Advancing Sustainability of Process Industries through Digital and Circular Water Use Innovations

Membranes

AquaSPICE Course 2024

Laurence Palmowski & Team

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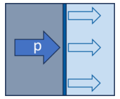
Content

- Membrane Fundamentals
- Membrane Processes

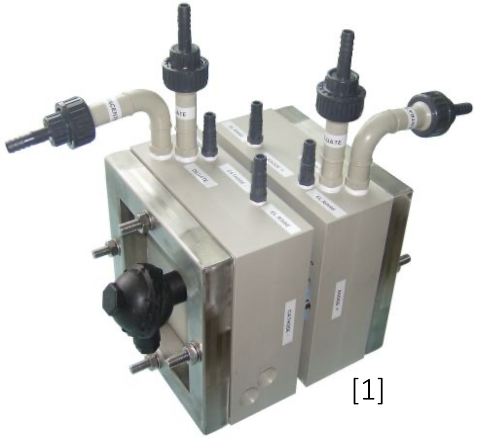


  - Pressure Driven Membrane Processes
  - Electrochemically Driven Membrane Processes
  - Temperature Driven Membrane Processes
- Economic Considerations
- AquaSPICE Case Study 1: Dow Boehlen

Membrane Fundamentals

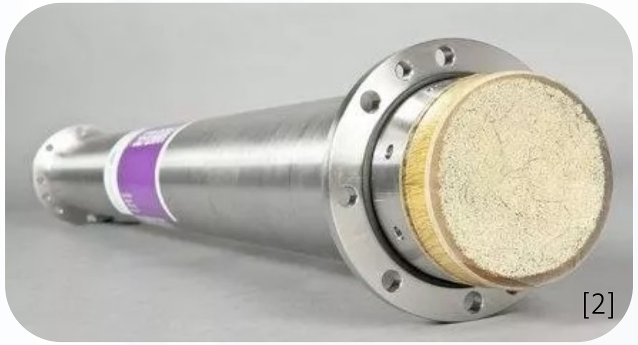
What are Membranes?

- **Membranes** :
  - Thin **selective barriers** designed to **separate** or **filter** substances based on size, charge, or other specific properties
  - Synthetic membranes can be made of organic and inorganic materials, mostly **polymers**



[1]

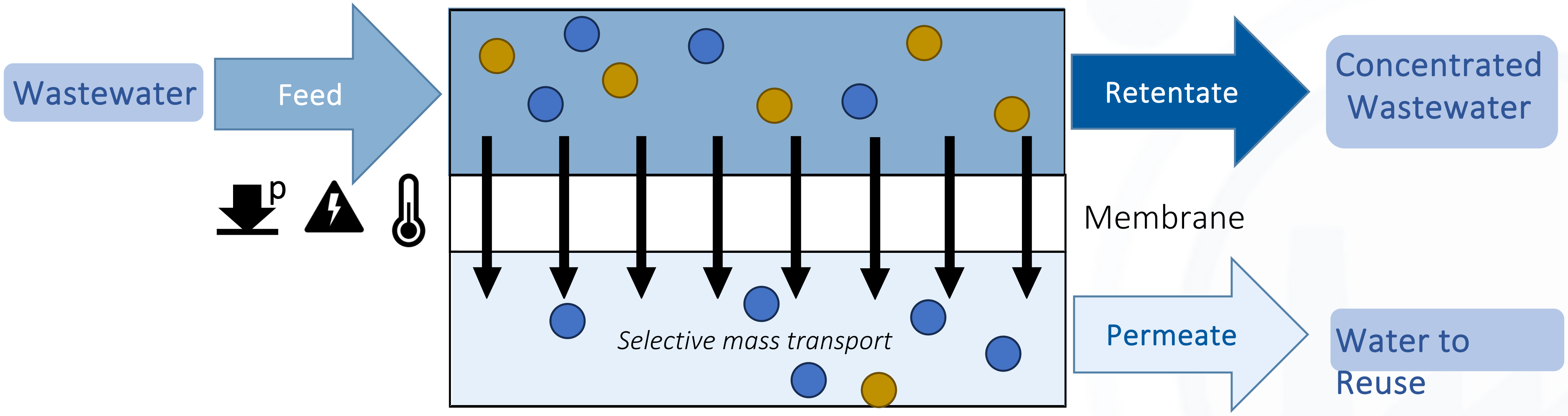
Electrodialysis membrane (left) and electrodialysis stack (right)



[2]

Hollow fibre membranes (left) and hollow fibre membrane module (right)

Membrane Process Terminology



- Different **driving forces** for mass transport through membrane
  - **Pressure** Δ_p driven membrane processes, e.g. Micro-, Nano-, Ultrafiltration, Reverse Osmosis
  - **Electrochemically** Δ_U driven membrane processes, e.g. Electrodialysis
  - **Temperature** Δ_T driven membrane processes, e.g. Membrane Distillation

Membrane Applications in Industry

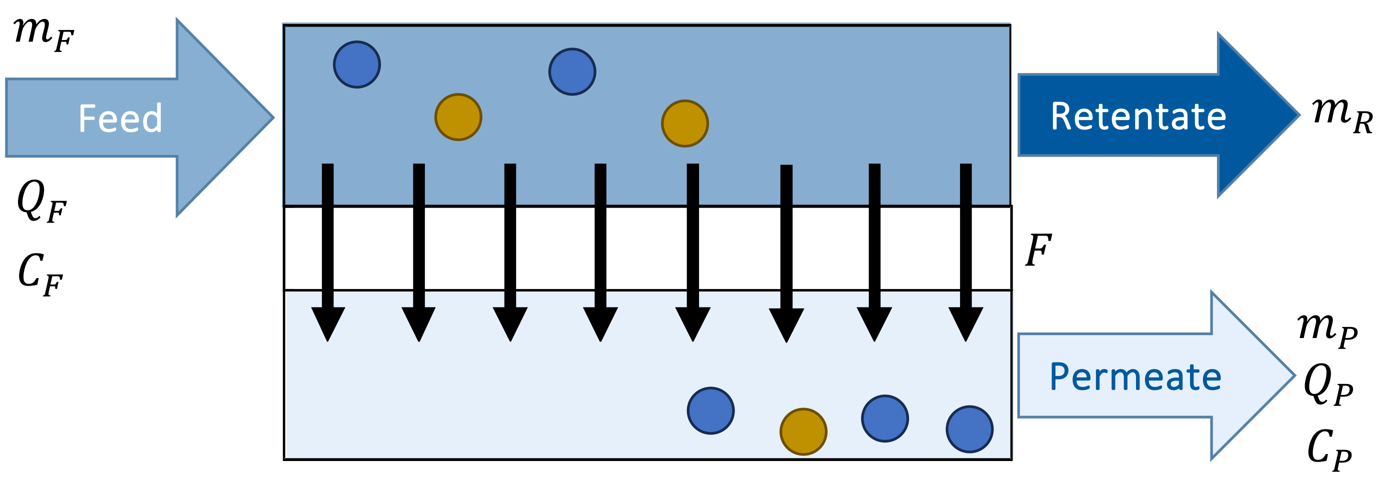
Preventing or **mitigating emissions** from industrial processes (waste water treatment)

Enabling the **recovery of valuable resources** from industrial process streams (water, heat, solvents or other raw materials)

Promoting **energy savings** in industry

Illustration sources:
3 - https://www.zfk.de/wasser-abwasser/abwasser/industrieabwasser-auch-moderne-anlagen-klaeren-nicht-alles
4 - https://naturschutz.ch/news/sauberes-trinkwasser-hat-keine-prioritaet/152837
5 - https://www.bund-naturschutz.de/oekologisch-leben/energie-sparen

Important Parameter for Membrane Processes I/II



Mass Balance $$\dot{m}_F = (\dot{m}_R + \dot{m}_P) \left[\frac{kg}{h}\right]$$

Membrane Flux $$F = \frac{Q_P}{A} \left[\frac{L}{m^2 * h}\right]$$

(Water) Recovery $$r = \frac{Q_P}{Q_F} * 100\ [\%]$$

(Solute) Rejection $$R = \frac{C_F - C_P}{C_F} * 100\ [\%]$$

Selectivity $$S_{ij} = \frac{C_{iP}/C_{jP}}{C_{iF}/C_{jF}}$$

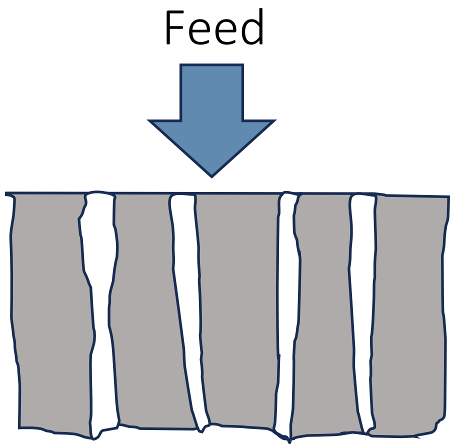
Parameter:

m – mass flow rate [kg/h]
Q – volumetric flow rate [L/h]
A – membrane surface area [m^2]
C – solute concentration [g/L]

Indices:

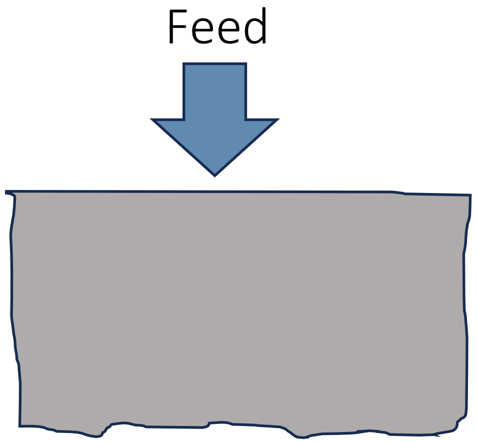
F – feed
P – permeate
R – retentate
i – substance i
j – substance j

Membrane Structures



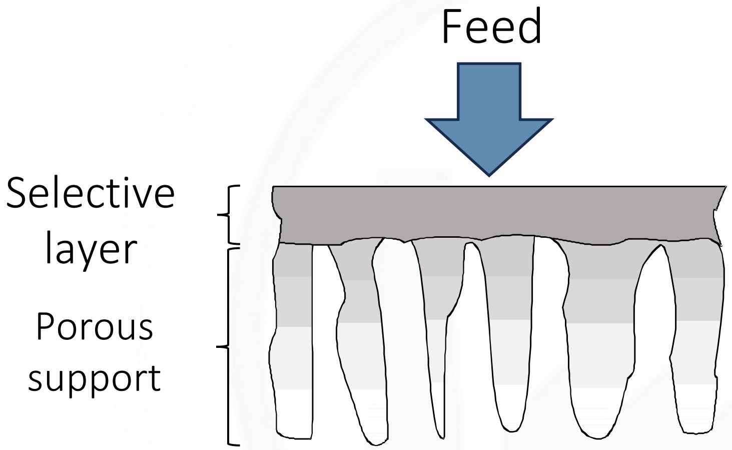
Porous

Separation by Sieve Effect



Dense

Separation by Solution-Diffusion Mechanism



Asymmetric

Membrane Morphology

Asymmetric Membranes

Why asymmetric membranes?

Requirement → High permeate flow

Consequences → Thin selective layer

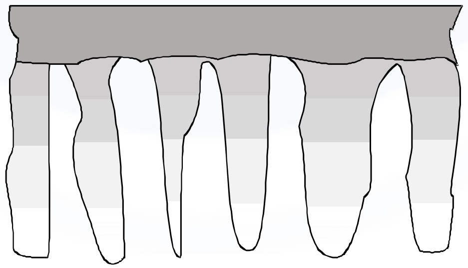
$$\boldsymbol{Flux \sim \frac{1}{Membrane\ thickness}}$$

Problem → Low mechanical stability

Solution

→ **Asymmetric membrane**

= very thin and selective layer **+** thick and porous supporting layer



Membrane Configurations

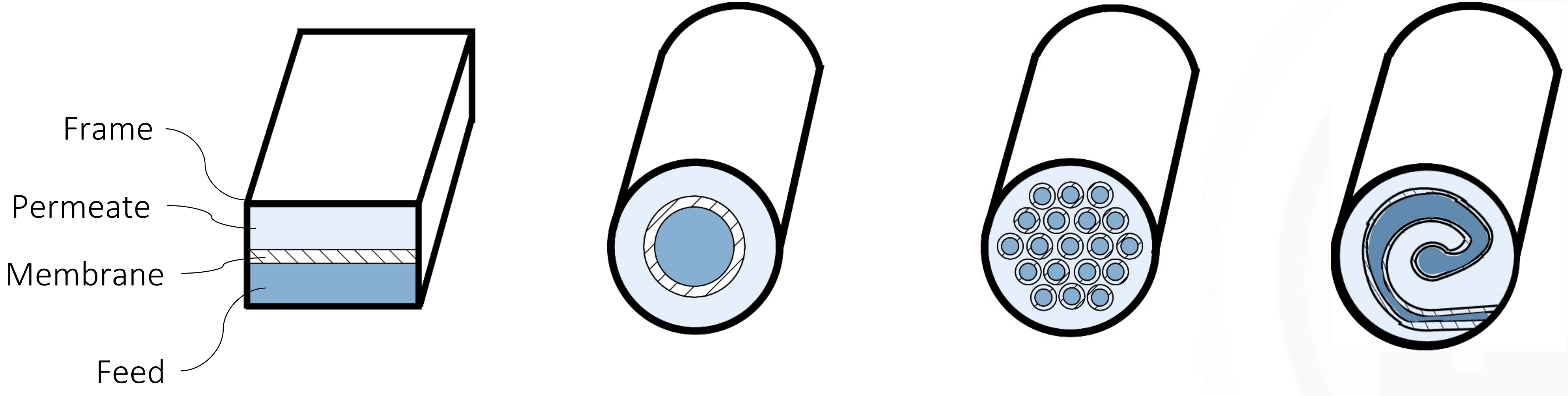
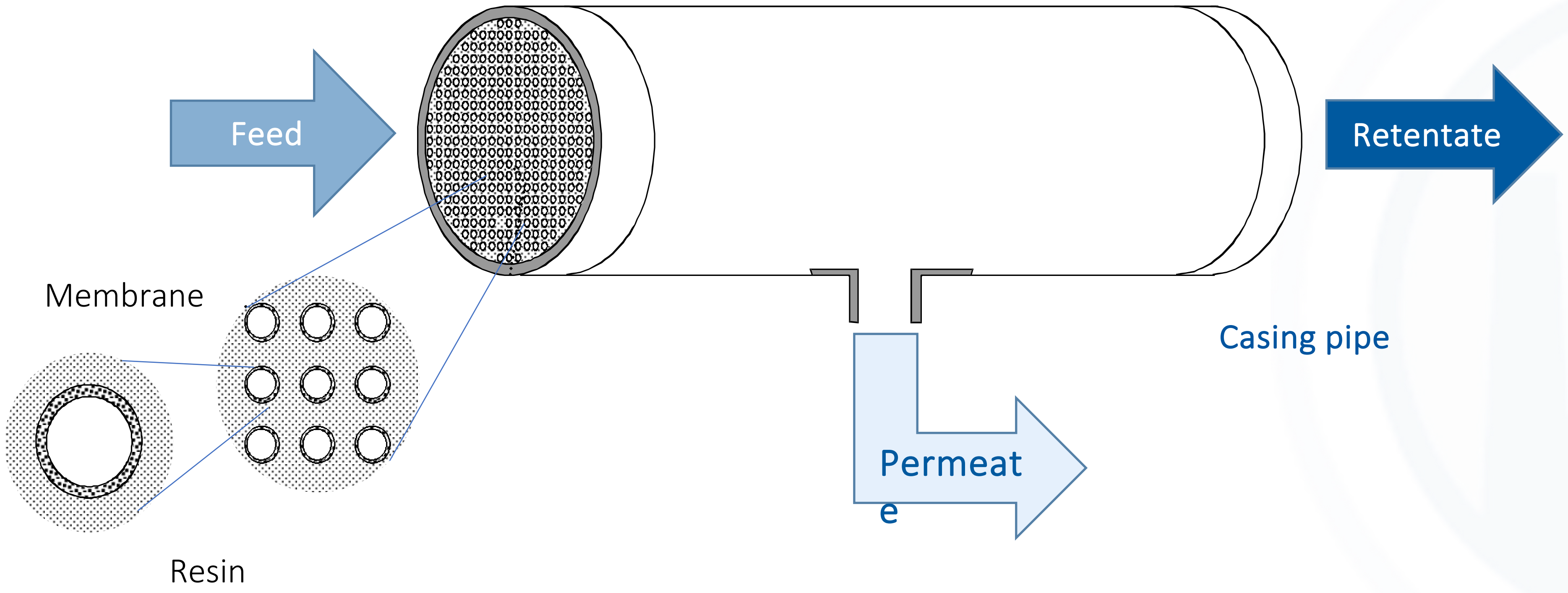


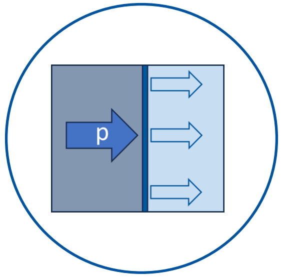
Plate and Frame | Tubular | Capillary/Hollow fiber | Spiral wound

