1. What is ZLD?

Zero Liquid Discharge (ZLD) is a treatment process that its goal is to remove all the liquid waste from a system. The focus of ZLD is to reduce economically wastewater and produce clean water that is suitable for reuse.

ZLD technologies consist traditionally from brine concentrators and crystallizers that use thermal evaporation to turn the brine into highly purified water and solid dry product ready for landfill disposal or for salt recovery. While evaporator/crystallizer systems are the most commonly used in ZLD processes, other promising technologies (ED/EDR, FO and MD which will be explained later) with high recoveries have taken foothold and are used in different combinations in order to lower the cost and raise the efficiency of the systems.

The increasingly tighter government regulations on the discharge of brine due to the environmental effect make ZLD necessary when water is scarce or the local water bodies are protected by law. Thus many industrial facilities and brine effluent contributors that up to now where either discharging brine to nearby available surface water or the sea and to wastewater treatment plants, are trying to find new ways to tackle this issue.

2. ZLD Drivers

The industrial involvement with brine is twofold. Many industrial processes require water which they contaminate and releasing it may cause irreversible damages to the local environment.

In India and during the last decade due to heavy contamination of local waters by industrial wastewater was followed by strict regulations that make ZLD necessary in order to ensure the future of their rivers and lakes. In Europe and North America, the drive towards zero ZLD has been applied due to the high costs of wastewater disposal at inland facilities. These costs increase exponentially by government fines and the costs of disposal technologies.

ZLD can also be used to recover valuable resources from the wastewater which can be sold or reused in the industrial process. Some examples are as follows,

- Generation of valuable potassium sulfate (K_2SO_4) fertilizer from a salt mine
- Concentration of caustic soda (NaOH) to 50 and 99% purity
- Recovery of pure, saleable sodium sulfate ($NaSO_4$) from a battery manufacturing facility

- Reduction of coal mine wastewater treatment costs by recovering pure sodium chloride (NaCl) which can be sold as road salt
- Lithium (Li) has been found in USA oil field brines at almost the same level as South American salars
- Gypsum ($CaSO_4.2H_2O$) can be recovered from mine water and flue gas desalinization (FGD) wastewater, which can then be sold to use in drywall manufacturing

Other advantages to the application of ZLD are:

- Decreased volume of wastewater lowers the costs of waste management.
- Recycling water on site thus decreasing the need for water intake and meeting with treatment needs.
- Reduce the truck transportation costs for off-site disposal and the related environmental risks.

Table 1, ZLD Drivers

1. Meeting tight brine disposal government regulations
2. Recovery of valuable materials in the waste streams
3. Decreased waste volumes and management costs
4. Recycling water on-site
5. Reducing truck costs for off-site disposal

3. ZLD applications

There is a wide diversity of sources for discharge flow streams that include:

- Cooling tower blowdown in heavy industry and power plants
- Ion exchange regenerative streams particularly in food and beverage processing
- Flue gas desulfurization, wet wastewater stream
- Municipal potable water systems, wastewater streams
- Process water reuse from agricultural, industrial and municipal streams
- Various industrial wastewater streams from the textile, coal-to-chemical, food and dairy or battery industries

More in particular, we can refer to the following applications (Table 2),

Table 2, ZLD Wastewater Stream Applications

Membrane System Reject (*NF, MF, UF, RO*)	**Mine Drainage**
Flue Gas Desulfurization (*FGD*) Blowdown / Purge	**Refinery, Gas to Liquid (*GTL*), and Coal to Chemical (*CTX*) Wastewaters**
Produced Water (*Conventional, Fracking, SAGD*)	**Scrubber Blowdown**
NO_x Injection Water	**Demineralization Waste**
Integrated Gasification Combined Cycle (*IGCC*) Gray Water	**Landfill Leachate**

The discharge sources can be further categorized according to volume and complexity. A ZLD solution must take the latter into consideration along with the location of the waste stream.

