



DESALINATION • WATER REUSE • ZLD

Water Desalination Technology Map –

A Summary of Techniques following a Novel Classification Approach

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Abstract:

With the emergence of more and more desalination techniques over recent years, sound methodological classification of the various desalination techniques has become increasingly difficult to achieve.

In the present paper classification criteria are identified to serve the purpose of prolonged stability in classification structure. Two novel desalination technology maps are proposed and discussed, one mapping desalination techniques according to the specific initiator driving the specific desalination process, and another one mapping the techniques by the separation principle of salt and water applicable to the specific desalination technique. For each of the 22 desalination techniques considered, detailed descriptions on desalination process and applicable classification criteria follow. The benefits and limitations of the novel classification formats are pointed out and elaborated on with invitation for further enriching discussion.

Keywords:

Water, Desalination, Technology, Technique, Classification, Separation Principle, Driving Force, Initiator, Chemical Potential Difference; Electrochemical Potential Difference

The "Deutsche Meerwasser Entsalzung – DME - e.V. is pleased to make this new approach to the classification of water desalination technologies available to interested readers as part of its charitable work as part of the "Water Desalination Technology Map" and hopes to make a contribution to improving the further availability of water in the future. Furthermore, we hope that with this work we can also bring young people closer to the often complicated topic of water desalination.

The entire document of the "Water Desalination Technology Map" is available to anyone to download and use in the English original and in the German translation free of charge.

German seawater desalination – DME- e.V., September 5th, 2022

1. Introduction

Who would need yet another classification for desalination techniques? Maybe a trivial question – but only at first glance. No doubt, desalination has seen numerous categorisation approaches giving insight into particular questions posed, e.g. "Are membranes applied or not?" or "Which desalination technique can work with thermal energy?" or "Is the technique working under vacuum?" or "Does the technique discharge chemicals?"

But would it not be most knowledgeable to find criteria that bring to light the very nature of desalination techniques? The present paper strives to identify criteria that categorise desalination techniques by their fundamental nature, to map them and to sketch them in a novel categorisation context. The authors believe that the new framework will serve scientists and students or other interested parties in the field of desalination to develop a more profound understanding regarding the intrinsic rationale of desalination techniques and to realise the inter-relational context of the different techniques.

Also, the categorisation discussion brings to light some inconsistency on technical nomenclature, which – due to fairly wide and loose use - has found its way into everyday's technical language. Yet, although merely of formal relevance, the methodological context of the present paper may be just right to devote at least a few thoughts on the need of maintaining awareness regarding the use of scientific language.

2. Classification Approach

2.1 The Subject of Classification: Water Desalination Techniques

2.1.1. Scope: Multi-Source Water Desalination for Multi-Purpose Use

When thinking about "desalination", the traditional connotation will most likely be the generation of drinking water from seawater to overcome serious water shortage in arid regions of the world. Of course, the desalination of seawater for this purpose is the classic and largest application of desalination [1], however, the use of desalination techniques today reaches a myriad of purposes, a good number of them to overcome the scarcity of water for human and agricultural consumption (e.g. brackish and seawater desalination to produce drinking water), but more and more also for industrial purposes such as ultrapure water generation, desalination for water reuse, zero liquid discharge applications or – not targeting for water, but for salt - recovery of valuable salts and metals from water.

In broader brackets, desalination comprises cases of

- non-selective reduction or elimination of salt content in water (reducing in bulk),
- selective reduction or elimination of salt content in water (specific reduction)
- concentration of brine to reduce its volume and to minimise environmental impact
- concentration of salts and metals in water and recovery of salts and metals from water

The more the term “desalination” is widened from its narrow classic purpose to generate drinking water, the more techniques come to mind that could potentially be usable for the specific desalination task.

For the purpose of this article, the term “water desalination” is used in its broadest context: it refers to the separation of water and salt, using saline water of any source (e.g. seawater, brackish water, ground water, etc.) and for any purpose (e.g. drinking water, ultrapure water, recovery of salts). In this way, the widest range of techniques to desalinate water is covered by the intended classification approach, thereby winning on substance and relevance.

2.1.2 Focus: The Core of the Desalination Process

As a further matter of clarification, it should be noted that water desalination plants typically comprise a sequence of process steps to accomplish the task of separating salt and water. Amongst others, the source water may need pretreatment prior to the desalination step and the desalinated water may need posttreatment after the desalination step to reach a specific water quality.

Solely the middle step in the sequence of “Pretreatment – Desalination – Posttreatment”, represents the core-process in desalination. Additionally, a desalination plant will need to incorporate secondary functions, e.g. solutions for energy supply, brine discharge and other functions to be able to properly operate and to comply with site specific environmental, safety and other requirements.

While all these functions assist to the plant’s capability of separating water from salt, solely in the “desalination step” water is separated from salt; all other process steps and functions, while important, solely assist the desalination step, the “heart” of a desalination plant. In consequence, this article focuses primarily on the desalination step of the process, where separation of salt from water factually happens.

2.1.3 Convention on Terminology: “Technologies” vs. “Techniques”

The use of the terms “Technology” and “Technique” has been quite loose in science and everyday language. In German (and other European languages), a distinction exists between “Technik” and “Technologie” that is absent in the Anglo-Saxon world, where both terms are usually translated by “technology.”

Etymologically “technology” means “science of craft”, from the τέχνη, *téchne*, “art, skill, cunning of hand”; and -λογία, standing for “science”. The term “technique” (in German: “Technik”) stems from the Greek τεχνικός, *technikós* which is also derived from the Greek word τέχνη, *téchne*, meaning “art, handcraft, craftsmanship”.

The term “technology” is a fairly young term and came to prominence in the early 20th century in connection with the Second Industrial Revolution. Before the 20th century, the term “technology” has been uncommon in English, and it was used either to refer

to the description or study of the or to allude to technical education. The term's meanings changed in the early 20th century when American social scientists, beginning with Thorstein Veblen translated ideas from the German concept of "Technik" into "technology." By the 1930s, "technology" referred not only to the study of the industrial arts, but also to the industrial arts themselves. In contrast to the Anglo-Saxon world, in German and European languages the original etymological connotation survived and traditionally interprets "technology" as the "science of techniques" (in German: "Die Wissenschaft der Technik") [2].

In an attempt to maintain the scientific precision given by its historic format, this article applies the etymological terminology. In consequence, in the present paper water desalination is referred to as a "technology", thus as an umbrella term representing the science of desalination as well as its techniques. "Techniques", in turn, refer to specific forms of technical execution of technology and include devices, skills and capabilities by applying desalination science and know how (e.g. Reverse Osmosis, Membrane Distillation, Electrodialysis etc.).

2.2 Classification Methodology

2.2.1 Existing Classification Approaches and Criteria

There is nothing like the one and only classification format for a particular technology. Several classification formats may exist at the same time for a given technology. The format of classification is simply a function of the question posed, i.e. the criterion of classification. Different questions will lead to differing classification maps. Typical classification criteria used in existing desalination literature are amongst others:

- Phase change vs. no phase change [3, 4, 5]
- Thermal versus non-thermal [6-8, 9]
- Thermal vs. membrane based [6, 8, 10]
- "Working principle" of desalination techniques [7, 11]

Furthermore, technology classification is not rigid over time but requires review due to innovation in the particular field of technology, thereby, outmoding prior classification approaches which may start suffering methodological fit.

All this is also true in water desalination, where - from the early boiling and condensing of water by ancient Greek sailors - innovation has enriched desalination diversity in a remarkable way: Today we count more than 20 desalination techniques (see Section 4) in use or potentially useful. Existing classification approaches are often faced with need to squeeze novel desalination techniques into historic mapping formats, however, at the cost of sacrificing methodological precision.

Review of publications in desalination science reveals some challenges in classifying desalination techniques, as the following examples show:

- Classification “Thermal – Membrane - Chemical - Adsorption”

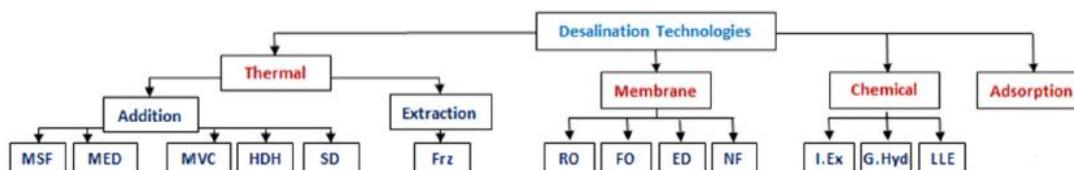


Fig. 1. Classification of desalination technology according to [8]

In this classification scheme the criteria chosen are not complementary to each other and do not add to one total.

- Classification “Phase change – No phase change – Alternative processes – Hybrid systems”

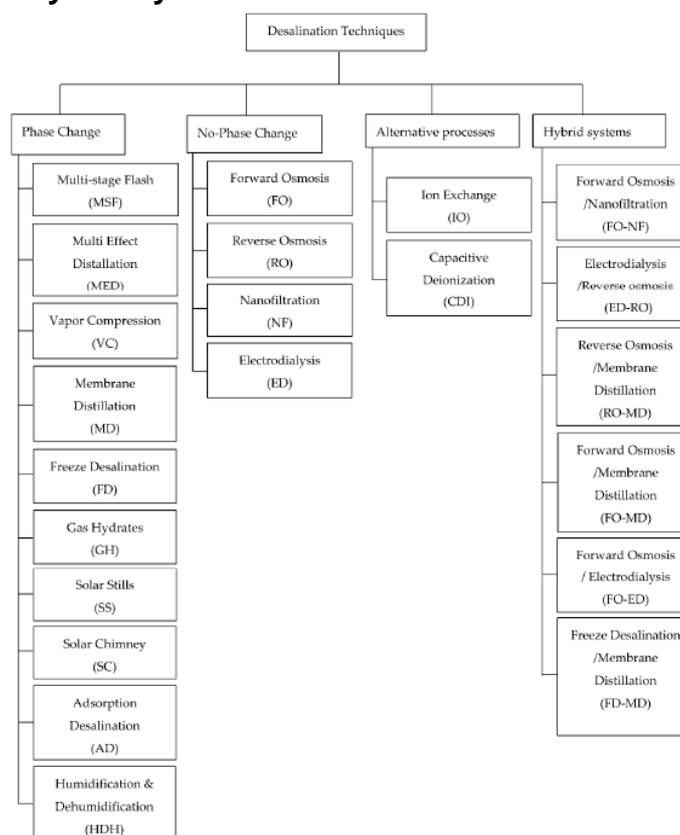


Fig. 2. Classification of desalination technology according to [3]

This classification shows a lack of consistency because the criteria pair “Phase change” and “No phase change” is already fully complementary and systematically adds to a consistent and fully complete total. It does, however, not allow for further techniques (like “Alternative processes” or “Hybrid systems”) being added over and above this already complete pair.

- **Classification “Thermal – Physical”**

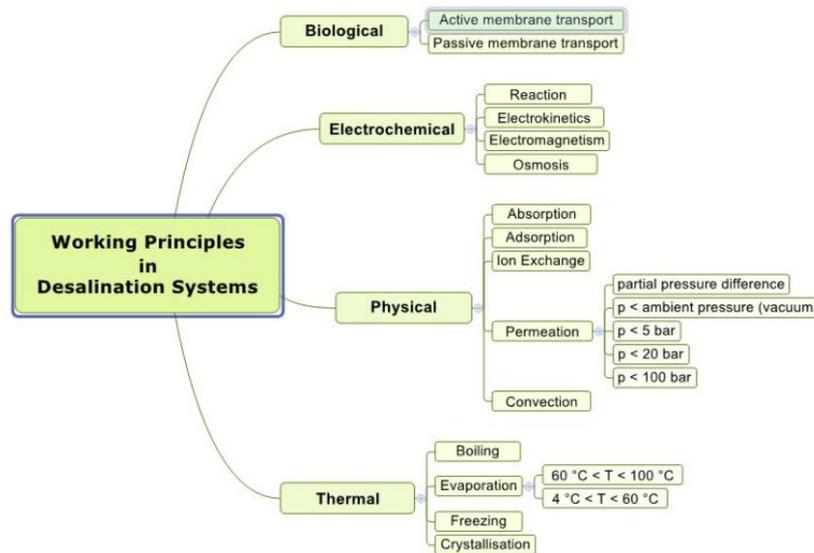


Fig. 3. Classification of desalination technology according to [11]

In this classification the chosen criteria are not mutually exclusive. Just as much as thermal science will typically be considered amongst scientists as a section of physics, a thermal desalination technique will also need to be considered physical.

- **Classification “Thermal – Membrane – Other”**

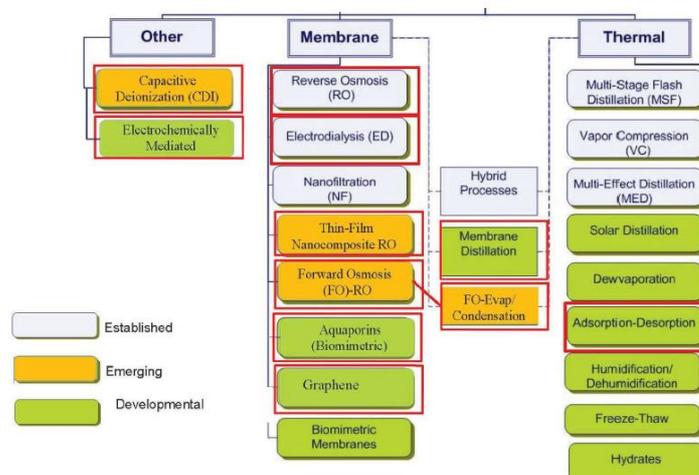


Fig. 4. Classification of desalination technology according to [10]

In this criteria arrangement the term “Other” may well be factually correct, however, does not render additional explanatory value.

- **Classification “Thermal – Membrane – Electrical – Chemical”**

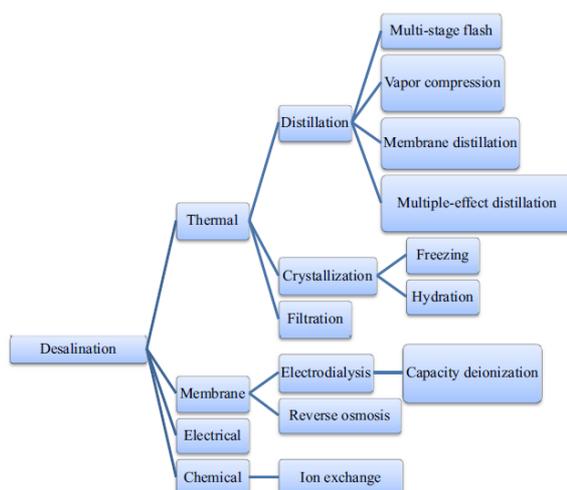


Fig. 5. Classification of desalination technology according to [6]

This pragmatic classification format has been in use for quite some time. However, with the emergence of Membrane Distillation, being both a “Membrane” as well as a “Thermal” technique, it does not permit unequivocal classification any more. Similarly, Electrodialysis shares both, “Membrane” and “Electrical” characteristics, and can, therefore, not be unequivocally be classified under either of the two criteria.

- **Classification of e.g. RO or ED under Filtration**

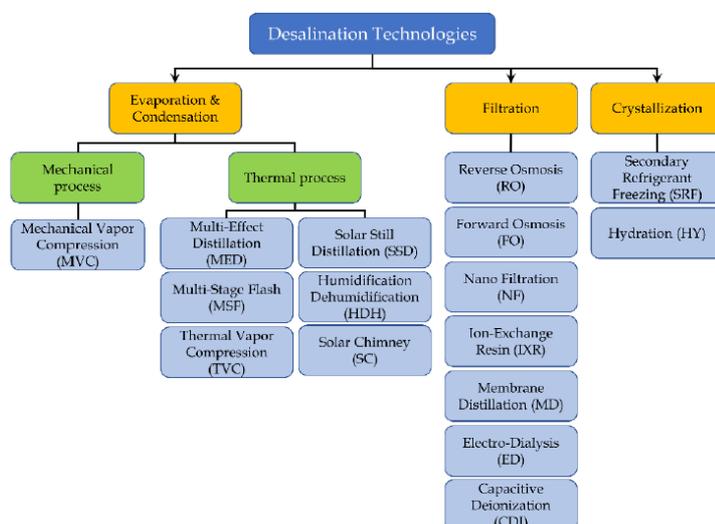


Fig. 6. Classification of desalination technology according to [7]

The clustering of such desalination techniques as Reverse Osmosis (RO) or Electrodialysis (ED) under the “working principle” criterion “filtration” [7] would probably be discussed controversially in terms of scientific adequacy in nomenclature. A good number of scientists would probably prefer classification of RO membranes as solution-diffusion membranes, being different in working principle from porous membranes used in filtration. Likewise, ED would presumably find preferential classification under the principle of electrophoretic mobility of ions in an electrical field (movement of ions according to their charge).

2.2.2 Conceptualising a Novel Classification Approach with Novel Classification Criteria

Challenges in classification methodology like the ones exemplarily addressed above, highlight the methodological difficulties encountered today in classifying desalination techniques.

Study of the literature regarding classification of water desalination technology also reveals that as of today only very limited research has been accomplished regarding classification of desalination techniques by more fundamental criteria. Examples of classification attempts by e.g. “working principle” of desalination techniques may be found under [2, 8]; a closer look, however, reveals that there is room for an update on terminology, methodological accuracy and consistency.

More importantly, the authors concentrated on identifying a classification approach that would yield both, a more persistent methodological consistency as well as a higher robustness against drastic alteration. In the past, this goal has been jeopardized in particular when the necessity to integrate a new desalination technique into an existing classification scheme arose and finally ended up with the need to reshuffle the existing criteria set rather than simply adding the new technique while maintaining the existing classification principles. Therefore, the achievement of a criteria set with higher stability and consistency over time has been the target.

In an attempt to accomplish this target, a classification solution is suggested in the present paper that addresses the fundamental principles of desalination, i.e. the very “heart” of the individual desalination techniques. The rationale for this approach: The nature of a desalination technique does not change over time, and, therefore, suggests stability in classification structure. It, therefore, appears meaningful to look for such categorizing criteria that would reflect the nature of the various desalination techniques best, in particular:

1. For a particular desalination technique, what exactly drives the salt-water separation process?
2. For a particular desalination technique, what exactly is the fundamental principle (mechanism) that separates water and salt?

As simple as these two questions may appear, an answer to these questions is not trivial at all as it requires identification of

- the various **salt removal techniques**
- the “**driving force**”, or more precisely, the “**initiator(s)**” driving the process
- the “**separation principle**” (separation mechanism) applicable to a particular desalination technique.

In the following Section 3, the novel technology classifications are presented in the form of two desalination technology maps being completely compatible with each other, one based on the initiators driving the desalination processes, the other one the criterion “Salt-Water Separation Principle”.

3. Desalination Technology Mapping under New Classification Criteria

3.1 Identification of Desalination Techniques

For the intended desalination technology map, 22 desalination techniques have been identified. They are either in commercial use or in an emerging stage or they are known but not (or not any more) in significant use, however, should be taken note of as unique desalination formats. All of them have found their mapping in the technology maps (Figure 7 and 8).

The various techniques differ from each other in their technical characteristic, however, they may share an identical initiating driving force or an identical separation principle thus forming clusters under the respective criterion shared.

In-depth descriptions pertaining to the initiators driving the desalination process or pertaining to the salt-water separation principle of the particular desalination technique can be found in Section 4 for a more detailed understanding.

3.2 Technology Mapping by Driving Force and the Initiators Driving the Desalination Process

3.2.1 A New Classification Criterion: The “Electrochemical Potential Difference”

When investigating the question of what drives a process, the classic response from scientists of the thermodynamic field is short and simple: Processes are driven because of a difference in “chemical potential” [12, 13, 14].

Unfortunately, the term “chemical potential” is rather non-descript and quite difficult to grasp compared to the notion of other thermodynamic variables like temperature or pressure. As the present paper is also intended to the interested layman, the authors wish to convey the notion of this quantity in a more intuitive way, describing its properties rather than relating it to energy change (change in Gibbs free energy) as customarily exercised in thermodynamics. In the present paper, the thermodynamic complexity is, therefore, reduced to a level considered commensurate to understanding the basic concept of the chemical potential:

Looking at the various substances on earth, every substance has some tendency to change, i.e.

- to react with other substances,
- to transform into another state of aggregation,
- to migrate to another place.” [13]

Examples for this would be the reaction of hydrogen and oxygen to form water ($2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O}$), the vaporisation and freezing of water, or the migration of Na ions or Cl ions in water under the influence of an electric potential. As another example, the perishing of chemicals, even in a sealed bottle, demonstrates that the driving force for this ubiquitous phenomenon is not the interaction between different substances, as believed by chemists in former times, but it is the intrinsic property of each substance itself. This tendency to change is described by a single physical quantity, the chemical potential μ [13].

The value of the chemical potential always refers to a specific substance. The unit of the chemical potential is Joule per mole. The substance must not necessarily be pure; it may well be composed of different substances [13].

Changes in the form of chemical reaction, phase change or migration take place voluntarily, because the tendency of substances for change is more compelling in the initial state A than in the final state B. In fact, substances tend to move from a higher chemical potential to a lower one because – as deeper knowledge of thermodynamic theory tells us – this reduces the free energy (also known as “Gibbs free energy”). The chemical potential represents the change in free energy (Gibbs free energy), and once the change in free energy comes to an end (becomes zero), the substances in the system - as a total - have no more motivation to change. They cannot - in total - reduce their free energy further and have reached a new equilibrium level at an energy level which has been reduced for the totality of substances participating in the system. The totality of substances has, therefore, reached a more stable energy level. The chemical

potential difference, therefore, represents the driving force of changes in a system [13-14].

