Zero Liquid Discharge using membrane distillation

- a solution to the scarcity of water

Problem to be solved

Water industry faces a problem in disposal of concentrate from water treatment processes. Zero Liquid Discharge (ZLD) systems offer solutions to concentrate disposal.

A ZLD-system produces a clean stream from wastewater suitable for reuse or for other types of recovery and a concentrate that can be disposed of as slurry or solid, or preferably reused as raw material.

ZLD systems are already in use in many instances, but they are complicated and expensive. This invention presents a simplified ZLD system.

State of the Art

Today most of the ZLD facilities are primarily industrial and power plant applications. Typical waste streams that produce large volumes of wastewater include cooling tower blow down, gas scrubber blow down, ion-exchange regeneration effluent and rinses, plant wash down and rain water runoff and process wastes. Typical industries producing these wastewaters are Power, Semiconductor manufacturing, Pulp and paper, Printed circuit board manufacturing, Plating and metal finishing, Food and beverage – in general, all industries create liquid waste.

As examples, a feed water flow to be treated in a power plant can be 5 million litres of water per day and a typical semiconductor fab consumes 1-2 million litres water per day. Both have to be of utmost purity.

For over 30 years, vapour compression evaporation has been the most used technology to achieve zero liquid discharge. Evaporation recovers about 95 % of a wastewater as distillate for reuse. Waste brine can then be reduced to solids in a crystalliser/dewatering device.

However, evaporation alone can be an expensive option when flow rates are considerable. One way to solve this problem is to integrate membrane processes with evaporation. These technologies are nowadays often combined to provide complete ZLD-systems. The most common membrane processes used so far are reverse osmosis (RO) and electro dialysis reversal (EDR).

By combining these technologies with evaporation and crystallization, ZLD-systems have become less expensive. They are combined differently depending on the circumstances. Together with these components, a variety of other well-known water treatment technologies are used in ZLD-systems for pre-treatment and polishing treatment, i.e., pH adjustment, degasifier, mixed bed ion-exchange, anion ion-exchange, cation ion exchange, oil/water separator, neutralization, oxidation (UV, ozone, sodium hypo chlorite), dissolved air flotation (DAF), carbon adsorption, anaerobic or aerobic digestion.

Water Recycling Systems in the power industry

The power-generation industry has one of the biggest wastewater streams in industry and also accounts for the largest part of the industrial wastewater recycling systems use. (Fig 1.). Most of the energy and water efficiency will evolve from the cooling tower. Cooling towers have the task of removing heat from water that is discharged from the condenser at a power plant and also to capture pollutants prior to eliminating waste into the atmosphere or ground water.

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General ZLD-system in a power plant