Membrane Module

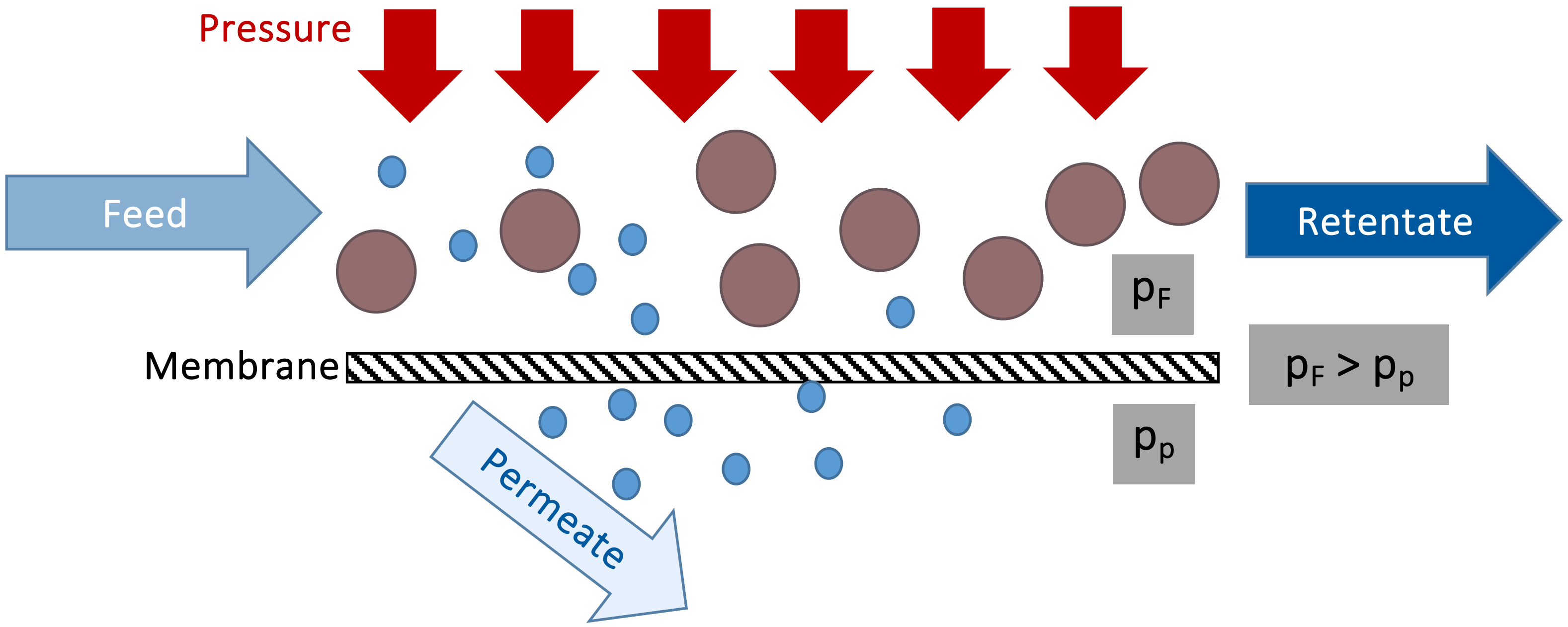
Scheme of a Capillary Module



Pressure Driven Membrane Processes



Principle of Pressure Driven Membrane Processes



Microfiltration:

Particles, algae, protozoa, bacteria

Ultrafiltration:

Viruses, colloids, macromolecules

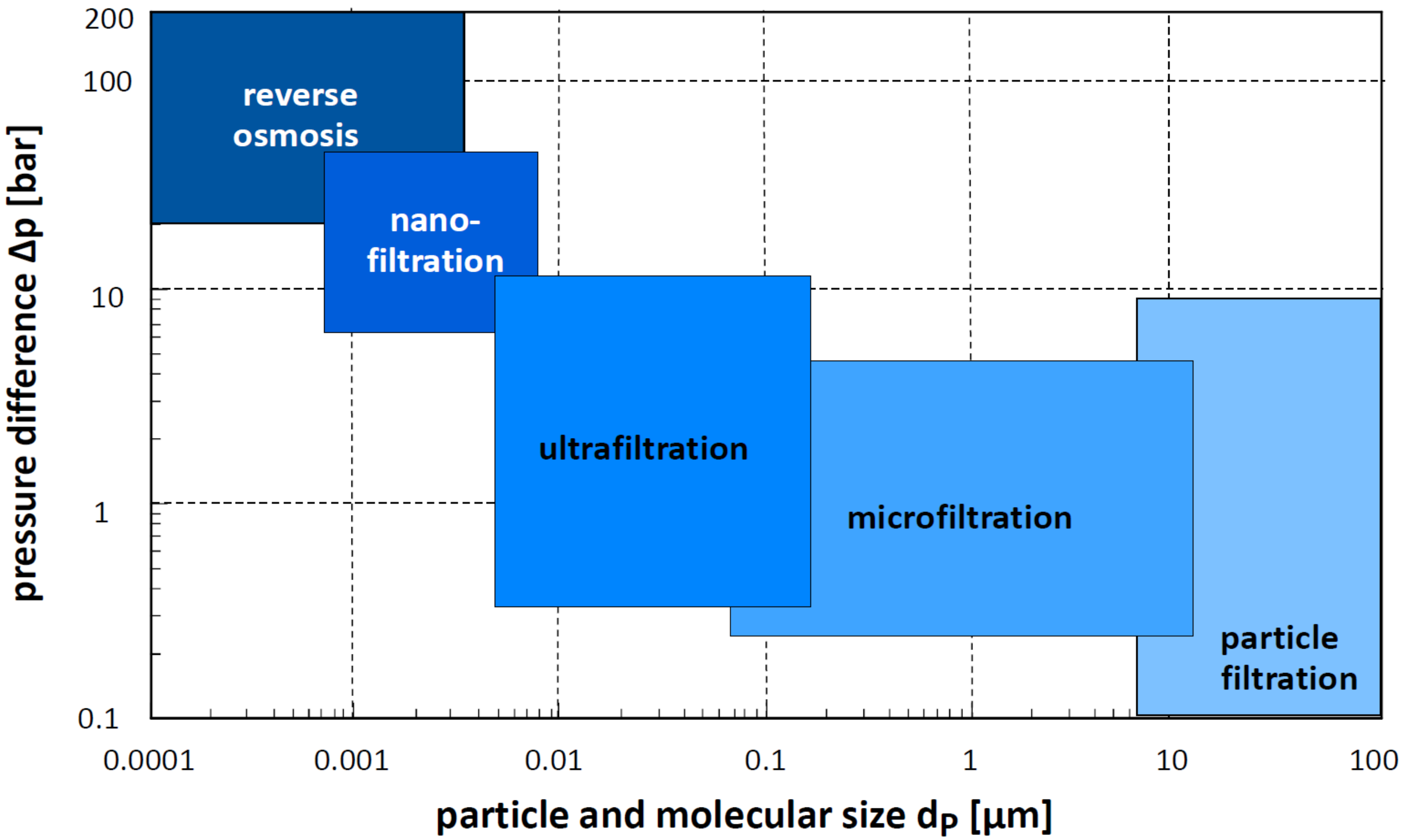
Nanofiltration:

Dissolved, org. substances, divalent ions

Reverse Osmosis:

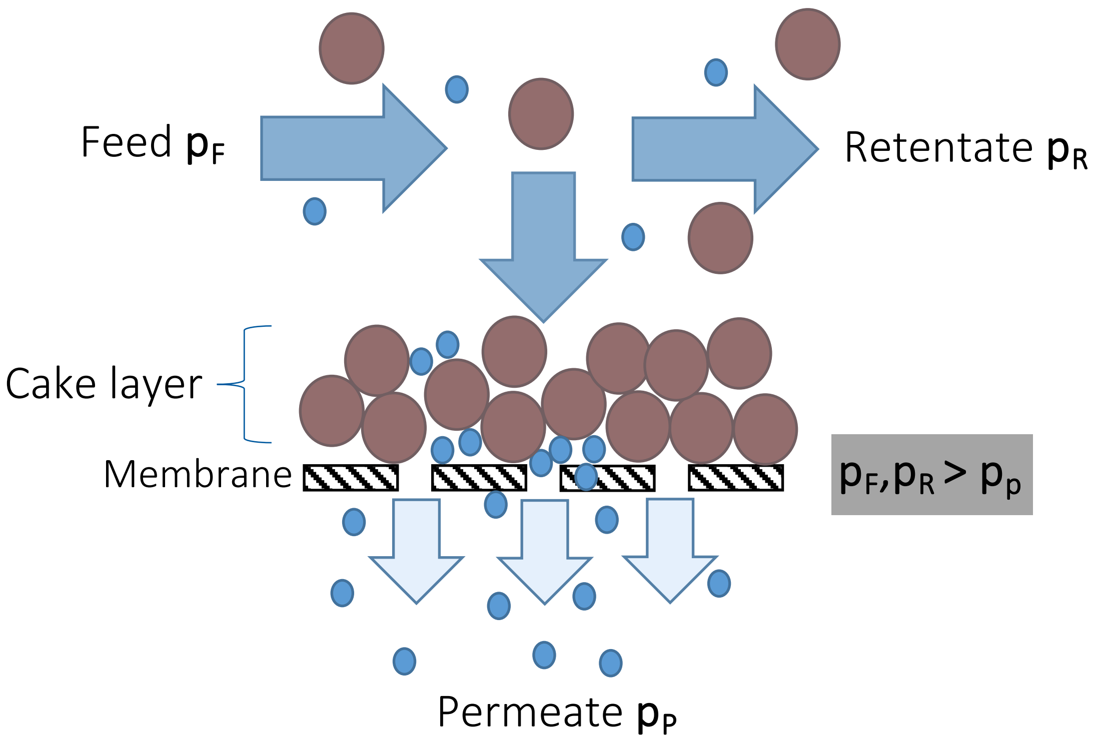
monovalent ions, small molecules

Classification of Pressure Driven Membrane Process



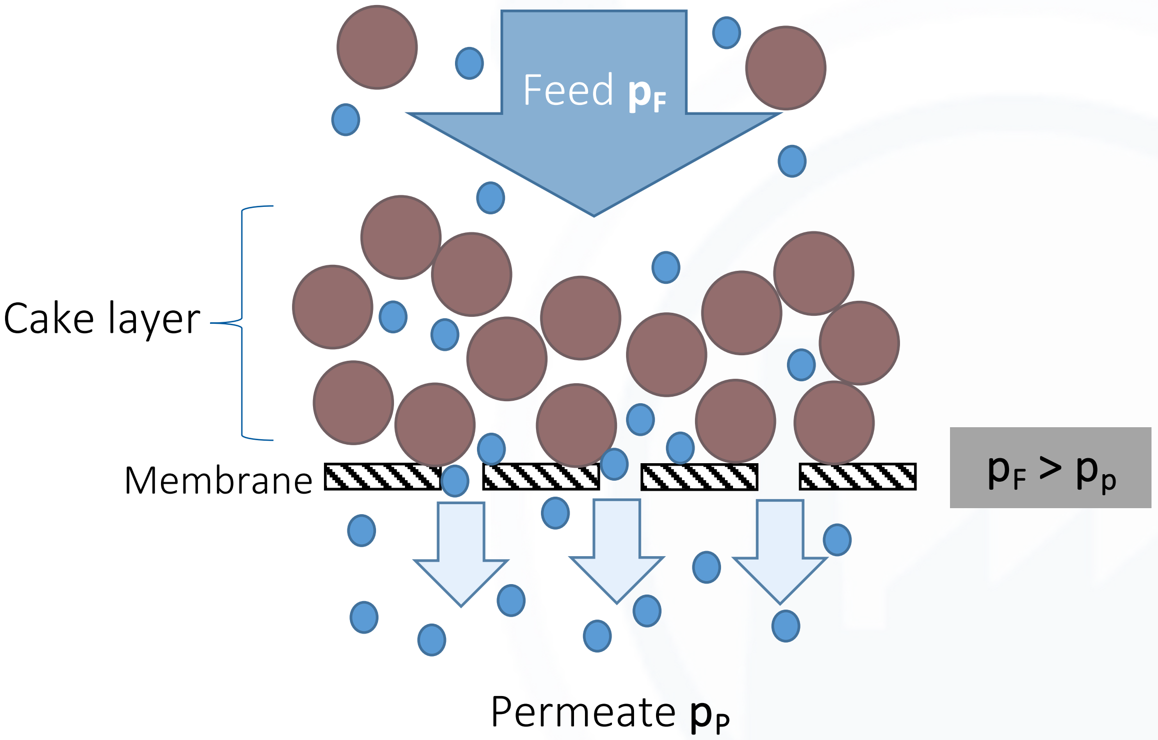
Operational Modes

Crossflow ||



$$\Delta p_{Transmembran} = \left(\frac{p_F - p_R}{2}\right) - p_P$$

Dead-End ⊥



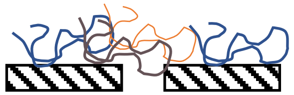
$$\Delta p_{Transmembran} = p_F - p_P$$

Performance Limiting Phenomena

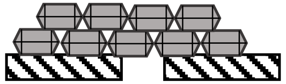
Membrane Fouling

- Membrane Fouling is the buildup of undesirable substances or particles on the membrane, impeding its filtration efficiency
- Classification of fouling

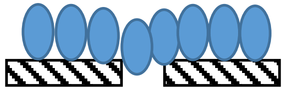
Organic fouling



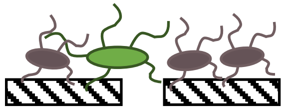
Inorganic fouling



Collodial fouling



Biofilms



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Backwashing, Chemical Cleaning

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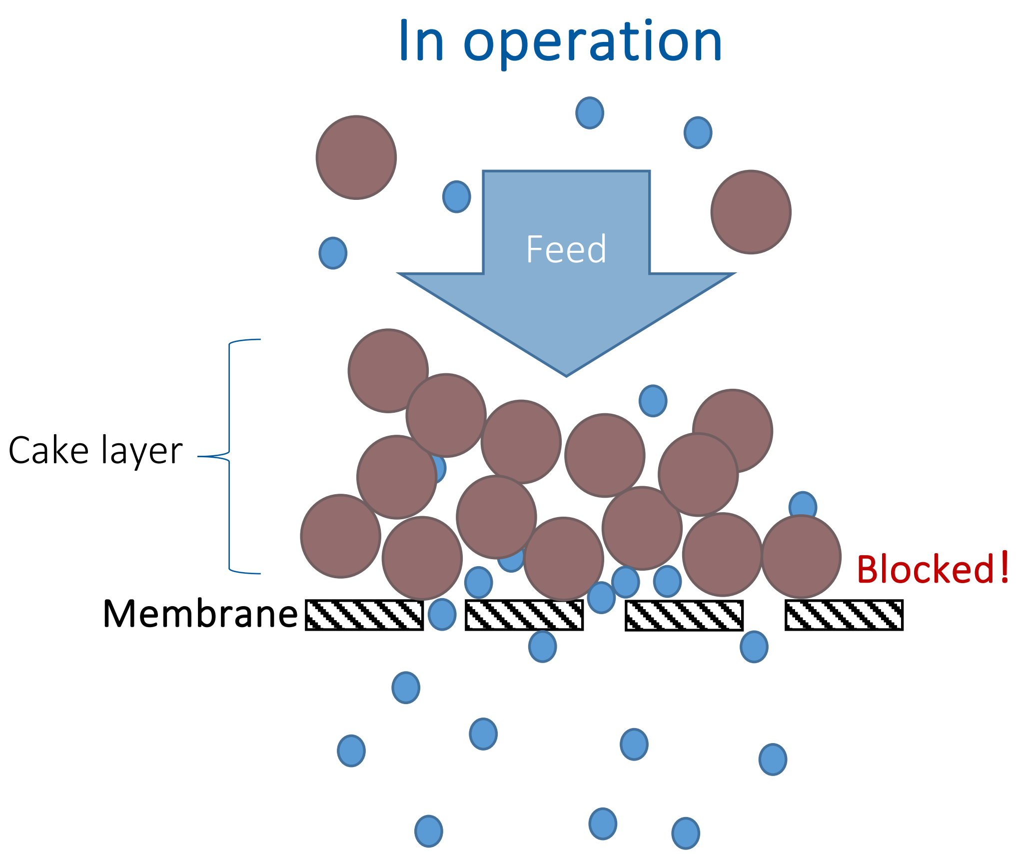
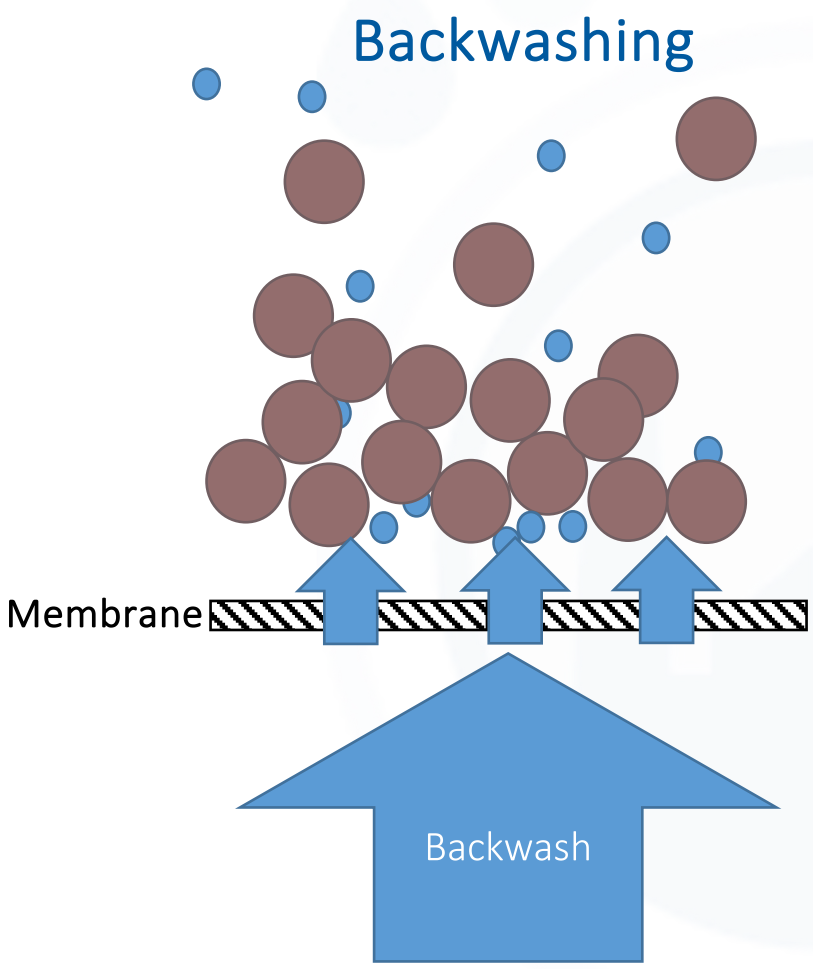
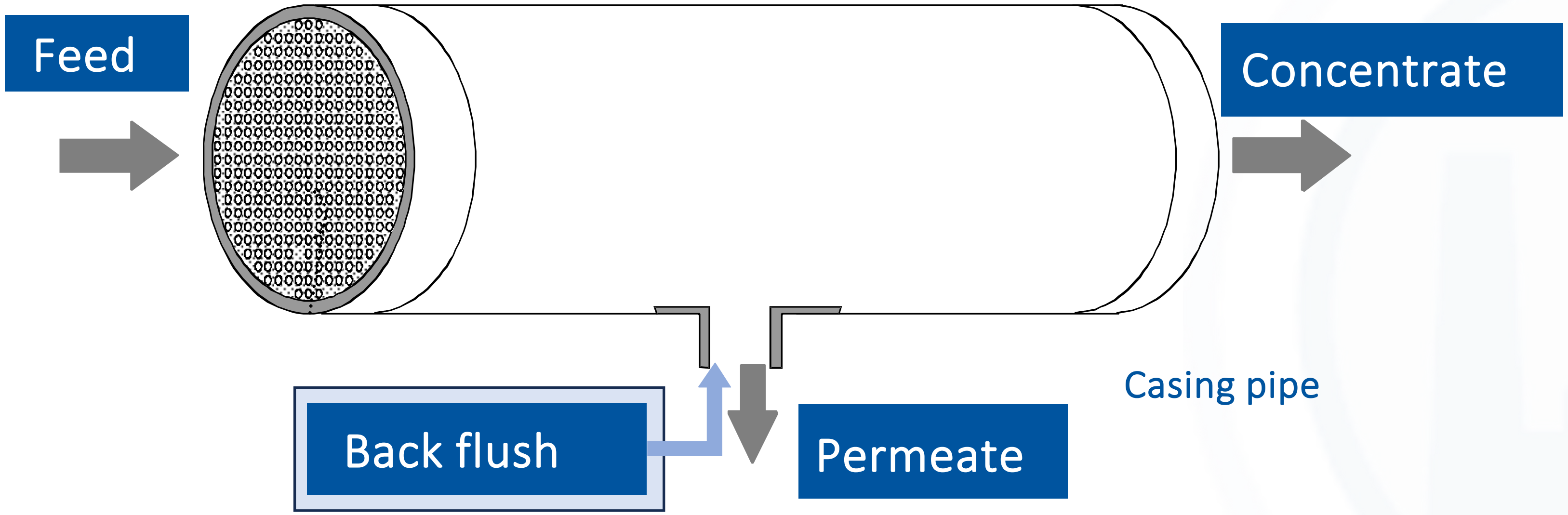
Backwashing I/II



