Produced Water-Aided Treatment of Blowdown Water for Value Creation

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Project Objective

Objective:
To develop a blowdown (BD) water treatment process utilizing produced water (PW) and low-grade heat

Expected Outcome:
Maximized water reuse for cooling operation at thermal electric power plants and saleable by-product generation while achieving a step-improvement of chemical and energy footprints of BD and PW water treatment

Makeup and blowdown waters

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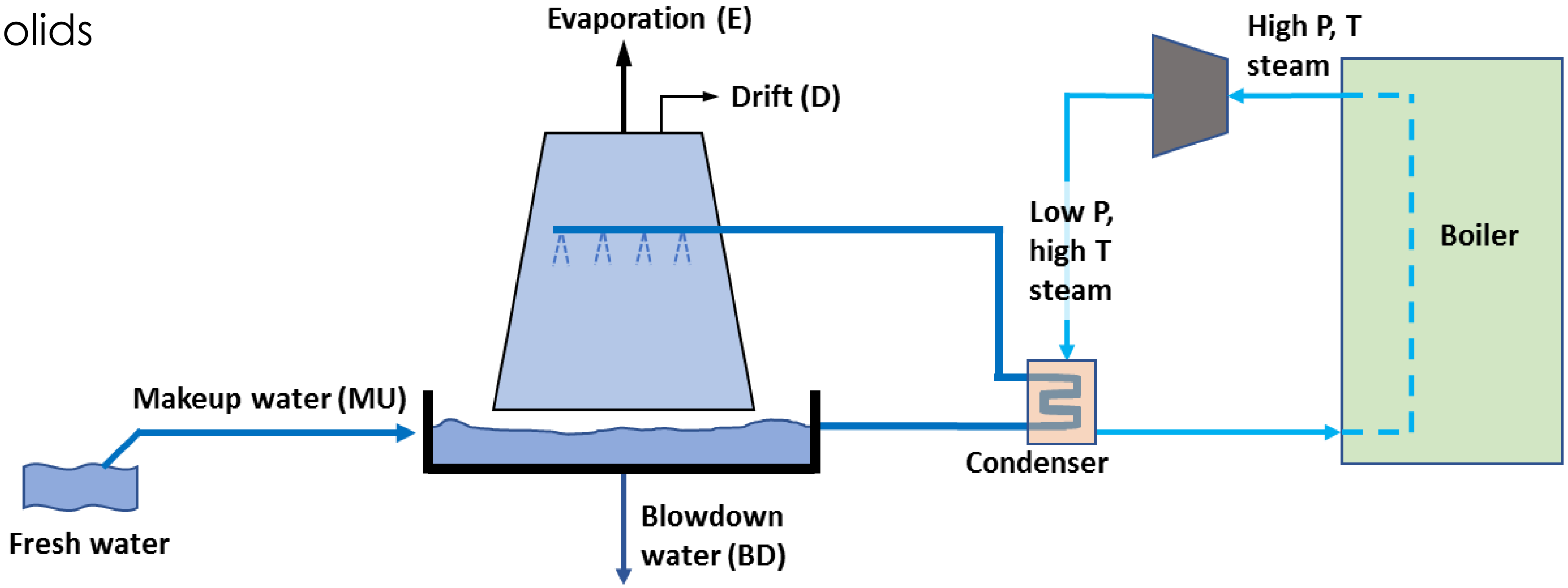
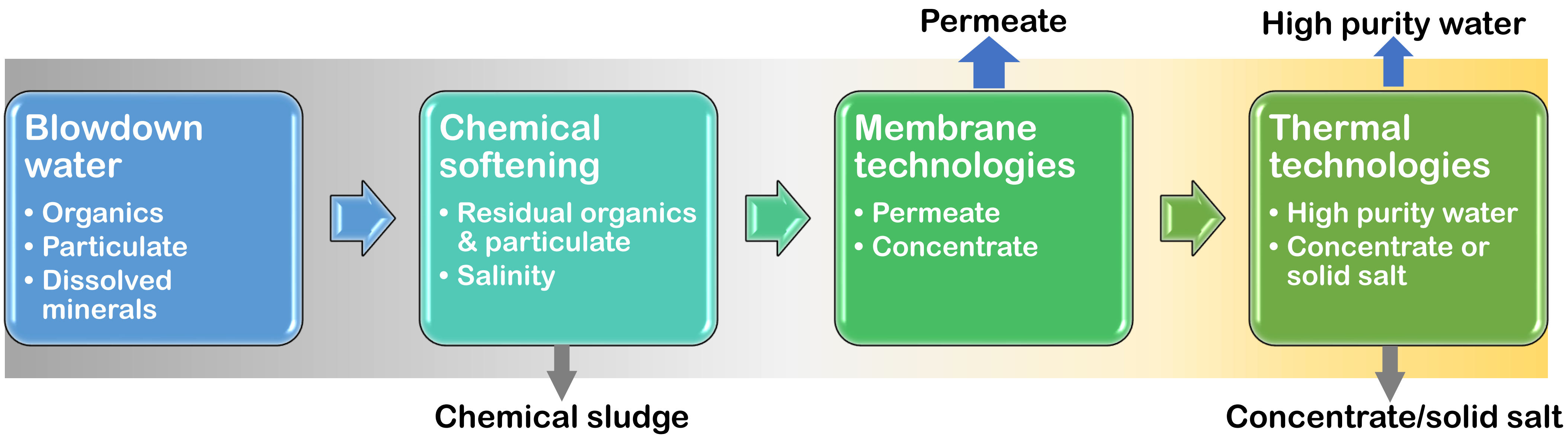
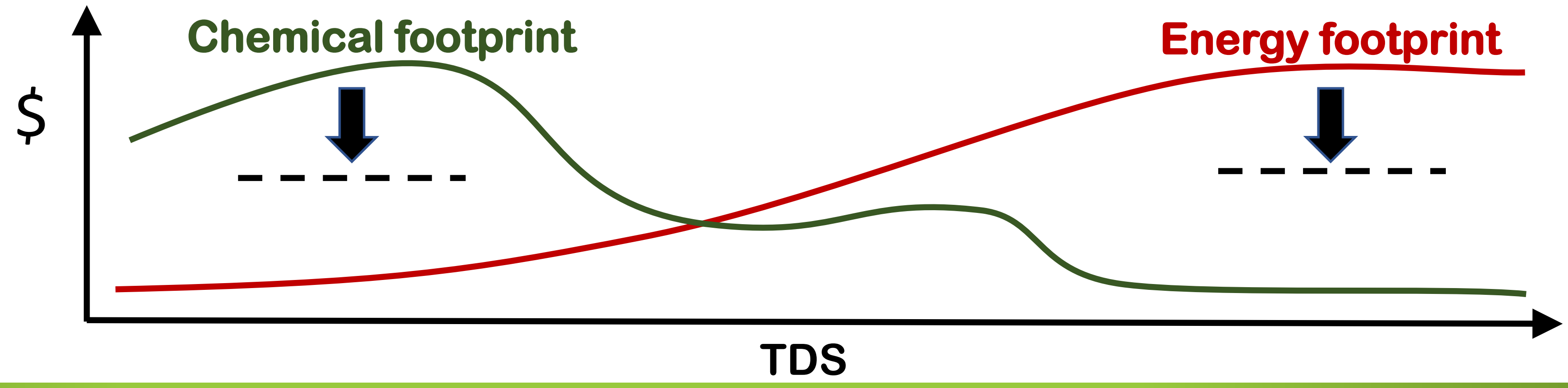
Scale-forming constituents in recirculating water (EPRI, 2003)
- Multi-valent metals (e.g., Ca, Mg, etc.)
- Sulfate, phosphate
- Alkalinity (e.g., bicarbonate)
- Silicate
- Suspended solids



