CHALMERS
UNIVERSITY OF TECHNOLOGY

Discussion of Zero Liquid Discharge as a solution for desalination brine management

A case study at Desolenator's project in Dubai

Master's thesis in Infrastructure and Environmental Engineering

Thekla Eleonore Hövel

DEPARTMENT OF ARCHITECTURE
AND CIVIL ENGINEERING

CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2021
www.chalmers.se

MASTER'S THESIS ACEX30

Discussion of Zero Liquid Discharge as a solution for desalination brine management

A case study at Desolenator's project in Dubai

Master's Thesis in the Master's Programme Infrastructure and Environmental Engineering

Thekla Eleonore Hövel

Department of Architecture and Civil Engineering
Division of Water Environment Technology
CHALMERS UNIVERSITY OF TECHNOLOGY

Göteborg, Sweden 2021

Discussion of Zero Liquid Discharge as a solution for desalination brine management
A case study at Desolenator's project in Dubai

Master's Thesis in the Master's Programme Infrastructure and Environmental Engineering

THEKLA ELEONORE HÖVEL

© THEKLA ELEONORE HÖVEL, 2021

Examensarbete ACEX30
Institutionen för arkitektur och samhällsbyggnadsteknik
Chalmers tekniska högskola, 2021

Department of Architecture and Civil Engineering
Division of Water Environment Technology
Chalmers University of Technology
SE-412 96 Göteborg
Sweden
Telephone: + 46 (0)31-772 1000

Department of Architecture and Civil Engineering
Göteborg, Sweden, 2021

Discussion of Zero Liquid Discharge as a solution for desalination brine management

A case study at Desolenator's project in Dubai

Master's thesis in the Master's Programme Infrastructure and Environmental Engineering

THEKLA ELEONORE HÖVEL

Department of Architecture and Civil Engineering
Division of Water Environment Technology
Chalmers University of Technology

ABSTRACT

Desalination is forecasted to have a key role in narrowing the worldwide water demand-supply gap. However, the negative environmental impact of desalination due to brine discharge is a major drawback. The recycling of brine following the Zero Liquid Discharge (ZLD) approach has been recently proposed as a sustainable brine management solution. The extraction of water and resources from the brine while producing valuable solids is considered to be an essential strategy to fulfil the water-supply and resource gap. A broader application of these ZLD technologies is currently limited because the technologies are still associated with very high capital and operation costs, custom-design on a case-to-case basis, and difficulties to deal with complex streams.

This report detailly summarizes conventional and emerging ZLD and resource recovery technologies to provide guidance for brine management aiming to decrease the environmental impact of desalination. Limited information concerning the actual economic data (capital and operation cost) of ZLD technologies have been identified. Thus, a market survey is conducted to assess the techno-economic data of commercially available ZLD technologies. The gained knowledge is applied to design and assess the best fitting ZLD chain for Desolenator's project in Dubai, the United Arab Emirates, using real-life feedwater data. Three different ZLD treatment chains have been designed considering the water composition, process performances, and market availability. The conducted multi-criteria analysis which includes environmental, social, economic, and technical dimensions, showed that the proposed traditional thermal ZLD chain is expected to have the least impact at Desolenator's project site. The subsequent techno-economic analysis concluded that the proposed treatment chain is just economically feasible if additional revenue via salt recovery is achieved.

Knowing the technical, environmental, social, and economic data of conventional and emerging ZLD technologies and systems is essential. Further research in the field to assess such data in combination with the development of less technically complex and cost intensive ZLD technologies is needed for a broader application of ZLD as a brine management solution worldwide. This is a worthwhile task for the future to decrease the environmental impact of desalination and lead to an increased contribution against the growing water scarcity.

Keywords: Desalination, brine management, Zero Liquid Discharge, Minimal Liquid Discharge, brine mining, resource recovery

Contents

List of Figures

List of Tables

Preface

This master's thesis was a part of the double degree master's program in M.Sc. Infrastructure and Environmental Engineering at Chalmers University of Technology and M.Sc. Water Resource Engineering and Management at University Stuttgart and was carried out individually. This project is done in collaboration with Desolenator who accepted the project and has provided background information and support on technological and social aspects.

Firstly, I would like to thank all three parties for giving me the opportunity to conduct this research. Many thanks to my examiner and supervisor Dr. Frank Persson at Chalmers University of Technology for the support and guidance I received beforehand and throughout the thesis process. Special thanks to Dr. Jiajun Cen and Catriona McGill at Desolenator for patiently answering all my questions and providing me with all the background knowledge. Finally, big thanks to my supervisor Dr. Carsten Meyer at University Stuttgart for all the academic help beforehand and throughout the thesis process. Without the flexibility and collaboration of Frank, Jiajun, Catriona, and Carsten, I would have not been able to successfully finish this thesis. Thank you for letting me explore my topic of interest and for challenging and training me in intercultural working.

I would also like to send my gratitude to Anne Weiß at University Stuttgart who has motivated me to enroll in this double degree program and to fully explore my opportunities.

Finally, thank you to my family and friends for being patient and supporting me during my days of absence in Sweden and the Netherlands.

Maastricht, January 2021

Thekla Eleonore Hövel

Abbreviations

APS	Accelerated Precipitation Softening
ASE	Advanced Solar Evaporator
BAC	Biological Activated Carbon
BC	Brine Concentrators
BCr	Brine Crystallizers
BW	Brackish water
CAPEX	Investment/Capital cost
COD	Chemical oxygen demand
DOC	Dissolved organic carbon
ED	Electrodialysis
EDM	Electrodialysis Metathesis
EDR	Electrodialysis Reversal
EFC	Eutectic Freeze Crystallization
EV	Evaporators
FBBR	Fluidized Bed Bioadsorber Reactor
FO	Forward Osmosis
GHG	Greenhouse gases
HDH	Humidification – Dehumidification
HPRO	High-Pressure Reverse Osmosis
IEX	Ion Exchange
MCA	Multi-criteria analysis
MCR	Membrane Crystallization
MD	Membrane Distillation
MED	Multi-Effect Distillation
MLD	Minimal Liquid Discharge
MSF	Multi-Stage Flash Distillation
MVR or MVC	Mechanical Vapor Recompression or Mechanical Vapor Compression
NF	Nanofiltration
OARO	Osmotically Assisted Reverse Osmosis
OPEX	Operation cost
PV-T	Photovoltaic–Thermal Collectors
RO	Reverse Osmosis
SBT	Soil Biotechnology
SD	Spray Dryer
SW	Seawater
TDS	Total dissolved solids
TEA	Techno-economic analysis
TOC	Total organic carbon
TSS	Total suspended solids
TSSE	Temperature Swing Solvent Extraction
TVR	Thermal Vapor Recompression
UF	Ultrafiltration
VSEP	Vibratory Shear Enhanced Processing
WAIV	Wind-Aided Intensified Evaporation
ZLD	Zero Liquid Discharge

1 Introduction

Water is the irreplaceable basis of all life on earth leading to extreme ecological, social, and economic importance. The worldwide population growth as well as the related water consuming and contaminating activities and lastly, climate change exert pressure on freshwater sources and exacerbating water scarcity in most world regions. The UNESCO World Water Assessment Programme (2020) states that around four billion people experience currently severe physical water scarcity for at least one month per year and by 2050, at least one in four people is likely to live in a country affected by chronic or recurring shortages of freshwater. The conventional approaches as collecting rainfall and river runoff applied in water-scarce areas are becoming to be insufficient to meet human demands. New and unconventional strategies as desalinated water are according to Jones et al. (2019) forecasted to be a key role in narrowing the water demand-supply gap.

1.1 Desalination

Desalination is defined as the process of salt removal from water by separating the feedwater intake into freshwater and concentrate stream. According to Jones et al. (2019), six feedwater sources can be used for desalination which differ in Total Dissolved Solids (TDS) concentration. Seawater (SW) has the highest TDS concentration (20,000 – 50,000 ppm TDS) and is the most common feedwater source accounting for 61 % of desalinated water on the global market in 2019 as seen in Figure 1-1 (Jones et al., 2019).

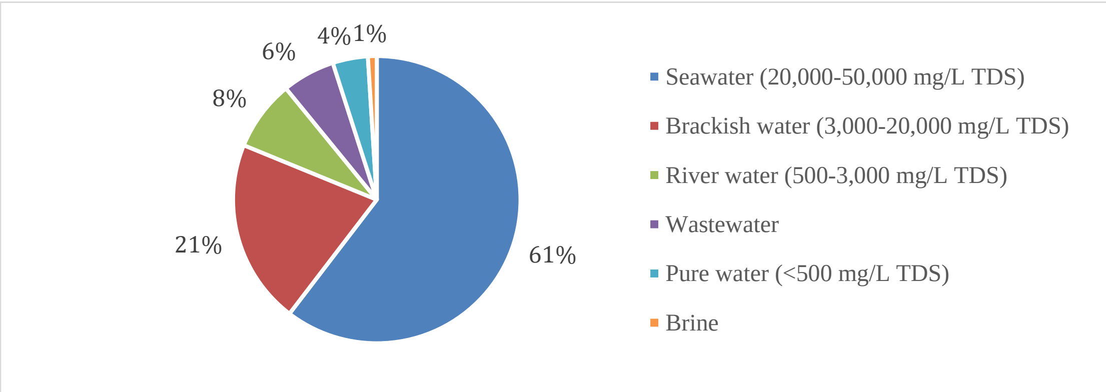

Figure 1-1: Global desalination installation capacity by water source in 2019 (based on (Jones et al., 2019))

The capacity of global installed desalination has steadily expanded from 2010 to 2019 at a rate of 7% per year, whereof SW and brackish water (BW) desalination had the highest capacity increase (Eke et al., 2020; Jones et al., 2019). The remaining need for the improvement of new freshwater supplies to meet the human demand will further lead to an increasing trend in global desalination capacity according to Missimer & Maliva (2018).

However, the majority of the currently in use desalination processes are associated with high capital and maintenance costs and negative impact on the environment due to high energy consumption and wastewater discharge (Pistocchi et al., 2020).

The high energy consumption during the desalination process results in the emission of greenhouse gases (GHG) if fossil fuels are used (Garg & Joshi, 2015). Pistocchi et al. (2020) state that until now it has not been sufficiently noted that desalination can be

100 % decarbonized by using renewable energy sources as solar energy. Another advantage of solar-driven desalination is the possibility of implementing plants in water-scarce remote regions, where the connection to the public electrical grid is not given, unreliable, or not cost-effective (Garg & Joshi, 2015). Thus, solar-driven desalination has a huge potential to environmentally friendly produce drinking water in water scare arid and semi-arid areas.

The outfall of the concentrate stream, called brine, is considered to be the major challenge associated with desalination technology (Jones et al., 2019). The safe discharge and/or treatment of the brine remains a major technical and economic challenge (Missimer & Maliva, 2018).

Desalination can be a promising water production process to meet the worldwide water demand if the environmental impact of brine disposal and energy consumption can be reduced in an economically feasible way (Pistocchi et al., 2020).

1.2 Desolenator

Desolenator is a clean-technology start-up company with offices in the United Kingdom, Netherlands, and United Arab Emirates (UAE) (C. McGill, personal communication, September 9, 2020). The start-up was founded in 2013 and developed a solar-driven thermal desalination technology. So far, Desolenator offers three products: Household Model (~ 20 L/day), Kiosk Unit (~100 L/day), and Community Model (~25 m^3/day). The company is aiming to provide in future a model that can serve 250 m^3/day of drinking water. The flow scheme of the community model can be seen in Figure 1-2

Desolenator’s approach differs from conventional desalination plants in the following aspects: The used technology harnesses both thermal and electrical energy for a process of optimized distillation, creating carbon-neutral water through 100 % solar energy (C. McGill, personal communication, September 9, 2020). Due to the storage of solar-generated heat and electricity, is the system able to operates 24 hours 7 days a week. Furthermore, the technology creates water closer to the end-user and substitutes the need for an entire water supply chain. The elimination of external energy, filters, and membranes and low maintenance of the entire water supply chain makes it possible to offer the Lowest Levelized Cost of water of US$ 1/m^3. To increase the sustainability of the system, Desolenator is interested in sustainable and economic-feasible brine management (C. McGill, personal communication, September 9, 2020).

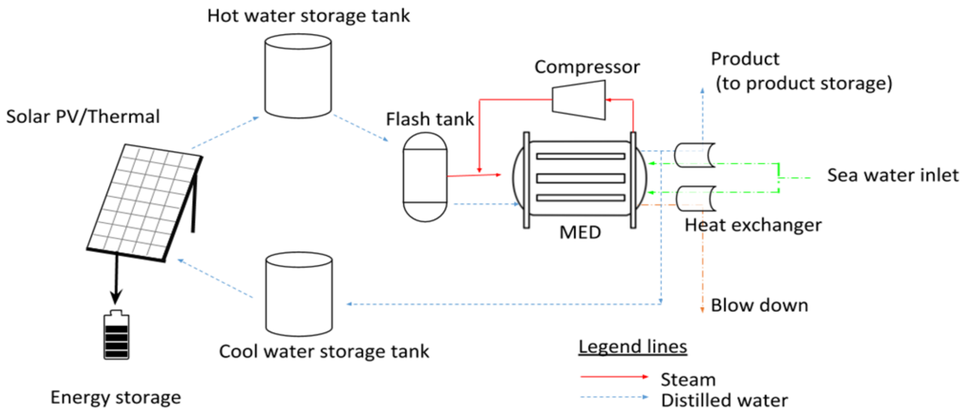

Figure 1-2: Schematic flow diagram of Desolenator’s Community Model (C. McGill, personal communication, September 9, 2020)

1.3 Brine Management

Brine management is classically associated with disposal including surface water discharge, sewer system blending, deep well injection, land application, and evaporation ponds (Ghernaout, 2019). Detailed descriptions of the environmental concerns associated with each disposal method can be found i.e. in Mezher et al. (2011). Many scientific investigations proofed the ecological disaster of brine disposal on soil deterioration, groundwater qualities, and the aquatic medium and organisms (Ghernaout, 2019). As an example, the salinity of the Arabian Gulf which is already used for large desalination capacity is expected to increase by some extra 2.24 mg/L by the year 2050 due to untreated brine discharge back to the sea, which could lead to the death of sensitive elements of the biota and marine organisms (Missimer & Maliva, 2018).

Different methods approaching brine recycling are considered to be crucial both for environmental and economic aspects (Ghernaout, 2019). The so-called Zero-Liquid-Discharge (ZLD) is the most known recycling technique, where theoretically all water is recovered, and contaminants are reduced to solid waste. Currently, several scientific papers are discussing the possibility of additional resource recovery e.g. minerals, nutrients, and metals from the brine in order to fulfil the present and future gap in the resource market and to offset the costs of the brine treatment and desalination itself (Pistocchi et al., 2020).

ZLD is currently just applied for few inland desalination facilities (Pistocchi et al., 2020). A broader application of these technologies is currently limited because the technologies are still associated with very high capital and operation costs, custom-design on a case-to-case basis, and difficulties to deal with complex streams (Freger, 2014). However, environmental regulations on the discharge of specific solutes and the connected growing social responsibility and education towards awareness of environmental issues motivate the implementation of ZLD for desalination brine management. An additional driver is the worldwide growing water scarcity and stress with the still negligible rate of wastewater recycling.

1.4 Aim and research question

This research aims to provide guidance for brine management to decrease the environmental impact of desalination worldwide. An investigation of all brine management options following the ZLD approach will be conducted. The implementation and maintenance requirements, market availability including technical and economic data will be assessed for such technologies. Additionally, the applicability of resource recovery technologies will be discussed also under consideration of current market availability, requirements, and technical data.

The retrieved knowledge will be used to develop brine management solution(s) that fit(s) and integrate(s) optimally to the Desolenator's pilot project in Dubai (UAE) as a specific case study. The solutions will be presented with relevant design steps. Therefore, the real-life water data of the projects as well as the site conditions will be analysed. The proposed solution(s) will be evaluated through a multi-criteria analysis (MCA) and techno-economic analysis (TEA).

The following research questions are formulated to assist in reaching the aim and are answered throughout the research:

1. What ZLD technologies exist for brine management?
2. What technologies and alternative methods exist to recover resources from brine?
3. What are the appropriate treatment options for waste produced during brine treatment?
4. What are the implementation and operational requirements of these technologies and methods? If needed, could the electricity be provided by renewable energy as photovoltaic–thermal (PV-T) collectors?
5. Are all these technologies and methods available on the global market? If so, who are the providers and what are the cost and reimbursement of brine management?
6. What brine management system(s) fit(s) optimally to the Desolenator technology under consideration of techno-economic, social, and environmental aspects?

The final research question which will motivate the installation of brine management is:

- Is the implementation of a brine management system at Desolenator's pilot plant economically profitable? If so, at what point does it breakeven?

Additionally, a hypothesis is formulated based on the status of knowledge which is going to be proofed correctly or false throughout the research study.

If ZLD systems are not only focusing on recovering freshwater but also resources, THEN it can be possible to create an economically feasible treatment chain BECAUSE the revenue is higher than the cost.

1.5 Limitations

Limitations refer to the limitation on data and calculation simplification. The process performance and energy demand of the proposed ZLD chains have been calculated under a variety of assumptions as seen in Chapter 3.3. Nevertheless, the validation of the calculated data has been done by comparing literature values and it has been found that despite the chosen assumption the calculated energy demand is similar to the literature values. However, the fluctuation of process performance has been neglected and thus the calculated processes just reflect a static value.

Missing economic, environmental, social, and technical data of ZLD technologies limited the qualitative analysis via multi-criteria and techno-economic of the proposed treatment chain(s). Missing data have been discussed on literature values and objective perspective. Validation of the results could not be made due to limited resources.

Due to the missing data of water composition, economic, environmental, social, and technical factors as well as the calculation simplification, the results of this study can be thus just seen as a basis for a more accurate discussion on ZLD including a detailed process performance modelling.

2 Literature review

2.1 Brine characteristics

Brine, also called concentrate or reject, is the highly concentrated water generated as a by-product of desalination processes. In general, brine consists of most of the dissolved solids such as heavy metals, nutrients, organic and microbial contaminants, pathogenic microorganisms of the feedwater as well as chemicals added during the pretreatment step (as antiscalants, coagulants, and flocculants) (Katal et al., 2020; Panagopoulos et al., 2019).

The brine quantity is dependent upon the desalination plant size and the water recovery rate, which is defined as the percentage of the volume of freshwater generated to the total volume of feedwater (Panagopoulos et al., 2019). The water recovery rate depends on the applied desalination technology and the feedwater source quality including salinity. A higher water recovery rate results in smaller brine volumes with higher salinity and contaminant concentration and vice versa (Panagopoulos et al., 2019). Meanwhile, the brine quality depends on the feedwater quality, salt rejection of the membranes (if membrane-based technologies are used), pretreatment steps, and the water recovery rate.

The constituents of concern in brine, which could harm the process performance and lead to a limited water recovery rate according to Charisiadis (2018) are shown in Table 2-1. Chemicals as acids, antiscalants, and biocides are commonly added in a pretreatment step of the desalination plant to improve the water recovery rate and avoid system failure (Panagopoulos et al., 2019). Katal et al. (2020) state that the addition of acids, antiscalants, and biocides has a direct consequential effect on the equilibria of the dissolved constituents. The matrix of the brine can therefore differ in constituents` concentration and characteristics even using the same feedwater and process. It can be concluded, that differences in brine composition occur due to the variation in feedwater quality, chemicals, and various operating conditions of the desalination technologies (Panagopoulos et al., 2019).

Table 2-1: Typical constituents of concern in brine (based on (Charisiadis, 2018))

Sodium (Na^+)	TDS/TSS	Phosphate (PO_4^{3-})	Strontium (Sr^{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	-

82 % of the feedwater used in desalination is SW and BW (Jones et al., 2019). The characteristics and ion composition of 16 different brines from various desalination plants using SW and BW can be obtained from Table 2-2 (Panagopoulos et al., 2019) Despite small variances, large amounts of sodium (Na^+) and chloride ($Cl^{-)}$, with other ions such as calcium (Ca^{2+}), magnesium (Mg^{2+}), and sulfate (SO_4^{2-}) are in the brine obtained from SW desalination plants. Such a conclusion cannot be made for BW desalination plants. The ion composition of BW desalination plants highly differs due to the difference in the feedwater origin, salt concentrations, and the water recovery rate in the desalination process.

Table 2-2: Characteristics of brine from various desalination plants (Panagopoulos et al., 2019)

Source	Technology	EC (mS/cm)	TDS (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^{+} (mg/L)	K^{+} (mg/L)	Cl^{-} (mg/L)	SO_4^{2-} (mg/L)	HCO_3^{-} (mg/L)	PO_4^{3-} (mg/L)
Brackish water	RO	–	7500	1032	318	991	–	2823	1553	576	0.4
	RO	–	17,500	819	386	5130	–	8960	1920	223	2
	RO	15.54	10,927.72	959.4	378.5	2024	70.4	4817	2560.3	–	–
	RO	11.5	7890	1030	515	879	–	3346	991	1013	–
	RO	19.2	14,800	612	326	3922	62	4440	3964	1354	–
	RO	24.9	21,035	1371	1348	3858	33	8018	4811	1362	0.8
	EDR	13.1	9579	960	344	1150	422	3443	1344	885	–
	RO	38.7	34,885	1855	1556	7359	241	14,428	8366	863	0.6
Seawater											
	RO	–	50,200	625	2020	15,500	–	20,250	–	199	–
	RO	85.2	79,660	960	2867	25,237.28	781.82	41,890	6050	1829	–
	MSF	76.8	57,400	521	1738	18,434	491	32,127	4025	–	2.5
	RO	–	55,000	879	1864	15,270	–	31,150	5264	432	–
	RO	–	70,488	790	2479	21,921	743	38,886	5316	173	–
	RO	–	68,967	845	2550	21,070	784	38,014	5342	274	–
	RO	–	80,028.4	891.2	2877.7	24,649.2	888	43,661.5	6745.1	315.3	–
	MSF	93.7	81,492	725.4	2504.8	20,993.4	739.7	35,377.9	–	–	–

Even though the displayed ions in Table 2-2 are the most known ones, SW and thus SW brine respectively contains almost all elements from hydrogen to uranium in the periodic table (Mavukkandy et al., 2019). The extraction of minerals from RO brine started in the 1990s and until now the research focus of resource harvesting of brine remains on RO brine (Shahmansouri et al., 2015). Historically, table salt (sodium chloride), and the by-products potassium chloride, magnesium salts, and bromide salts are extracted via evaporation (Mavukkandy et al., 2019). The development of resource recovery from seawater and brine is displayed in Figure 2-1.

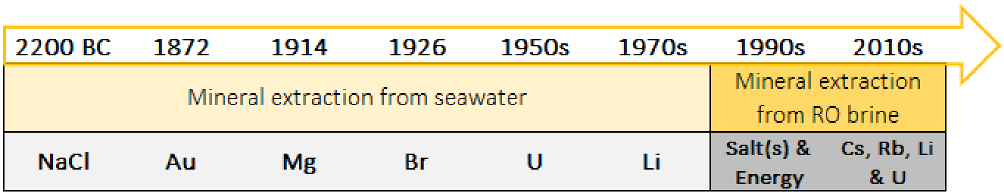

Figure 2-1: Timeline representing the development of resource recovery from seawater and brine (based on (Mavukkandy et al., 2019))

2.2 Zero-Liquid-Discharge technologies

Zero Liquid Discharge (ZLD) is the recycling strategy where all liquid is removed/recovered from the brine producing clean water and solid waste (Charisiadis, 2018; Giwa et al., 2017). The recovery of the highly concentrated last 5 to 10 % of the water is both operating and capital cost-intensive and in many cases doubles the treatment costs (see Chapter 2.5) (Perry, 2016). The approach of recovering up to 95 % of the water from the brine is called Minimal Liquid Discharge (MLD). MLD is discussed as an alternative to ZLD due to the higher economic feasibility of the system while following the same idea and using the same technologies (Giwa et al., 2017). ZLD systems consist in general of three treatment steps: pretreatment step (I), pre-concentration (II), evaporation/crystallization (III) as seen in Figure 2-2 (Panagopoulos & Haralambous, 2020). MLD systems differ from ZLD, as they miss the last treatment step and thus consist just of pretreatment (I) and pre-concentration (II) (Charisiadis, 2018; Panagopoulos & Haralambous, 2020). However, the implementation of each treatment step depends highly on the water characteristics.

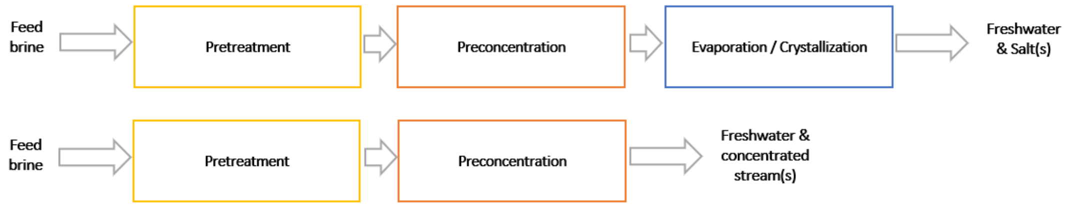

Figure 2-2: Treatment stages of a ZLD framework (top) and MLD framework (bottom) (based on (Panagopoulos & Haralambous, 2020))

Similar to desalination technologies, ZLD treatment technologies are based on pressure-driven and electrical potential-driven membranes, thermal-based technologies, and other technologies (Giwa et al., 2017). In general, low-salinity brines produced by BW and wastewater feedwater sources, tend to be treated with a membrane-based ZLD/MLD approach including intensive pretreatment. On the other hand, high-salinity brines are treated commonly with only thermal ZLD methods and incorporate regular to no pretreatment (Giwa et al., 2017). The intensive pretreatment in membrane-based approaches is needed as the membrane permeability decreases by certain water constituents resulting in increased operating and maintenance costs and could lead to system failures (Muhammad & Lee, 2019). The pretreatment and treatment technologies used for a ZLD system are classified in Figure 2-3. Throughout this chapter, the displayed technologies are introduced.

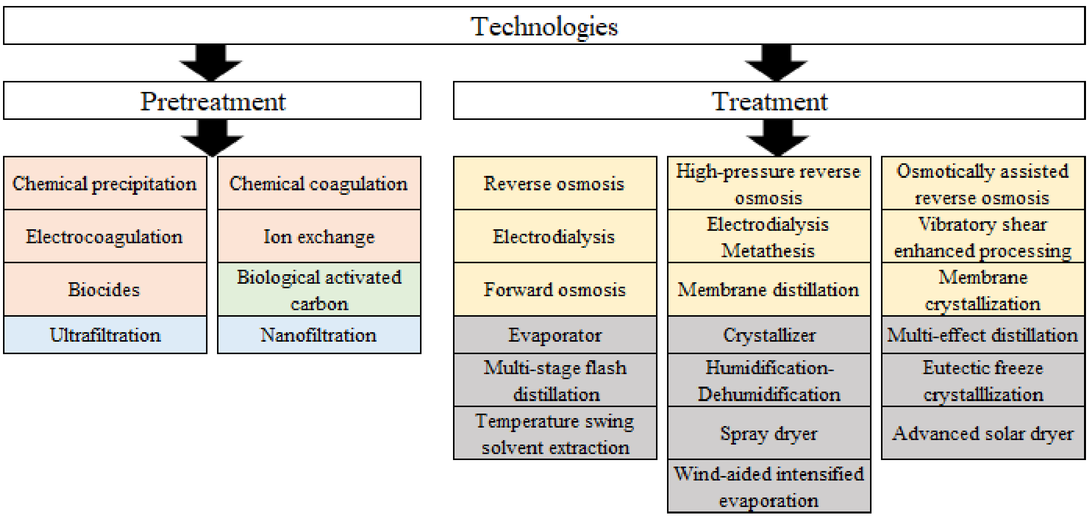

Figure 2-3: ZLD technologies classified in pretreatment (chemical=orange, biological=green, physical=blue) and treatment (membrane=yellow, thermal=grey)

2.2.1 Pretreatment technologies and their removal efficiency

Pretreatment is meant to remove all constituents that could negatively affect the process performance of the subsequent technologies. Problems that are associated with creating the largest negative impact on technology performance are scaling, fouling, corrosion, and foaming (Kress, 2019). The so-called scale removal is especially needed if the ZLD system include membrane technologies (Giwa et al., 2017).

In general, pretreatment technologies are based on physical, chemical, and/or biological methods (Kress, 2019). The pretreatment step could consist of a single or two-step system. Appropriate pretreatment technologies and processes depend highly on the nature of the contaminations in the brine, and thus an analysis of brine compounds is mandatory (Panagopoulos & Haralambous, 2020).

2.2.1.1 Chemical pretreatment

Chemical pretreatment is in general associated with the addition of chemicals at several stages along the process chains for the removal of scaling and inorganic fouling precursors such as calcium and magnesium from brine before secondary treatment (Giwa et al., 2017; Panagopoulos & Haralambous, 2020).

Conventional chemical pretreatment technologies are chemical precipitation and coagulation-flocculation. **Chemical precipitation or softening** has been broadly utilized for brine treatment with lime softeners (e.g. calcium hydroxide) to remove mainly scale-forming ions like magnesium, calcium, and silica from the brine which otherwise would be responsible for early membrane fouling (Giwa et al., 2017; Katal et al., 2020; Mavukkandy et al., 2019). Calcium and magnesium removal could be additionally done using salts such as NaOH and Na_2CO_3 as precipitants at high temperatures, which effectiveness has been studied by Atkins et al. (2018) and Sanmartino et al. (2017).

Coagulation-flocculation is a chemical process that forces small particles to form bigger agglomerations that precipitate and are removed by filtration techniques (Münk, 2008). Giwa et al. (2017) state that the coagulant iron chloride ($FeCl_3$) provides the most outstanding performance in recent studies for brackish water treatment especially for the destabilization of the organic compound in Reverse Osmosis brine. Despite being a well-known process, coagulation has not been considered broadly for usage in brine treatment due to high salt concentrations (Katal et al., 2020).

These conventional chemical pretreatment results in intensive use of chemicals and the production of wet sludge which needs additional care for legitimate management creating an application limitation of the method and lead to increased operating costs (Katal et al., 2020; Muhammad & Lee, 2019; Panagopoulos & Haralambous, 2020). Currently, extensive efforts are being made to improve chemical precipitation (e.g. due to the addition of seed material) and to search for alternative strategies that may involve techniques of various kinds (Panagopoulos & Haralambous, 2020).

Conventional chemical softening could be substituted using a **Pellet Reactor** to remove hardness from the brine. Pellet reactors are fluidized bed reactors that contain calcium carbonate crystals that grow on the surface of the pellets ensuring heterogeneous nucleation and growth (Giwa et al., 2017). The main advantage of pellet softening compared to conventional chemical softening (lime softening) is the production of relatively dry sludge. Despite the efficient removal of silica and calcium, pellet softening is inefficient for magnesium removal because of the more pronounced solubility (Giwa et al., 2017).

Another alternative approach is the usage of an **Accelerated Precipitation Softening (APS)** as an alkali-induced precipitation step before secondary membrane treatment, which prevents pH disruptions and ensures accelerated removal of recalcitrant scale-forming ions (Giwa et al., 2017). Similar to the pellet reactor, the improved surface areas provide accelerated kinetics of mineral salt precipitation and brine softening.

Electrocoagulation is one of the purification methods within the field of electrokinetic applications aiming to change the surface charge of particles by continuously providing metallic ions as a coagulant sources with the aid of a sacrificial anodic electrode (Giwa et al., 2017). The advantage of using the alternative process of electrocoagulation compared to conventional chemical coagulation is the lower production of sludge volume and a smaller footprint (Panagopoulos & Haralambous, 2020). However, the disadvantages and remaining challenges are the high operating and support costs (Katal et al., 2020). Panagopoulos and Haralambous (2020) state the need for more research to investigate the removal efficiency of electrocoagulation and the applicability in brine management.

Another attempt has been directed towards the use of **Ion Exchange (IEX)** which uses resins to remove undesirable ions in water (Giwa et al., 2017). The undesirable ions are exchanged with an equivalent amount of equal charged ions in the resins and thus removed from the water. Another method of Ion Exchange is ion-exchange membranes which follow the same principle and are mainly incorporated in electrodialysis. The process is considered to be efficient and cost-effective, where the costs associated with the process are mainly reliant on the regeneration of the membranes or resins (Panagopoulos & Haralambous, 2020). However further research is needed to validate the long-term suitability of ion-exchange membranes for brine treatment and to increase the resin efficiency by the usage of multiple resins to simultaneously remove various substances (Giwa et al., 2017).

Additional chemical addition of **biocides as ozone and ultraviolet (UV) radiation** may be used to eliminate organic matter and prevent biofouling (Pellegrin et al., 2016). Studies by Umar et al. (2013) and Zhou et al. (2011) showed that the removal efficiency of dissolved organic carbon (DOC) and chemical oxygen demand (COD) by ozone or UV was only minimally influenced by the salinity. However, currently only a few studies have analysed the impact of salinity on the process performance for organics removal (Katal et al., 2020).

2.2.1.2 Physical pretreatment via filtration

Ultrafiltration and nanofiltration are the most commonly discussed filtration techniques for brine treatment (Münk, 2008). Filtration techniques are fairly reliable and, unlike chemical pretreatment technologies, do not produce sludge (Panagopoulos & Haralambous, 2020).

Ultrafiltration (UF) removes substances down to 0.01 µm due to a sieving mechanism combined and applied pressure of up to 5 bars (Mezher et al., 2011; Münk, 2008). UF is applied to decrease and eliminates contaminants affecting color as high-weight dissolved organic compounds, dissolved macromolecules, colloids, some viruses, smaller bacteria as well as scale-forming ions (Morillo et al., 2014; Münk, 2008). UF as pretreatment for ZLD systems is currently still tested but seems promising. Especially if used before membrane technologies. One pilot project observed that UF removed most of the suspended solids, iron, and approximately 50 % of oil and grease from treated seawater (Muhammad & Lee, 2019).

