g. filtration of frac water in Oil and Gas
  - Assists in adoption of membranes

Measure of Success

Through the end of this 3 year program (April 30, 2017)

- Continued engagement and buy-in from paper industry
- Achievement of technical objectives and milestones
- **TRL 5** demo at pulp and paper mill site
- Confirmation of quantified energy savings to end-user

Beyond this program

- Development of **TRL 8** prototype: will require funding beyond this program from DOE and/or paper industry

Energy savings estimate by paper consortium

- Reduction in energy from 3.5 MMBtu/adt to <2.8 MMBtu/adt
  - **~55 TBtu/yr** energy savings

Project Management & Budget

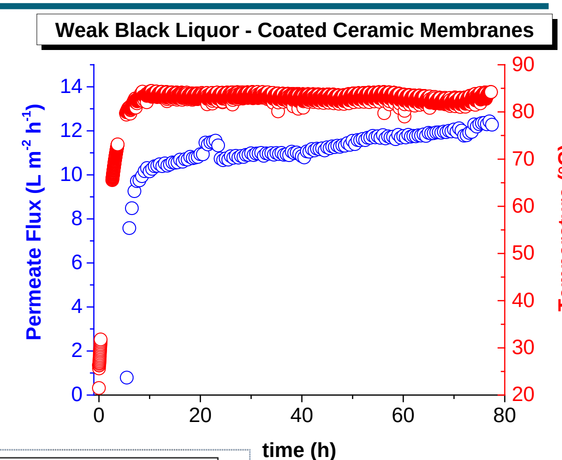
- Project duration: 36 months (Year 3 started May 1st)
- Progress measured by quantitative milestones
  - October 31, 2016: Document optimal parameters for in-place coating and backflushing
  - April 30, 2017: Demonstrate black liquor treatment process for >7 days with <20% drop in total flux with semi-automated backflush, chemical clean, and in-place coating reformation

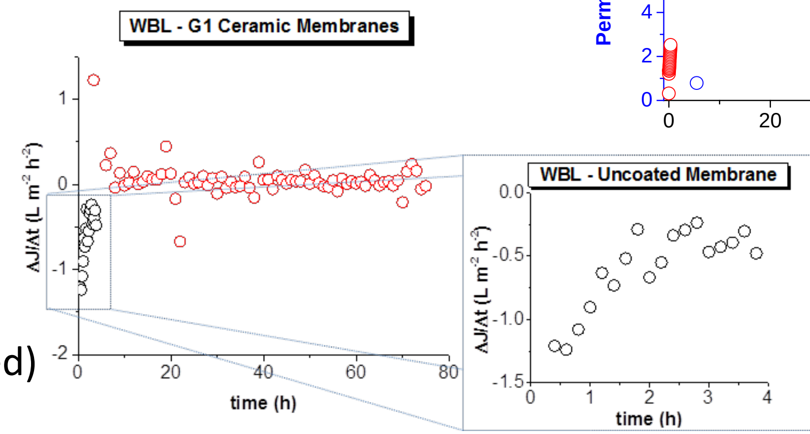
Total Project Budget	
DOE Investment	$ 2,109,297
Cost Share	$ 973,888
Project Total	$ 3,083,185

Results and Accomplishments

Go/No-Go successfully completed

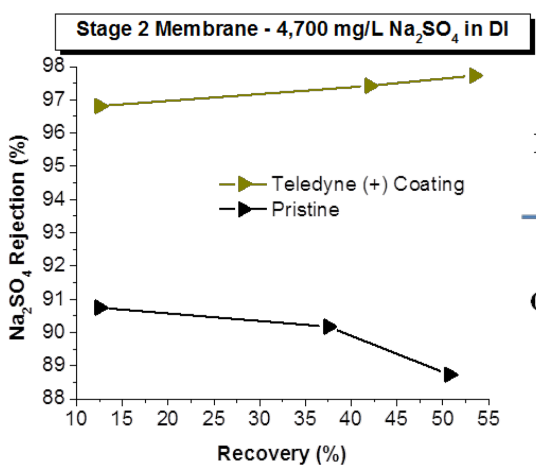
- 85 °C weak black liquor (WBL) processed with Stage 1 coated membranes for >3 days with no decrease in permeate flux
  - ➢ 15% solids WBL concentrated to 23% solids at 85% permeate recovery
  - ➢ ΔJ/Δt = **+0.2** L·m^{-2}·h^{-2} **with coating** after 72 h
  - ➢ ΔJ/Δt = **–0.4** L·m^{-2}·h^{-2} after 3 h **without coating**

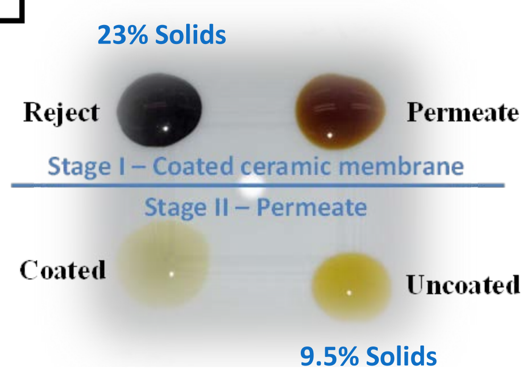




Teledyne charged coatings

- ↑sulfate rejection with ↑ recovery (compared to ↓ rejection with uncoated)
- 380 mg L^{-1} sulfate and 13 g L^{-1} total organic carbon using WBL permeate feed





Remaining work

- Optimize coating, cleaning and re-coating on large scale membranes (~1 m²)
- Demonstrate WBL concentration for >7 days at the paper mill with less than 20% drop in permeate flux with semi-automated backflush, chemical clean, and in-place coating reformation