Baseline Treatment Process and Opportunities



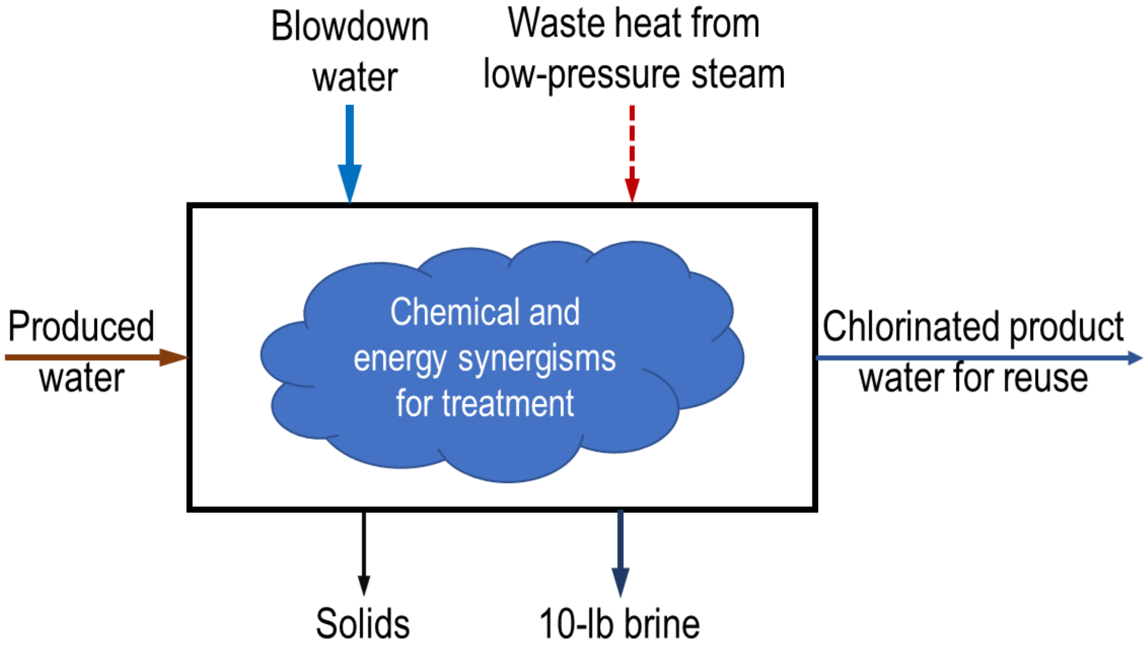


A Regional Solution

- Innovative approach for co-treatment of PW and BD water

- Chemical and energy synergisms

- Useful products
  - RO permeate for cooling makeup
  - 10-lb brine as saleable product
  - NaOH and Cl_2 generation

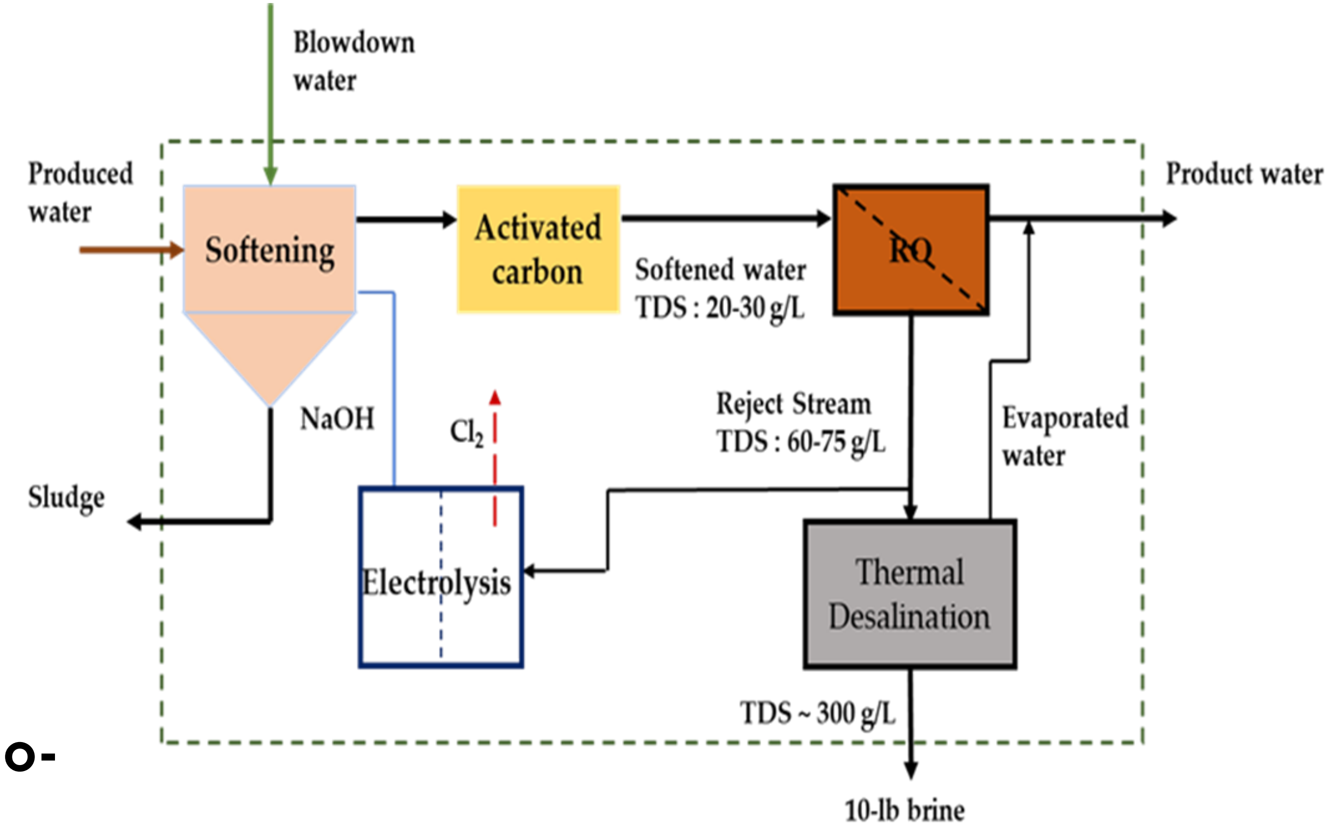


- **Align with DOE Office of Fossil Energy and the National Energy Technology Laboratory (NETL) mission by supporting long-term, high-risk meritorious fundamental research that advances the science of coal technologies**