Nanofiltration (NF), removes substances down to 0.001 µm via a combination of sieving and solution diffusion (Mezher et al., 2011; Münk, 2008). NF is defined as a process intermediate between Reverse Osmosis (RO) and UF (Tsai et al., 2017). NF uses significantly lower pressure than RO and removes particles based on their size characteristics and charge (NF rejects highly multivalent ions). NF softens the water by the removal of hardness ions and efficiently reduces TDS, turbidity, organics, sulfate, virus, dissolved organic carbon, and a fraction of the salts and silica (Panagopoulos & Haralambous, 2020). Furthermore, NF can be applied to separate and extract bi-valent metal ions, such as calcium (Ca^{2+}) and sulfate (SO_4^{2-}) from brine if coupled with crystallization units. Dong et al. (2015) studied the process performance of commercially available NF membranes in salt solutions equal to seawater`s salinity. It was concluded that NF has an outstanding performance in the removal of hardness ions and is leading to higher water recovery. NF as a membrane-based process poses fouling problems and is thus limited to brines with salinities lower than 55,000 mg/L TDS due to osmotic pressure constraints (Panagopoulos & Haralambous, 2020).

2.1.1.1 Biological pretreatment

Biological processes as pretreatment is a major technique and an integral part of ZLD when using wastewater as feedwater (Shah et al., 2020). Biological pretreatment methods are based on microbial activity to break down biodegradable organics and nutrients in aerobic (in presence of oxygen) or anaerobic (in absence of oxygen) milieu (Kress, 2019; Shah et al., 2020). The milieu terms are related to both the type of microorganisms used for contaminant degradation and the operating conditions of the bioreactor. Several biological pretreatment methods such as **Soil Biotechnology (SBT), Biological Activated Carbon (BAC), Fluidized Bed Bioadsorber Reactor (FBBR), Willow Field** have been discussed by scientists (Katal et al., 2020).

Factors that might affect the biological process performance in brine treatment are (1) bio-refractory organic compounds and (2) chromium and copper (inhibit the efficiency of nitrifying bacteria) (Katal et al., 2020). The biggest factor affecting the efficiency of biological processes is high salt concentrations which results in unbalanced osmotic stress across microbial cells leading to system failure (Katal et al., 2020). However, according to Giwa et al. (2017) and Katal et al. (2020), biological pretreatment technologies are still useful to sufficiently remove certain foulants or scalants from low salinity brine (>2,000 mg/L). Biological processes for brine treatment are still in the pilot stage and rarely used, despite their promising treatment performance for low to moderate-saline brine (Pellegrin et al., 2016).

The only literature found that tested the performance of a biological pre-treatment on moderate saline brine solution is by Lu et al. (2013), who applied a Biological Activated Carbon (BAC) system on a moderate saline brine solution with TDS concentrations of 10,000 mg/L. It was concluded that the COD and DOC removal efficiency of approximately 50 to 60 % was achieved (Katal et al., 2020). This shows the effectiveness of biological treatment for activated sludge to be acclimated to moderate-saline environments (Katal et al., 2020). However, further research is needed to evaluate the BAC process performance in a higher saline environment.

2.2.1.3 Conclusion

Physical and biological pretreatment technologies are restricted to the treatment of moderate and low salinity brine (Katal et al., 2020; Panagopoulos & Haralambous, 2020). Chemical pretreatment technologies are the most effective for the removal of hardness and scaling ions in high saline water, but conventional technologies are associated with a high cost for the chemical demand and waste disposal (Katal et al., 2020; Muhammad & Lee, 2019; Panagopoulos & Haralambous, 2020). Several alternative chemical methods have been developed as APS. Nonetheless, conventional chemical pretreatments, in particular chemical precipitation, remains extremely important in ZLD and MLD systems due to the lack of research regarding the technical and economic sustainability of other pretreatment methods and technologies (Panagopoulos & Haralambous, 2020). Table 2-3 summarizes with which chemical, biological and physical pretreatment methods the constituents of concern (see Table 2-1) are mostly reduced and/or treated in brine management.

Table 2-3: Pretreatment methods used for the treatment of the constituents of concern (chemical=orange; physical=blue, biological=green)

	Ca^{2+}	Mg^{2+}	Ba^{2+}	Sr^{2+}	Silica	$SO4^{2-}$	K^{+}	B^{+}	Nitrogen	$PO4^{3-}$	Cl^{-}	Na^{+}	F	Alkalinity / pH	TDS / TSS	COD/ TOC/ BOD	Oil& Grease
Chemical precipitation																	
Coagulation-Flocculation																	
Pellet reactor																	
APS																	
Electrokinetic Treatment																	
IEX																	
Biocides																	
UF																	
NF																	
SBT																	
BAC																	
FBBR																	
Willow field																	

2.2.2 Membrane technologies

Membrane technologies are historically applied for the preconcentration of brine before the application of thermal technologies which are limited by certain TDS concentration (Panagopoulos et al., 2019). However, the current trend is to develop more resistant membranes to resist higher TDS concentrations, so-called emerging technologies. In the following chapter established as well as emerging membrane technologies are described in regard to their efficiency and process performance in brine treatment. Appendix A provides the summary of the literature review for established and emerging membrane technologies.

2.2.2.1 Conventional membrane technologies

In **Reverse osmosis (RO)** processes, hydraulic pressure is applied to overcome the osmotic pressure between the concentrated and the permeate liquid resulting in the movement of water molecules through a semipermeable membrane from the high to a lower salt concentrated compartment as seen in Figure 2-4 (a) (Panagopoulos et al., 2019). However, the salinity constraint of conventional RO makes it unpromising for the application for high-saline brine treatment (Panagopoulos et al., 2019). The conventional RO membranes and modules currently available can operate up to 82 bar and TDS feed concentrations of up to around 70,000 mg/L with around 50% water recovery rate (Panagopoulos et al., 2019). The practical pressure limitations of RO membranes and modules, the decreasing efficiency, and the increasing energy demand for separation with increasing concentration, and the scaling and fouling risk due to hardness ions result in the fact that the conventional RO technology is only applicable for TDS concentrations of up to 70,000 mg/L (Panagopoulos et al., 2019).

Electrodialysis (ED) is another established membrane technology that differs from RO as ions are removed from the water molecules (Charisiadis, 2018). Alternating anion-selective membranes (AMs) and cation-selective membranes (CMs) are placed within an electric field generated by electrodes leading to the movement of negative and positive ions through the semipermeable membranes with attached positively or negatively charged species respectively as seen in Figure 2-4 (b) (Morillo et al., 2014). Therefore, ED is producing a flow with low ion concentration, a so-called dilutant, and a process flow with high ion concentration, a so-called concentrate while just using electricity which could be supplied by PV panels (Morillo et al., 2014).

Charisiadis (2018) states, that ED can treat high concentration solutions (>70,000 ppm) with no concentration limit. Additional research confirms that ED can effectively treat high-salinity brine. For example, Jiang et al. (2014) studied the direct application of ED for the treatment of RO brine with 7 % to 10.5 % (m/v) concentrations. It has been found that the tested ED membranes were able to produce a highly diluted (refresh water) and highly concentrated stream (up to 27.13 % (m/v)) with a water recovery rate of 67.78 %. However, the process performance of ED can be affected by the deposition of suspended solids as well as the precipitation of scaling ions on the membrane`s surface (Morillo et al., 2014). Especially, when the brine becomes significantly high in concentration, the risk of scaling increases resulting in a reduced yield of the electric field and decreased process performance. Therefore, pretreatment is needed to remove such constituents from the feedwater, whereof the most common approach is NF (Liu et al., 2016).

Electrodialysis Reversal (EDR) is an approach used to minimize the precipitation problem via the reversal of the polarity of the electrical potential at certain time intervals (Charisiadis, 2018). Due to the reversal of the electrical field, electrically charged substances on the surface of the membranes are removed without any additional energy demand.

ED was proposed to be used in brine management not only to concentrate the brine but also to harvest salt (Liu et al., 2016). The implementation of the selective ion exchange membranes in ED makes the selective extraction of specific ions possible and ED attractive as a resource recovery approach. The ion-selective ion-exchange membranes are still costly according to Liu et al. (2016).

It is concluded that ED has become a perspective technology in handling low to high-saline brine due to the high concentration production, low operation pressure, and lower fouling potential compared to RO membranes. However, further research is needed to improve the permeability and selectivity of membranes to eliminate the risk of scaling (Morillo et al., 2014).

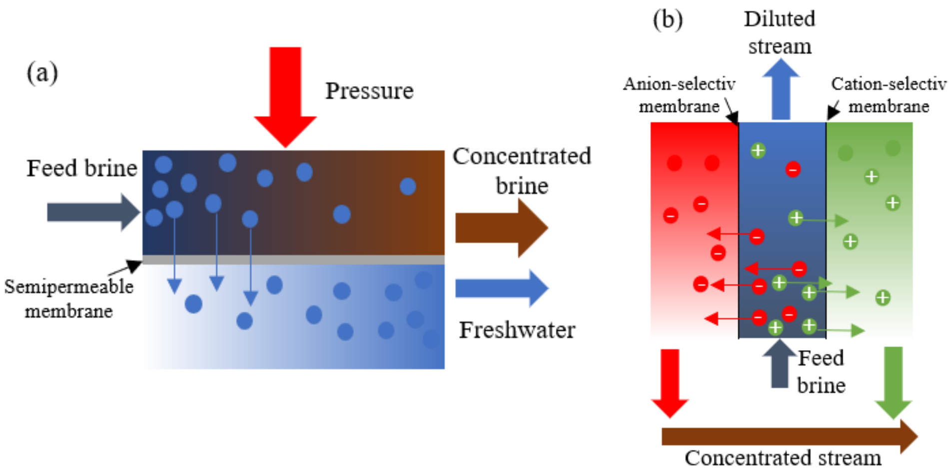

Figure 2-4: Schematic flow diagram of Reverse Osmosis (a) and Electrodialysis (b)

2.2.2.2 Emerging technologies

Due to the limitations of conventional membrane technologies, alternative membrane methods have to be developed that are less energy-consuming than thermal technologies and have a higher tolerance for high salinity concentrations than conventional membrane technologies (Tsai et al., 2017). These approaches include the further development of conventional membranes by material or process modification. Modification of RO includes High-Pressure RO (HPRO), Osmotically Assisted Reverse Osmosis (OARO), and Vibratory Shear Enhanced Processing (VSEP):

HPRO membranes can handle pressure above 82 bar and thus treat brine with a concentration of over 70,000 mg/L (Panagopoulos et al., 2019). However, such HPRO membranes are rarely commercially available and those accessible achieve a low water recovery rate (8 % to 50 %) and higher energy consumption than RO. The main disadvantage is the remaining scaling and fouling risk of HPRO membranes resulting in the need for intensive pretreatment.

OARO is a recently developed membrane-based technology that uses a lower pressure sweep solution on the membrane`s permeate side and thus decreases the difference in the needed osmotic pressure (treatment of higher TDS possible) and increases the water flux and recovery (up to 92 %) (Panagopoulos et al., 2019). However, the specific energy consumption and the treatment costs are higher than in previous osmosis-related technologies due to the immaturity of OARO (Panagopoulos et al., 2019). Further development in membrane performance is needed to increase the commercial availability of OARO.

VSEP improves the filtration efficiency by the creation of vibratory shear by torsional oscillation at the membrane`s surface resulting in operation independence from the solubility of salt or the presence of suspended solids or colloids in brine (Subramani et al., 2012). The advantages of VSEP are: (1) high rates of filtration water recovery of 80-93 % from brackish brine, (2) resistance to membrane scaling, and (3) decreased footprint than thermal technologies (Giwa et al., 2017). Nonetheless, the energy consumption (three times of RO) to maintain oscillatory vibration by a torsional spring is high and just a few studies that discuss the application of VSEP in brine treatment (Subramani et al., 2012).

Electrodialysis Metathesis (EDM) is a modification of ED that uses an additional solution compartment for sodium chloride (NaCl) (Giwa et al., 2017; Panagopoulos et al., 2019). Due to the addition of NaCl to the adjacent cell, various salts as calcium chloride are formed. Zarzo (2018) concludes that the advantages in comparison to conventional ED are: (1) lower membrane fouling potential due to the generation of soluble salts; (2) higher water recovery rate and efficiency due to recirculation of the product to the feedwater. However, EDM is currently rarely commercially available and no literature has been found to report the pilot-scale testing of EDM on brine treatment (Panagopoulos et al., 2019).

Alternative emerging processes are **Forward Osmosis (FO), Membrane Distillation (MD), and Membrane Crystallization (MCR). FO** uses a highly concentrated solution generally referred to as a draw solution to produce high osmotic pressure differential across a semipermeable membrane (Morillo et al., 2014; Subramani & Jacangelo, 2015). Due to the difference in the osmotic pressure between the feedwater and the draw solution, water molecules start moving from the less concentrated feed stream to the highly concentrated draw solution as seen in Figure 2-5 (a). The draw solutes are afterward removed from the diluted draw solution via e.g. external heat input to potentially recycle the solutes and to generate clean water (Subramani & Jacangelo, 2015). The draw solution regeneration is important to minimize the draw solution quantity and the waste production, respectively. The energy consumption of FO is low without the regeneration of the draw solution as no external pressure is needed, but could be higher than conventional membrane processes with the withdraw solution recovery (Panagopoulos et al., 2019). In order to keep the energy requirement of FO minimal, researchers developed draw solutions that do not need separation treatment, which remain to be tested sufficiently (Subramani & Jacangelo, 2015). However, FO is capable to run on a variety of heat sources which makes the usage of alternative energy sources like waste heat and renewable energy possible (Subramani & Jacangelo, 2015).

It is concluded that FO can recover up to 70 % of water and treat high concentrated brine (up to 200,000 mg/L TDS) while having a lower contamination potential and energy consumption (Charisiadis, 2018; Panagopoulos et al., 2019). However, the unavailability of an efficient and universal draw solution and the energy demand of FO, if draw solution regeneration is applied are challenges for FO (Panagopoulos et al., 2019). Another challenge is the rare existence of enhanced and stable specifically designed membranes (Subramani & Jacangelo, 2015). Currently, just a few FO membranes are commercially available that can treat high-TDS brines (Panagopoulos et al., 2019). Even though FO membranes were indicated in previous studies to below-fouling, according to Panagopoulos et al. (2019), a high risk of fouling is occurring at FO membranes.

MD is a non-isothermal evaporative technology that incorporates a hydrophobic microporous membrane (Morillo et al., 2014). The vapor pressure difference resulting from the different temperatures between the two sides of the hydrophobic membrane is the driving force that causes the mass and heat transfer of volatile solution components as water to the cold side as seen in Figure 2.5 (b) (Charisiadis, 2018). MD can treat high-TDS brine of over 200,000 mg/L due to the theoretical nonexistent salinity restriction for the feedwater while recovering up to 90 % of water (Panagopoulos et al., 2019). An advantage of MD compared to conventional distillation is the lower operating temperature (30 to 80 °C) (Charisiadis, 2018; Panagopoulos et al., 2019). The low-grade energy needed for MD can be taken from waste heat and/or alternative energy sources such as solar or geothermal. Despite the low-temperature requirements the amount of thermal energy needed for the MD process is a major disadvantage (Panagopoulos et al., 2019). Furthermore, the costs of the membrane materials, the low permeate flux, pore wetting, flux reduction due to concentration polarization, and poor thermal efficiency, are all limiting factors for large-scale implementation (Panagopoulos et al., 2019; Subramani & Jacangelo, 2015). Innovative materials that offer microporous membranes with desired porosity, hydrophobicity, low thermal conductivity, and low fouling are needed to increase the MD commercialization opportunities (Panagopoulos et al., 2019; Subramani & Jacangelo, 2015).

MCr is according to Panagopoulos et al. (2019) an extension of the MD that provides the opportunity not just to recover water from the brine but also valuable solid crystal salts at the same time. A hydrophobic and microporous membrane is applied in MCr to separate the constituents of the brine (Katal et al., 2020). The process performs until the supersaturation is reached and nucleation of crystals is induced. The generated crystals are collected after the supersaturation in an external crystallizer (Mavukkandy et al., 2019). MCr can “form specific crystal size distribution and these crystals can be modified to form specific crystal superstructures” (Mavukkandy et al., 2019, p.8). Due to this characteristic, MCr is associated with well-controlled nucleation and growth kinetics, as well as higher crystallization rates. According to Panagopoulos et al. (2019), MCr is applicable for high-saline brine of up to 350,000 mg/L. Other advantages are that MCr has no feed pressure requirements, low fouling propensity modular, and low-grade thermal energy can be used to overcome the high energy demand. However, the issues of membrane wetting, low membrane flux, poor thermal efficiency, and the need for intensive pretreatment processes to avoid scaling and fouling remain the challenges faced by MCr. However, the resource recovery potential of MCr makes the technology interesting for the treatment of brine despite these disadvantages, which remains to be evaluated practically (Mavukkandy et al., 2019).

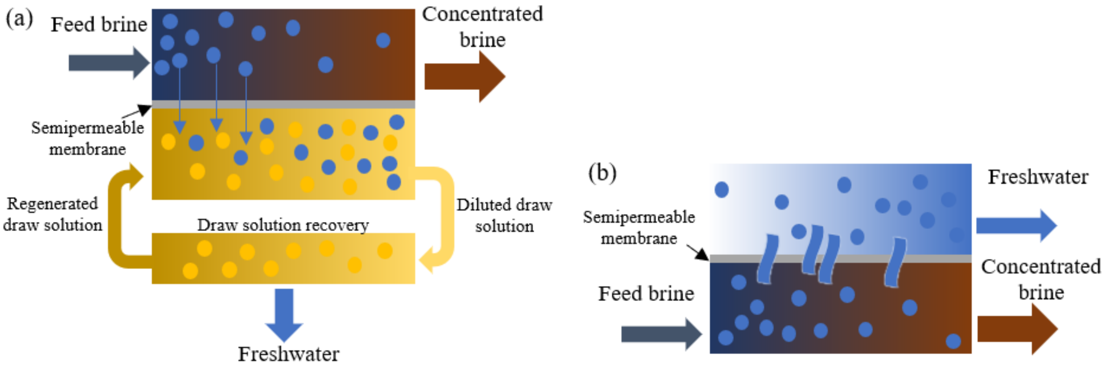

Figure 2-5: Schematic diagram of Forward Osmosis with draw solution recovery (a) and Membrane Distillation (b)

2.2.2.3 Conclusion

The literature study showed that the only technologies tested on brine on a pilot scale are RO, ED/EDR, MD, and FO. The other emerging technologies are still in the initial phase of development or the phase of experimental testing. RO is limited to the treatment of moderate saline brine (up to 70,000 mg/L) and the application of RO in high saline brine could be only possible through the future development of pressure-resistant membrane material (HPRO) (Panagopoulos et al., 2019). FO could be applied for higher TDS concentration but the increasing membrane scaling risk with increasing concentration remains currently a limitation for broader application of FO (Panagopoulos et al., 2019). In the conducted experiments it has been seen that MD has higher reliability than FO and RO while achieving a higher water recovery rate under higher TDS concentration (Charisiadis, 2018). However, the high energy consumption of MD and the insufficient testing in SW brine from thermal technologies creates a challenge (Katal et al., 2020). ED/EDR, which is an established desalination technology, has been successfully tested on SW brine for the concentration of the brine above 200,000 mg/L with a smaller risk of membrane failures than RO (Panagopoulos et al., 2019). However, the main disadvantage of ED/EDR is the poor quality of the water which creates a limitation as a stand-alone technology for drinking water production (Charisiadis, 2018).

Figure 2-6 shows the comparison of the above-described technologies in terms of their maximum TDS concentration and ranged according to the minimum specific energy consumption. FO and MD do not have a TDS treatment limit according to the literature reviewed and could theoretically treat brine above 200,000 mg/L TDS concentrations. However, it can be concluded that only MCr has been proven to concentrate the brine until saturation level due to the addition of an external crystallizer and that most of the technologies are operating until 175,000 mg/L TDS concentration. Additionally, the energy demand range is the highest for FO but in general high for all emerging technologies.

A lot of promising emerging technologies have been developed recently. However, most of them are yet to be sufficiently tested and commercially available (Panagopoulos et al., 2019). Further research on the improvement of membrane material to minimize the risk of scaling is expected to lead to fast growth in the implementation of membrane technologies in the future.

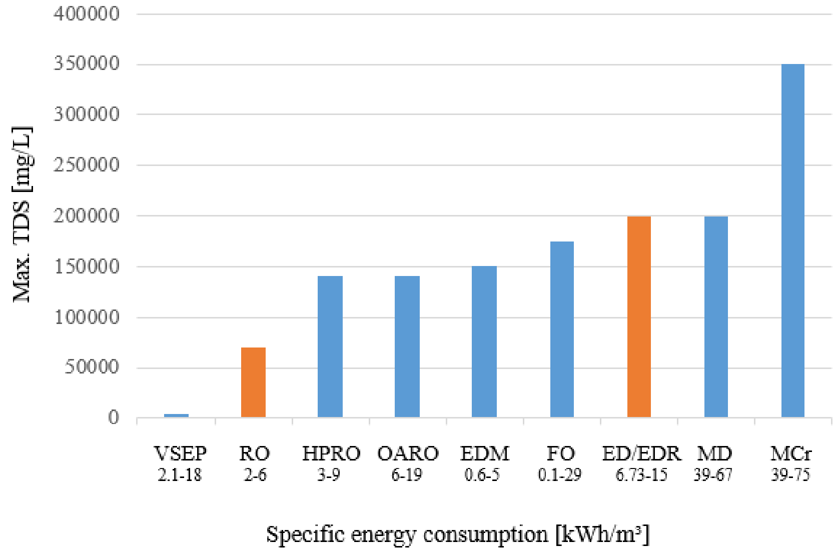

Figure 2-6: Comparison of membrane technologies regarding maximal TDS concentration and energy demand (conventional=orange, emerging=blue)

2.2.3 Thermal technologies

Thermal-based technologies are generally applied to minimize the volume of high-salinity brines where membrane treatment processes fail due to the difficult constituent concentrations in the brine (Giwa et al., 2017). Brine Concentrator (BC), also called an evaporator, and Brine Crystallizer (BCr) are the most commonly used technologies in ZLD brine treatment chains (Panagopoulos et al., 2019). According to Zarzo (2018), evaporation-crystallization technologies are the most technically feasible systems for the complete elimination of brine by solid waste formation. The results of the literature study are presented in Appendix B and below conventional as well as emerging thermal technologies are introduced.

2.2.3.1 Conventional thermal technologies

Brine Concentrators (BC), also called **Evaporators (EV)**, are conventional ZLD technologies that use thermal energy to create distillate and concentrated brine via evaporation (Panagopoulos et al., 2019). BC can be categorized according to their length and the positioning (horizontal or vertical) of the tubes as seen in Figure 2-7 (Charisiadis, 2018). The main BC designs used are vertical tube, falling film, horizontal spray-film, or plate-type evaporators according to Panagopoulos et al. (2019), and falling film and thin-film evaporators according to Ahirrao (2014) and Charisiadis (2018). The common factor between all these different BC designs and configurations is that the brine gets evaporated inside the tube while being heated up by the latent heat of vaporization supplied by vapor condensing on the outside of the tube (Giwa et al., 2017).

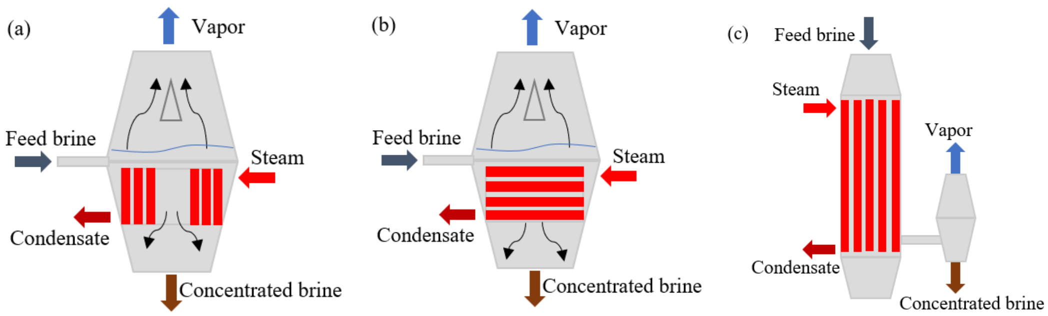

Figure 2-7:Schematic diagram of Evaporator types: Horizontal-tube (a), Vertical-tube (b) and Longtube-vertical/Falling film (c)

According to Giwa et al. (2017) are the three limitation factors of BC: "(1) the boiling point elevation of the brine [due to the salt concentration], (2) the relative concentrations of sulfate and chloride, and (3) the solubility of the sodium salts" (p.8). With increasing temperatures, the corrosion risk on the evaporators heat exchanger is raised. Thus, evaporators operate normally at reduced pressure to reduce the boiling point (Charisiadis, 2018). This means that a vacuum pump or jet ejector vacuum system is required, also referred to as a vacuum evaporator.

The water recovery rate achievable with BC lies between 90 to 99 % for high-quality freshwater (with a TDS concentration between 5 to 20 mg/L) and for a TDS inlet concentration of maximal 250,000 mg/L (Panagopoulos et al., 2019). However, a drawback of the technologies is the capital costs of BC which mainly rely on the requirements of high-priced material (e.g. titanium) that avoid corrosion by boiling brine and the specific energy consumption of BC (see Chapter 2.5) (Panagopoulos et al., 2019).

Different systems have been developed to reduce the energy consumption of evaporators and other evaporative thermal technologies (Ahirrao, 2014). The most common ones are evaporators with Thermal Vapor Recompression (TVR) and Mechanical Vapor Recompression or Mechanical Vapor Compression (MVR or MVC). Table 2-4 shows a basic comparison of TVR and MVR, whereof MVR is the most energy-efficient system for evaporation and can work with any kind of evaporative technology (Ahirrao, 2014).

Table 2-4: Main characteristics of mechanical vapor and thermal vapor recompression (based on (Ahirrao, 2014)).

	Main characteristics	Capital cost	Operating cost	Electrical energy	Thermal energy
TVR	In TVR a steam jet ejector is used to increase the temperature and pressure of vapor produced from the first effect of the evaporator (Ahirrao, 2014). The motive steam is mixed with vapor generated from the first effect and utilized in the first effect of condensation.	Medium	Medium	Low	Low
MVR	MVR compresses vapor by mechanically driven equipment such as compressors (Ahirrao, 2014). The MVR produces superheated steam from vapor, which is desuperheated before returning to the evaporator.	Relatively high	Low	High	Low

Multi-Effect Distillation (MED) is a traditional thermal desalination technology that consists of multiple cells operated at decreasing levels of pressure (leading to decreasing boiling point) and uses vapor pressure difference as the driving force (Giwa et al., 2017). The generated vapor from the feedwater in one effect subsequently condenses in the next effect due to lower temperatures and pressure providing extra heat of vaporization (Kress, 2019). Figure 2-8 presents the schematic diagram of MED. The application of MED for brine treatment has been limited or not reported in literature according to Panagopoulos et al. (2019). Currently, MED systems are made of common stainless grades, that are not suitable for high TDS brine treatment due to corrosion problems (Panagopoulos et al., 2019). However, this can be avoided if cost-intensive anticorrosion materials such as titanium are used (Panagopoulos et al., 2019). Scaling is considered to be another major issue for these systems resulting in the need for pretreatment (e.g. addition of antiscalants) (Panagopoulos & Haralambous, 2020). Despite having a lower energy demand than BC, the energy input of MED is still considerably high and considered to be another drawback (Panagopoulos et al., 2019). Thermal and electrical energy could be generated through renewable energy sources or waste heat, thus making it more sustainable (Kress, 2019). While MED has a theoretically lower water recovery than emerging membrane technologies as MD or FO, MED has the advantage of producing higher-purity freshwater (<10 mg/L TDS) (Panagopoulos et al., 2019; Panagopoulos, 2020a).

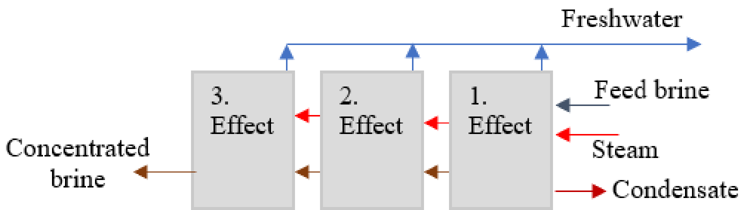

Figure 2-8: Schematic diagram of Multi-Effect Distillation.

Multi-Stage Flash Distillation (MSF) is a highly similar technology to MED that could be used in brine treatment for high purity water recovery after material upgrade (Panagopoulos et al., 2019). MED differs from MSF in two points: (1) vapor condensation occurs in heat exchange with the liquid in the subsequent distillation effect and (2) the maximum temperature is up to 70-75°C" while MSF reaches temperatures up to 110 to 120 °C (Panagopoulos et al., 2019, p.13) The higher maximum brine temperatures enhance flashing and performance ratio but also increase scaling (Kress, 2019). Thus, pretreatment is recommended for scale inhabitation. Furthermore, the specific high energy consumption of MSF presents as another disadvantage of the technology (Kress, 2019; Panagopoulos et al., 2019).

Brine Crystallizers (BCr) are applied in general for the last step of a ZLD brine treatment system (Katal et al., 2020). The water and salt recovery potential from brine as well as lowering the environmental impact are the main advantages of BCr compared to disposal methods (Giwa et al., 2017).

BCr is designed "primarily as vertical cylindrical vessels with heat input from an available steam source or vapor compressor" (Panagopoulos et al., 2019, p.12). These BCr are called evaporative crystallizers because the incoming and recirculating brine is heated by vapor leading to the evaporation of water and the formation of salt crystals (Giwa et al., 2017). The most commonly used type of BCr is the forced circulation crystallizer, where the vapor is recycled to reduce energy consumption and incoming brine is mixed with the circulating brine after entering the crystallizer sump as seen in the schematic diagram of BCr in Figure 2-9 (Charisiadis, 2018; Panagopoulos et al., 2019). In the final step of the BCr, freshwater is collected, and dry solids are produced, which can be disposed of in landfills or used for other applications (Giwa et al., 2017).

Brine could be directly applied to BCr in which the brine is driven into saturation concentration levels leading to an exceptionally high water recovery rate (up to 99 %) (Charisiadis, 2018; Panagopoulos, 2020a). Similar to an evaporator, the high capital costs and energy demand are the limiting factors of BCr (see Chapter 2.5). Preconcentration is important to reduce the operating and capital costs of crystallization (Charisiadis, 2018). Therefore, BCr is just applied as a final step of ZLD after a sufficient reduction in brine volume.

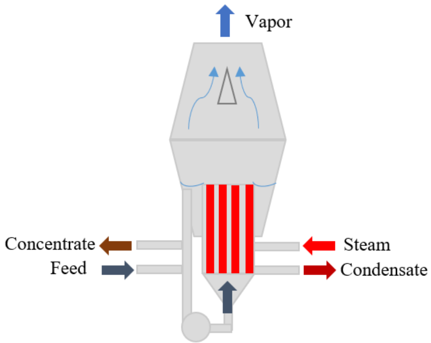

Figure 2-9: Schematic diagram of a Forced Circulation Crystallizer

2.2.3.2 Emerging thermal technologies

Humidification – Dehumidification (HDH) is a system that imitates the natural water cycle of evaporation and condensation to generate pure water (Lawal & Qasem, 2020). The system is based on the ability of air to carry water vapor at higher temperatures (Subramani & Jacangelo, 2015). Renewable and low-grade energy sources can be used to drive the HDH systems, whereof solar energy is the most common one (Lawal & Qasem, 2020). HDH systems have been so far just applied as a desalination technology but due to the ability to handle high salinity brine the application for the brine treatment is nowadays discussed (Narayan et al., 2010). Narayan et al. (2010) state that further research needs to be carried out to assess the full potential of HDH in brine treatment.

Eutectic Freeze Crystallization (EFC) is a technology that utilizes the different densities between the ice and the salt produced (Panagopoulos et al., 2019). EFC operates at the specific concentration, also known as eutectic temperature (ET), at which ice crystals are no longer formed and the salt reaches saturation (Mavukkandy et al., 2019). Pure water is produced by washing and remelting the crystals of ice (Giwa et al., 2017). EFC can produce freshwater and high-purity salts using less energy than traditional evaporation-based separation processes (Giwa et al., 2017; Mavukkandy et al., 2019; Panagopoulos, 2020a). So far only a few studies have discussed EFC for brine treatment due to the complex nature of desalination of brine (Panagopoulos & Haralambous, 2020). Furthermore, the capital expenditures for EFC are high resulting in another drawback of the technology (Panagopoulos & Haralambous, 2020). According to Giwa et al. (2017), the number of plants employing EFC for brine treatment on a large-scale, pilot-scale, or demonstration-scale is low primarily due to the low productivity of this method.

Temperature Swing Solvent Extraction (TSSE) is a non-evaporative thermal technology that uses a low-polarity solvent with temperature-dependent water solubility for the selective extraction of water over salt (Boo et al., 2020). TSSE has been just recently studied for ZLD application of high-salinity brine by Boo et al. (2020). The energy needed for TSSE is significantly lower than evaporation technologies as no phase change of water occurs (Boo et al., 2020). Due to the lower operating temperature, TSSE can be operated with low-grade heat sources. However, the amount of solvent needed for the complete extraction of water is a drawback of the technology. Further research is needed to confirm the effectiveness of high saline brine treatment and energy consumption.