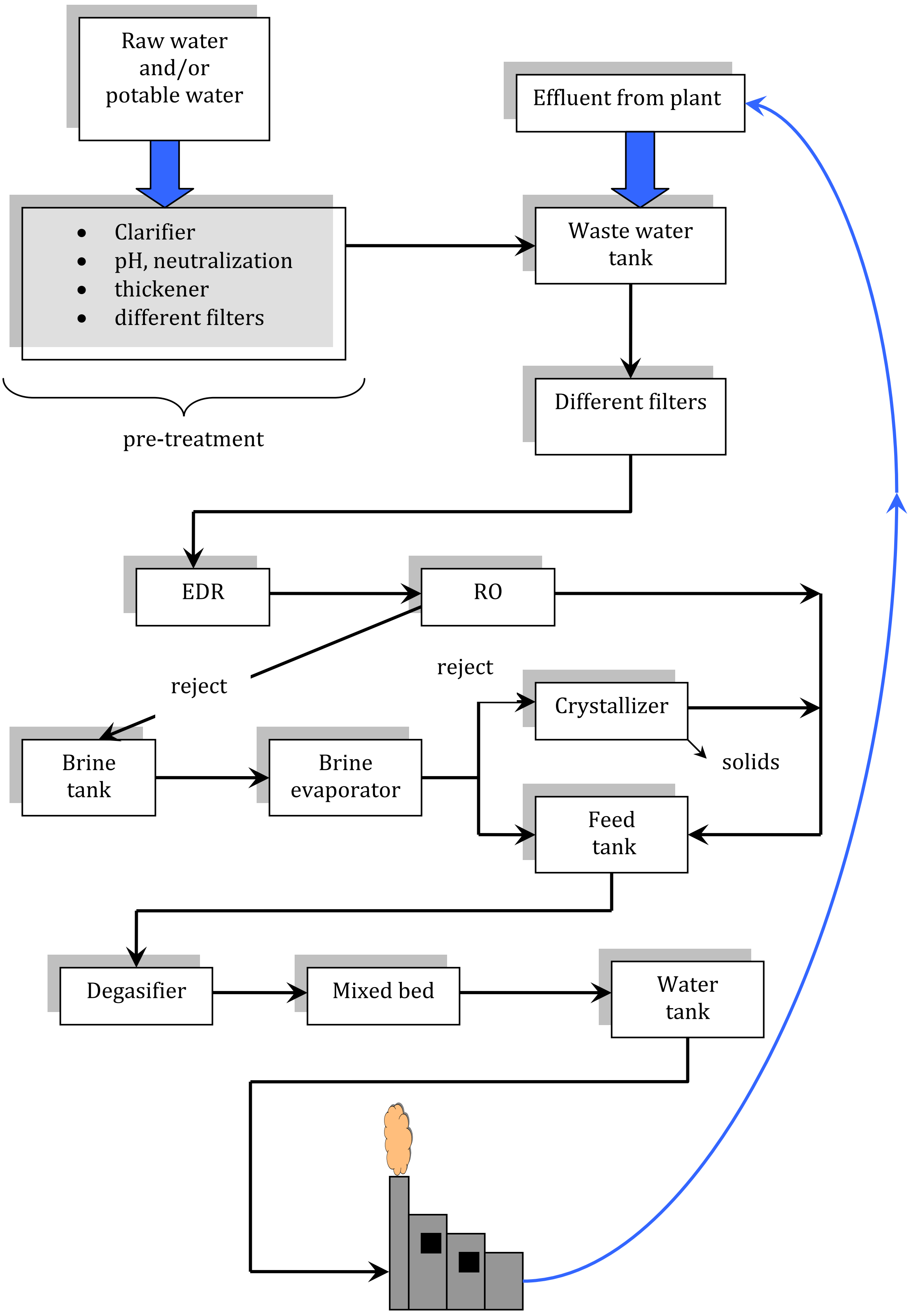

Figure 1 Example of how a present ZLD-system is integrated in a power plant.

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Reuse of Rinse Water for Semiconductor use

The economic incentive to recycle spent rinse water from an ultra pure water system is considerable. A major semiconductor manufacturer may use one or several million liter water per day, which may cost more than $6 per 1,000 liters.

The electric characteristics, including the withstand voltage of oxide film and carrier life times determine the reliability of semiconductor devices. These are improved by cleaning wafer surfaces with ultra pure water, whereby a high quality of semiconductor devices is reached.

Impurities contained in recovered raw water vary. For example, metallic ion (inorganic ion, heavy metal ion), organic matter (TOC, Total Organic Carbon), particles, colloidal silica (SiO_2), microbes and bacteria. These impurities can be removed by combining systems that have various impurities removal functions (coagulation filtration, membrane separation, ion exchange, ultra violet sterilization, degassing, biological processing, evaporative concentration, substituted reaction systems, etc.).

Quality control items for ultra pure water for a semiconductor manufacturing plant are for instance resistivity, TOC, heavy metal ion, silica and dissolved oxygen. It is important to maintain the impurities concentration at an extremely low level. Resistivity must be maintained close to the theoretical value of 18.24MΩ • cm. The TOC concentration must be less than 1 µg/l (1 part per billion - ppb).

Materials / components used are of high purity and have a minimal dissolution of contaminants.

Recovery of a large number of substances, such as hydrofluoric acid, ammonia, calcium fluoride and various metals should be possible within a ZLD system.

With a ZLD system the spent water can be reclaimed for reuse. As an example separate rinse streams can be combined with make-up water and fed to the system. The systems may operate at 90% recovery. Over 80% of the spent water, which was formerly discharged to sewer, may be recycled on a continuous basis. (Fig 2).