Project Description

Co-treatment process design

1. BD/PW Mixing
2. Chemical Softening
3. Activated Carbon Adsorption
4. Reverse osmosis
5. Thermal desalination
   → 10-lb brine
6. Brine electrolysis
   → NaOH and Cl_2 generation
7. Process modeling/simulations and techno-economic analysis (TEA)
   → treatment process optimization

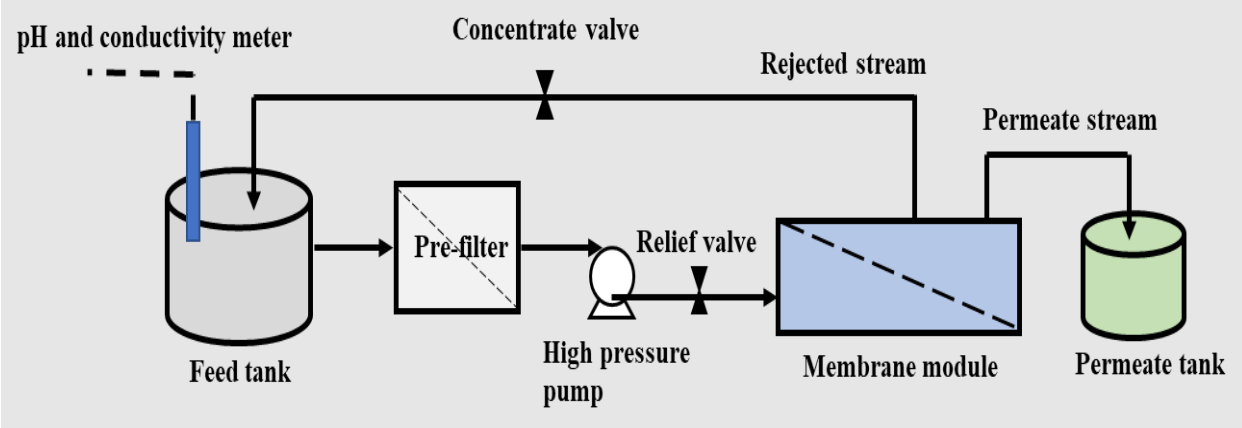


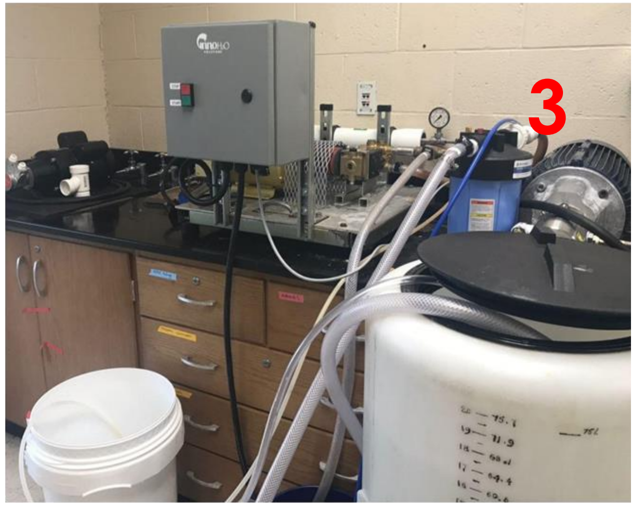
Laboratory-scale Process

Experimental Set-Up

1. Mixing and softening
2. Activated Carbon Filtration
3. Reverse Osmosis (RO)

Schematic of RO Set-Up





Results

Mixing, Softening and Activated Carbon Filtration

- BD/PW mixing at 10:1 volumetric ratio resulted in 70% sulfate and 90% barium removal without any chemical use.

- Chemical Softening: use of alkaline chemicals further removed scale-forming ions with >99% efficiencies for Ca, Mg, Ba, Sr, and Fe.

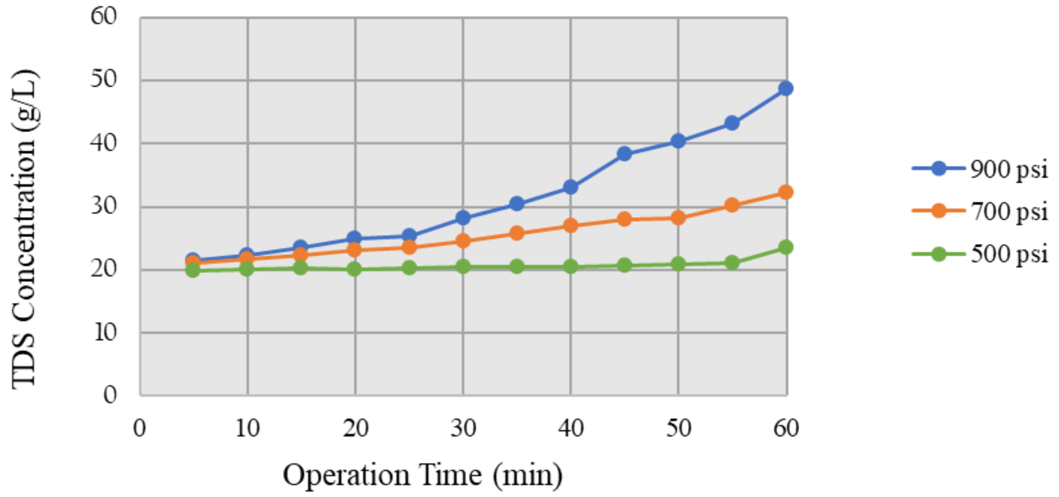
- Activated carbon filtration achieved >90% TOC removal and further reduced calcium, barium, and strontium concentrations by >98%.