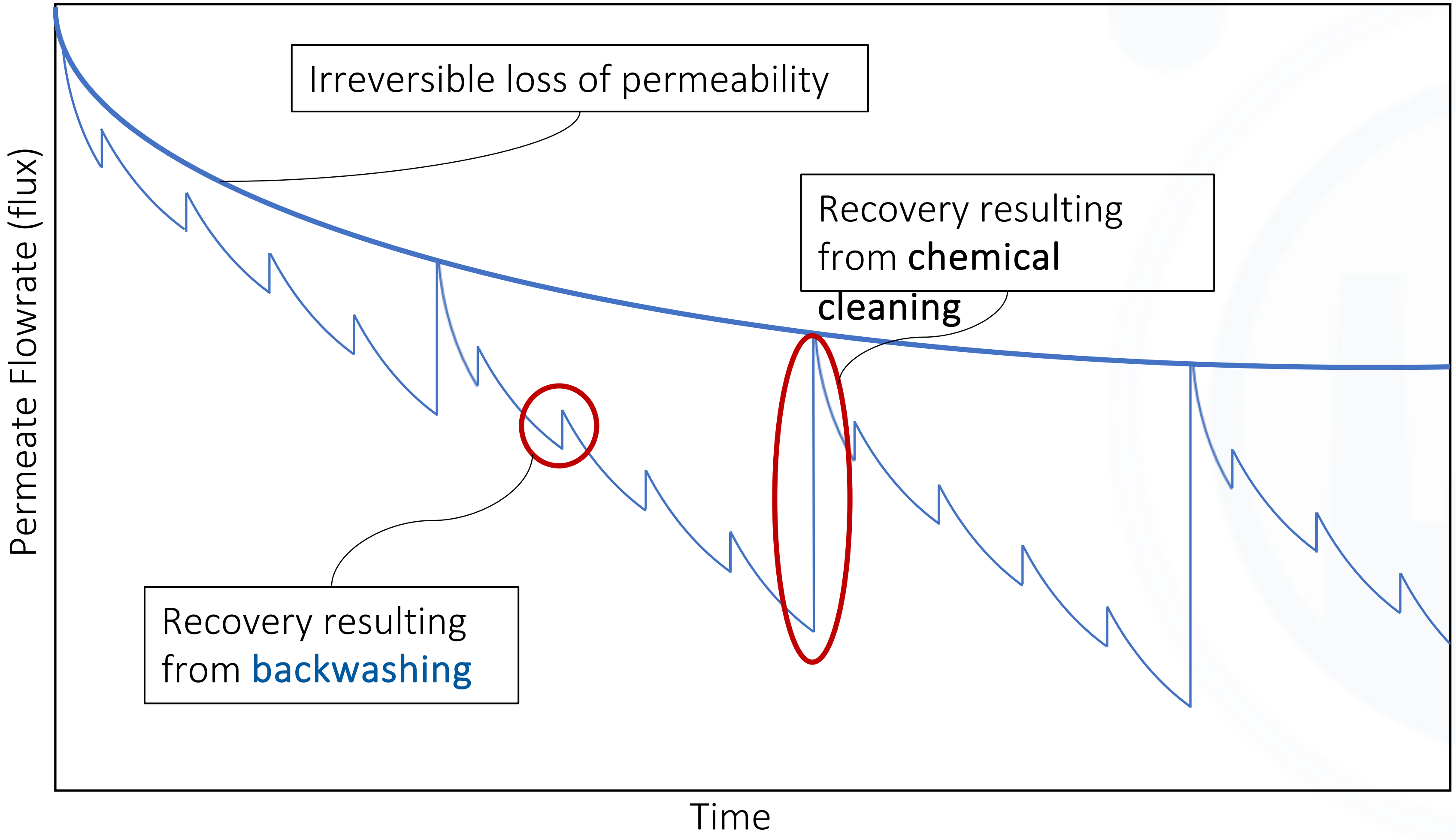


Backwashing II/II

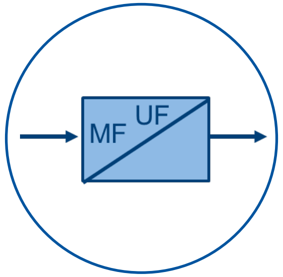
Module-scale Backwashing



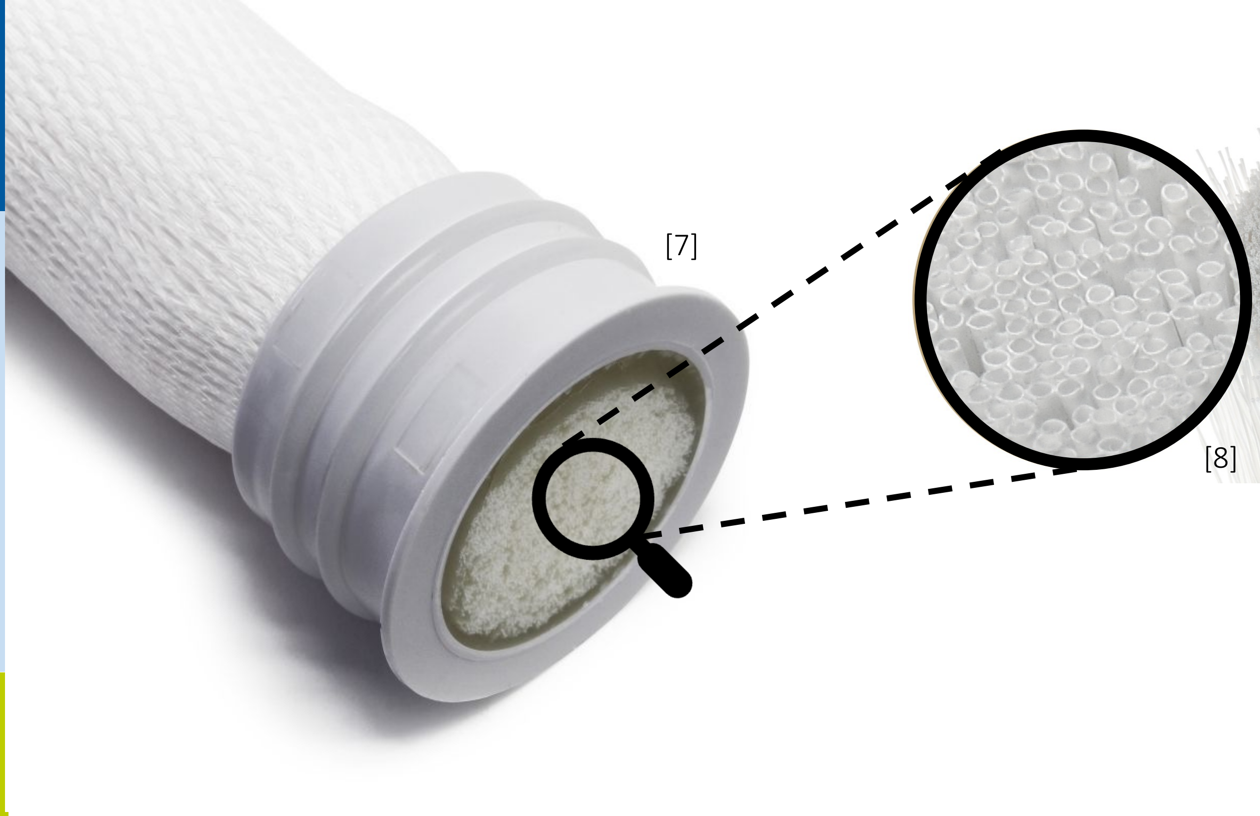
Membrane Cleaning



Micro- and Ultrafiltration



Micro- and Ultrafiltration



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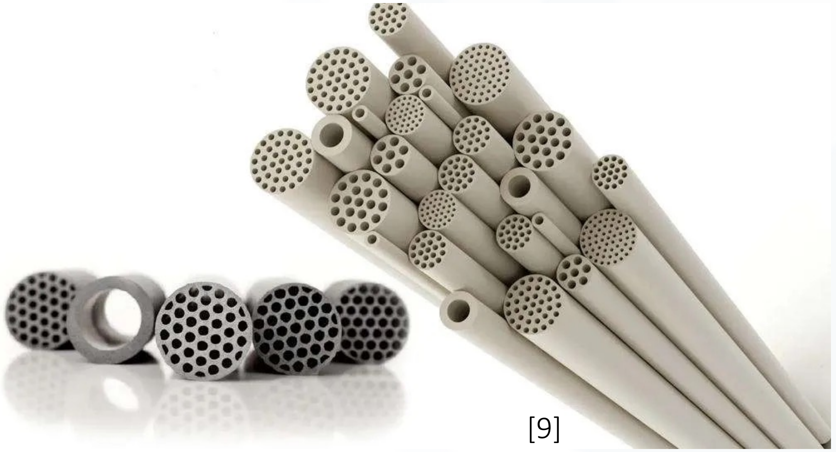

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Main Applications of Micro- and Ultrafiltration

Examples

- Leachate treatment
- Concentration of aqueous coating from spray booth water

Environmental engineering

Metalworking industry

- Concentration of oil/water emulsion
- Treatment of degreasing baths

- Concentration of gelatin and chicken proteins
- Clarifying filtration of wine

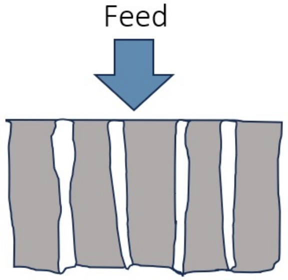
Pharmaceutical industry

Food industry

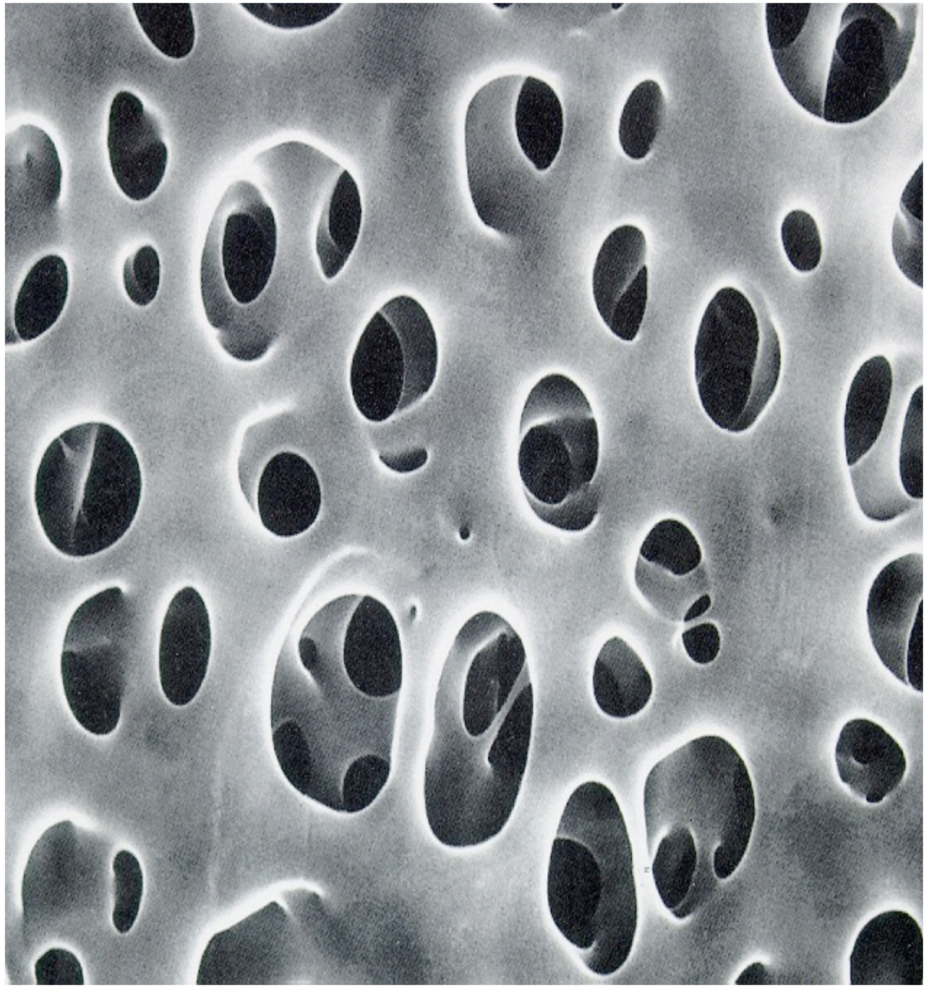
- Purification of antibiotics
- Concentration, separation and purification of vaccines and enzymes