4. ZLD Determining Factors

The most important factors that determine the ZLD design depend on,

1. The specific contaminants in the discharge stream
2. The volume of the dissolved material
3. The required design flow rate

The contaminants of concern are presented in Table 3,

Table 3, Typical Chemical Constituents of Concern

Sodium (Na^+)	**TDS/TSS**	**Phosphate (PO_4^{3-})**	**Strontium (S^{2+})**	**Sulfate (SO_4^{2-})**
Potassium (K^+)	**COD/TOC/BOD**	**Ammonia (NH_3)**	**Oil & Grease**	**Fluoride (F^-)**
Calcium ($Ca^{2+)}$	**pH**	**Boron (B^+)**	**Barium (Ba^{2+})**	**Nitrate (NO_3^-)**
Magnesium (Mg^{2+})	**Chloride (Cl^-)**	**Alkalinity**	**Silica**	**-**

These parameters need to be accurately measured before requesting a quote in order so as to get an accurate estimation of the system’s cost. If the feed is prone to changes in flow and the concentration of the contaminants, inlet buffering tanks regulate the peaks.

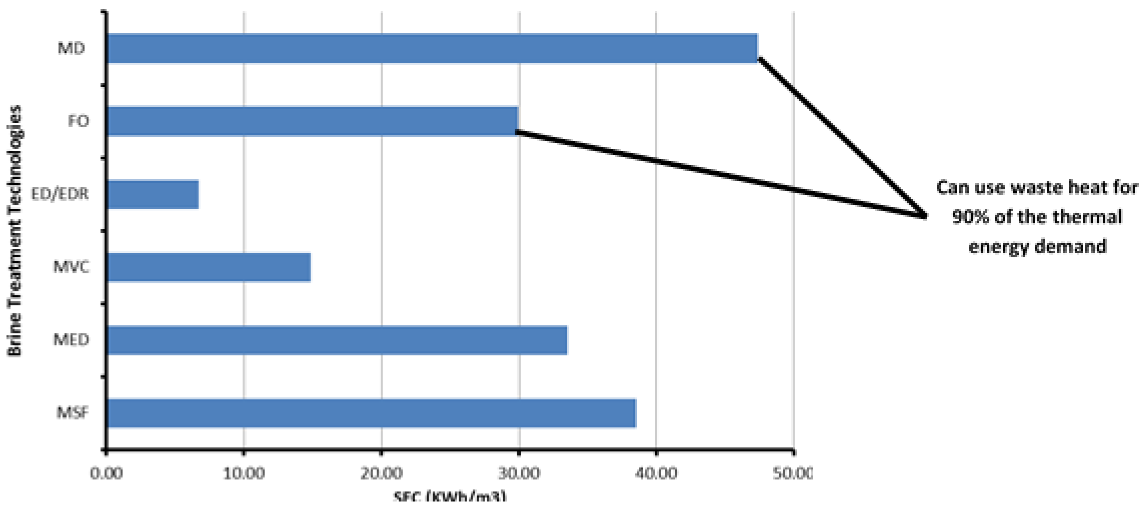
5. Operation costs

Each technology that makes up the ZLD chain has a certain purchasing cost, but an important parameter for calculating the costs and eventually the payback period are the operating costs. The OPEX can change drastically based on what process is selected especially for electrical power and steam-generating facilities. For a long term investment the benefits and drawbacks of each choice have to be weighed as well as what works better for each company and their working staff. This will help to get an initial versus a long-term cost investment.

Brine Treatment Technology	Electrical Energy (KWh/m3)	Thermal Energy (kWh/m3)	Total El. Equivalent (kWh/m3)	Typical Size (m3/d)	Investment ($/m3/d)	max TDS (mg/L)
MSF	**3.68**	**77.5**	**38.56**	**<75,000**	**1,800**	**250,000**
MED	**2.22**	**69.52**	**33.50**	**<28,000**	**1,375**	**250,000**
MVC	**14.86**	**0**	**14.86**	**<3,000**	**1,750**	**250,000**
ED/EDR	**6.73**	**0**	**6.73**	**/**	**/**	**150,000**
FO	**0.475**	**65.4**	**29.91**	**/**	**/**	**200,000**
MD	**2.03**	**100.85**	**47.41**	**/**	**/**	**250,000**