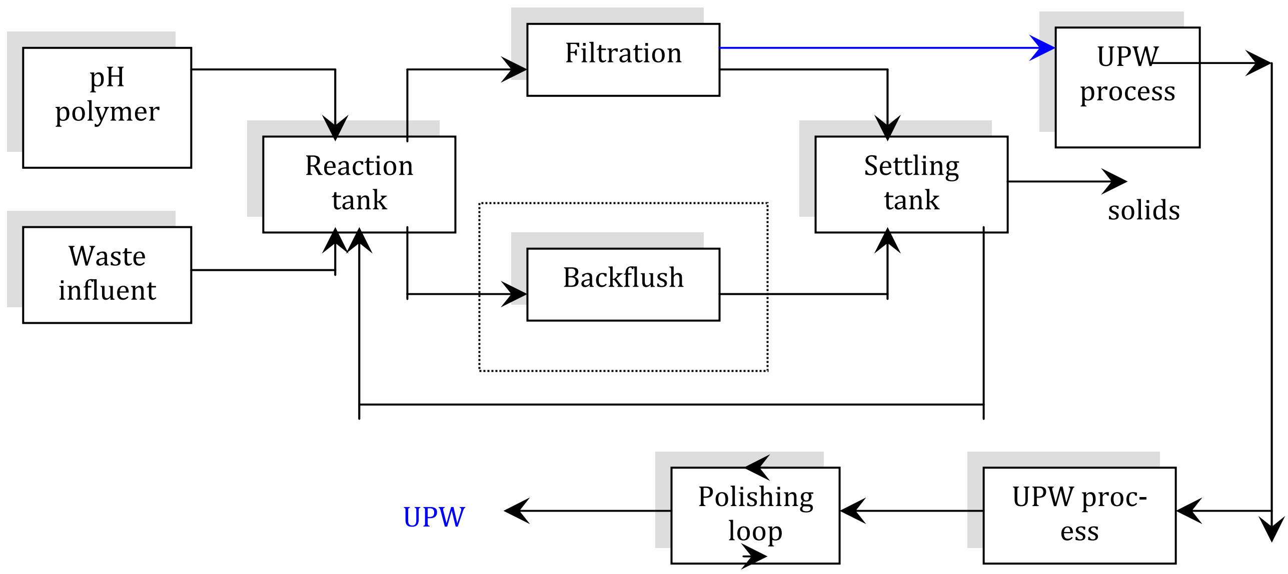

Figure 2 ZLD-system for the semiconductor industry

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An UPW-system for semiconductor rinse water must remove more than 99% of the contaminating materials. It should also be capable to reduce water usage during the semiconductor manufacturing process by up to 85% through reclaim.

The water to be recovered has to go through four recovery steps; through the reaction tank, on to the filtration, on to the back flush and finally to de-watering.

Reaction step. Influent waste water is pH adjusted, then mixed with organic and inorganic coagulant additives. The polymers react with the contaminants to form spheres. The reaction is complete in a few minutes.

Filtration. The filtration is accomplished through low pressure membranes. The clean water then exits the filter while solids are retained on the filter membrane. Operating pressures remain below 15 psi (1 bar).

Back flush. The membranes are pulsed to remove solids and then solids are pumped to a settling tank.

Solids formation/De-watering. Solids are pumped to a holding tank for further settling. Conventional filter presses can be used to further separate and de-water solids. Overflow filter press water is returned to the reaction tank.

Reuse. The treated water is then used as make up for the UPW process, containing RO and possibly a dozen other steps.

Example metal plating

In the Ni and Cr plating industry filtration may be combined with separate ion-exchange beds and an evaporator. The system can typically handle flow rates of 50 gpm. In the pre-treatment step ultra filtration (UF) is combined with carbon filter. UF is used for removal of virus and bacteria and suspended solids. The carbon filters contain granular activated carbon media that adsorb impurities, including volatile organics, within molecule-sized pores. Oxidants such as chlorine are also removed during their interaction with the carbon surface.

After pre-treatment the water passes through the polishing step, which consists of separate bed demineralises, where the salts in the water are separated into positively charged cations and negatively charged anions. Separate bed means that there are two tanks, one containing cation resin and the other containing anion resin.

The process begins when the water is passed through cation exchange resin. The cation resin is in the hydrogen form (H^+) and exchanges all the positively charged ions for hydrogen, thus converting all the impurities in the water into acids.

The water from the cation exchange is then passed through anion exchange resin. The anion resin is in the hydroxyl form (OH^-) and exchanges all the negatively charged ions into the hydroxyl form, completing the conversion of all impurities into water ($H^+ + OH^- \rightarrow H_2O$), thus providing pure demineralised water.

The concentrate is finally fed to an evaporator providing clean water for plating, thus completing the closed ZLD-system. (Fig 3).