Just as a ball rolls down the hill and thereby reduces its gravitational potential, molecules of substances react, transform or move. In doing so, they tend naturally to go from a higher to a lower chemical potential, thereby changing the amount of substance, i.e. their concentration in a solute. In principle, the following three cases can happen:

- $\mu_A > \mu_B$: transformation of substance A into substance B or transport from place A to place B
- $\mu_A = \mu_B$: no transformation, no transport; chemical equilibrium
- $\mu_A < \mu_B$: transformation of substance B into substance A or transport from place B to place A [13].

A phase change is initiated by a difference in chemical potential between the two phases A and B. When e.g. temperature increases, the chemical potential decreases. It does so for almost all substances and for all states of aggregation. The decrease is greater for gases than for liquids, and greater for liquids than for solids. For example, at 1 bar and temperatures deviating from 0 °C, liquid water and solid ice have different chemical potentials. Depending on the temperature, the phase transition is running in one or the other direction. At 0 °C the two phases are in equilibrium [13].

As we can derive from the above, the difference of the chemical potential is the driving force for substances to change (change in location, chemical composition or state of aggregation). However, we would also like to know which specific variable of the chemical potential is responsible for the change, i.e. which trigger needs to be pulled to get momentum on the process. This knowledge would also help identify the intensity, by which a process is driven.

Classic thermodynamic theory provides an answer to this question. It reveals (in a simplified way) that a change in chemical potential may result from a change in any of the three following variables, namely a change in

- temperature,
- pressure and
- amount of substance [13]

So, initiating a process or changing either of these variables will change the chemical potential. In line with this notion, the term “**Initiator**” is used in the present paper to reflect these three variables influencing the chemical potential.

While the classic thermodynamic theory is capable of explaining the driving force for a good number of desalination processes by the **difference in chemical potential**, this explanation is not sufficient for those processes, which are not purely initiated by a change in temperature, pressure or amount of substance. In particular, there are a number of desalination techniques which are triggered by an electrical potential difference.

In consequence, a more comprehensive explanation model is needed that includes the electrical potential difference as a fourth variable. The concept of **difference in electrochemical potential** is the answer to the question [13, 15]. The electrochemical potential comprises the chemical potential and the electrostatic potential of the particles

[12]. It is a concept with all-inclusive explanatory capacity and can give an explanation for how a desalination process is driven, when one of the four possible triggers are activated to initiate a deviation from an existing equilibrium, i.e. either a difference in:

- temperature,
- pressure,
- amount of substance or
- electrical potential.

While the difference in electrochemical potential is the ultimate and unique explanation of science to the question of what drives a desalination process [12], it does not yield differentiating capacity for classifying or clustering of desalination techniques. The “flying altitude” of explanation is simply too high. It is, therefore, necessary to take a lower observation altitude to gain the capability to truly form clusters, i.e. to classify. The four variables introduced in the previous section serve this task.

3.2.2 Desalination Technology Map by Driving Force (Difference in Electrochemical Potential) and its Initiators

Figure 7 represents the Desalination Technology Map responding to the question of what drives the individual desalination techniques identified in Section 3.1.2, and, more precisely, what are the initiating variables (all of which marked in green colour in Figure 7) driving the process of a particular desalination technique.

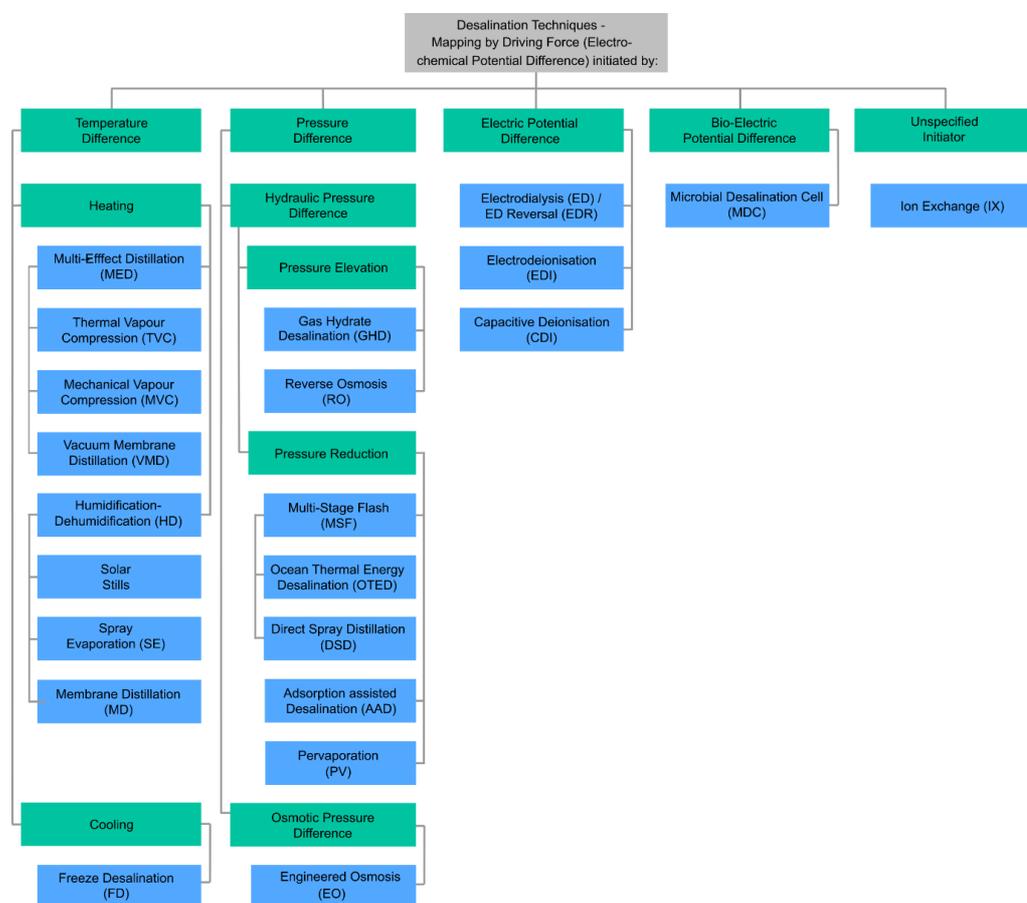


Fig. 7. Desalination Technology Mapping according to Driving Force and the Initiators Driving the Desalination Process.

A few aspects regarding the classification logic of this technology map appear worthwhile to mention:

- On the top level, the “electrochemical potential difference” represents the ultimate driving force for all desalination processes. As can be derived from the preceding Section 3.2.1 the use of a uniform criterion does not permit differentiation as needed for classification purposes. To gain classification capability, on the level below the notion of the “**Initiators**” driving the desalination process, i.e. the variables triggering a desalination process, has been introduced. They correspond in nature to the functional variables on which the electrochemical potential difference (the driving force) depends, i.e. temperature, pressure, amount of substance or electrical potential difference. For example, a pump needs to be switched on to build up the pressure necessary for driving desalination by Reverse Osmosis (RO), or, the supply of heat is the initiating variable for driving a Multi-Effect Distillation (MED) process, or, an electrical circuit must be closed for achieving the electrical potential difference necessary to drive desalination via Electrodialysis (ED).
- As far as the criterion temperature difference is concerned, it is opportune to sub-cluster the desalination techniques further into heating and cooling. As far as the criterion pressure difference is concerned, a primary sub-clustering into the type of pressure (hydraulically or osmotically induced) applied and a secondary sub-clustering into elevation and reduction of pressure appeared helpful to differentiate the criteria initiating the process.
- What may appear unknown and may need further explanation is the introduction of a new type of initiator, the “bio-electric potential difference” which is a peculiarity of the Microbial Desalination Cell (MDC). On the one hand, the MDC desalination process requires an electric potential difference to operate. In this respect it does not differ from other electrically driven techniques like Electrodialysis (ED), Electrodialysis Reversal (EDR), Electrodeionisation (EDI) or Capacitive Deionisation (CDI), and hence, would also justify joint classification with these techniques.

On the other hand, MDC differs from the other electrically driven techniques, as the electrical field is not induced by supply of electric power from outside the system, but instead, by an integral feature of this technique, i.e. the generation of electrical power by the activity of special bacteria inside the desalination cell. In MDC, the power generation part is inseparably integrated into the desalination cell, a unique case amongst all desalination techniques. A higher recognition to this unique aspect of MDC, therefore, appears justified. In consequence, the “bio-electric” potential difference has been recognised in the present paper as a further criterion distinct from the conventional “electric” potential difference. As a result, MDC has been subsumed under the criterion of bio-electric potential difference, and not under the criterion of electrical potential difference. Mind well that MDC still needs the supply of energy from outside the system, however, such energy (nutrition in the feed water for the work of the bacteria) does not have to be separately organised or paid for (unless special nutritious substances are added to the feed water).

- Also, readers may be confused by seeing the desalination technique Ion Exchange (IX) classified under the criterion “chemical potential difference – unspecified initiator”. The authors have opted for this classification knowing that it is unsatisfactory to not identify a specific initiation variable that drives the IX process as done in all other cases. However, until today, literature on IX has not really come up with a uniform response on the exact driver applicable to this technique. [16, 17] Traditional literature from the chemical field uses the notion of “affinity” as explanatory model to respond to the question of what drives the process. This notion was based on the opinion of former chemical scientists who understood chemical reactions as interactions resulting from the relation between substances [13]. As already outlined in Section 3.2.1, it is known today, however, that it is not the interaction between substances, but the intrinsic property of each individual substance itself (called “chemical potential”), that, when changed, represents the driving force of IX [13]. Unfortunately, however, there seems to be no uniform scientific understanding today in identifying the more specific initiator driving the IX process. For this reason, it is suggested to leave the initiator unspecified until science has come up with a sufficiently uniform understanding. [16]

3.3 Desalination Technology Map by Separation Principle of Water and Salt

A further desalination technology map has been developed to respond to the question of what is the underlying principle for the separation of water and salt for each of the 22 desalination techniques. The result of this analysis is presented in Figure 8.

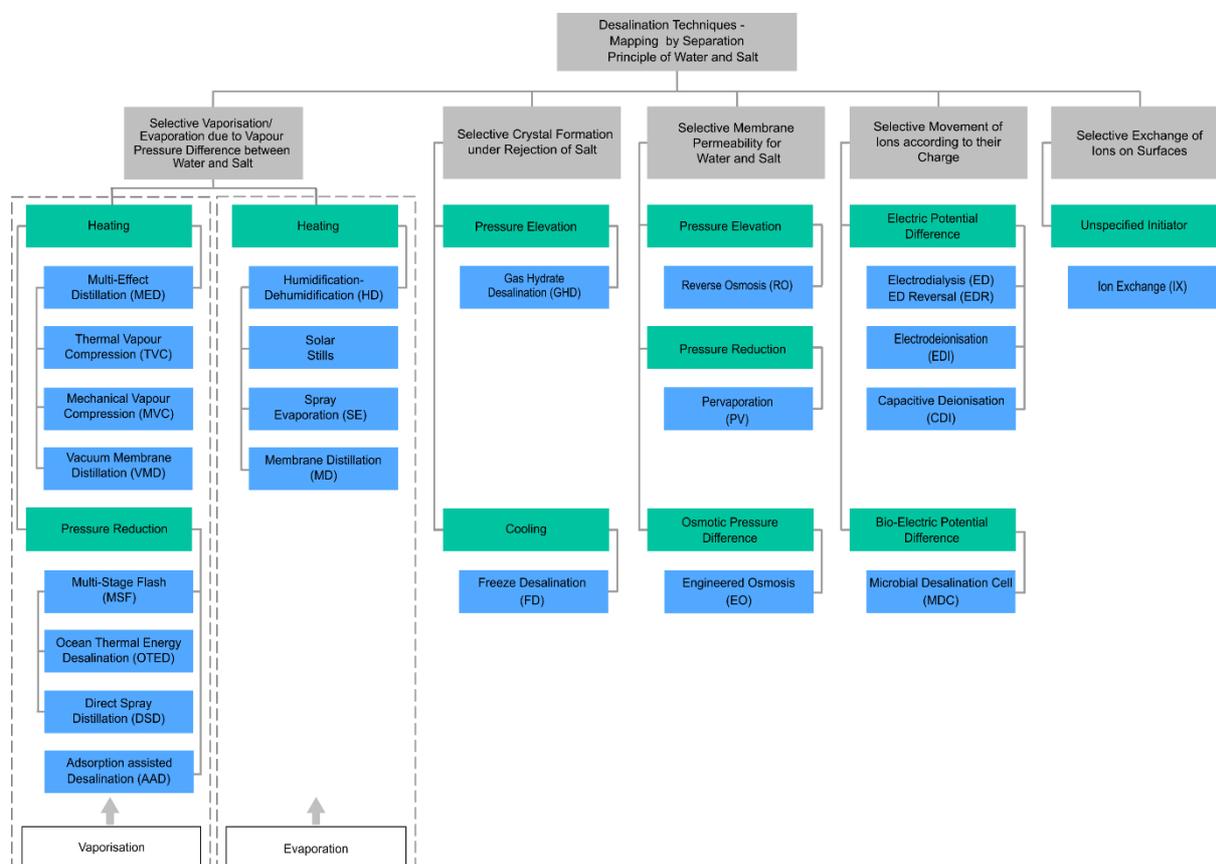


Fig. 8. Mapping according to the Separation Principle of Water and Salt

Five distinct separation principles (all marked in grey colour) have been selected as classification criteria and all 22 desalination techniques identified (all marked in blue colour) have been classified accordingly thereunder.

This technology mapping will probably be more intuitive and easier to understand than the analysis on the initiators of the driving force as the separation principles are more intuitive than the concept of the electrochemical potential. As can be seen in Figure 8, there are only 5 separation principles on which the 22 identified desalination techniques are founded.

- Selective vaporisation/evaporation due to vapour pressure difference between water and salt
- Selective crystal formation under rejection of salt
- Selective membrane permeability for water and salt
- Selective movement of ions according to their charge
- Selective exchange of ions on surfaces

While the first four classification criteria may be intuitively easy to understand, the 5th criterion may need explanation: As already experienced in Section 3.2.2, solely the Ion Exchange (IX) technique falls under the criterion of “Selective exchange of ions on surfaces. To better understand this notion, it should first be noted that amongst researchers there is no uniform consensus on the fundamental technological principles of this technique. It would have been possible to subsume IX under the criterion of “Selective movement of ions according to their charge”. However, IX differs in this context from all other desalination techniques, in that the criterion of “movement of ions according to their charge” is a necessary condition for IX, but not a sufficient one. Ion Exchange (IX) requires more, it requires the “exchange” of ions; simple movement is not enough, a true one-to-one exchange on the surfaces of the IX resin bed is required. The authors have opted to highlight this aspect, and they have, therefore, given preference to subsuming IX under a separate 5th criterion.

As an interesting and hopefully valuable add-on, the various variables initiating the driving force have also integrated into this map (in green colour), thereby making this map a very comprehensive and hopefully very useful one-pager tool on separation principles of desalination techniques and on the corresponding initiators of the driving force.

3.4 Discussion of the Novel Technology Mapping Formats

A number of interesting peculiarities have come to light when developing the Desalination Technology Maps introduced in Sections 3.2.2 and 3.3 which may be noteworthy:

- The technology map in Figure 8 classifying by separation principle of water and salt brings to light an interesting additional differentiation aspect, i.e. the differentiation of thermal technologies into those based on “evaporation” and those based on “vaporisation” (marked as boxes without colour in Figure 8). A clear differentiation between these two terms has somewhat disappeared in colloquial language. For the purpose of the present paper, the following notion is used:

“Evaporation” refers to a phase change from liquid to gas at a temperature and pressure level below the boiling point, while “Vaporisation” refers to a phase change from liquid to gas at a temperature and pressure level at boiling point. This terminology is chosen to remind of maintaining this important thermodynamic difference in technical language. In line with this terminology, the present paper uses the term “Vaporiser” when referring to an apparatus in which vaporisation occurs (rather than the term “evaporator” which - for unknown reasons - has found its way into colloquial language).

- Somewhat surprising may be the fact that two conventionally undifferentiated desalination techniques, Membrane Distillation (MD) and Vacuum Membrane Distillation (VMD), do not share the identical separation principle, as MD by its nature is based on evaporation and VMD is based on vaporisation.
- As already determined in Section 2.1.2, the present paper primarily focuses on the core step of desalination, thereby abstracting from other important aspects of desalination, for example the supply of power. A problem of consistency arises, when the supply of power is an integral part of the core desalination cell and cannot be separated any more for the desalination step (e.g. in the case of the Microbial Desalination Cell (MDC)).
- By the same token, the question might occur, whether Mechanical Vapour Compression (MVC) and Thermal Vapour Compression (TVC) should be considered “variations” of Multi-Effect Distillation (MED), as they do not differ in the core desalination characteristics from each other (separation principle and driving force). Or, should they be listed as separate desalination techniques, because they differ from MED in that they are able to recover energy (via vapour compression)?

In recognition of the significant value added from the energy recovery function, MVC and TVC would well qualify as separate desalination techniques next to MED. This option was chosen for the present paper. Nevertheless, classifying TVC and MVC as variations of MED would be a justifiable classification alternative.

Inversely again, Capacitive Deionisation (CDI) and Membrane Capacitive Deionisation (MCDI) have been kept as one desalination technique (in two variations), as MCDI simply represents an improvement to CDI.

- Furthermore, it may be argued to classify Direct Spray Distillation (DSD) and Multi-Stage Flash (MSF) as simple variations of one and the same desalination technique because the two techniques do not differ in separation principle nor in how the process is initiated and driven. In particular, flashing induced by a sudden pressure reduction and subsequent condensation of the vapour is true for DSD as well as for MSF, which would speak for classifying them as variations of a single technique. However, there are some peculiar differences in technical execution which would justify MSF and DSD as two separate desalination techniques, namely: flashing of water droplets in DSD versus flashing of an open-channel flow in MSF, and, direct contact condensation in DSD versus surface condensation in MSF (see Section 4). For the purpose of the present paper, the latter classification format has been chosen.

- Generalising on the previous peculiarities, the discussion of when a technical format of technology deserves categorisation as “technique” or as “variation” or as mere “improvement” is a generic issue of categorisation consistency. This issue is also encountered when designing Figures 7 and 8. As a matter of convention regarding the mapping, simple “improvements” of a technique have not been made visible in these Figures, but are referred to in Section 4 when explaining a particular desalination technique in more detail. Desalination techniques qualifying for alternative classification have been listed in Figures 7 and 8 persistently as distinct techniques and have been marked with a connecting line on their left side. For example, in Figure 8, MVC, TVC and Vacuum Membrane Distillation (VMD) are listed as independent techniques. To show that they may alternatively be regarded as variations of MED, they are connected by left side line. The same applies to Solar Stills, Solar Evaporation (SE) and Membrane Distillation (MD) which may alternatively be regarded as variations of Humidification-Dehumidification (HD). Furthermore, Ocean Thermal Energy Desalination (OTED) and Direct Spray Distillation (DSD) may be regarded as independent techniques, or alternatively, as variations of MSF as made visible by interconnecting left side line.
- Taking reference to Engineered Osmosis (EO), it should be pointed out that EO does not represent a stand-alone desalination technique, but is merely a pretreatment step to ensure an optimal separation result - as in Forward Osmosis, (FO) - or an attempt to reduce the energy consumption for a downstream Reverse Osmosis (RO) unit (as in Osmotic Dilution, OD). However, for the sake of comprehensiveness and to reflect the growing awareness for EO applications in the desalination community, it was decided to assign one place in the present technology map to the group of EO and its related variations, namely FO, OD, Direct Osmotic Concentration (DOC) and Pressure Retarded Osmosis (PRO).

Summarising on the benefits and pitfalls of the novel classification maps, the authors believe that the newly developed desalination technology maps may have merit as a comprehensive structural learning tool on water desalination technology, in particular when conveying a clear methodological understanding on fundamental differences and similarities pertaining to the various techniques. Harmonisation in technical language and illustration have been didactic targets. Last, not least, the classification approach in the present paper is meant to provide a high level of consistency for long-term use. However, the authors acknowledge that there are still remaining challenges as pointed out above. The authors invite the interested reader for enriching discussion to further solidify and mature these maps.

In Section 4, the identified desalination techniques are presented individually. The driving force, the process initiators and the separation principle of each technique are explained in more detail and the processes are shortly described.

In desalination systems that work on the basis of vaporisation and evaporation, the “vapour pressure” plays a decisive role. An explanatory note has been added to Annex 1 to facilitate ease of understanding and to simplify language use in the subsequent Sections.

4. Desalination Techniques according to Separation Principles

4.1 Selective Vaporisation

4.1.1. Multi-Effect Distillation (MED) also known as Multiple-Effect Distillation

Dr. Heike Glade

Distillation usually means separation of the components from a liquid mixture by using selective vaporisation (transition of liquid state to gas state) and subsequent condensation (transition of gas state to liquid state). It exploits differences in vapour pressure, in other words volatility, between the components in the mixture. In the present paper, vaporisation refers to the transition of the liquid state to the gas state at the boiling temperature, whereas evaporation refers to the change from the liquid state to the gas state that takes place below the boiling temperature as already explained in Section 3.4. Heat exchangers used for vaporisation are usually called evaporators or vaporisers. In the present paper, for the sake of linguistic consistency, the heat exchangers used for vaporisation are called vaporisers.

