Zero Liquid Discharge (ZLD)
Concept, Evolution and Technology Options

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Outline

- History and motivation
- Conventional ZLD
- Hybrid ZLD
- Emerging ZLD and near-ZLD alternatives
- Outlook

Some History

- ZLD sector was apparently born in 1970s in USA, driven by the regulator
  - ✓ Tight federal regulations on salt discharge to surface waters introduced, especially, due to salinity problems in the Colorado River
  - ✓ Regulations were mainly concerned with power plant discharges from cooling tower blowdowns and scrubbers (in the wake of previously introduced regulations on flu gas discharges)
  - ✓ Clean Water Act 1974, revised 1977, 1982
- First ZLDs installed were 500-2,000 GPM units based on evaporation/crystallization
- Regulations are expected to keep tightening: new EPA's guidelines (ELG) expected in 2017 and 2022 on various types of discharges (many have to be ZLD)

Sources: GWI Report, 2009; G. Maller/URS, 2013

Current Drivers and Limitations

- Presently, the major driver for using ZLD are
  - ✓ Environmental regulation on discharge of specific solutes (salt, toxic elements, nitrate-nitrite etc);
  - ✓ Water scarcity/water stress growing world-wide along with still negligible rate of waste water recycling;
  - ✓ Economics: recycled water becomes more affordable as the water supply from conventional sources becomes more expensive;
  - ✓ Growing social responsibility and education towards awareness of environmental issues
  - ✓ While ZLD cost is high in most cases, it might be a more economic solution when waste needs to be transported in large volumes over long distances
- Still ZLD has drawbacks, probably, the most significant are
  - ✓ Very high cost (both CAPEX and OPEX)
  - ✓ Custom-design on case-to-case basis
  - ✓ Difficulties to deal with complex streams (e.g., petrochemical)

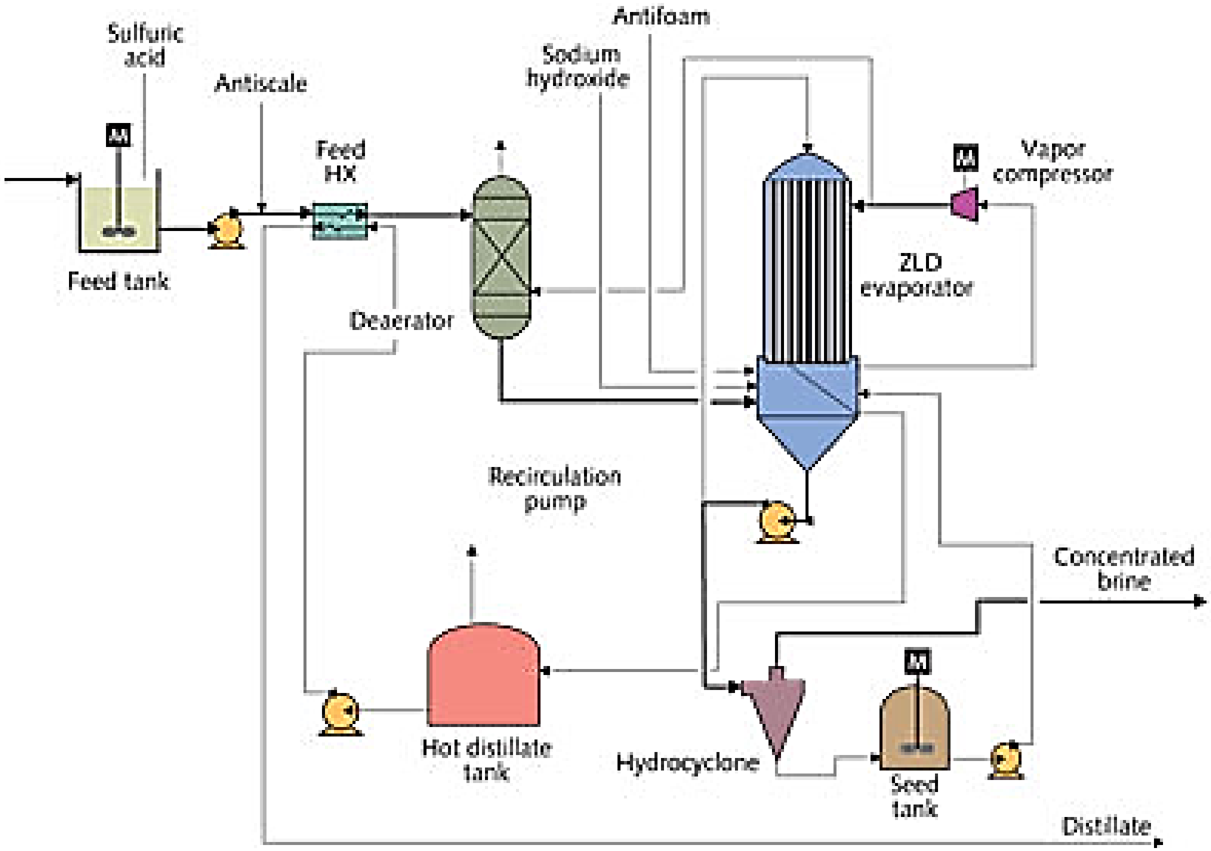
Current and Potential Markets for ZLD

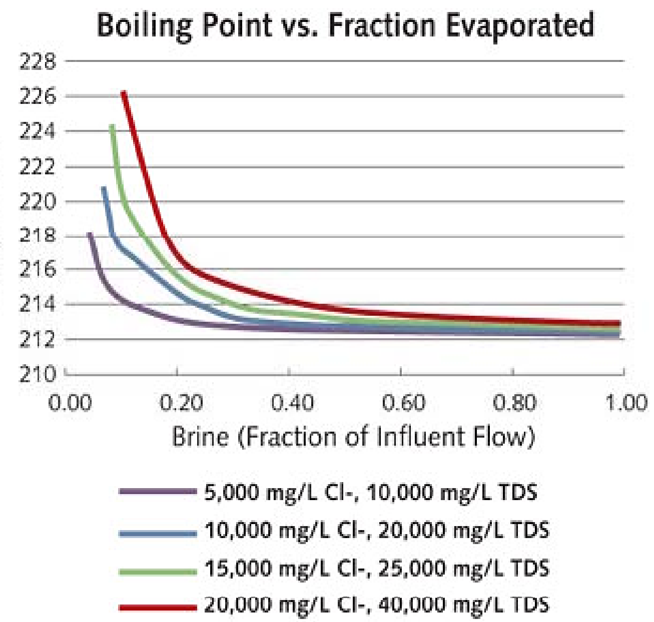
- Treatment and recycling of industrial waste effluents
  - Power
  - Synthetic fuels
  - Primary metals processing
  - Microelectronics
  - Chemical
  - Pulp and paper
  - Coal mining
  - Battery manufacturing
  - PVC manufacturing
  - Uranium mining
  - Petroleum and petrochemical
  - Oil refining
  - Steam Assisted Gravity Drainage (SAGD) heavy oil recovery
  - Cogeneration
  - Fertilizer
  - Solid waste (leachate and secondary sewage effluent)
  - Coal liquefaction
  - Ethanol production
- Tertiary treatment of municipal waste effluents
- Inland desalination…

Conventional Thermal ZLD Technology

- The conventional ZLD is based on evaporation and crystallization operations
- Evaporation (MVC or live steam) usually aims at >90% water recovery
- crystallization may achieve 100% recovery
- solids can be further dewatered on a filter-press for landfill
- Latent heat of evaporation is partly recovered (especially, for MVC)
- Operational and capital costs are still very high due to high energy consumption (20-40 kWh/m^3 vs. 2-3 kWh/m^3 in desalination), use of chemicals and expensive corrosion-resistant materials.