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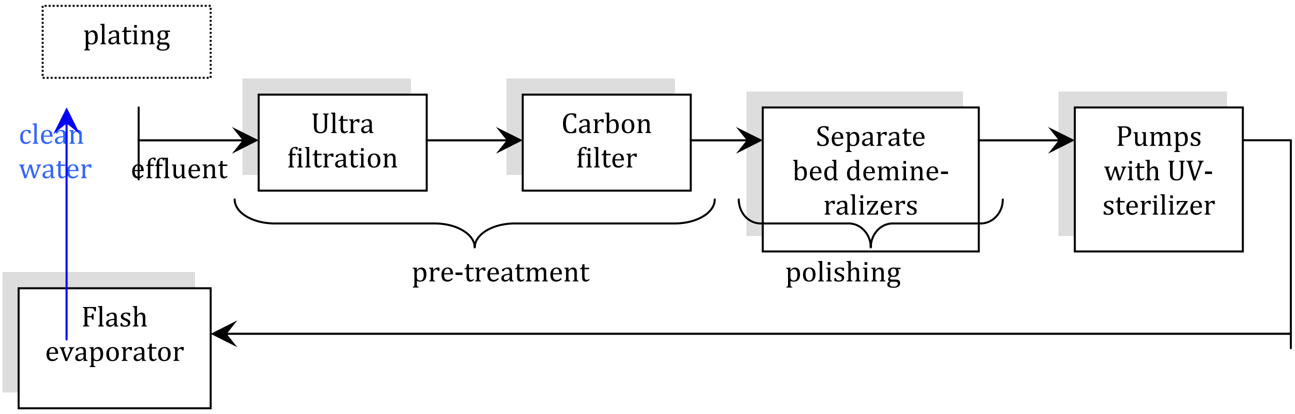

Figure 3 ZLD-system for the plating industry.

Also for desalination of sea-water

Given the right systems, the right components and the correct specifications, used water can be recovered in a ZLD system. Using a ZLD system for water produced by desalination of sea-water not only minimizes the proportion of sea-water feed needed for any given application, it also guarantees that the brine from the production from this sea-water feed does not cause environmental damage.

Selection of ZLD-systems

Characterizing the waste stream is difficult yet essential when designing a ZLD-system. It is important to start off with a realistic estimate of composition, feed chemistry and flow rate. A poorly described waste stream will likely lead to a design which is far from its optimum. The system will either be too large and expensive or too small to achieve the required separation.

The selection of the waste water flow rate typically determines the size and therefore the initial capital cost of the ZLD-system. It also determines what compositions of systems are being used. The following are general guidelines:

- Below 10 gpm of feed – crystallisers and/or spray dyers can be combined.
- 10 – 50 gpm of feed – use a crystalliser alone.
- 50 – 100 gpm of unsaturated feed – use an RO/EDR/crystalliser combination.
- 50 – 100 gpm of saturated feed – use an evaporator/crystalliser combination.
- 100 – 500 gpm of feed – either an RO/crystalliser or an evaporator/crystalliser combination may be the most economical.
- 500 – 1000 gpm of feed – all three should be used

The waste stream compositions can be measured directly, preferably on multiple occasions to characterize a range of compositions. The most common measurements today include organics, for example, chemical oxygen demand (COD), biochemical oxygen demand (BOD), total organic carbon (TOC) and inorganics (anions, cations, silica).

Depending on the process, the feed chemistry may change occasionally and sometimes unexpectedly and this may disrupt the working and even damage existing ZLD-systems.

Apart from complexity and cost, this is probably one of the greatest disadvantages of available state-of-the art systems. The proposed system is simpler and much more robust to changes in chemical composition of the feed.

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Components in ZLD-systems

RO

Reverse osmosis is a process where water is pressurized so that it passes through a semi-permeable membrane, leaving particles, dissolved inorganic salts and silica behind. As a rough guide to performance, RO can produce a concentrate containing 30000 ppm total dissolved solids (TDS). Two problems with RO are that organics will seriously foul RO systems and that RO requires a feed stream that is free of suspended solids. Because of this it is advisable to remove organics from wastewater before it enters the RO, so extensive front-end filtration equipment is required. Some membranes are pH and temperature sensitive, so pH control and feed equalization may be necessary. RO is thus a sensitive technology. However, the advantage of RO over evaporation is that the life cycle costs of RO, assuming correct pre-treatment and correct maintenance, are about half those of evaporators.

EDR

Electro dialysis reversal (EDR) is a membrane process in which electrolytes migrate across charge-selective membranes in response to an electrical field. 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. EDR differs from RO in that the ions are removed and the water is left behind, whereas in RO, the water is removed and the ions are left behind. Because of this, silica and dissolved organics are not removed with an EDR process, which is an important aspect to remember when the clean stream is reused. Like RO, EDR requires solids and organics removal from the feed for reliable operation.