Multi-Effect Distillation (MED) is used for the separation of water from a saline solution by vaporisation of the water during heat supply and subsequent condensation.

Driving Force and Initiator

The saline water, which is a mixture (solution) of water (solvent) and soluble salts (solutes), is brought into contact with a heat transfer surface that is held at a higher temperature than the saturation temperature (boiling temperature) of the saline water corresponding to its prevailing pressure. Thus, the temperature of the saline water is raised to its boiling temperature and then the water vaporises at constant pressure and constant temperature by heating. The enthalpy of vaporisation (latent heat) must be supplied to the saline water to effect vaporisation. The system undergoes a phase transition and strives toward phase equilibrium. Thus, water particles (molecules) are transferred from one phase to the other until equilibrium is attained.

From a thermodynamic point of view, for a closed system (no mass can cross the boundary of the system, i.e., the total number of particles in both phases is constant) at constant pressure and held at constant temperature in contact with a heat reservoir, the Gibbs energy, which depends on the temperature, the pressure and the number of particles of each component in the two phases, decreases and the system moves toward a stable state. The Gibbs energy reaches its minimum at equilibrium, i.e. the infinitesimal change of the Gibbs energy will be zero, which is characterised by a uniform chemical potential. The chemical potential of a component in a mixture is defined as the rate of change of Gibbs energy of the system with respect to the change in the number of particles of the component when pressure, temperature and the number of particles of the other components are constant. Particles tend to move from higher chemical potential to lower chemical potential because this reduces the Gibbs energy. The condition of coexistence of the liquid and the vapour phase in equilibrium implies that the chemical potential of each component is the same in both phases.

Thus, the **chemical potential difference** is the **driving force** for the transfer of particles between the phases which is **triggered by heating (initiator)** [1, 2].

Separation Principle

The separation of water from salt is based on the large vapour pressure difference between water and salt. Water has a low boiling point and can readily change from a liquid state to a gas state with high vapour pressure, whereas salt has a negligibly small vapour pressure and is considered as non-volatile. The water changes from a liquid state to a vapour state leaving behind the dissolved salts. Thus, the vapour phase is only composed of pure water. The water vapour is subsequently condensed and the condensate is collected. Hence, the **selective vaporisation of water due to the large vapour pressure difference between water and salt** represents the fundamental separation principle.

The term 'multi-effect distillation' refers to the use of vaporisers in multiple stages which are also called effects. The multi-stage nature of a vaporisation plant should not be confused with the multi-stage nature of a distillation column. In the latter case, the multi-stage nature is necessary for the generation of a pure product, as the vapour pressures of the substances to be separated are close to each other (e.g., water and alcohol) [3]. In desalination, pure water can be produced in a single stage, as the vapour pressure of salt is negligibly small. Multiple stages are solely used to lower the specific thermal energy consumption. In single-stage distillation under real conditions, the mass of water produced is less than the mass of heating steam used to operate the system. As single-effect distillation is not efficient in terms of thermal energy consumption, multi-effect distillation is usually applied.

In the following, Multi-Effect Distillation (MED) without vapour compression is described. Single-Effect or Multi-Effect Distillation with Mechanical Vapour Compression (MVC) and Multi-Effect Distillation with Thermal Vapour Compression (TVC) are described in separate sections as explained in Section 3.4.

Process

A Multi-Effect Distillation plant is composed of several vaporisers called stages or effects and a final condenser. Different types of heat exchangers can be used for vaporisation. Submerged tube vaporisers, falling film vaporisers with vertical tubes or with horizontal tubes and plate vaporisers have been used [4]. In today's land-based MED plants, horizontal tube falling film vaporisers are commonly employed. For marine vessels and offshore applications, single-stage and multi-stage systems with plate vaporisers, vertical tube rising film vaporisers and vertical tube falling film vaporisers are often used.

In a horizontal tube falling film vaporiser, seawater is distributed onto a horizontal tube bundle by spraying nozzles, as shown in Figure 1. In small plants, perforated plates are sometimes used for liquid distribution. Steam condenses inside the horizontal tubes, while the seawater flows as a thin film over the outside of the tubes. Heat is transferred from the condensing steam inside the tubes to the seawater on the outside of the tubes through the tube wall. Hence, the seawater is preheated to the saturation

temperature corresponding to the prevailing pressure on the top tube rows and partly vaporises on the following tube rows. The generated vapour flows through a droplet separator, mostly a knitted wire mesh or a vane-type separator, in order to remove the entrained brine droplets. The vapour must be free of brine droplets to prevent the contamination of the distillate.

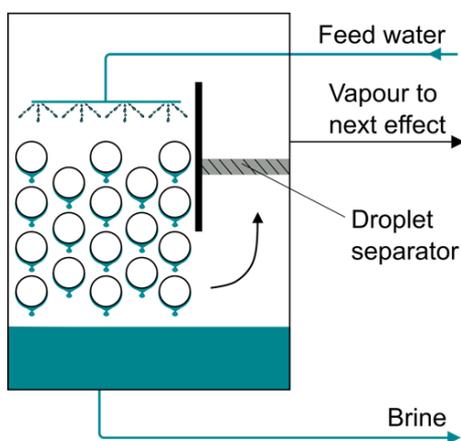


Fig. 1. Horizontal tube falling film vaporiser.

In MED plants, the vaporisers are arranged in a way that the vapour, which is generated in one stage, is used as heating steam in the following stage. A heating medium from an external source, mostly heating steam (e.g., the exhaust steam of a steam turbine in a power plant) or sometimes hot water, is fed to the first stage. The vapour of the last stage is condensed in the final condenser. Forward, backward, parallel and mixed feeding configurations can be distinguished [3-6]. The configurations differ in the brine flow direction relative to the vapour flow direction from stage to stage.

Figure 2 shows the most common process configuration where the feed water flow is distributed in parallel to all the stages, usually in equal shares (parallel feeding configuration). Seawater flows through the final condenser which is usually a shell-and-tube heat exchanger. The water vapour generated in the last stage condenses on the outside of the tubes. Heat is transferred from the condensing vapour to the seawater flowing through the tubes and, thus, the seawater is preheated. At the outlet of the final condenser, part of the seawater, which served as cooling water, is discharged back to the sea while the remaining part, which is the feed water, is fed to the stages where it is distributed onto the horizontal tube bundles.

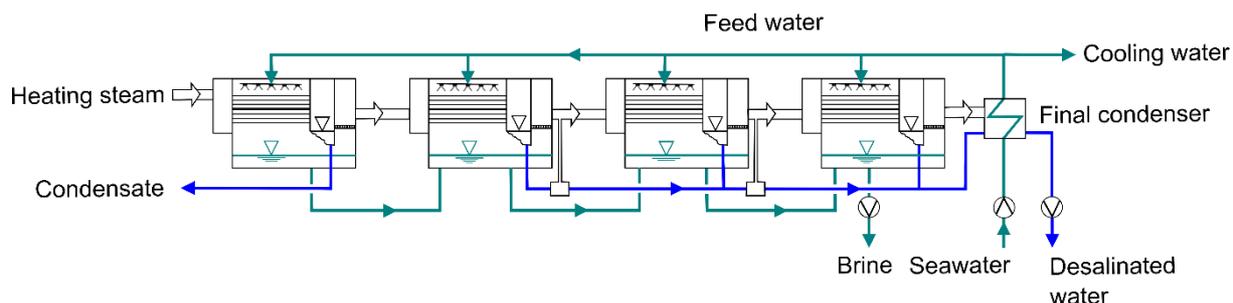


Fig. 2. Multi-Effect Distillation (MED) plant with parallel feeding configuration.

The heating steam fed into the first stage condenses inside the horizontal tubes and the condensate is led back to the external source. The vapour produced in the first stage is directed to the tubes of the next stage. It condenses inside the tubes, while a fraction of the seawater on the outside of the tubes vaporises. This process continues in subsequent stages at decreasing temperature and pressure. In doing so, the enthalpy of vaporisation of the heating steam which is introduced into the first stage can be reused several times by passing the generated vapour from stage to stage with decreasing pressure. The pressure of the heating steam to the first stage and the pressure in the final condenser are controlled. The temperatures and corresponding pressures of the intermediate stages set themselves in accordance with the heat transfer resistances. Thus, the temperatures and pressures decrease from the first to the last stage.

In order to improve the process, the concentrated brine and the distillate leaving the stages are directed to the following stages. The concentrated brine leaving the first stage is directed to the vaporiser sump of the next stage where the pressure is lower than that in the first stage. Thus, a small fraction of the brine vaporises due to the sudden pressure reduction (flashing) and the vapour mixes with the vapour which is generated through heat transfer on the horizontal tubes. The brine from the second stage is directed to the sump of the third stage where a small fraction vaporises due to sudden pressure reduction and so on. Finally, the brine from the last stage is extracted by means of a pump and discharged to the sea.

The distillate leaving the second stage flows through a distillate flashing box which is connected to the heating steam duct of the third stage where the pressure is lower. Thus, a small fraction of the distillate vaporises due to the sudden pressure reduction (flashing) and the vapour mixes with the vapour which flows into the tubes of the third stage. The distillate leaving the third stage flows through a distillate flashing box, which is connected to the heating steam duct of the following stage and so on. Finally, the distillate (desalinated water) is extracted from the final condenser by means a pump.

Gases which are present in the vapour space of a condenser and do not condense at the prevailing temperatures and pressures such as oxygen, nitrogen, carbon dioxide are called non-condensable (NC) gases. The presence of NC gases is caused by the release of dissolved gases from the vaporising brine [7] and by the leakage of ambient air through flanges, inspection openings, instrumentation nozzles, etc. into the parts of the vaporiser operating under ambient pressure. Even low concentrations of NC gases significantly reduce the heat transfer coefficient on the condensation side and, thus, the overall heat transfer coefficient and the performance of distillation plants. Due to the detrimental effect of NC gases on the heat transfer during condensation, they must be continuously removed from the condensers by a venting system (not shown in Figure 2). A start-up steam jet ejector is usually used to evacuate the system during start-up and a steam jet ejector system is employed for the continuous extraction of the NC gases during operation. The vapour extracted with the NC gases is condensed in shell-and-tube condensers arranged after the steam jet ejectors.

The highest brine temperature is limited by the risk of severe crystallization fouling on the heat transfer surfaces (precipitation and deposition of inversely soluble salts on the heat transfer surface, also called scaling [15-17]) and corrosion and by the temperature of the heating steam that is available from an external source. Most MED plants

operate at low top brine temperatures of less than 70 °C [4, 8-14]. The required heating steam pressure for MED plants can thus be about 0.35 bar or even lower [9, 14, 18].

The lowest process temperature is the temperature of the seawater which is usually between 5 °C and 35 °C (sometimes also higher in some regions) [10]. Thus, there is a maximum temperature span available for the process in multiple stages whereas a temperature difference is necessary for heat transfer in each stage. Thus, the temperature difference in each stage decreases with increasing number of stages.

In falling film vaporisers, small temperature differences are applied in order to avoid nucleate boiling with vapour bubble formation on the tube wall which may cause dry spots and severe scaling. In horizontal tube falling film vaporisers used for desalination applications, the temperature difference between condensation and evaporation side is usually between 2.5 and 7 K or even lower [14, 19, 20]. Thus, vaporisation takes place at the free surface of the falling film.

The specific thermal energy consumption and, thus, the operating costs decrease with increasing number of stages. At the same time, the driving temperature difference for heat transfer decreases with increasing number of stages which leads to an increase in the specific heat transfer surface area and, thus, in the investment costs. As a consequence, there is an optimum number of stages with regard to operating costs and investment costs [21]. MED plants usually have between 4 and 12 stages and their specific thermal energy consumption ranges from 60 to 220 kWh per m³ of distillate [3, 4, 8-10]. The Gained Output Ratio (*GOR*), which is the mass flow rate of distillate produced per mass flow rate of heating steam fed to the first stage, is often used to quantify the thermal efficiency. It usually ranges from 3 to 10 for MED plants with 4 to 12 stages. The specific electric energy consumption, mainly required for conveying liquid streams using pumps, is between 1.5 to 2.5 kWh per m³ of distillate [9, 10, 22].

MED plants are built with single-unit capacities of 100 to 15000 m³/d while bigger plants with a single-unit capacity of up to 68000 m³/d are mostly built with thermal vapour compression [9].

Motivation of Use

Multi-Effect Distillation is a mature and well-established process in the desalination industry where it is preferably used for the production of potable and process water from seawater in medium-scale to large-scale plants. Massive field experiences exist. An MED plant is robust and relatively easy to operate, requiring minimum supervision. Staff which is skilled to operate thermal processes like common power generation systems can easily operate MED plants. Maintenance costs are relatively low because there are no rotating parts except low-pressure pumps. Plant reliability and availability are high [3, 4, 8-10].

The process does not need complex pre-treatment of seawater and is tolerant to variations of seawater conditions. The plant performance is not much influenced by the feed water quality. Thus, challenging feed water conditions and high feed water salinities can be treated. Multi-Effect Distillation plants steadily produce distillate with a very low salinity (Total Dissolved Solids (*TDS*) below 10 ppm down to below 2 ppm). Thus, the high purity of distillate allows for direct use in industrial applications, with or

without minor polishing, e.g., in boilers for steam production or in closed loop cooling systems. Furthermore, 'low grade' or 'waste' heat at a low temperature level can be used as thermal energy source [3, 4, 8-10, 18].

References Multi-Effect Distillation

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4.1.2 Thermal Vapour Compression (TVC)

Dr. Heike Glade

Multi-Effect Distillation with Thermal Vapour Compression, or simply Thermal Vapour Compression (TVC), combines the basic MED system (see Section ‘Multi-Effect Distillation (MED)’) with a steam jet ejector in order to recycle low-pressure process vapour and, thus, to utilise its enthalpy, lowering the specific thermal energy consumption and enhancing the thermal efficiency of the system.

Driving Force and Initiator

As the core process of desalination is the same as in Multi-Effect Distillation (MED) plants (without vapour compression), the driving force is the same.

The saline water, which is a mixture (solution) of water (solvent) and soluble salts (solutes), is brought into contact with a heat transfer surface that is held at a higher temperature than the saturation temperature (boiling temperature) of the saline water corresponding to its prevailing pressure. Thus, the temperature of the saline water is raised to its boiling temperature and then the water vaporises at constant pressure and constant temperature by heating. The enthalpy of vaporisation (latent heat) must be supplied to the saline water to effect vaporisation. The system undergoes a phase transition and strives toward phase equilibrium. Thus, water particles (molecules) are transferred from one phase to the other until equilibrium is attained.

From a thermodynamic point of view, for a closed system (no mass can cross the boundary of the system, i.e., the total number of particles in both phases is constant) at constant pressure and held at constant temperature in contact with a heat reservoir, the Gibbs energy, which depends on the temperature, the pressure and the number of particles of each component in the two phases, decreases and the system moves toward a stable state. The Gibbs energy reaches its minimum at equilibrium, i.e. the infinitesimal change of the Gibbs energy will be zero, which is characterised by a uniform chemical potential. The chemical potential of a component in a mixture is defined as the rate of change of Gibbs energy of the system with respect to the change in the number of particles of the component when pressure, temperature and the number of particles of the other components are constant. Particles tend to move from higher chemical potential to lower chemical potential because this reduces the Gibbs energy. The condition of coexistence of the liquid and the vapour phase in equilibrium implies that the chemical potential of each component is the same in both phases. Thus, the **chemical potential difference** is the **driving force** for the transfer of particles between the phases which is **triggered by heating (initiator)** [1, 2].

Separation Principle

As the core process of desalination is the same as in Multi-Effect Distillation (MED) plants (without vapour compression), the separation principle is the same.

The separation of water from salt is based on the large vapour pressure difference between water and salt. Water has a low boiling point and can readily change from a liquid state to a gas state with high vapour pressure, whereas salt has a negligibly small vapour pressure and is considered as non-volatile. The water changes from a liquid state to a vapour state leaving behind the dissolved salts. Thus, the vapour phase is only composed of pure water. The water vapour is subsequently condensed and the condensate is collected. Hence, the **selective vaporisation of water due to the large vapour pressure difference between water and salt** represents the fundamental separation principle.

Process

Vapour compression can be applied to different types of vaporisers with single or multiple stages. In general, vapour compression refers to the principle of compressing the vapour, which is generated in a vaporiser, and raising its pressure. Thus, the condensation temperature is increased, and the vapour can be used as heating steam in the same stage or in preceding stages. Vapour can be compressed by means of a mechanical compressor, called Mechanical Vapour Compression (MVC), or by means of a steam jet ejector, called Thermal Vapour Compression (TVC). In the following, Thermal Vapour Compression is described. Mechanical Vapour Compression is considered in a separate section.

In today's land-based TVC plants, horizontal tube falling film vaporisers are commonly employed [3]. The basic MED process scheme with horizontal tube falling film vaporisers is described in Section "Multi-Effect Distillation (MED)".

Figure 1 shows a common MED process (parallel feeding configuration) combined with thermal vapour compression. Steam jet ejectors consist of a nozzle, a mixing zone and a diffuser. Steam at a high pressure, referred to as motive steam in the following, enters the nozzle. The motive steam expands through the nozzle. The pressure of the steam decreases and its flow velocity rises. In the mixing zone between nozzle outlet and diffuser inlet, the pressure is the lowest so that the low-pressure vapour to be compressed can be drawn in. Both flows are combined in the mixing zone. When the two flows are mixed, part of the motive flow's kinetic energy is transferred to the suction flow. The mixed flow is then slowed down in the subsequent diffuser and an increase in pressure occurs at the same time. The mixture of motive steam and suction vapour has an intermediate pressure at the outlet of the diffuser and can be used as heating steam [4, 5].

As shown in Figure 1, the vapour generated in the last stage is split. Part of the vapour condenses in the final condenser, whereby the seawater is preheated. The other part of the vapour is passed to the steam jet ejector, where it is compressed by means of the motive steam. The mixed flow is directed to the first stage, where it is used as heating steam. Instead of compressing part of the vapour from the last stage, part of the vapour from an intermediate stage can be compressed by the steam jet ejector.

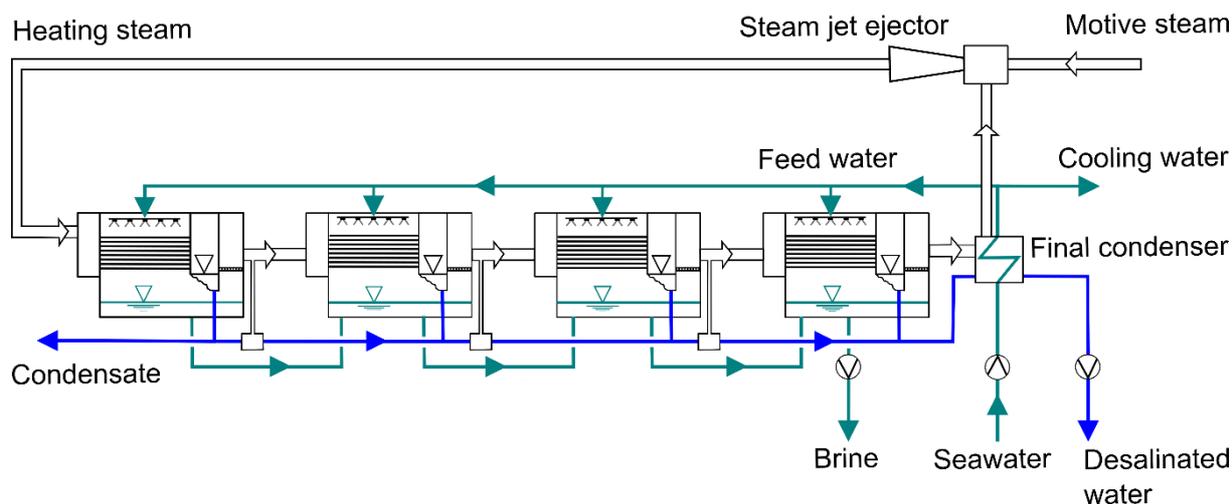


Fig. 1. Multi-Effect Distillation plant (parallel feeding configuration) with Thermal Vapour Compression (TVC).

Motive steam pressure for the steam jet ejector in TVC plants is in most cases between 2.5 and 20 bar [6, 7]. Like MED plants, most TVC plants operate at low top brine temperatures of less than 70 °C in order to limit the risk of severe scaling on heat transfer surfaces and corrosion [3-7].

Multi-Effect Distillation plants with Thermal Vapour Compression usually have between two and six stages [3-6]. The Gained Output Ratio (*GOR*), which is the ratio of the mass flow rate of the distillate to the mass flow rate of the heating steam to the first stage, is higher for TVC plants than for MED plants with the same number of stages, typically between 4 and 10 using 2 to 6 stages. It can increase up to 16 for more stages [3, 8, 9]. The specific thermal energy consumption of TVC plants is usually between 60 and 160 kWh per m³ of distillate. When comparing a TVC and an MED plant with a similar thermal performance, the heat transfer surface area of the TVC plant is considerably reduced for the same distillate mass flow rate or the TVC plant requires a similar heat transfer surface area for a considerably higher distillate mass flow rate. Thus, TVC plants are built with single-unit capacities up to 68000 m³/d [4, 9]. Like MED plants, TVC plants have a low specific electric energy consumption between 1.5 and 2.5 kWh per m³ of distillate [6, 8].