MVC Evaporation (Falling Film)

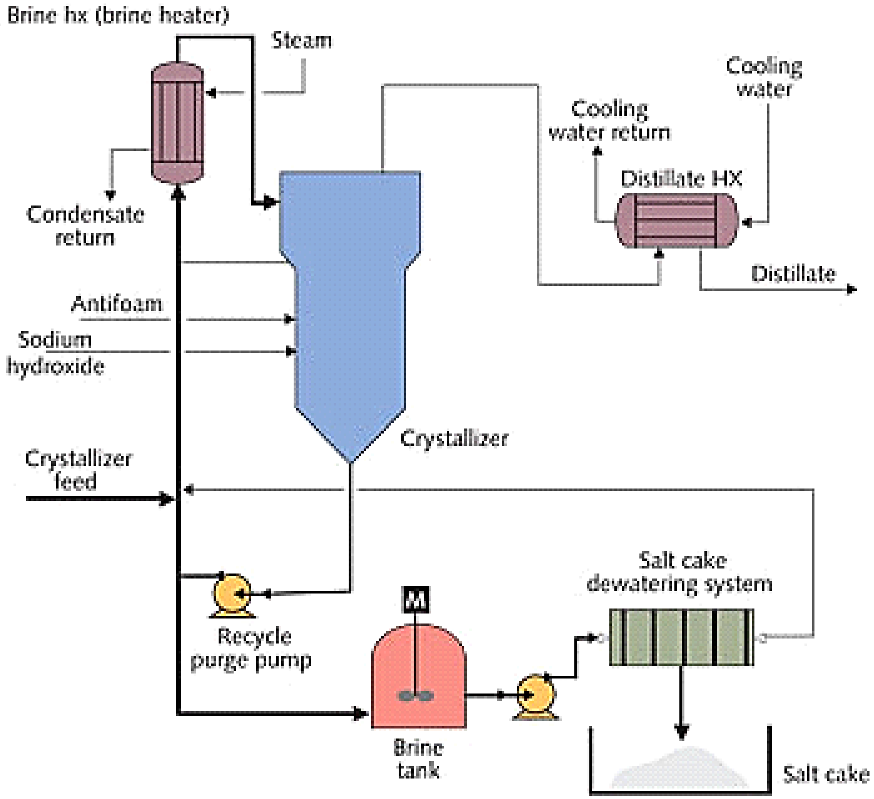


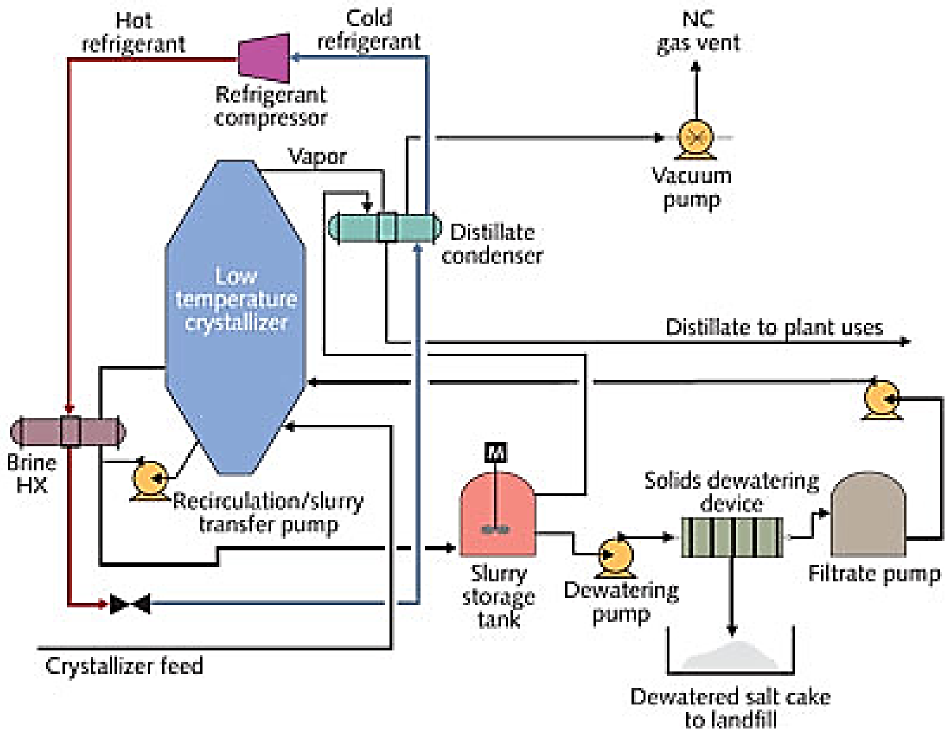


Potential issues:

- T_{boil} elevation (for MVC)
- Prior removal of SS and Ca required
- $Mg(OH)_2$ precipitation (scaling and corrosion)
- High $MgCl_2$ and $CaCl_2$ solubility

Crystallization





Atmospheric Crystallization with Softening Pretreatment

(T_{boil} may be too high for $MgCl_2$ and $CaCl_2$)

Vacuum crystallization

(lower T_{boil}, higher salt concentration)