Table 4, Specific Energy Consumptions (SECs) of Brine Treatment Technologies, Multistage Flash (MSF), Multi-Effect Distillation (MED), Mechanical Vapor Compression (MVC), Electrodialysis (ED/EDR), Forward Osmosis (FO), Membrane Distillation. The energy consumption values are the average of 13 comparative studies on ZLD technologies ranging from 2002 -2017. Clarifications are needed for ED/EDR, FO and MD. 1) ED/EDR SEC depends on the salinity of the feed as higher salinities require higher SECs, 2) FO SEC depends on the Draw Solution and the Regeneration Method. Most papers assume the use of thermolytic salts and their regeneration at a 60^{o}C temperature. 90% of the thermal energy needed can be acquired by waste heat if it's available, 3) MD SEC depends on the configuration. Most common MD configuration in the studies is Direct Contact MD (DCMD) due to its simplicity. 90% of the thermal energy needed can be acquired by waste heat if it's available and finally 4) the total electrical equivalent was taken using the following, Total El. Equivalent = El. Energy + 0.45 x Thermal Energy due to modern power plant efficiency (according to relevant paper).

Fig.1 Brine Treatment Technologies SECs graph comparison (see clarifications in the description of table 4)



On a last note for a cost benefit analysis you must always take into consideration factors like,

- Taxes or additional purchasing fees
- Possible utility costs in the installation area
- Environmental regulatory fees or permits
- Regular compliance testing

6. **Basic ZLD Design - ZLD Blocks**

Despite the variable sources of a wastewater stream, a ZLD system is generally comprised by two steps which are represented in Figure 1.

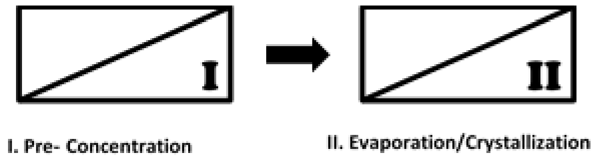


Fig.2, ZLD Basic Blocks

1. **Pre-Concentration;** Pre-concentrating the brine is usually achieved with membrane brine concentrators or electrodialysis (ED). These technologies concentrate the stream to a high salinity and are able to recover up to 60–80% of the water.
2. **Evaporation/Crystallization;** The next step with thermal processes or evaporation, evaporates all the leftover water, collect it, and drives it for reuse. The waste that is left behind then goes to a crystallizer which boils all the water until all the impurities crystallize and are filtered out as a solid.

6.1. Pre-concentration

The pre-concentration of the liquid waste stream is a very important step due to the fact that it reduces the volume of the waste and downsizes significantly the very costly evaporation/crystallization step. Usually it is achieved with electrodialysis (ED) or membrane processes which consist of Forward Osmosis (FO) and Membrane Distillation (MD) (Figure 3).

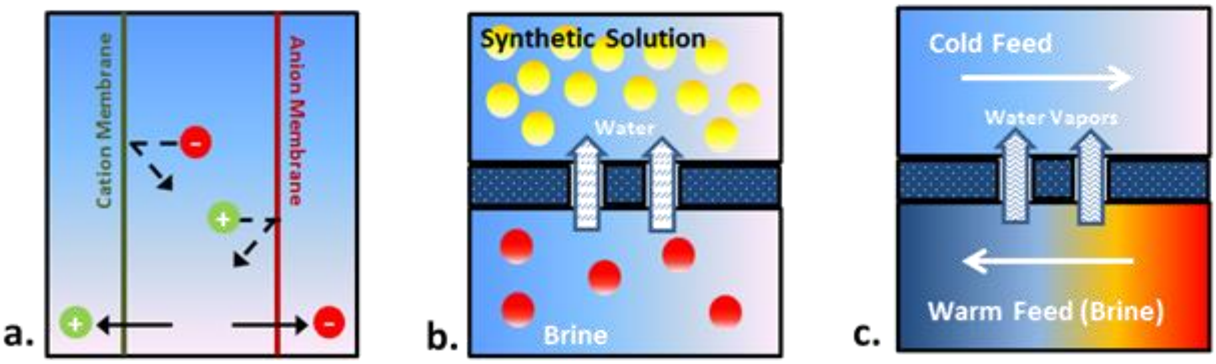


Fig.3, Brine treatment technologies, (a) Electrodialysis, (b) Forward Osmosis, (c) Membrane Distillation