Motivation of Use

Multi-Effect Distillation combined with Thermal Vapour Compression is a mature and well-established process in the desalination industry where it is preferably used for the production of potable and process water from seawater in large-scale installations. Massive field experiences exist [3-8].

As the core process of desalination is the same, many advantages of MED, which are mentioned in the Section 'Multi-Effect Distillation (MED)', also apply to TVC. A TVC plant is robust and relatively easy to operate, requiring minimum supervision. Staff which is skilled to operate thermal processes like common power generation systems can easily operate TVC plants. Maintenance costs are relatively low because there are no rotating parts except low-pressure pumps. Plant reliability and availability are high [3-8].

The process does not need complex pre-treatment of seawater and is tolerant to variations of seawater conditions. The plant performance is not much influenced by the feed water quality. Thus, challenging feed water conditions and high feed water salinities can be treated. Multi-Effect Distillation plants with Thermal Vapour Compression steadily produce distillate with a very low salinity (Total Dissolved Solids (*TDS*) below 10 ppm down to below 2 ppm). Thus, the high purity of distillate allows for direct use in industrial applications, with or without minor polishing, e.g., in boilers for steam production or in closed loop cooling systems [3-8].

Compared with MED, the thermal efficiency can be considerably enhanced by using thermal vapour compression. However, a major drawback of TVC is that it requires motive steam at a pressure above 2 bar [6].

References Thermal Vapour Compression

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4.1.3 Mechanical Vapour Compression (MVC)

Dr. Heike Glade

Single-Effect or Multi-Effect Distillation with Mechanical Vapour Compression, often just called Mechanical Vapour Compression (MVC), combines Single-Effect or Multi-Effect Distillation (see Section 'Multi-Effect Distillation (MED)') with a mechanical compressor in order to recycle low-pressure process vapour and, thus, to utilise its enthalpy, lowering the primary energy consumption.

Driving Force and Initiator

As the core process of desalination is the same as in Multi-Effect Distillation (MED) plants (without vapour compression), the driving force is the same.

The saline water, which is a mixture (solution) of water (solvent) and soluble salts (solutes), is brought into contact with a heat transfer surface that is held at a higher temperature than the saturation temperature (boiling temperature) of the saline water corresponding to its prevailing pressure. Thus, the temperature of the saline water is raised to its boiling temperature and then the water vaporises at constant pressure and constant temperature by heating. The enthalpy of vaporisation (latent heat) must be supplied to the saline water to effect vaporisation. The system undergoes a phase transition and strives toward phase equilibrium. Thus, water particles (molecules) are transferred from one phase to the other until equilibrium is attained.

From a thermodynamic point of view, for a closed system (no mass can cross the boundary of the system, i.e., the total number of particles in both phases is constant) at constant pressure and held at constant temperature in contact with a heat reservoir, the Gibbs energy, which depends on the temperature, the pressure and the number of particles of each component in the two phases, decreases and the system moves toward a stable state. The Gibbs energy reaches its minimum at equilibrium, i.e. the infinitesimal change of the Gibbs energy will be zero, which is characterised by a uniform chemical potential. The chemical potential of a component in a mixture is defined as the rate of change of Gibbs energy of the system with respect to the change in the number of particles of the component when pressure, temperature and the number of particles of the other components are constant. Particles tend to move from higher chemical potential to lower chemical potential because this reduces the Gibbs energy. The condition of coexistence of the liquid and the vapour phase in equilibrium implies that the chemical potential of each component is the same in both phases. Thus, the **chemical potential difference** is the **driving force** for the transfer of particles between the phases which is **triggered by heating (initiator)** [1, 2].

Separation Principle

As the core process of desalination is the same as in Multi-Effect Distillation (MED) plants (without vapour compression), the separation principle is the same.

The separation of water from salt is based on the large vapour pressure difference between water and salt. Water has a low boiling point and can readily change from a liquid state to a gas state with high vapour pressure, whereas salt has a negligibly small vapour pressure and is considered as non-volatile. The water changes from a liquid state to a vapour state leaving behind the dissolved salts. Thus, the vapour phase is only composed of pure water. The water vapour is subsequently condensed and the condensate is collected. Hence, the **selective vaporisation of water due to the large vapour pressure difference between water and salt** represents the fundamental separation principle.

Process

Vapour compression can be applied to different types of vaporisers with single or multiple stages. In general, vapour compression refers to the principle of compressing the vapour, which is generated in a vaporiser, and raising its pressure. Thus, the condensation temperature is increased, and the vapour can be used as heating steam in the same stage or in preceding stages. Vapour can be compressed by means of a mechanical compressor, called Mechanical Vapour Compression (MVC), or by means of a steam jet ejector, called Thermal Vapour Compression (TVC). In the following, Mechanical Vapour Compression is described. Thermal Vapour Compression is considered in a separate section.

Different types of heat exchangers can be used for vaporisation. Horizontal tube falling film vaporisers are commonly employed. Figure 1 shows a single-stage distillation plant with mechanical vapour compression. An MVC plant consists of a mechanical vapour compressor, a horizontal tube falling film vaporiser, preheaters for the intake seawater, brine and product pumps and a venting system, as illustrated in Figure 1.

The feed water is usually preheated by cooling down the distillate (desalinated water) and the brine exiting the vaporiser in plate heat exchangers. Subsequently, the seawater enters the deaerator that removes dissolved gases such as oxygen and nitrogen, which would otherwise deteriorate the heat transfer during condensation. A vacuum system without a separate deaerator can also be used.

In a horizontal tube falling film vaporiser, the feed water is distributed onto a horizontal tube bundle by spraying nozzles. Steam condenses inside the horizontal tubes, while the feed water flows as a thin film over the outside of the tubes. Heat is transferred from the condensing steam inside the tubes to the feed water on the outside of the tubes through the tube wall. Hence, the feed water is preheated to the saturation temperature corresponding to the prevailing pressure on the top tube rows and partly vaporises on the following tube rows. Part of the concentrated brine is mixed with the feed water and conveyed by a pump to the top of the vaporiser. The remaining part of the brine is extracted by a pump and passed to the feed water preheater. The generated vapour flows through a droplet separator, mostly a knitted wire mesh or a vane-type separator, in order to remove the entrained brine droplets, which would otherwise damage the compressor blades and deteriorate the quality of the distillate.

In MVC plants, the vapour is compressed by means of a centrifugal compressor driven by an electric motor. Thus, the pressure and the condensation temperature of the vapour are increased, and the vapour can be used as heating steam in the same stage.

As the heating steam passes the horizontal tubes, it condenses and is collected as distillate. The distillate (desalinated water) is extracted by a pump and passed to the feed water preheater.

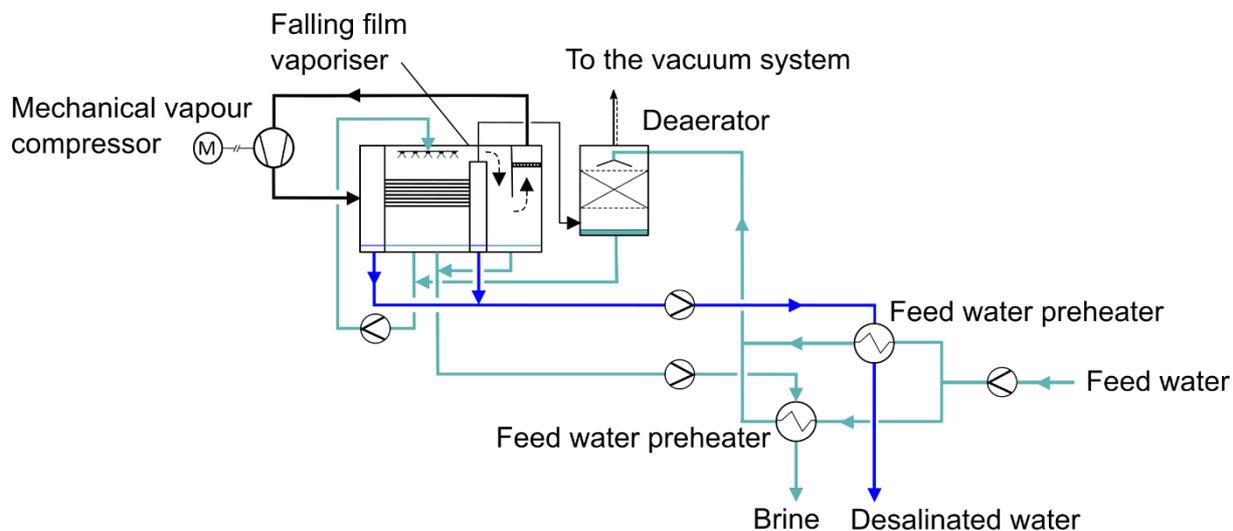


Fig. 1. Single-Stage Distillation with Mechanical Vapour Compression (MVC)

The specific electric energy consumption of MVC plants is in the range of 8 to 15 kWh per m³ up to 17 kWh per m³ of distillate [3-7]. MVC plants are mostly built with one stage, but they can have up to three stages. They are built with single-unit capacities between 100 and 5000 m³/d [3-7]. Maximum distillate production is limited by limitations in compressor capacity. Like MED plants, most MVC plants operate at low top brine temperatures of less than 70 °C in order to limit the risk of severe scaling on heat transfer surfaces and corrosion [3-7].

Motivation of Use

Single-Effect or Multi-Effect Distillation with Mechanical Vapour Compression is a mature and well-established process in the desalination industry where it is preferably used for the production of potable and process water from seawater in small-scale to medium-scale plants [3-7].

As the core process of desalination is the same, the advantages of MED, which are mentioned in the Section 'Multi-Effect Distillation (MED)', also apply to MVC. An MVC plant is robust and relatively easy to operate, requiring minimum supervision. Staff which is skilled to operate thermal processes like common power generation systems can easily operate MVC plants. The process does not need complex pre-treatment of seawater and is tolerant to variations of seawater conditions. The plant performance is not much influenced by the feed water quality. Thus, challenging feed water conditions and high feed water salinities can be treated. Mechanical Vapour Compression plants steadily produce distillate with a very low salinity (Total Dissolved Solids (TDS) below 10 ppm down to below 2 ppm) [3-7].

Mechanical Vapour Compression plants are often factory-assembled and tested with all auxiliaries on a skid so that the installation requirements on site are minimised. Due to their robustness and compactness, MVC plants are suitable for remote areas. Since

no external heating medium is required, MVC plants can be operated at any place with access to a power grid [3-7].

References Mechanical Vapour Compression

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4.1.4 Vacuum Membrane Distillation (VMD)

Dr. Markus Spinnler

Separation Principle

Vacuum membrane distillation (VMD) is a variant of Membrane distillation (MD) based on the principle of vaporisation of pure water in a feed channel, diffusion of water vapour across a porous membrane and subsequent condensation of the water vapour at a condenser [1]. The separation of pure water and salt is due to a substantially lower **vapour pressure** of salt compared to water, see Annex 1. Thus, at a given temperature and pressure, pure water will vaporise while the salt ions remain dissolved in the liquid brine.

The role of the membrane in the VMD process is to contain and stabilise the feed water channel. Due to the open pores of the membrane, it provides a free vaporisation surface, but it is not involved in the separation process itself [2]. Different to conventional MD systems, where water is evaporated into air-filled membrane pores, VMD does not involve Non-Condensable Gases (NCG) like air [3-4]. Therefore, VMD has to be classified as a stand-alone **vaporisation**-based desalination technique.

Driving Force and Initiator

The fundamental driver of VMD systems is the establishment of a difference in the partial vapour pressure of water in the saline feed water, the pressure of water vapour in membrane pores and permeate channel and the saturation vapour pressure of the condensate. As vapour pressure is an exponential function of temperature, this is done by building up a temperature difference between the feed water channel and the condenser. Mostly, the vapour pressure difference is achieved by heating the feed water or by heating the feed channel itself [1, 5]. Analogous to MD, **heating** can therefore be identified as main initiator for driving VMD processes.

The temperature-induced vapour pressure difference is assisted by evacuating the permeate channel. This is mainly done to remove NCG from the permeate channel and serves two purposes: First, the amount of water vapour in membrane pores and permeate channel is higher than in air filled systems. Second, NCG are severely impeding the condensation process. Removing NCG improves the condensation efficiency by more than 30 % [6].

Process

Figure 1 is illustrating the basic principle of a VMD system. In a VMD cell, feed water is flowing through a channel with a solid, non-permeable boundary on the left and a porous, hydrophobic VMD membrane on the right side. In consequence, the feed water is held back in the feed channel. The voids formed by the membrane pores provide a free vaporisation surface. Therefore, only water vapour is passing through the pores and hence across the membrane. Similar to all MD designs, in VMD the feed water or

the feed channel itself is heated in order to raise the heat of vaporisation and to establish the required temperature and thus vapour pressure difference between feed water and condensate. Similar to Multi-Effect Distillation (MED) and Humidification-Dehumidification (HD) systems, the Top Brine Temperature (*TBT*) can be up to 85 °C.

Through the pores of the membrane, the feed channel releases pure water molecules from the feed water to the pores. Due to the vapour pressure gradient, the water vapour is diffusing through pores and permeate gap and reaches the condenser surface. Here, the water vapour molecules are taken up in a condensate film. The heat of condensation is released and can be recovered. In multi-effect designs, this can serve for heating the feed water of the following effect, see Figure 2. Note that the mass flow of pure water molecules is always following the gradient from high to low vapour pressure or in other words from high temperature in the feed water to low temperature in the condensate. Note also that in all MD applications, the condensate is commonly called “permeate”, as in Reverse Osmosis (RO). Even though MD is mainly a thermally driven process, MD nomenclature is based on membrane systems.

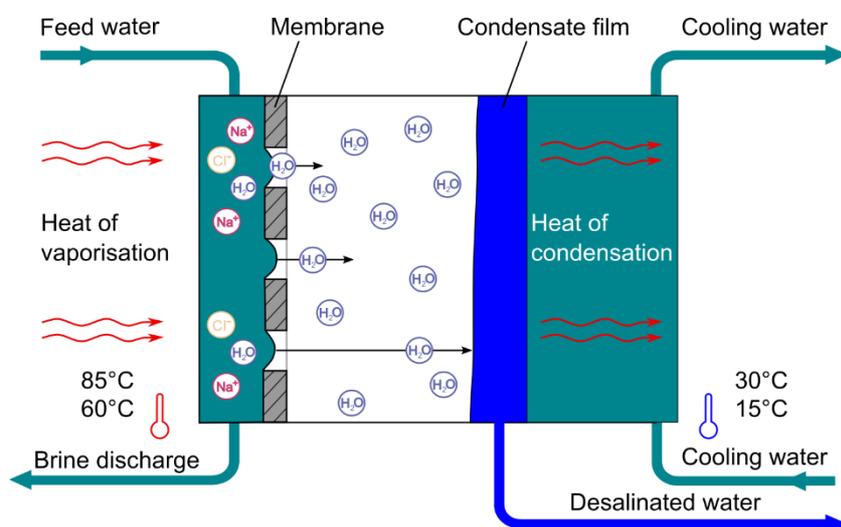


Fig. 1. Principle of water mass transfer in VMD systems.

Regarding pressure control, the prevailing pressure in the permeate channel will automatically correspond to the saturation vapour pressure of water at the actual condensation temperature. For building up the mentioned vapour pressure gradient between water in the feed water and condensate, the condensation temperature has to be lower than the temperature of the feed water.

Besides temperature, the partial vapour pressure of water in aqueous solutions is also a function of salinity. Increasing salinity means decreasing the concentration of water in the solution and hence decreasing the partial vapour pressure of water. Especially in applications with high salinity, for example in Zero Liquid Discharge (ZLD), the temperature-induced vapour pressure increase has to overcome the salinity-induced vapour pressure reduction, which demands higher feed water operation temperatures. With increasing salinity, this leads to an increasing Specific Energy Consumption (*SEC*) [7].

So far, the basic mechanisms are similar to an MED process. The main difference is that MED is vaporising water vapour from a free surface – the liquid feed water film on

the vaporiser tubes – whereas VMD is vaporising from a surface which is fixed by the porous membrane. Theoretically, this allows for a smaller installation space.

In all MD processes, the liquid water film on the feed side of the membrane has to be stabilised using a hydrophobic membrane. This means, that in VMD, common MD membranes can be applied. MD membranes have a pore size from 0.1 to 0.45 microns and are mostly manufactured from PTFE (Teflon), more seldom from PVDF (Polyvinylidene fluoride) or PP (Polypropylene) [1]. For more details, please refer to the article on MD.

In Figure 2, a standard VMD setup is shown [5]. Here, the similarities to MED plants become apparent. In commercial systems, the heat supply is mostly provided by a water-based heating system, steam input or a steam raiser. In the single effects, the heat of vaporisation is provided by the sensible heat of the feed water. For this reason, the feed water gradually cools down and both the vaporisation (feed water) and condensation temperatures decrease with the number of effects. In most cases, the heat rejection part is designed as a final condenser using e.g. seawater as a coolant. Thus, the required gradient in saturation vapour pressures in each effect is adjusted by the overall temperature difference between the heat supply and rejection sections. As already said, the prevailing pressure in each effect is determined by the condensation temperature. The vacuum system is only there to remove NCG. Therefore, VMD is basically a self-regulating system. [1, 5]

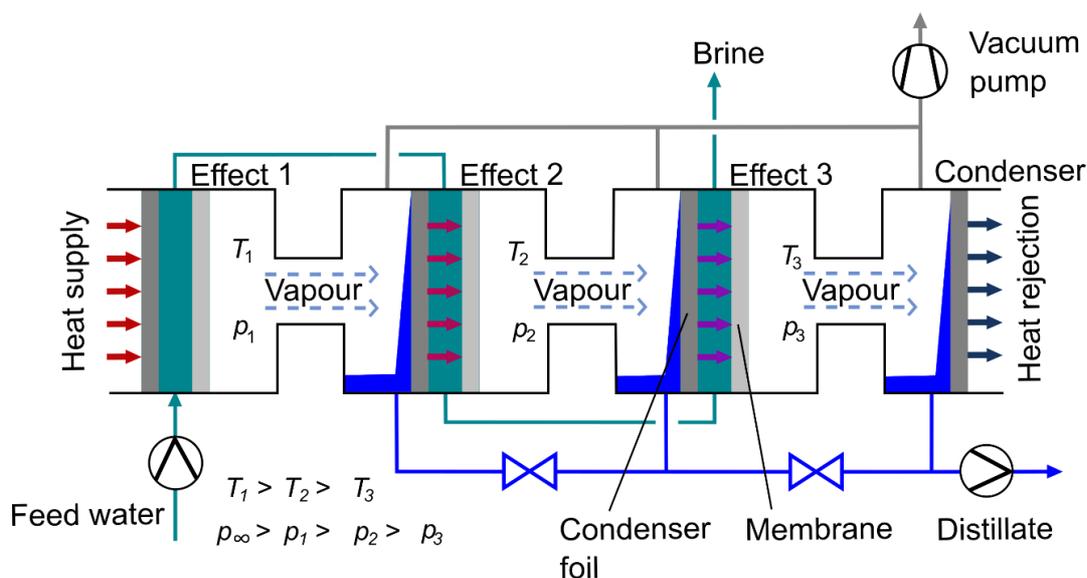


Fig. 2. Multi-effect VMD arrangement using flat-plate membranes with heat supply (left) and rejection (right). Adapted from [5].

Motivation of Use

A major advantage of VMD processes is their capability to be operated with thermal energy at a low temperature level (60 °C – 85 °C). Thus, one particular benefit is the possibility to drive VMD processes with solar irradiation or waste heat. Another key advantage is their robustness towards the feed water quality and their suitability for Zero Liquid Discharge (ZLD) applications, e.g. [1, 7]. The plant sizes of VMD plants are relatively small in the range of 1 – 50 m³/day installed capacity, but can be modularly extended up to 10'000 m³/day [8]. Compared to conventional MD systems,

VMD has a higher Performance Ratio PR due to the absence of NCG. This comes at the cost of a higher technical complexity. Strongly depending on the plant configuration and its operation parameters, PR s between $PR = 1.8 \dots 8$ have been reported [1,7,9]. However, as the upper limits are determined theoretically it would be more realistic to assume $PR = 4$ ($SEC = 160 \text{ kWh/m}^3$) for a commercial plant [10]. Generally, in all vaporisation- or evaporation-based MD systems, the use of chemicals is very limited [1].

References Vacuum Membrane Distillation

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4.1.5 Multi-Stage Flash (MSF) also known as Multi-Stage Flash Distillation or Multiple-Stage Flash Evaporation

Dr. Heike Glade

Multi-Stage Flash (MSF) is used for the separation of water from salt in a saline solution by using selective vaporisation and subsequent condensation similar to Multi-Effect Distillation (MED), but the principal mode of vaporisation is different. In contrast to Multi-Effect Distillation, where vaporisation is effected by heating of the saline water through a solid heat transfer surface under constant pressure, vaporisation in MSF plants is induced by a sudden pressure drop below the vapour pressure.