2.2.3.3 Drying technologies

Alternatively, conventional or alternative drying technologies could be used as a final step of the ZLD chain, which produce solids without water recovery. **Spray Dryer (SD)** is another commercially available crystallization technology that converts the brine into a dry powder of mixed solid salts and has the advantage to produce solid salt products with desired quality standards (Panagopoulos et al., 2019; Panagopoulos & Haralambous, 2020). According to Panagopoulos et al. (2019), SD systems are currently commercially available with a water evaporation capability from 0.5 kg/h to 70 kg/h with specific energy consumption of 52–64 kWh/m^3. However, SD does not recover freshwater from the brine and is so far only used for low-volume flows of around 54.51 m^3/d (Mickley, 2008; Panagopoulos, 2020a).

Shi et al. (2018) and Wu et al. (2020) developed recently 3D structures for **Advanced Solar Evaporation (ADS).** The A3D cup-shaped solar evaporator by Shi et al. (2018) consists of three layers of silica/carbon/silica (SCS) (Mavukkandy et al., 2019). The cup has almost 100 % solar evaporation efficiency and 99.35 % light absorption. Furthermore, it has been observed that the evaporation rate just slightly decreases for hypersaline streams (25 wt.%) making it applicable for high-saline brine treatment (Shi et al., 2018). Due to the separation of the salt precipitation surface from the light-absorbing surface, it is possible to treat near-saturated NaCl brine (25 wt.%) for up to 120 hours with a stable and high water evaporation rate of 1.26 kg/m^2. The freshwater production is just slightly decreasing from 0.55 kg/m^2h to 0.5 kg/m^2h when the brine concentration is increasing from 15 wt.% to 25 wt.% brine (Shi et al., 2018). The study by Wu et al. (2020) suggested the improvement of solar energy efficiency by the usage of a bio-mimetic 3D structure for an evaporator. It has been shown that the spontaneously formed water film fully utilizes the solar energy through the Marangoni effect, which results in localized salt crystallization. With the designed 3D module an evaporation rate of 2.63 kg/m2*h with over 96 % energy efficiency and a water collecting rate of 1.72 kg/m2*h has been achieved under high salinity (25 wt. % NaCl) (Wu et al., 2020). It has been observed that the energy efficiency and water evaporation rate are independent based on the salt accumulation showing the potential for sustainable and practical applications.

Wind-Aided Intensified Evaporation (WAIV) is an alternative intensive evaporation process that uses vertical wetted packing towers that “utilizes wind power to evaporate densely-packed wetted surfaces” (Giwa et al., 2017, p.8). WAIV systems can achieve up to 90 % evaporation ratio compared to traditional evaporation ponds with one-fifth lower land requirement (Giwa et al., 2017). Furthermore, WAIV has the lowest specific energy consumption of up to 1 kWh/m3 as energy is only required for the pumps (Panagopoulos et al., 2019). Thus, WAIV is especially suitable for areas where energy costs and aridity are high (Morillo et al., 2014). It has been observed that the precipitation of less soluble gypsum in the WAIV has led to an enrichment of magnesium salts which has the potential to be recovered as a mineral by-product from brine (Giwa et al., 2017). Thus, WAIV could be favourable for resource recovery. However, the potential of salt recovery using WAIV needs to be further studied (Morillo et al., 2014).

2.2.3.4 Conclusion

Conventional thermal technologies for the initial volume reduction of brine are evaporator, MED, and MSF, of which the Evaporator is proven performance reliably for high-saline brine (Panagopoulos et al., 2019). Crystallizer is a conventional thermal technology applied as the final step of the ZLD chain for the concentration of the brine up to saturation level and the production of final solids (Giwa et al., 2017). However, all these conventional technologies have a higher energy demand than membrane technologies but producing water with higher quality, and the process performance is currently more reliable as the membrane's performance is still easily affected by scaling ions (Panagopoulos et al., 2019). The energy demand for all these technologies could be lowered by the incorporation of MVC or TVC (Ahirrao, 2014). However, the techno-economic feasibility of these conventional thermal ZLD systems remains difficult at present according to Morillo et al. (2014) and Zarzo (2018). Emerging technologies such as HDH, EFC, and TSSE have been developed but remain to be tested sufficiently on high saline brine treatment (Panagopoulos et al., 2019). Alternatively, for the crystallization and final production of solids, drying technologies such as SD, WAIV, and advanced solar dryer could be implemented. These technologies have the advantage to run mainly on solar or wind energy. However, no water recovery could be achieved with these technologies, and the production of solids remains dependent on climatic conditions (Panagopoulos et al., 2019).

Figure 2-10 shows the maximum TDS concentration of the inlet and the range of the specific energy consumption found in the literature for the different thermal technologies. The majority of technologies are operational for a TDS concentration of 250,000 mg/L. BCr, SD, WAIV, HDH, and TSSE operate until or above the solubility level of the brine resulting in solid salt precipitation. It can be found that the energy demand range of all these technologies is significantly higher than for membrane-based technologies. Additional and future research should focus on the minimization of energy demand by the recovery of heat or steam and alternative technologies (Panagopoulos et al., 2019).

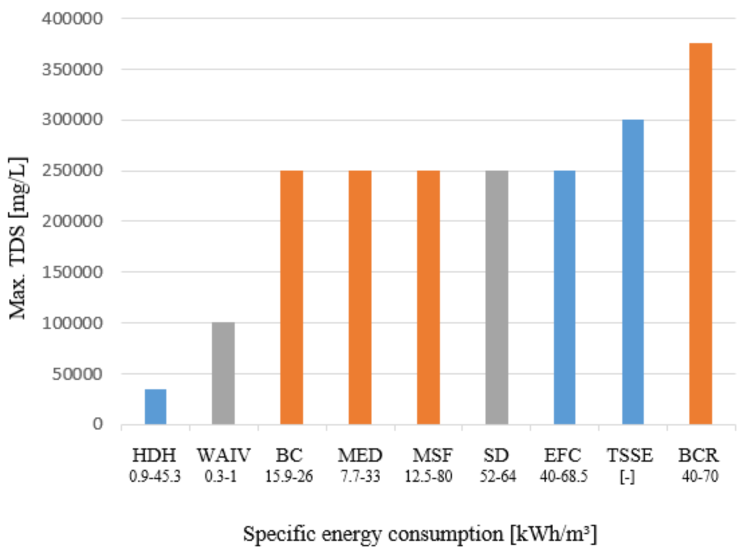

Figure 2-10: Comparison of thermal technologies regarding maximal TDS concentration and energy demand (conventional=orange, emerging=blue, drying=grey)

2.3 Resource recovery technologies

ZLD and MLD systems aim mainly to reduce the brine volume while recovering the water and producing solids. Resource recovery methods on the other hand focus on the extraction of a specific constituent from brine (Shahmansouri et al., 2015). However, the integration of ZLD and MLD technologies for resource recovery and/or the usage of the same technologies in the ZLD and MLD is common. The extraction of valuable resources from brine to offset the costs and to decrease the environmental impact of brine management has been receiving a lot of attention lately.

Several researchers have investigated different methods for the extraction of individual valuable minerals from seawater and to lesser extent desalination brine. To my knowledge, only Shahmansouri et al. (2015), Loganathan et al. (2017), and Mavukkandy et al. (2019) performed a comprehensive literature review on resource recovery from brine. Shahmansouri et al. (2015) set the focus on a cost-benefit analysis for individual minerals while Loganathan et al. (2017) and Mavukkandy et al. (2019) discussed different methods for potentially profitable mineral extraction. Pistocchi et al. (2020) however just shortly discussed resource recovery from brine.

Loganathan et al. (2017) concluded in their study that the extraction of sodium, calcium, magnesium, potassium, lithium, strontium, bromine, boron, and uranium are economically attractive based on the market price and concentration. Pistocchi et al. (2020) state that the extraction of minerals from brine could be just feasible for the elements if the concentration is comparable with, or higher than the average abundance in the upper Earth crust. Figure 2-11 shows the concentration of elements in SW brine after 90 % recovery vs the concentration in the upper Earth crust. It was concluded by Pistocchi et al. (2020) that sodium, chloride, strontium, magnesium, boron, and bromine could be extracted profitable comparing the concentration in the Earth crust to brine.

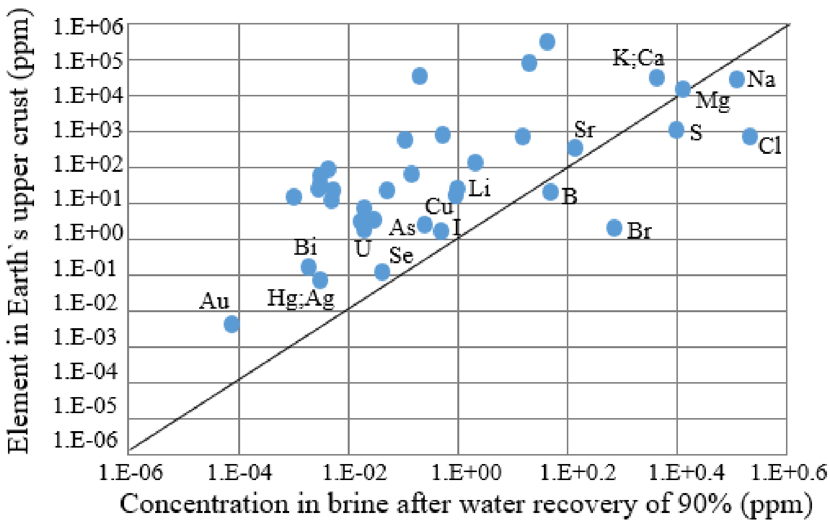

Figure 2-11: Comparison of average concentrations in seawater brine and upper Earth crust (with 1:1 line) (based on (Pistocchi et al., 2020))

However, suitable methods of extraction need to be provided that are more economically beneficial than land mining methods (Mavukkandy et al., 2019). Shahmansouri et al. (2015) observed that the primary cost analysis concluded that the extraction of the majority of compounds would not be profitable considering the current market price and available technologies. Sodium, chloride, potassium, and magnesium could be profitably extracted but the feasibility of extraction is highly dependent on commodity pricing, final product purity, and applied method (Shahmansouri et al., 2015).

This chapter is going to provide an overview of the main resource recovery methods including challenges and future perspectives. The generation of chlorine, acids, and bases from desalination brine has been also discussed as an alternative approach, which is however not further discussed in this research.

2.3.1 Adsorption/desorption process

During adsorption/desorption processes the mineral of interest is taken up by a selective adsorbent while other minerals remain in the water (Loganathan et al., 2017). Afterward, the adsorbed mineral has to be quantitively desorbed from the media using the minimum volume and concentration of the desorbent. Unwanted minerals are removed from the desorbed solution by selective adsorbents to them or by chemical precipitation before finally being crystallized (Loganathan et al., 2017).

Adsorption has the advantage to be a simple, low-cost, and an already established process for wastewater treatment (Loganathan et al., 2017). The adsorption of minerals from brine might be easier than from seawater due to the high concentrations. However, according to Mavukkandy et al. (2019), it is generally complicated to retain a particular mineral at a high concentration because of the low adsorption capacities and selectivity's at the current stage. The adsorbent needs to have high adsorption capacity and selectivity towards the mineral of interest (Loganathan et al., 2017). Some conducted studies indicate that the extraction of minerals from brine is lower than from seawater due to the competition of other ions. Wiechert et al. (2018) for example, states that the amount of uranium absorbed on an amidoxime functionalized adsorbent declined from seawater to brine by 47 %. "The complete selectivity of adsorption/desorption of specific minerals has not been established yet, because of the presence of much higher concentrations of other minerals that compete for adsorption" (Mavukkandy et al., 2019, p.11). Further development of highly selective absorbents is needed for the successful economic-feasible extraction of minerals.

An innovative approach suggests the combination of absorbents with MD, which could increase the economics. So far just studies for the extraction of rubidium from SWRO brine via an MD-adsorption system have been reported (Mavukkandy et al., 2019). It was shown that the system showed a good process performance in terms of rubidium extraction and freshwater recovery. It was concluded that "a continuous supply of feed solution, adsorbent separation and generation enhances the performance of the process" (Mavukkandy et al., 2019, p.8). However, scaling posed a major challenge as. calcium sulfate crystallized and deposited on the membrane surface. Thus, there is a need for further research in the prevention and delay of scaling on membrane surfaces.

2.3.2 Electrodialysis

The usage of monovalent ion-selective membranes to separate monovalent from divalent ions in ED/EDR could generate solutions enriched with the ion of interest (Loganathan et al., 2017). Selective Electrodialysis technology (S-ED) has been studied for the enrichment of sodium chloride as well as recently lithium from seawater (Mavukkandy et al., 2019). Hoshino (2015) studied the recovery of lithium from seawater via dialysis with ion conductive glass-ceramics (Li ionic superconductor) as the ion-selective membrane (LISM) for the recovery of lithium. LISM functions as a salt bridge which made the transport of Li^+ from high- to low-concentration solution possible. During the process, electricity was generated and a lithium recovery ratio of 7 % was achieved after 72 hours without any external power supply. It was concluded further that S-ED and LISM should be applicable for lithium recovery from brine containing lithium but this remains to be tested sufficiently (Hoshino, 2015).

The remaining limitation of this resource recovery process is the precipitation of carbonate and sulfate on the membrane's surface (Mavukkandy et al., 2019). Furthermore, further research is needed to improve the ions` selectivity permeability similar to adsorption/desorption.

2.3.3 Chemical precipitation

Chemical precipitation for the extraction of hardness ions as calcium and magnesium is a known pretreatment technology. However, chemical precipitation has been tested also for the extraction of valuable calcium and magnesium products from brine (Shahmansouri et al., 2015). The extraction of saleable calcium products including calcium sulfate from seawater or brine has garnered very little attention, while magnesium extraction has been studied in more detail.

Magnesium is typically recovered from seawater as magnesium hydroxide via successive precipitation using lime followed by washing and filtration to concentrate the magnesium hydroxide slurry (Shahmansouri et al., 2015). The slurry is then sold or further refined to an end product as magnesia. In general, synthetic magnesia (from seawater) contains fewer impurities than natural magnesia (containing between 92 and 99.5% magnesium oxide) and thus the magnesium market is expected to increase in the future (Shahmansouri et al., 2015). Just recently Dong et al. (2018) and Safar et al. (2020) studied the recovery of MgO from brine via precipitation with NaOH as an alkaline source to react with Mg^{2+}. Both studies showed that the extraction of MgOH at a high temperature is the best. Safar et al. (2020) investigated that 98 % of magnesium could be extracted from SWRO brine at a pH of 10 and 90°C. Dong et al. (2018) studied further that MgO could be further calcined under a range of temperature (500 to 700 °C) and duration (2 to 12 hours) to generate the reactive MgOH as the final product applicable as an additive and a binder for many industries (Mavukkandy et al., 2019) The determination of the optimum $NaOH/Mg^{2+}$ ratio is essential for the production of the highest amount of yield. It was observed, that the synthesized MgO from brine shows much higher purity and reactivity to the commercial MgO.

Mohammad et al. (2019) studied the magnesium recovery potential from brine via precipitating Mg^{2+} with ammonia. The process is based on the precipitation of magnesium hydroxide by the reaction of $MgCO_3$ in the brine with ammonium hydroxide. The recovered $Mg(OH)_2$ could be used for the remineralization of pure water produced by desalination (Mavukkandy et al., 2019). Maximum recovery of 99 % was achieved at a temperature of 15 °C, brine salinity of 85,000 mg/L, and a molar ratio of 4.4 NH_3:1 (Mohammad et al., 2019). The solubility of $Mg(OH)_2$ is proportional to the temperature leading to the recommendation to operate at low temperatures for a complete magnesium recovery. The limitation of chemical precipitation remains the high quantity of chemicals and the possibility of precipitation of other ions resulting in lower purities (Mavukkandy et al., 2019).

2.3.4 Solar evaporation

The application of solar evaporation ponds for the evaporation of water to recover the solely sodium chloride from seawater is widely known. (Loganathan et al., 2017). Traditional salt farming uses several evaporator pans feeding into the final crystallizer pan. Solar evaporation ponds have also been proven successful for potassium chloride, potassium sulfate, sodium sulfate, lithium sulfate, and boric acid recovery (Giwa et al., 2017). Although evaporation ponds are easy to construct and low maintenance, they require a large footprint and are susceptible to land contamination. The pond needs to be lined to prevent groundwater contamination. Thus, the trend is to substitute solar evaporation ponds with alternative drying technologies as WAIV, SD, or ASE (see Chapter 2.2.3.3)

2.3.5 Membrane Crystallization

Membrane Crystallization (MCr) creates supersaturation in solution and creates a metastable state in which crystallization occurs (Loganathan et al., 2017). The advantage of MCr is the controlled optimum supersaturation level resulting in higher quality compared to evaporative separation techniques. According to Loganathan et al. (2017), MCr has been just tested for the production of NaCl and $MgSO_4$ on laboratory-scale experiments. The first attempt for the resource recovery of lithium with MCr from LiCl salt solutions was done by Quist-Jensen et al. (2016). It has been concluded that vacuum MD was the only application that could treat the solution to saturation level, making crystallization and thus lithium recovery successful. It was also concluded that the focus should be on investigating lithium recovery from mixed salt solutions.

The limitations of MCr are the high concentration of major salts in seawater and brine (Loganathan et al., 2017). The selectively fractionalize valuable minerals present at low concentration could be just achieved at high water recovery rates. However, at high water recovery, the effect of polarization and increased resistance to vapor transport within the membrane pores, and the increased risk of membrane scaling will reduce the performance of MCr.

2.3.6 Eutectic Freeze Crystallization

Eutectic Freeze Crystallization (EFC) similar to MCr can simultaneously recover water and resources. EFC can obtain different salts with high purity due to different eutectic points (EP) (Mavukkandy et al., 2019). Katal et al. (2020) present a study where EFC was applied on RO brine. The experiment showed that a water recovery rate of 97 %, as well as recovery of pure Na2SO4 (96.4 % purity) and pure CaSO4 (98 % purity), can be achieved. The investigation of several researchers show that EFC can successfully treat various binary aqueous solutions, such as $CuSO_4$.(Panagopoulos et al., 2019). Nonetheless, the possibility to apply EFC for the separation of multiple salts from multicomponent brine remains to be fully investigated (Panagopoulos et al., 2019).

2.3.7 Conclusion

So far, the majority of extraction schemes in scientific papers for mineral recovery from brine have been proposed or tested only at a laboratory scale (to less extent with actual brine samples) (Shahmansouri et al., 2015). Until now, only a few studies have investigated the potential of mineral extraction from RO brine at a pilot scale. The minerals most widely researched for extraction are sodium, magnesium, lithium, and uranium. Pistocchi et al. (2020) and Shahmansouri et al. (2015) state that currently, the extraction of sodium, chloride, potassium, and magnesium could be economically-feasible. “Mineral recovery could be justified at specific desalination plants, where the logistics foster access to markets” (Pistocchi et al., 2020, p.4). Pistocchi et al. (2020) accounted that if salt production would be implemented universally, the generated salt would exceed the global demand by a factor of 10 resulting in reduced prices and/or impossibility to sell the product. The only resource found to meet the global demand is potassium. “However, technologies to economically separate [potassium] from seawater are not yet available” (Pistocchi et al., 2020, p.4).

It was concluded by Mavukkandy et al. (2019) that the extraction of several materials from desalination brine is technically possible but currently expensive which largely restricts the commercialization. Shahmansouri et al. (2015) state “due to the marginally attractive economics of extraction and significant uncertainties associated with producing commodities, this study suggests that extraction from desalination concentrate is unlikely to significantly improve the economics of desalination unless concentrate disposal costs were significantly reduced as a result” (p.4). “Thus, while an intriguing challenge for the future, [brine] mining is currently hardly a game changer for desalination” (Pistocchi et al., 2020, p.4). “It may gain some traction with the development of separation technologies, as land reserves dwindle, or because of escalating social or geopolitical tensions” according to Pistocchi et al. (2020, p.4). Recently, more and more research projects, such as Sea4value (2020), focus on increasing the economic feasibility of resource recovery techniques via the development of radical innovations got financially supported by inter alia the European Union. This shows the importance of improving resource recovery methods in order to make brine mining economically feasible in the future.

2.4 Solid and liquid waste management

ZLD describes a process that removes all water from the brine aiming to leave no liquid waste. The liquid waste management, traditionally surface water disposal or deep well injection, is thus not needed. The product of a ZLD system is a solid residue of precipitated salts (Erdal, n.d.).

However, in most cases, the product generated in ZLD chains is a concentrated brine, also known as salt slurry, mother liquid, or salt cake (Ahirrao, 2014). Further solid separation treatment is needed to separate the generated crystals from the liquid via centrifuges and dryers. Such technologies are sometimes incorporated in crystallizer but not always or are already applied as the last step of a ZLD chain (see Chapter 2.2.3.3). Thus, sometimes external solid separation technologies are needed. The most common type of centrifuge applied for the chemical and mineral industries is a pusher centrifuge, which provides a continuous filtering of the mixture. The capacity sizing of the centrifuge depends mainly upon two types of inorganic salt: sodium chloride and sodium sulfate (Ahirrao, 2014). The operation of such a pusher centrifuge depends on many parameters such as particle size, viscosity, solids concentration, cake quality, and particle attrition. Dryers, on the other hand apply thermal energy for the separation of solids from the liquid (Ahirrao, 2014). The most common types of dryers are Rotary Drum Dryer, Spray Dryers, or Agitated Thin Film Dryer.

Currently, the only treatment option mentioned in the literature for solids is the transfer to adequate solid waste disposal facilities, e.g. landfills if they do not have any economic value (Erdal, n.d.). In general, toxicity tests are conducted on the residues to determine the type of landfill (municipal solids waste landfill or hazardous waste landfill). The landfills need to be lined and monitored appropriately to avoid the contamination of soil and groundwater via salts and chemicals (Tong & Elimelech, 2016). No research has been found that studied alternative reuse or solid waste management options than the disposal of the less economic value and mixed salts from brine. Giwa et al. (2017) states also that the deposition of solids at landfills “is not the ultimate solution for the brine problem” (p.2).

Often MLD is implemented instead of ZLD due to techno-economic restraints. In such cases, the remaining liquid waste stream needs treatment. The current disposal strategies for brine are surface water discharge, deep well injection, evaporation ponds, land application, and direct reuse application (Pramanik et al., 2017). The choice of the most suitable brine disposal method depends on factors such as "quantity, quality and composition of the brine, availability of receiving site; the permissibility of the option; public acceptance; capital and operating costs and the capacity of the facility for future expansion" (Panagopoulos et al., 2019, p.4). All disposal methods could cause a negative environmental impact and should as much as possible be avoided. "Although there have been advances in desalination process technology, there is a need for further improvements in the disposal of reject brine" (Mustafa et al., 2020, p.1).

2.5 Market analysis and economic aspects

The ZLD and MLD market is closely related to the brine concentration market but is not equal as high-recovery treatment of low salinity feedwaters is not included (Weaver & Birch, 2020). However, the brine concentration market is a growing market with a capital expenditure of around US$ 257 million and a compound annual growth rate of 6.7 % according to Weaver and Birch (2020). Until 2025 the brine concentration technologies are expected to grow steadily.

The market is currently highly dominated by thermal technologies even though emerging technologies and Reverse Osmosis are growing as the innovation is focused on using thermal technologies less (Weaver & Birch, 2020). The key technology segments of the brine concentration market in 2020 are falling film evaporators (>100 m^3/d), crystallizers, small/mid-scale evaporators (10-100 m^3/d) and non-conventional ZLD encompass (including membrane technologies as HPRO). Small/mid-scale evaporator ranges from small kettle boilers to larger more technologically sophisticated evaporator units, which operate like falling film evaporator but at a reduced scale.

Just a few companies provide large-scale brine concentration systems and dominate this market, while the market for mid-range solutions is more crowded (Weaver & Birch, 2020). There is a greater number of local players active in a small quantity of regional or national markets. However, Weaver and Birch (2020) state: "even at this smaller scale, this is a low volume market" (p.14) with 35 companies working in the brine concentration field.

To my knowledge, no comprehensive literature study has been conducted that assesses the total costs of ZLD technologies. The cost associated with ZLD technologies is capital cost, energy cost, and non-energy related operation cost (e.g. labour cost, maintenance, and replacement costs) (Weaver & Birch, 2020). Information of specific unit costs per m^3 however has been given for some ZLD technologies by Weaver and Birch (2020), Panagopoulos et al. (2019), and Panagopoulos (2020a).

The typical unit costs assessed by Weaver and Birch (2020) for the key technologies in US$/$m^3$ split within amortized capital (10 years), energy and non-energy operation costs can be seen in Figure 2-12 (Weaver & Birch, 2020). It can be concluded that non-energy operation costs are neglectable in comparison to capital and energy costs for all technologies. Conventional RO and HPRO have the lowest capital as well as energy costs. Mid-sized evaporators have the highest costs with over US$ 10/m^3 of amortized capital costs making the highest contribution (Weaver & Birch, 2020). The total unit costs of crystallizer result in almost 50 % of energy costs (Weaver & Birch, 2020).

The specific costs assessed by Weaver and Birch (2020) are significantly higher (up to 10 times) than the specific costs of freshwater produced assessed by Panagopoulos (2020a) and Panagopoulos et al. (2019) for several ZLD units, especially for mid-sized evaporator presented in Appendix A and B. However, both studies state that membrane technologies are cheaper than thermal technologies in both capital and operation costs. The capital cost impact of membranes lies in the cost of membranes, whereof the capital cost of thermal technologies are influenced by the usage of expensive anticorrosion material (Charisiadis, 2018; Panagopoulos et al., 2019). It is additionally concluded that with increasing brine concentration, the energy required, and thus energy costs, to separate the remaining free water rises exponentially (Weaver & Birch, 2020). Figure 2-13 shows the specific energy consumption for a variety of ZLD technologies according to their application stages. Crystallization technologies have the highest energy consumption., while the preconcentration step has lower than the evaporation step. “This means that the final step to ZLD (crystallization) can represent the majority of a ZLD system’s total energy consumption” (Weaver & Birch, 2020, p.15). The minimization of brine volume beforehand through preconcentration and evaporation stages is essential to decrease the energy cost of the system.

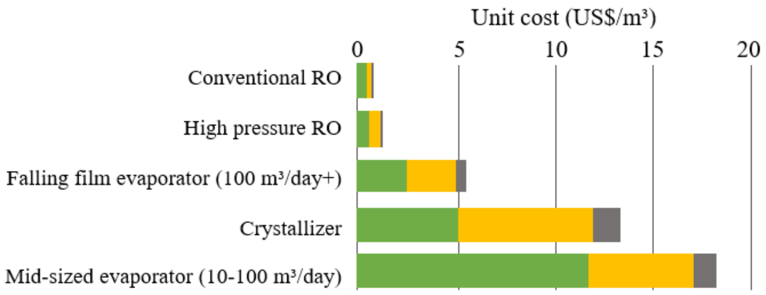

Figure 2-12: Specific costs of the key technologies of the brine concentration market (amortized capital costs (10 years)=green, energy cost=yellow, non-energy operation costs=grey)(based on (Weaver & Birch, 2020))

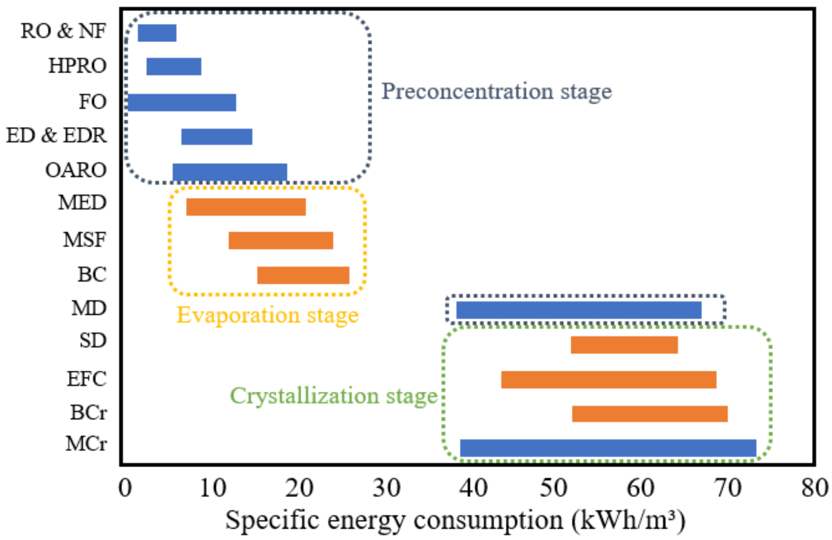

Figure 2-13: Specific energy consumption of ZLD technologies (thermal=blue, membrane=orange) (based on (Panagopoulos, 2020a))

3 Method

3.1 Literature review

The literature study of this thesis is following the qualitative approach (Qchieng, 2009). Qualitative data as reports, books, scientific papers, articles, and additional data are retrieved from Chalmers library and academic research portals as e.g., Scopus with the use of the following search terms: ZLD, MLD, desalination brine management, solid waste management, liquid waste management, seawater and brine mining, resource recovery from saline solution, ZLD market.

3.2 Market survey

Technical and economic data of available technologies are collected by personal communication with companies. To produce more generic answers from the companies, a survey is created and sent out, which includes questions about possible ZLD technologies, capital costs, implementation, and operation requirements including the energy consumption of those.

The companies providing ZLD and MLD technologies have been assessed as follow: The companies working in the ZLD field has been firstly identified by the comparison of ten different market analysis of the global ZLD and MLD market. These reports provide a detailed overview of companies and their ZLD and MLD products as well as the current status and forecast of the global zero liquid discharge. However, they are not freely accessible and thus just the name of 29 companies have been able to be withdrawn from the table of content. Additional 32 companies in the ZLD and MLD market have been assessed by extensive literature review. Those were compared with the companies mentioned by Weaver and Birch (2020) and the final list of the total 61 companies which has been contacted throughout this study is presented in Table C.1 in Appendix C.

3.3 Case study

The result of the literature review, market survey, and personal communication are used to design the ZLD system(s) at the Desolenator's project site as a specific case study. The designed system(s) and associated resource flows are visualized in a schematic flow diagram using the software Excel.

3.3.1 Site characteristics

The pilot project of Desolenator is located in Dubai in the United Arabic Emirates as seen in Figure 3-1. The climate in Dubai is characterized as a tropical desert climate with hot, sunny conditions with temperatures up to 42 °C in summer and 29 °C in winter (Weather Atlas, n.d.). The desalination plant lies within an industrial area located directly at the Arabic Gulf, where the feedwater is taken from.

Figure 3-1: Location of Desolenator's project in the United Arab Emirates (Google, n.d.)

Real-life feedwater data from the Dubai project site have been given for January to November 2018. The water samples have been taken from the intake seawater station at the Arabic Gulf around the 15th of each month and laboratory analysed. The water composition after the simple prefiltration unit which is placed before the MED as well as information about the process performance of such is not available. Furthermore, the sodium, potassium, and bicarbonate concentration in the feedwater was not measured.

Following simplification have been assumed regarding the feedwater composition:

- The total suspended solids, turbidity, and organic content are reduced by the prefiltration unit to a neglectable small amount. Meanwhile, the ion composition has been assumed to remain the same as the feedwater.
- The sodium concentration is assumed to be 10,000 mg/L according to the average seawater constituent concentrations from Lenntech (2020).

The measured concentrations of the feedwater indicate high TDS concentration throughout the year from 40,221 to 46,371 mg/L with a yearly average of 44,293 mg/L. Most of the total TDS concentration is chloride which makes up around 60 % indicating the high salinity of the brine. Based on the seawater composition data retrieved from Lenntech (2020), the sodium and chloride concentration are therefore around 85 % of the total TDS concentration. Scaling ions such as magnesium, calcium, sulfate contribute around 13.5 % to the total TDS concentration with magnesium contributing the most with a yearly average of 1,494 mg/L. The carbonate hardness of the brine measured as $CaCO_3$ is around 8,248 mg/L on the yearly average. The pH of the water is on average 8.31 indicating that the brine is slightly alkaline and leads to a higher risk of scaling. Figure 3-2 shows the variation within the measured concentration of TDS and chloride in 2018. It can be found that 50 % of the TDS and chloride values lie between 42,500 to 46,250 mg/L and 23,700 to 25,300 mg/L, respectively. The upper quarter is close to the maximum value indicating that higher concentration occurred more often. The maximum value of TDS and chloride is around 5 % higher than the average value. However, the average feedwater concentrations were used as a basis for the ZLD design chain.