- Industrial partners
  - Longview Power
  - Northeast Natural Energy
  - InnoH2O Solutions

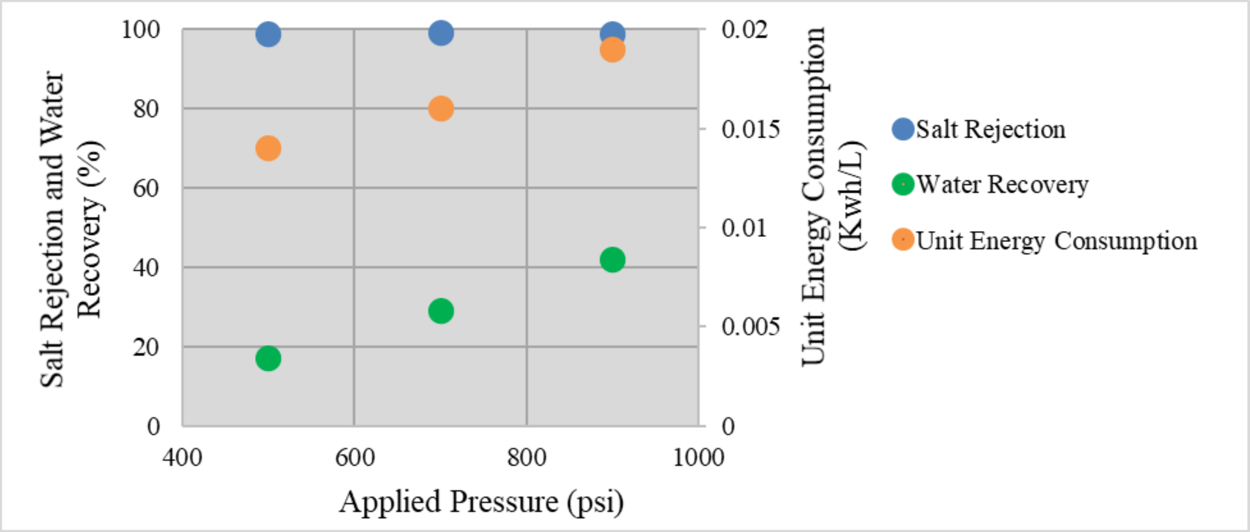
Results

Reverse Osmosis Desalination

- **Working Volume ~ 70 L**
- **Initial TDS ~ 20 g/L**
- **Operation Time = 60 min**
- **Initial pH ~ 10.5**



Applied Pressure (psi)	500	700	900
Salt Rejection (%)	99	99	99
Water Recovery (%)	17	29	42
Unit Energy Consumption (Kwh/L)	0.014	0.016	0.019
Final TDS concentration (g/L)	23	32	50



Results

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Brine Electrolysis

- Brine electrolysis was used to generate hydroxide and hypochlorite
- Developed a brine electrolysis cell with a Covestro oxygen depolarizing cathode.
- Evaluated four cation exchange membranes from Chemours.
- Use of 80 g/L and 110 g/L NaCl solutions in brine electrolysis
  - Faradaic efficiency is near 80%
  - Specific energies:
    0.3 kWh per kg NaCl transferred and 15-20 kWh per cubic meter of dilute product
- Industrial partners
  - Covestro
  - Chemours