Driving Force and Initiator

Saline water is passed through a throttling device to a vessel, often called flash chamber (or flashing chamber), at a lower pressure than the vapour pressure corresponding to the liquid temperature. Part of the water vaporises. The pressure must be reduced below the vapour pressure to effect vaporisation. The process is called flashing because the vaporisation is extremely rapid after the liquid enters the flash chamber. Flashing is an isenthalpic process (i.e., the enthalpy stays constant) and often referred to as an adiabatic process (i.e., no transfer of heat between the system and its environment). The enthalpy of vaporisation that is required for vaporisation is not supplied by external heating during the flashing process but by the residual liquid stream which cools down to saturation temperature.

The system undergoes a phase transition and strives toward phase equilibrium. From a thermodynamic point of view, the entropy of the system increases and is maximal in the stationary equilibrium. Both phases will interchange water particles (molecules) and energy until equilibrium is attained. The condition of coexistence of the liquid and the vapour phase in equilibrium implies that the temperature and the pressure as well as the chemical potential of each component are the same in both phases. The **chemical potential difference** is the **driving force** for the transfer of water particles between the phases which is **initiated by** the sudden **pressure reduction** [1, 2].

Separation Principle

The separation of water from salt is based on the large vapour pressure difference between water and salt. Water has a low boiling point and can readily change from a liquid state to a gas state with high vapour pressure, whereas salt has a negligibly small vapour pressure and is considered as non-volatile. The water changes from a liquid state to a vapour state leaving behind the dissolved salts. Thus, the vapour phase is only composed of pure water. The water vapour is subsequently condensed and the condensate is collected. Hence, the **selective vaporisation of water due to the large vapour pressure difference between water and salt** represents the fundamental **separation principle**.

Process

In a single-stage flash process, saline feed water is heated in a heat exchanger called brine heater. The brine is prevented from vaporisation by keeping its pressure throughout the heating process above the saturation vapour pressure corresponding to its temperature. The brine is then throttled to a flash chamber at a lower pressure than the saturation vapour pressure corresponding to its temperature. Part of the water vaporises. Both the vapour and the residual liquid cool down to the saturation temperature corresponding to the reduced pressure. The vapour is subsequently condensed by heat transfer to a cooling stream, part of which constitutes the feed water.

In Multi-Stage Flash plants, the processes of flashing and condensation are repeated in multiple stages. The multiple-stage nature of a vaporisation plant should not be confused with the multiple-stage nature of a distillation column. In the latter case, the multiple-stage nature is necessary for the generation of a pure product, as the vapour pressures of the substances to be separated are close to each other (e.g., water and alcohol). In desalination, pure water can be produced in a single stage, as the vapour pressure of salt is negligibly small. Multiple stages are solely used to lower the specific thermal energy consumption. As single-stage flash is not efficient in terms of thermal energy consumption, multi-stage flash is usually applied.

A Multi-Stage Flash plant is composed of several flash chambers with a rectangular base area. The schematic of a flash chamber is shown in Figure 1. The brine flows through orifices, i.e., slots in the stage partition wall, into the bottom of the flash chamber where the pressure is lower than the vapour pressure corresponding to the temperature of the entering brine. The sudden pressure drop at the orifice causes flashing. Simple slot orifices or slot orifices and a weir are used as brine transfer devices, as shown in Figure 1. The brine flows within the flash chamber with a free surface (open-channel flow). It cools down towards the saturation temperature corresponding to the pressure in that stage and a fraction of the brine vaporises.

The vapour passes through a wire-mesh droplet separator to remove the entrained brine droplets and, thus, to prevent an increase in the salinity of the distillate. Then the vapour condenses on the outer surface of a horizontal tube bundle. Thereby, heat is transferred to the brine flowing inside the tubes and the brine temperature is raised. This energy recovery is essential to lower the specific thermal energy consumption. The condenser is placed in the upper part of the flash chamber. Most large modern MSF distillers are of the cross-flow design (also called cross-tube design) with the condenser tube axis crosswise to the flashing brine flow, as shown in Figure 1. The tube bundles of MSF condensers have a cylindrical or a rectangular cross section and are placed at one side or in the middle of the stage. Leaving the condenser tubes of one stage, the brine flows through a so-called water box and enters the condenser tubes of the following stage. Non-condensable (NC) gases which deteriorate the heat transfer during condensation are removed from the vapour space of the condenser by a venting system. The condensate is collected in a distillate tray.

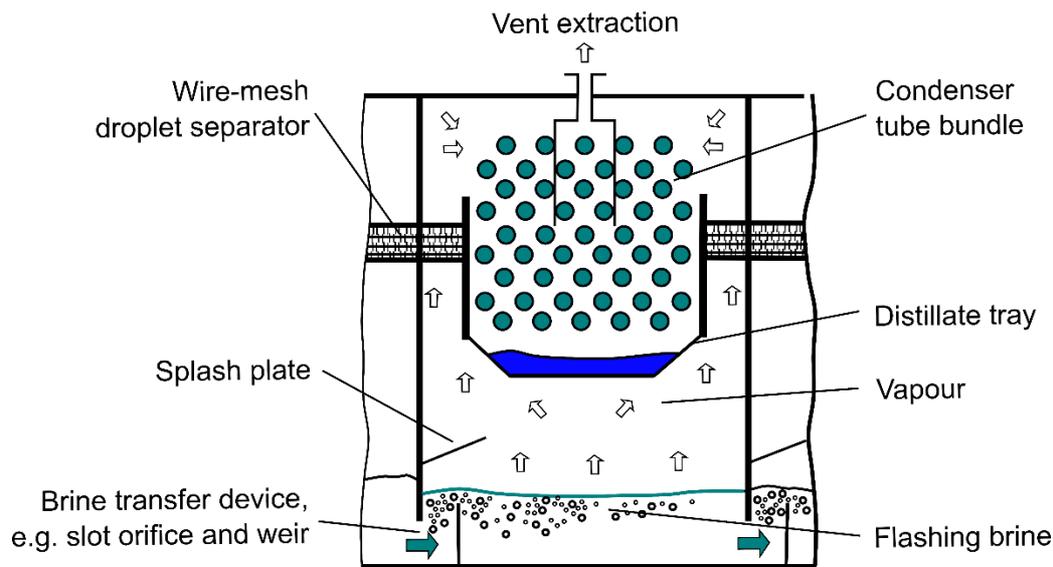


Fig. 1. Flash chamber in an MSF plant.

There are two main MSF process configurations, the brine once-through system and the brine recirculation system [3-6]. The first MSF distillers were once-through distillers. Corrosion problems and high consumption of chemicals led to the preference of brine recirculation distillers. Figure 2 shows the flow diagram of an MSF plant with brine recirculation configuration.

The seawater flows through the condenser tubes of the stages of the so-called heat rejection section. The vapour, generated in the respective flash chamber, condenses on the outer surface of the condenser tubes and the seawater flowing through the tubes is heated. After leaving the heat rejection section, part of the seawater, which served as cooling water, is discharged back to the sea while the remaining part is used as feed water. During winter operation, part of the cooling water is recycled and mixed with the intake seawater in order to increase the intake seawater temperature.

In a deaerator, the non-condensable gases which are dissolved in the seawater and do not react chemically such as nitrogen and oxygen are removed from the feed water. The deaerated feed water is mixed with a portion of the brine from the last stage. A circulation pump drives the brine recirculation flow through the condensers of the so-called heat recovery section. The vapour, generated in the respective flash chamber, condenses on the outer surface of the condenser tubes and the brine flowing through the tubes is heated.

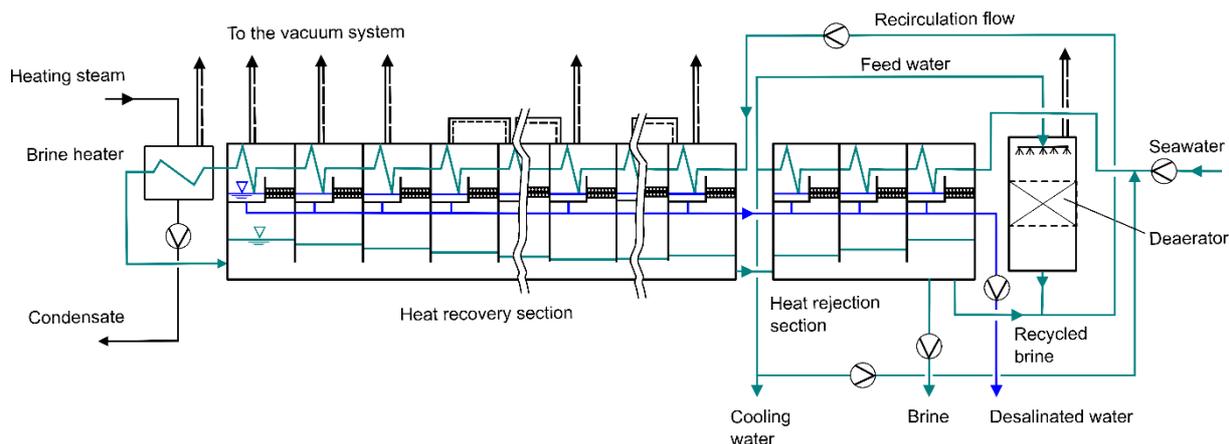


Fig. 2. Flow diagram of the Multi-Stage Flash (MSF) process with brine recirculation configuration.

After leaving the condenser tubes of the first stage, the brine enters a shell-and-tube heat exchanger, called brine heater, in which its temperature is raised to the top brine temperature by condensing steam from an external source, e.g., steam extracted from the steam turbine of a power plant. During heating in the heat rejection section, heat recovery section and in the brine heater, the brine is kept at a pressure that is higher than the saturation vapour pressure to avoid vaporisation inside the condenser tubes. After leaving the brine heater, the brine flows through an orifice into the bottom of the first flash chamber where the pressure is lower than the vapour pressure corresponding to the brine temperature. The sudden pressure drop at the orifice causes flashing. The brine cools down towards the saturation temperature corresponding to the pressure in that stage and a fraction of the brine vaporises. The vapour passes through a wire-mesh droplet separator, thus reducing the entrainment of brine droplets, and condenses on the outer surface of the condenser tube bundle.

The brine flows through orifices into the next stage in which the pressure is lower. Here and in all subsequent stages the flashing process is repeated, so that the brine partly flashes into vapour and cools down in the bottom of the chamber, the vapour condenses on the tubes and the brine in the tubes is heated. The salinity of the brine flowing through the flash chambers increases stage by stage. Part of the concentrated brine in the last stage is extracted with the brine pump and discharged back to the sea. The other part is combined with the deaerated feed water and enters the heat recovery section.

The condensate is collected in the distillate tray, directed to the distillate channel, passed through all stages via inter-stage transfer orifices and undergoes a flashing process. The vapour formed from the flashing distillate is mixed with the vapour from the flashing brine and condenses on the tubes. The distillate (desalinated water) is extracted from the last stage with the distillate pump and conveyed to the post-treatment plant.

The presence of NC gases in MSF distillers is caused by the leakage of ambient air into the parts of the evaporator operating under vacuum and the release of dissolved gases from the evaporating brine. Nitrogen, oxygen and argon can be removed almost completely in the deaerator. However, carbon dioxide, which chemically reacts in seawater, cannot be removed by simple deaeration. It is released from the brine during flashing and must be extracted by a venting system [7].

For flashing, there is no solid heat transfer surface area necessary which could be susceptible to crystallization fouling (precipitation and deposition of inversely soluble salts on the heat transfer surface, also called scaling). However, scaling occurs on the inner surfaces of the condenser tubes where the brine is being heated. A common method to reduce scaling is the addition of a chemical additive (anti-scalant) to the feed water in ppm concentrations combined with the application of a sponge ball cleaning system inside the brine heater and condenser tubes during plant operation.

Typically, MSF plants have between 16 and 22 stages, each of which operating at a lower pressure and temperature. The enthalpy of vaporisation is provided by the brine flow which cools down after being preheated before. Therefore, a large mass flow rate of flashing brine and a large temperature difference for flashing are required for vapour generation. The maximum brine temperature in the first stage is limited by the risk of severe scaling on the inside surfaces of the brine heater and condenser tubes. Multi-Stage Flash plants usually operate at top brine temperatures between 90 °C and 112 °C. The MSF process can be applied when heating steam is available at a pressure of 2.5 bar and above [8-11]. The lowest process temperature is the seawater temperature which is usually between 5 °C and 35 °C (sometimes also higher in some regions) [8].

MSF plants are built in large units of about 5000 to 90000 m³ of distillate per day. The specific thermal energy consumption ranges from 70 to 110 kWh per m³ of distillate down to 65 to 70 kWh per m³ for modern large MSF plants. The specific electric energy consumption, mainly required for conveying the large liquid streams using pumps, is between 2.5 to 5 kWh per m³ of distillate [8-11].

Motivation of Use

Multi-Stage Flash is a mature and well-established process in the desalination industry where it is preferably used for the production of potable and process water from seawater in very large installations. Massive field experiences exist. An MSF plant is very robust and relatively easy to operate, requiring minimum supervision. Staff which is skilled to operate thermal processes like common power generation systems can easily operate MSF plants. Plant reliability and availability are high [4-6, 8-11]. Currently, MSF plants can be operated for periods varying from 2 to 5 years before a major overhaul is necessary [4].

The process does not need complex pre-treatment of seawater and is tolerant to variations of seawater conditions. The plant performance is not much influenced by the feed water quality. Thus, challenging feed water conditions and high feed water salinities can be treated. MSF plants steadily produce distillate with a very low salinity (Total Dissolved Solids (TDS) below 10 ppm). Thus, the high purity of distillate allows for direct use in industrial applications, with or without minor polishing, e.g., in boilers for steam production or in closed loop cooling systems [4-6, 8-11].

References Multi-Stage Flash

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4.1.6 Ocean Thermal Energy Desalination (OTED) also known as Ocean Thermal Energy Conversion (OTEC) or Low Temperature Thermal Desalination (LTTD) or Thermocline Driven Desalination

Dr. Heike Glade

Ocean Thermal Energy Conversion (OTEC) techniques use the temperature difference between warm seawater at the surface of the open ocean and cold seawater at between 800 m to 1000 metres depth to produce electricity [1]. The warm surface seawater and the cold deep seawater serve as heat source and heat sink, respectively, for the working fluid in a heat engine which converts the thermal energy into mechanical work that is further transformed into electricity through a generator.

In addition to electricity, desalinated water can be produced by separating the water from the salt in the warm seawater stream using selective vaporisation and subsequent condensation. The desalination process is based on flash vaporisation of the warm seawater induced by a sudden pressure drop below the vapour pressure. The cold seawater is used to condense the water vapour. The present paper is focussed on the desalination process using ocean thermal energy. Therefore, the process is named Ocean Thermal Energy Desalination (OTED). The part of the OTEC techniques that deals with desalination is sometimes also called 'Low Temperature Thermal Desalination' (LTTD) or 'Thermocline Driven Desalination' [2]. Figure 1 illustrates the basic principle.

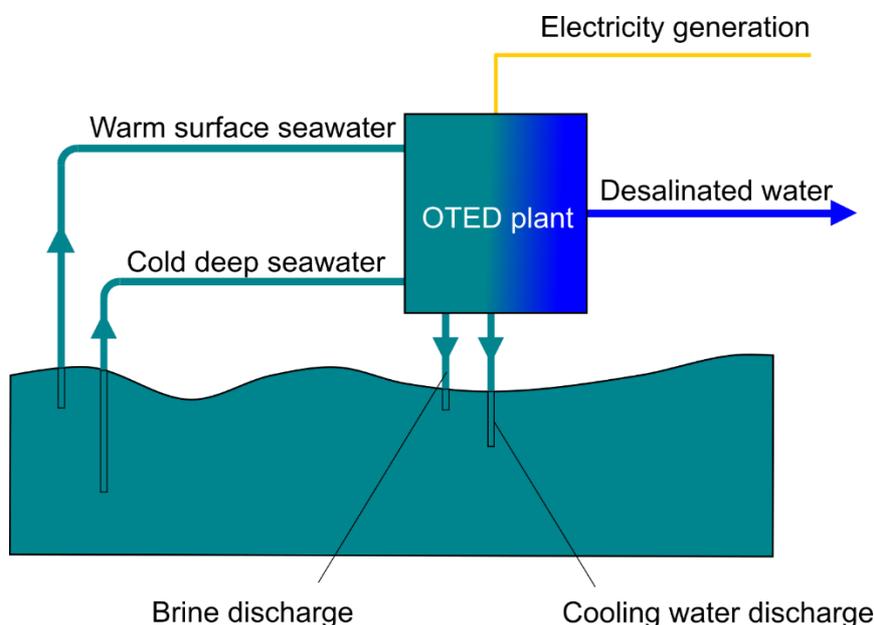


Fig. 1. Schematic of Ocean Thermal Energy Desalination (OTED).

Driving Force and Initiator

As the core process of desalination is the same as in Multi-Stage Flash (MSF), the driving force is the same.

Saline water is passed through a throttling device to a vessel, often called flash chamber (or flashing chamber), at a lower pressure than the vapour pressure

corresponding to the liquid temperature. Part of the water vaporises. The pressure must be reduced below the vapour pressure to effect vaporisation. The process is called flashing because the vaporisation is extremely rapid after the liquid enters the flash chamber. Flashing is an isenthalpic process (i.e., the enthalpy stays constant) and often referred to as an adiabatic process (i.e., no transfer of heat between the system and its environment). The enthalpy of vaporisation that is required for vaporisation is not supplied by external heating during the flashing process but by the residual liquid stream which cools down to saturation temperature.

The system undergoes a phase transition and strives toward phase equilibrium. From a thermodynamic point of view, the entropy of the system increases and is maximal in the stationary equilibrium. Both phases will interchange water particles (molecules) and energy until equilibrium is attained. The condition of coexistence of the liquid and the vapour phase in equilibrium implies that the temperature and the pressure as well as the chemical potential of each component are the same in both phases. The **chemical potential difference** is the **driving force** for the transfer of water particles between the phases which is **initiated by** the sudden **pressure reduction** [3, 4].

Separation Principle

As the core process of desalination is the same as in Multi-Stage Flash (MSF), the separation principle is the same.

The separation of water from salt is based on the large vapour pressure difference between water and salt. Water has a low boiling point and can readily change from a liquid state to a gas state with high vapour pressure, whereas salt has a negligibly small vapour pressure and is considered as non-volatile. The water changes from a liquid state to a vapour state leaving behind the dissolved salts. Thus, the vapour phase is only composed of pure water. The water vapour is subsequently condensed and the condensate is collected. Hence, the **selective vaporisation of water due to the large vapour pressure difference between water and salt** represents the fundamental separation principle.

Process

For OTED processes, the natural vertical temperature distribution in the open ocean is used. Most solar energy is absorbed by a thin layer of the ocean surface and there is barely any sunlight that penetrates below 200 m. Thus, the upper layer of the ocean is warmed by the sun and mixed to depths of about 100 m by wave motion. The bottom layer consists of colder water formed at high latitudes. Deep seawater temperature is maintained at 4 °C to 8 °C at 600 m to 1000 m depth. The interface or thermocline is sometimes marked by an abrupt change in temperature but more often the change is gradual. The temperature difference between the upper (warm) and bottom (cold) seawater layers ranges from 10 K to 25 K, with the higher values found in equatorial waters. Thus, there are two enormous water reservoirs providing the heat source and the heat sink required for a heat engine. When warm surface and cold deep seawater have at least a temperature difference of 20 K, electric power and/or desalinated water can be produced using the temperature difference [5].

Four main OTEC techniques have been proposed: open cycle, closed cycle, Kalina cycle as a variation of the closed cycle and hybrid cycle. Though only the open cycle and the hybrid cycle are used for the production of desalinated water, all four processes are shortly described in the following in order to allow a better understanding of OTEC techniques.

Open Cycle OTED (OC-OTED):

As shown in Figure 2, the open cycle consists of the following steps:

- (i) Warm surface seawater is throttled to a flash chamber at a lower pressure than the saturation vapour pressure corresponding to its temperature. Flash vaporisation of a fraction of the water occurs by the sudden pressure reduction. Both the vapour and the residual seawater cool down to the saturation temperature corresponding to the reduced pressure.
- (ii) The water vapour expands in a turbine, producing mechanical work that is further transformed into electric energy through a generator.
- (iii) Heat is transferred from the water vapour to the cold seawater in a condenser resulting in condensation of the water vapour. If a direct condenser is used, the condensed water is simply mixed with cold deep seawater and then discharged to the ocean surface. If a surface condenser is used, the condensed desalinated water can be collected as one of the final products and used for various purposes.
- (iv) The non-condensable gases that are released from the seawater at the low operating pressure and the in-leakage air are extracted from the flash chamber and the condenser, compressed and discharged to the ambient by a vacuum pump.