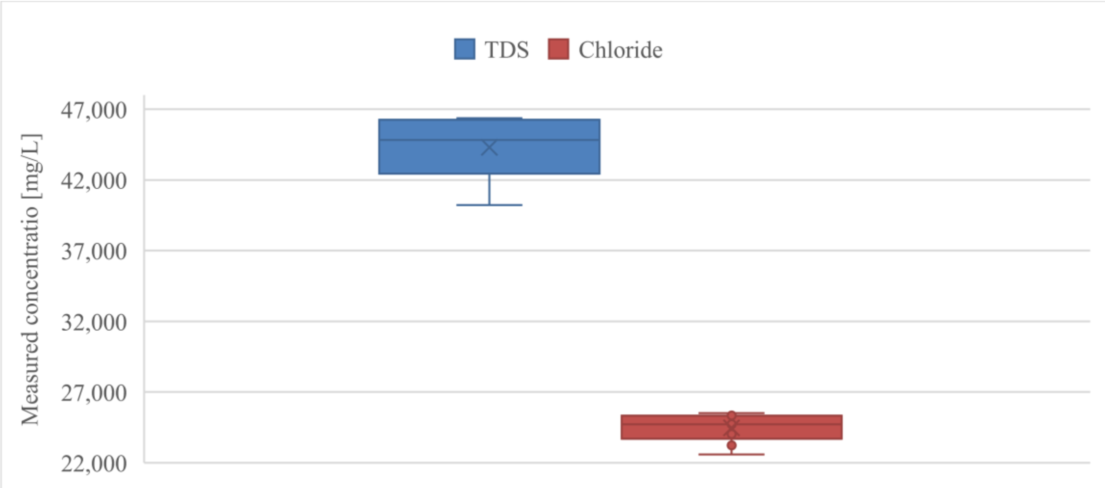

Figure 3-2: Variation within the measured total dissolved solids and chloride concentration in 2018(cross=median, box=lower and upper quartile, whiskers=min. and max. value (based on (C. McGill, personal communication, December 23, 2020)))

3.3.2 Calculation of brine volume and composition

The feedwater data were used to calculate the average yearly concentration of the brine coming from the Desolenator's desalination facility. The incoming brine is separated into distillate and concentrated brine stream in the MED as in all thermal technologies by the addition of external heat as seen in Figure 3-3. The volumetric water recovery rate of the MED without recirculation was given as 42 % for a drinking water production of 20 m^3 (C. McGill, personal communication, December 23, 2020) The brine flow rate under these circumstances was calculated with Equation (1) to 27 m^3 per day. It is assumed that the distilled water from the MED does not contain any constituent concentration resulting in the concentration balance seen in Equation (2). The concentration factor was assessed using Equation (3) and applied in Equation (4) to assess the brine composition and constituent concentrations. The operation hours of the MED system were set to 8 hours and used to receive the flow rate per hour. The water recovery rate and brine composition for thermal technologies as evaporator and crystallizer have been calculated with the same approach, while the selectiveness of ion extraction from brine by membranes has been taken from literature.

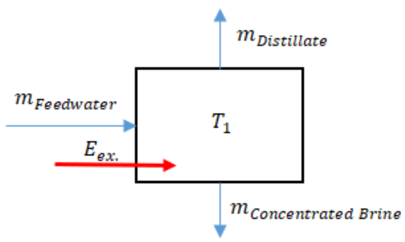

Figure 3-3: Energy-mass balance on an evaporative system.

$$Q_B = \frac{Q_D}{WRR} - Q_D \ (1)$$
$$c_F * Q_F = c_B * Q_B + 0 \ (2)$$
$$c = \frac{1}{1-WRR} = \frac{Q_F}{Q_B} \ (3)$$
$$C_B = c * C_F \ (4)$$

Q_B: Brine flow rate [m^3/d] Q_D: Freshwater flow rate [m^3/d] WRR: Water recovery rate [-] Q_F: Feedwater flow rate [m^3/d]	c: Concentration factor [-] C_B: Brine constituent concentration [mg/L] C_F: Feedwater constituent concentration [mg/L]

The following simplifications have been assumed for the calculation of the water compositions:

- The concentration factor was unified for all concentrations in thermal technologies based on the assumption that the distillate does not contain any constituent concentration. Due to do chemical reactions of constituents to each other and different solubilities at different temperatures could the concentration factor highly differ from the calculated concentrations.
- The maximum TDS concentration in the crystallizer has been set to the solubility level of sodium chloride which has the highest concentration in the brine. However, other constituents are less soluble and precipitation of those at the calculated TDS concentration could occur.
- The process performance of membrane and resource recovery technologies has been taken from studies that were conducted on RO brine. The water composition of the thermal desalination technologies differs from RO brine and could lead to different process performances in praxis.
- Furthermore, it has been assumed that the filtration unit for the extraction of resources after chemical precipitation is removing a neglectable small amount of water.
- For all technologies, the fluctuation of process performance has been neglected and thus the calculated processes just reflect a static value.

3.3.3 Energy calculation

Thermal technologies are commonly based on phase change through evaporation to achieve a further concentration of the brine. The higher the feed concentration, the water recovery rate, and the final concentration of the brine, the more energy is needed to separate the water from the brine (Vane, 2017; Weaver & Birch, 2020). Figure 3-4 shows the minimum work per freshwater produced in dependency of the sodium chloride concentration in the feed.

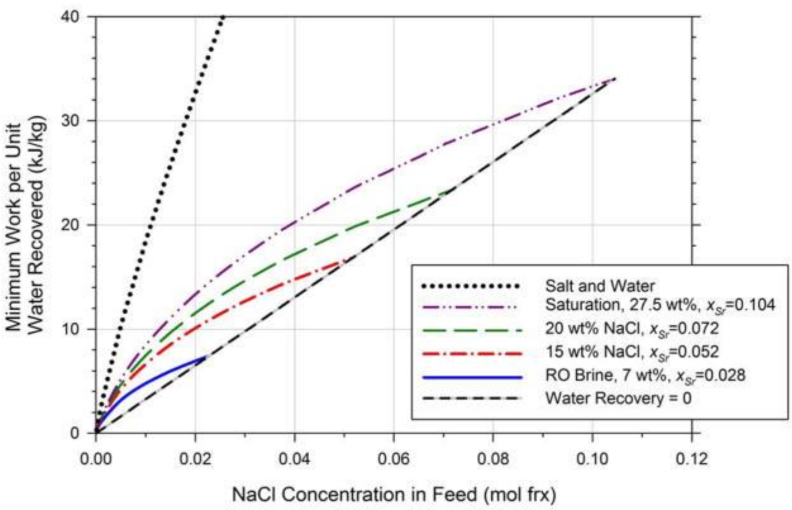

Figure 3-4: Effect of NaCl concentration in the feed streams on the minimum work required at 25 °C to produce water as further functions of the brine reject stream concentration (Vane, 2017)

The theoretical least work of separation per freshwater produced on a mass basis can be calculated for the arbitrary thermal technologies according to Equation (5) (Mistry & Lienhard, 2013). A problem with brine in thermal applications is the so-called boiling point elevation as a result of the high salt concentration in the brine. Therefore, the boiling point of the brine needs to be calculated in dependency on the desired final concentration according to Equation (6) (Atkins et al., 2018). An assumption made for the boiling point calculation was that the total TDS concentration equals the sodium chloride concentration, which just makes up 85 % according to the mass balance of the feedwater data. The Gibb`s free energy of the feedwater, distillate, and concentrated brine needed for the calculation of the least work or heat of separation is the enthalpy minus the entropy of the streams at a specific temperature as seen in Equation (7) (Atkins et al., 2018). The enthalpy is a sum of the temperature and specific heat capacity. The specific heat capacity of the feedwater and concentrated brine depends on the temperature and salinity and was calculated according to Equation (8) to (13) (Ramalingam & Arumugam, 2012). Like the enthalpy is the entropy also influenced by temperature and salinity. The entropy of the streams has been taken from the calculation by Sharqawy et al. (2010).

$$\frac{W_{Least}}{m_D} = \left[(g_D - g_c) - \frac{1}{WRR} * \left(g_f - g_c\right)\right] \text{ (5)}$$

$$T_1 = T_W + K_b * i * m \text{ (6)}$$

$$g = h - T * s = c_p * T - T * s \text{ (7)}$$

- $c_p = 4180 - 4.396 * \left(\frac{S}{100}\right) * \rho + 0.0048 \left(\frac{S}{100}\right)^2 * \rho^2$ (8)
- $\rho(S,T) = a1 + a2T + a3T^2 + a4T^3$ (9)
- $a1(S) = 999.9 + 7.6374 * S + 7.3624 * 10^{-4} * S^2 + 4.7088 * 10^{-4} * S^3$ (10)
- $a2(S) = 0.02592 - 0.033946 * S + 7.7952 * 10^{-4} * S^2 - 9.3073 * 10^{-6} * S^3$ (11)
- $a3(S) = -5.9922 * 10^{-3} + 3.7422 * 10^{-4} * S - 1.0436 * 10^{-5} * S^2 + 1.4816 * 10^{-7} * S^3$ (12)
- $a4(S) = 1.5332 * 10^{-5} - 9.386\,x * 10^{-7} * S + 3.2836 * 10^{-9} * S^2 + 4.0083 * 10^{-10} * S^3$ (13)

W_{Least}: Least work of separation [kJ/h] g_D: Gibb`s free energy of the distillate [kJ/kg] $g_f$: Gibb`s free energy of the feedwater [kJ/kg] T_W: Boiling point of water [°C] i: Van't Hoff factor is 2 for NaCl m: Molarity [mol/kg] h: Specific enthalpy [kJ/kg] s: Specific entropy [kJ/kg*K] S: Salinity [% by weight] ρ: Density of water [kg/m^3]	m_D: Distillate mass flow [kg/h] g_c: Gibb`s free energy of the concentrated brine [kJ/kg] $WRR$: Water recovery rate [%] $T_1$: Boiling point/Heat source temperature [K] $K_b$: Ebullioscopic constant=0.51[°C*kg/mol] $g$: Gibb`s free energy [kJ/kg] T: Temperature [K] or [°C] c_p: Specific heat capacity [kJ/kg*°C]

The actual energy demand differs highly from the minimum energy demand due to the non-existence of 100 % energy efficiency (Vane, 2017). This leads to the definition of Second Law Efficiency for the generic steady-state separation process, which is defined as the ratio of the minimum work to the actual work as seen in Equation (14) (Vane, 2017). Thiel et al. (2015) defined different Second Law Efficiencies of desalination technologies, which has been taken as input for Equation (14). Figure 3-5 shows the Second Law Efficiency of MVC in dependency of the feed salinity, compressor efficiency, and terminal temperature difference in the evaporator-condenser unit. The heat needed for raising the temperature if the separation of the stream is not desired can be calculated with Equation (15) and multiplied with the efficiency of a heat exchanger to access the actual energy demand.

$$\frac{W_{Least}}{m_D} * \frac{1}{n_{II}} = \frac{W_i + Q_i * (1 - \frac{T_o}{T_H})}{m_D} = \frac{E_{Actual}}{m_D} \quad (14)$$

$$\frac{Q_{ex.}}{m_F} = c_p * (T_1 - T_f) * L \quad (15)$$

W_{Least}: Least work of separation [kJ/h] n_{II}: Second Law Efficiency [-] Q_i: Net heat input [kJ/kg] T_H: Heat source temperature [K] $Q_{ex.}$: External Heat [kJ/kg] m_F: Feed mass flow [kg/h] c_p: Specific heat capacity [kJ/kg*°C] L: Energy loss factor [%]	m_D: Distillate mass flow [kg/h] W_i: Net work input [kJ/kg] T_o: Ambient Temperature [K] E_{Actual}: Actual Energy of separation [kJ/h] T_f: Feed water temperature [K] T_1: Boiling point/Heat source temperature [K]

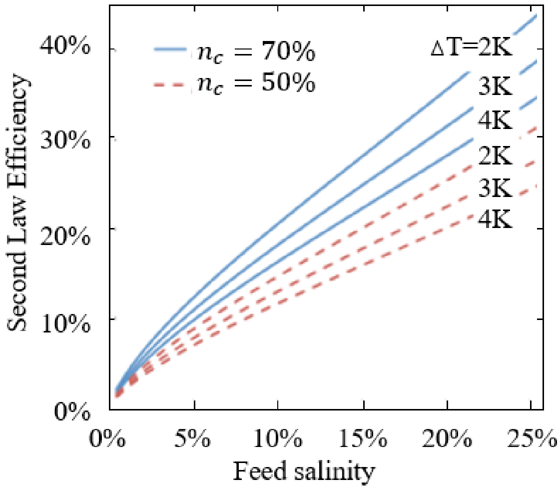

Figure 3-5: Second Law Efficiency of thermal technologies with MVC in dependency of the feed salinity (based on (Thiel et al., 2015))

Alternatively, preconcentration by **membrane technologies** to reduce energy consumption could be implemented (Panagopoulos et al., 2019). ED separates the brine into a diluted and a more concentrated saltwater stream. The efficiency of the process depends on the membrane specifications, current density, and the duration of the process. Figure 3-6 shows the process efficiency of an ED membrane in dependency of the time and current density (Jiang et al., 2014). The selectiveness of ED was based on literature studies (Casas et al., 2012; Jiang et al., 2014; Liu et al., 2016). The energy of ED is the sum of the energy needed to reduce the salinity and energy for pumping. The energy needed for the ED process is calculated according to Korngold (1982) using Equation (16). The energy needed for pumping could not be calculated but adjusted according to Tonner and Tonner (2004) who define the relationship between the energy of separation to energy for pumping as 1:2.

$$E_D = \frac{26.8 * (C_1 - C_2) * i * r}{n * 1000} \quad (16)$$

E_D: Energy requirement (Wh/m^3) n: Desalination efficiency [-] r: Specific resistance of a cell pair (Ω cm^2)	C_1: Initial concentration (meq/L) C_2: Final concentration (meq/L) i: Current density (mA/cm^2),

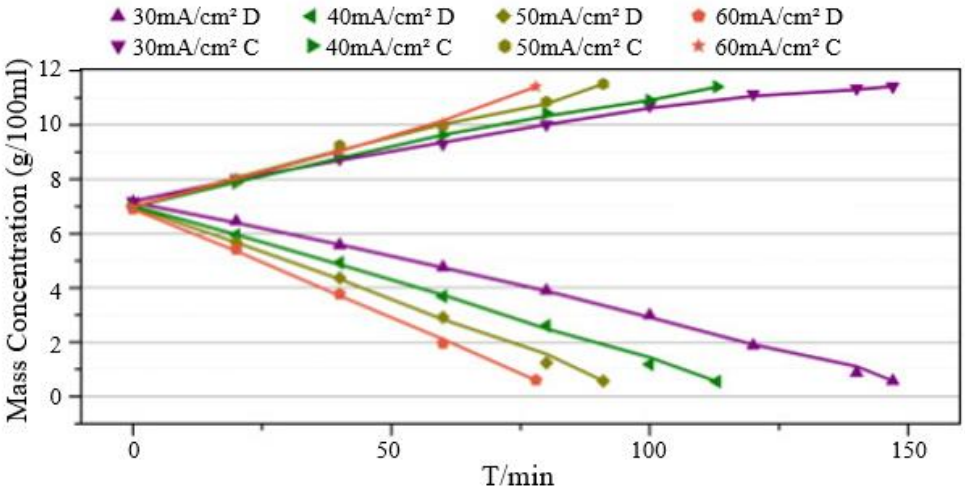

Figure 3-6: Mass concentration vs. time curve of an ED membrane at different current densities, initial mass concentration is 7.0% (m/v) (C=concentrated stream; D=diluted stream) (based on (Jiang et al., 2014))

The following limitations and simplification have been identified:

- The needed specific heat capacity, enthalpy, and entropy were calculated by Equation (7) to (8) and taken from data that have been just validated at atmospheric pressure and until concentration up to 120,000 mg/L with an accuracy of +/- 5 %.
- The heat exchanger efficiency has been set to 80 % for the brine heating in non-separation processes, which is exceptionally high.
- The specific resistance of membranes has been taken as an average from the studied membranes by Jiang et al. (2014).

Nevertheless, the validation of the calculated energy data has been done by comparing literature values and it has been found that despite the chosen assumption the calculated energy demand is similar to the literature values.

3.3.4 Quantity of chemicals and resources

The theoretical amount of chemicals needed to reach the desired pH for chemical precipitation has been calculated by Equation (17) to (18). The molar concentration of the chemicals as NaOH was chosen as 0.7 M because it is the most common concentration (Katal et al., 2020).

$$[H^+] + [OH^-] = 10^{-14} \quad (17)$$

$$Q_S = \frac{[OH^-]*Q_B}{c-[OH^-]} \quad (18)$$

Q_S: Flow rate of chemical [l/h] Q_B: Flow rate of brine [l/h]	c: Molar concentration of the chemical [M]

The assessment of the quantity of extracted resources is relevant for the economic evaluation of the ZLD design. The total quantity of solids has been calculated as the sum of TDS concentration and the flow, which refers in the dependency of the purity to sodium chloride. The amount of magnesium oxide, which is the product of the chemical precipitation of magnesium with NaOH has been calculated based on the molar mass: 1 kg of magnesium results in 1.658 kg magnesium oxide (Safar et al., 2020).

3.3.5 Multi-criteria analysis

In order to assess the best fitting technology, the three different design ideas are compared by a multi-criteria analysis (MCA). No literature has been found that uses a MCA for the evaluation of proposed ZLD treatment chains. Panagopoulos and Haralambous (2020) did however compare a MLD to a ZLD treatment chain under the consideration of the following 9 criteria: Framework stages, technologies, freshwater recovery target, feed brine salinity, energy consumption of each technology, GHGs emissions, cost impact, resource recovery, and social impact.

These criteria have been combined with the criteria used by Cossio et al. (2020) for the assessment of the sustainability of small wastewater treatment systems in low-income countries. The ZLD design ideas are compared in the following dimensions: environmental, social, economic, technical, and institutional. Appendix D shows the indicators for each dimension including a description and suggested units.

In the Desolenator case study, the indicators are discussed based on the calculation and/or literature values. For indicators based on calculated values, three stages have been defined according to literature values (Charisiadis, 2018; Kress, 2019; Mavukkandy et al., 2019; Panagopoulos et al., 2019). The calculated values for each design idea are assigned to the three stages (green-lowest, yellow-moderate, red-highest), respectively. For the indicators where the value could not be calculated, the indicators are discussed based on literature values and a ranking system from 1 to 3 (lowest to highest impact) is applied. Institutional dimensions are neglected for the comparison of the three design chains as the provider of the ZLD chain remains Desolenator and the value is expected to be the same.

3.3.6 Techno-economic analysis

The best-fitting technology of the proposed design ideas chosen by MCA is also economically evaluated. In order to answer the last research question regarding at what point the ZLD treatment chain would break even, a techno-economic analysis is conducted.

Lauer (n.d.) explains several options in his methodology guideline on techno-economic assessment (TEA). Out of the presented TEA methods the net cash flow table is chosen. This method gives according to Lauer (n.d.) "an excellent overview on the timeline of incomes and payments over [the] project period" (p.20).

The net cash flow table compares revenue, operation cost (OPEX), investment related OPEX as well as investment cost (CAPEX) to each other:

- The **revenue** of a ZLD treatment chain is the reimbursement of the water and if applied resources/salts.
- The **OPEX** is a sum of the maintenance, energy, labour, and other costs (e.g. waste disposal) (Lauer, n.d.).
- The **investment related OPEX** includes the administrative and insurance cost, the periodical cost for infrastructure, location, and building, as well as planning and consulting costs (Lauer, n.d.).
- The **CAPEX** reflects the capital costs of all equipment as well as the construction and shipping costs (Lauer, n.d.).

The main difficulty of techno-economic analysis is to produce realistic data for the cost components (Lauer, n.d.). The cost data for revenue and the majority of investment costs have been assessed through literature review, market survey, and given by

Desolenator. The specific capital cost parameter by Weaver and Birch (2020) has been found to correlate with the specific capital cost by the market survey. Thus, the specific OPEX given by Weaver and Birch (2020) is taken as an input parameter for the thermal technologies. Lauer (n.d.) states: "cost assessment can only be made on comparative basis looking at existing similar technologies or applications with data available" (p.9). Missing cost data are taken from Panagopoulos (2020b) and Smets et al. (2016), which are comparative to the case study. The techno-economic analysis has been done in Euro. For the conversion of USD to EUR, the rate of exchange has been taken from the stock market on the 29th of December using Finanzen (https://www.finanzen.net/waehrungsrechner).

The following simplification has been made:

- It is assumed that the planning and implementation time of the project will take one year. Thus, the investment cost will be spent in the first year of project development. It is furthermore assumed, that the investment is paid from own capital without a bank loan.
- The investment cost for land development as well as the periodical cost for infrastructure, location, and building of the ZLD chain are neglected because the project site is already owned and developed by Desolenator. Furthermore, the planning and consulting cost has been neglected in this case study as the engineering work will be mainly done by Desolenator staff.
- Cost parameters for pipes and pumps are simplified and assumed to be included in the investment costs of the ZLD technologies. Additionally, it is first assumed that the crystallizer includes an internal drying technology.
- The interest and inflation rates are neglected in this study as the water price is set to the Lowest Levelized Cost of water and the energy is generated by Desolenator which neglects and lowers dependency on the market.

It is explained how each of the cost parameters are defined below:

- **Revenue:** Desolenator wants to keep the Lowest Levelized Cost of water drinking water of US\$ 1/m^3 (C. McGill, personal communication, December 23, 2020). The reimbursement of salt has been set to a minimum of US\$ 180/ton (Nayar et al., 2019; Panagopoulos, 2020b).
- **OPEX:** The non-energy related OPEX for crystallizer and evaporator are defined as EUR 1.08/m^3 and EUR 0.62/m^3 by Weaver and Birch (2020), respectively. The variable and fixed OPEX for the PV-T panels are taken from Smets et al. (2016) as EUR 0.009/kWh for electrical and EUR 0.038/kWh for solar thermal energy. Desolenator's PV-T panels generate 1.4 kWh/ day electrical and 4.8 kWh/ day thermal energy resulting in OPEX of EUR 0.0312/kWh per panel (C. McGill, personal communication, December 23, 2020). Another considered OPEX is the waste disposal fee. This cost data for Dubai for 2020 has been taken from a newspaper article as US\$ 27/ton (Writer, 2018).
- **Investment related OPEX:** The administrative and insurance cost are just considered as investment related operation cost, which is set according to Lauer (n.d.) to 2 % of the CAPEX.

- **CAPEX:** The average investment cost per litre per year for evaporator and crystallizer has been assessed by the market study. The data retrieved from companies are indicating an average cost of 0.0244 EUR/litre/year for an evaporator and 0.05826 EUR/litre/year for a crystallizer. Desolenator provided the cost parameter for the PV-T panels as 400 EUR/panel (C. McGill, personal communication, December 23, 2020). The shipping and installation cost for the ZLD technologies has been defined as 70.1 times the daily freshwater production by Panagopoulos (2020b).

The number of PV-T panels required to power the ZLD process has been assessed according to Equations (19) and (20) for the calculated energy requirement. It has been assessed based on the energy data retrieved from the ZLD technology provider that for evaporator and crystallizer the electrical energy demand is around 0.2-0.5 % of the total energy requirement. Based on these data (0.2 % electrical energy demand for evaporator and crystallizer) the minimal number of panels needed results in 295 for thermal energy and 3 for electrical energy. The remaining electrical energy is assumed to be sufficient to provide the energy for pumping and a centrifuge. According to Szepessy and Thorwid (2018) is the minimum specific energy consumption for a high-speed centrifuge at the flow rate of around 5.5m^3/d at 13 kWh/m^3, which is highly comparable to the 13.5 kWh power consumption of the Condorchem centrifuge (Condorchem, personal communication, November 12, 2020). According to Equation (19), 53 panels are needed to provide this electricity. Thus, more than 200 panels remain to provide electricity for pumping. The time until the initial investment is paid back is calculated with Equation (21) as the ratio of CAPEX to the annual net cash flow.

$$n_{Panels} = \frac{E_{electrical}}{1.4} \quad (19)$$

$$n_{Panels} = \frac{E_{thermal}}{4.8} \quad (20)$$

$$Payback\ time = \frac{Inital\ Investment}{Annual\ Net\ Cash\ Flow} \quad (21)$$

n_{Panels}: Number of PV-T panels [-] $E_{thermal}$: Minimal thermal energy [kWh/d]	$E_{electrical}$:Minimal electrical energy [kWh/d]

4 Market survey

In order to assess the actual capital costs and energy demand of ZLD technologies, a market analysis is conducted. The companies presented in Table C.1 in Appendix C have been contacted by email and/or phone to assess techno-economic data of their technologies for 7 to 30 m^3/d of brine with TDS concentration in the range of 40,000 mg/L to 70,000 mg/L. As seen in Figure 4-1, 34.42 % of the companies did reply or provided more details. Out of the 21 companies replying just 47.62 % provide technologies suitable to the given flow and TDS concentration.

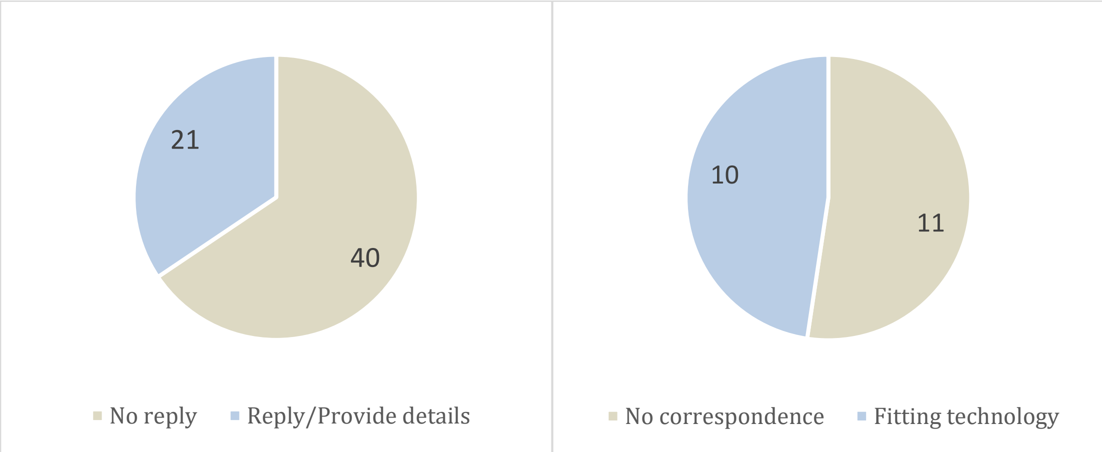

Figure 4-1: Companies interaction: Number of companies replying/providing details (a); Number of companies providing fitting technologies (b)

The 10 companies providing suitable technologies suggested and/or only shared information about thermal technologies mainly vacuum evaporators. Table C.2 in Appendix C provides the summary of the market survey. Figure 4-2 shows the capital costs (CAPEX) of evaporator and crystallizer in dependency on the maximum water flow. It can be concluded that the cost of evaporators, as well as crystallizers, tends to raise with increasing water flow rate. However, prices range from up to double the price could be also found for the same flow rate. This could be explained due to the application of different anticorrosive materials, which could make up half of the total CAPEX costs (Weaver & Birch, 2020). It can be found that the CAPEX cost (e.g. Aquatech) which has been just roughly given differ highly from the norm.

It can be concluded, the CAPEX cost for crystallizers tends to be slightly lower than those for evaporators. However, in dependency of the flow rate, it can be found that that the cost of crystallizer for 125 l/h is more or less the same for evaporator for 1250 l/h. The average CAPEX for evaporator has been calculated to around 24.45 EUR/m^3/yr and for crystallizer to 58.27 EUR/m^3/yr without the outlying values. The amortized capital cost from Weaver and Birch (2020) for a lifetime of 10 years has been given to US$ 5/m^3 for crystallizer, US$ 2.5/m^3 for falling film evaporators, and US$ 12/m^3 for mid-sized evaporators. According to the conversion rate of USD to EUR from the stock market on the 29th of December using Finanzen (https://www.finanzen.net/waehrungsrechner), this results in 41.1 EUR/m^3/yr for crystallizer, 20.55 EUR/m^3/yr for falling film evaporator, and 98.63 EUR/m^3/yr for mid-sized evaporators. It can be found that the assessed CAPEX per m^3/yr for crystallizer and evaporator are highly comparable to the values given by Weaver and Birch (2020) for crystallizer and falling film evaporator showing that the costs of the mid-sized evaporator are lower than reported.

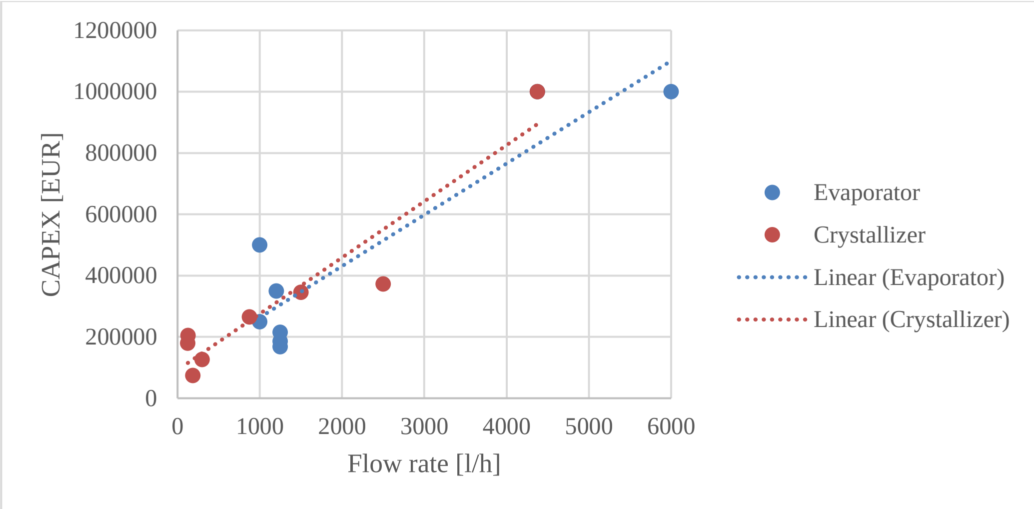

Figure 4-2: Market survey: Capital cost of evaporator and crystallizer in relation to flow rate.

The technologies are driven by a variety of energy sources like electricity or steam and were given in several units as seen in Table C.2 in Appendix C. Thus, the energy demand per-flow rate cannot be compared for all technologies. Figure 4-3 shows the specific energy demand in kWh per m^3 in dependency of the flow rate for some of the technologies where electrical energy is just needed or the alternative energy demand was transferable to the required unit. Despite the limited amount of data, it is apparent that in general the higher the flow rate the lower the energy consumption. This agrees with the observation from Weaver and Birch (2020) that the specific energy demand of large scale evaporator is lower than of small/mid-sized evaporator.

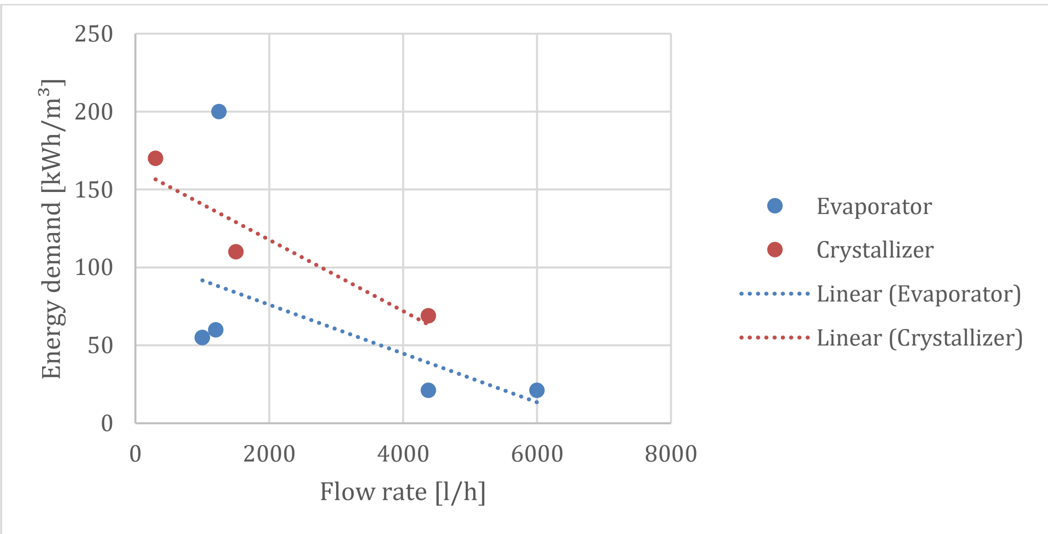

Figure 4-3: Market survey: Specific energy demand of evaporator and crystallizer in relation to the flow.

Figure 4-4 shows the minimum CAPEX costs per litre and year of evaporators in relation to the theoretical water recovery rate. The CAPEX per litre a year is the lowest for the lowest water recovery rate from high saline brine indicating the usage of less cost-intensive robust material. In general, a minimal trend towards higher water recovery rates with increasing CAPEX per litre a year can found.

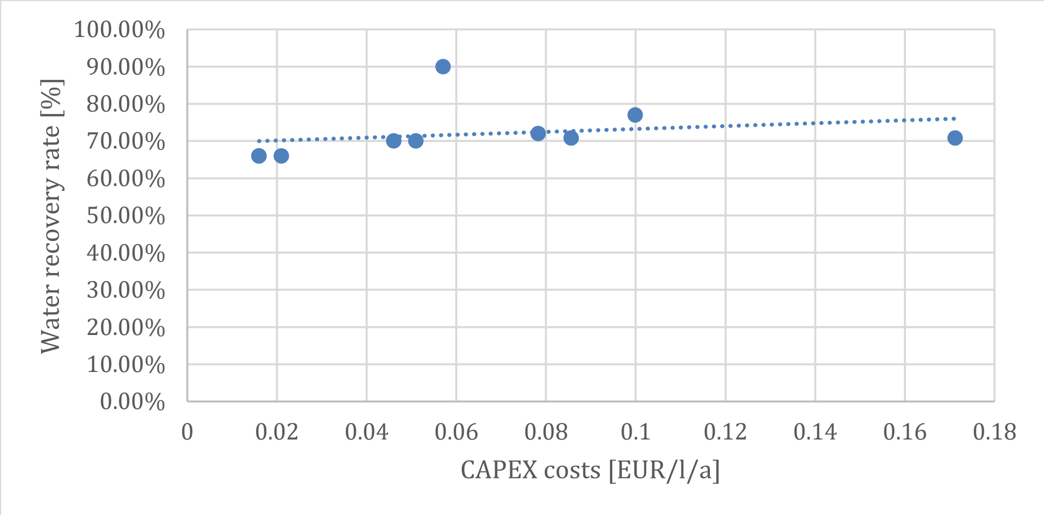

Figure 4-4: Market survey: Theoretical maximum water recovery rate for evaporator in relation to specific capital cost.