K. Jenkins et al/CH2M Hill, WaterWorld, 2013

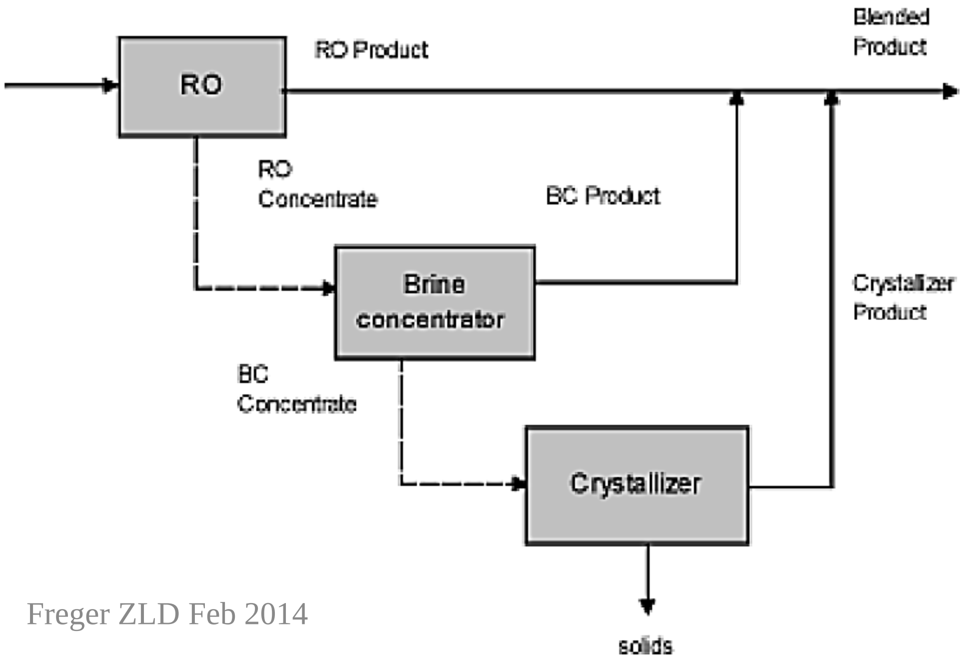
Hybrid ZLD Technologies

- Due to the high cost there is a strong motivation to employ more energy-saving process to minimize the MVC/Crystallization share.
  (Compare with costs of desalination technologies: RO << ED << Thermal.)
  - ✓ Reverse Osmosis* (RO) – rejects salt, passes water, 2-4 kWh/m^3
  - ✓ Nanofiltration* (NF) – similar to RO, but passes some salt
  - ✓ Electrodialysis* (ED) or ED reversal (EDR) – removes ion, costs intermediate to RO and MVC
  - ✓ Natural Evaporation – slow, large footprints
- Another possible motivation is presence of organics, volatiles, colloids etc., which complicates the treatment and water reuse. Available solutions:
  - ✓ Conventional bioremediation
  - ✓ MBR/UF pretreatment

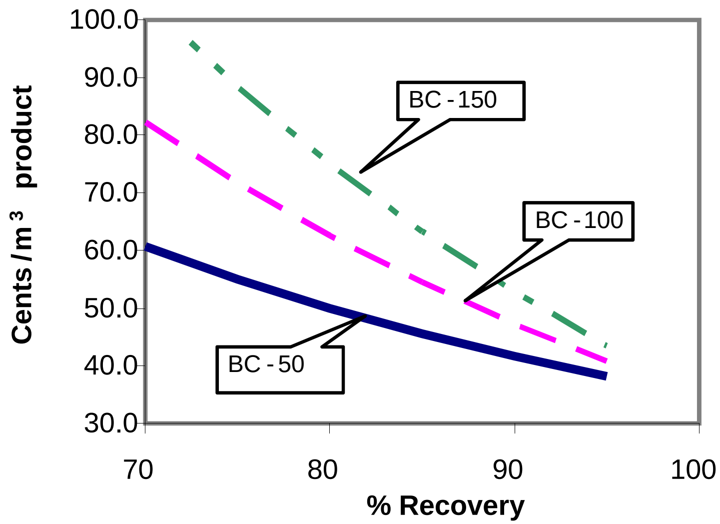
*RO, NF and ED will be covered in detail on 2nd day

ZLD Combined with RO

- RO is presently the best and most energy-saving available technology for desalting. The purpose is then to use RO to recover as much water as possible before MVC. The ZLD cost drops as RO recovery increases.
- The recovery in RO is however limited by 3 main factors
  - ✓ Osmotic pressure becomes too high for TDS ~ 80,000 ppm
  - ✓ Scaling by sparingly soluble salts (Ca, Mg, SO4, PO4, silica), maybe alleviated to some degree using anti-scalants
  - ✓ Fouling (by organics, colloids, biofilms etc.)