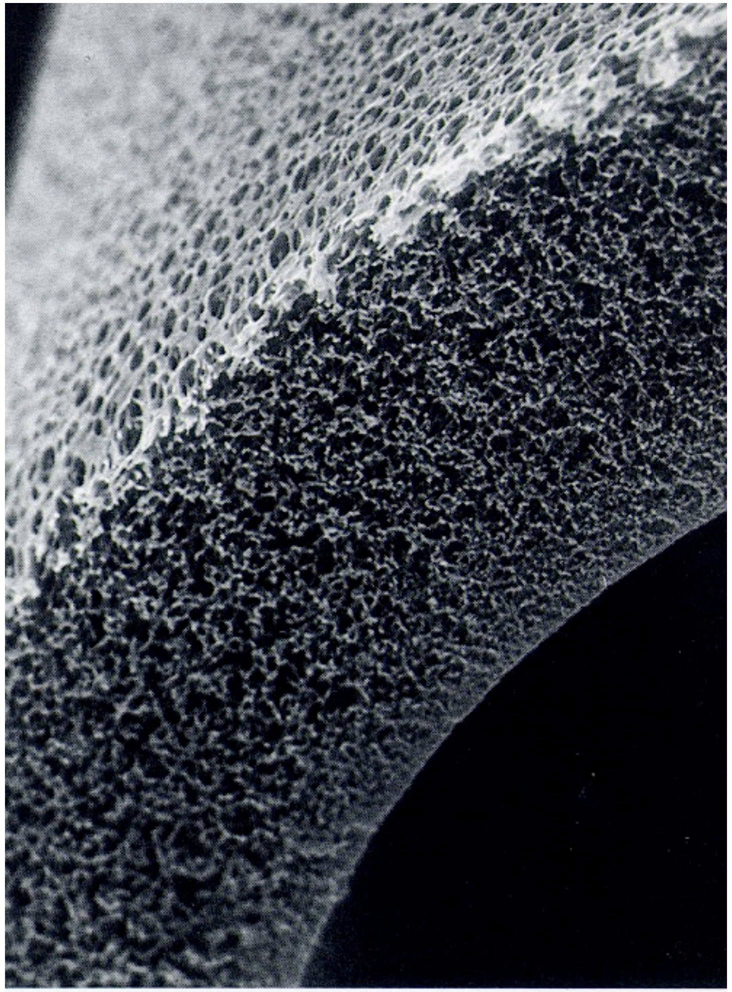
Membranes for Microfiltration

SEM Images



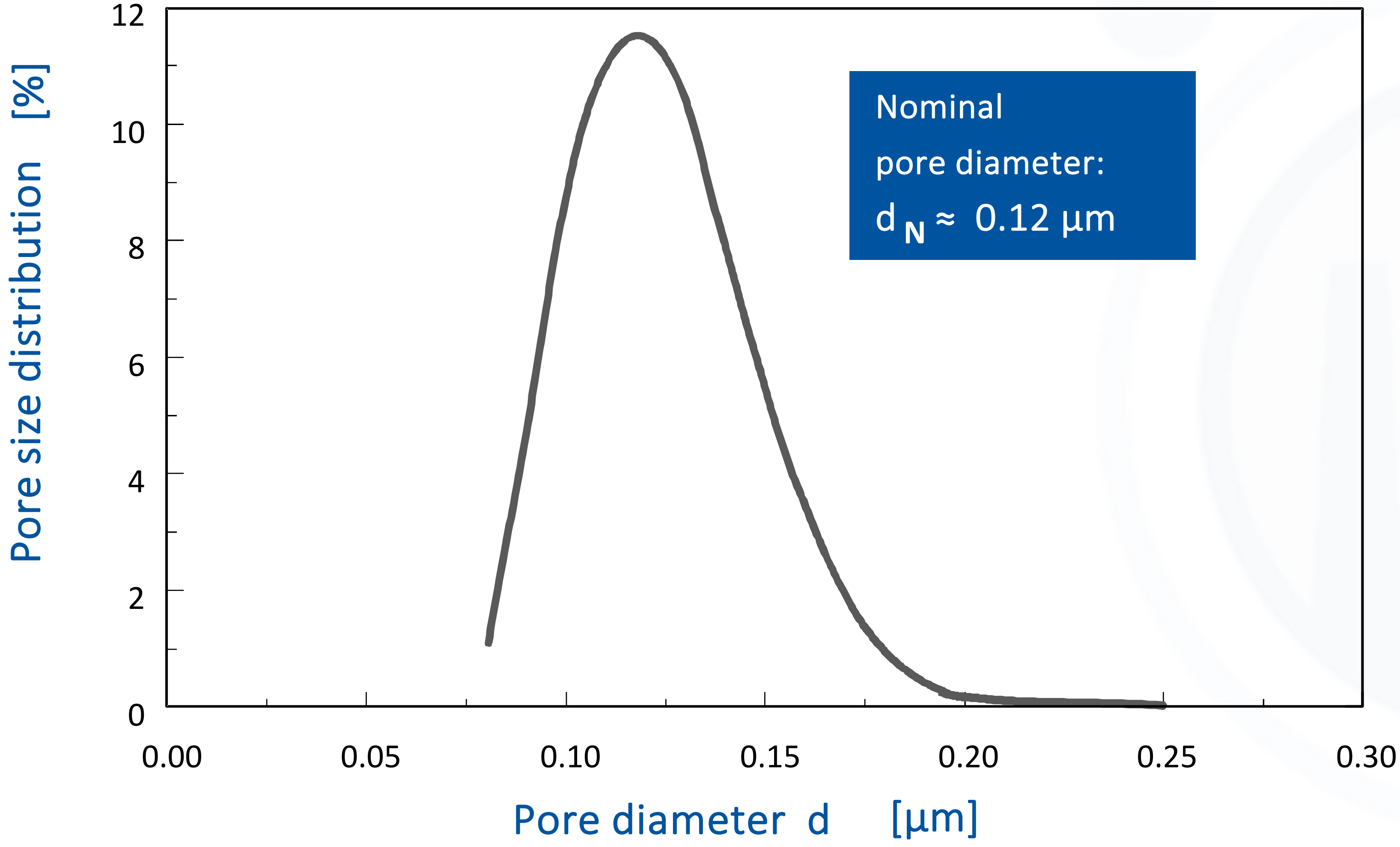
Symmetric polysulfone membranes: pore structure





Membranes for Microfiltration

Exemplary pore size distribution of microfiltration membranes

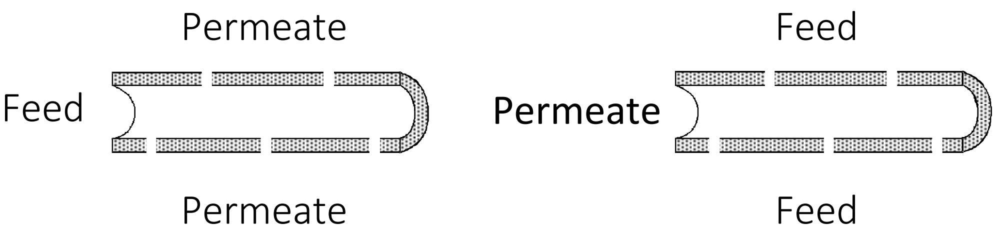


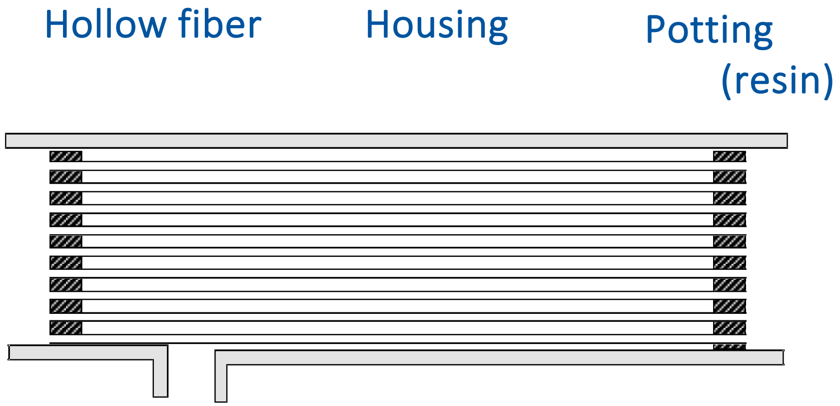
Module Design for Micro- and Ultrafiltration

Capillary/ Hollow Fiber Module

- Hollow fiber module

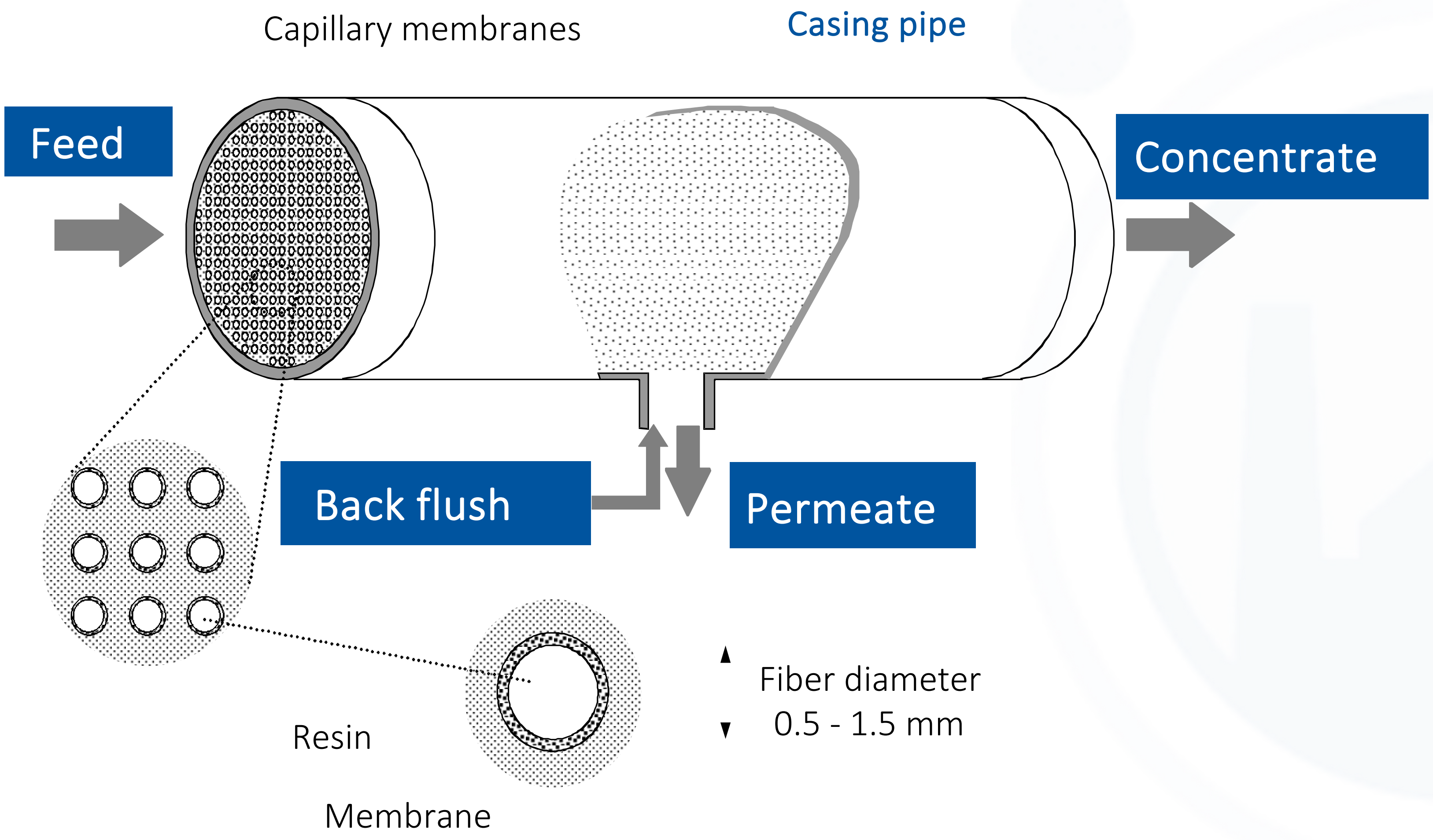
Feed: lumen side	Feed: shell side





Modules for Micro- and Ultrafiltration

Scheme of a Capillary Module



Plants for Micro- and Ultrafiltration

Example from Palm Islands Dubai (7700 m^3/h)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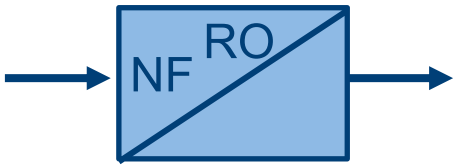
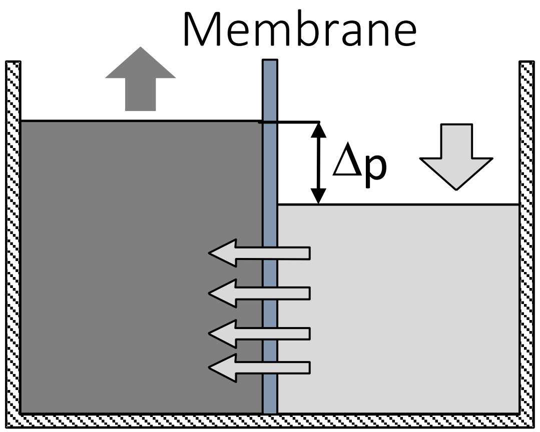
Many modules are assembled to so called racks or stages.

Nanofiltration (NF)
and Reverse Osmosis (RO)

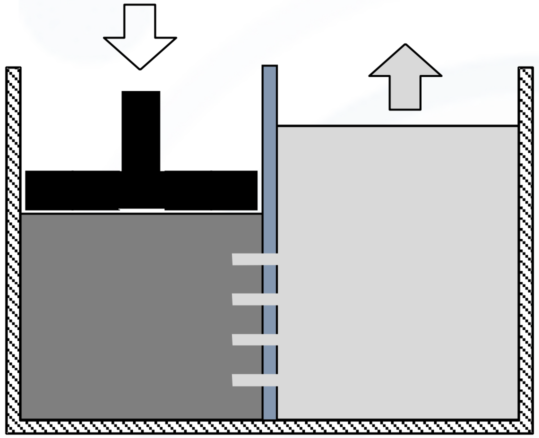


Principles of Reverse Osmosis



high concentration

low concentration

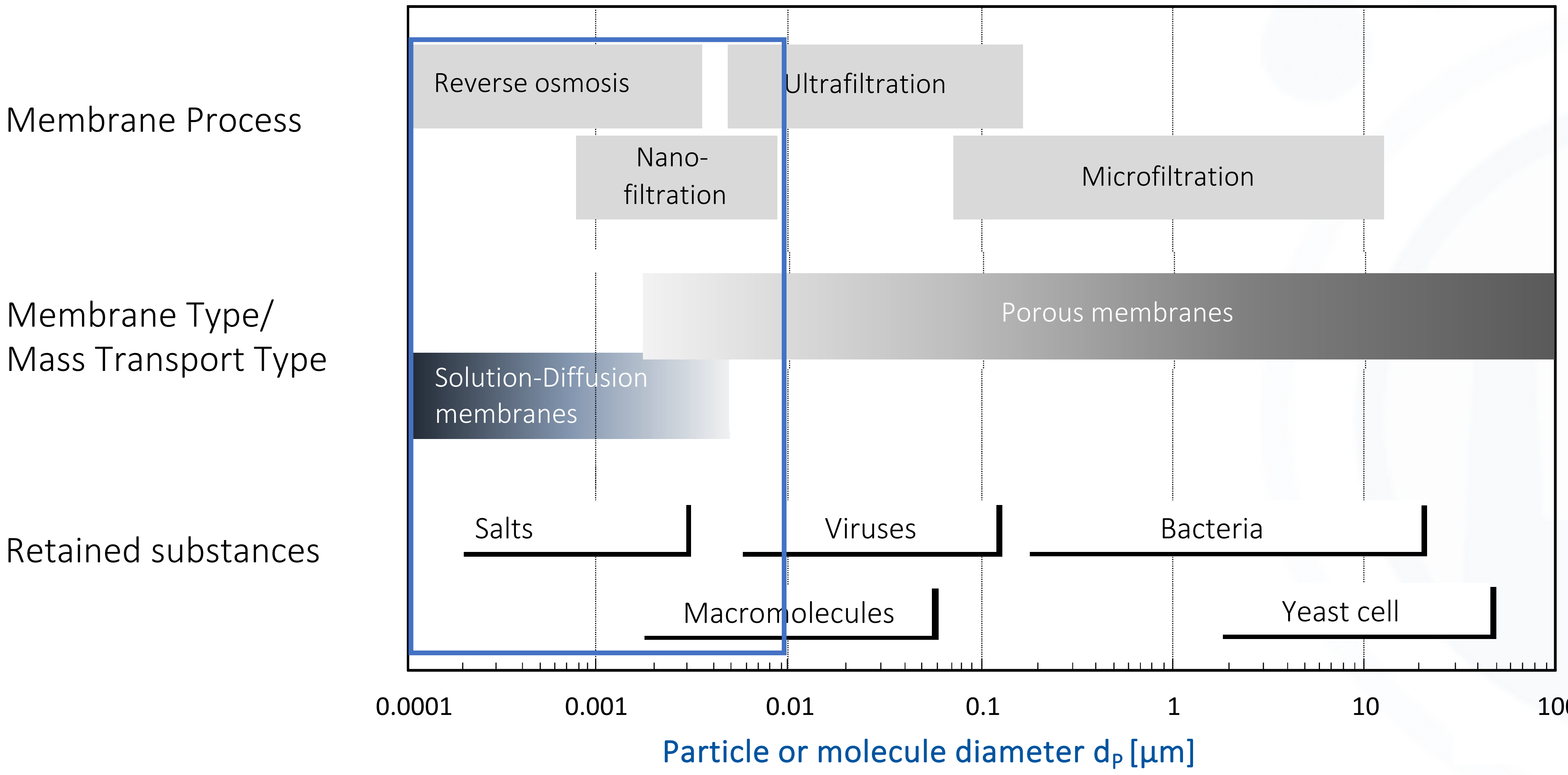


Osmosis : $\Delta p < \Delta \pi$

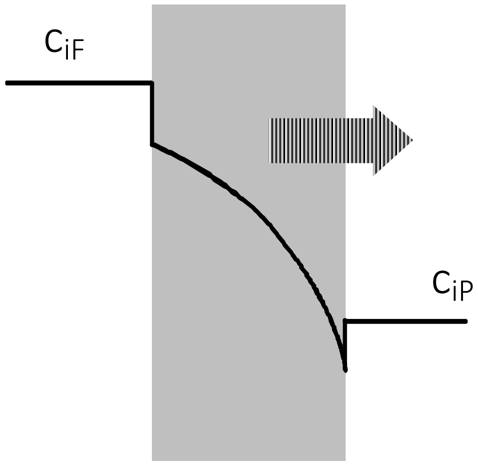
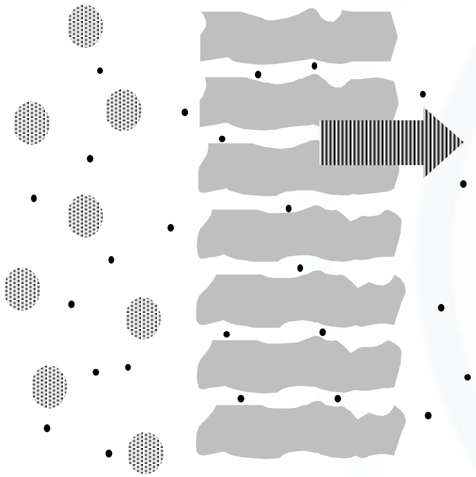
Reverse osmosis: $\Delta p > \Delta \pi$