A similar comparison for crystallizer is difficult to make due to the lack of information from companies. Most of the companies indicate that their crystallization technology treats up to ZLD, the definition in terms of water recovery rate has not been given. Some companies indicate that their crystallization technologies remove the remaining water until a dry residue content of the salt is reached. Therefore, it is assumed that such technologies must incorporate a solid separation technology as e.g. centrifuge. Just one company states that the crystallizer can concentrate the brine until saturation level and an additional centrifuge is needed. This technology has the lowest specific costs per year at below 0.02 EUR/l.

5 Zero-liquid discharge system at Desolenator's project site

The aim of the study is to propose a Zero Liquid Discharge (ZLD) system that can be coupled with Desolenator's technology in terms of water recovery and energy efficiency as well as accessing the feasibility of such a design. Real-life feedwater data of the Desolenator's project site in Dubai is used for the analysis, which includes basic mass-energy balance calculations. The proposed systems are compared via a multi-criteria analysis to assess the best fitting technology. Afterward, the economic feasibility of the best fitting technology is evaluated using a techno-economic analysis.

5.1 Design

Below three different ZLD design ideas are described including the energy-mass balance. The first two are based on thermal technologies while the third one is incorporating ED as a membrane-based minimization technology.

5.1.1 First design idea (Evaporator+Crystallizer)

In the following chapter, the combination of an evaporator to reduce the volume followed by a crystallizer to harvest the salts is investigated. Considering the composition of the brine at the DEWA site, it is suggested to concentrate the brine up to 200,000 mg/L TDS concentration with a vacuum evaporator using moderate anti-corrosive material (up to 120,000 mg/L Cl^-) with a 5 % safety factor to remain throughout the year within the concentration limitation. Afterwards, the brine is concentrated in the crystallizer up to saturation level to produce a mother liquid with salt crystals, the so-called salt cake. The schematic flow diagram of the system can be seen in Figure 5-1 (a).

The concentration of the brine to 190,000 mg/L at a temperature of around 60 °C results in a theoretical water recovery rate of 59.8 %. The theoretical constituent concentration has been calculated with the concentration factor and the results are shown in Table E.2 in Appendix E. The minimum work required for the separation into pure water and 20 % salinity brine with a feed brine salinity of 7.7 % has been calculated according to Equation (5) to 17.27 kJ/kg (Mistry & Lienhard, 2013). The actual energy demand of thermal technologies with MVC has been calculated with the Second Law Efficiency (Thiel et al., 2015). It has been found that the second law efficiency of MVC at a feed salinity of 7.7 % is at a maximum of 16 % (Thiel et al., 2015). Thus, the calculated minimum actual energy demand results in 107.94 kJ/kg (~29.98 kWh/m^3).

The concentrated brine from the evaporator is treated up to 370,000 mg/L which refers to the saturation level of NaCl at 60 °C according to Pavuluri et al. (2014). The theoretical water recovery rate results in 45,95 % including the 5 % safety factor. The minimum work of separation has been calculated to 67.18 kJ/kg. The incorporation of an MVC would lead at 20 % feed concentration to a Second Law Efficiency of maximal 35 % (Thiel et al., 2015). Therefore, the minimum actual energy needed for separation is calculated to 191.94 kJ/kg (~53.32 kWh/m^3). The sodium chloride purity according to the mass balance is calculated to **84.86 %** in this scenario, whereof the water quality is assumed to be **0 mg/L TDS concentration** without any chemical usage.

The theoretical water recovery of the total system results in around **78.27 %** with a total calculated actual energy consumption of **83,3 kWh/m^3** for the freshwater produced. Figure 5-1 (b) shows the expected specific energy consumption in relation to the water recovery rate for the proposed system. Figure 5-1 (c) shows the variation of TDS concentration within the treatment chain throughout the year. It can be found that the safety factor of 5 % is sufficient to be below the concentration limit.

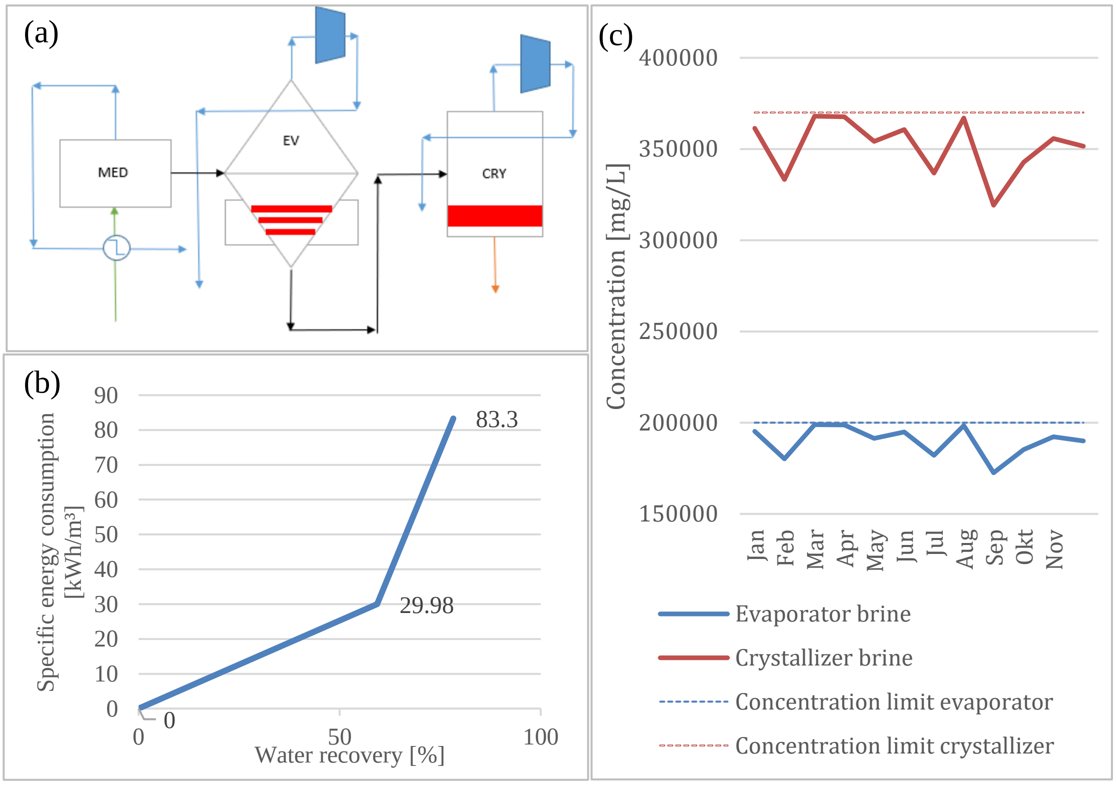

Figure 5-1: Schematic flow diagram of first design idea (EV+CRY) (feedwater=green, freshwater=blue, brine=black, resources/salts=orange) (a). Theoretical specific energy consumption of the system`s technology as a function of the water recovery rate (b). Variation of TDS concentration throughout the year within the evaporator and crystallizer (c).

5.1.2 Second design idea (Evaporator+Advanced Solar Evaporator)

Alternatively, the brine could be concentrated by an evaporator until 300,000 mg/L (30 % saline concentration) if highly anti-corrosive material is used and afterwards be treated by Advanced Solar Evaporation (ASE). The constituents of concern, e.g. hardness as magnesium, should be reduced by chemical precipitation. Table E.2 in Appendix E shows the calculated flow and concentration for each step of the design idea.

According to Safar et al. (2020) and Sanmartino et al. (2017) is the precipitation of magnesium the most effective when adding NaOH at high temperatures (above 78 °C). Safar et al. (2020) showed in the experiment that a pH of 10 and a temperature of 90 °C could lead up to 98 % magnesium, 20 % calcium, and 25 % sulfate removal from brine. The magnesium is expected to precipitate as $Mg(OH)_2$ resulting in a possible reimbursement. To reach the desired pH of 10 an addition of **0.49 l/h** of NaOH (0.7 M) is needed. The heat required to elevate the temperature to 90 °C results in 214.13 kJ/kg (~59.48 kWh/m^3) without recirculation according to Equation (15). It is assumed that the brine could be preheated to 80 °C by the recirculating brine resulting in energy consumption of 38.9 kJ/kg (~10.81 kWh/m^3) and a heat exchange efficiency of around 80 % (first law efficiency). Heat exchange efficiencies of 80 % or above can be theoretically achieved in dependency of the heat exchange area (Chávez & Godínez, 2020; Deethayat et al., 2015; IPIECA, 2020) The brine is afterward cooled down to ambient temperature before filtration (needed pore space around 0.45 µm). The filtrated brine needs to be adjusted to a neutral pH to prevent precipitation and corrosion within the evaporator. Polycarboxylic-acid used commonly before membrane desalination as an antiscalant could be added. With a molar concentration of 0.7 M, **0.49 ml/h** of polycarboxylic-acid is needed. This refers to a total chemical consumption of **0.157 ml** per litre freshwater produced.

Due to the remaining high concentration of scaling ions and hardness in the brine, a safety factor of 5% is applied in the evaporator which results in a final TDS concentration of 285,000 mg/L. For such a concentration, the water recovery rate results in 74.33 %. The least work of separation has been calculated according to 24.74 kJ/kg (6.87 kWh/m^3). The Second Law Efficiency for MVC remains maximal for 7.7 % saline brine at 16 % resulting in minimal actual energy of 154.63 kJ/kg (~42.95 kWh/m^3) (Thiel et al., 2015). The concentrated brine could be afterward dried by ASE. The research by Wu et al. (2020) showed that the designed three-dimensional solar evaporator could effectively evaporate high-salinity brine (25 wt.% NaCl). The solar-driven evaporation rate of 2.63 kg/m^2h with an energy-efficiency of over 96 % and a water collecting rate of 1.72 kg/m^2h was achieved using high-saline water (Wu et al., 2020). According to this research data, a water collecting rate of 65.4 % would be possible with at least 320 m^2 evaporation area. However, information about the water quality is not given by Wu et al. (2020) and it is simply assumed that the evaporated water does not contain any constituents.

The total system could therefore recover **91.11 %** of the water with specific minimal energy requirements of **53.76 kWh/m³**. Figure 5-2 shows a schematic diagram of the process scheme and Figure 5-3 the theoretical specific energy demand. The extracted magnesium in form of $Mg(OH)_2$, as well as the final crystals sodium chloride of **90.18 %**, could create a reimbursement of the system.

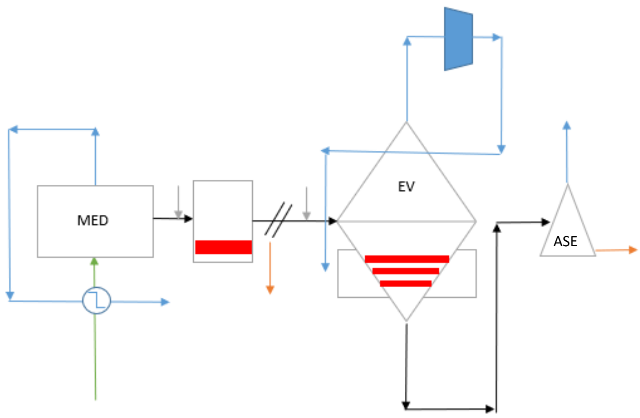

Figure 5-2: Schematic flow diagram of second design idea (EV+ASE) (feedwater=green, freshwater=blue, brine=black, resources/salts=orange, chemicals=grey)

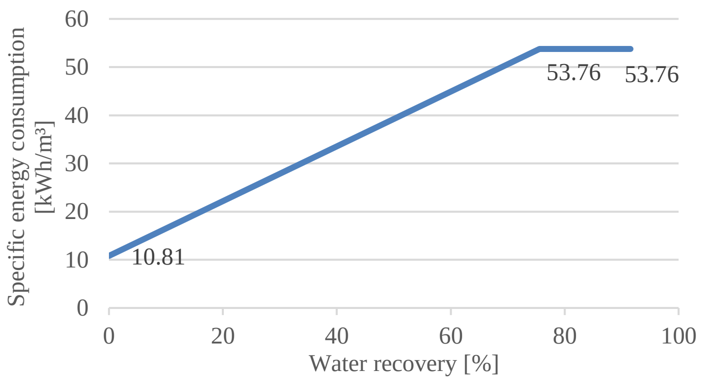

Figure 5-3: Theoretical specific energy consumption of the second design system`s technology as a function of the water recovery rate

5.1.3 Third design idea (Electrodialysis+Crystallizer)

Membrane-based processes such as ED could be applied to reduce the energy demand of the total treatment chain. Jiang et al. (2014) conducted experiments where ED was directly applied for the treatment of SWRO brine. It has been shown that the two tested brines with 70,000 and 105,000 mg/L TDS could be diluted until 470 mg/L TDS concentration with all tested ion-exchange membranes concerning time and current density, while concentrating the brine to 114,100 mg/L and 160,000 mg/L, respectively. The TDS concentration of the diluted brine lies slightly over the WHO standard guidelines (300 mg/L TDS). However, mixing the brine with the distilled water of the crystallizer and MED would be reducing the total TDS concentration to around **256 mg/L** which is below the drinking-water quality limit.

The brine used in the experiments of Jiang et al. (2014) has a significantly lower concentration of hardness, e.g. calcium and magnesium. Despite the low concentration, the precipitation of magnesium on the membrane's surface has been observed with operation time reducing the process performance of the ED. Therefore, the hardness of the DEWA brine has to be reduced. Giwa et al. (2017) mention that the application of the pellet reactor on brine has successfully removed 98 % of calcium hardness in the water after adjusting the pH to 9 with a mixture of lime and caustic soda while removing 5 % of the water. The main advantage compared to traditional chemical softening is the production of relatively dry sludge, which can be directly disposed of at landfills. However, pellet reactors are not able to remove magnesium. Therefore, the chemical precipitation of magnesium with NaOH at a pH of 10 and a temperature of 90 °C according to the experiment by Safar et al. (2020) is suggested.

The theoretical heat needed for raising the temperature has been like in the second design idea (EV+ASE) calculated to 38.9 kJ/kg (~10.81 kWh/m^3) assuming a heat exchanger efficiency of 80 % (Chávez & Godínez, 2020; Deethayat et al., 2015; IPIECA, 2020). The need for the adjustment of 10 results in the need of **0.49 l/h** of NaOH with a molar concentration of 0.7 M. Decreasing the pH after the chemical precipitation to 7 leads to the need of around **0.47 ml/h** of polycarboxylic-acid acids, which also works as an antiscalant. This results in a total demand of chemicals of **0.148 ml** per litre of freshwater produced.

The softened brine is afterward treated by the first ED stack to a concentration of around 110,000 mg/L and in the second stack to 160,000 mg/L. The increasing TDS inlet concentration into the second ED results in lower water recovery efficiency. While the first stack can recover a maximum of 77.75 % of the water, the second ED recovers

64.5 % (Jiang et al., 2014). The required energy of the ED stacks to reduce the salinity has been calculated using the equation from Korngold (1982). The average specific resistance has been set to 2.965 $\Omega*cm^2$ calculated as the average of the membranes used by Jiang et al. (2014). The required energy was calculated for the range of minimum and maximum current density (30 to 60 mA/m^2). The energy demand for decreasing the salinity of the first ED results in 2.82 to 5.64 kWh/m^3 with a desalination efficiency of 98.51 % and for the second ED in 4.53 to 9.06 kWh/m^3 with a desalination efficiency of 98.57 % per freshwater produced. The relationship between the energy needed to reduce the salinity to the energy for pumping is according to Tonner and Tonner (2004) 1:2. Therefore, the total energy of the first ED stack is 8.46 to 16.92 kWh/m^3 and for the second ED 13.59 to 27.18 kWh/m^3.

The concentrated ED brine with a concentration of around 160,000 mg/L is fed into a crystallizer where the brine is concentrated until 370,000 mg/L with a 5 % safety factor. The theoretical water recovery in the crystallizer results in 54.48 %. The minimum work of separation has been calculated to 73.22 kJ/kg (~20.24 kWh/m^3). According to Thiel et al. (2015) is the maximal second law efficiency of MVC 30 % for a 16 % feed salinity. Therefore, the minimal actual energy requirement results in 244.07 kJ/kg (~67.47 kWh/m^3). Figure 5-4 shows the schematic diagram of the treatment chain and Table E.3 in Appendix E the calculated concentrations and flow parameters of the designed system.

The total theoretical water recovery of the system is **91.58 %** and the specific energy in the range of **100.33** to 122.38 kWh/m^3 per freshwater produced assuming that the water flows by gravity through the pellet reactor. Figure 5-5 shows the theoretical minimum specific energy consumption in dependency on the water recovery rate for the proposed system. The extraction of calcium, magnesium, and NaCl (with a purity of **91.17 %)** could create a possible reimbursement for the treatment chain.

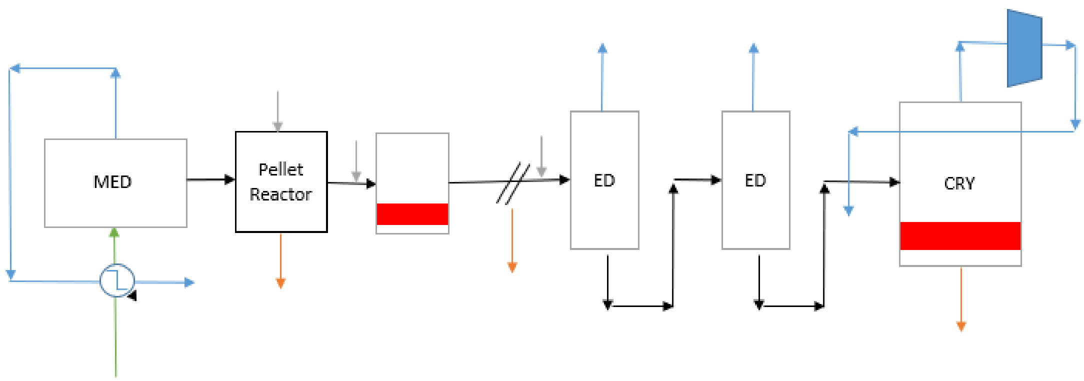

Figure 5-4 Schematic flow diagram of third design idea (ED+CRY) (feedwater=green, freshwater=blue, brine=black, resources/salts=orange, chemicals=grey)

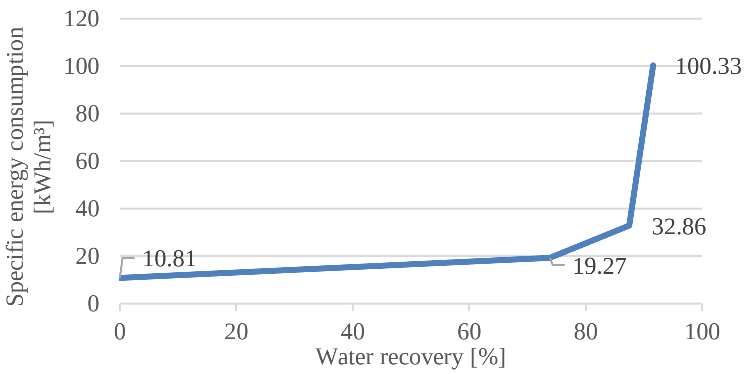

Figure 5-5. Theoretical minimal specific energy consumption of the third design system`s technology as a function of water recovery rate

5.2 Multi-criteria analysis

For the assessment of the best-fitting technology, the three proposed design ideas are compared by a multi-criteria analysis considering environmental, social, economic, and technical dimensions.

5.2.1 Environmental dimension

The theoretical minimal energy demand, water recovery rate, water quality, recovered salt quality, chemical usage of the treatment chains has been calculated according to the presented method in Chapter 3.3 and presented in Chapter 5.1 for each of the design ideas and assigned to the stages as seen in Table 5-1.

Further environmental indicators are global warming potential, land area, and soil and groundwater contamination, which are discussed and if possible, assigned with a ranking from 1 to 3 (lowest to highest impact).

The **global warming potential** refers to the generation of greenhouse gas (GHG) emissions during energy production, transport of the solids to the consumer or landfills, and during the treatment. Tong and Elimelech (2016) mention the implementation of ED, as in the third design idea (ED-CRY), increases the carbon dioxide emissions due to the decarbonization for the scaling control. GHG are also emitted due to the transportation of solids to the consumer or landfills. The number of emissions is highly dependent on the chosen transport method, e.g. trains or transporter. It is expected that those emissions like the emissions during treatment are minor. Due to the difficulty to assess the quantity of those, they are neglected in this case study.

The emissions associated with energy production are highly dependent on the energy source and energy demand (Panagopoulos et al., 2019). The usage of renewable energy sources such as solar could reduce carbon dioxide emissions compared to fossil fuels by 98 % according to the calculation of Song (2020). In the case of Desolenator, the required energy will be produced by PV-T panels which reduces the GHG significantly to a minimum. For a complete assessment of the global warming potential, the GHG emitted during the production of the PV-T panels has to be included. It can be assumed that GHG emissions are proportional to energy demand (Song, 2020). Thus, the global warming potential is considered to be the highest for the third design idea (ED+CRY) and the lowest for the second design idea (EV+ASE).

The **land requirement** of the design ideas is highly dependent on the stages of the treatment chain as well as the design of each of the technologies. The first idea (EV+CRY) has the lowest stage number of frameworks, two stages, compared to the second (EV+ASE) (three stages) and the third idea (ED+CRY) (five stages) leading to the assumption that the first idea has the lowest land requirement. Little to no information has been found about the land requirement of each of the proposed ZLD technologies. Thus, the discussion regarding land requirement below cannot be taken as an absolute value but rather more as a preliminary check.

According to one supplier of thermal technologies, the land requirement of an evaporator is around 120 m^2 for a 30m^3/d flow rate, of which the tank contributes the most (Geer Qile, personal communication, September 9, 2020). As the flowrate in the crystallizer is around half of the one in the evaporator, it is assumed that the land requirement of the crystallizer is around half of the one for the evaporator. The land requirement of the first idea (EV+CRY) would be therefore around 180 m^2. The land demand for the second idea (EV-ASE) is higher due to the implementation of Advanced Solar Evaporation. The minimum area required has been calculated just for the last treatment step to a minimum of 320 m^2 (excluding the safety factor). The land requirement of the second idea including the assumption of 120 m^2 land requirement for evaporator would be therefore at least 2.5-fold higher than the first idea. Additionally, a tank for chemical precipitation as well as for the cooling of the brine after the chemical precipitation is needed, which is simplified assumed to be at least twice the area of the evaporator as the flow rate is the same. Thus, the land requirement results in higher land demand of at least 4-fold. The third idea (ED+CRY) has three more framework stages than the first design idea (EV+CRY) including stages with large tanks as pellet reactor and chemical precipitation including cooling tanks, which are assumed to have each the land requirement of an evaporator. Furthermore, at least 250 stacks of membranes are needed for each ED step to achieve the flow rate of 27 m^3/day. However, no information has been found about the space demand for such ED stacks. Excluding the space demand for ED, the land requirement is assumed to be at least 2-fold higher than the one for the first design idea (EV+CRY). It is therefore concluded that the first idea would most likely have the lowest land requirement and the second idea the highest.

Groundwater and soil contamination occurs if the solids are disposed of on landfills or by the usage of evaporation ponds which are not accurately monitored and protected by e.g. impervious lining (Tong & Elimelech, 2016). The contamination of soil and groundwater by solids from desalination plants is an important environmental indicator, which has until now not been discussed properly in literature. Contamination from chemicals used during the treatment as well as due to the natural salts might occur. The first design idea does not use any chemicals and thus the soil and groundwater could be just contaminated by the natural salts. The other two design ideas include chemical precipitation and therefore, contamination might happen due to the chemicals and natural salts if the harvested solids cannot be sold. However, the usage of biodegradable chemicals reduces environmental contamination highly. Accurate information about the landfill sites in Dubai has not been found. Therefore, this indicator is impossible to assess at the current stage of knowledge. Additional site information is needed to estimate the potential of soil and groundwater contamination of each of the design ideas.

Table 5-1: MCA – Environmental dimension evaluated for each of the proposed design ideas.

Dimension	*Indicator*	*Units*	*Stages*		*1. Design idea (EV-CRY)*	*2. Design idea (EV-ASE)*	*3. Design idea (ED-CRY)*
Environmental	Energy demand	kWh/m^3	0-60 60-85 >85		83,3*	53.76*	100.43*
	Global warming potential	kg CO_2 eq./m^3			2	1	3
	Water recovery	%	>95 85-95 <85		78.27*	91.11*	91.58*
	Land area	m^2			1	3	2
	Quality of water	mg/L	<10 10-250 >250		~0*	~0*	256*
	Recovered salt quality	%	>95 85-95 >85		84.86*	90.18*	91.17*
	Chemical usage	litre/h	<0.3 0.3-0.6 >0.6		~0*	0.49 l/h NaOH, 0.49ml/h antiscalant*	0.49 l/h NaoH and 0.47 ml/h antiscalant*
	Soil and groundwater pollution	Scoring system			-		-

*These numbers have been calculated according to Chapter 3.3 and presented in Chapter 5.1.

5.2.2 Social dimension

Social aspects such as public acceptance and aesthetics should be also considered when choosing a ZLD treatment chain. Those indicators are highly dependent on the project location and should be assessed by interviewing local inhabitants and/or workers. To my knowledge, no evaluation of the social impacts of different ZLD chains has been conducted. Song (2020) evaluated that the human health impact is dependent on the energy source and energy demand. However, too little information is given to be evaluated for the given case study. The public acceptance of implementing a ZLD chain at the site is assumed to be the same for all three design ideas as the location remains the same. Tong and Elimelech (2016) mention that solar ponds have raised concerns about their odor. Thus, it is assumed that the aesthetic acceptance is lower for the second design idea as this incorporates Advanced Solar Evaporation (ASE). High land requirements disturb most likely the visual interference as e.g. by the implementation of ASE (Tong & Elimelech, 2016). Thus, it is estimated that social acceptance based on aesthetic values is lower for the second design idea while the other two remain the same as seen in Table 5-2.

Table 5-2: MCA- Social dimension evaluated for each of the proposed design ideas.

Dimension	*Indicator*	*Suggested units*		*1. Design idea (EV-CRY)*	*2. Design idea (EV-ASE)*	*3. Design idea (ED-CRY)*
Social	Public acceptance	Scoring system		-	-	-
	Aesthetics	Scoring system		1	2	1
		Total score		*1*	*2*	*1*

5.2.3 Economic dimension

The economic dimension includes the investment cost, operating and maintenance cost, water price, and resource reimbursement. Desolenator is aiming to provide the drinking water still at the Lowest Levelized Cost of water of US $ 1/L despite the cost of the different ZLD treatment chains (C. McGill, personal communication, December 23, 2020). Thus, the product water price has been neglected. Table 5-3 shows the below discussed ranking of the economic indicators.

Little information about the actual cost values can be found. To my knowledge, the only literature that provides cost information about a variety of ZLD technologies is given by Panagopoulos et al. (2019), which is very low for thermal technologies compared to the assessed values from the market survey which correlates with the data from Weaver and Birch (2020). However, the data from Panagopoulos et al. (2019) can be used to estimate the relation of investment costs for each of the design ideas to each other. According to Panagopoulos et al. (2019), the cost impact for evaporators is given as US $ 1.11/m^3 and for crystallizers as US $ 1.22/m^3 of freshwater produced. ED/EDR has the lowest cost impact with US $0.85/m^3 of freshwater produced which is comparative with the cost impact of chemical precipitation US $0.82–0.93/m^3 (Panagopoulos & Haralambous, 2020). The cost impact of ASE is dominated by the land cost and the protection structure to avoid the contamination of groundwater and soil (Panagopoulos et al., 2019). However, no information about the cost of ASE has been found and it is thus neglected in this comparison. Based on the data from Panagopoulos et al. (2019), the first design idea (EV+CRY) would have a cost impact of US $ 2.33/m^3, the second (ED+ASE) US $1.93/m^{3,} and the third (ED+CRY) US $2.89/m^3.

The implementation of PV-T panels for the energy production for each design idea is needed. As the third design idea (ED+CRY) has the highest theoretical energy demand, the associated capital cost for the energy provision will be the most, while the second (EV+ASE) has the lowest. Considering the additional capital cost for the PV-T panels for the energy production, it is concluded that the investment cost for the third design idea (ED+CRY) is the highest, while the second (EV+ASE) has the lowest.

Operating and maintenance costs refer to the non-energy-related operation and maintenance costs, which include inter alia chemical usage, labor, and replacement costs (Weaver & Birch, 2020). Operating and maintenance costs are lower for the first design idea (EV+CRY) as the least chemical usage and replacement cost is expected (application of 5 % safety factor). No information about the frequency of ED membrane replacement in high saline or seawater has been found. It is assumed that the ED membranes must be at least as often replaced as RO membranes in desalination plants. RO membranes have a lifetime of 2 to 3 years in seawater despite backwashing every 4 months (ESP Water Products, 2020; United Nations Environment Programme, 1997). Therefore, the third design idea (ED+CRY) is expected to have the highest non-energy-related operating and maintenance costs due to the membrane replacement effort and the highest expected chemical usage. The operating and maintenance costs for the second design idea (ED+ASE) would be driven by the chemical usage and the labor cost for the collection of the solids from the ASE, which is expected to exceed the cost of the first design idea (EV+CRY). It is concluded that the third design idea (ED+CRY) has the highest operating and maintenance costs and the first (EV+CRY) the lowest.

The **revenue via resource recovery** is analyzed for the three different design ideas. In the second and third design option magnesium via chemical precipitation is additionally recovered to sodium chloride. The price of sodium chloride as salt for human consumption has been defined by Panagopoulos (2020b) to US$ 180/ton for the purity of around 90 % and by Nayar et al. (2019) between US$ 80 to US$ 200/ton for purities between 97 to 99.8 % in dependency of the location, whereas the price in Saudi Arabia is US$ 190/ton. The price of magnesium has been reported to be around US$ 2000/ton by Loganathan et al. (2017) (Loganathan et al., 2017) and the price of the precipitated magnesium oxide to US$ 2500/ton by Safar et al. (2020) in Kuwait. Based on these price data a rough estimate about the resource reimbursement for each of the design ideas is done.

The amount of salt results in the first (EV+CRY), second (EV+ASE), and third ideas (ED+CRY) to 2.11 ton/day, 2.02 ton/day, and 0.33 ton/day, respectively. The estimated purity of the salt based on the mass balance is in the first idea around 85 % and the second and third around 91 %. It is assumed for now, that just the sodium chloride produced in the second and third design idea can be sold for US$180 to US$190/ton. This results in an income of US$ 363.72/day to US$ 383.92/day for the second (EV+ASE) and US$ 59.69/day to US$ 63.00/day for the third design option (ED+CRY).

The amount of magnesium oxide produced in the second and third option results in 0.11557 ton/day, and 0.10979 ton/day, respectively. The expected reimbursement of the magnesium precipitation has been calculated for a price of US$ 2000 to US$ 2500/ton. The reimbursement of the second design idea (EV+ASE) results in US$ 231.15 to US$ 288.94 per day and for the third (ED+CRY) to US$ 219.58 to US$ 274.48 per day. The total income per day for the second option would be around US$ 594.87 to US$ 671.86 and for the third results in around half of these values, between US$ 279.266 and US$ 337.48. The calculated expected ranking of the reimbursement can be seen in Table 5-3.

Table 5-3: MCA – Economic dimension evaluated for each of the proposed design ideas.

Dimension	*Indicator*	*Suggested units*		*1. Design idea (EV-CRY)*	*2. Design idea (EV-ASE)*	*3. Design idea (ED-CRY)*
Economic	Investment costs	EUR/m^3		2	1	3
	Operating and maintenance cost	EUR/m^{3}per year		1	2	3
	Product water price	EUR/l		-	-	-
	Resource reimbursement	EUR/kg		3	1	2
		Total score		6	4	8

5.2.4 Technical dimension

The technical dimension includes the reliability of the plant, complexity of construction as well as operation and maintenance effort at site. Table 5-4 presents the below-discussed ranking of the technical dimension for the three design ideas.

The **reliability of the plant** regarding changes in concentration, water flow fluctuations, and climate fluctuation is evaluated. The safety factor of concentration (~5%) in the thermal technologies in the first (EV+CRY) and second design (EV+ASE) idea leads to the assumption that temporary concentration fluctuation would not affect the process performance (e.g. corrosion on heat exchanger). However, the reduction of hardness ions via chemical precipitation in the second design idea (EV+ASE) is still needed to avoid damages. Similarly, the third design idea (ED+CRY) based on ED is highly dependent on the accurate performance of the pre-treatment steps. If they are not working or cannot efficiently decrease the scaling ion concentration to a minimum, these could quickly lead to early membrane failures. All the design processes are designed for a certain flow rate. However, if flow fluctuations occur the process performance of the ED membranes would be the most affected (Tong & Elimelech, 2016). The Advanced Solar Evaporation incorporated in the second option (EV+ASE) is also highly dependent on the sun's efficiency. If for a certain period it should be cloudy or less warm this will affect the process performance of the advanced evaporation highly. However, as all design ideas would be driven by solar energy, all of them are dependent on climate fluctuation. It is concluded that the first option (EV+CRY) would be the most reliable in terms of concentration and flow. Additionally, it is assumed that the third option (ED+CRY) is the most unreliable in terms of concentration and flow fluctuation, while the second (EV+ASE) is expected to have moderate reliability.

The **complexity of the construction** can be just evaluated if looking at the framework stages and the associated connection. The first option (EV+CRY) is based on two stages, thus the possibility of misconstruction of the connection pipes is lower than in the other two options. The highest complexity results in the correct construction of the ED stacks.