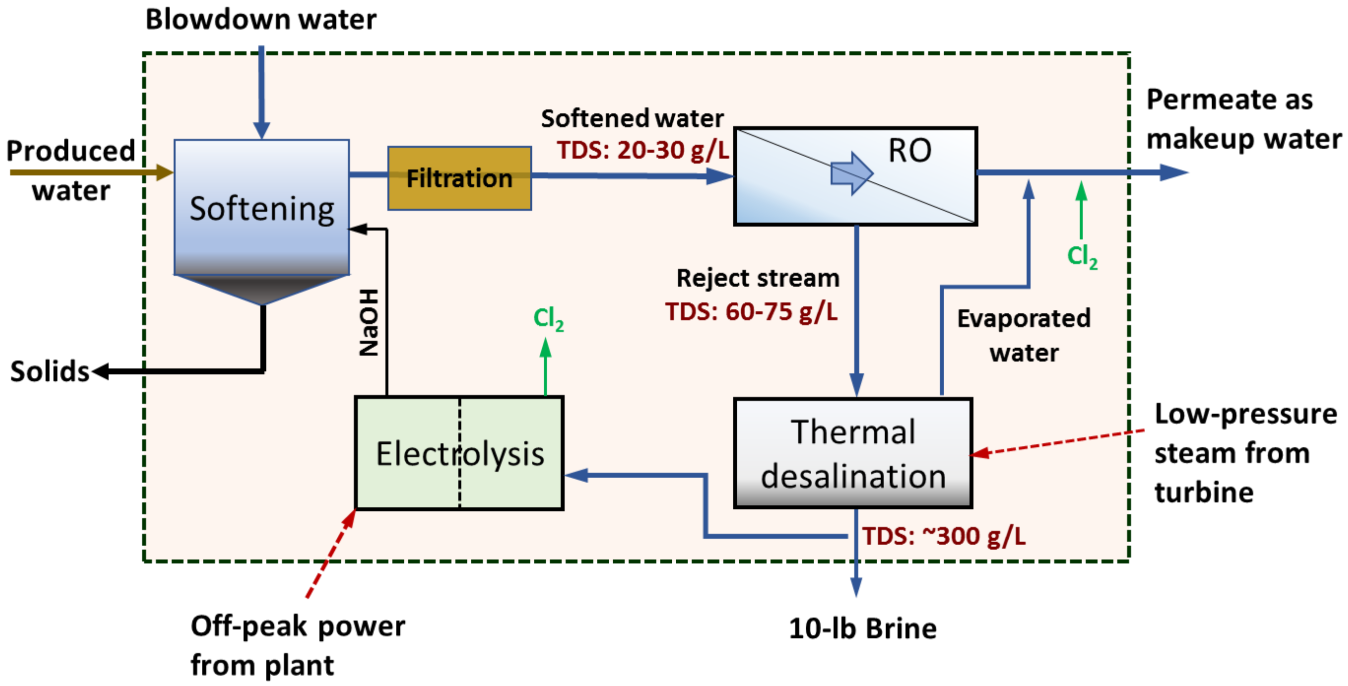
covestro

Chemours

Results

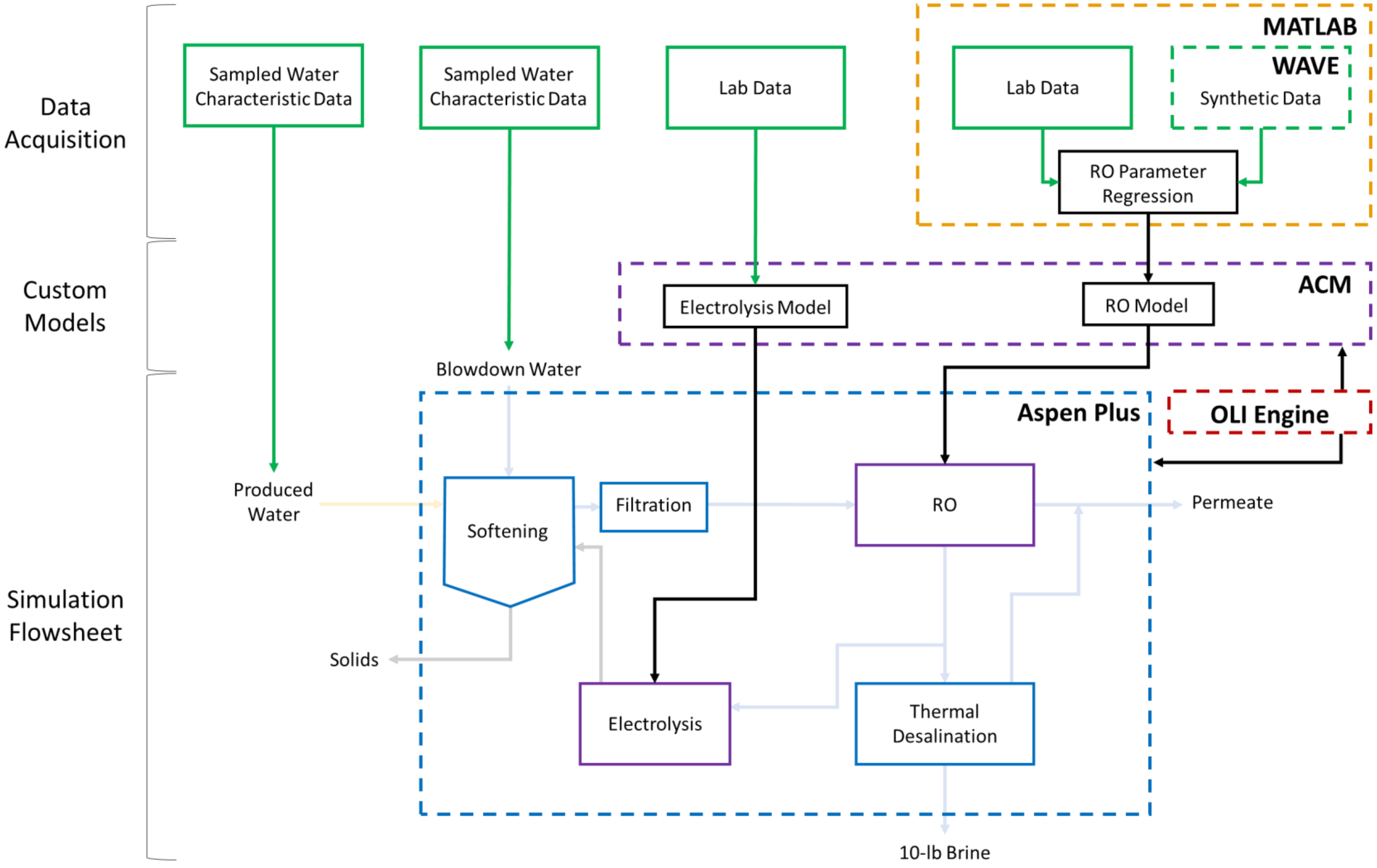
Process Modeling and Simulations

- Simulation flowsheet created in **Aspen Plus** with supplementary imported software models and calculations