$\Delta \pi$ Osmotic pressure
Δp Hydrostatic pressure

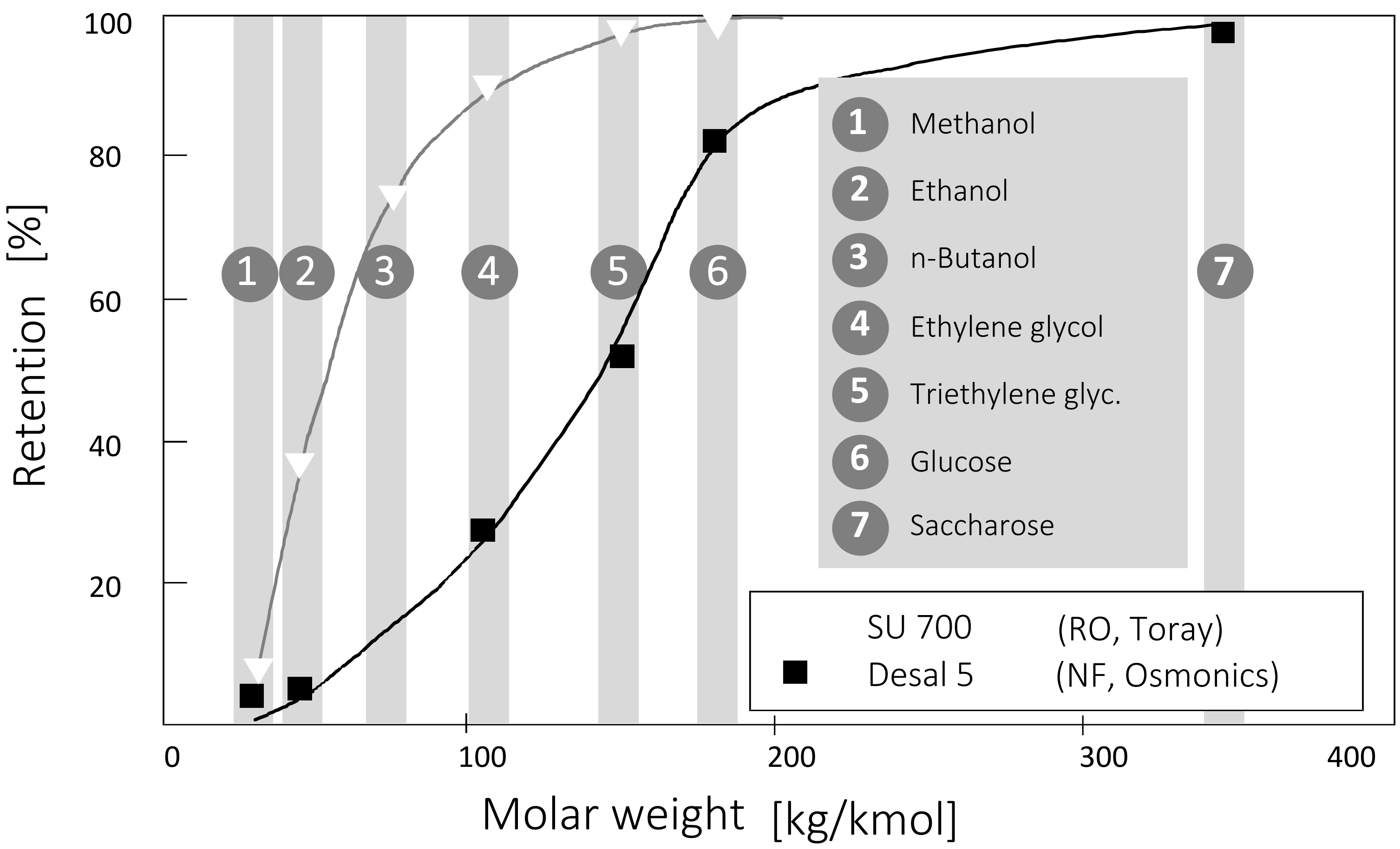
Modeling of the Mass Transport in Membranes



Models for the Mass Transport Through Membranes

Solution-diffusion membrane	Porous membrane
	
• Reverse osmosis • Electrodialysis • Pervaporation	• Microfiltration • Ultrafiltration • Nanofiltration

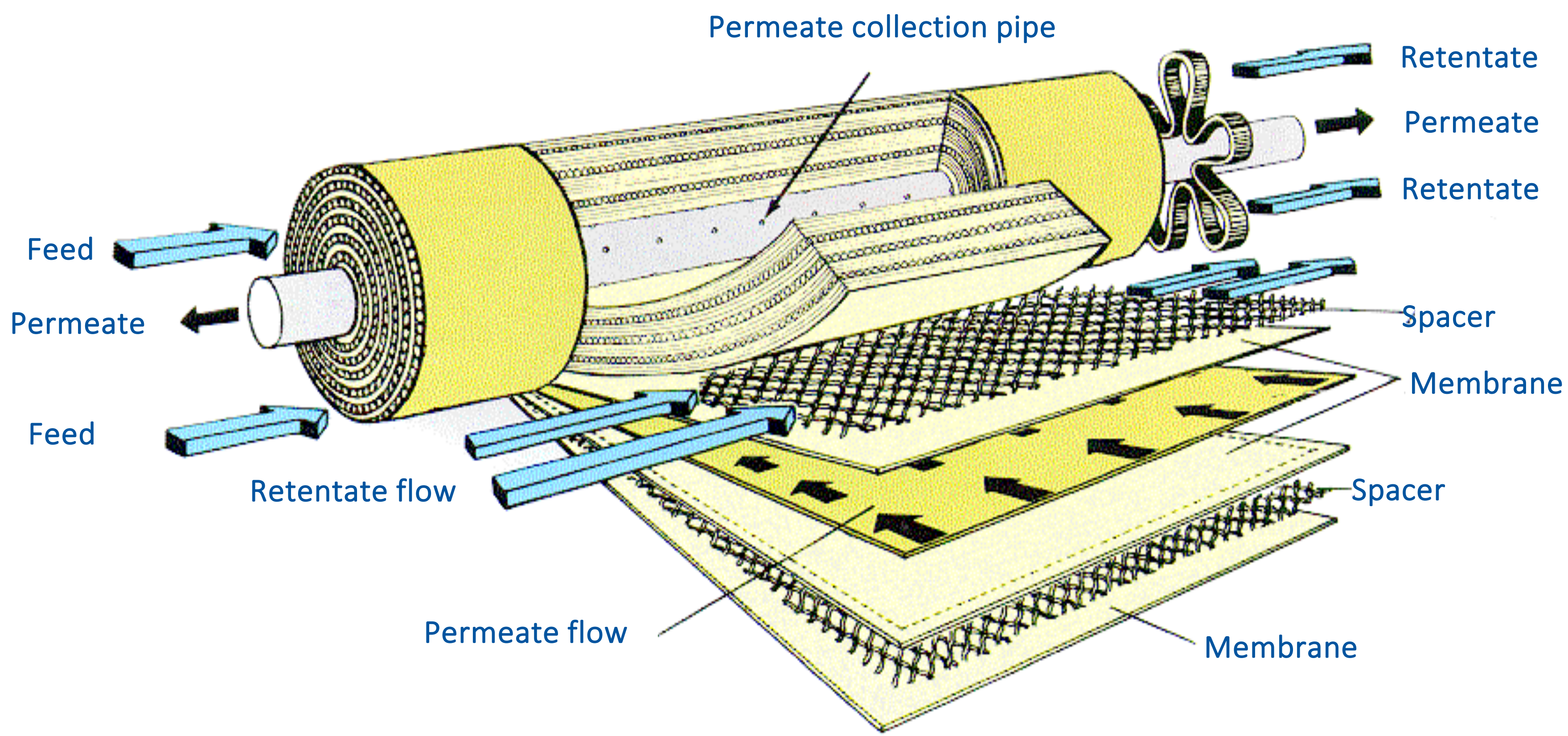
Comparison of Retention of RO / NF Membranes



- RO:
  - Good retention of ions and organic molecules
- NF:
  - Weak retention of monovalent ions (e.g. Na+ , Cl-)
  - Good retention of multivalent ions (eg. SO42-) and low molecular weight organics > 200 kg/kmol

Membrane and Modules for RO/NF

Design of a Spiral Wound Membrane Module

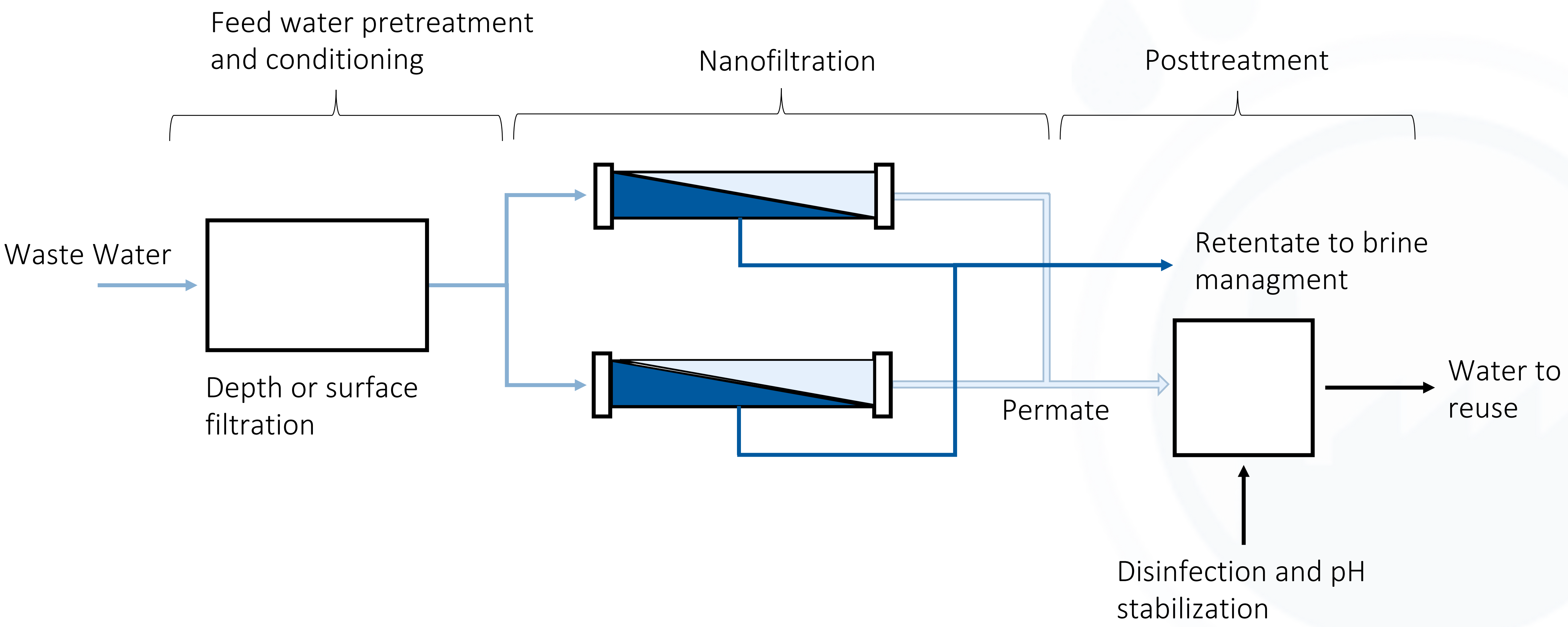


Height of feed channel fixed due to spacer: 0.5 - 1.0 mm

Membrane and Modules for RO/NF

- Plant with spiral wound membrane modules in Ashkelon

Exemplary Membrane Process Flow Chart



Factors Influencing the Performance of UF/MF Modules

Characteristics of membrane module

Characteristics of membrane
- Morphology and structure
- phys.-chem. properties
- chem./mech./therm. stability

Module design
- Feed-side hydrodynamics
- Packing density/Dead zone
- Backwash ability

Performance of membrane modules

Membrane permeability
- Reversible cake layer
- Membrane fouling
- Membrane aging

Filtering membrane area
- Module blocking due to high particulate concentration
- Blocking/Accumulation of sludge

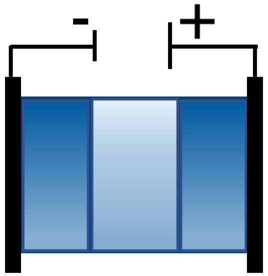
Operation and feed parameter

Chemical cleaning
- Cleaning agents
- Cleaning frequency
- Cleaning parameter

Plant design
- Operation parameter
- Module rinsing
- Chemically supported cleaning

Feed (pretreatment)
- Feed components and concentrations
- Dissolved substances, colloids
- pH-Value, conductivity
- Pretreatment, Flocculation

Electrochemically Driven Membrane Processes: Electrodialysis



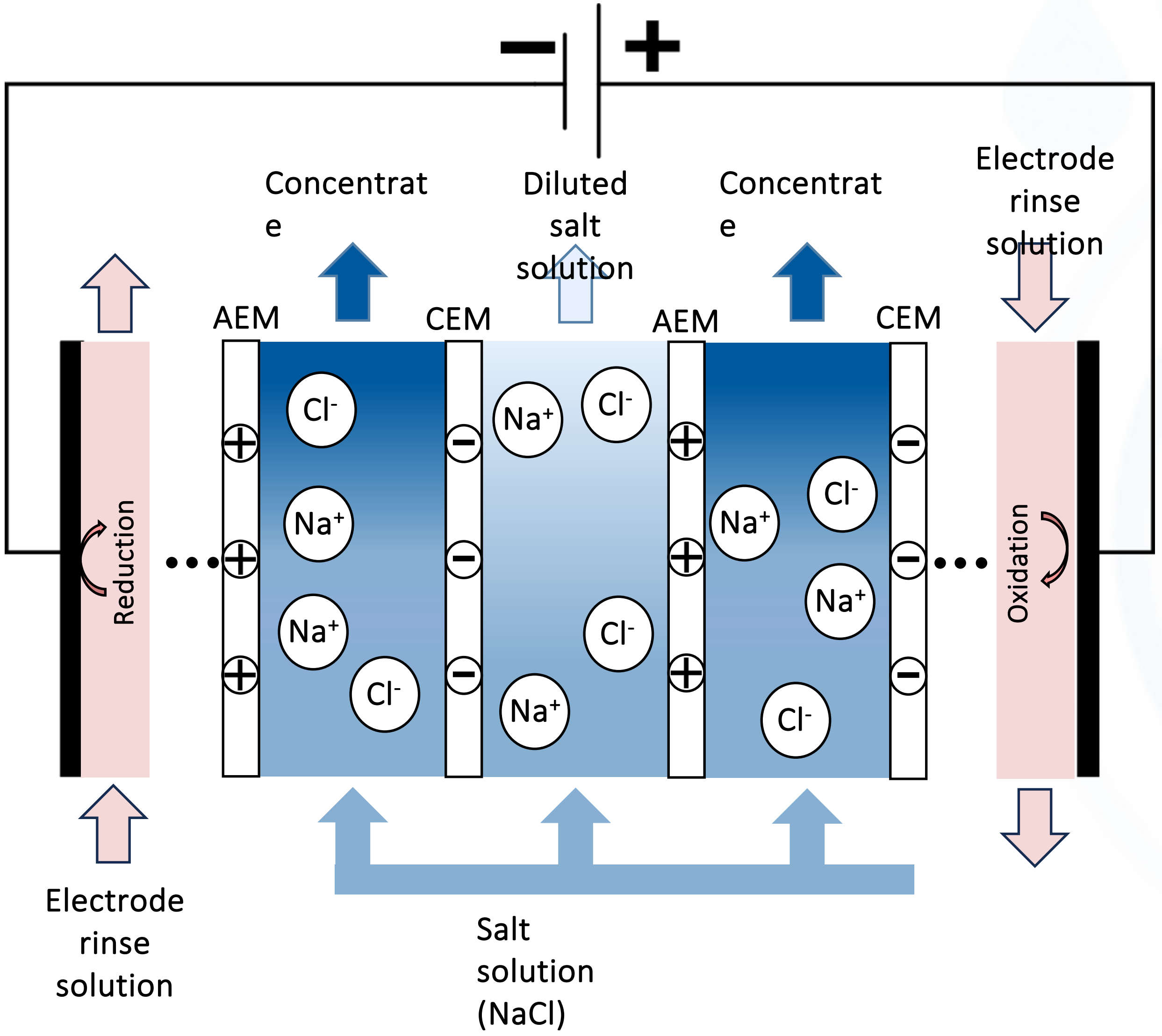
Electrodialysis Fundamentals

- Process principle:
  - Setup: Ion exchange membranes (positively and negatively charged) are positioned between two electrodes in alternating order
  - The channels between membranes is flooded with the solution (containing ions) that is to be treated
  - Voltage applied → electrical field between electrodes makes ions migrate:
    - Cations (+ charge) migrate towards cathode (- charge) through cation exchange membranes (- charge)
    - Anions (- charge) migrate towards anode (+ charge) through anion exchange membranes (+ charge)

    →2 product streams: concentrate and diluate
- Applications:
  - Concentration or removal of salts in aqueous solutions
  - Separation of charged substances from neutral substances

Electrodialysis

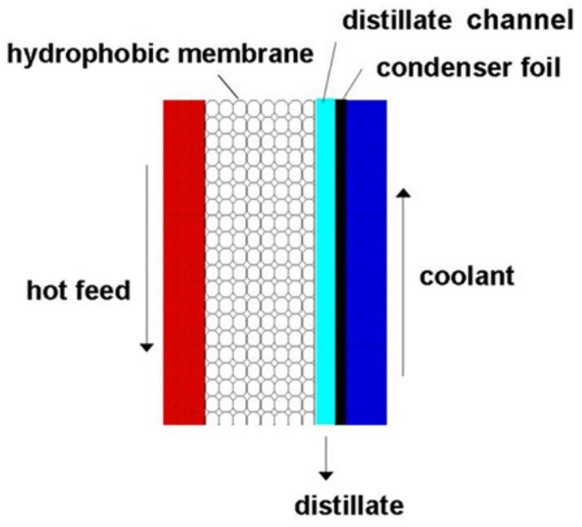
Exemplary Process with NaCl Solution

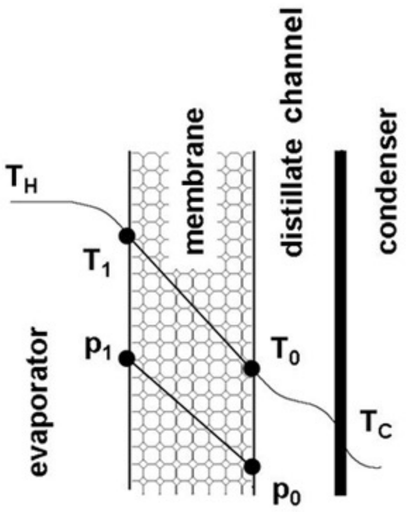


Temperature Driven Membrane Processes

Membrane Distillation

- Membrane Distillation (MD) is a thermally-driven separation process, in which only vapour molecules transfer through a microporous hydrophobic membrane.
- The driving force in the MD process is the vapour pressure difference induced by the temperature difference across the hydrophobic membrane.
- Use of mild heat (60 to 850C) to desalt highly saline waters.
- A hydrophobic membrane (microporous PTFE) retains heated aqueous solution but allows steam to permeate and condense as distilled water.