Finally, the **operation and maintenance effort** is evaluated. The labour workers at the project site of Desolenator are already trained to operate a MED vessel which is a thermal technology and similar to evaporator and crystallizer. Thus, it seems plausible to assume that the first option (EV+CRY) has the lowest difficulty in operation and maintenance for the workers. The third option (ED+CRY) has the highest maintenance effort with the membranes being in need to be backwashed and replaced in certain time intervals (United Nations Environment Programme, 1997). The staff would have to receive additional training to operate the third design idea (ED+CRY) accurately. Also, the salt collection in the second option (EV+ASE) results in higher operation and maintenance effort than the first one.

Table 5-4: MCA – Technical dimension evaluated for each of the proposed design ideas.

Dimension	*Indicator*	*Suggested units*		*1. Design idea (EV-CRY)*	*2. Design idea (EV-ASE)*	*3. Design idea (ED-CRY)*
Technical	Reliability	Scoring system		1	2	3
	Complexity of construction	Scoring system		1	2	3
	O&M effort	Scoring system		1	2	3
		Total score		3	6	9

5.2.5 Conclusion

For the final comparison of the design ideas, the calculated values of the environmental dimension are assigned with a ranking of 1 to 3 according to the stage level and the four dimensions are summed up in Table 5-5. Due to missing data and actual values, most of the indicators are discussed on literature values and/or objective values which leads to the conclusion that the results of the MCA should be seen as guidance and not as an accurate reflection of the situation.

Nonetheless, it can be found that the second design idea (EV+ASE) has the lowest environmental impact despite the highest land requirement. The social dimension has been just evaluated for the aesthetic indicator where the second design (EV+ASE) idea is expected to have a higher negative impact than the other two. The economic dimension is similar for all three design ideas, whereof the second idea (EV+ASE) is expected to be less economically impactful. For the technical dimension, the first idea (EV+CRY) has the lowest impact, and the third (ED+CRY) the highest. Without any further weighting factor, the total score of the first design idea (EV+CRY) is the lowest with just one point difference to the second design idea (EV+ASE).

Weighting factors for the Desolenator's project site in Dubai have been assigned for a further evaluation of the treatment chain as seen in Table 5-5. The project site is located in an industrial area with a greater distance to domestic properties, therefore the social dimension is less important than the environmental, economic, and technical dimension. For the environmental dimension, the land area and energy demand are of greater importance than the other environmental indicator. The project site has a limited land area, and the energy demand reflects the space required by PV-T panels. Besides that, all the economic indicators have been also defined to greater importance for Desolenator. With the weighting system, the first design idea (EV-CRY) is around half of the score of the second design idea (EV-ASE) and one-fourth of the third design idea (ED-CRY), indicating that this design idea is expected to have the lowest impact at Desolenator's project site.

Table 5-5: MCA – Total score evaluated for each of the proposed design ideas.

Dimension	*Indicator*	*Units*	*1. Design idea (EV-CRY)*	*2. Design idea (EV-ASE)*	*3. Design idea (ED-CRY)*	*Weighting factor*
Environ-mental	Energy demand	kWh/m^3	2	1	3	3
	Global warming potential	kg CO_2 eq./m^3	2	1	3	2
	Water recovery	%	3	2	1	2
	Land area	m^2	1	3	2	3
	Quality of water	mg/L	1	1	3	2
	Recovered salt quality	%	3	2	2	2
	Chemical usage	liter/h	1	2	2	2
	Soil and groundwater contamination	Scoring system	-	-	-	2
Score of environmental dimension			***13***	***12***	***17***	
Social	Public acceptance	Scoring system	-	-	-	1
	Aesthetics	Scoring system	1	2	1	1
Score of social dimension			***1***	***2***	***1***	
Economic	Investment costs	EUR/m^3	2	1	3	3
	Operating and maintenance cost	EUR/m^{3}per year	1	2	3	3
	Product water price	EUR/l	-	-	-	3
	Resource reimbursement	EUR/kg	3	1	2	3
Score of economic dimension			***6***	***4***	***8***	
Technical	Reliability	Scoring system	1	2	3	2
	Complexity of construction	Scoring system	1	2	3	2
	O&M effort	Scoring system	1	2	3	2
Score of technical dimension			***3***	***6***	***9***	
Total score excluding weighting factor			**23**	**24**	**35**	
Total score including weighting factor			**56**	**95**	**202**	

5.3 Techno-economic analysis

The first design idea (EV+CRY) is expected to have the least negative impact considering the sum of environmental, social, economic, and technical dimensions. Below the economic feasibility will be evaluated with a techno-economic analysis in two scenarios.

5.3.1 First scenario excluding salt reimbursement

Firstly, it is assumed that the assumption of 10,000 mg/L sodium in the feedwater is correct which results in a sodium chloride purity of around 85 % in the final solids based on the mass balance. It has been found that a minimum of 90 % purity is needed to sell the salt. Thus, the solids would be in need to be disposed of on landfills which leads to an additional operating cost.

Table 5-6 presents the calculation of the cost parameters and Figure 5-6 shows the net cash flow table for the first 10 years of project development based on the calculated cost parameters with an increasing OPEX of 5 % per year according to Lauer (n.d.). It can be seen that the income of the water with the Lowest Levelized Cost of water is not enough to offset the expected OPEX and investment related OPEX. Therefore, the net cash flow is negative for all years of project development indicating an annual cost of EUR 53,976.59 in the first year (tendency increasing). Even with neglecting the insurance and administrative cost, which has not been considered in the techno-economic analysis by Panagopoulos (2020b), the net cash flow remains negative with an annual cost of EUR 41,924.72 in the first year. It can be found that the waste disposal fee contributes besides the OPEX of the PV-T panels the most to the OPEX.

In order to payback the treatment chain within the plant life, which has been set according to Panagopoulos (2020b) to 20 to 35 years, the annual net cash flow has to be between EUR 17,216 to 30,128 (Lauer, n.d.). This can be achieved if the water price is raised to EUR 7.39 – 9.00/m^3 excluding and EUR 8.90 – 10.51/m^3 including investment related OPEX. However, raising the water price above the Lowest Levelized Cost of water is not in compliance with Desolenator's philosophy (C. McGill, personal communication, December 23, 2020).

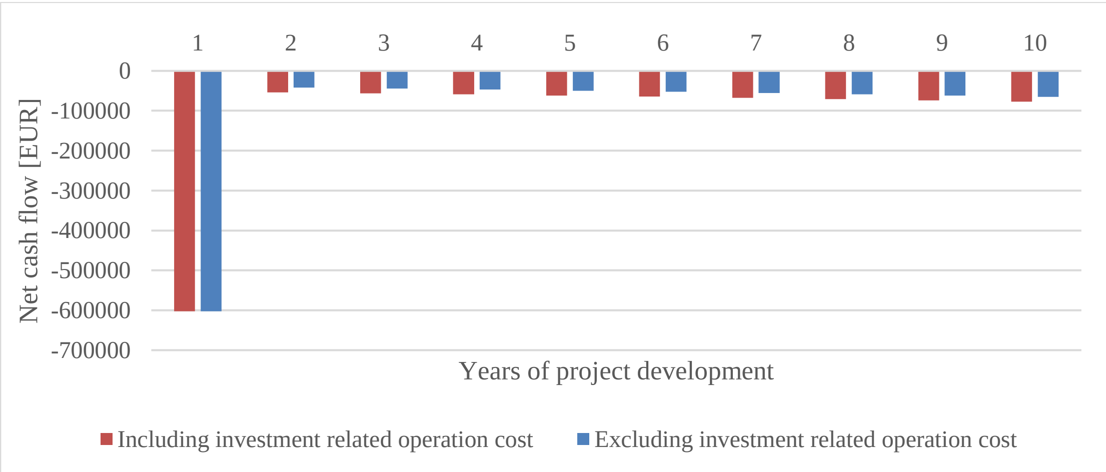

Figure 5-6: Net cash flow table of the first scenario excluding salt reimbursement for the first 10 years of project development

Table 5-6: TEA - Calculated cost parameter for the first scenario excluding salt reimbursement

Annual cost parameters			
Revenue			
	Price [EUR/ m³]	*Amount of freshwater [m³/yr]*	*Annual income [EUR/yr]*
Product water	0.8203	8,000.23	6,562,59
		Total	**6,562,59**
OPEX			
	Cost [EUR/ m³]	*Amount of freshwater [m³/yr]*	*Annual cost [EUR/yr]*
Evaporator	0.62	10,081.3	6,250.41
Crystallizer	1.08	4051.93	4,376.08
	Cost [EUR/ kWh]	*Amount of Energy* [kWh/yr]	*Annual cost [EUR/yr]*
PV-T	0.0312	667,585	20,810
	Price [EUR/T]	*Amount [T/yr]*	*Annual cost [EUR/yr]*
Waste disposal fee	22.1475	769.87	17,050,76
		Total	**48,487.31**
Investment related OPEX			
	Factor [%]	*Investment cost [EUR]*	*Annual cost [EUR/yr]*
Administrative and insurance costs	2.00	602,564.6	12,051.29
		Total	**12,051.29**

One-off cost parameters			
CAPEX			
	Cost [EUR/ m³/yr]	*Amount of brine [m³/yr]*	*Total Cost [EUR]*
Evaporator	24.4540	10,081.3	246,527.8
Crystallizer	58.2687	4,051.93	236,100.6
	Cost [EUR/ panel]	*Number of panels*	*Total Cost [EUR]*
PV-T panel	400	295	118,000
	Factor	*Produced water [m³/d]*	*Total Cost [EUR]*
Shipping and installation cost	70.10	27.62	1,936.16
		Total	**602,564.6**

5.3.2 Second scenario including salt reimbursement

In this scenario, it is assumed that the initial concentration of sodium has been underestimated and the resulting solids have a purity of at least 90 %. Therefore, the produced solids can be sold, creating an additional income, and reducing the OPEX due to the neglection of waste disposal fees. For 90 % sodium chloride purity, the sodium concentration must be at least 15,000 mg/L in the feedwater.

Assuming that the produced salts can be sold for EUR 147.65/ton, the revenue is high enough to cover the OPEX and investment related OPEX resulting in a positive annual net cash flow of EUR 76,745.90 in the first year and EUR 61,736.30 in the tenth year. Figure 5-7 and Table 5-7 present the net cash flow table of the first ten years of project development and the calculated cost parameter, respectively. The payback time for this scenario result in 8.85 years including and 7.78 years excluding the investment related OPEX. Even, if an external centrifuge is needed which would result in an additional EUR 119,595 CAPEX, the plant would breakeven after 10.41 years including and 9.13 years excluding investment related OPEX after project implementation (Condorchem, personal communication, November 12, 2020). Thus, the plant would have been paid off at least 10-15 years before the end of the plant lifetime keeping the Lowest Levelized Cost of water of US$ 1/m^3.

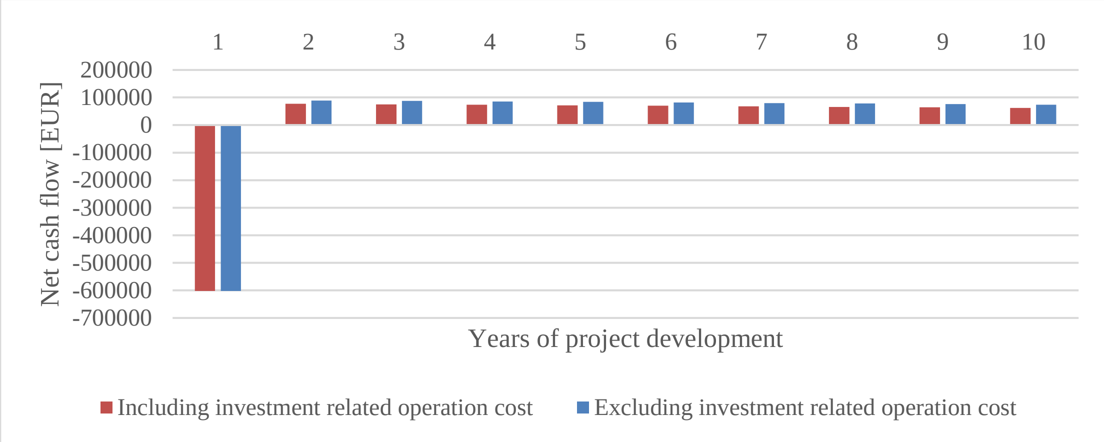

Figure 5-7: Net cash flow table of the second scenario including salt reimbursement for the first 10 years of project development

Table 5-7: TEA - Calculated cost parameter for the second scenario including salt reimbursement.

Annual cost parameters			
Revenue			
	Price [EUR/ m³]	*Amount of freshwater [m³/yr]*	*Annual income [EUR/yr]*
Product water	0.8203	8,000.23	6,562.59
	Price [EUR/T]	*Amount of salt [T/yr]*	*Annual income [EUR/yr]*
Product salt	147.6499	769.871	113,671.23
		Total	**120,233.82**
OPEX			
	Cost [EUR/ m³]	*Amount of freshwater [m³/yr]*	*Annual cost [EUR/yr]*
Evaporator	0.62	10,081.3	6,250.41
Crystallizer	1.08	4051.93	4,376.08
	Cost [EUR/ kWh]	*Amount of Energy [kWh/yr]*	*Annual cost [EUR/yr]*
PV-T	0.0312	667,585	20,810
		Total	**31,436.62**
Investment related OPEX			
	Factor [%]	*Investment cost [EUR]*	*Annual cost [EUR/yr]*
Administrative and insurance costs	2.00	602,564.6	12,051.29
		Total	**12,051.29**

One-off cost parameters			
CAPEX			
	Cost [EUR/ m³/yr]	*Amount of brine [m³/yr]*	*Total Cost [EUR]*
Evaporator	24.4540	10,081.3	246,527.8
Crystallizer	58.2687	4,051.93	236,100.6
	Cost [EUR/ panel]	*Number of panels*	*Total Cost [EUR]*
PV-T panel	400	295	118,000
	Factor	*Freshwater production [m³/d]*	*Total Cost [EUR]*
Shipping and installation cost	70.10	27.62	1,936.16
		Total	**602,564.6**

5.4 Discussion

The techno-economic analysis with the net cash flow method has been calculated for the proposed treatment chain of an evaporator coupled with a crystallizer. The majority of real-life data for the investment cost and revenue have been assessed by the market study and given by Desolenator. The missing cost parameters as the majority of operation and investment related operation cost has been taken according to Lauer (n.d.) from Smets et al. (2016) and Panagopoulos (2020b) creating a limitation. The cost parameter for the shipping and installation, administrative and insurance as well as the reimbursement of sodium chloride has the highest insecurity. It is expected that these values differ the most in real-life. Furthermore, inflation and interest rate and the market price fluctuation of sodium chloride have been neglected. The number of PV-T panels needed has been calculated based on the calculated theoretical energy requirement which is despite the chosen simplification reflecting the literature values and some of the ZLD technology data provided by companies. However, it is expected that the number of PV-T panels needed would be higher in real-life due to the additional energy needed for heat up in the morning, which has not been taken into account in the calculations. The replacement and maintenance cost of the thermal technologies, as well as the PV-T panels, have been calculated as an annual cost. It is expected, however, that the cost of replacement is not spread equally throughout the years of project development.

The net cash flow method refers thus more to a static cost-benefit assessment. Therefore, the conducted techno-economic analysis of the Desolenator case study can be seen as a preliminary check to investigate whether further investigation should be done or not (Lauer, n.d.).

It is observed that the operation cost for the proposed treatment chain, especially the waste disposal fee is too high in Dubai as if they can be offset by the reimbursement of the Lowest Levelized Cost of water. Therefore, with the chosen assumption and simplification, the proposed ZLD treatment chain is not economically feasible without additional reimbursement if the water price is kept at the minimum. Thus, the additional reimbursement of resources as sodium chloride is mandatory in the calculated scenario to create a positive net cash flow. If sodium chloride can be sold for around 150 EUR/tonne, the cost would breakeven after around 10 years including and after 9 years excluding investment related OPEX. Based on this preliminary check it can be concluded that a thermal-based ZLD treatment chain could be just economically feasible for this case study if at last sodium chloride could be recovered in high purity form and the market demand remains stable.

Alternative suggestions to increase the economic feasibility of a ZLD system at Desolenator's project site are:

The investment cost could be decreased by the recirculation of the brine in the existing MED up to 2-3 times the TDS concentration (140,000 to 210,000 mg/L). Thus, the concentrated brine could be sent directly to a crystallizer and centrifuge neglecting the investment cost of an evaporator. This would also lead to a reduced feedwater intake and total freshwater production of the treatment chain. However, it needs to be accurately investigated if Desolenator's MED vessel would be able to handle such high concentrations.

Furthermore, if a pre-treatment step as Nanofiltration would be implemented ahead of the MED, the resulting brine would have a significantly reduced hardness. This would create the opportunity for the implementation of membrane technologies without extensive pre-treatment of the brine via chemical precipitation, higher water recovery rates, and higher sodium chloride purity within the thermal technologies resulting in increased economic feasibility. However, the MCA showed that the installation of membrane technology is not recommended as the operation and maintenance effort would be significantly higher and additional training of the staff is needed.

For a more accurate assessment and evaluation of the economic feasibility of a ZLD treatment chain at Desolenator's project site, the following investigation and research have to be done:

- A detailed water analysis of the feed water as well as of the brine is mandatory.
- The calculation of water concentration and energy demand should be done in more detail using process engineering simulation tools.
- Further research in and investigation on the real-life cost parameter of ZLD projects especially operation and investment related operation cost.
- It should be also followed up if and when new ZLD technologies and resource recovery methods have been successfully tested and are commercially available.

It is recommended to further investigate the implementation of a ZLD treatment chain at Desolenator's project if the missing data and uncertainties regarding water concentration, energy demand, cost parameter could be found and solved by the recommended additional research in the field.

6 Discussion

Desalination is according to Jones et al. (2019) one of the unconventional strategies which is forecasted to be a key role in narrowing the global water demand-supply gap. However, increasing concerns about the environmental impact of desalination, especially the high energy demand and discharge of brine in the ambient water sources, leads to the need for the incorporation of renewable energy sources and sustainable brine management in an economically feasible way (Pistocchi et al., 2020).

Zero-Liquid-Discharge (ZLD) as a sustainable desalination brine management and an additional freshwater source has recently gained a lot of attention (Panagopoulos & Haralambous, 2020). ZLD is however not always the most reasonable choice for all given the high costs. The recovery of the highly concentrated last 5 to 10 % of water is both operating and capital cost-intensive and in many cases doubles the treatment costs according to Perry (2016). “To this end, when regulatory and environmental needs and requirements are fulfilled, the MLD strategy [which recovers up to 95 % of freshwater] appears to be a promising and more cost-effective option for industries“ (Panagopoulos & Haralambous, 2020, p.5). Therefore, MLD has been discussed lately to be the new ZLD solution from an economic point of view (Perry, 2016; Pistocchi et al., 2020).

ZLD systems consist in general of three treatment steps, pretreatment (I), pre-concentration (II), evaporation/crystallization (III), while the MLD system incorporates just the pretreatment (I) and pre-concentration (II) step (Charisiadis, 2018; Panagopoulos & Haralambous, 2020). The pretreatment step refers to the reduction of harmful constituent concentration via chemical, physical, and biological treatment, whereof the chemical is applied the most in high concentrated brine (Panagopoulos et al., 2019). The pre-concentration step is based on membrane technologies and the final step refers to thermal technologies. To my knowledge, most literature discusses crystallization as the final step of a ZLD treatment chain (Giwa et al., 2017; Panagopoulos et al., 2019). However, crystallization concentrates the brine just up to the salt saturation level and the implementation of an internal or external centrifuge or dryer is needed for the production of solids (Ahirrao, 2014). This should be stated more clearly in the literature cause the potentially recovered water from the centrifuge is of poor quality and cannot be counted as freshwater (Brandt et al., 2016). Thus, the 100 % freshwater recovery from seawater brine as advertised by inter alia Perry (2016) in a ZLD chain is currently impossible.

Thermal technologies, traditionally Evaporator (Brine Concentrator) and Crystallizer are based on evaporation for the separation of water from the brine (Panagopoulos, 2020a). Due to the required phase change of the water, the energy requirement in thermal technologies is high. Furthermore, thermal technologies have been reported to be investment intensive due to the usage of highly anti-corrosive material (Panagopoulos et al., 2019; Weaver & Birch, 2020). Several authors reported that similar to desalination, the future of ZLD is not thermal-based and the tendency goes towards membrane-based approaches (Giwa et al., 2017; Panagopoulos et al., 2019; Pistocchi et al., 2020). However, the thermal energy required to heat the brine could be provided by renewable energy sources, e.g., PV-T, or alternative energy sources, e.g., low-grade waste heat (Panagopoulos et al., 2019). Furthermore, thermal technologies as Evaporator and Crystallizer are known technologies, which has been implemented and tested for decades as desalination technologies (Jones et al., 2019). Therefore, thermal technologies are favourably implemented for high concentrated brine with a high quantity of scaling ions (Panagopoulos et al., 2019). Additionally, the reliability of these technologies regarding small concentration- and flow fluctuation is higher than with membrane-based technologies. It can be concluded that thermal technologies have despite being associated with high energy-related operation and maintenance cost the advantage to reliably operate in high saline water and under small flow and concentration fluctuations.

Membrane-based technologies are considered to have lower costs and are less energy-intensive and for those reasons are preferred than thermal technologies for the application in brine management (Panagopoulos et al., 2019). RO, which is the most implemented desalination technology is however limited to a moderate salt concentration level cause the pressure needed to separate highly concentrated solution is exceeding the practical pressure limit of the membranes (Panagopoulos et al., 2019). Therefore, new membrane-based approaches as FO and MD have been developed, which are promising alternatives due to higher membrane resistance and lower energy demand than thermal technologies (Charisiadis, 2018). However, the membrane-based approaches have been mainly tested in laboratory testing and just minimal in pilot projects and to less extend on seawater brine. Panagopoulos et al. (2019) mention that despite being advertised as robust, that in MD, FO, and ED testing membrane failing occurred in conducted experiments due to scaling and hardness ions resulting in less reliable process performance and the need for extensive pre-treatment. No literature has been identified, that evaluates or states how often membranes need to be replaced if applied as ZLD technology. For an accurate statement about the process performance in seawater brine management, membrane technologies must be tested more in pilot projects. The development of new highly resistant membrane materials is needed to make the membrane process performance more reliable (Panagopoulos et al., 2019). It can be concluded that membranes can depending on the water composition, be successfully operated in low concentrated brine with lower energy demand and investment cost (Giwa et al., 2017). At the current stage, it does not seem technically feasible to implement membrane technologies without extensive pre-treatment in moderate and high concentrated brine as a substitution of thermal technologies. However, further development in membrane material and pilot-scale testing could create the possibility for a wider and increased use of membrane technologies.

The market study and survey confirmed what has been discussed above. Despite the fact, that new membrane-based technologies are researched on and the tendency goes toward using those more, currently, more than half of the technologies offered in the brine concentrating market are thermal (Weaver & Birch, 2020). 61 companies have been identified to provide ZLD technologies on the global market. The absolute majority of those are only offering thermal technologies, mainly vacuum evaporators, and crystallizers, only a few have been found to provide ED/EDR, FO, and MD membranes. Despite the research on and the development of innovative membrane technologies, it can be found that those are not yet available on the global market. It has been also proven that the investment cost is increasing with higher flow rates for evaporators and crystallizers. If the efficiency of desalination plants could be increased, the total cost of brine management could be reduced due to minimized brine production.

The idea to offset the cost of desalination and/or ZLD/ MLD treatment chain via resource recovery has gained major attention since the mid-90s (Shahmansouri et al., 2015). At the moment just the highest concentrated minerals are extracted as sodium chloride and magnesium salts (Loganathan et al., 2017). The additional extraction of resources of interest as lithium and uranium has been gained a lot of attention lately due to the increasing global demand (Loganathan et al., 2017). However, the feasibility of the extraction of the majority of compounds is currently not profitable considering the concentration, the current market price, and available technologies (Shahmansouri et al., 2015). The further development in highly selective adsorption material and crystallization of different salts simultaneously are promising approaches that could make resource recovery in future economic feasible for minerals whose abundance in seawater is comparable with, or higher than their average abundance in the upper Earth crust (Pistocchi et al., 2020). Pistocchi et al. (2020) mention that if salt production would be implemented universally, the global market would be over satisfied resulting in a decreased market value of the resources. Thus, it has been concluded that "mining is currently hardly a game changer for desalination" (Pistocchi et al., 2020, p.4). From an environmental point of view could the extraction of resources from brine in the future substituting the way more environmentally impactful land mining and thus it should be followed up (Mavukkandy et al., 2019).

The remaining problem with ZLD and MLD is the appropriate treatment of waste produced during brine treatment and which has been until now not discussed accurately in literature. ZLD aims to produce solids that can be sold. However, as stated already currently the resource recovery options are at the initial development and it has to be expected that not all ZLD plants are producing sellable solids (Mavukkandy et al., 2019). Thus, there is a need for appropriate solid waste management for the produced solids. Until now, the only treatment option mention in the literature is the disposition of the solids at landfills. However, the landfills need to be lined and monitored appropriately to avoid the contamination of soil and groundwater via salts and chemicals (Tong & Elimelech, 2016). This is not always given especially in low and middle–income countries. Giwa et al. (2017) states also that the deposition of solids at landfills "is not the ultimate solution for the brine problem" (p.2). The handling of MLD waste brine has been to my knowledge not discussed at all yet. MLD produces highly concentrated brine which would even create a higher environmental impact than desalination brine when discharged to the ambient water sources. Alternative, drying technologies as Evaporation Ponds, Advanced Solar Evaporation, or WAIV are needed to produce solid waste. These approaches have however a high land requirement and the efficiency is highly dependent on the climate. Thus, MLD seems from an environmental point of view not to be the best brine management solution. Further research on solid and liquid waste management is needed.

The Desolenator project site in Dubai has been chosen as a case study to discuss the implementation of a ZLD treatment chain under consideration of social, environmental, and economic aspects. Three design ideas have been developed based on the feedwater data given by Desolenator and technology performance data from literature studies. The first design idea incorporates the traditional thermal technologies, the second Evaporator with Advanced Solar Evaporation, and the third uses membrane technologies for concentrating the brine. Considering all four dimensions, the treatment chain based on traditional thermal technologies has been analysed to have the lowest impact, despite high energy demand and investment cost, which is against the current research trend.

Most research in the ZLD field has been focused on providing an overview about and comparison of technologies and their process performance including energy requirements, e.g. (Charisiadis, 2018; Giwa et al., 2017; Panagopoulos et al., 2019). To my knowledge, until now none has analysed ZLD chains under the consideration of social, environmental, technical, and economic dimensions. The research by Song (2020) has been found to be the only detailed life cycle analysis on ZLD. However, solid waste management is not included in this study as well as economic, social, and economic parameters insufficiently. The conducted MCA has been based on the minimal data found and is not expected to reflect accurately the real-life situation. However, the defined dimension and indicators for comparison on the ZLD system could be guidance for the way forward. It is recommended that for an accurate evaluation of the ZLD chain in the future, more analysis in social, technical, economic, and environmental dimensions should be done and less focus on investment cost and energy demand.

The subsequent techno-economic analysis of the ZLD chain with the net cash flow method has been based on real-life capital cost data and literature values. It has been evaluated that with the Lowest Levelized Cost of water of US\$ 1/m^3 the water cost could not offset the annual operation cost. Just if the final solids could be sold resulting in the neglection of waste disposal fees, the annual operation cost could be offset. In general, other case studies show a way more optimistic view on ZLD treatment chains, (e.g. (Panagopoulos, 2020b)). It has been found, that in previous techno-economic analysis, additional cost as waste disposal fees and administrative and insurance costs are not considered. However, the case study confirms what has been discussed by inter alia Pistocchi et al. (2020) that currently, available ZLD technologies are hardly economically feasible without additional reimbursement.

ZLD and MLD have been discussed and forecasted to be a sustainable solution for brine management (Giwa et al., 2017). However, it can be found that the total environmental impact of such treatment chains has only recently gained more attention and has not been analysed accurately until now. The handling of the discharge of MLD treatment chains as well as the solids of a ZLD treatment chain has also not been discussed and evaluated properly. Additionally, advertising ZLD as the possibility to extract all water from the brine with a high freshwater recovery of over 95 % for all feedwater qualities is critical. Up to 100% freshwater recovery from seawater desalination brine in an economically feasible way seems impossible at the current state of development.

It can be concluded, that ZLD and MLD should not be advertised as sustainable brine management solutions while achieving high freshwater recoveries if the total environmental impact has not been researched, and promising technologies for high saline water are still under development. However, the problem of brine management remains, and following suggestions for further research should be done in this field to minimize the environmental impact of desalination:

- Accurate assessments of the environmental, social, economic, and technical impact of ZLD and MLD chains.
- New research on appropriate solid waste management including possible reuse options.
- Guidance tool/handbook that provides sufficient information about each ZLD technology considering the social, environmental, economic, and technical impact.
- More research on the process performance of innovative new technologies in the pilot stage including the assessment of membrane replacement in ZLD treatment chains.
- Research and development of new solutions for resource recovery and reuse options of brine.

Finally, from an environmental point of view and according to the waste pyramid, which is universally applied to eliminate and minimize waste, the steps towards sustainability are the prevention and reduction of waste, the preparation for reuse, recycling, and energy recovery, and then disposal. Thus, the reduction of desalination brine by increasing the efficiency of desalination plants must be the first step towards sustainability. Secondly, the brine should be reused via recirculation and or sustainable land and water application. And just afterward recycling and energy recovery via ZLD should be considered. Thus, from an environmental point of view, it is more relevant to increase the efficiency of desalination and to develop alternative reuse options of the brine than recycling via ZLD. However, considering the increasing global water-supply gap is the recycling of wastewater including brine an essential strategy to secure access to freshwater especially in arid and semi-arid regions. Nevertheless, the implementation of SW ZLD treatment is similar to the majority of SW desalination at the current stage restricted to high or middle-income countries due to the high investment and operation cost and technical complexity (Jones et al., 2019). In order to change this, less technical complex and cost intensive ZLD and desalination technologies have to be developed. This is a worthwhile task for the future.

7 Conclusion

In order to decrease the environmental impact of desalination, the incorporation of renewable energy sources and sustainable brine management is essential (Jones et al., 2019). The recycling of brine via ZLD is the most known sustainable brine management strategy. ZLD uses technologies to recover freshwater from brine while producing solid waste (Panagopoulos et al., 2019). The ZLD technologies can be splitted into pretreatment (chemical, biological, physical) and treatment technologies (membrane, thermal). Pretreatment is especially needed if membrane technologies are applied as they are currently more sensitive than thermal towards harmful constituents in the brine. Despite the current research trend towards new and innovative membrane technologies, traditional thermal technologies are still dominant on the market (Weaver & Birch, 2020). The market study showed furthermore that the ZLD market is a low volume market with the most provider offering thermal technologies at a small range. Resource recovery from brine has been discussed to offset the treatment costs and to fulfil the resource recovery gap. Resource recovery could be done using ZLD technologies as chemical precipitation but also alternative approaches as adsorption/desorption. However, techno-economic feasible resource recovery from brine is at the current stage still limited to the resources with the highest concentration (Pistocchi et al., 2020). Accurate waste management strategies for solids produced during ZLD and liquid generated in MLD chains have not been developed yet (Giwa et al., 2017). The development of a ZLD chain at the Desolenator's project site showed the design chain with traditional thermal technologies including an evaporator and crystallizer is expected to have the least impact considering social, environmental, economic, and technical dimensions in comparison to other commercially available technologies. The most sensitive parameter to lead to the final decision of this specific design idea were techno-economic indicators as well as the land requirement. The subsequent techno-economic analysis showed that the proposed design idea (EV+CRY) could be just economic feasible if additional reimbursement via salt recovery is achieved while keeping the Minimum Levelized Water Cost. However, due to limitations in data and calculation simplification, is the study just a preliminary investigation and can be used as a basis for further investigation.

The study confirms that research on improving and new technologies for water and resource recovery from brine as well as solid and liquid waste management is needed for techno-economic feasible sustainable brine management. Additional assessments about the social, environmental, and economic impact of ZLD are recommended. The recycling of brine following the ZLD approach is an essential strategy to decrease the environmental impact of desalination if coupled with renewable energy and to contribute to secure water accessibility worldwide.

References

Ahirrao, S. (2014). Zero Liquid Discharge Solutions. In V. V. Ranade & V. M. Bhandari (Eds.), *Industrial wastewater treatment, recycling and reuse* (pp. 489–520). Butterworth-Heinemann. https://doi.org/10.1016/B978-0-08-099968-5.00013-1

Atkins, P. W., Paula, J. de, & Keeler, J. (2018). *Atkins' physical chemistry* (Eleventh edition). Oxford University Press.