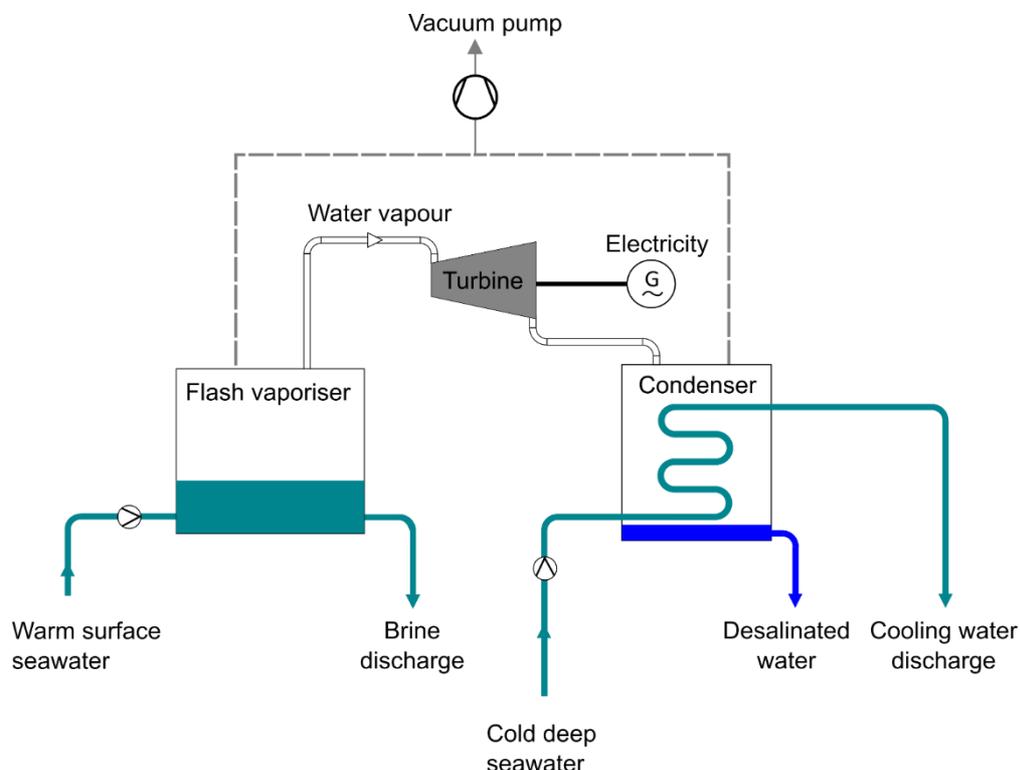


Fig. 2. Open cycle OTED system.

The open-cycle process can, therefore, be configured to simultaneously produce electricity as well as desalinated water, which is about 0.5 - 0.6 % by volume of the input warm surface seawater [5]. Additionally, the cold seawater pumped up from

deeper regions of the ocean, after being used to facilitate condensation, can be introduced in an air-conditioning system. As such, systems can produce electricity, desalinated water and air-conditioning. Furthermore, the cold water can potentially be used for aquaculture purposes, as the seawater from the deeper regions close to the seabed contains various nutrients, like nitrogen and phosphates [1].

The relative production rate of power and desalinated water is rigidly fixed because the turbine and the condenser are connected in series. Therefore, the conventional OC-OTED design is restricted by the fixed ratio of power and water production. A novel design was proposed by Kim et al. [5] to flexibly adjust power and water production rates using multiple condensers. Furthermore, the potential of using a modular set of hollow fibre vacuum membrane distillation systems as replacement of the huge flash vaporiser was explored by Kim et al. [5].

There are some fundamental problems with conventional OC-OTED systems. The evaporator, turbine and condenser operate at very low pressures ranging from 3 percent to 1 percent of the atmospheric pressure, i.e. 30 mbar to 10 mbar. Thus, the system must be carefully sealed to prevent in-leakage of atmospheric air that can severely degrade or shut down operation. Additionally, the dissolved gases released from seawater during the flashing process as well as the in-leakage air cannot be easily removed. Furthermore, the specific volume of the low-pressure vapour is very large compared to that of the pressurised working fluid used in closed cycle OTEC, as described below. This means that components must have large flow areas to ensure that vapour velocities do not attain excessively high values. Thus, an OC-OTED system is extraordinarily bulky and costly because it uses the warm seawater as a working fluid, which requires a huge vaporiser and a gigantic turbine [7].

In spite of the aforementioned complications, the open cycle has certain benefits from the selection of water as the working fluid. Water, unlike ammonia, is non-toxic and environmentally friendly.

Closed Cycle OTEC (CC-OTEC):

In the CC-OTEC system, warm surface seawater (heat source) is used to vaporise, and cold seawater (heat sink) is used to condense a working fluid which drives a turbine in a closed loop. The working fluid has a lower boiling temperature at ambient pressure and, thus, provides a higher vapour pressure at low temperatures compared with water. Most commonly ammonia is used as a working fluid, although propylene and refrigerants have also been studied [1].

The CC-OTEC is based on the thermodynamic Rankine cycle. Heat is transferred from the warm seawater to the working fluid and, thus, the working fluid is vaporised. The vapour expands in a turbine to a lower pressure. Then heat is transferred from the vapour to the cold seawater and, thus, the vapour is condensed. The pressure of the working fluid is raised by a pump before it enters again the vaporiser.

In comparison to open cycle systems, the use of ammonia as a working fluid reduces the size of the turbine and the surface area required by heat exchangers for effective heat transfer. However, closed cycle systems cannot be used for seawater desalination.

Kalina Cycle OTEC:

The OTEC process based on the so-called Kalina cycle, developed by Alexander Kalina, is a variation of the closed cycle OTEC, whereby instead of pure ammonia, a mixture of water and ammonia is used as the working fluid. The Kalina process takes better advantage of the temperature difference between the heat source and the heat sink. More heat can be converted and efficiencies are enhanced [1].

Hybrid Cycle OTED (HC-OTED):

Hybrid cycle OTED attempts to use advantages of the closed cycle and the open cycle in an optimised way, i.e., high power generation rate followed by desalinated water production.

In a two-stage Hybrid Cycle OTED, electricity is generated in a closed cycle system in a first stage followed by water production in a second stage in order to maximise the use of the thermal resource available to produce electricity and desalinated water, as shown in Figure 3. In the second stage, the temperature difference available in the seawater effluents from a Closed Cycle OTEC system (e.g., 12 K) is used to produce desalinated water through a system consisting of a flash vaporiser and a surface condenser (basically, an open cycle without a turbine) [6].

Since desalination in the second stage of HC-OTED uses the thermal energy after power generation in the first stage, the desalination rate is not as high as that of OC-OTED [5].

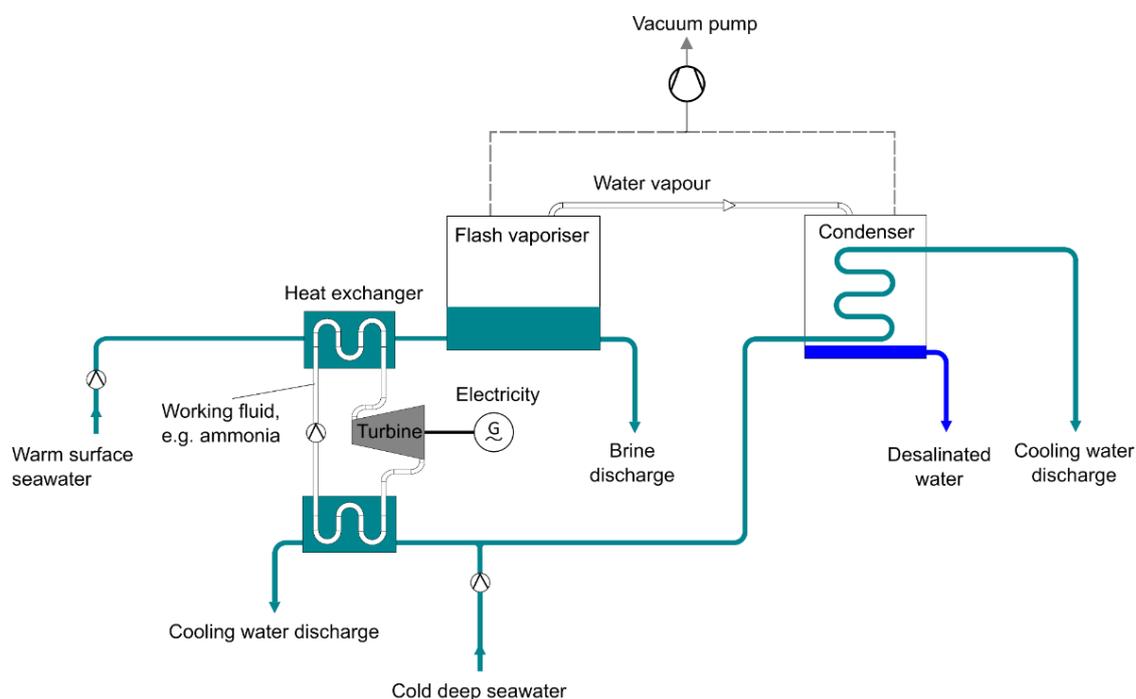


Fig. 3. Hybrid cycle OTED system.

A number of possible configurations for OTED plants have been proposed. These configurations range from floating plants to land-based plants, including shelf-mounted towers and other offshore structures [6]. Important components of the OTED plants are the electricity cables to transfer electricity back to shore and the water ducting systems. The technical challenge is the size of the water ducting systems that need to be deployed in large-scale OTED plants. In particular, a 100 MW OTED plant requires cold water pipes of 10 m diameter or more and a length of 1000 m, which need to be securely connected to the platforms [1].

All OTEC plants are still research or demonstration plants or at an early stage of commercialisation. Currently, the largest OTEC plant built is still a 1 MW plant located in Hawaii, which ran from 1993 to 1998. Smaller plants were built in Japan. There are a number of 10 MW plants that are in various stages of development. Besides these projects, ideas and prototypes are being explored for plants, e.g., in China, Curacao, France (La Réunion), Japan, Malaysia, Oman, Philippines, South Korea, the USA (Hawaii, Guam, Puerto Rico), and Zanzibar. Also, sites are being explored on some parts of the African coast. An overview is given by Kim et al. [5] and the International Renewable Energy Agency [1].

Motivation of Use

Ocean thermal energy is a renewable energy source which allows the production of electricity and desalinated water on a continuous (non-intermittent) basis, while also providing cooling without electricity consumption. The ocean water temperature changes only slightly during the night and day and in various seasons. Therefore, the use of inverter and additional storage systems is eliminated. It is expected that OTED systems can generate about 5×10^6 MW power in the world [7]. Assuming warm surface seawater at 26 °C and cold deep seawater at 4 °C, the ideal energy conversion is about 7 percent. An actual OTED plant will irreversibly transfer heat and produce entropy at various points in the cycle yielding an energy conversion of 3 to 4 percent. These values are small compared to efficiencies obtained for conventional power plants. However, OTED uses a resource that is constantly renewed by the sun [6].

As shown in Figure 4, another advantage is the multi-functionality of OTEC techniques being able to simultaneously provide electricity, desalinated water, microalgae streams and air-conditioning. Given that deep seawater is typically free of pathogens and contaminants, whilst being rich in nutrients (nitrogen, phosphates, etc.), land-based systems could further benefit from the possibility of using the deep seawater for parallel applications, such as cooling for buildings and infrastructure, seawater cooled greenhouses for agriculture, and enhanced aquaculture among other synergetic uses. Furthermore, OTEC power production may be used to provide electricity for a reverse osmosis desalination plant to increase the production of desalinated water [1].

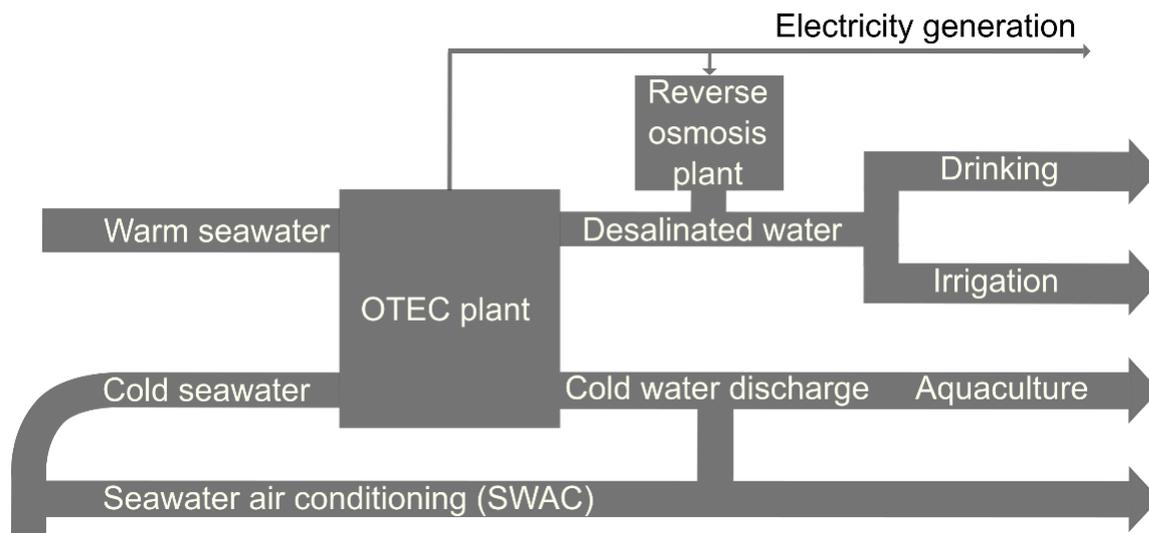


Fig. 4. Multi-functionality of an OTEC plant (based on [1]).

Ocean Thermal Energy Conversion (OTEC) has the highest potential when comparing all ocean energy techniques, and as many as 98 nations and territories have been identified that have viable OTEC resources. A large number of island states in the Caribbean and Pacific Ocean have OTEC resources within 10 kilometres of their shores [1]. OTEC is considered to be especially suitable for remote islands in tropical seas where electricity generation can be combined with other functions, e.g., fresh water production and air-conditioning.

The technological challenge is that the small temperature difference between warm and cold seawater requires very large volumes of seawater at minimum pressure losses. Thus, large seawater pumps, large piping systems, and large cold water pipes are required, operating almost continuously in a hostile and corrosive environment.

The existing barriers are high up-front capital costs, and the lack of experience building OTEC plants at larger scale. From an environmental point of view, OTEC plants at scale will require large pipelines to transport the volumes of water, which might have an impact on marine life, as well as the infrastructures to transfer the water (for land-based systems) or electricity (for off-shore systems). Since it is not a tested technology at large scale, there are unknown risks to marine life at depth and on the seabed where there is large-scale upward transfer of cold water with high nutrient content. From a technical point of view, the large-scale pipes, bio-fouling of the pipes and the heat exchangers, the corrosive environment, and discharge of seawater are still being researched [1].

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4.1.7 Direct Spray Distillation (DSD) also known as Spray-Assisted Low-Temperature Desalination or Low-Temperature Distillation (LTD) or Direct-Contact Spray-Assisted Evaporation and Condensation (DCSEC)

Dr. Heike Glade

Direct Spray Distillation (DSD) can be used for the separation of water from a saline solution and concentration of the saline water toward salt crystallization. Heated saline water is sprayed with nozzles into a flash chamber at a lower pressure than the saturation vapour pressure corresponding to its temperature. It undergoes flash vaporisation induced by the sudden pressure reduction. Concurrently, cooled distillate is sprayed into the condenser and the water vapour generated in the flash chamber condenses on the droplets of the sprayed distillate.

At first, research was focussed on breaking up the saline water into droplets and subsequent flashing. The water vapour was condensed on a solid heat transfer surface [1, 2]. In recent years, spray-assisted flashing and spray-assisted direct contact condensation have been studied. Furthermore, multi-stage configurations are in the focus of research [3-5].

The main principle of the Direct Spray Distillation process is similar to the Multi-Stage Flash (MSF) process (see Section 4.1.5 'Multi-Stage Flash (MSF)'). However, there are some peculiar differences, namely flashing of water droplets in DSD versus flashing of an open-channel flow in MSF and direct contact condensation in DSD versus surface condensation in MSF. Furthermore, the DSD process is primarily aimed at enhancing the ratio of produced desalinated water to feed water and strongly concentrating the brine to reduce brine discharge toward Zero Liquid Discharge (ZLD).

The DSD process, where heated saline water is sprayed with nozzles into a flash chamber and undergoes flash vaporisation induced by pressure reduction, should not be confused with Spray Evaporation (SE), where saline water is sprayed with nozzles into hot air at atmospheric pressure and evaporates.

Driving Force and Initiator

As the core process of desalination is the same as in Multi-Stage Flash (MSF), the driving force is the same.

Saline water is passed through a throttling device to a vessel, often called flash chamber (or flashing chamber), at a lower pressure than the vapour pressure corresponding to the liquid temperature. Part of the water vaporises. The pressure must be reduced below the vapour pressure to effect vaporisation. The process is called flashing because the vaporisation is extremely rapid after the liquid enters the flash chamber. Flashing is an isenthalpic process (i.e., the enthalpy stays constant) and often referred to as an adiabatic process (i.e., no transfer of heat between the system and its environment). The enthalpy of vaporisation that is required for vaporisation is not supplied by external heating during the flashing process but by the residual liquid stream which cools down to saturation temperature.

The system undergoes a phase transition and strives toward phase equilibrium. From a thermodynamic point of view, the entropy of the system increases and is maximal in the stationary equilibrium. Both phases will interchange water particles (molecules) and energy until equilibrium is attained. The condition of coexistence of the liquid and the vapour phase in equilibrium implies that the temperature and the pressure as well as the chemical potential of each component are the same in both phases. The **chemical potential difference** is the **driving force** for the transfer of water particles between the phases which is **initiated by** the sudden **pressure reduction** [6, 7].

Separation Principle

As the core process of desalination is the same as in Multi-Stage Flash (MSF), the separation principle is the same.

The separation of water from salt is based on the large vapour pressure difference between water and salt. Water has a low boiling point and can readily change from a liquid state to a gas state with high vapour pressure, whereas salt has a negligibly small vapour pressure and is considered as non-volatile. The water changes from a liquid state to a vapour state leaving behind the dissolved salts. Thus, the vapour phase is only composed of pure water. The water vapour is subsequently condensed and the condensate is collected. Hence, the **selective vaporisation of water due to the large vapour pressure difference between water and salt** represents the fundamental separation principle.

Process

Figure 1 shows a schematic diagram of a single-stage Direct Spray Distillation system. Saline feed water is heated in a heat exchanger. The saline water is prevented from vaporisation by keeping its pressure throughout the heating process above the saturation vapour pressure corresponding to its temperature. The brine is then sprayed using nozzles into a flash chamber at a lower pressure than the saturation vapour pressure corresponding to its temperature. Part of the water vaporises. Vaporisation occurs instantly from the droplet surfaces within milliseconds. Both the vapour and the residual liquid cool down to the saturation temperature corresponding to the reduced pressure. The remaining brine leaves the flash chamber. Part of the brine is discharged and the other part is recirculated.

The flash chamber and condenser are connected to allow vapour flow. The vapour generated in the flash chamber moves to the adjacent condenser chamber due to a small pressure difference induced by the condensation of vapour. A wire-mesh droplet separator is placed between the flash chamber and the condenser to prevent the entrainment of saline water droplets.

Distillate is cooled down to a lower temperature than the saturation temperature corresponding to the vapour pressure and sprayed into the condenser chamber. Water vapour is brought into contact with the cold distillate droplets and direct contact condensation occurs. The process of direct contact condensation is **very fast** and efficient. As the cooling water and the condensed water vapour are mixed up, pure distillate must be used as cooling water.

Specially designed spray systems are applied in the flash and condenser chambers to enlarge the specific liquid-gas phase interface areas and realize better heat and mass transfer.

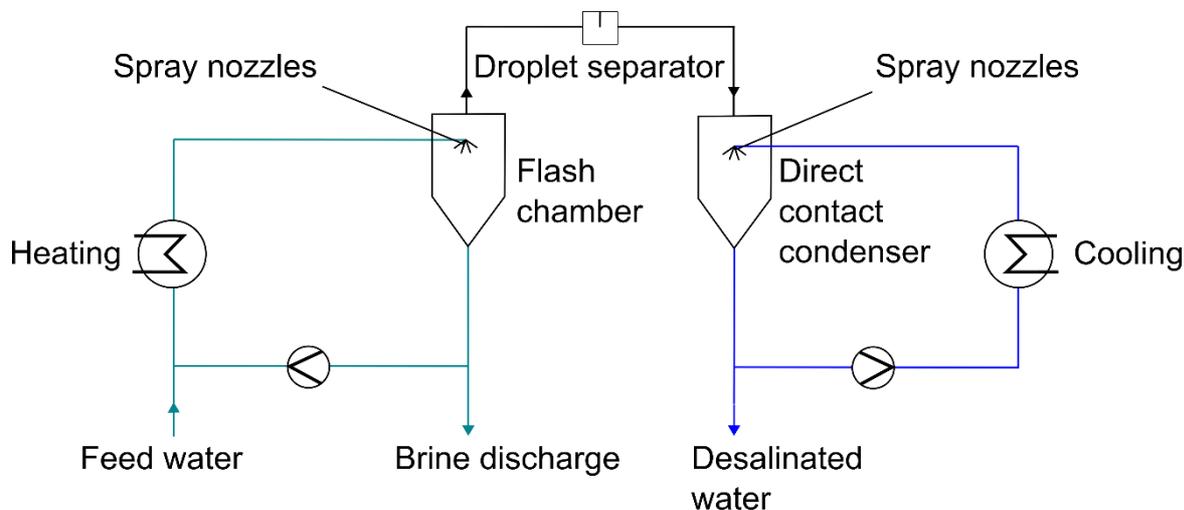


Fig. 1. Process scheme of a single-stage Direct Spray Distillation (DSD) system (based on [3]).

A multi-stage configuration is shown in Figure 2. Each stage comprises a spray flash chamber and a spray condenser. The flash chamber and the condenser chamber are connected to allow vapour flow. A wire-mesh droplet separator is placed between the flash chamber and the condenser chamber to prevent the entrainment of saline water droplets.