Source: Alkhudhiri et al., 2011

Common Properties of Membrane Processes

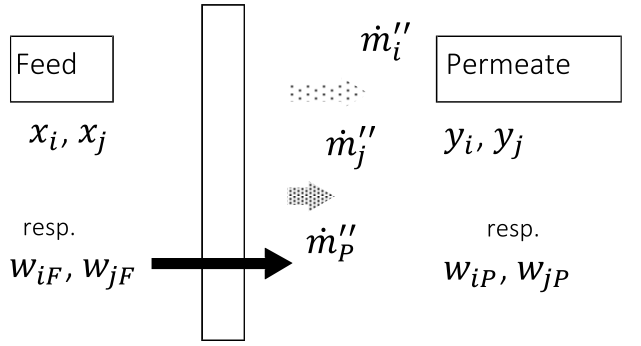
- Limited selectivity (effective for large classes of compounds)
- Modular construction
  - scalable and easily expandable
- Relatively compact compared to sedimentation
  → low footprint
- Only separation, no elimination of pollutants
  → Treatment/disposal of pollutant-rich concentrate is needed
- Moderate energy demand
  - Yet critical for cheap products, such as water
- Large contact surface
  → Membrane fouling and durability are critical aspects

Economic Considerations

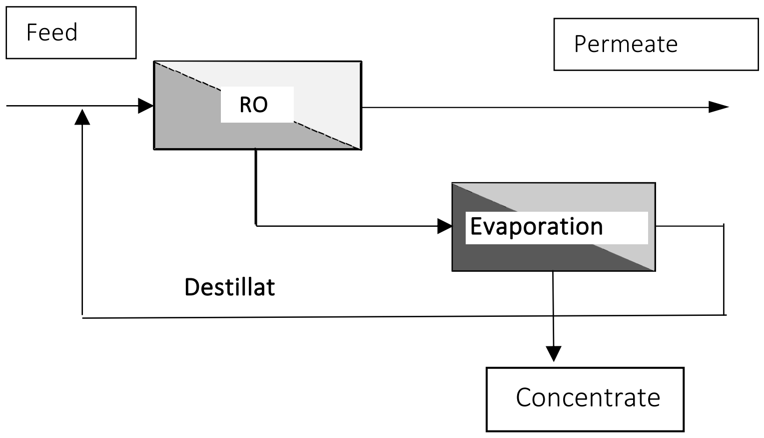
Technical and Economic Aspects

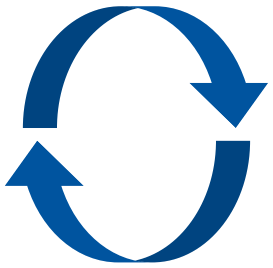
Different Levels of Process Development

Membrane element

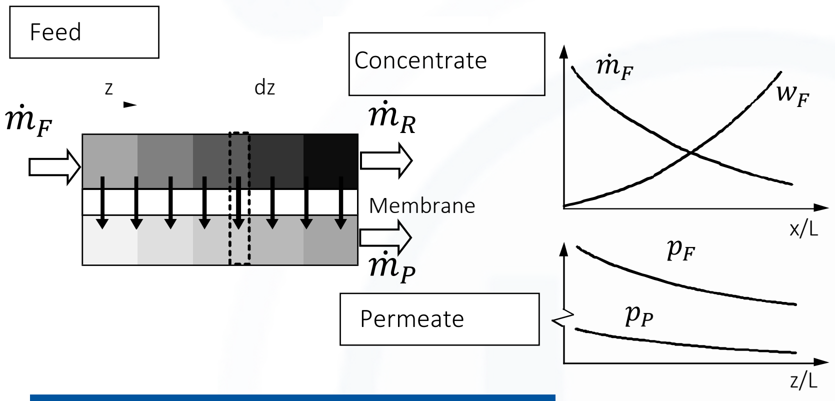


Full process

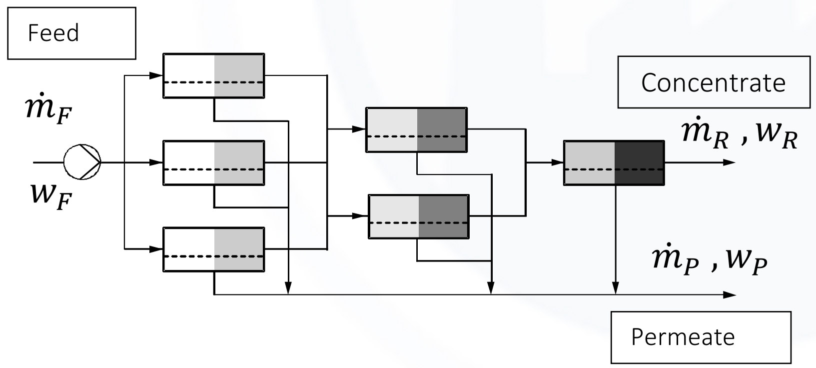




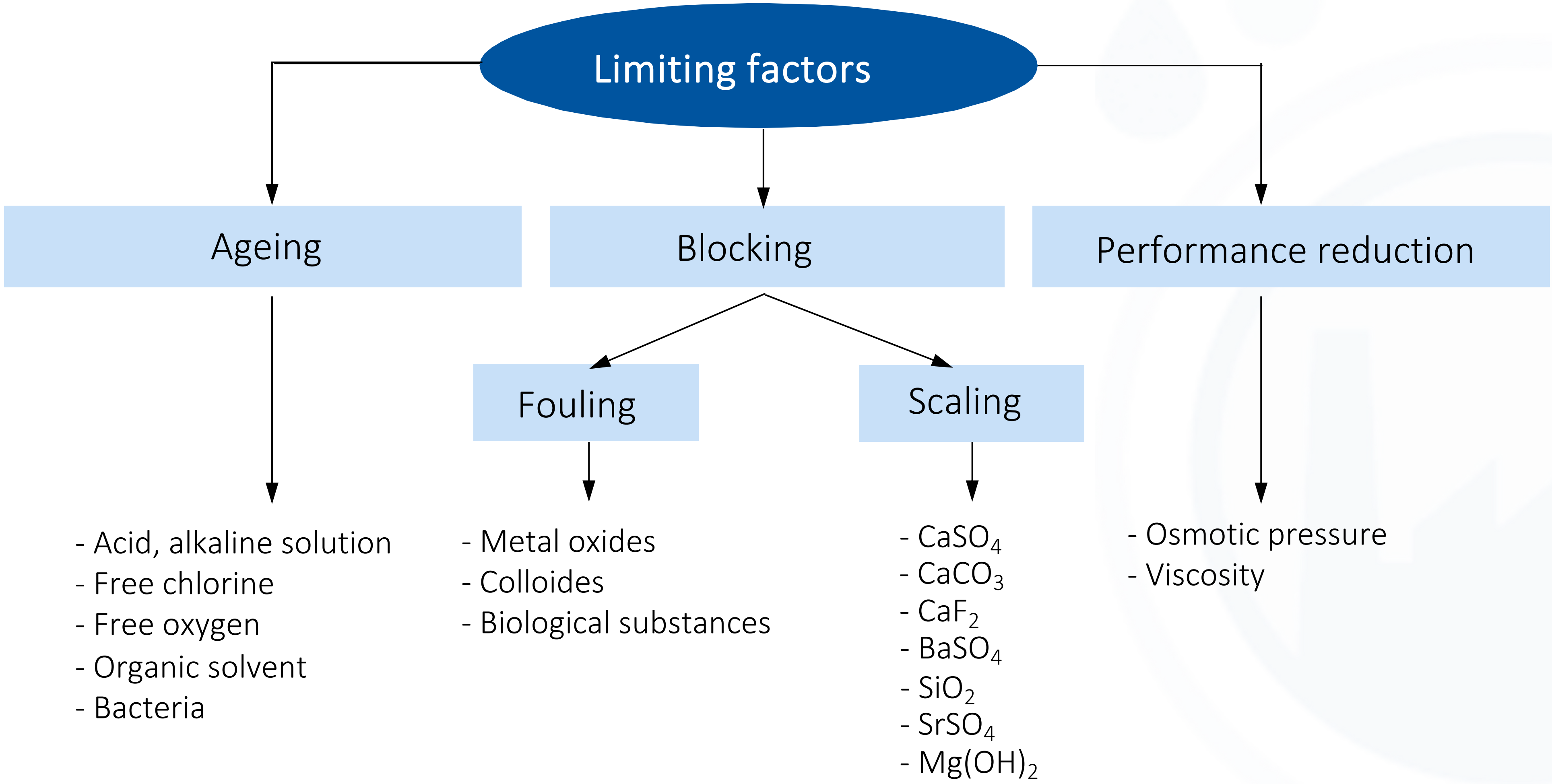
Module



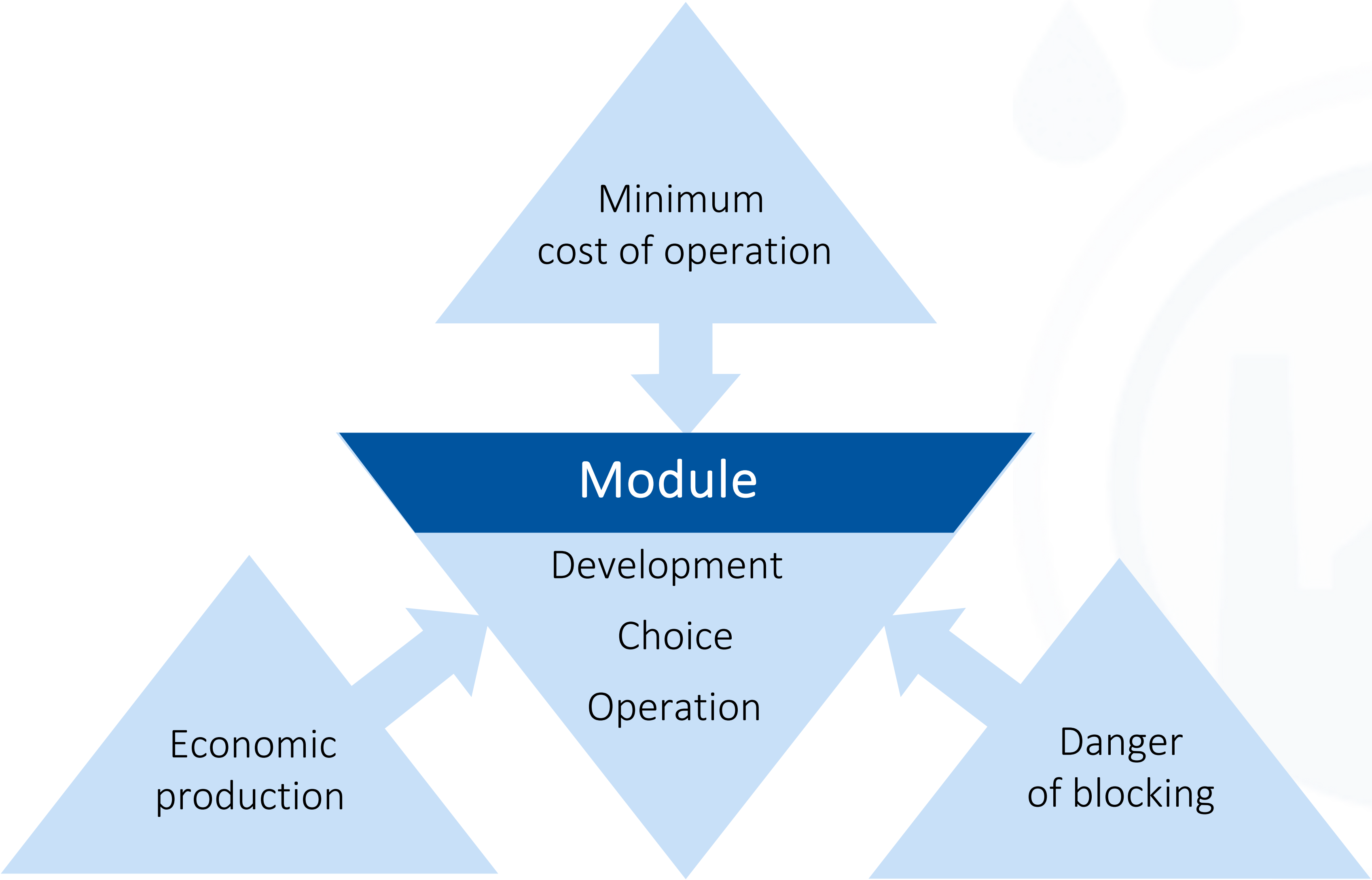
Module arrangement



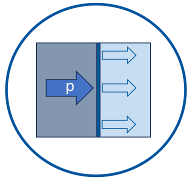
Limiting Factors of Membrane Processes



Viewpoints of Module Development, Choice and Operation



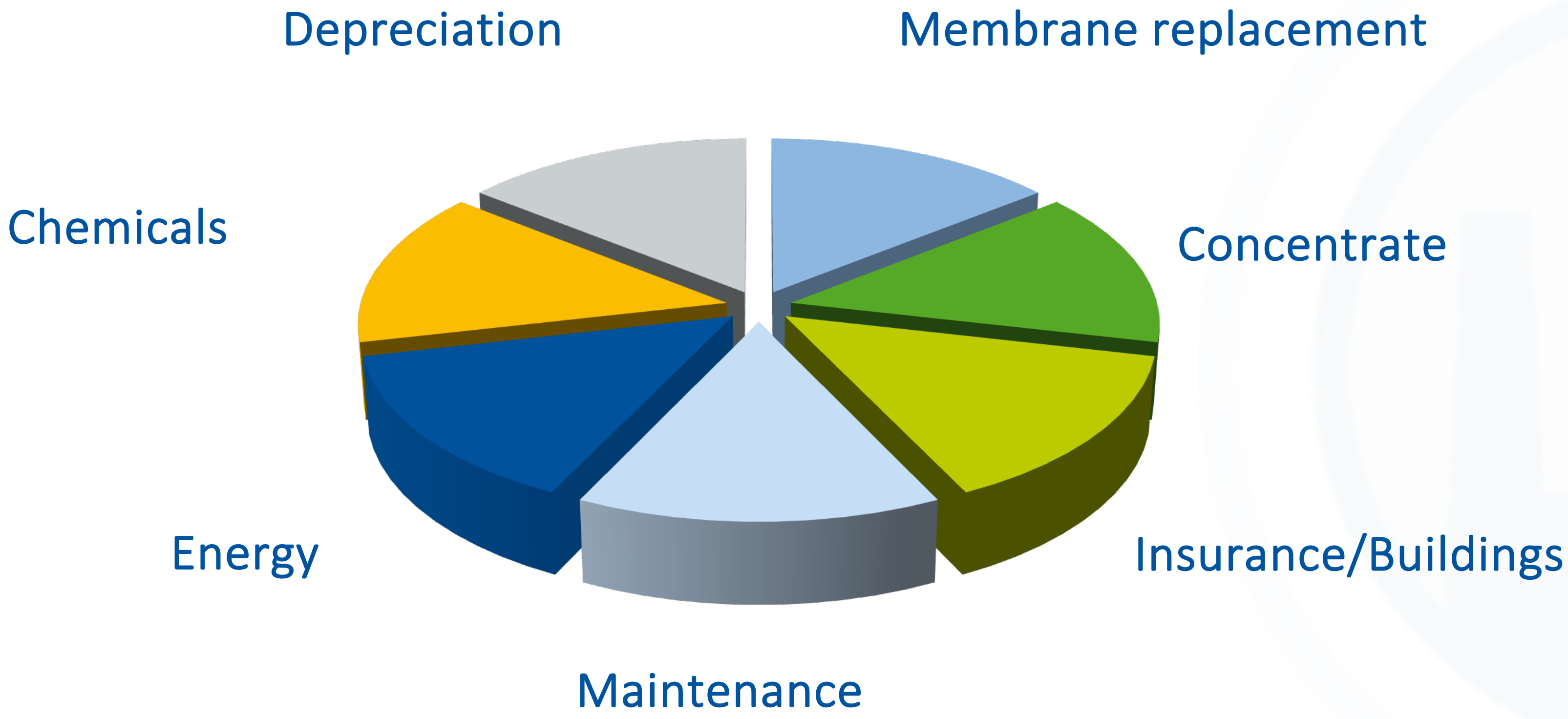
Demands on Module Construction



- Economic production:
  - High packing density
  - Low-cost materials that guarantee sufficient thermal, chemical and mechanical stability
- Minimum cost of operation:
  - Low pressure drop
  - Low energy demand
  - Good cleaning performance
  - Cost-efficient membrane change
- Low danger of blocking:
  - High load capacity for solids
  - Steady flow
  - Prevention of dead zones
  - Prevention of channelling

Technical and Economic Aspects

- Shares of **operation cost** of membrane plants



Literature Reference Membrane processes

The material on membrane processes presented is mainly based on the book „Membranverfahren“ and course material of Aachener Verfahrenstechnik which are kindly acknowledged.

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Advancing Sustainability of Process Industries through Digital and Circular Water Use Innovations

Thank you!

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Illustration sources

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Advancing Sustainability of Process Industries through Digital and Circular Water Use Innovations

Assessment of Cooling Tower Blowdown Reuse Feasibility at Chemical Industrial Site

Sarah Isabell Müller, Eduard de las Heras García, Lies Hamelink, David Moed, Lisa Wyseure, Ivaylo Hitsov, Gergana Chapanova, Thomas Diekow, Christian Kaiser, Laurence Palmowski, Thomas Wintgens

The AquaSPICE project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 958396.

