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/m³ vs. 2-3 kWh/m³ in desalination), use of chemicals and expensive corrosion-resistant materials.
MVC Evaporation (Falling Film)

Potential issues:
- $T_{\text{boil}}$ 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
($T_{\text{boil}}$ may be too high for MgCl$_2$ and CaCl$_2$)

Vacuum crystallization
(lower $T_{\text{boil}}$, higher salt concentration)

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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/m³
  - 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.)

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**Cost of Brine Concentration for BWRO**

- Glueckstern, Proc. 6th IDS, 2003
RO Limitations on Recovery

Brine Osmotic Pressure vs. Recovery

\[ J_v = L_p(\Delta P - \Delta \pi) \]

Scaling Potential vs. Recovery

\[ LSI = SP/SP_c \sim C^n, \ n \sim 2-5 \]
Increasing RO Recovery: 2-Stage RO/NF

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

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/m³ 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.

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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

Formation of sparingly soluble salts prevented using a stack of 4-compartment units
RO+EDM+Off-Stack Precipitation ZLD Process

Biological (Pre-)Treatment

- Removes TOC (most organics) as CO₂ and sludge, may leave some recalcitrant organics
- 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 Research 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 (McCUTCHION et al., 2005)
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.

![Evaporation Pond Image](Courtesy, Lesico Ltd.)

![Bar Graph Image](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