The feed water is heated up in heat exchangers (HEX 1 and HEX 2) by hot distillate which cools down. Then the feed water is heated to the top brine temperature below 100 °C, typically up to 65 °C [4], in the main heat exchanger (HEX 3) by an external heat source. The saline water is prevented from vaporisation by keeping its pressure throughout the heating process above the saturation vapour pressure corresponding to its temperature. In the flash vaporisation cycle, the hot saline water is sprayed into flash chambers, flashes and the remaining brine flows by gravity to the subsequent chambers with lowered temperature and pressure. The generated vapour flows from the flash chamber to the condenser in every stage. In the condenser cycle, the cooled distillate is sprayed into the condenser chambers to allow for direct contact condensation on cooled droplets. During this process, the temperature and pressure of the cooling water increases from stage to stage. In heat exchanger HEX 2, heat is transferred from the hot cooling water to the cold feed water. The gained distillate (desalinated water) cools down in an optional heat exchanger HEX 1 and the feed water is preheated. The heat exchanger HEX 4 reduces the temperature of the cooling water before it is pumped to the condenser cycle.

The brine is extracted from the last flash chamber. Part of the brine is discharged and the remaining brine is recirculated.

In order to run the process, a vacuum system extracts non-condensable (NC) gases, such as N₂, O₂, CO₂, from the chambers. In the connection duct to the vacuum pump, an optional heat exchanger, which is not shown in Figure 2, cools down the extracted gas mixture of non-condensable gases and water vapour to condense as much water vapour as possible.

The precipitation of salts for Zero Liquid Discharge (ZLD) applications requires a crystallizer which is not shown in Figure 2.

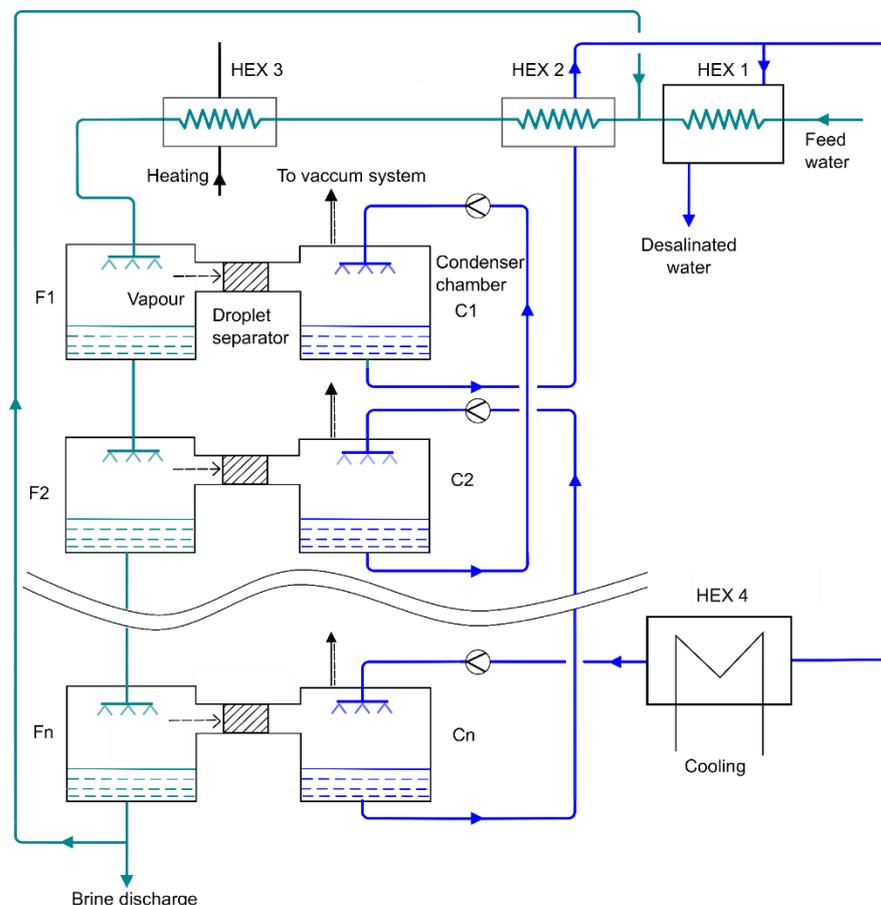


Fig. 2. Process scheme of a multi-stage Direct Spray Distillation (DSD) system (based on [3-5]).

Motivation of Use

The plants are still lab-scale or pilot plants. Instead of relying on solid heat transfer surfaces, flash vaporisation and direct contact condensation are applied. The advantages of the DSD process include higher heat and mass transfer rates, simplicity of design (no internal parts except for the spray nozzles), and the capacity to operate at relatively small temperature differences. Being devoid of any solid heat transfer surface area, the risk of corrosion and scale formation is drastically lowered, and no chemicals are needed to pre-treat the feed water [4].

Furthermore, DSD is tolerant to high salinities, impurities and fluctuating feed water qualities [3, 4]. It is assumed that a high ratio of desalinated water to feed water (i.e., recovery ratio) can be achieved and, thus, the brine volume can be reduced, leading to a lower environmental impact of brine discharge. The precipitation of salts seems possible in order to allow for Zero Liquid Discharge operation [3].

Furthermore, 'low grade' or 'waste' heat at a low temperature level can be used as thermal energy source. Thus, a particular benefit is the possibility to drive the DSD process with solar irradiation or industrial waste heat [3, 4].

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4.1.8 Adsorption assisted Desalination (AAD)

Dr. Markus Spinnler

Separation Principle

Adsorption Desalination (AD) uses the principle of vaporisation of pure water in a vaporiser and the subsequent adsorption of the pure water vapour in an adsorption bed. In a second step, the adsorbed water vapour is being desorbed from the adsorption bed and liquified in a downstream condenser. Analysing the process brings to light that the core of AD consists of vaporisation with subsequent condensation. The adsorption bed serves exclusively as an aid to maintain the required low vaporisation pressure.

Even though the term “Adsorption Desalination” has found its way into the related literature, e.g. [1-5], the authors of the present article propose using the term “Adsorption *assisted* Desalination” (AAD) as it is less misleading and offers higher scientific precision.

However, like in any vaporisation process, the separation of pure water and salt is due to a substantially lower **vapour pressure** of salt compared to water, see Annex 1. Thus, at a given temperature and pressure, pure water will vaporise while the salt ions remain dissolved in the liquid brine.

Driving Force and Initiator

The fundamental driver of AAD systems is the establishment of a difference in the partial vapour pressure of water in the saline feed water and the pressure of the surrounding pure water vapour in the vaporiser. In other words, at a given temperature, the absolute pressure inside the vaporiser (see Figure 1) has to be below the partial vapour pressure of water in the feed water. In AAD systems, the pressure reduction in the vaporiser is achieved by the water vapour uptake of the adsorbent in the adsorber bed.

But why is an adsorption bed reducing the pressure in the vaporiser? In a general sense, adsorption is a physical process, in which molecules adhere to a solid surface and accumulate on this surface. The attachment of molecules to the solid grains of the adsorbent is caused by van der Waals forces [6]. To say it simply, the water vapour is extracted from the vaporiser by the attachment of water (vapour) molecules to the adsorbent. Hence, no additional vacuum system is required.

For these reasons, **pressure reduction** can be identified as initiator driving the vaporisation of water in AAD. Heating is only required to supply the necessary heat of vaporisation. Working at temperatures and pressures around the boiling point of saline water and with no air or other Non-Condensable Gases (NGC) involved, AAD can be classified as **vaporisation** process. Due to the vaporisation and subsequent desorption from the adsorption bed, AAD is a double-distillation process offering a higher separation efficiency than in single-effect distillation.

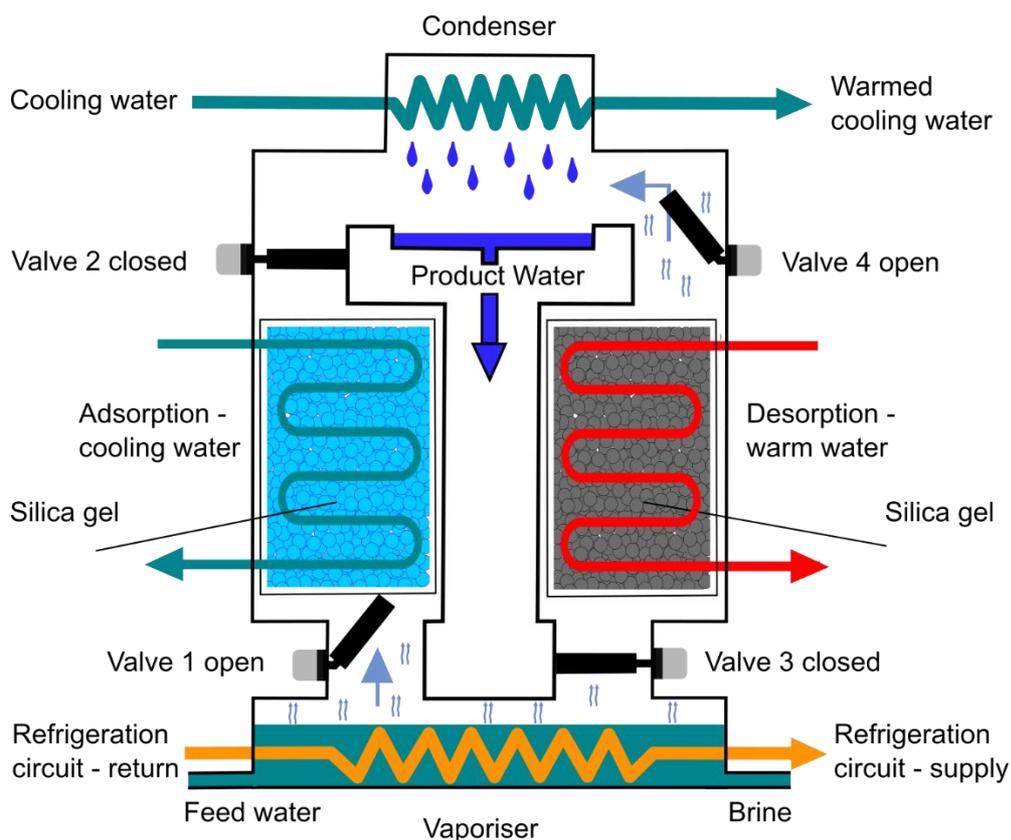


Fig. 1. Schematic set-up of a two-bed AAD system in adsorption mode (left, blue) and in desorption mode (right, red). Adapted from [5]. Note that the connection to a refrigeration circuit (orange) is optional.

Process

Figure 1 is illustrating the basic configuration of an AAD system with two adsorption beds [5]. A typical plant consists of three main components: (1st) the vaporiser, (2nd) a single or several reactor beds, where the adsorbent is placed and (3rd) the condenser [2].

Feed water is pumped into the vaporiser, where the pressure lies below the partial vapour pressure of pure water in the saline solution at the targeted vaporisation temperature. The heat of vaporisation is provided by a heat exchanger, which stabilises the vaporisation temperature and hence pressure. Similar to the set-up of a conventional adsorption chiller [7], this heat exchanger can be operated at low vaporisation temperatures, for instance at 7 °C and a corresponding 9.4 hPa saturation pressure of water in seawater at 35'000 ppm. Thus, AAD systems have the big advantage to be integrable into district cooling circuits and to provide both cooling capacity and high-grade potable water at the same time. For this reason, the technique is sometimes defined as Adsorption Desalination with Cooling (ADC) [1].

The low vaporisation pressure level is maintained by the water vapour uptake of the adsorbent, which mostly is either silica gel or zeolite. To operate the process in adsorption mode, valve 1 is open while valve 2 remains closed, see also Figure 1. Due to the exothermic nature of the adsorption process, the adsorber bed has to be cooled

to remove the heat of adsorption as shown in the left reactor in Figure 1. The adsorption process can continue until the adsorbent is saturated, i.e. until an equilibrium between the number of molecules in gas and solid phase and the free surface of the adsorbent is achieved. Again, this equilibrium is a function of pressure and temperature [6].

Once saturated, the adsorbent can easily be regenerated, which in AAD is mostly achieved by heating the reactor bed. In Figure 1, the reactor on the right shows the desorption process. Providing heat at a low temperature level from 55 ... 85 °C [1] desorbs the water vapour molecules. To operate the process in desorption mode, valve 3 is closed while valve 4 remains open. The required heat of desorption equals the heat of adsorption that was purged during the adsorption process. Thus, AAD has the capability to be operated with low temperature heat sources like solar thermal or waste heat. The regeneration has two objectives: (1st) to restore the adsorption capacity of the exhausted adsorbent and (2nd) to recover the water vapour present in the adsorbed phase [2].

The desorbed water vapour is set free and subsequently is liquefied in the condenser unit. The pressure in the condenser unit is defined by the condensation temperature. The condensate is trickling down from the condenser surface and is collected as product water.

Due to the transient loading behaviour of the adsorber, AAD systems have to be operated in a batch mode. This is the main reason behind installing two or four beds. Silica gel is a common adsorbent because it takes up water vapour without significant structural or volume change and readily releases it under mild heating. The time for the regeneration process is a function of the regeneration temperature – the lower the temperature, the longer it takes to release the water vapour [3]. It should be noted that in AAD, the fresh water is distilled twice (i.e. double-distilled), leading to an even better separation result as in other vaporisation- or evaporation-based desalination systems. High Recovery Ratios of 65...80 % were achieved with no significant increase in product water salinity [3, 5]. In order to reduce the Specific Energy Consumption (*SEC*), the possibilities for heat recovery, for instance between adsorption and regeneration step or between condenser and vaporiser are manifold.

Motivation of Use

In experimental studies, a nominal water production of roughly 12 m³/d per ton of silica gel and a cooling capacity of 88 kW at rated conditions of 85 °C for the regeneration heat source, 30 °C for the condenser cooling water and 7 °C for the chilled water in the vaporiser was reported, proving the feasibility of ADC systems [1,3]. In pilot plants, a very low *SEC* < 1.5 kWh/m³ of electrical energy was determined [1]. Unfortunately, as commonly done in the adsorption business, the thermal energy requirements for regenerating the adsorbent are considered to be for free and therefore neglected, which is kind of misleading. However, Ng [3] reports a primary energy consumption of 38.8 kWh/m³, which lies in the range of optimised Multistage Flash (MSF) or Multi-Effect Distillation (MED) plants.

Compared to other desalination techniques, there are several significant advantages of AAD: (1st) it requires only low-grade heat e. g. from solar thermal or waste heat, (2nd) it has fewer moving parts, e.g. no vacuum system, which reduces the maintenance

costs, (3rd) it shows a reduced fouling and corrosion propensity due to the low operation temperature and the confinement of the saline solution to few parts of the total system, (4th) it has the ability to co-generate high-grade potable water and cooling, (5th) due to the double distillation both pre- and posttreatment requirements are reduced [5].

A further important advantage might be achieved by combining AAD with other multi-stage distillation processes. Due to the vapour uptake of the absorbent and the resulting low vaporisation pressure and temperature, the last stages of MSF or MED plants can be operated below ambient temperatures. Integrating AAD with the final condenser of an MED system enables the combined cycle to use energy from the ambient, as the difference between Top Brine Temperature (*TBT*) and condensation temperature (which is the vaporising temperature in the downstream AAD system) can be expanded from 80 °C ... 40 °C to 80 °C ... 10 °C. This allows to significantly increase the number of MED stages and thereby the Gained Output Ratio (*GOR*) [3]. Experiments from a laboratory-scale pilot have shown an increase in water production by more than a factor of 2 [4].

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4.2 Selective Evaporation

4.2.1. Humidification-Dehumidification (HD or HDH) and Multi-Effect Humidification (MEH)

Dr. Markus Spinnler

Separation Principle

Humidification-Dehumidification (HD), sometimes also named HDH or in case of multiple effects “Multi-Effect Humidification” (MEH) imitates the natural rain cycle in an artificial environment. In the natural rain cycle, only pure water evaporates from the surface of the oceans, while the salt ions remain in the seawater. The separation of pure water and salt is due to a substantially lower **vapour pressure** of salt compared to water, see Annex 1. Thus, at a given temperature, pure water will evaporate while the salt ions remain dissolved in the liquid brine. The HD process uses this principle of evaporation of pure water in a humidifier and subsequent condensation of the pure water vapour in a dehumidifier.

Driving Force and Initiator

The fundamental driver of HD systems is the establishment of a difference in partial vapour pressure between the water in the saline feed water, the water vapour in the surrounding air and the vapour pressure of the condensate. As vapour pressure is an exponential function of temperature, this is done by building up a temperature difference between the humidifier and the dehumidifier, mostly by heating the feed water [1-2]. Therefore, **heating** is identified as main initiator for driving HD processes. The majority of HD set-ups uses air as a carrier medium. For this reason, HD can be classified as a diffusion-driven, **evaporative** process.

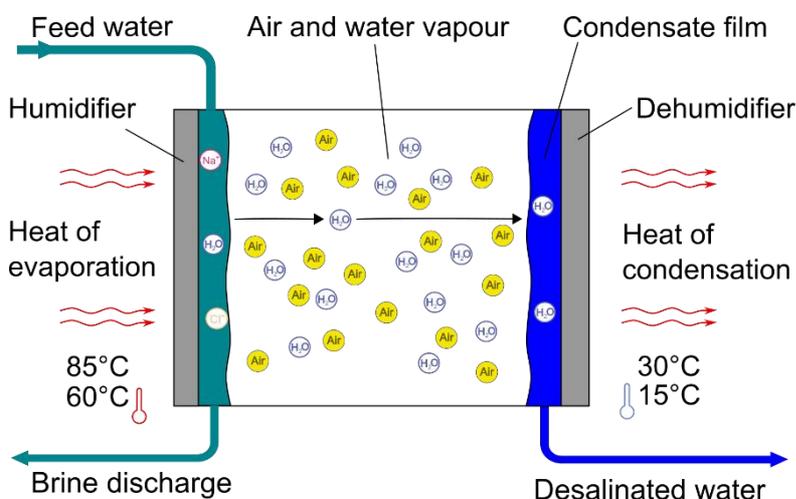


Fig. 1. Principle of water mass transfer in HD systems with air as carrier medium.

Figure 1 is illustrating the basic principle of HD. In an HD system the humidifier (sometimes “evaporator”) or the feed water itself is heated in order to raise the heat of evaporation and to establish a temperature difference between humidifier and dehumidifier. The humidifier releases water molecules from the feed water to the air, where they appear as pure water vapour (evaporation). A dehumidifier (often “condenser”) captures the water vapour molecules in the humid air in a condensate film. The heat of condensation is released and can be recovered for preheating the feed water. It is important to realise that the mass flow of pure water molecules is always following the gradient from high to low vapour pressure. Thus, the vapour pressure difference or in other words the temperature gradient drives the net water flow from feed (humidifier) to humid air and from humid air to condensate (dehumidifier).

Besides temperature, the partial vapour pressure of water in aqueous solutions is also a function of salinity. Increasing salinity means decreasing the concentration of water in the solution and hence decreasing the partial vapour pressure of water (Raoult’s law, see Annex 1). Especially in applications with high salinity, for example in Zero Liquid Discharge (ZLD), the temperature-induced vapour pressure increase has to overcome the salinity-induced vapour pressure reduction, which demands high feed water operation temperatures. With increasing salinity, this leads to an increasing Specific Energy Consumption (*SEC*). [3]

Process

In literature, a large variety of HD configurations is reported. Exemplarily, Figure 2 shows the configuration of a single-stage, closed air, water heated HD system.

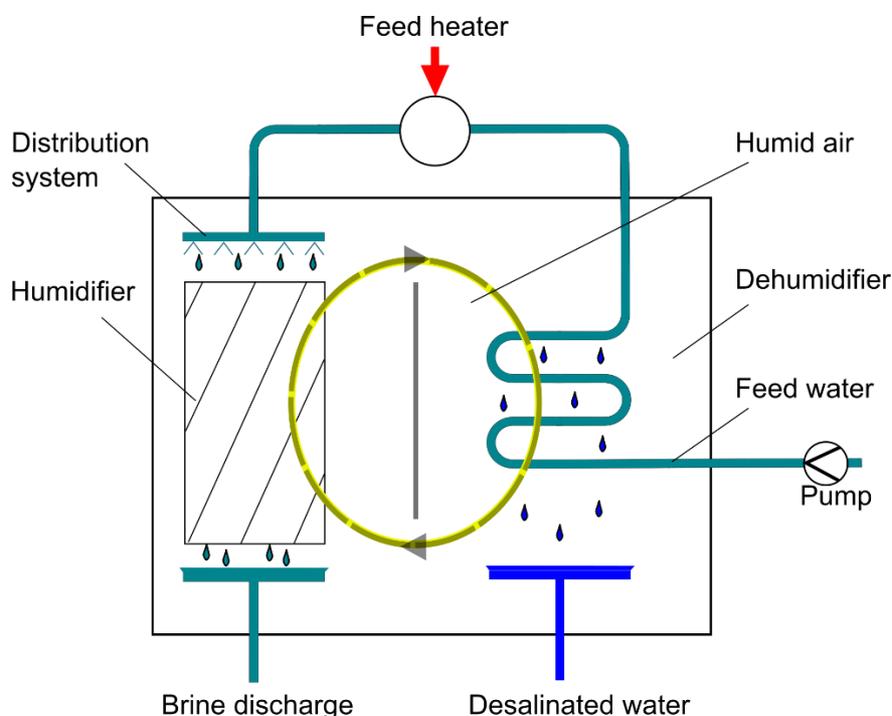


Fig. 2. Process scheme of a single-stage, closed air, water heated HD system.