Results

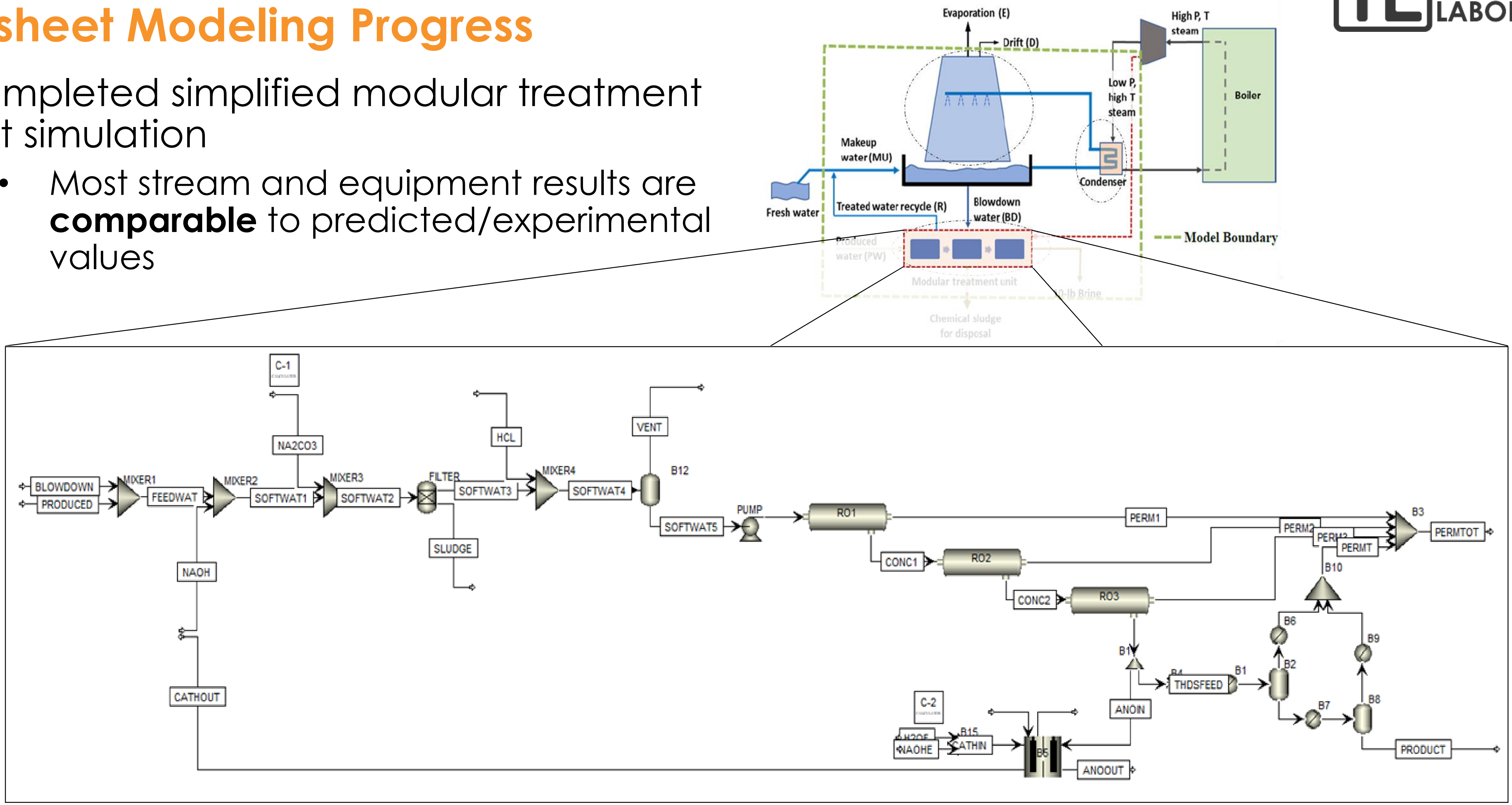
Data and Software Workflow



Results

Flowsheet Modeling Progress

- Completed simplified modular treatment unit simulation
    - Most stream and equipment results are **comparable** to predicted/experimental values



Results

Model Overview and Preliminary Results of Modular Unit

Softening and Filtration

- Phase and equilibrium calculations performed by OLI Engine package
- NaOH and $NaHCO_3$ additions bring stream to a **pH** of **12**, **35 g/L total TDS** and **3 mg/L 2+ ion TDS**

Thermal Desalination

- Phase and equilibrium calculations performed by OLI Engine package
- Modeled as sequential heat exchangers in Aspen Plus

Reverse Osmosis

- Custom model developed in ACM using Spiegler-Kedem-Katchalsky model
- Synthetic data from 5000+ designs simulated in WAVE
- Membrane performance parameters regressed in MATLAB using WAVE data
- 850+ simulated designs
- 50 designs considered viable by operating within the membrane constraints
- Potential annual savings of **$250,000** when comparing best to worst viable designs

Electrolysis

- Custom model developed in ACM using Faraday's law
- Faradaic efficiencies applied to conversion at each electrode determined by experimental data
- Chlorine-hypochlorous acid-hypochlorite equilibrium determined by OLI equilibrium model
- **1% of RO concentrate** flow may be diverted to the unit to maintain equal volume compartments and **sufficient NaOH production**

Conference presentation and Publication

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- G. Khajouei, H. Park, H. Finklea, P. Ziemkiewicz, L.-S. Lin. "Co-treatment of Produced water and Blowdown Water to Reduce Chemical and Energy Footprint of Water Reuse and Byproduct Generation", WEFTEC, October, 2020 (**selected as one of <u>top 10 academic papers</u>**)

- L.-S. Lin, H. Finklea, P. Ziemkiewicz, F. Lima, and H. Li, Co-management of Produced Water and Power Plant Brines for Value Creation, Shale Insight Conference, Technology Showcase Program, virtual event, Sep. 29 – Oct. 1, 2020.

- G. Khajouei, H. I. Park, H. O. Finklea, P. F. Ziemkiewicz, E. F. Peltier, and L.-S. Lin, Produced water softening using high-pH catholyte from brine electrolysis: reducing chemical transportation and environmental footprint, *Journal of Water Process Engineering* (revised manuscript submitted).