Evaporator

Evaporators come in all sizes and shapes, for example; falling film-, rising film-, forced circulation-, scraped surface/thin film- and combination evaporator. Evaporators produce a distillate stream that is very clean, typically containing less than 10 ppm of TDS, which is one of the main reasons why evaporators are used in a ZLD-system. The most prevalent type is the falling film evaporator, also called brine concentrator (Fig 4). The waste produced is often treated in a filter press reducing the waste to dry solids. An evaporator may treat RO or EDR concentrates to a total solids (TS) concentration of 300 000 ppm. At this value the boiling point rise of the brine results in either an excessively large heat-transfer area (large capital cost) or an excessively large temperature difference (large operating cost). Values higher than 300 000 ppm makes the combination with a crystalliser more economical than an evaporator alone.

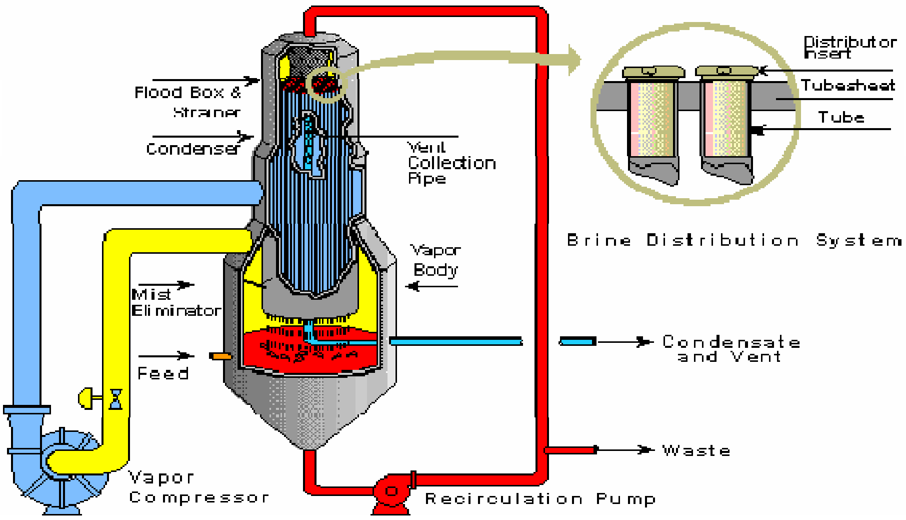

Figure 4 A falling film evaporator, also called a brine concentrator.

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Crystalliser

The crystalliser reduces highly saturated wastewater to dry solids for disposal. The last step is usually a filter press. High purity water is recovered from the crystalliser for recycling. A crystal-liser may also recover specific salts from a mixed salt waste stream. The crystalliser is a forced circulation evaporator which uses a mechanical vapour compressor or plant steam as the energy source. (Fig 5.)