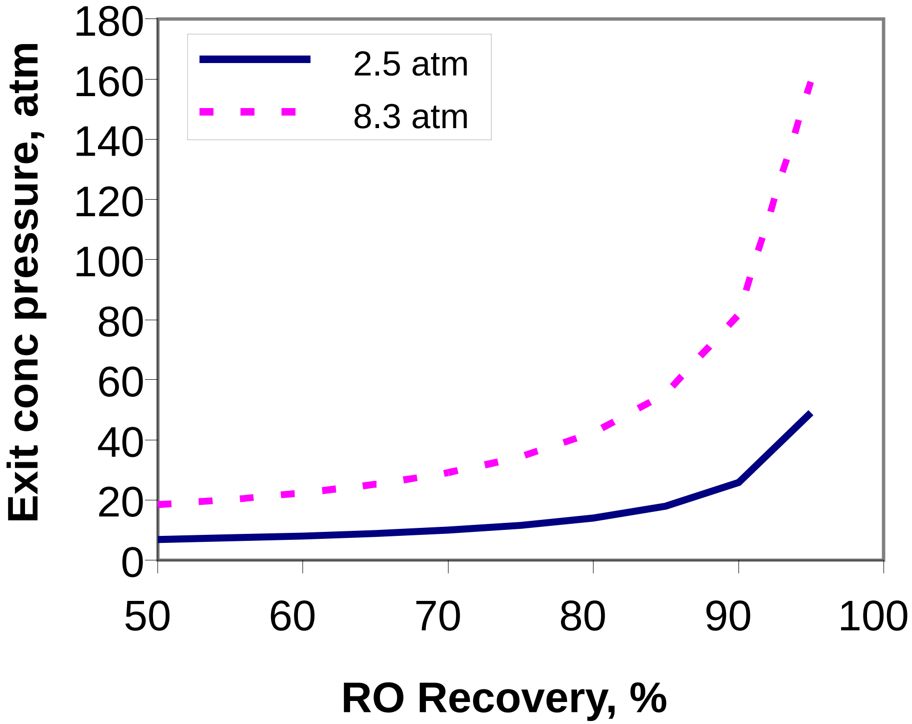


Cost of Brine Concentration for BWRO

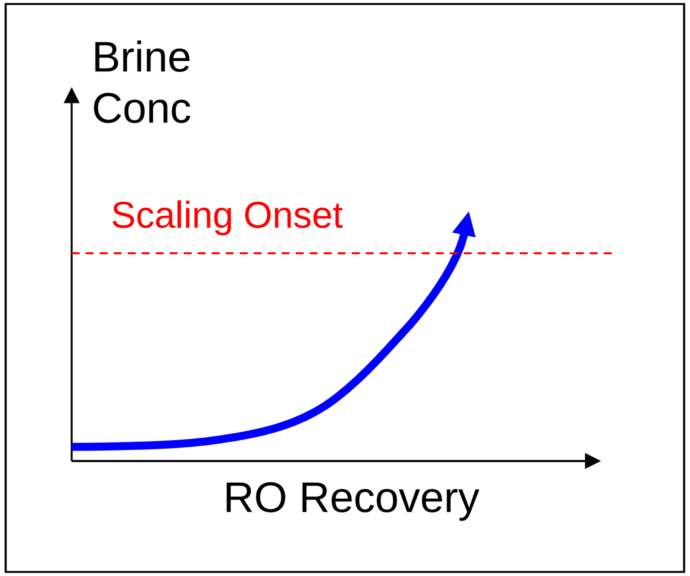


Glueckstern, Proc. 6th IDS, 2003

RO Limitations on Recovery



Brine Osmotic Pressure vs. Recovery



Scaling Potential vs. Recovery

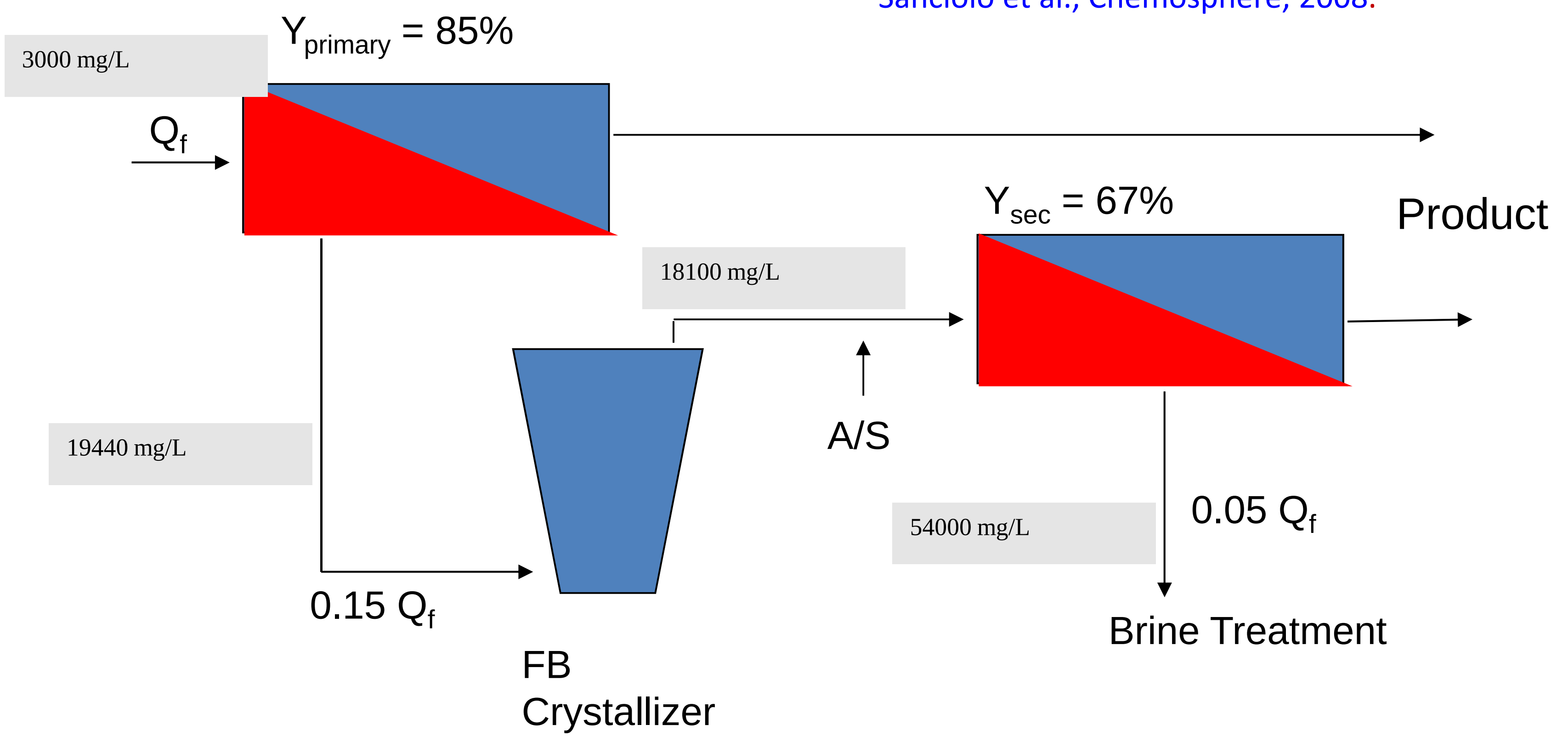
$$J_v = L_p(\Delta P - \Delta\pi)$$

$$LSI = SP/SP_c \sim C^n,\ n \sim 2\text{-}5$$

Increasing RO Recovery: 2-Stage RO/NF

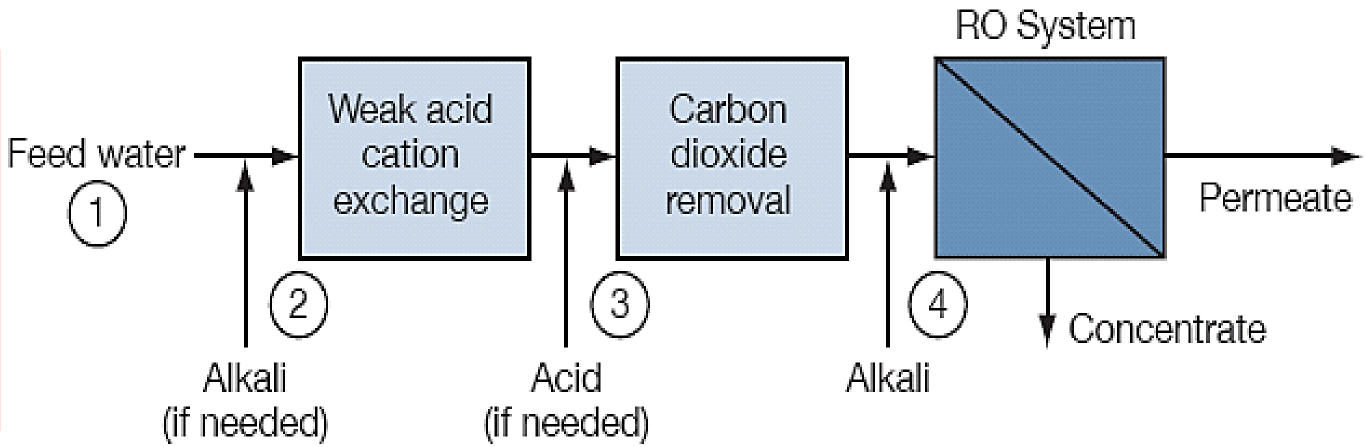
- ✓ A simple 2-stage (different membranes & pressures used at each stage)
- ✓ Interstage softening/precipitation (more chemicals used)

Rahardianto, et al., JMS 2007; EST, 2008; Des. 2010, Sanciolo et al., Chemosphere, 2008.



High Efficiency RO (HERO) Process

- High Silica Water
- Cooling Tower Blowdown
- Tertiary Treated Effluent (Sewage)
- High/TOC Biologically Active Water