Boo, C., Billinge, I. H., Chen, X., Shah, K. M., & Yip, N. Y. (2020). Zero Liquid Discharge of Ultrahigh-Salinity Brines with Temperature Swing Solvent Extraction. *Environmental Science & Technology*, *54*(14), 9124–9131. https://doi.org/10.1021/acs.est.0c02555

Brandt, M. J., Johnson, K. M., Elphinston, A. J., & Ratnayaka, D. D. (2016). Energy Use, Sustainability and Waste Treatment. In M. J. Brandt, K. M. Johnson, A. J. Elphinston, & D. D. Ratnayaka (Eds.), *Twort's Water Supply* (7th ed., pp. 553–580). Elsevier Science. https://doi.org/10.1016/B978-0-08-100025-0.00013-2

Casas, S., Aladjem, C., Cortina, J. L., Larrotcha, E., & Cremades, L. V. (2012). Seawater Reverse Osmosis Brines as a New Salt Source for the Chlor-Alkali Industry: Integration of NaCl Concentration by Electrodialysis. *Solvent Extraction and Ion Exchange*, *30*(4), 322–332. https://doi.org/10.1080/07366299.2012.686849

Charisiadis, C. (2018). *Brine Zero Liquid Discharge (ZLD) Fundamentals and Design: A guide to the basic conceptualization of the ZLD/MLD process design and the relative technologies involved*. Unpublished. https://doi.org/10.13140/RG.2.2.19645.31205

Chávez, O., & Godínez, F. (2020). Polygeneration Study of Low-to-Medium Enthalpy Geothermal Reservoirs in Mexico. *Journal of Thermal Science*, 1–11. https://doi.org/10.1007/s11630-020-1271-9

Cossio, C., McConville, J. R., Mattsson, A., Mercado, A., & Norrman, J. (2020). Evas - a practical tool to assess the sustainability of small wastewater treatment systems in low and lower-middle-income countries. *The Science of the Total Environment*, *746*, 140938. https://doi.org/10.1016/j.scitotenv.2020.140938

Deethayat, T., Kiatsiriroat, T., & Thawonngamyingsakul, C. (2015). Performance analysis of an organic Rankine cycle with internal heat exchanger having zeotropic working fluid. *Case Studies in Thermal Engineering*, *6*, 155–161. https://doi.org/10.1016/j.csite.2015.09.003

Dong, H., Unluer, C., Yang, E.-H., & Al-Tabbaa, A. (2018). Recovery of reactive MgO from reject brine via the addition of NaOH. *Desalination*, *429*, 88–95. https://doi.org/10.1016/j.desal.2017.12.021

Eke, J., Yusuf, A., Giwa, A [Adewale], & Sodiq, A. (2020). The global status of desalination: An assessment of current desalination technologies, plants and capacity. *Desalination*, *495*, 114633. https://doi.org/10.1016/j.desal.2020.114633

Erdal, U. G. (n.d.). *Brine-Concentrate Treatment and Disposal Options Report: Compounds of Emerging Concern: ZLD.* Southern California Regional Brine-Concentrate Management Study – Phase I. https://www.usbr.gov/lc/socal/reports/brineconcentrate/6TreatmentandDisposal_part2.pdf

ESP Water Products. (2020, December 22). *How to change RO Filters and Membranes*. https://www.espwaterproducts.com/how-to-change-an-ro-filter-and-membranes/

Freger, V. (January 2014). *Zero Liquid Discharge (ZLD) - Concept, Evolution and Technology Options*. ZLD Workshop, Gandhinagar. https://gpcb.gov.in/images/pdf/ZLD_PRESENTATION_3.PDF

Garg, M. C., & Joshi, H. (2015). A Review on PV-RO Process: Solution to Drinking Water Scarcity due to High Salinity in Non-Electrified Rural Areas. *Separation Science and Technology*, *50*(8), 1270–1283. https://doi.org/10.1080/01496395.2014.951725

Ghernaout, D. (2019). Brine Recycling: Towards Membrane Processes as the Best Available Technology. *Applied Engineering, 3*(2), 71–84. https://doi.org/10.11648/j.ae.20190302.11

Giwa, A [A.], Dufour, V., Al Marzooqi, F., Al Kaabi, M., & Hasan, S. W. (2017). Brine management methods: Recent innovations and current status. *Desalination, 407*, 1–23. https://doi.org/10.1016/j.desal.2016.12.008

Google. (n.d.). *Google Maps location of Desolenator`s project in Dubai*. Retrieved January 15, 2021, from https://www.google.com/maps/@25.0522392,55.1167644,5949m/data=!3m1!1e3

Hoshino, T. (2015). Innovative lithium recovery technique from seawater by using world-first dialysis with a lithium ionic superconductor. *Desalination, 359*, 59–63. https://doi.org/10.1016/j.desal.2014.12.018

IPIECA. (2020, December 13). *Heat Exchangers*. https://www.ipieca.org/resources/energy-efficiency-solutions/efficient-use-of-heat/heat-exchangers/

Jiang, C., Wang, Y., Zhang, Z., & Xu, T. (2014). Electrodialysis of concentrated brine from RO plant to produce coarse salt and freshwater. *Journal of Membrane Science*, *450*, 323–330. https://doi.org/10.1016/j.memsci.2013.09.020

Jones, E., Qadir, M., van Vliet, M. T. H., Smakhtin, V., & Kang, S.-M. (2019). The state of desalination and brine production: A global outlook. *The Science of the Total Environment*, *657*, 1343–1356. https://doi.org/10.1016/j.scitotenv.2018.12.076

Katal, R., Ying Shen, T., Jafari, I., Masudy-Panah, S., & Hossein Davood Abadi Farahani, M. (2020). An Overview on the Treatment and Management of the Desalination Brine Solution. In M. Hossein Davood Abadi Farahani, V. Vatanpour, & A. Hooshang Taheri (Eds.), *Desalination - Challenges and Opportunities: An Overview on the Treatment and Management of the Desalination Brine Solution.* IntechOpen. https://doi.org/10.5772/intechopen.92661

Korngold, E. (1982). Electrodialysis unit: Optimization and calculation of energy requirement. *Desalination*, *40*(1-2), 171–179. https://doi.org/10.1016/S0011-9164(00)88681-6

Kress, N. (2019). Desalination Technologies. In N. Kress (Ed.), *Marine Impacts of Seawater Desalination* (pp. 11–34). Elsevier. https://doi.org/10.1016/B978-0-12-811953-2.00002-5

Lauer, M. (n.d.). *Methodology guideline on techno economic assessment (TEA).* ThermalNet WP3B Economics. https://ec.europa.eu/energy/intelligent/projects/sites/ieeprojects/files/projects/documents/thermalnet_methodology_guideline_on_techno_economic_assessment.pdf

Lawal, D. U., & Qasem, N. A. (2020). Humidification-dehumidification desalination systems driven by thermal-based renewable and low-grade energy sources: A critical review. *Renewable and Sustainable Energy Reviews, 125*, 109817. https://doi.org/10.1016/j.rser.2020.109817

Lenntech. (2020, December 7). *Composition of seawater: Major ion composition of seawater*. https://www.lenntech.com/composition-seawater.htm

Liu, J., Yuan, J., Ji, Z., Wang, B., Hao, Y., & Guo, X. (2016). Concentrating brine from seawater desalination process by nanofiltration–electrodialysis integrated membrane technology. *Desalination*, *390*, 53–61. https://doi.org/10.1016/j.desal.2016.03.012

Loganathan, P., Naidu, G., & Vigneswaran, S. (2017). Mining valuable minerals from seawater: A critical review. *Environmental Science: Water Research & Technology, 3*(1), 37–53. https://doi.org/10.1039/C6EW00268D

Lu, J., Fan, L [L.], & Roddick, F. A. (2013). Potential of BAC combined with UVC/H2O2 for reducing organic matter from highly saline reverse osmosis concentrate produced from municipal wastewater reclamation. *Chemosphere*, *93*(4), 683–688. https://doi.org/10.1016/j.chemosphere.2013.06.008

Mavukkandy, M. O., Chabib, C. M., Mustafa, I., Al Ghaferi, A., & AlMarzooqi, F. (2019). Brine management in desalination industry: From waste to resources generation. *Desalination*, *472*(114187). https://doi.org/10.1016/j.desal.2019.114187

Mezher, T., Fath, H., Abbas, Z., & Khaled, A. (2011). Techno-economic assessment and environmental impacts of desalination technologies. *Desalination*, *266*(1-3), 263–273. https://doi.org/10.1016/j.desal.2010.08.035

Mickley, M. (2008). *Survey of High-recovery and Zero Liquid Discharge Technologies for Water Utilities.* WateReuse Foundation. https://www.waterboards.ca.gov/water_issues/programs/grants_loans/water_recycling/research/02_006a_01.pdf

Missimer, T. M., & Maliva, R. G. (2018). Environmental issues in seawater reverse osmosis desalination: Intakes and outfalls. *Desalination*, *434*, 198–215. https://doi.org/10.1016/j.desal.2017.07.012

Mistry, K., & Lienhard, J. (2013). Generalized Least Energy of Separation for Desalination and Other Chemical Separation Processes. *Entropy*, *15*(12), 2046–2080. https://doi.org/10.3390/e15062046

Mohammad, A. F., El-Naas, M. H [M. H.], Al-Marzouqi, A. H [A. H.], Suleiman, M. I., & Al Musharfy, M. (2019). Optimization of magnesium recovery from reject brine for reuse in desalination post-treatment. *Journal of Water Process Engineering*, *31*, 100810. https://doi.org/10.1016/j.jwpe.2019.100810

Morillo, J., Usero, J., Rosado, D., El Bakouri, H., Riaza, A., & Bernaola, F.-J. (2014). Comparative study of brine management technologies for desalination plants. *Desalination*, *336*, 32–49. https://doi.org/10.1016/j.desal.2013.12.038

Muhammad, Y., & Lee, W. (2019). Zero-liquid discharge (ZLD) technology for resource recovery from wastewater: A review. *The Science of the Total Environment*, *681*, 551–563. https://doi.org/10.1016/j.scitotenv.2019.05.062

Münk, F. (2008). *Ecological and economic analysis of seawater desalination plants*. Diploma Thesis. University of Karlsruhe Institute for Hydromechanics. http://www.ifh.uni-karlsruhe.de/science/envflu/research/brinedis/muenk-diplomathesis.pdf

Mustafa, J., Mourad, A. A.-H., Al-Marzouqi, A. H [Ali H.], & El-Naas, M. H [Muftah H.] (2020). Simultaneous treatment of reject brine and capture of carbon dioxide: A comprehensive review. *Desalination*, *483*(114386). https://doi.org/10.1016/j.desal.2020.114386

Narayan, G. P., Sharqawy, M. H., Summers, E. K., Lienhard, J. H., Zubair, S. M., & Antar, M. A. (2010). The potential of solar-driven humidification–dehumidification desalination for small-scale decentralized water production. *Renewable and Sustainable Energy Reviews*, *14*(4), 1187–1201. https://doi.org/10.1016/j.rser.2009.11.014

Nayar, K. G., Fernandes, J., McGovern, R. K., Dominguez, K. P., McCance, A., Al-Anzi, B. S., & Lienhard, J. H. (2019). Cost and energy requirements of hybrid RO and ED brine concentration systems for salt production. *Desalination*, *456*, 97–120. https://doi.org/10.1016/j.desal.2018.11.018

Panagopoulos, A. (2020a). A comparative study on minimum and actual energy consumption for the treatment of desalination brine. *Energy*, 118733. https://doi.org/10.1016/j.energy.2020.118733

Panagopoulos, A. (2020b). Techno-economic evaluation of a solar multi-effect distillation/thermal vapor compression hybrid system for brine treatment and salt recovery. *Chemical Engineering and Processing - Process Intensification, 152*, 107934. https://doi.org/10.1016/j.cep.2020.107934

Panagopoulos, A., & Haralambous, K.-J. (2020). Minimal Liquid Discharge (MLD) and Zero Liquid Discharge (ZLD) strategies for wastewater management and resource recovery – Analysis, challenges and prospects. *Journal of Environmental Chemical Engineering*, 104418. https://doi.org/10.1016/j.jece.2020.104418

Panagopoulos, A., Haralambous, K.-J., & Loizidou, M. (2019). Desalination brine disposal methods and treatment technologies - A review. *The Science of the Total Environment*, *693*, 133545. https://doi.org/10.1016/j.scitotenv.2019.07.351

Pavuluri, S., Jambhekar, V., & Hommel, J. (2014). *Kinetic approach for modeling salt precipitation in porous-media.* Universität Stuttgart. https://www.researchgate.net/publication/262495450_Kinetic_approach_for_modeling_salt_precipitation_in_porous-media

Pellegrin, M.-L., Burbano, M. S., Sadler, M. E., Diamond, J., Baker, S., Greiner, A. D., Arabi, S., Wong, J., Doody, A., Padhye, L. P., Sears, K., Kistenmacher, P., Kent, F., Tootchi, L., Aguinaldo, J., Saddredini, S., Schilling, B., Min, K., McCandless, R., . . . Aerts, P. (2016). Membrane Processes. *Water Environment Research : A Research Publication of the Water Environment Federation*, *88*(10), 1050–1124. https://doi.org/10.2175/106143016X14696400494579

Perry, M. (2016, August 30). Is MLD the new ZLD for forward osmosis technologies? *ForwardOsmosisTech*. https://www.forwardosmosistech.com/is-mld-the-new-zld-for-forward-osmosis-technologies/

Pistocchi, A., Bleninger, T., Breyer, C., Caldera, U., Dorati, C., Ganora, D., Millán, M. M., Paton, C., Poullis, D., Herrero, F. S., Sapiano, M., Semiat, R., Sommariva, C., Yuece, S., & Zaragoza, G. (2020). Can seawater desalination be a win-win fix to our water cycle? *Water Research*, *182*(115906). https://doi.org/10.1016/j.watres.2020.115906

Pramanik, B. K., Shu, L., & Jegatheesan, V. (2017). A review of the management and treatment of brine solutions. *Environmental Science: Water Research & Technology*, *3*(4), 625–658. https://doi.org/10.1039/C6EW00339G

Qchieng, P. (2009). An Analysis of the Strengths and Limitation of Qualitative and Quantitative Research Paradigms. *Problems of Education in the 21st Century*, *13*, 13–18. http://www.scientiasocialis.lt/pec/files/pdf/Atieno_Vol.13.pdf

Quist-Jensen, C. A., Ali, A., Mondal, S., Macedonio, F., & Drioli, E. (2016). A study of membrane distillation and crystallization for lithium recovery from high-concentrated aqueous solutions. *Journal of Membrane Science*, *505*, 167–173. https://doi.org/10.1016/j.memsci.2016.01.033

Ramalingam, A., & Arumugam, S. (2012). Experimental Study on Specific Heat of Hot Brine for Salt Gradient Solar Pond Application, *4*(3), 956–961. http://www.sphinxsai.com/2012/july_sept12/Chem/pdfchem/CT=18(956-961)%20JS%2012.pdf

Safar, M., Garudachari, B., Al-Muqahwi, S., & Ahmad, M. (2020). Extraction of valuable minerals from reverse osmosis brine in Kuwait. *Desalination and Water Treatment*, *176*, 243–251. https://doi.org/10.5004/dwt.2020.25525

Sanmartino, J. A., Khayet, M., García-Payo, M. C., El-Bakouri, H., & Riaza, A. (2017). Treatment of reverse osmosis brine by direct contact membrane distillation: Chemical pretreatment approach. *Desalination*, *420*, 79–90. https://doi.org/10.1016/j.desal.2017.06.030

Sea4value. (2020, November 2). *The Project - Sea4value*. https://sea4value.eu/the-project/#technologies

Shah, A. V., Varjani, S., Srivastava, V. K., & Bhatnagar, A. (2020). Zero Liquid Discharge (ZLD) as Sustainable Technology - Challenges and Perspectives. *Indian Journal of Experimental Biology*, *8*(58), 508–514. https://doi.org/10.3389/fenvs.2017.00070

Shahmansouri, A., Min, J., Jin, L., & Bellona, C. (2015). Feasibility of extracting valuable minerals from desalination concentrate: a comprehensive literature review. *Journal of Cleaner Production*, *100*, 4–16. https://doi.org/10.1016/J.JCLEPRO.2015.03.031

Sharqawy, M. H., Lienhard, J. H., & Zubair, S. M. (2010). Thermophysical properties of seawater: a review of existing correlations and data. *Desalination and Water Treatment*, *16*(1-3), 354–380. https://doi.org/10.5004/dwt.2010.1079

Shi, Y., Zhang, C., Li, R., Zhuo, S., Jin, Y., Le Shi, Hong, S., Chang, J., Ong, C., & Wang, P. (2018). Solar Evaporator with Controlled Salt Precipitation for Zero Liquid Discharge Desalination. *Environmental Science & Technology*, *52*(20), 11822–11830. https://doi.org/10.1021/acs.est.8b03300

Smets, A., Jäger, K., Isabella, O., van Swaaij, R., & Zeman, M. (2016). *Solar Energy: The physics and engineering of photovoltaic conversion technologies and systems*. UIT Cambridge Ltd.

Song, Y. (2020). *Environmental impacts of zero liquid discharge technologies.* University of Michigan. https://deepblue.lib.umich.edu/bitstream/handle/2027.42/154870/Song%2c%20Yichuan%20Thesis.pdf?sequence=1&isAllowed=y

Subramani, A., DeCarolis, J., Pearce, W., & Jacangelo, J. G. (2012). Vibratory shear enhanced process (VSEP) for treating brackish water reverse osmosis concentrate with high silica content. *Desalination*, *291*, 15–22. https://doi.org/10.1016/j.desal.2012.01.020

Subramani, A., & Jacangelo, J. G. (2015). Emerging desalination technologies for water treatment: A critical review. *Water Research*, *75*, 164–187. https://doi.org/10.1016/j.watres.2015.02.032

Szepessy, S., & Thorwid, P. (2018). Low Energy Consumption of High-Speed Centrifuges. *Chemical Engineering & Technology*, *41*(12), 2375–2384. https://doi.org/10.1002/ceat.201800292

Thiel, G. P., Tow, E. W., Banchik, L. D., Chung, H. W., & Lienhard, J. H. (2015). Energy consumption in desalinating produced water from shale oil and gas extraction. *Desalination*, *366*, 94–112. https://doi.org/10.1016/j.desal.2014.12.038

Tong, T., & Elimelech, M. (2016). The Global Rise of Zero Liquid Discharge for Wastewater Management: Drivers, Technologies, and Future Directions. *Environmental Science & Technology*, *50*(13), 6846–6855. https://doi.org/10.1021/acs.est.6b01000

Tonner, J. B., & Tonner, J. (2004). Desalination and Energy Use. In C. J. Cleveland (Ed.), *Encyclopedia of energy* (pp. 791–799). Elsevier. https://doi.org/10.1016/B0-12-176480-X/00403-4

Tsai, J.-H., Macedonio, F., Drioli, E., Giorno, L., Chou, C.-Y., Hu, F.-C., Li, C.-L., Chuang, C.-J., & Tung, K.-L. (2017). Membrane-based zero liquid discharge: Myth or reality? *Journal of the Taiwan Institute of Chemical Engineers*, *80*, 192–202. https://doi.org/10.1016/j.jtice.2017.06.050

Umar, M., Roddick, F., & Fan, L [Linhua] (2013). Assessing the potential of a UV-based AOP for treating high-salinity municipal wastewater reverse osmosis concentrate. *Water Science and Technology : A Journal of the International Association on Water Pollution Research*, *68*(9), 1994–1999. https://doi.org/10.2166/wst.2013.417

UNESCO World Water Assessment Programme. (2020). *The United Nations World Water Development Report 2020: Water and climate change*. United Nations Educational, Scientific and Cultural Organization.

United Nations Environment Programme. (1997). *Source Book of Alternative Technologies for Freshwater Augmentation in Latin America and the Carribbean: 2.1 Desalination by reverse osmosis*. https://www.oas.org/dsd/publications/unit/oea59e/ch20.htm

Vane, L. M. (2017). Review: Water recovery from brines and salt-saturated solutions: Operability and thermodynamic efficiency considerations for desalination technologies. *Journal of Chemical Technology and Biotechnology*, *92*(10), 2506–2518. https://doi.org/10.1002/jctb.5225

Weather Atlas. (n.d.). *Monthly weather forecast and climate Dubai, United Arab Emirates*. Retrieved January 19, 2021, from https://www.weather-atlas.com/en/united-arab-emirates/dubai-climate#climate_text_1

Weaver, R., & Birch, H. (August 2020). *Desalination Market Update: GWI DesalData Market Assessment Webinar.* GWI DESALDATA.

Wiechert, A. I., Ladshaw, A. P., Gill, G. A., Wood, J. R., Yiacoumi, S., & Tsouris, C. (2018). Uranium Resource Recovery from Desalination Plant Feed and Reject

Water Using Amidoxime Functionalized Adsorbent. *Industrial & Engineering Chemistry Research*, *57*(50), 17237–17244. https://doi.org/10.1021/ACS.IECR.8B04673

Writer, S. (2018, August 2). Dubai announces new waste disposal fees. *Gulf Business*. https://gulfbusiness.com/dubai-announces-new-waste-disposal-fees/

Wu, L., Dong, Z., Cai, Z., Ganapathy, T., Fang, N. X., Li, C., Yu, C., Zhang, Y., & Song, Y. (2020). Highly efficient three-dimensional solar evaporator for high salinity desalination by localized crystallization. *Nature Communications*, *11*(1), 521. https://doi.org/10.1038/s41467-020-14366-1

Zarzo, D. (2018). Beneficial uses and valorization of reverse osmosis brines. In G. Gude (Ed.), *Emerging Technologies for Sustainable Desalination Handbook* (pp. 365–397). Elsevier Science & Technology.

Zhou, T., Lim, T.-T., Chin, S.-S., & Fane, A. G. (2011). Treatment of organics in reverse osmosis concentrate from a municipal wastewater reclamation plant: Feasibility test of advanced oxidation processes with/without pretreatment. *Chemical Engineering Journal*, *166*(3), 932–939. https://doi.org/10.1016/j.cej.2010.11.078

Appendices

Appendix A: Summary of literature study on membrane technologies

Technology	Advantages	Disadvantages	Water recovery from brine	Energy consumption	Cost impacts	Specific cost
Reverse Osmosis (RO)	•Commercially available (Panagopoulos et al., 2019) •Known technology (Panagopoulos et al., 2019) •Less energy-intensive technology (Panagopoulos et al., 2019)	•Just applicable to low TDS concentration of up to 70,000 mg/L (Panagopoulos et al., 2019) •Applied pressure needed and thus high electrical demand (Panagopoulos et al., 2019) •Intensive pretreatment needed due to high risk of fouling and scaling (Panagopoulos et al., 2019) • Not effective as a stand-alone technology for brine treatment (Panagopoulos et al., 2019)	•Up to 50% for <70,000mg/L TDS feed brine (Panagopoulos et al., 2019) •Up to 10% for 85,000mg/L TDS feed brine (Panagopoulos et al., 2019) •~98 % in combination with evaporation processes for industrial wastewater treatment (Tsai et al., 2017)	Specific energy consumption (SEC) 2-6kWh/m³ of freshwater produced (Panagopoulos et al., 2019)	•CAPEX costs of membranes (Panagopoulos et al., 2019) •Pretreatment costs (Panagopoulos et al., 2019) •Energy consumption (Panagopoulos et al., 2019)	•US$ 0.75/m³ of freshwater produced (Panagopoulos et al., 2019) •~US$ 1/m³ (Weaver & Birch, 2020, August)
Electrodialysis/ Electrodialysis Reversal (ED/DER)	•Application for high concentration feed (> 70,000 ppm with no concentration limit) (Charisiadis, 2018) •Lower membrane fouling (EDR doesn`t have a compact fouling layer like RO) and less need for chemical usage (Liu et al., 2016) (Charisiadis, 2018) •Low operation pressure (no applied pressure) (Liu et al., 2016) •High concentration production and water recovery (Liu et al., 2016) • Lower energy consumption due to the absence of applied pressure. (Charisiadis, 2018) •Only electrical energy is needed and can be provided by renewable energies as PV (Morillo et al., 2014)	•Beyond the current density limit water dissociation occurs resulting in lower performance efficiency (Mavukkandy et al., 2019) •Limited removal efficiency (no elimination of suspended solids, dissolved solids, microorganisms, and organic contaminants) (Charisiadis, 2018) •Need for pretreatment (Liu et al., 2016). • With increasing salinity of the feed, the energy consumption is increasing (Charisiadis, 2018) •High CAPEX costs as ED membranes (Liu et al., 2016).	•up to 97% water recovery with pretreatment (Morillo et al., 2014) •Up to 86% (Panagopoulos et al., 2019)	•6.73 kWh/m³ (Charisiadis, 2018) •7-8 KWh/m3 (Morillo et al., 2014) •7-15 KWh/m³ of freshwater produced (Panagopoulos, 2020)	• CAPEX costs of membranes (Morillo et al., 2014) • Electricity consumption (Charisiadis, 2018) •Pretreatment required (Morillo et al., 2014)	US$ 0.85/m³ of freshwater produced (Panagopoulos et al., 2019)
High-Pressure Reverse Osmosis (RO)	•Application for high concentration feed (>70,000 mg/L) (Panagopoulos et al., 2019) •Only electrical energy is needed (Panagopoulos et al., 2019) •Known technology (works the same way as RO) (Panagopoulos et al., 2019) •Successful reduction of brine volume (Panagopoulos et al., 2019) •Less energy-intensive technology (Panagopoulos et al., 2019)	•Needs applied pressure (Panagopoulos et al., 2019) • Need for intensive pretreatment due to high risk of scaling and fouling (Panagopoulos et al., 2019) •Low water recovery rate and freshwater production (Panagopoulos et al., 2019) •Application of up to 120 bar are rarely commercially available (Panagopoulos et al., 2019) •Max. concentration reachable is 175000 mg/L (Weaver & Birch, 2020, August)	Up to 50% water recovery (Panagopoulos et al., 2019)	Specific energy consumption (SEC):3-9 kWh/m³ for freshwater produced (Panagopoulos et al., 2019)	•CAPEX costs of membranes (Panagopoulos et al., 2019) •Pretreatment costs (Panagopoulos et al., 2019) •Energy consumption (Panagopoulos et al., 2019)	•US$ 0.79/m³ of freshwater produced (Panagopoulos et al., 2019) •~US$ 1.5/m³ (Weaver & Birch, 2020, August)

Technology	Advantages	Disadvantages	Water recovery from brine	Energy consumption	Cost impacts	Specific cost
Osmotically Assisted Reverse Osmosis (OARO)	• Application for high concentration feed (up to 140,000 mg/L) (Panagopoulos et al., 2019) •No feed pressure requirements (Panagopoulos et al., 2019) •Low fouling propensity modular (Panagopoulos et al., 2019) •High rejection of many contaminants (Panagopoulos et al., 2019) •Less energy-intensive technology (Panagopoulos et al., 2019)	• Selection of the appropriate draw solution (Panagopoulos et al., 2019) •Intensive pretreatment processes to avoid fouling and scaling problems (Panagopoulos et al., 2019)	Up to 72% (Panagopoulos et al., 2019)	6-19 kWh/m³ of freshwater produced (Panagopoulos et al., 2019)	•high CAPEX costs due to usage of multiple RO and FO stages	US$ 2.4/m³ of freshwater produced (Panagopoulos et al., 2019)
Vibratory Shear Enhanced Processing (VSEP)	•High rates of filtration/high fluxes (Giwa et al., 2017) •Higher resistance to membrane scaling (Giwa et al., 2017) •Decreased footprint (Giwa et al., 2017) •High resistance against silica (Subramani et al., 2012)	•Increased energy consumption (Giwa et al., 2017) • Precipitation of barium sulfate could occur and thus cleaning is needed (Giwa et al., 2017) •Has been just successfully tested at low TDS (around 5,000 mg/L) (Subramani et al., 2012)	•93% (Giwa et al., 2017) •80% (Subramani et al., 2012)	•SEC is three times as RO (Subramani et al., 2012) •At TDS of 5 000 and flux of 20.4 L/m²*h SEC is 2.1 kWh/m³ (Subramani et al., 2012)	•Energy costs (Giwa et al., 2017) •CAPEX cost membranes (Giwa et al., 2017)	
Electrodialysis Metathesis (EDM)	•Application for high concentration feed up to 150,000 mg/L (Panagopoulos et al., 2019) •Low fouling propensity modular (Panagopoulos et al., 2019) • Effective brine treatment of high silica content (Panagopoulos et al., 2019)	• Energy costs increase with TDS of feedwater (Panagopoulos et al., 2019) •Organic fouling of membranes could be a problem and may require additional pretreatment (Panagopoulos et al., 2019)	Up to 92% (Panagopoulos et al., 2019)	0.6-5.1 kWh/m³ of freshwater produced (Panagopoulos et al., 2019)	•CAPEX costs of membranes (Panagopoulos et al., 2019) •Electricity consumption (Panagopoulos et al., 2019)	US$ 0.60/m³ of freshwater produced (Panagopoulos et al., 2019)
Forward Osmosis (FO)	•Osmotically-driven process (elimination of applied pressure) (Subramani & Jacangelo, 2015) •Application for high concentration feed (>70,000 ppm (until 175,000 ppm) (Charisiadis, 2018) (Subramani & Jacangelo, 2015) •Low energy consumption (due to the absence of applied pressure) (Charisiadis, 2018) •Thermal heat sources could be waste heat or renewable energies (Subramani & Jacangelo, 2015) •High feed water recovery (Subramani & Jacangelo, 2015) •Lower fouling potential (without the need for applied pressure) (Subramani & Jacangelo, 2015) •Physical cleaning can be applied. Lower pretreatment needed: substitution of chemicals (Charisiadis, 2018) •High rejection of many contaminants (Panagopoulos et al., 2019)	• Limited full-scale installation (Subramani & Jacangelo, 2015) •Difficult to choose optimal draw solution (reverse salt flux might occur) (Charisiadis, 2018) •Salt precipitation inhibits flux and recovery (Panagopoulos et al., 2019) •Lower flux rate than RO resulting in the need of higher membrane area requirement (Subramani & Jacangelo, 2015) • Difficult to choose the right membrane. Requires certain membranes just applicable for FO applications. (Charisiadis, 2018) •Internal and external concentration polarization might occur (Charisiadis, 2018; Panagopoulos et al., 2019) • Intensive pretreatment process to avoid scaling and fouling (Panagopoulos et al., 2019)	•~70% water recovery (Charisiadis, 2018) •up to 98% (Panagopoulos et al., 2019)	• 29.91 KWh/m³=0.46 kWh/m³ Electrical+ 29.45 KWh/m³ Thermal (Charisiadis, 2018) •SEC: 0.1-0.85 kWh/m³ (or up to 13 kWh/m³ if draw regeneration step is included) (Panagopoulos et al., 2019)	•Independency of the application of the technology: In strict FO applications with gaseous mixtures as draw solutions, thermal energy for the regeneration of the draw solution will be the major cost. (Subramani & Jacangelo, 2015) •Membrane costs (Panagopoulos et al., 2019) •Pretreatment costs (Panagopoulos et al., 2019)	US$ 0.63/m³ of freshwater produced (Panagopoulos et al., 2019)

Technology	Advantages	Disadvantages	Water recovery from brine	Energy consumption	Cost impacts	Specific cost
Membrane Distillation (MD)	•Low energy/temperature requirements (30-60°C) (Charisiadis, 2018) •Usage of renewable energy sources as waste heat and solar possible (Charisiadis, 2018) •Less effectiveness to concentration polarization thus fewer flux limitations (Charisiadis, 2018) •Application for high (salinity) concentration feed with no concentration limit (>200,000 ppm) (Charisiadis, 2018) •100 % theoretical rejection of non-volatile components (Lu et al., 2019) •Less sensitive to feed concentration (Lu et al., 2019) •No extensive pretreatment needed (Morillo et al., 2014) •Less membrane fouling than RO (Kress, 2019)	• Relatively high energy consumption (especially thermal) (Charisiadis, 2018) •High CAPEX module costs (Charisiadis, 2018) •Low flux compared to pressure-driven membranes (Charisiadis, 2018) •Surfactants or amphiphilic contaminants may cause wetting of the membrane (Charisiadis, 2018) •Precipitation of inorganic salt limits the process performance (Morillo et al., 2014) •Lack of specific MD membranes (Kress, 2019)	•~85% water recovery (Charisiadis, 2018) •81% for brackish RO brine (Morillo et al., 2014) •Up to 100% (Kress, 2019) •Up to 90% (Panagopoulos et al., 2019)	•47.41 kW/m³= 45.38 kW/m³ thermal + 2.03 kWh/m³ electrical (Charisiadis, 2018) • 43kW/m³ or 10kWh/m³ if waste heat is used (Kress, 2019) •39-67kWh/m³ of freshwater produced (Panagopoulos et al., 2019)	•Energy costs (Charisiadis, 2018) •Membrane module costs (Charisiadis, 2018) •Pretreatment costs to avoid flux reduction (Kress, 2019)	US$ 1.17/m³ of freshwater produced (Panagopoulos et al., 2019)
Membrane Crystallization (MCr)	•Application for high concentration feed (up to 350,000 mg/L) (Panagopoulos et al., 2019) •No feed pressure requirements (Panagopoulos et al., 2019) •Low fouling propensity modular (Panagopoulos et al., 2019) •Possibility of utilization low-grade thermal energy allowing to reduce operating costs and carbon footprint (Panagopoulos et al., 2019) •Solid product is collected (Panagopoulos et al., 2019)	•Potential of membrane wetting (Panagopoulos et al., 2019) •Low membrane flux and poor thermal efficiency (Panagopoulos et al., 2019) •Intensive pretreatment processes to avoid scaling and fouling problems •Post-treatment is needed if volatile pollutants are present (Panagopoulos et al., 2019)	up to 90% (Panagopoulos et al., 2019)	•SEC: 39-73 kWh/m³ of freshwater produced (Panagopoulos et al., 2019) •SEC: 40-75kWh/m³ (Katal et al., 2020).	•Treatment costs are higher than MD (Katal et al., 2020). •Energy cost (Katal et al., 2020).	US$ 1.24/m³ of freshwater produced (Panagopoulos et al., 2019)