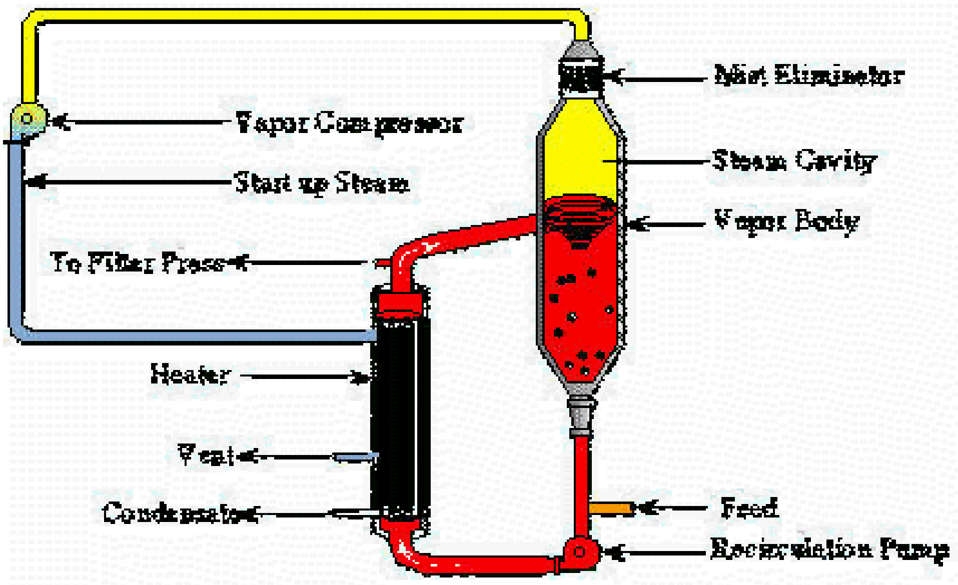

Figure 5 The heat flows in a crystalliser

Spray dryer

When a crystalliser is not appropriate, the spray dryer is another method for dewatering the concentrated slurry left over from the brine concentrator. The spray dryer transforms the slurry into a fine powder of mixed salts for disposal by atomising the wastewater slurry inside a hot chamber, instantly vaporizing the water droplets and leaving only dry salts behind. (Fig 6.)

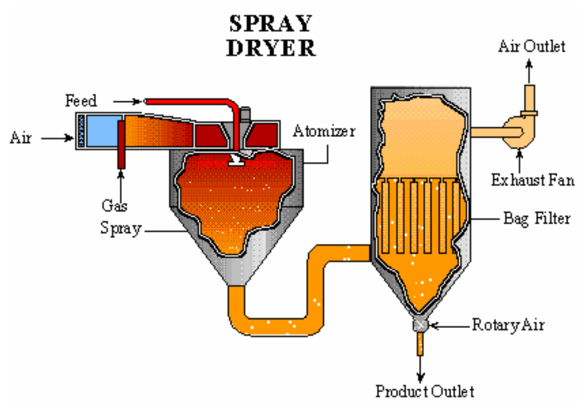

Figure 6 Spray dryer.

Use of membranes in ZLD

Membranes are expected to play critical roles in future ZLD solutions. Membrane technologies are available in a range of configurations and operating modes, and can be pressure or vacuum-

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driven, or use electrical potential as the driving force as in the case of EDR membranes. The membrane technologies commercially available today consist of the following:

- Micro filtration (MF) membranes – used for removal of suspended solids and bacteria.
- Ultra filtration (UF) membranes – used for volatile organics and virus removal, as well as the removal capabilities listed for MF membranes.
- Nano filtration (NF) membranes – used for water softening and sulphate removal.
- Reverse osmosis (RO) membranes – used for salt removal for brackish and seawater.
- Electro dialysis reversal (EDR) membranes – used for salt removal for brackish water.

The prevalent membrane technologies used to day in ZLD-systems are RO and EDR. These technologies have both advantages and disadvantages. One possible solution instead of RO and EDR is MD technology.

Membrane Distillation

Membrane Distillation (MD) is a new unit operation that uses hydrophobic membranes as a barrier for contaminated water from which mass transport of vapor is driven by differences in vapor pressure. Temperature levels are such that low-grade heat sources may be used to supply the required energy to the process. Unlike other membrane processes, MD does not require a mechanical pressure pump and is not limited by the osmotic pressure.

The advantages of MD are 100% (theoretical) rejection of ions, macromolecules, colloids, cells, and other non-volatiles, lower operating temperatures than conventional distillation, no vacuum is used, lower operating pressure than conventional pressure-driven membrane separation processes, low sensitivity to variations in process variables (e.g. pH and salts), good to excellent mechanical properties and chemical resistance, lower capital costs as compared to RO (Reverse Osmosis) and distillation, and opportunity to use waste energy from sources with temperatures below 100°C.

The disadvantages of MD are, high energy intensity, volatiles cannot be completely separated unless degassing module is added, membranes used are sensitive for surfactants

In summary the technology specifications are: ambient pressure and low temperature means no metals – and no metals means no corrosion – and low capital cost. Waste heat power means minimal exergy use. No chemicals, filters and other consumables mean low running cost. Fully automated operation means complete safety. Minimal sensitivity to changes in composition of feed means reliable performance.

In practical systems, water is first passed through a pre-treatment filter in order to remove solid particulate matter. Volatiles are then removed in a degasser and, finally, non-volatiles in the MD – module.

Installed equipment will be able to remove all conceivable contaminants from sea-water, brackish water, industrial and municipal effluents and from contaminated ground- and surface water. It produces Ultra Pure Water from any feed.

Typical test results for Membrane Distillation

Test results prove that MD is more efficient in separating non-volatile contaminants/components from water than conventional distillation or RO. The following results for various types of contaminants are typical.