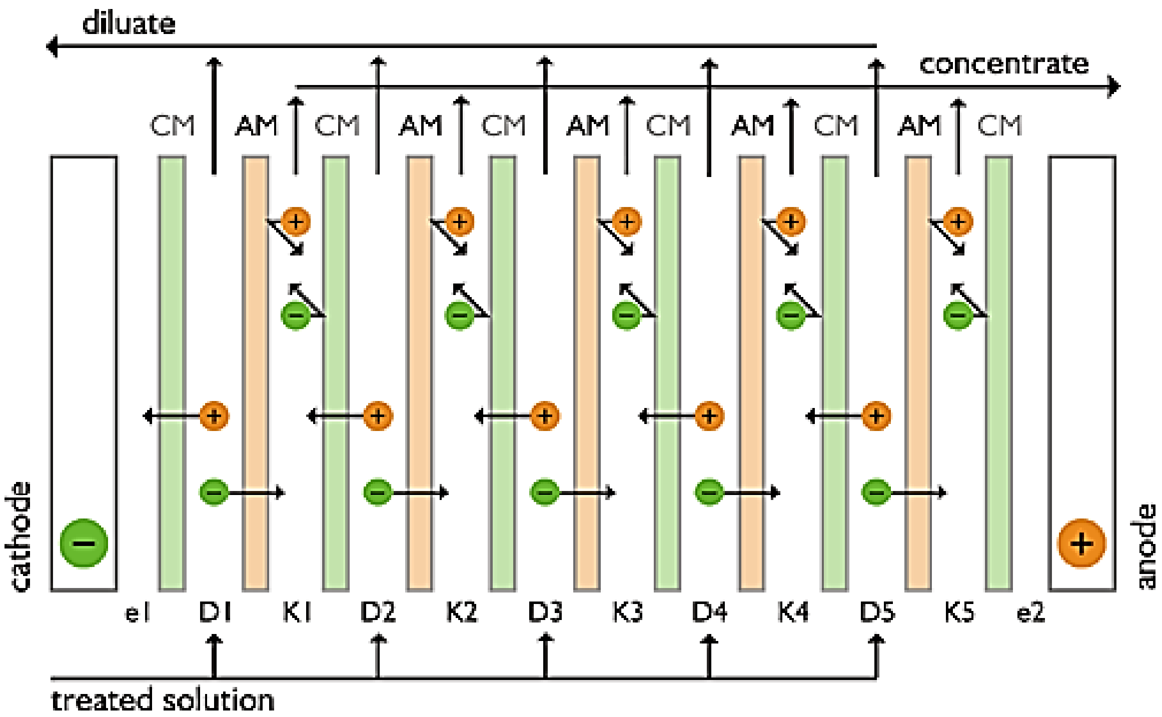


- By removing Ca and carbonate hardness RO can run at pH >10.5
  - ✓ High pH creates a “cleaning environment” => low fouling
  - ✓ Silica solubility very high, hardness removed => low scaling
  - ✓ Salt rejection and flux are increased
- Recovery >90%
- However, high chemical costs add ~\$0.13/m^3 overall product

Source: FEMP Bulletin, DOE/EE – 0294; aquatech.com

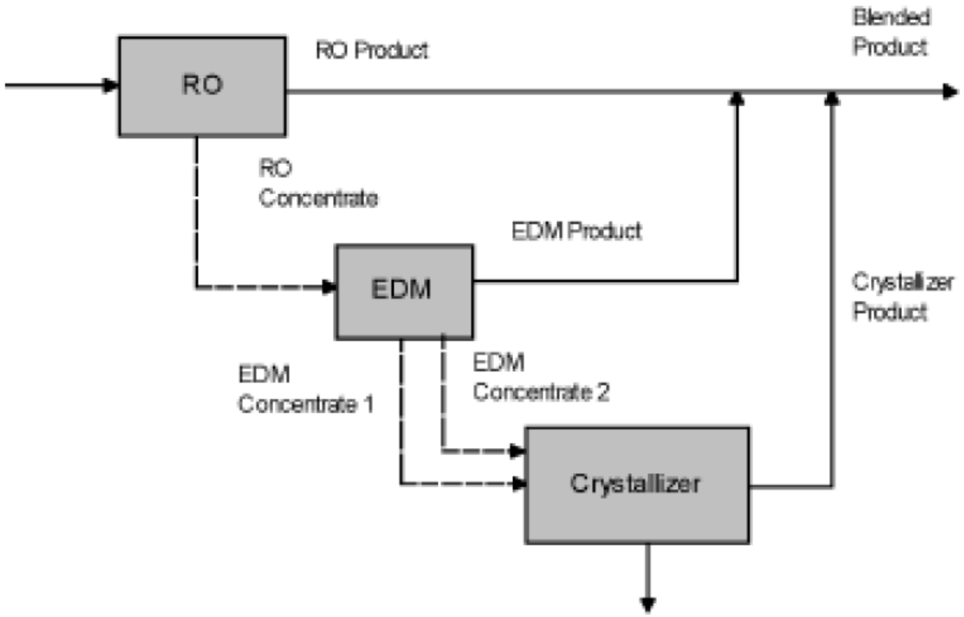
ZLD Combined with ED

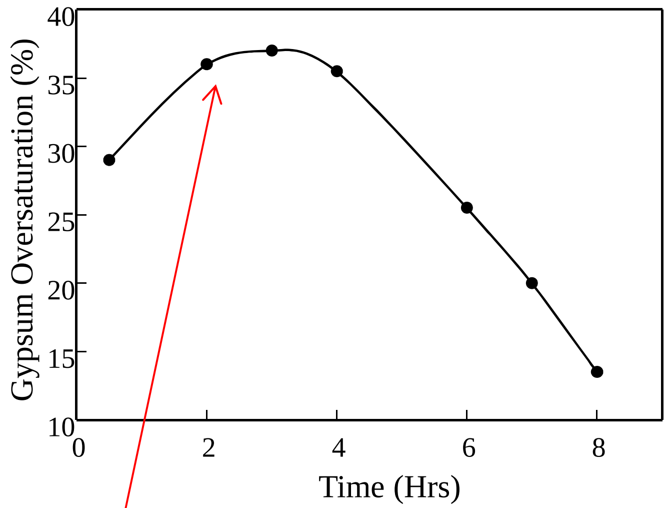
- ED is not limited by osmotic pressure and thus it can achieve a much higher recovery.
- Typically, ED desalting cost is higher than RO but lower than MVC/crystallization. The optimal placement of ED is then between RO and evaporation.



Increasing ED recovery for ZLD

- As in RO, precipitation of sparingly soluble salts in the brine limits recovery. Proposed solutions include
  - Off-stack precipitation (seeded)
  - EDM in place of regular ED