ED, FO and MD can function efficiently with a much higher salinity content than RO (150,000 ppm, 200,000 ppm, 250,000 ppm and 70,000 ppm respectively).

6.1.1. Electrodialysis/ Electrodialysis Reversal

Electrodialysis is a membrane process that uses electrodes to create an electric field which pushes negative and positive ions through semipermeable membranes with attached positively or negatively charged species respectively. ED is used in multiple stages to concentrate the brine to saturation levels. It is often used together with RO for very high water recovery. ED differs from RO because it removes the ions and not the water and vice versa for RO. Due to this fact silica and dissolved organics are not removed with ED which is important if the clean stream is to be reused. ED requires solids, as does RO, solids and organics removal from the feed.

Electrodialysis reversal (EDR)

In EDR the polarity of the electrodes is reversed several times an hour and the fresh water and the concentrated wastewater are exchanged within the membrane stack to remove fouling and scaling.

6.1.2. Forward Osmosis

FO is an osmotic membrane process with a semipermeable membrane that unlike RO doesn't use applied pressure in order to achieve separation of water from dissolved solutes like ions, molecules and larger particles. That means a lot less of energy for the process in comparison to RO. In general FO uses thermal and electrical energy. Thermal energy can be substituted with low grade waste heat which can be found everywhere in most industrial or nearby areas.

6.1.3. Membrane Distillation

MD is a thermally driven transport process that uses hydrophobic membranes. The driving force in the method is the vapor pressure difference between the two sides of the membrane pores, allowing for mass and heat transfer of the volatile solution components (e.g. water). The simplicity of MD along with the fact that it can use waste heat and/or alternative energy sources, such as solar and geothermal energy, enables MD to be combined with other processes in integrated systems, making it a promising separation technique.

6.1.4 The importance of Pre-Concentration in a ZLD Process

The pre-concentration technologies have very high recoveries but usually not enough like the typical thermal evaporation technologies to drive the brine into saturation concentration levels. So why are they so important? The reason is the CAPEX/OPEX of the evaporators/crystallizers. 1) Due to the corrosive nature of the brine it takes more and more resistant metal alloys in order to resist corrosion as the concentration rises. That means that the bigger is the evaporation/crystallizer module, the bigger will be the CAPEX required (which can be 60-70% of the whole process). 2) High energy demand due to the rise of the boiling point of the brine as concentration goes higher. Both points will be explained more analytically in the evaporation/crystallization Lenntech webpages.

Let's try to formulate a visual example of the situation. Let's suppose that we have 100 m^3/d brine and we want to treat it with a MD-MVC-Crystallizer combination. Let's suppose that we have (rough approaches from available values in related papers),

- MD (75% recovery)/available waste heat combination → 90% of Thermal Energy can be substituted by waste heat → Energy consumption will go from 47.41 down to 6.57 KWh/m^3
- MVC with 90% recovery → Average of 14.86 KWh/m^3
- Crystallizer with 50% recovery → Average of 50 KWh/m^3

So, given all the latter values, let's see how the brine process will play out.