Technological and collaborative challenges

- The proposed co-treatment technology uses mature treatment methods. Integrating the different treatment units that have a wide range of treatment kinetics is a challenge.

- The project team has presented and discussed with energy and power producers the co-treatment technology, and received positive feedback. However, the energy and power market fluctuations are an uncertainty for the industries to adopt the technology.

Future Work of the Project

- Reverse osmosis
  - effects of pH and applied pressure on water recovery and energy consumption using different BD/PW mixtures
- Thermal desalination treatment of the RO concentrate
- Brine electrolysis using the brine from the thermal desalination
- Process integration
- Perform Techno-Economic Analysis (TEA)
- Optimize flowsheet performance for a variety of scenarios

Preparing Project for Next Steps

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Market Benefits/Assessment

- This technology addresses water management/treatment for coal-power generation and shale gas production.
- Successful development of the technology is expected to help achieve the DOE-led Water Security Grand Challenge Goal 3 "Achieve near-zero water impact for new thermoelectric power plants, and significantly lower freshwater use intensity within the existing fleet".
- Adoption and implementation of the technology is expected to provide power plants with flexibility for managing water; yield chemical/energy savings; and help achieve zero liquid discharge footprint.

Preparing Project for Next Steps

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Technology-to-Market Path

- The future project work of process integration and optimization is a key step for scale-up design, construction, and commercial applications.
- Scaling up the treatment process from laboratory to pilot-scale testing is a logical step upon the completion of laboratory process testing.
- Potential new research directions include comparison of different co-treatment process configurations and regional application scenarios.
- Industrial collaborators include power and energy producers, technology developers and providers, and treatment equipment/material providers.