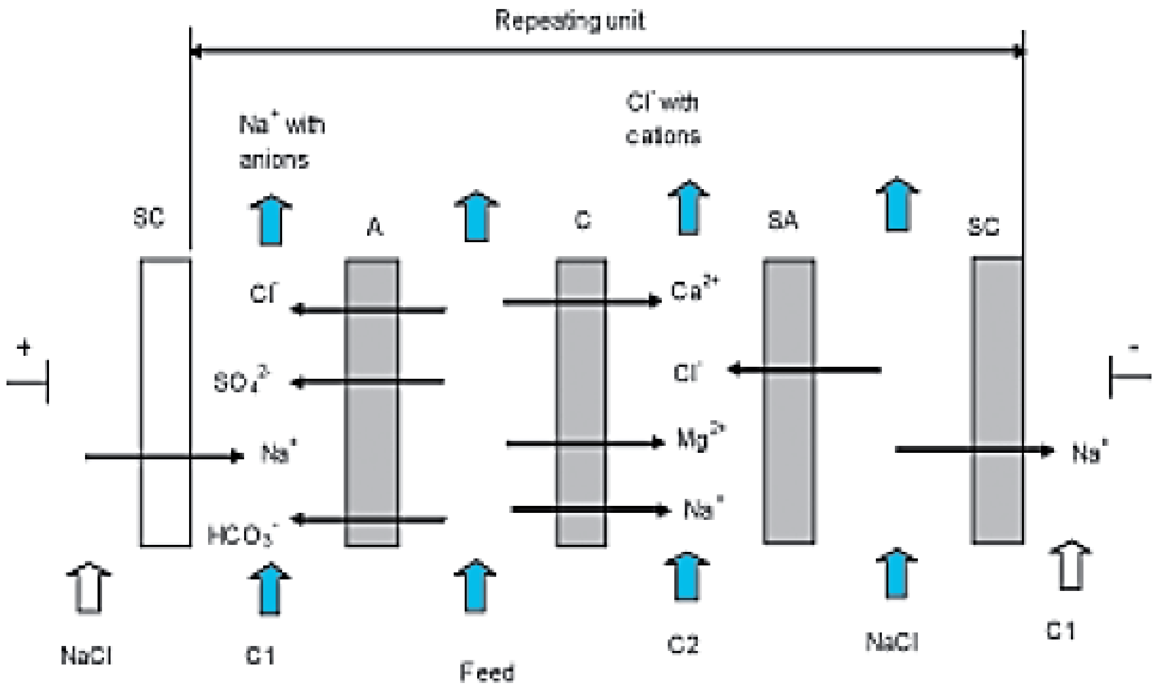




Onset of precipitation
place crystallizer in brine loop

R. Bond et al, 2011, Florida Water Res J; J. Gilron, Wetsus, 2013.

ED Metathesis

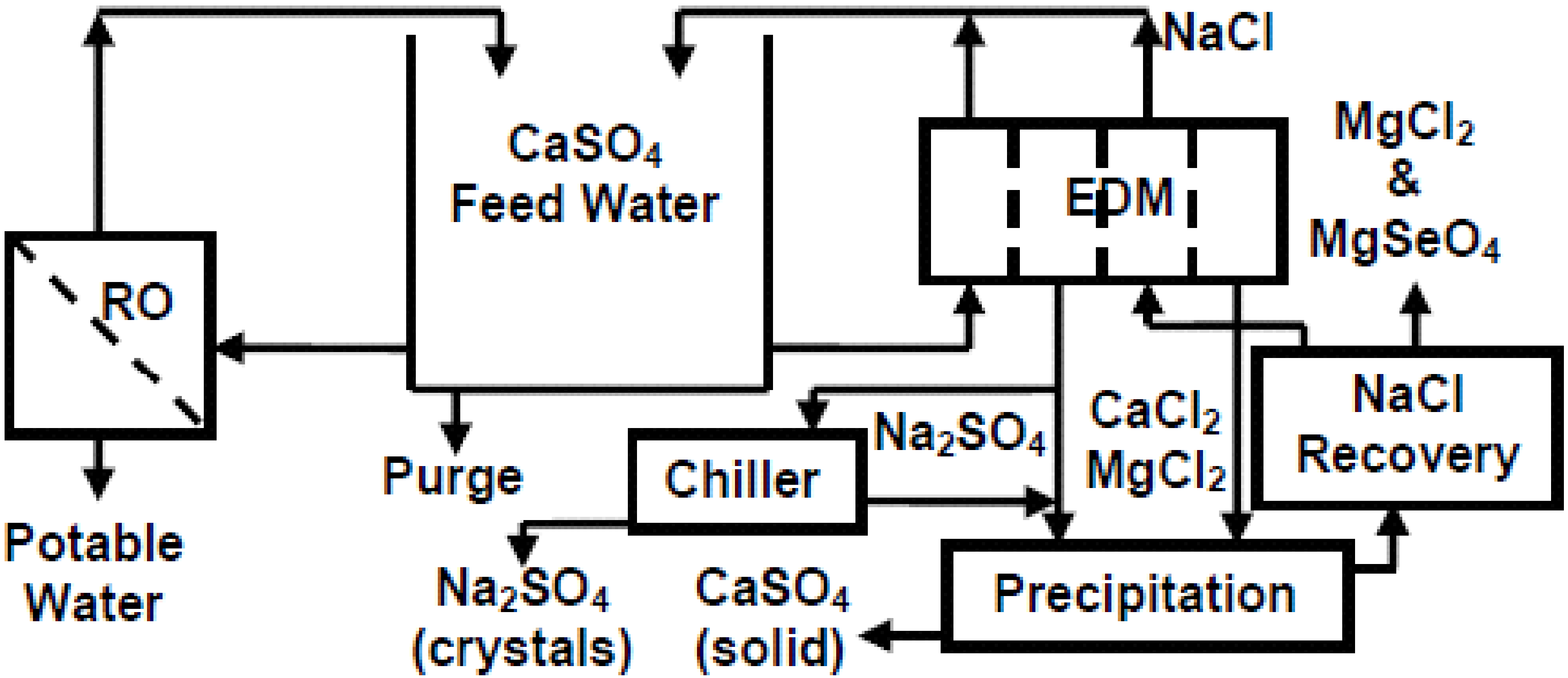


Formation of sparingly soluble salts prevented using a stack of 4-compartment units

Analyte	RO Concentrate (mg/L)	EDM Feed (mg/L)	EDM Concentrate 1 (mg/L)	EDM Concentrate 2 (mg/L)
Calcium	450	322	34	10,200
Magnesium	500	417	9	6500
Sodium	4700	4200	60,800	37,900
Chloride	7800	6280	65,800	102,000
Sulfate	2580	2220	34,200	nondetect
Silica	43.5	49.0	16	11

R. Bond et al, 2011, Florida Water Res J; T. Davis, USBR Rpt. 135.

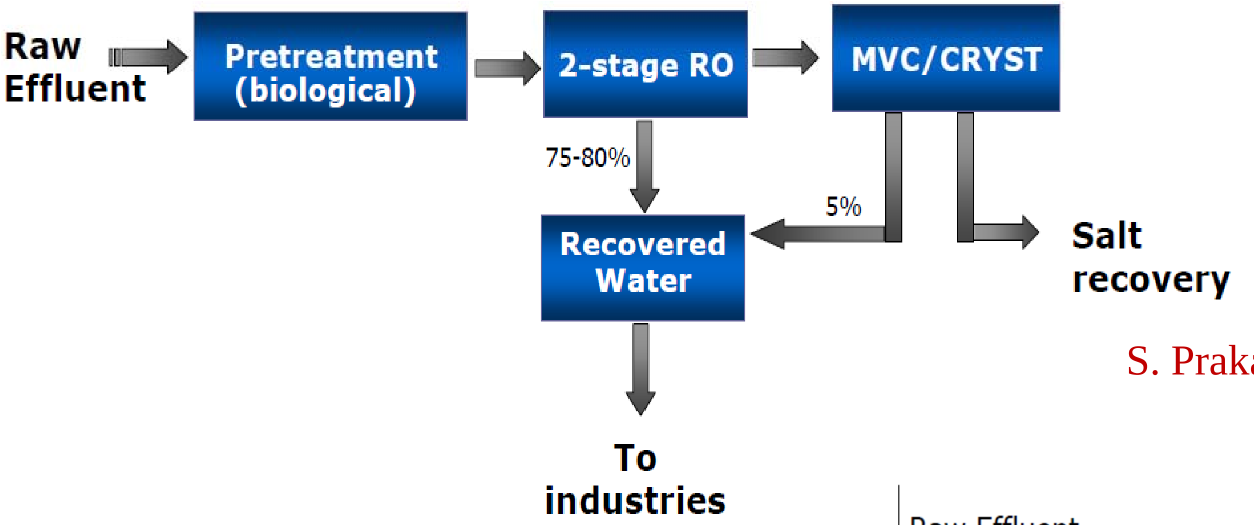
RO+EDM+Off-Stack Precipitation ZLD Process