DOW CHEMICAL COMPANY @BOEHLEN

Quick Facts

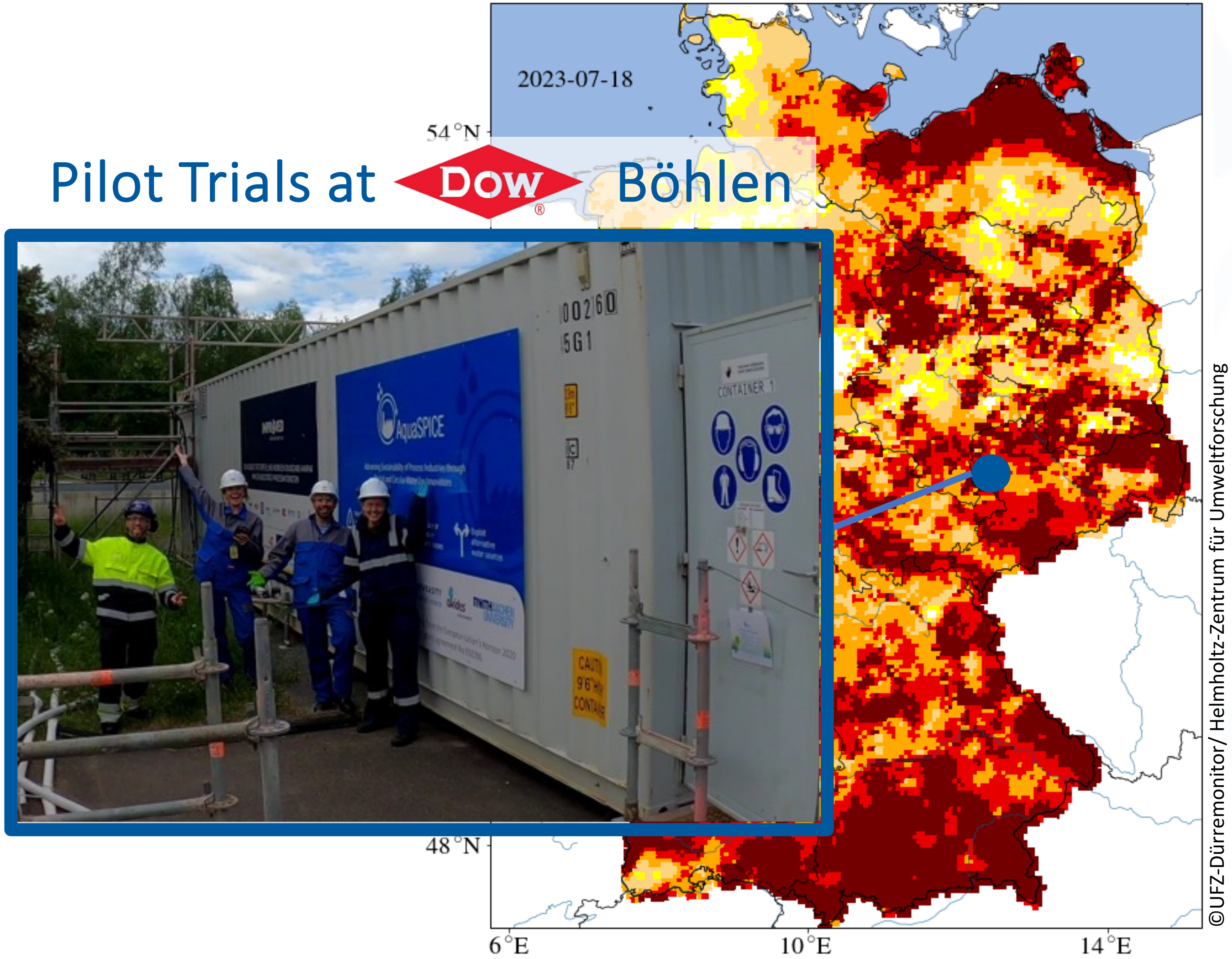
- Dow chemical company
  - Founded in 1897
  - Multinational corporation, headquarters in Midland, Michigan (USA)
  - Products:
    - Basic and performance plastics
    - Basic and performance chemicals
    - …
  - Target industries/applications:
    - Automotive
    - Construction
    - Pharmaceutical
    - Agriculture
    - …

@ Terneuzen, The Netherlands
@ Boehlen, Germany

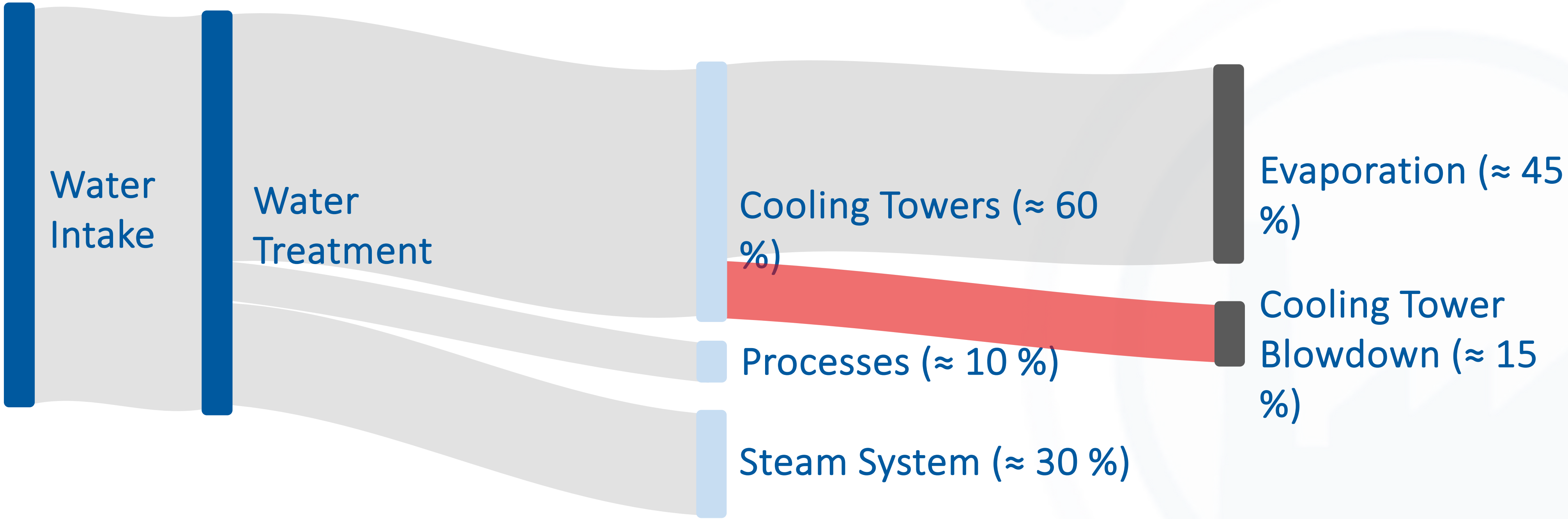
WATER STRESS IN GERMANY

Current Drought Map of July 2023

Pilot Trials at Dow Böhlen

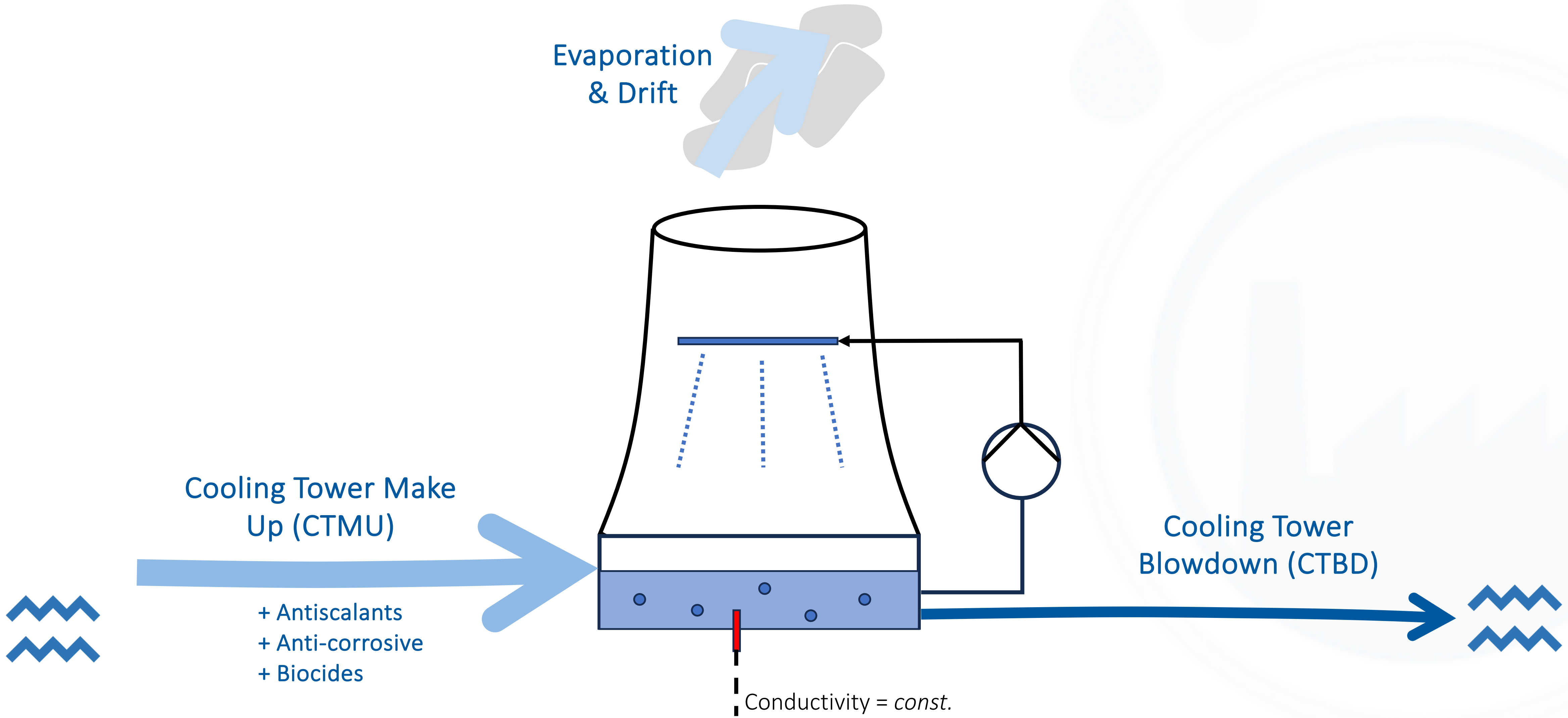


WATER USAGE IN THE CHEMICAL INDUSTRY

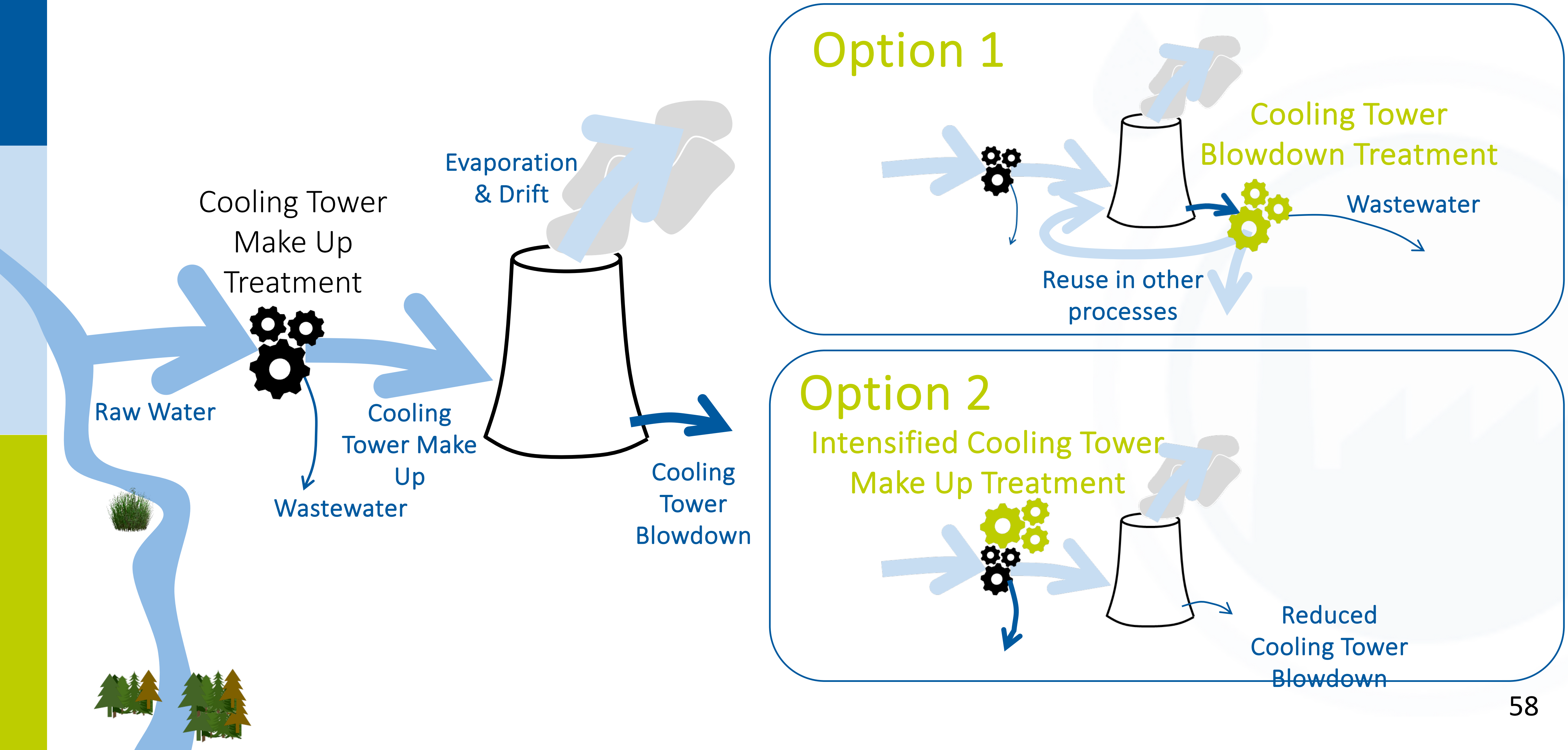


According to AquaSPICE D2.2 (2021)

COOLING TOWER BLOWDOWN



OPTIONS OF WATER USE MINIMIZATION



TRIALS: COOLING TOWER BLOWDOWN (CTBD)

Average CTBD

pH	7
Turbidity	7 NTU
EC	1950 µS/cm
TOC	22 mg/L

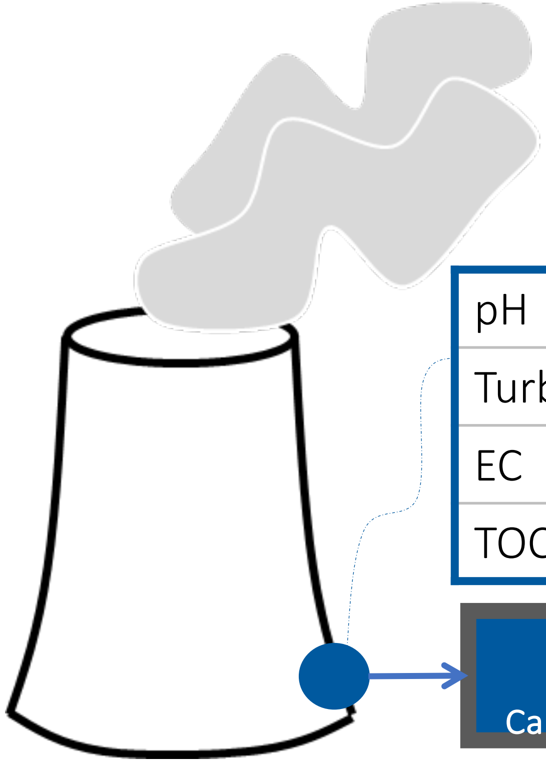
Targets:

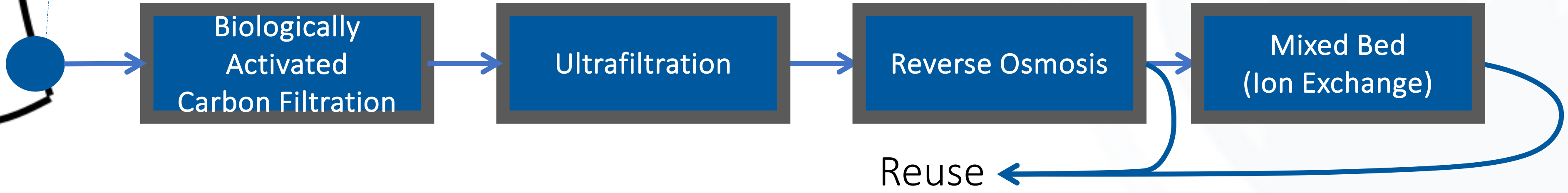
Water Quality

Water Efficiency

Cooling Tower Make Up Water:
TOC < 3 mg/L
EC < 500 µS/cm

Boiler Feed Water:
TOC < 0.2 mg/L
EC < 0.2 µS/cm





TRIALS: PRE-TREATMENT

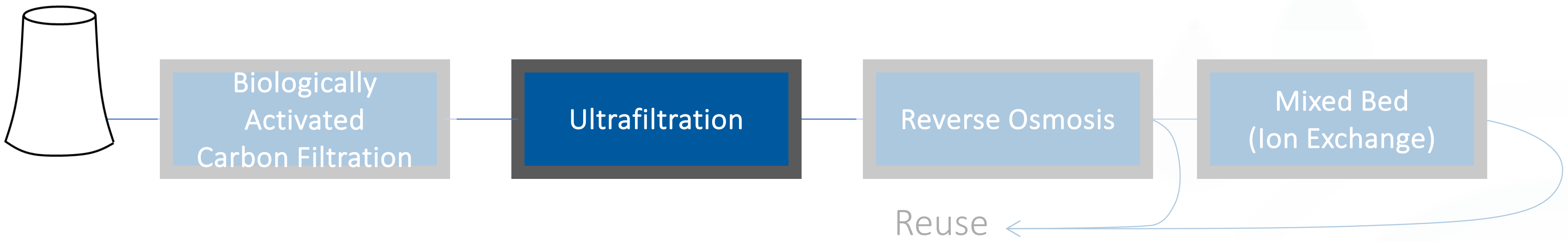
Biologically Activated Carbon Filtration → Ultrafiltration → Reverse Osmosis → Mixed Bed (Ion Exchange) → Reuse

- 3 cylindrical columns operated in series (50 L), top down
- Biologically activated GAC (NORIT GAC 830 W)
- Volume Flow: 500 L/h
- Filtration Velocity: 15 m/h
- EBCT: 5 min per column

	Average Quality	Rejection
TOC	16 mg/L	≈ 20 %
EC	2 mS/cm	-
Turbidity	3 NTU	≈ 55 %

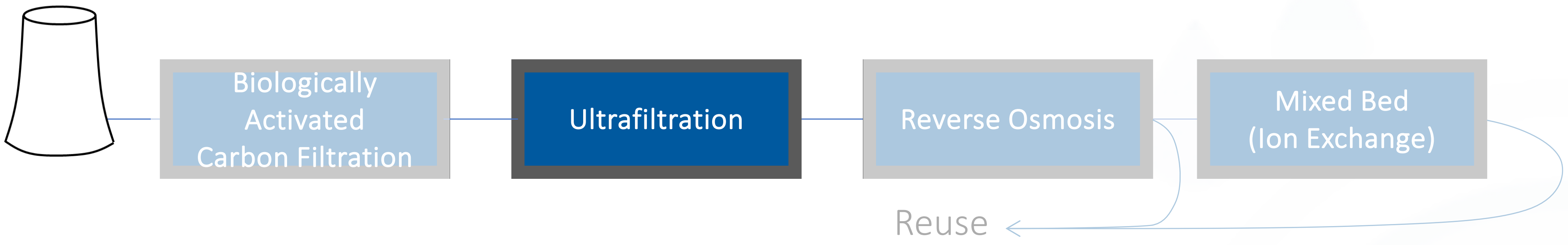
Specific Energy Consumption: ≈ 0.04 kWh/m³
Water Recovery: 99.9 %