100 m^3 Brine → MD (-75%) → 25m^3 Brine → MVC (-90%) → 2.5 m^3 Brine → Crystallizer (-50%) → 1.25 m^3 Brine → Driven to Centrifuge or Belt Press

This translates into 100 m^3 x 6.57 KWh/m^3 + 25 m^3 x 14.86 KWh/m^3 + 2.5 m^3 x 50 KWh/m^3 = 657KWh + 371.5 KWh + 125 KWh = 1,153.5 KWh/100 m^3 Brine

If we hadn't a pre-concentration step and drove the brine straight to an evaporator then the energy demand would be,

$100\ m^3 \times 14.86\ KWh/m^3 + 10\ m^3 \times 50\ KWh/m^3 = 1{,}486\ KWh + 500\ KWh = 1{,}986\ KWh/\ 100\ m^3$ Brine

1,986 KWh (MVC-Crystallizer)/ 1,153.5 KWh (MD-MVC-Crystallizer) = 1.72 or 172% increase to the energy consumption of the brine treatment without a pre-concentration step!

Table 5, Relative water recoveries (%) of each combination (with and without pre-concentration) along with the SECs for each technology

	ZLD with Pre-Concentration		ZLD without Pre-Concentration	
	Recovery (%)	SEC (kWh/m3)	Recovery (%)	SEC (kWh/m3)
MD	75	6.75	0	0
MVC	97.5	14.86	90	14.86
Crystallizer	98.75	50	95	50

The graphical visualization of Table 5 gives us Figure 4,

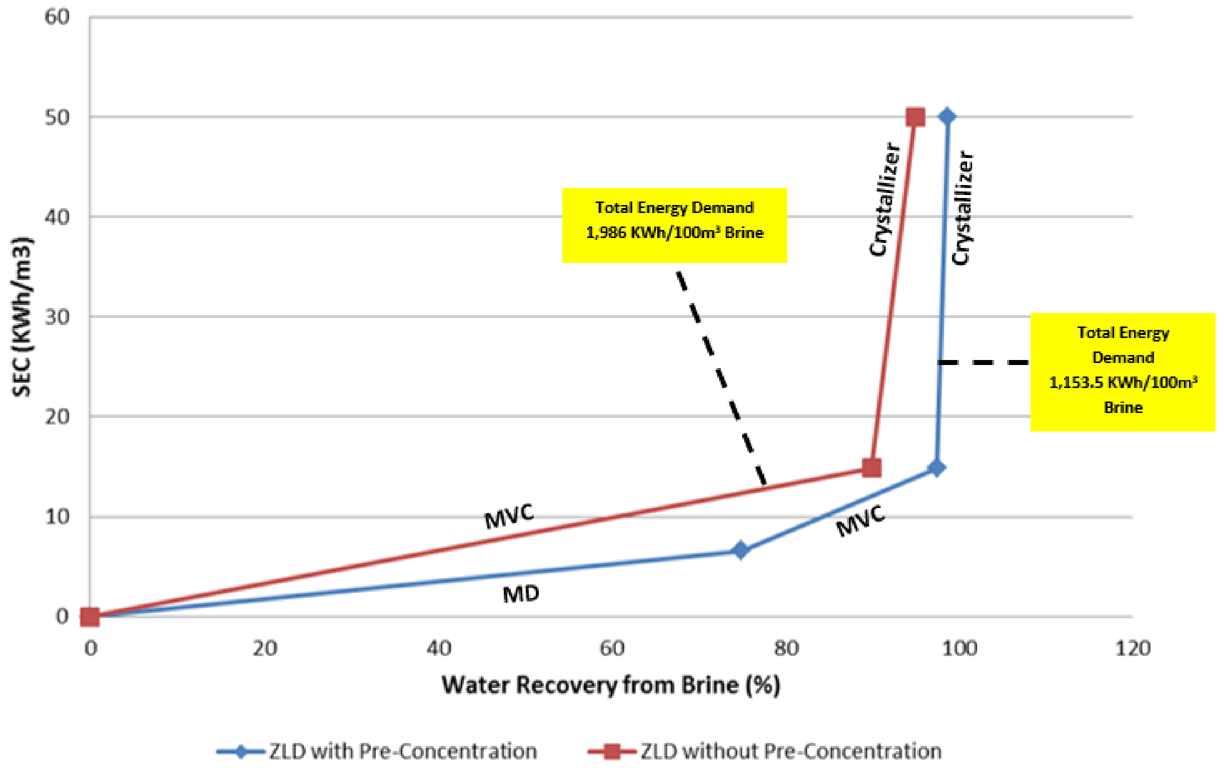


Fig.4, Relative water recoveries (%) of each combination (with and without pre-concentration) along with the SECs for each technology