T. Davis, USBR Rpt. 135.

Biological (Pre-)Treatment

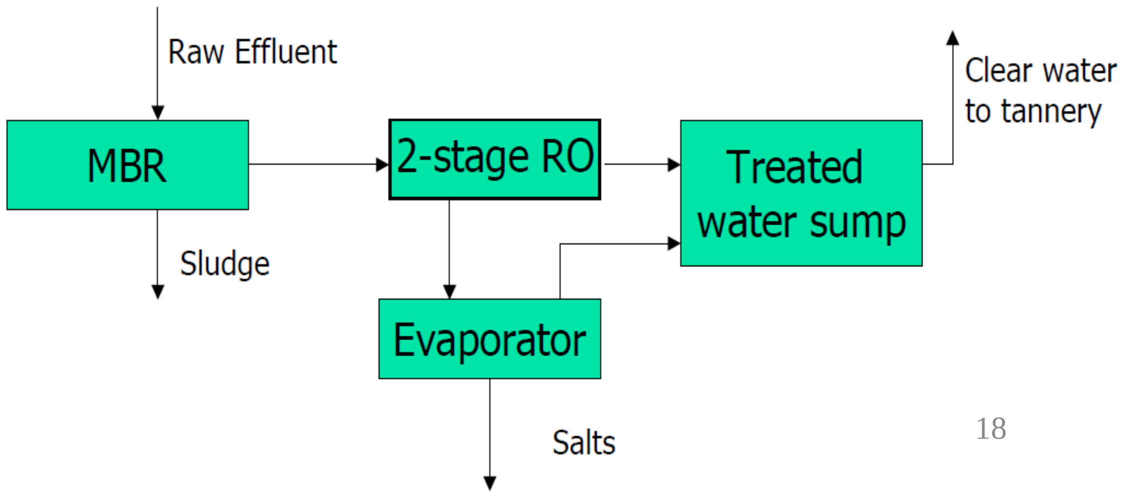
- Removes TOC (most organics) as CO_2 and sludge, may leave some recalcitrant organicss
- MBR/UF is significantly more expensive, but offers a smaller footprint and a more robust process



Tirupur Project
Textile Effluent,
54 MLD, 2007

S. Prakash, GWI, Barcelona, 2007

Ambur–Vaniyambadi
Tannery Effluent
7 MLD, 2007



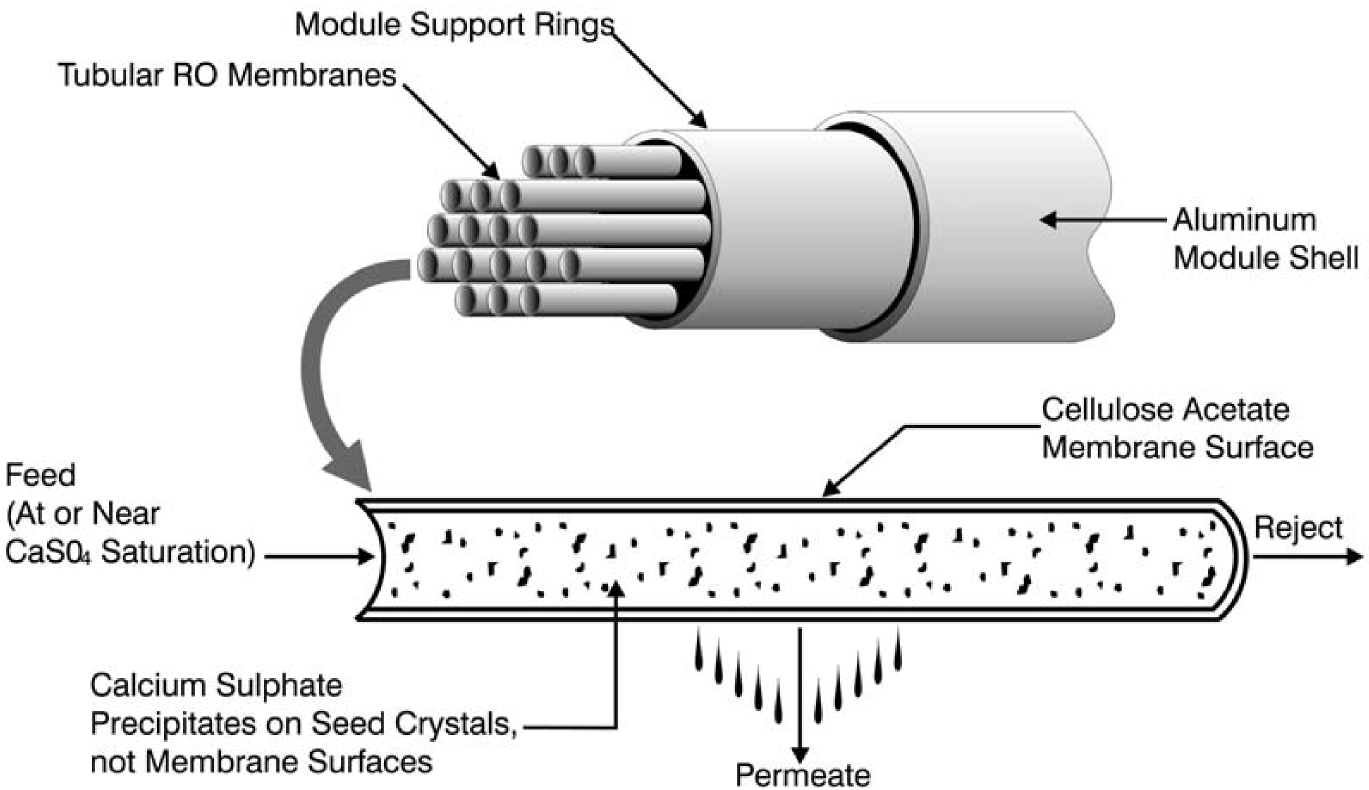
Emerging and State-of-the-Art ZLD Solutions

- Several alternative technologies or hybrids are in use or being examined for ZLD.
  - SPARRO (Seeded RO)
  - ARROW (O'Brien and Gere, 2007) – pH elevation + IX + RO
  - VSEP (by New Logic Rerearch Inc.) – membranes vibrated
  - HEEPM (by EET Corporation) – ED treats the feed to RO
  - Forward Osmosis (FO)
  - Molecular distillation (MD)
  - Wind-assisted intensified evaporation (WAIV)

Mickley, WaterReuse Foundation, 2008

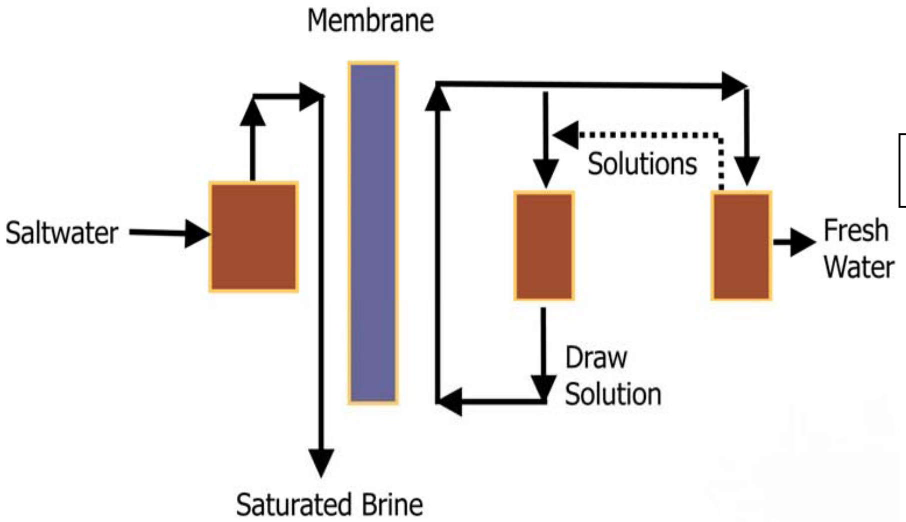
SPARRO Process

- Developed for treating hard waste water from mining industry.