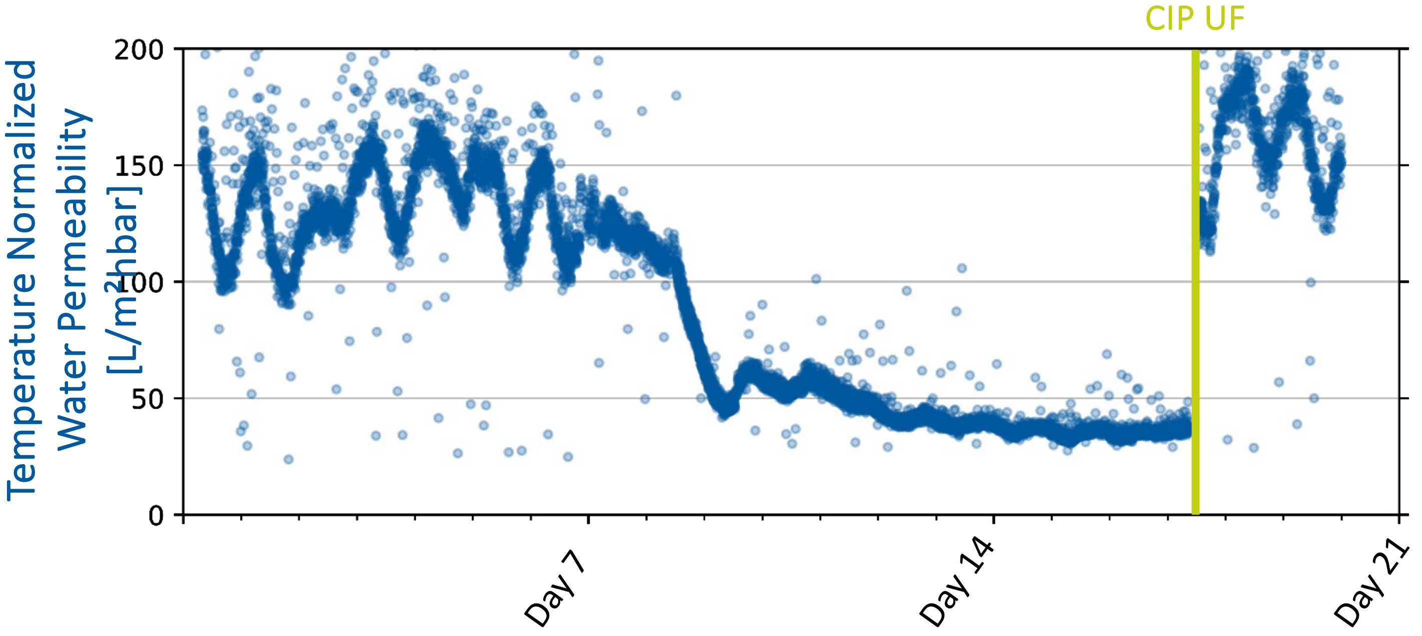
TRIALS: PRE-TREATMENT



- 2 modules of 4“ inge dizzer® P Multibore® 0.9 membranes operated in parallel (dead-end)
- Permeate Flux: **35 LMH**
- Filtration Time: **30 min**
- Backwash Time: **15 s**
- Forward Flush Time: **30 s**

TRIALS: PRE-TREATMENT

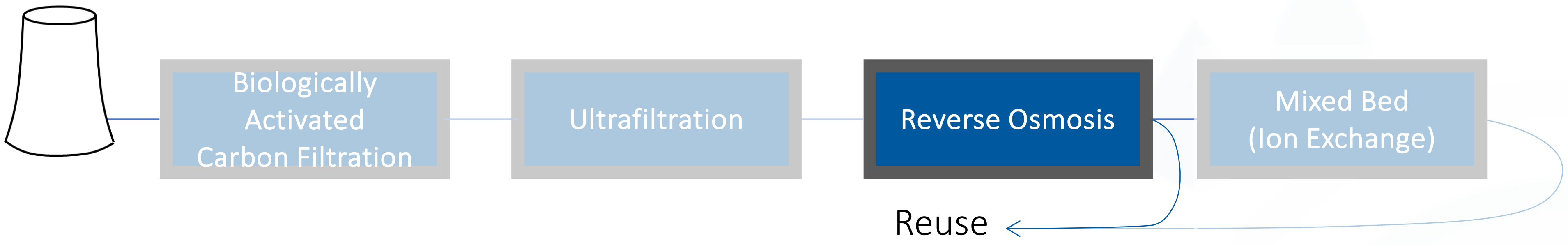




	Average Quality	Rejection
TOC	14 mg/L	≈ 10 %
EC	n.a.	-
Turbidity	0.5 NTU	≈ 80 %

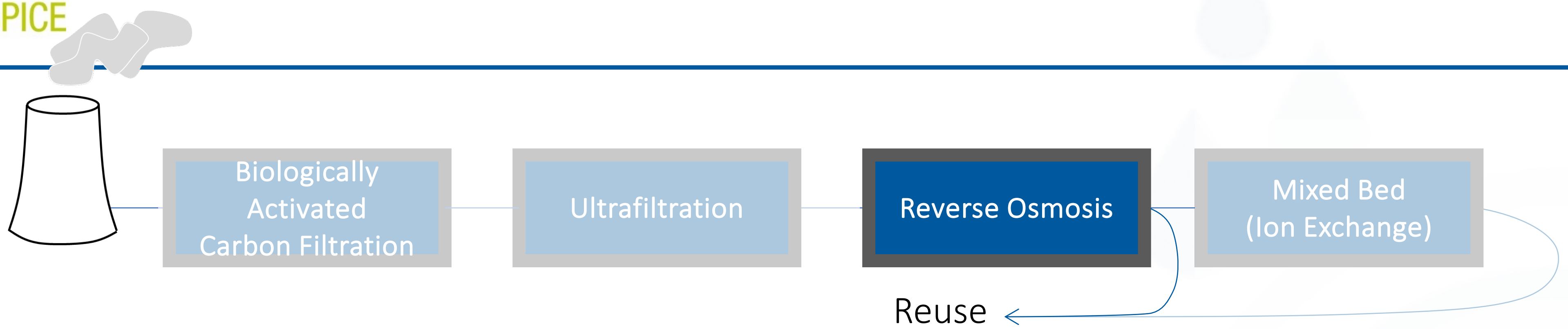
Specific Energy Consumption: ≈ 0.04 kWh/m^3
Water Recovery: 95.4 %

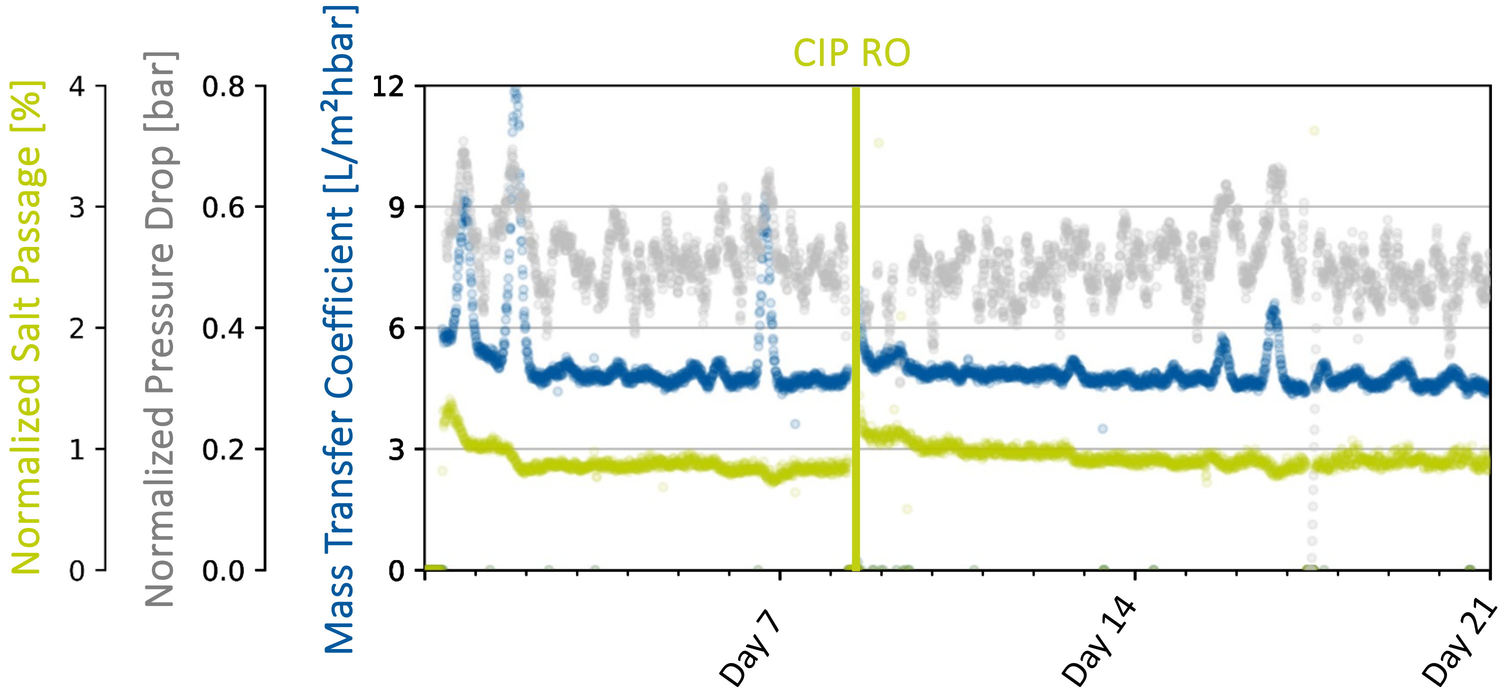
TRIALS: DESALINATION



- 4" module DuPont FilmTec™ LCLE-4040 (8.7 m²):
  - Partial Recirculation of Concentrate: higher system recovery
- Module Feed Flow: **~ 1100 L/h**
- Permeate Flux: **20 LMH**
- Feed adjustments:
  - 20 w-% HCl for pH (pH = 6.1)
  - Antiscalant (Genesys LF: 4 mg/L to Feed)

TRIALS: DESALINATION



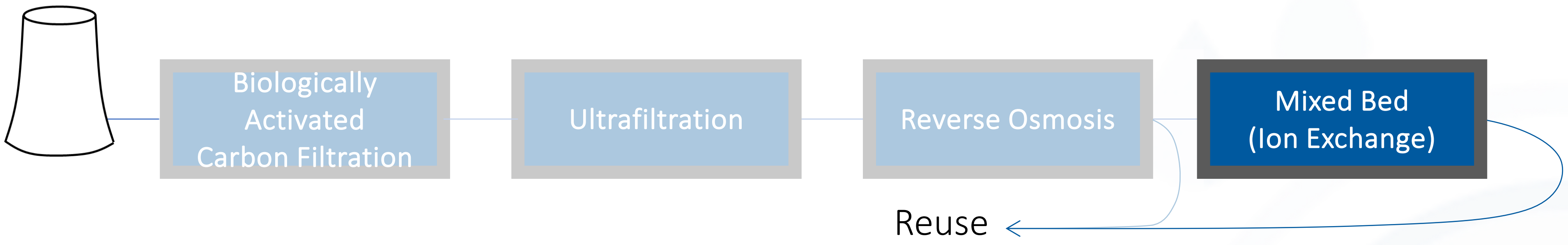


	Average Quality	Rejection
TOC	0.1 mg/L	≈ 99.3 %
EC	80 µS/cm	≈ 96 %
Turbidity	0.2 NTU	≈ 60 %

Specific Energy Consumption: ≈ 2 kWh/m³

Water Recovery: 75 %

TRIALS: DESALINATION



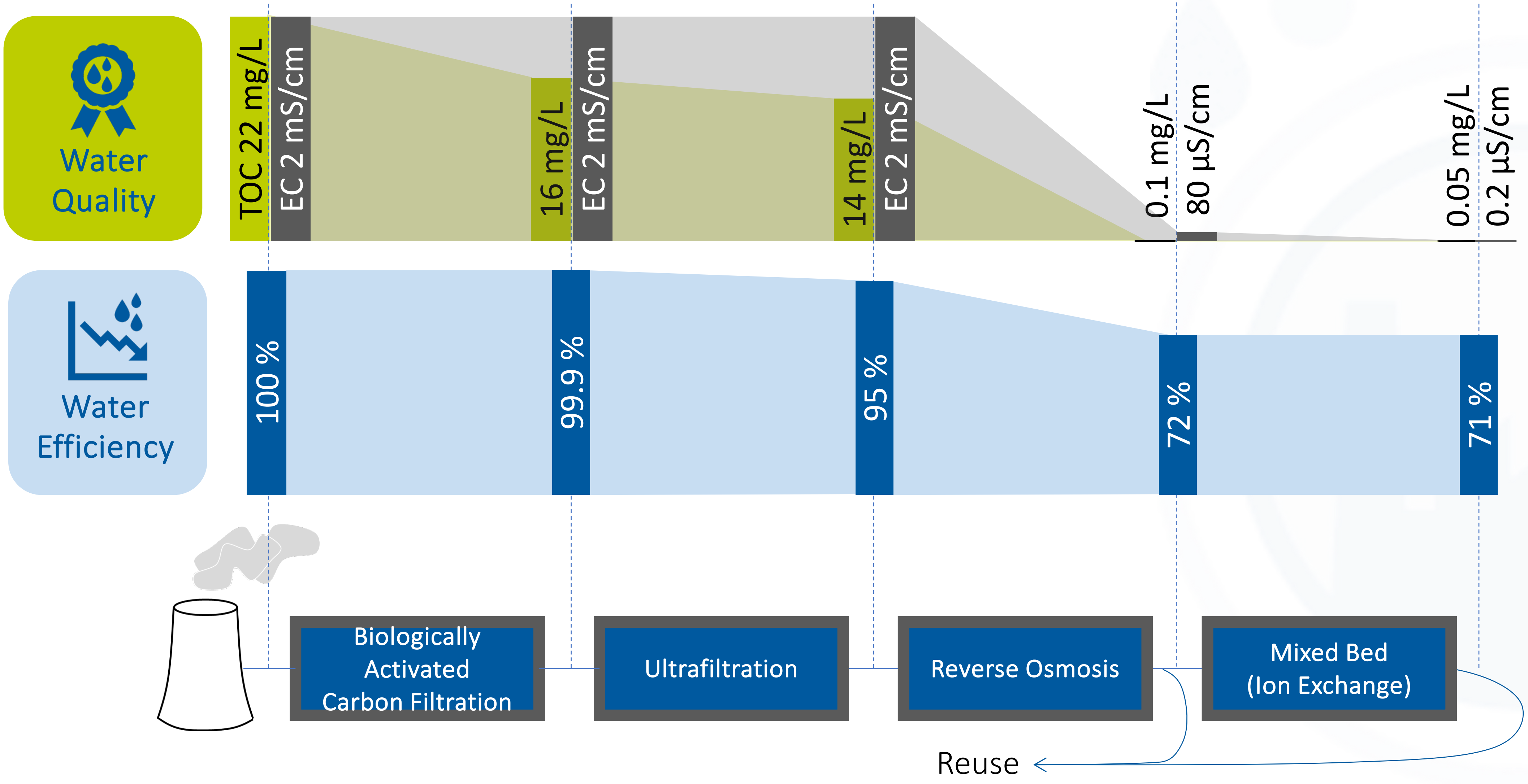
- Resin: Amberlite™ MB20
- 1 day operation (till exhaustion)
- Throughput: 16 BV/h
- Filtration velocity: 22 m/h

	Average Quality	Rejection
TOC	0.05 mg/L	≈ 50 %
EC	0.2 µS/cm	≈ 99 %
Turbidity	n.a.	-

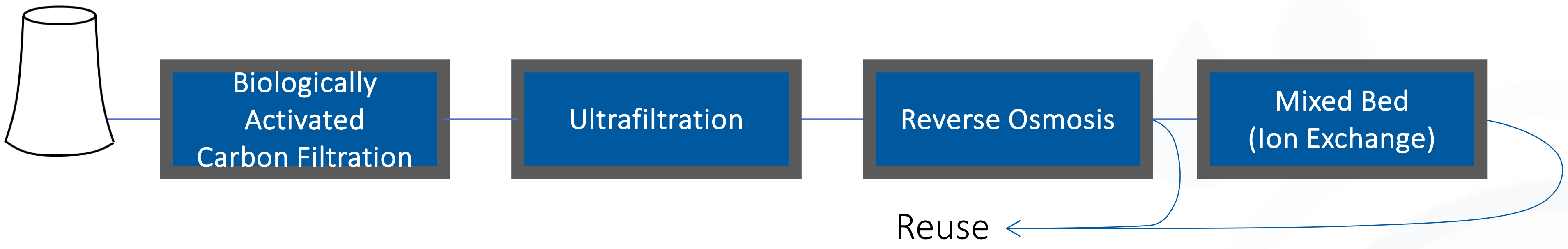
Specific Energy Consumption: ≈ 0.02 kWh/m³

Water Recovery: 99 %

SUMMARY: TARGETS



CONCLUSION



Water Efficiency

- Total treatment train operated with **71 % Water Recovery**
  - Cooling tower's water footprint reduction of > 15 %

Water Quality

- **Recommendation:** Reuse of treated water as boiler feed water (high quality even of RO permeate→ boiler feed water (deionate) is more valuable)
- Good **operational stability** of all technologies was shown
- **Barrier for implementation:** Effects of reduced and more concentrated water amount on receiving water bodies need to be studied

AquaSPICE

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Thank you!

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