U.S. DEPARTMENT OF
ENERGY

Office of
ENERGY EFFICIENCY &
RENEWABLE ENERGY

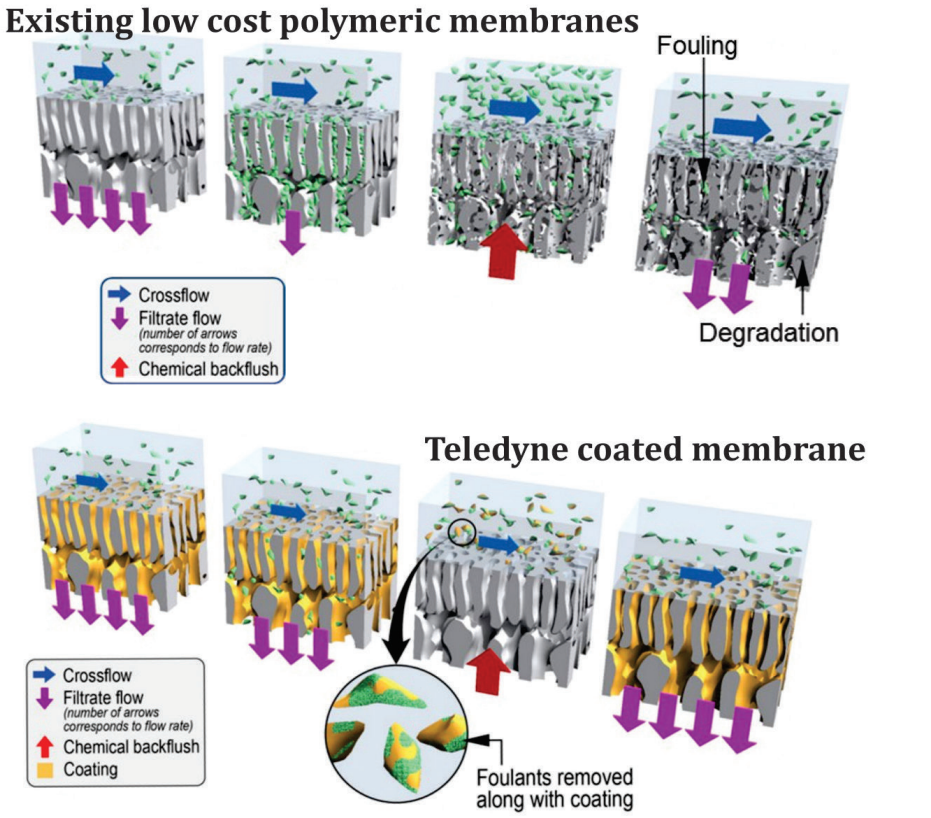
Sacrificial Protective Coating Materials that can be Regenerated *In-Situ* to Enable High-Performance Membranes

Among the various manufacturing processes employed across all U.S. industries, the process of concentrating weak black liquor (WBL) in the pulp and paper industry is identified as one of the largest energy reduction opportunities for separation technologies.

The concentration of WBL in the pulping process is currently performed by multiple stages of steam-heated evaporators, which concentrate the liquor from approximately 15% solids to about 65%–80% solids. This process consumes large amounts of energy due to the high heat needed to vaporize water.

The technical feasibility of ceramic membrane separation offering a non-evaporative, pressure-driven alternative to concentrating WBL has been demonstrated, but ceramic membranes have higher capital costs, making them prohibitively expensive. Polymeric membranes are available at much lower cost but, untreated, the membranes are attacked by the harsh nature of the WBL. Moreover, membrane fouling leads to clogging, increasing operation costs.

Replacing the first two evaporators with membrane-based separation would allow WBL to be concentrated from about 15% solids to about 30% solids without the use of thermal evaporation.



A protective coating (yellow) on the polymer membrane provides chemical and fouling resistance. Removing the foulants and/or coating during chemical backflush and subsequent in-place regeneration increases longevity.

Graphic image credit Teledyne.