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1. Water, containing 3.4 mg/l of chlorine. After treatment, the content of chlorine was below detection level, i.e. below 0.01 mg/l. *Photometric analysis (Perkin Elmer) by the Water Protection Association of South West Finland.*

2. Water containing 1.000 µg/l of trihalomethanes. After treatment, the content of trihalomethanes was below detection level, i.e. below 1 µg/l. *Gas Chromatography by the University of Turku, Finland.*

3. Water containing 31.000 ppm of chloride. After treatment, the content of chlorides was below detection level, i.e. below 1 ppm. *Ion Chromatography by VBB Viak in Stockholm, Sweden.* Conductivity of permeate in test 3 was measured to 0.24 mS/m at 25 degrees – i.e. 4 MegOhm. *Kemotron Tetramatic by VBB Viak, Stockholm, Sweden.*

4. Water with a 134 Cs activity of 2.4 Bequerel. After processing, the activity was below detection level, i.e. below 0.1 Bq. Also tests with Radium, Strontium and Plutonium were below detection levels. *Lithium Drifted Germanium Detector by the Radiation Physics Department, Lund University, Sweden*

5. Water containing large amounts of Bacteria. After two days, the number of bacteria was measured in both feed and treated water and then again after seven days. The results were as follows:

Number of bacteria per milliliter	Feed water	Treated water
after 2 days	3.300	0
after 7 days	14.000	0

Membrane filter count by the National Bacteriological Laboratory of Sweden in Stockholm.

Variations of the technology

The basic technology described above is a variation of MD called Air Gap Membrane Distillation (AGMD) but there are also other possible variations of the technology. By using vacuum instead of atmospheric pressure on the retentate side, production can be increased considerably, but a trade-off is more complicated construction and more advanced materials.

Instead of Air-Gap also "Direct Contact MD" is possible, i.e. wherein the vapour condenses directly into a cooling stream instead of on a film that is indirectly cooled as in AGMD.

Another variation is "Sweeping Gas MD" where the vapour is transported from the down-side of the membrane by a gas stream to be condensed in another location.

All these variations can also be included in different configurations forming module types that are common in membrane technology, such as plate and frame, spiral wound and hollow fibre.

The advantages of MD in a ZLD-context

A ZLD-system built on MD technology is less complicated than state-of-the art-systems in that an MD module plus a degasser theoretically executes complete removal of all contaminants in water. (Fig. 7)

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Example of a ZLD-system containing a MD-module

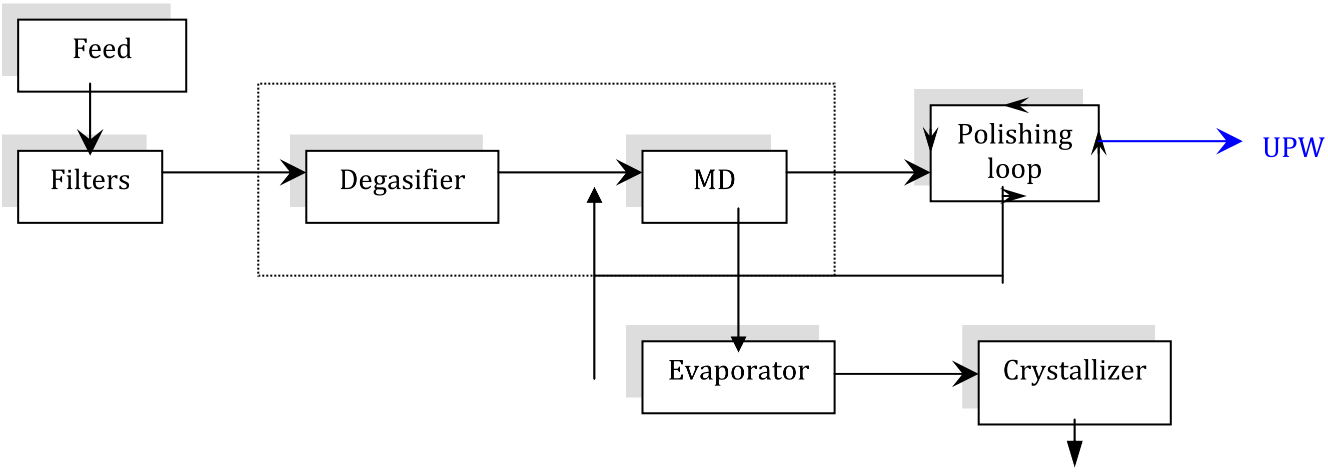

Figure 7. The MD technology integrated into a ZLD-system

The MD unit is not sensitive for high or low pH or for changes in pH and it is not sensitive for any other changes in the feed chemistry. Mo matter what feed, the purity of the water is even and constantly higher than for state-of-the-art systems of similar and higher complexity.