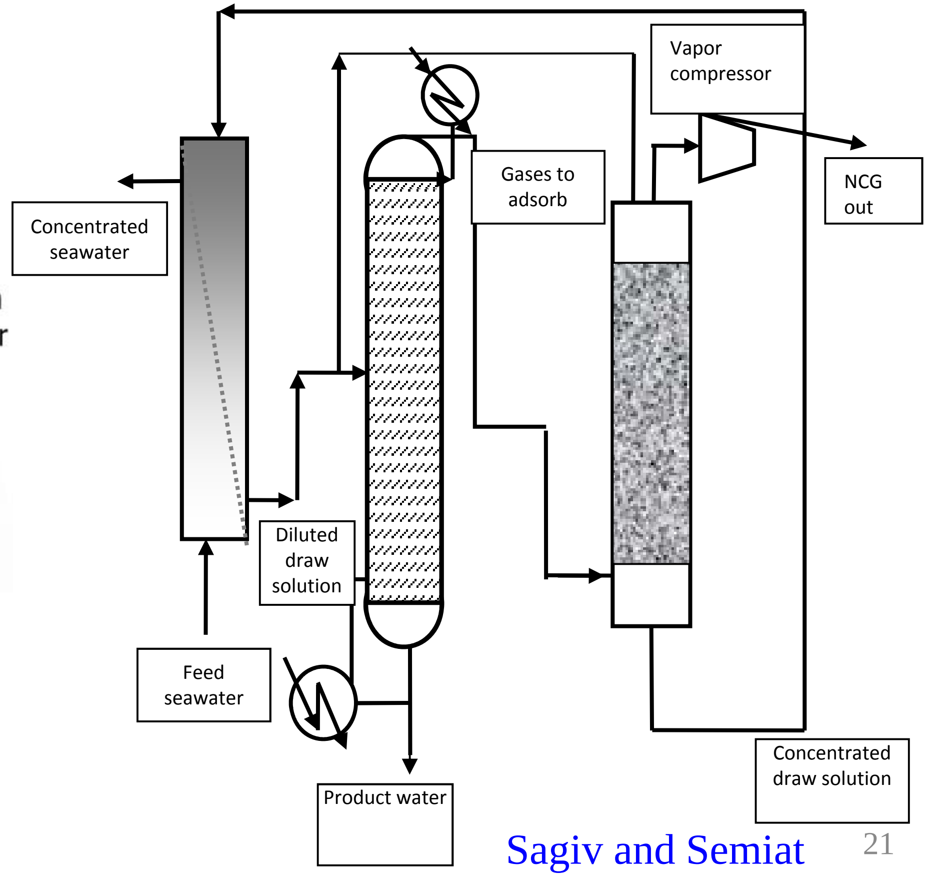


Forward Osmosis

- FO is used today for treating produced water in oil industry (generating a larger volumes of waste water – no ZLD)
- FO was proposed as an alternative to RO. Viable only when a waste energy (heat or osmotic) is available.



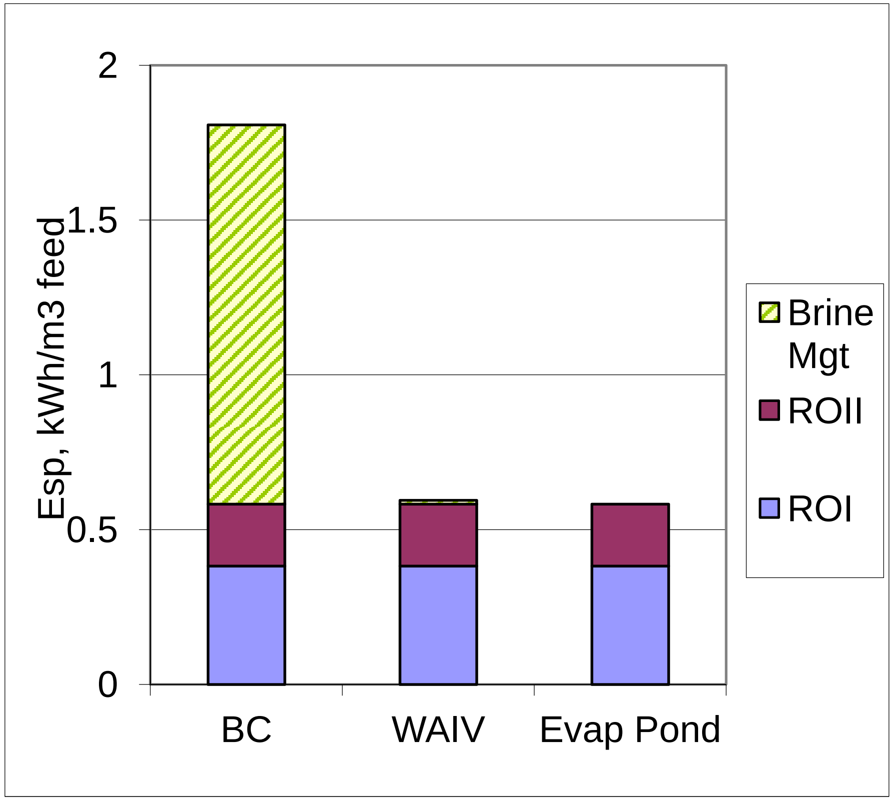
Proposed concept
(McCutcheon et al., 2005)



Sagiv and Semiat

WAIV (enhanced natural evaporation)

- Evaporation ponds (EP) are widely used as part of ZLD, but their footprint may be excessively large.
- WAIV may offer a 1/15 land and 1/3 CAPEX of EP for the same evaporation rate



J. Gilron, Wetsus, 2013

Outlook

- Efforts continue to find alternatives to energy-intensive evaporator/crystallizer systems.
- Hybrids systems with increased recovery are and will be the dominant approach
- Progress is being made in lowering capital costs; a total installed cost factor is down from 5 to 1.8-2.
- "… *industry analysts predict a cumulative annual growth rate for recovery/ reuse systems in excess of 200% over the next decade, of which a significant portion could be accounted for by ZLD capacity. … The economic and regulatory climate is such that ZLD or near zero discharge is going to continue to grow rapidly*…"
  [G. Cope, "From zero to hero", globalwaterintel.com]

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ZLD Workshop Organizers