So the pre-concentration step not only decreased the energy costs to less than half but also increased the recovery availability of the system. Not to mention the possible downsize of the MVC from 100 to 25m^3 and the Crystallizer from 10 to 2.5m^3 which means huge savings in CAPEX/OPEX.

Here it's important that we start talking about the concept of Minimum Liquid Discharge (MLD). MLD is a high recovery system without going all the way to ZLD due to the costs and complexity related to the latter. MLD is discussed further on a separate Lenntech webpage.

6.2 Evaporation and Crystallization

After pre-concentration of the waste stream the next step is to use thermal processes or evaporation to generate solid and reuse the evaporated water. Evaporation is essentially heat transfer to a boiling liquid with the intent to concentrate a non-volatile solute from a solvent, which is usually water, by boiling off the solvent. The evaporation process normally stops just before the solute begins to precipitate, otherwise it is considered as crystallization.

Falling film evaporation is an energy efficient method of evaporation that concentrates the water up to the initial crystallization point (super saturation). Adding acid will neutralize the solution so, when heating it, as to prevent scaling and harming the heat exchangers. De-aeration is also often used in order to release dissolved oxygen, carbon dioxide, and other non-condensable gases.

The exiting brine from the evaporator goes into a *forced-circulation* crystallizer where the water is concentrated beyond the solubility of the contaminants and formed crystals. The result product is dewatered by a filter press or a centrifuge and the centrate (mother liquor) is returned to the crystallizer.

The collected condensate (water) from the three steps returns to the process, eliminating the discharge of liquids in the system. If organics are present, condensate polishing may be required before reusing it. The product water is then driven to a holding tank.

The solid waste, at this point, will go either to a landfill or for reusing.

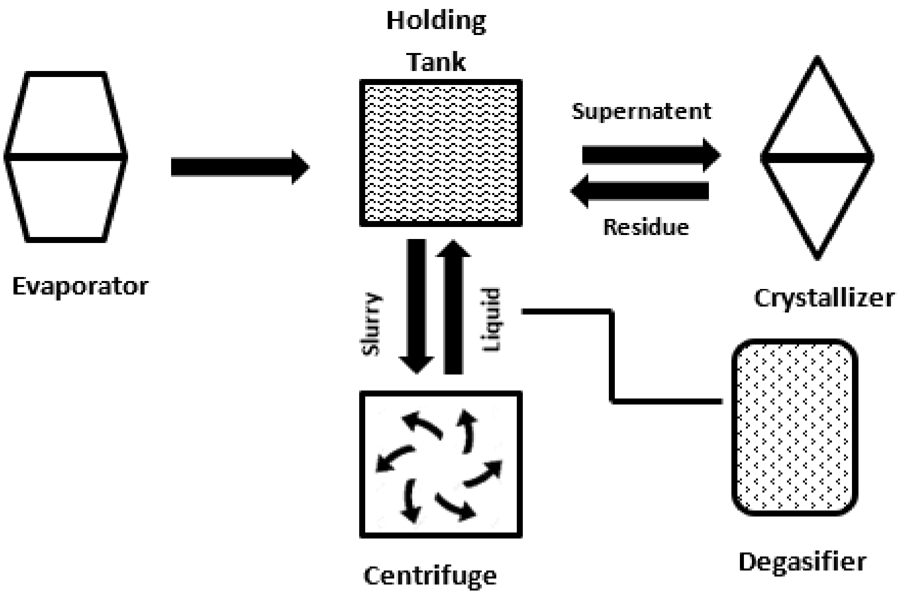


Fig.5, ZLD Evaporation/Crystallization phase