A complete MD ZLD-system guarantees complete purity of water both for absolutely safe human consumption for the most exacting industrial use. At the same time it achieves a complete recovery of water and deposition or reuse of the contaminants. An example of such a system is shown in Fig. 8.

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Example of use of MD-ZLD system

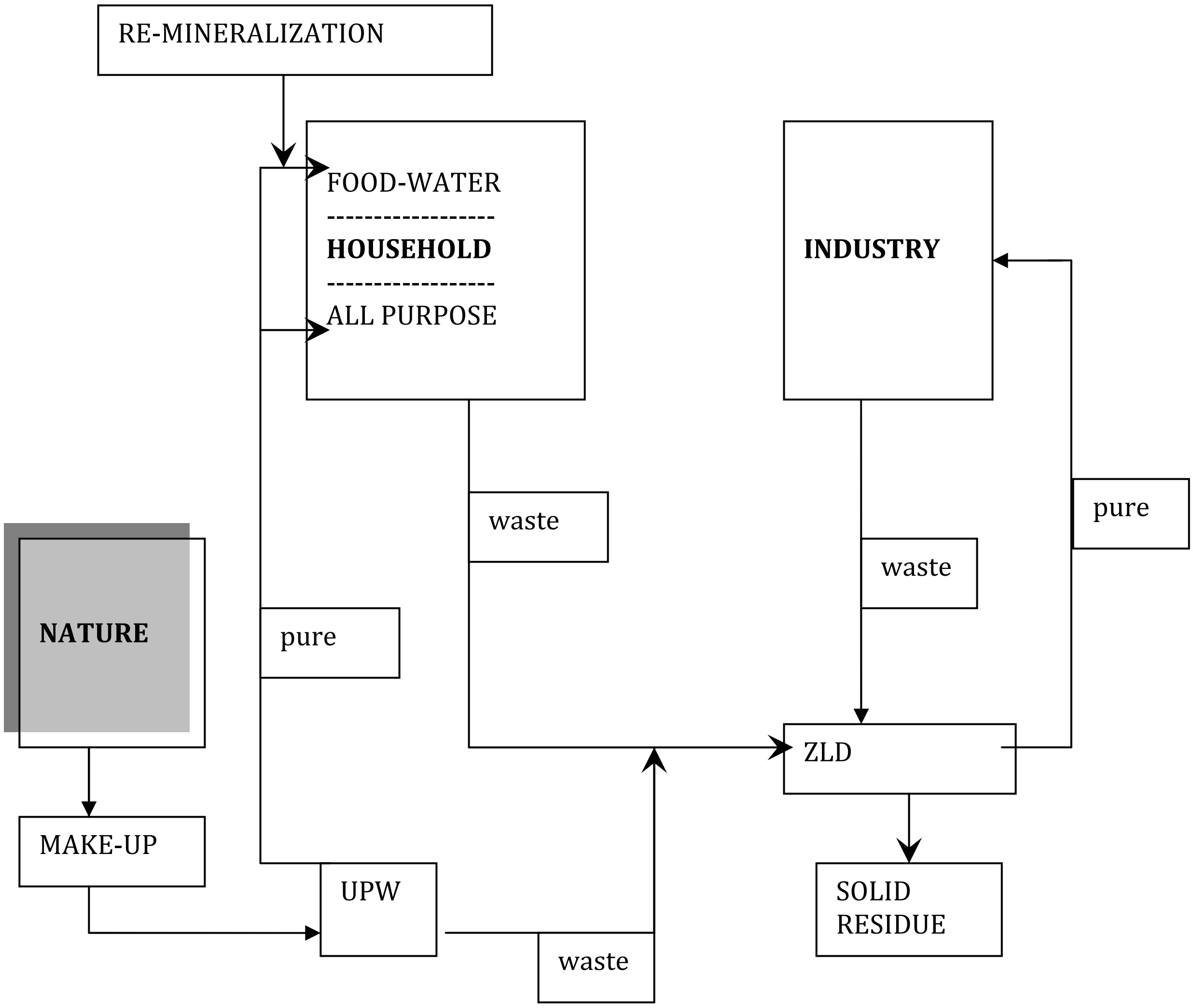

Figure 8. Example of a complete ZLD system

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