This project developed a pressure-driven membrane-based WBL concentration process that maintains high product flow by mitigating membrane fouling. The chemically-resistant and antifouling coating can be deposited on ceramic and polymeric membranes to enable economical implementation of the concentration process. The protective coating makes it difficult for various foulants in the WBL to adhere to the membranes while also providing protection from harsh conditions. The low cost, superhydrophilic, and sacrificial coating can be regenerated in-situ and on demand to combat membrane degradation and fouling from black liquor. Such a coating makes membrane-based WBL concentration feasible since it increases the filtrate flow for longer periods of time. As a result, the overall membrane cost is lower because the membrane lifetime is increased.

Benefits for Our Industry and Our Nation

The chemically resistant, antifouling, low-cost membrane coatings have the potential to provide the following benefits:

- Reducing energy requirements and greenhouse gas emissions of black liquor concentration
- Reducing water demand in the separation step, which will require less energy to heat process water
- Projected payback period for an optimized industrial scale process is less than 3 years with lower operating costs, providing a competitive advantage to the U.S. pulp and paper industry.
- Potential production of higher value-added products by fractionation of lignin and hemicellulose with an optimal choice of membrane pore size

Applications in Our Nation's Industry

This novel technology could enable major reductions in energy use in the paper industry, while also making membrane separation of challenging feed streams in other industries commercially viable. Applications in other industries include treatment of water in oil and gas drilling, waste streams from metal and mining, and biologically loaded streams in food processing.

Project Description

A chemically resistant, antifouling, low-cost membrane coating was developed for application in the pulp and paper industry. The coated membranes are designed to be used in place of the first two multi-stage, steam- heated evaporators for concentration of WBL in paper pulping. The novel renewable coating protects the membranes against the harsh feed and reduces fouling.

Barriers

Major barriers to be overcome include the following:

- Lifetime uncertainty for the polymeric membranes and coating materials in constant contact with hot, caustic black liquor
- Feasibility of cleaning and recoating the membranes while in place

Pathways

To ensure successful maturation of the technology, the project:

- Developed critical proof-of-concept of membrane protection and antifouling and refined target specifications for the membrane separation process;
- Provided lab-scale demonstration of all components, including membrane cleaning and recoating and a plan to meet target specifications;
- Demonstrated hot black liquor filtration in a lab-scale unit; and
- Developed a detailed business case for commercializing the demonstrated technology.

Milestones

This project began in 2012 and was completed successfully in 2017.

- Achieved environmental stability (pH 13-14, temperature >80°C) of coating materials on chosen membranes
- Demonstrated coating regeneration after black liquor filtration with <10% drop in flux after recoating process
- Established a black liquor treatment process for >3 days with <20% drop in total flux
- Established a black liquor treatment process for >7 days with <20% drop in total flux with backflush, chemical clean and in-place coating reformation
- Demonstrated a black liquor concentration process in a lab unit on both hardwood and softwood black liquor streams for >14 days of continuous operation and analysis of black liquor and filtrate streams

Accomplishments

- Developed antifouling coatings and demonstrated multistage concentration of WBL. Crossflow performance was significantly improved with the coating at pH >13 and T >80°C.
- Continuously filtered WBL for 3 days using coated ceramic membranes in a laboratory-scale unit without any observable fouling or need for backflushing.
- Successfully demonstrated in-place, pilot-scale, antifouling properties of the coating using WBL instantaneously supplied by an operational paper mill.

Technology Transition

Early engagement of pulp and paper manufacturing partners has been a key contributor to the successful development of this technology. The industrial partners provided expertise in industrial operations, including the design of filtration modules and the complete design of filtration systems appropriate for black liquor concentrations. Industrial partners also provided on-site lab demonstration and validation trials to ensure an adequate supply of black liquor and validate test results to the end users.

Teledyne is leveraging their market penetration strategies in the municipal water filtration market and antifouling of streamer cables used in oil exploration to refine the commercialization approach for this project. Data from these other markets will also help to further establish a robust business case. Given the size of the pulp and paper market and the relatively simple coating operation, other markets should not be needed to justify a commercially feasible coating operation. However, additional research is needed to fully optimize the anti-fouling coating process for the large-scale industrial membranes.

Project Partners

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Project final report available at:
www.osti. gov/scitech
OSTI Identifier 1429323

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DOE/EE-1685 • March 2019