Appendix B: Summary of literature study on thermal technologies

Technology	Advantages	Disadvantages	Water recovery from brine	Energy consumption	Cost impacts	Specific cost
Evaporator (EV)/ Concentrator (BC)	•"Application for high salinity concentration (inlet TDS up to 250,000 mg/L)" (Panagopoulos et al., 2019, p.7) •Typical maximum TDS concentration reached within BC 250,000 mg/L (Weaver & Birch, 2020, August) •"Established technology specifically developed for the treatment of high-TDS brine" (Panagopoulos et al., 2019, p.7) •"High-quality freshwater is produced (<20 mg/L TDS)"(Panagopoulos et al., 2019, p.7)	•"High capital costs due to the expensive materials required to avoid corrosion" (Panagopoulos et al., 2019, p.7) •"Salt contains impurities, so improvement can be considered through brine pretreatment or specialized design" (Panagopoulos et al., 2019, p.7) •"Energy-intensive technology" (Panagopoulos et al., 2019, p.7)	•90 to 99% (Panagopoulos et al., 2019) •~95% (Charisiadis, 2018) •95 to 99% (Giwa et al., 2017)	•SEC: 15.86-26kWh/m³ of freshwater produced (Panagopoulos et al., 2019) •18-20kWh/m³ (Charisiadis, 2018)	•High CAPEX due to the expensive anticorrosion materials (Panagopoulos & Haralambous, 2020) •Energy costs (Panagopoulos et al., 2019)	•US$ 1.11/m³ of freshwater produced (Panagopoulos et al., 2019) •~US$ 5.5-18/m³ (Weaver & Birch, 2020, August)
Crystallizer (BCR)	•Application for high salinity concentration (TDS inlet up to 300,000 mg/L (Panagopoulos et al., 2019) or final TDS up to 375,000 mg/L (Tsai et al., 2017) and 500,000 mg/L (Weaver & Birch, 2020, August)) •"Solid product is filtered and dried" (Panagopoulos et al., 2019, p.7) •"Established technology specifically developed for the treatment of high-TDS brine" (Panagopoulos et al., 2019) •"High-quality freshwater is produced (<20 mg/L TDS)"(Panagopoulos et al., 2019, p.7)	•"High capital costs due to the expensive materials required to avoid corrosion" (Panagopoulos et al., 2019, p.7) •"Salt contains impurities, so improvement can be considered through brine pretreatment or specialized design" (Panagopoulos et al., 2019, p.7) •"Energy-intensive technology" (Panagopoulos et al., 2019, p.7)	Up to 99% (Panagopoulos et al., 2019)	•SEC: 52-70kWh/m³ of freshwater produced (Panagopoulos et al., 2019) •SEC: 40-70 kWh/m³ (Tsai et al., 2017) •50kWh/m³ (Charisiadis, 2018)	•High CAPEX due to the expensive anticorrosion materials (Panagopoulos & Haralambous, 2020) •Energy costs (Panagopoulos et al., 2019)	•US$ 1.22/m³ of freshwater produced (Panagopoulos et al., 2019) •~US$ 13.5/m³ (Weaver & Birch, 2020, August)
Multi-Stage Flash Distillation (MSF)	•Better than RO for high TDS feedwater (Kress, 2019) •Commercially operating large-sized plants (Kress, 2019) •Long-term operation record (Kress, 2019) •Easy to manage and operate (Kress, 2019) •"Commercially available and can be further upgraded to treat high-TDS brine" (Panagopoulos et al., 2019, p.7). •"High-quality freshwater is produced" (Panagopoulos et al., 2019, p.7) •"Application for medium salinity level (70,000 to 180,000 mg/L) if corrosion-resistant materials are used" (Panagopoulos et al., 2019, p.7) •maximum TDS 250,000 mg/L (Charisiadis, 2018) •Possibility of utilization low-grade thermal energy as waste heat allowing to reduce operating costs and carbon footprint (Kress, 2019; Panagopoulos et al., 2019)	•"High capital costs due to expensive anti-corrosion material" (Panagopoulos et al., 2019, p.7) •"Intensive pretreatment processes to avoid scaling and fouling problems" (Panagopoulos et al., 2019, p.7) •"Energy intensive technology" (Panagopoulos et al., 2019, p.7) •Corrosion and scaling problems (Kress, 2019; Panagopoulos & Haralambous, 2020) •Higher energy requirement than RO and MED (Kress, 2019) •Lower recovery than RO (Kress, 2019) •Brine hotter by up to 15°C receiving environment (Kress, 2019) •Cannot operate under 60 % capacity (Kress, 2019)	•up to 85-90% (Panagopoulos et al., 2019) •up to 85% (Panagopoulos & Haralambous, 2020)	•12.5-24 kWh/m³ (Panagopoulos, 2020) •~38 kWh/m³ (Charisiadis, 2018) •50 to 80 kWh/m³ (Kress, 2019)	•Capital costs (Panagopoulos et al., 2019). •Energy consumption if fossil fuels are used (Panagopoulos et al., 2019).	US$ 1.40/m³ of freshwater produced (Panagopoulos et al., 2019)

Technology	Advantages	Disadvantages	Water recovery from brine	Energy consumption	Cost impacts	Specific cost
Multi-Effect Distillation (MED)	•"Application for medium salinity level (70,000 to 180,000 mg/L) if corrosion-resistant materials are used" (Panagopoulos et al., 2019, p.7). •Maximum TDS 250,000 mg/L (Charisiadis, 2018) •Better than RO for high TDS feedwater (Kress, 2019) •Commercially operating large-sized plants (Kress, 2019) •Lower operation temperature than MSF (Kress, 2019) •Can be incorporated with mechanical or thermal vapor compression system to increase efficiency (Kress, 2019) •Possibility of utilization low-grade thermal energy as waste heat allowing to reduce operating costs and carbon footprint (Kress, 2019; Panagopoulos et al., 2019) •Operation with renewable energy possible (Kress, 2019) •"Moderate capital costs" (Panagopoulos & Haralambous, 2020, p.4) •"Commercially available and can be further upgraded to treat high-TDS brine" (Panagopoulos et al., 2019, p.7). •"High-quality freshwater is produced" (Panagopoulos et al., 2019, p.7)	•Higher energy requirement than RO (Kress, 2019) •More costly than MSF (Kress, 2019) •Lower recovery than RO (Kress, 2019) • Brine hotter by up to 15°C than receiving environment (Kress, 2019) •Corrosion and scaling problems (Kress, 2019; Panagopoulos & Haralambous, 2020) •"Current systems are not designed for the treatment of brine" (Panagopoulos et al., 2019, p.7) •"High capital costs due to expensive anti-corrosion material" (Panagopoulos et al., 2019, p.7) •"Intensive pretreatment processes to avoid scaling and fouling problems" (Panagopoulos et al., 2019, p.7) •"Energy intensive technology" (Panagopoulos et al., 2019, p.7)	•up to 85% (Panagopoulos & Haralambous, 2020) •up to 93% (Giwa et al., 2017) •up to 85-90% (Panagopoulos et al., 2019).	•7.7-21 kWh/m³ of freshwater produced (Panagopoulos, 2020) •~33 kWh/m³ (Charisiac 2018)	•Capital costs (Panagopoulos et al., 2019). •Energy consumption if fossil fuels are used (Panagopoulos et al., 2019).	US$ 1.10/m³ of freshwater produced (Panagopoulos et al., 2019)
Eutectic Freeze Cyrstallization (EFC)	•"Application for high salinity brine (up to 250,000 mg/L)" (Panagopoulos & Haralambous, 2020, p.4) •"No addition of chemicals required" (Panagopoulos et al., 2019, p.7) •"Corrosion of materials is reduced due to the low operating temperature" (Panagopoulos et al., 2019, p.7) •"Production of high-purity salt (<90 %)" (Panagopoulos et al., 2019, p.7) •Less energy needed than traditional evaporation methods (Giwa et al., 2017) •Offers an environmentally friendly way for energy storage (Mavukkandy et al., 2019, p.7) •Recovering valuable resources could offset the treatment costs (Mavukkandy et al., 2019)	•"High capital costs" (Panagopoulos & Haralambous, 2020, p.4) •"This technology hasn`t been applied extensively in multicomponent brine solutions" (Panagopoulos & Haralambous, 2020, p.4) •"Formation of an ice scale layer in the crystallizer surfaces" (Panagopoulos et al., 2019, p.7) •Low productivity (Giwa et al., 2017)	•98% (Panagopoulos & Haralambous, 2020) •Theoretically 100% possible (Panagopoulos et al., 2019)	•43.8 - 68.5 kWh/m³ of freshwater produced (Panagopoulos & Haralambous, 2020) •minimum of 40 kWh/m (Panagopoulos, 2020)	•High capital costs (Panagopoulos & Haralambous, 2020)	US$ 1.42/m³ of freshwater produced (Panagopoulos et al., 2019)
Temperature Swing Solvent Extraction (TSSE)	•Low energy demand as water does not need to be evaporated (Boo et al., 2020) •Application of low-grade heat sources possible (Boo et al., 2020) •Mainly thermal energy needed (Boo et al., 2020) •Treatment of high saline brine (over 200,000mg/L) (Boo et al., 2020)	•Large amount of chemicals needed (Boo et al., 2020) •Less information about treatment performance on brine •Application for large-scale questionable	91.2-95.9% (Boo et al., 2020)	172 kWh/m³ of thermal energy needed (Boo et al., 2020)		

Technology	Advantages	Disadvantages	Water recovery from brine	Energy consumption	Cost impacts	Specific cost
Humidification–Dehumidification (HDH)	•Inexpensive and reliable desalination system if adequate heat sources applied (Dehghani et al., 2019) •Usage of low-grade heat sources or renewable energy sources possible (Dehghani et al., 2019) •Low pre-treatment and disposal requirements resulting in simplified operation and maintenance (Narayan et al., 2010) •If solar-driven: decentralized application possible (Subramani & Jacangelo, 2015) •Production of two effects, distillation, and cooling (Subramani & Jacangelo, 2015)	•HDH less efficient at high salinity concentrations (Dehghani et al., 2019) •Application for moderate salinity concentrations (just up to seawater salinities have been evaluated (Subramani & Jacangelo, 2015)) (Dehghani et al., 2019) •Increase of energy demand with increasing salinity concentration (Dehghani et al., 2019) •Extreme high thermal energy consumption (Narayan et al., 2010) •Requirement of waste heat or renewable energy source for cost-effective application (Subramani & Jacangelo, 2015) •Large footprint requirement due to humidifier and dehumidifier chambers (Subramani & Jacangelo, 2015) •Optimization of carrier gas flow rate and feed water type essential (Subramani & Jacangelo, 2015)	•up to 88% at salinity concentration of 30 % (Dehghani et al., 2019) •100% achievable (Lawal & Qasem, 2020) •More than 97,5% (Subramani & Jacangelo, 2015)	• Thermal: 140 to 550 kWh/m3 at a water production rate of 4-12 kg/m² (Narayan et al., 2010) •Electrical: minimum 0.9 kWh/m³ at 11L/h. (Lawal & Qasem, 2020) •45.3 kWh/m³ electrical energy consumption (Subramani & Jacangelo, 2015)	•Capital costs (Panagopoulos et al., 2019). •Thermal energy consumption (Panagopoulos et al., 2019).	
Wind-Aided Intensified Evaporation (WAIV)	•"Application for TDS up to 100,000 mg/L" (Panagopoulos & Haralambous, 2020, p.4) •Uses natural energy source to recover resources (Mavukkandy et al., 2019) •Low cost (Mavukkandy et al., 2019) •"Solid product is collected" (Panagopoulos et al., 2019, p.7) •"Simple technology" (Panagopoulos et al., 2019, p.7) •"Compact and modular design" (Panagopoulos et al., 2019, p.7) •Higher evaporation rate than evaporation pond (50 to 90 %) (Morillo et al., 2014; Panagopoulos et al., 2019) •Low economic cost (Morillo et al., 2014)	•"No freshwater recovery" (Panagopoulos & Haralambous, 2020, p.4) •"No selective salt production" (Panagopoulos & Haralambous, 2020, p.4) •Low productivity (Mavukkandy et al., 2019) • Not feasible for a large amount of brine (Mavukkandy et al., 2019) •"Higher capital and operating costs than evaporation ponds" (Panagopoulos et al., 2019, p.7) •"Salt contains purities" (Panagopoulos et al., 2019, p.7) •Large extents of land (Morillo et al., 2014) •Possible contamination of groundwater (Morillo et al., 2014)	No recovery (Panagopoulos & Haralambous, 2020)	0.3-1kWh/m³ (Panagopoulos & Haralambous, 2020)	•Capital costs (Panagopoulos et al., 2019).	US$ 1.37/m³ of freshwater produced (Panagopoulos et al., 2019)
Spray Dryer (SD)	•"Application for high salinity brine (up to 250,000 mg/L TDS)" (Panagopoulos et al., 2019, p.7) •"Recovery of high-purity salts with certain standards possible" (Panagopoulos & Haralambous, 2020, p.4) •"Simple technology" (Panagopoulos et al., 2019, p.7)	•"Highly unlikely to be economically viable on a large scale" (Panagopoulos & Haralambous, 2020, p.4) •"Recovery of freshwater from outlet gas would be difficult and expensive" (Panagopoulos et al., 2019, p.7) •"Salt could contain impurities: Improvement through pretreatment and specialized design possible" (Panagopoulos et al., 2019, p.7)	No recovery (Panagopoulos & Haralambous, 2020)	•52-64kWh/m³ of freshwater produced (Panagopoulos & Haralambous, 2020)		US$ 0.09/kg of solid produced (Panagopoulos et al., 2019)

Appendix C: Zero liquid discharge market survey

Table C.1: Zero liquid discharge technology provider

ZLD & MLD market analysis	*Own literature research*
1. 3v Green Eagle S.p.A.	1. Saltworkstech
2. Alfa Laval	2. Lenntech
3. Aquarion AG	3. Dupont Water Solutions
4. Aquatech International Corporation	4. Mitsubishi Hitachi Power Systems, Ltd.
5. Arvind Envisol Limited	5. Leheng
6. Austro Chemicals & Bio Technologies Pvt Ltd	6. Eco-Techno
7. Awas International GMBH	7. KMU loft
8. Bionics Advanced Filtration Systems Ltd	8. Encon evaporator
9. Condorchem Envitech	9. 3Vtech
10. Dew Envirotech Pvt. Ltd	10. Samsco
11. Doosan Hydro Technology	11. Cirtec
12. Evoqua Water Technologies LCC	12. RunDry
13. GEA Group AG	13. Epcon
14. H2O GMBH	14. C&G wastewater
15. Hydro Air Research Italia	15. Slipstream Ecotech
16. IDE Technologies	16. TMW
17. Kelvin Water Technologies Pvt. Ltd.	17. Salttech
18. Memsys GmbH	18. Memsift
19. Oasys Water	19. Fluid Technology Solutions Inc.
20. Petro Sep Corporation	20. Hyrec
21. Praj Industries	21. Aquastill
22. Safbon Water Technology	22. CTFT
23. Samco Technologies Inc	23. Modern Water
24. Suez	24. Fujifilm
25. Thermax Global	25. Ampac
26. Transparent Energy System Private Ltd.	26. Astom
27. Veolia	27. Genesis Water Technologies
28. Water next solutions private limited	28. Tangent Fluid Technology
29. ZLD Technologies PVT LTD	29. Pure Water Group
	30. Aquaswiss
	31. Formeco
	32. Mega

Table C.2: Techno-economic data of ZLD market survey

- The companies` names have been defaced because of confidential concerns.

Company	Technology	Average flux capacity	WRR and final concentration	Operation temperature	Energy consumption	Costs	Limitations and comments	Source
[redacted]	Vacuum evaporator	1200 l/h	33 % residual water content	85°C	50-60 kWh/m^3	350,000 EUR with vacuum pump and two chemical containers	•High resistance material (stainless steel) fabrication can handle up to 120 000 mg/L chloride concentration •Hardness and salt ions are expected to precipitate leading to decreased process performance •Intensive maintenance with chemical washing and visual inspection needed to avoid precipitation	([redacted], personal communication, October 21, 2020)
[redacted]	Vacuum evaporator	131 l/h - 1000 l/h	until 30 % saline solution is reached	Until 120 °C hot steam produced	45-55 kWh/m^3	250,000 EUR	•Escalade material (1.4539) can handle up to 120,000 mg/L chloride concentration •Risk of precipitation of salt and hardness ions leaves to safety factors (just operating until maximal 30 % saline solution)	([redacted], personal communication, October 20, 2020)
	Vacuum evaporator	131 l/h - 1000 l/h	until 30 % saline solution is reached	Until 120 °C hot steam produced	45-55 kWh/m^3	500,000 EUR	•Hastelloy material has no concentration limit •Risk of precipitation of salt and hardness ions leaves to safety factors remains (just operating until maximal 30 % saline solution)	([redacted] personal communication, October 20, 2020)
	Crystallizer	300-400 m^3/a (~1m^3/d)	20 % residual water content	operated with 120°C hot steam produced from VACUDEST module	4kW and steam produced (1 bar) from VACUDEST or external sources	180,000 EUR	•ZLD module adjustable to VACUDEST unit •Usage of Hastelloy material •Several ZLD units are needed for higher brine production due to the safety factor of VACUDEST. Thus, external steam production needed at 120 °C	([redacted], personal communication, October 20, 2020)
[redacted]	Vacuum evaporator	6.25 to 740 l/h 7 to 20 m^3/d	~70 % water recovery. Concentration of brine until maximal 210 g/L		Installed energy is 120 kW and absorbed power about 100 kW (150 to 200 kWh/t of wastewater or 150-200 W/l of distillate produced)	186,000 EUR	•Titanium usage for high salt concentrations •Could run with electric energy (using a heat pump/compressor circuit) or hot water for evaporation and cooling water for condensation of distillate •Produced saturated solution at about 210,000 mg/L of salts (80% water and 20% salt)	([redacted], personal communication, October 22, 2020)
	Vacuum evaporator	~10m^3/d	Concentrates up to 2 times		Power required is 320 kWt (36-44 m^3/h of hot water at 60°C; 20 to 25 W/l of distillate)	168,000 EUR	•Uses alternative energy (e.g. hot water and steam) •Use of special stainless-steel alloys for aggressive effluents •Just one unit needed to keep the boiling temperature low in the boiling chamber (necessary due to the presence of chlorides)	([redacted], personal communication, October 22, 2020)
	Horizontal evaporator/ crystallizer	1-1.5m^3/d	Remove all water from a saturated solution		170 to 200 W/litre of distillate produced	73,750 EUR	•Runs with alternative energy (hot water /steam) •Made from stainless steel to avoid precipitation	([redacted], personal communication, October 22, 2020)
[redacted]	Horizontal vacuum evaporator/ Crystallizer	127 L/h	Above 70 % and up to 90 % dry residues		Thermal requirement 86 kWt, equal to 140 kg/h steam (1bar) and 15 m^3/h hot water (90°C)	205,000 EUR	•Uses steam or hot water (fed by thermal energy) •Operates 24/7 •External heat exchanger •Build from Superdublex stainless steel to avoid precipitation •Need cooling water (14 m^3/h at 28°C)	([redacted] personal communication, October 21, 2020)

Company	Technology	Average flux capacity	WRR and final product	Operation temperature	Energy consumption	Costs	Limitations and comments	Source
[redacted]	Evaporator	10m³/d	Dry residue of 50-60%	Condensate outlet temperature depending on the used thermal vector could differ between 35-55°C and 50-70°C	Thermal requirement 290 kWt, Installed power 10 kW equal to 480 kg/h steam and 50 m³/h hot water (90°C)	215,000 EUR	•Fed with thermal energy (hot water 85-90°C or steam at 1 bar) •Upgrade to super-duplex (austenitic-ferritic) stainless steel for service in highly corrosive conditions	([redacted] personal communication, October 21, 2020)
[redacted]	HPRO and UF	For flow more than 100 m³/d	50 % reduction in volume (up to 2x at 60 000 mg/L TDS)		1 to 1.2 kWh/BBL ~6.289 to 7.5476 kWh/m³	Total costs 0.75 to 2 $/BBL Ballpark, 5 yrs	•Just electrical energy needed •Some pre-treatment needed dependent on inlet chem •TDS inlet concentration up to 80 000 mg/L •Can concentrate up to 130 000 mg/L TDS •Xtreme RO (ultra-high pressure RO) with Xtreme UF robust ceramic UF pre-treatment	([redacted] personal communication, September 9, 2020)
	Evaporator	10-35 m³/d	66 % reduction in volume (up to 3x at 100 000 mg/L TDS)		0.6 MMBTU/BBL for thermal energy and 2 to 3 kWh/BBL for eletrical energy	~3$/BBL Ballpark	•TDS inlet range up to 280 000 mg/L TDS •Can concentrate up to 350 000+mg/L TDS •Simple TSS filtration as pre-treatment needed •High resistance material used (FRP, CPVC, titanium wetted parts) •Some air emissions, VOC risks, water chemistry dependent	([redacted] personal communication, September 9, 2020)
	Crystallizer		ZLD		0.7 MMBTU/BBL for thermal energy and 3 to 4 kWh/BBL for electrical energy	~3$/BBL Ballpark	•TDS inlet range up to 280 000 mg/L TDS •Can concentrate up to saturation/ZLD •Simple TSS filtration as pre-treatment needed •High resistance material used (FRP, CPVC, titanium wetted parts) •Some air emissions, VOC risks, water chemistry dependent	([redacted] personal communication, September 9, 2020)
	Evaporator	10-35 m³/d	66 % reduction in volume (up to 3x at 100 000 mg/L TDS)		~0.7 MMBTU/BBL (~17.6MMBTU/hr per AB100) and 4 to 5 KWH/BBL volume reduced	4 to 6$/BBL Ballpark	•TDS inlet range up to 280 000 mg/L TDS •Can concentrate up to 350 000+mg/L TDS •Simple TSS filtration as pre-treatment needed •High resistance material used (FRP, CPVC, titanium wetted parts) •Closed hybrid system, no direct produced water contact with the atmosphere (no air emission risk)	([redacted] personal communication, September 9, 2020)
[redacted]	Crystallizer		Saturation/ZLD		0.8 MMBTU/BBL thermal energy and 5 to 6 kWh/BBL Volume reduced	4 to 6$/BBL Ballpark	•TDS inlet range up to 280 000 mg/L TDS •Can concentrate up to saturation/ZLD •Simple TSS filtration as pre-treatment needed •High resistance material used (FRP, CPVC, titanium wetted parts) •Closed hybrid system, no direct produced water contact with the atmosphere (no air emission risk)	([redacted] personal communication, September 9, 2020)
	Evaporator and MVR	10-35 m³/d	66 % reduction in volume (up to 3x at 100 000 mg/L TDS)		7 to 10 kWh/m³ Volume reduced electrical energy	~3 to 6 $/BBL Volume reduced	•TDS inlet range up to 280 000 mg/L TDS •Can concentrate up to 350 000+mg/L TDS •Simple TSS filtration and chemical softening as pre-treatment needed if sulfate concentration >50 g/L •High resistance material used (FRP, CPVC, titanium wetted parts) •Closed system (no air emission risk) •Just electrical energy needed	[redacted] personal communication, September 9, 2020)

Company	Technology	Average flux capacity	WRR and final product	Operation temperature	Energy consumption	Costs	Limitations and comments	Source
[redacted]	BC (MVC + Falling film evaporator)	10-35 m³/d	up to a 20-25% concentration		21kWh/m³	around 1,000,000 EUR	•MVC combined with falling film evaporator •Treatment up to 250,000 mg/L	([redacted] personal communication, November 30, 2020)
	Crystallizer	10-35 m³/d	ZLD, final salt		69kWh/m³	around 1,000,000 EUR	•Forced circulation •Anti-corrosive material (Titanium HE duplex) used for the treatment of high saline water	([redacted] personal communication, November 30, 2020)
	Vacuum MD	12-48m³/d	up to 90 % recovery	70-90 °C	21kWh/m³	below 1,000,000 EUR	•Feed brine concentration of around 10-12% •Salt rejection of 99.5-99.9%	([redacted] personal communication, November 30, 2020)
[redacted]	Heat pump vacuum evaporator (forced circulation)	300 l/h	ZLD		0.17 kWh/l of distillate	126,000 EUR	•Built out of super duplex steel •Fully automatic •Suitable to work 24h continuously •Single effect	([redacted], personal communication, November 13, 2020)
	Heat pump vacuum evaporator (forced circulation)	1.500 l/h	ZLD	35-55 °C	0.11 kWh/l of distillate	346,000 EUR	•Built out of superdublex steel •Fully automatic •Suitable to work 24h continuously •Double effect resulting in energy savings	([redacted] personal communication, November 13, 2020)
[redacted]	Vacuum crystallization	7m³/d, 6000 L/d distillate production	ZLD		Absorbed power= 2.6 kWh; Saturated steam 3 barg= 325kg/h; Cooling water at 27°C= 23m³/h; Cooling water at 8°C = 2.3 m³/h	265,445.00 EUR	•24 hours operation • Condensation by a heat exchanger with cooling water circuit or air condenser •Supporting structure made of stainless steel	([redacted] personal communication, November 12, 2020)
	Vacuum crystallization	20m³/d, 24 000 L/d distillate production	ZLD		Absorbed power= 10 kWh; Saturated steam 3 barg= 1,300kg/h; Cooling water at 27°C= 120m³/h	372,635.00 EUR	•24 hours operation • Condensation by a heat exchanger with cooling water circuit or air condenser •Supporting structure made of stainless steel	([redacted] personal communication, November 12, 2020)
	Centrifuge	500 kg/h	Final salt	45°C	13.5 kWh	119,595.00 EUR	•Continuous centrifugal separator suitable for solid-liquid separation • The final result is the obtaining of salts or sludge with a residual humidity	([redacted] personal communication, November 12, 2020)
[redacted]	MD + Crystallizer	25 m³/d			50 kWh/m³	around 500,000 EUR	•MD concentrates up to 200 000 mg/L and Crystallization up to 400 000 mg/L •Made from anticorrosive Duplex steel	([redacted] personal communication, September 29, 2020)
[redacted]	MD	1 m³/h			1.5 kWh electrical demand for pumps	220,000-230,000 EUR		([redacted] personal communication, September 14, 2020)
	EV + CRY	1m³/h	ZLD	65°C	EV: 15-20 kWh/m³ CRYST: 50-100 kWh/m³	600,000 – 800,000 EUR	•Recommendation to reduce the brine flow by MD and RO bevor thermal processes	([redacted] personal communication, September 14, 2020)

Appendix D: Multi-criteria analysis - Definition of dimensions for ZLD treatment chains (based on (Cossio et al., 2020)

Dimension	*Indicator*	*Description*	*Suggested units*	*Stages*
Environmental	Energy demand	Specific energy demand according to (actual or simulated) monitoring parameters	kWh/m^3	0-60 60-85 >85
	Global warming potential	Specific emission during treatment, energy production, salt disposal according to (actual or simulated) monitoring parameters	kg CO_2 eq./m^3	Discussion
	Water recovery	Water recovery efficiency according to (actual or simulated) monitoring parameters	%	>95 85-95 >85
	Land area	Land area requirement according to technical and design data	m^2	Discussion
	Quality of water	Water quality according to (actual or simulated) monitoring parameters	mg/L	<10mg/L TDS 10-250 mg/L TDS >250 mg/L TDS
	Recovered resource quality	Resource quality according to (actual or simulated) monitoring parameters	%	>95 85-95 <85
	Chemical usage	Chemical usage according to (actual or simulated) monitoring parameters	ml/h or ml/litre of freshwater produced	<0.3 0.3-0.5 >0.5
	Soil and groundwater pollution	Soil and groundwater contamination by the deposition of salt at landfills according to (actual or simulated) monitoring parameters	Scoring system	Discussion
Social	Public acceptance	Acceptance of the brine management before implementation following consent by the population	Scoring system	Discussion
	Aesthetics	Acceptance of noise, odour, visual interference	Scoring system	Discussion
Economic	Investment costs	Investments costs of the brine treatment chain considering the expected plant life	EUR/m^3	Discussion
	Operating and maintenance cost	Operation and maintenance costs of the brine treatment chain including chemical usage	EUR/m^3per year	Discussion
	Product water price	Water price	EUR/l	>1 EUR/l 1-3 >3 EUR
	Resource reimbursement	Reimbursement/ Price of recovered resource	EUR/kg	Discussion
Technical	Reliability	Reliability including effectiveness by water flow fluctuation	Scoring system	Discussion
	Complexity of construction	Appropriate technology designed in line with the local context and available resources	Scoring system	Discussion
	O&M effort	Operation and Maintenance effort	Scoring system	Discussion
Institutional	Information	Information/training to users during pre-investment and construction of the project. Technical information for operators to manage the plant	Scoring system	Discussion
	Interactions	Collaboration between the water provider and the municipality, local universities, and health institutions	Number of events/years	Discussion

Appendix E: Calculated brine composition for the proposed ZLD systems

Table E.1: Calculated flow and concentration of the first design idea (EV+CRY)

		MED			Evaporator		Crystallizer	
Description	Unit	Feedwater	Brine	Distillate	Concentrated Brine	Distillate	Concentrated Brine	Distillate
Flow rate	m³/d	47.62	27.62	20.00	11.10	16.52	6.00	5.10
Flow rate	l/h	5,952.38	3,452.38	2,500.00	1,387.65	2,064.73	750.08	637.57
pH		8.31	8.31	8.31	8.31	8.31	8.31	8.31
Temperature	°C	32.57	35.00	35.00	63.16	60.00	65.85	60.00
TDS	mg/L	44,293.73	76368.50	0.00	190,000	0.00	351500.00	0.00
Salinity		41.30	76.23	0.00	189.66	0.00	350.87	0.00
Total Hardness	mg/L	8,248.91	14,222.26	0.00	35,384.08	0.00	65460.54	0.00
Calcium	mg/L	810.09	1,396.71	0.00	3,474.92	0.00	6428.61	0.00
Magnesium	mg/L	1,493.64	2,575.24	0.00	6,407.02	0.00	11852.99	0.00
Chloride	mg/L	24,473.00	42,194.83	0.00	104,978.06	0.00	194209.42	0.00
Sulphate	mg/L	3,102.64	5,349.37	0.00	13,308.90	0.00	24621.47	0.00
Sodium	mg/L	10,000.00	17,241.38	0.00	42,895.46	0.00	95227.93	0.00

Table E.2: Calculated flow and concentration of the second design idea (EV+ASE)

		MED			Chemical Precipitation			Evaporator		Solar still
Description	Unit	Feedwater	Brine	Distillate	Brine	Brine	Brine	Concentrated Brine	Distillate	Distillate
Flow rate	m³/d	47.62	27.62	20.00	27.62	27.62	27.62	7.09	20.53	4.64
Flow rate	l/h	5,952.4	3,452.38	2,500	3,452.38	3,452.38	3,452.38	886.25	2,566.13	579.61
pH		8.31	8.31	8.31	10.00	10.00	7.00	7.00	7.00	7.00
Temperature	°C	32.57	35.00	35.00	90.00	35.00	35.00	64.74	60.00	
TDS	mg/L	44,835	77,301.7	0.00	77,301.72	73,161.31	73,161.31	285000	0.00	0.00
Salinity		41.30	76.23	0.00	76.23	76.23	76.23	296.96	0.00	0.00
Total Hardness	mg/L	8,248.9	14,222.3	0.00	14,222.26	3005.612	3,005.62	11,708.38	0.00	0.00
Calcium	mg/L	810.09	1,396.71	0.00	1,396.71	1,117.37	1,117.37	4,352.70	0.00	0.00
Magnesium	mg/L	1,493.6	2,575.24	0.00	2,575.24	51.50	51.50	200.64	0.00	0.00
Chloride	mg/L	24,473	42,194.8	0.00	42,194.83	42,194.83	42,194.83	164,370	0.00	0.00
Sulphate	mg/L	3,102.6	5,349.37	0.00	5,349.37	4,012.03	4,012.03	15,628.87	0.00	0.00
Sodium	mg/L	10,000	17,241.38	0.00	17,241.38	17,241.38	17,241.38	6,7163.82	0.00	0.00

Table E.3: Calculated flow and concentration of the third design idea (ED+CRY)

		MED			Pellet Reactor	Chemical Precipitation		1. Stack Electrodialysis		2. Stack Electrodialysis		Crystallizer	
Description	Unit	Feedwater	Brine	Distillate	Softened Brine	Brine	Brine	Concentrated Brine	Diluted Brine	Concentrated Brine	Diluted Brine	Concentrated Brine	Distillate
Flow rate	m³/d	47.62	27.62	20.00	26.23809524	26.24	26.24	5.84	20.40	2.07	3.77	0.94	1.13
Flow rate	l/h	5952.38	3452.38	2500.00	3279.76	3279.76	3279.76	729.75	2550.01	259.06	470.69	117.92	141.14
pH		8.31	8.31	8.31	9.00	10.00	7.00	7.00	7.00	7.00	7.00	7.00	7.00
Temperature	°C	32.57	35.00	35.00	35.00	90.00	35.00	35.00	35.00	35.00	35.00	61.26	60
TDS	mg/L	44835.00	77301.72	0.00	75932.95	75932.95	72066.29	110000	470	160000	470	351500	0
Salinity		41.30	76.23	0.00	76.23	76.23	76.23	116.36	0.47	169.25	0.50	371.81	0
Total Hardness	mg/L	8248.91	14222.26	0.00	10679.80	10679.80	268.07	409.17	1.66	595.16	1.75	1307.49	0
Calcium	mg/L	810.09	1396.71	0.00	27.93	27.93	22.35	34.11	0.17	49.62	0.15	109.00	0
Magnesium	mg/L	1493.64	2575.24	0.00	2575.24	2575.24	51.50	78.62	0.32	114.35	0.34	251.21	0
Chloride	mg/L	24473.00	42194.83	0.00	42194.83	42194.83	42194.83	64405.02	261.17	93680.03	275.19	205803.32	0
Sulphate	mg/L	3102.64	5349.37	0.00	5349.37	5349.37	4012.03	6123.85	24.83	8907.42	26.17	19568.49	0
Sodium	mg/L	10000.00	17241.38	0.00	17241.38	17241.38	17241.38	26316.77	106.72	38278.93	112.44	84094.03	0