Here, feed water (i.e. seawater) is heated to Top Brine Temperatures (*TBT*) of up to 85 °C. This is done to establish the required temperature difference and hence driving vapour pressure difference between feed, air and condensate and to provide the immense heat of evaporation. The warm feed water is sprayed into the so-called humidifier through a distribution system. To enhance the heat and mass exchange area at minimum feed mass flow, packing material is installed in the humidifier, where the feed water is trickling down forming a saline water film. Relatively cold and therefore dry air gets into contact with the warm feed water film in the humidifier. Due to the difference in temperatures and in partial water vapour pressures between feed water film and air, evaporation and sensible heat transfer take place. Both temperature and humidity of the air increase. Therefore, its density decreases. Thanks to the so created buoyant forces (free convection) or, in most plant configurations assisted by a fan (forced convection), the air is rising and entering the dehumidifier [4].

The dehumidifier is mostly realised as heat exchanger, in which the warm, humid air flow is cooled down to temperatures lower than the dew point temperature. Air moisture – which is the water vapour in the air – is condensing outside the heat exchanger coils and is releasing the heat of condensation. The condensing water vapour is trickling down and collected as condensate. In potable water production, the condensate is the product water. As coolant inside the heat exchanger coils, feed water is used, which is being preheated by the heat of condensation.

In some approaches, the condenser is not implemented as latent-sensible heat exchanger as described above, but as so-called direct contact heat exchanger. Here, cold fresh water is sprayed into a condensation column providing by itself a condensation surface. Even though providing a higher condensation efficiency, this option yields problems in recovering the heat of condensation. [5]

Other HD configurations rely on heating the air flow [4], on forming air bubbles in a saline water pond to achieve low feed water flow rates, e.g. [6] and on multistaging several effects, e.g. [7].

Motivation of Use

HD is a relatively robust technique, where any kind of aqueous solution with vapour pressure of the solvents lower than that of desalinated water can be treated. Feed water needs to be coarsely filtered and volatile components need to be separated. As in HD, scaling is a minor issue and basically no chemicals are needed for its operation. HD is one of the few desalination processes suitable for Zero Liquid Discharge (ZLD) applications, even though the Performance Ratio *PR* tremendously suffers from rising salt concentrations in the feed water [8].

A major advantage of the HD process compared to other phase change technologies is that it needs thermal energy at a low temperature level (60 °C – 85 °C). Thus, one particular benefit is the possibility to drive HD processes with solar irradiation or waste heat. The plant sizes of HD plants are relatively small in the range of 0.01 to 50 m³/day [9–10]. Depending on the plant configuration, *PR* lies between 4.7 and 1.2, which corresponds to an *SEC* of 140 kWh/m³ to 550 kWh/m³ [2] for standard seawater (approximately 35'000 ppm). Furthermore, no special qualification is needed to operate an HD system, making HD suitable for remote areas of application. According to [11], no chemicals are required for HD operation.

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4.2.2 Solar Stills

Dr. Markus Spinnler

In principle, Solar Stills are the simplest and oldest form of Humidification-Dehumidification (HD) processes [1-2]. One early and remarkable example for the application of Solar Stills is the desalination system in Las Salinas in Chile. Built in 1872, its setup can be seen as a major milestone in the history of desalination. The engineer Carlos Wilson designed and built a Solar Still covering an area of 4'700 m² using glass and timber. The production rate was 4.9 kg of water per m² of glass surface on a summer day, which is outstanding even for today's standards [1, 3-4].

Compared to classic HD systems, one of the peculiarities of Solar Stills is that the energy supply section is already integrated into the system. In fact, Solar Stills consist of a solar thermal collector with integrated HD unit. Solar Stills are therefore capable to operate autonomous and fully based on renewable energy. In addition, they don't need any auxiliary power or chemical pretreatment. Furthermore, they are able to work up to the crystallisation limits of saline water and beyond and are therefore well suited for Zero Liquid Discharge (ZLD) applications. Thus, it can be said that Solar Stills are an early form of sustainable desalination.

Due to these advantages and the very simple setup but nevertheless complex heat and mass transfer mechanisms involved, a huge Solar Still community, mostly working in science and development aid has emerged since the 1950ies [2]. In the author's experience, when asked to design a desalination system based on renewable energy and targeting developing countries, one of the first ideas students usually come up with is a Solar Still [5].

In view of these facts and considering the large community working on and with Solar Stills, the authors have decided to dedicate a separate article to this technique. As Solar Stills suffer from some severe drawbacks in energy and in condensation efficiency, it will be shown, that HD is a consequent evolution from the basic form of Solar Stills.

Separation Principle

Similar to all HD-related processes including Membrane Distillation (MD), Solar Stills imitate the natural rain cycle in an artificial environment. In the natural rain cycle, only pure water evaporates from the surface of the oceans, while the salt ions remain in the seawater. The separation of pure water and salt is due to a substantially lower **vapour pressure** of salt compared to water, see Section 4. Thus, at a given temperature, pure water will evaporate while the salt ions remain dissolved in the liquid brine. Solar Stills use the principle of evaporation of pure water from the surface of a saline water reservoir and subsequent condensation of the pure water vapour at the cover of the containment.

Driving Force and Initiator

The fundamental driver of Solar Stills is the establishment of a difference between (1st) the partial vapour pressure of water in the feed water reservoir, (2nd) the partial vapour pressure of water vapour in the air inside the Solar Still and (3rd) the saturation vapour pressure of the condensate on the transparent cover. As vapour pressure is an exponential function of temperature, this is done by building up a temperature difference between the feed water and the transparent cover.

Figure 1 is illustrating the basic principle of Solar Stills. The basic structure of Solar Stills is very similar to solar thermal collectors: the required temperature difference is built up by absorbing solar irradiation at the bottom of the feed water basin and thereby heating the feed water [6-8]. Therefore, **heating** can be identified as main initiator driving the desired mass transfer of pure water in Solar Stills.

As all Solar Stills are filled with humid air from the ambient, they can be classified as diffusion-driven **evaporation** systems. However, this reveals another example for inconsistency in technical nomenclature. The term “Still” is usually a short form of “Distiller”, describing a Solar Still as a distillation apparatus driven by solar power. Incorporating an evaporative process, the application of the term “distillation” is scientifically imprecise.

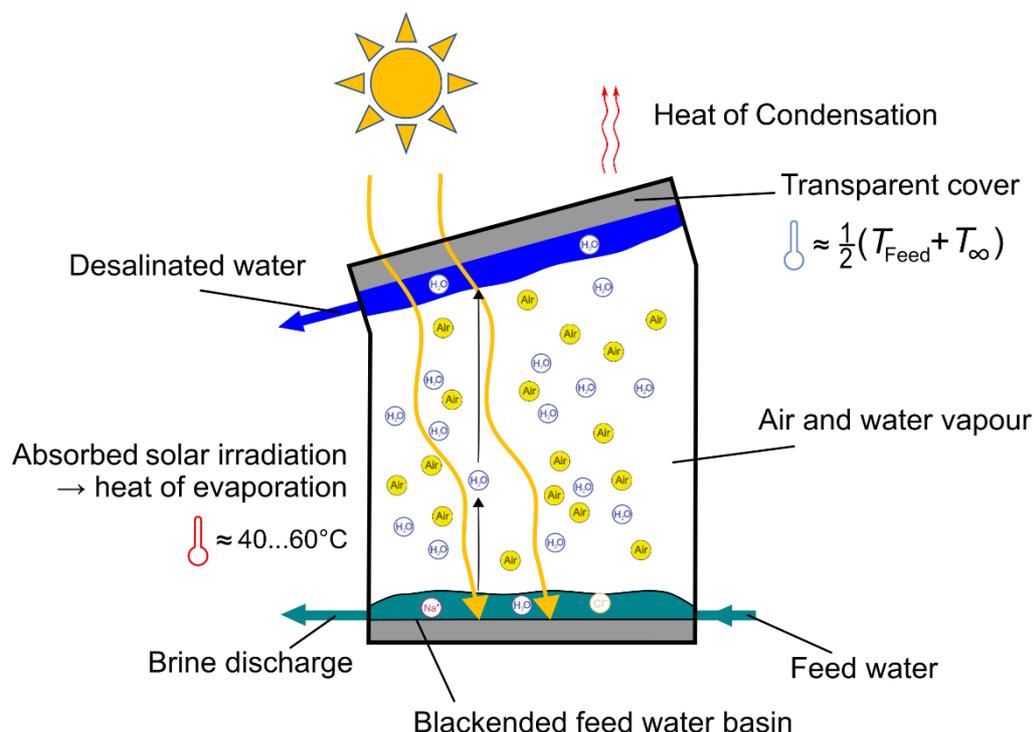


Fig. 1. Principle of water mass transfer in Solar Stills.

In a classical Solar Still, solar irradiation is captured by transmission through the transparent glass cover and the feed water and finally by absorption at the bottom of the feed water basin. The absorbed solar power is used to heat the feed water and thereby to provide the heat of evaporation and to establish a temperature difference between the feed water and the transparent cover. Giving a rough order of magnitude, the temperature of the transparent cover is a trifle higher than the average of feed water and ambient temperature [9-11]. At the surface of the feed water reservoir, water molecules are released to the air, where they appear as pure water vapour (evaporation). In an HD system, this part would correspond to the “humidifier”.

One of the crucial points of the process is to keep the temperature of the transparent cover below the dew point temperature of the humid air inside the Solar Still. The lower the cover temperature, the higher the condensate mass flow will be. Getting in contact with the relatively cold cover, the adjoining humid air will reach saturation and condensate droplets will start to form on the inside. Depending on the condensation mass flow rate, the droplets will coagulate and form a condensate film which can be used as desalinated water. In a corresponding HD plant, the transparent cover would take over the role of the “dehumidifier” or “condenser”.

The heat of condensation is released to the transparent cover which transfers it to the environment. Different from HD, it cannot be recovered for preheating the feed water. It is important to realise that the mass flow of pure water molecules is always following the gradient from high to low vapour pressure. Thus, the vapour pressure difference or in other words the temperature gradient drives the net water flow from feed water surface to humid air and from humid air to the surface of the condensate on the cover.

Besides temperature, the partial vapour pressure of water in aqueous solutions is also a function of salinity. Increasing salinity means decreasing the concentration of water in the solution and hence decreasing the partial vapour pressure of water (Raoult's law, see Annex 1). Especially in applications with high salinity, for example in Zero Liquid Discharge (ZLD), the temperature-induced vapour pressure increase has to overcome the salinity-induced vapour pressure reduction, which demands high feed water operation temperatures. However, the usable solar power in Solar Stills is characterised by their solar thermal collector efficiency. Collector efficiency is a negative linear function of the difference between feed water and environmental temperature divided by the solar irradiation power [9]. In other words, at higher feed water temperatures required due to higher feed salinity, the collector efficiency and thus the fresh water output will decrease.

Process

In literature, a large variety of Solar Still configurations is reported [3, 6-8, 12]. Exemplarily, Figure 2 shows the most basic Solar Still configuration.

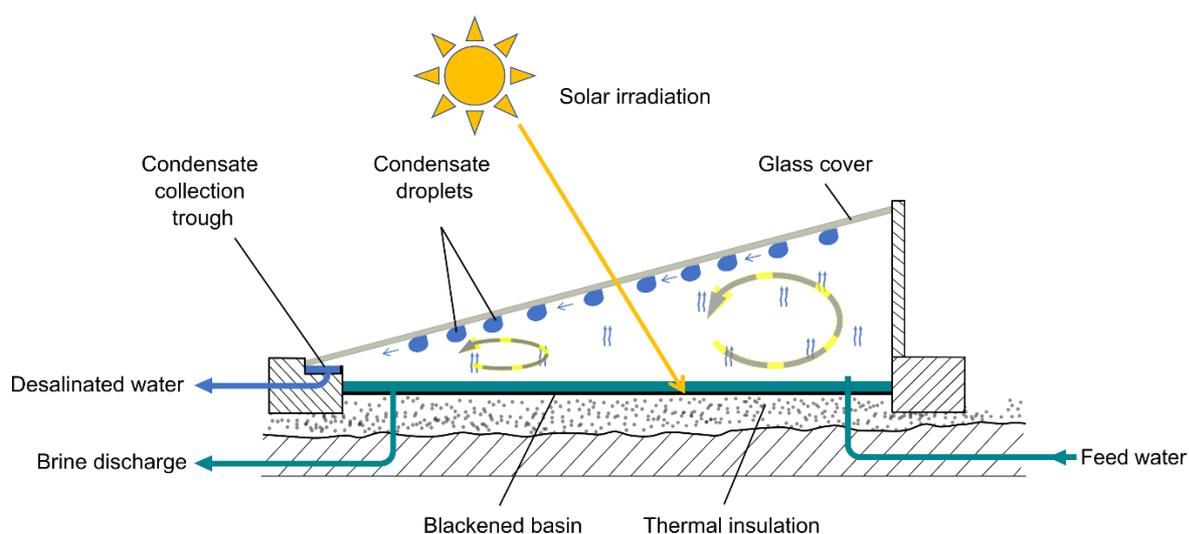


Fig. 2. Process scheme of a Solar Still.

After being transmitted through the transparent cover and the feed water, the solar irradiation is absorbed at the bottom of the feed water basin. Through convection, the

absorbed heat is released to the feed water and heats it to Top Brine Temperatures (*TBT*) of 40 °C to 60 °C [7, 13]. This is done to establish the required temperature difference and hence driving vapour pressure difference between feed, humid air and condensate and to provide the immense heat of evaporation. The feed water can be pumped into the basin continuously or in batch mode. In the simplest configuration, it can be filled into the basin manually. [4]

One of the main drawbacks in Solar Stills' energetic efficiency is that standard selective absorber materials do not comply with the corrosive feed water. Selective absorbers as used in standard solar thermal collectors provide a high absorptivity in the short wavelength spectrum of solar irradiation and low emissivity in the long wavelength region of thermal radiation. Working as a radiation trap, these materials reduce thermal radiation heat losses and allow high efficiency even at high absorber temperatures [9, 11]. In order to minimise this drawback, packing material can be added directly to the feed water basin. Like this, volumetric absorption of solar radiation in the feed water can be achieved and selective radiation characteristics can at least be emulated. For simplified use in remote areas, charcoal as filling material has been proposed [14], while for more advanced systems, blackened filter paper or even nanoparticles are under investigation [15].

Another drawback is the long matutinal start-up time due to the high thermal inertia of the feed water in the basin. As possible improvements, the use of porous absorbers (e.g. blackened tissues or fleeces) that are transporting minimal amounts of feed water by capillary forces have been proposed [7, 15-16]. As a welcome side effect, some porous absorbers also provide selective radiation properties [9, 16]. Other approaches lie in installing feed water troughs or minimised basins with reduced thermal inertia [12, 17].

The warm feed water surface gets into contact with the relatively cold and therefore dry air in the Solar Still. Due to the difference in temperatures and in partial water vapour pressures between feed water surface and air, evaporation and sensible heat transfer take place. Both temperature and humidity of the air increase. Therefore, its density decreases. Thanks to the so created buoyant forces (free convection), the air is rising and comes into contact with the cover plate.

The cover plate mostly is realised as a glass pane, sometimes e.g. in emergency systems also as a plastic foil [18]. In the ideal case, the glass plate is made of solar glass, which provides a 5 % higher transmissivity than conventional float glass [11]. Very seldom, it is made of the more expensive acrylic glass or polycarbonate, which are robust and also provide high transmissivity. This comes at the cost of a lower thermal conductivity, which leads to higher glass temperatures and a lower condensation rate [11, 19].

Air moisture – which is the water vapour in the air – is condensing on the inside of the glass cover and is releasing the heat of condensation, which cannot be recovered. Together with the absorbed solar irradiation this adds to heating up the glass pane, enhancing the glass pane temperature and thus throttles the condensation rate as the temperature and vapour pressure difference between feed water and glass is decreasing. After reaching a thermal equilibrium at a temperature slightly higher than the average between feed water and ambient temperature, the heat of condensation is released to the environment. The humid air is cooled down and depleted from water vapour. This makes it denser and creates a downforce, which adds to build up a free convection vortex between feed water surface and cover pane.

Besides the unwelcome heating of the glass plate due to absorption and heat of condensation, the formation of condensate droplets and to a lower extent also of a condensate film reduces the optical transmissivity of the glass cover and thus reduces the available solar thermal power and thermal efficiency.

The condensate is running down the inside of the glass plate and is collected as product water. In order to optimise the collection process, a tilt angle of the glass plate of roughly 30 ° is recommended. On one hand, the tilt angle must be optimised according to the solar irradiation, on the other hand, the angle must not become too flat in order to prevent condensate dripping back into the feed water basin. [7, 12-13]

Motivation of Use

Solar Stills are the ultimately robust technique, where any kind of aqueous solution with vapour pressure of the solvents lower than that of pure water can be treated. As in HD, scaling is a minor issue and no chemicals are needed for operating a Solar Still. Feed water doesn't even need to be filtered [4]. Solar Stills represent one of the few desalination processes suitable for Zero Liquid Discharge (ZLD) applications, even though the output suffers tremendously from rising salt concentrations in the feed water [20]. As was already described, Solar Stills work 100 % autonomously and only need a minimum of maintenance like periodical cleaning. They are automatically powered by 100 % solar energy and are therefore completely sustainable.

However, thanks to their limitations in heat recovery and the undesirable heating of the transparent condenser surface by solar absorption and the released heat of condensation, the main drawback of Solar Stills lies in their low energetic efficiency and the resulting low specific output of 1 to 5 litres per day and m² collector area [8, 13]. This leads to high specific investment costs and a large land use.

The approaches to improve the performance of Solar Stills are manifold and for the sake of brevity only some examples can be given here: Optimising the solar power supply led to multiple approaches in tilt angles and shapes of the glass cover [12, 15]. Optimising the feed water supply by minimising the thermal inertia was already discussed above. Quite contrary to this approach, some researchers are investigating methods to store the diurnal solar power for prolonged nocturnal operation. Research on thermal storage integration is targeting on latent heat storage systems (PCM) [7, 15, 21].

Another possibility would be to actively cool the transparent cover [22]. However, besides higher plant complexity and limited possibilities for recovering the heat of condensation this evokes problems with cooling water consumption and biofouling which endangers the transmissivity of the front plate [8, 22].

Further ideas aim towards installing external, actively cooled condensers to both improve the optical collector efficiency and to maintain high temperature differences between feed water and condenser. Going into the same direction is the idea to install external solar collectors to heat the feed water. Another approach that always helps to reduce the Specific Energy Consumption (*SEC*) is to multistage several Solar Stills in series. However, all these approaches are coming at the cost of a much higher complexity. [7-8, 15, 19]

Furthermore, the ongoing development towards HD systems becomes obvious: classic HD features both a separated, optimised humidifier and an actively cooled condenser as well as an external (solar) heat supply, see the main article on HD in section 4.2.1.

Numerous attempts for commercialisation of Solar Stills have been undertaken, mainly going into the direction of NGOs and development aid. In this context, the famous Watercone™ [23-24] has to be mentioned, which besides its desalination features is also a well-known design icon. With the Rosendahl Solar Still [13, 23] a mature system came onto the market but it did not survive the growing pressure from more effective desalination techniques.

Notwithstanding the drawbacks, the absence of any maintenance requirements as well as their robustness and their autonomous and sustainable operation makes Solar Stills the ideal choice for sunny, remote areas in developing countries with demand for low drinking water quantities, i.e. small communities, schools, etc.

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4.2.3 Spray Evaporation (SE) also known as Rapid Spray Evaporation (RSE)

Dr. Heike Glade

Spray Evaporation (SE) can be used for the separation of water from a saline solution and concentration of the saline water toward salt crystallization. Saline water is broken up into small droplets through spray nozzles and then evaporates in ambient air at atmospheric pressure. The water in the small droplets can be fully evaporated leaving behind solid salts which are separated from the gas phase. The water vapour carried away by the air condenses and the condensate is collected.

Related to the patent “Method for solid-liquid separation in water-based solutions” by U.S. Aquasonics Corporation, Albuquerque, USA (date of patent Oct. 9, 2001) [1], Aquasonics International, Albuquerque, USA, applied for a patent “Apparatus and method for thermal desalination based on pressurized formation and evaporation of droplets” (date of patent March 2, 2004) [2] and called the process Rapid Spray Evaporation. In the following years, variations of the Spray Evaporation process were subject to research and development.

In principle, the Spray Evaporation process is a Humidification-Dehumidification (HD) process. In addition to the Section “Humidification-Dehumidification (HD)”, this present extra section is devoted to Spray Evaporation because the process is primarily aimed at enhancing the ratio of desalinated water to feed water and strongly concentrating the brine to reduce brine discharge toward Zero Liquid Discharge (ZLD).

Spray Evaporation in ambient air at atmospheric pressure should not be confused with a process where superheated saline water is sprayed with nozzles into a flash chamber at a lower pressure than the saturation vapour pressure corresponding to its temperature and it undergoes flash vaporisation induced by the sudden pressure reduction, as applied in the Direct Spray Distillation (DSD) process.

Driving Force and Initiator

If the saline water gets in contact with air and the partial pressure of water vapour in the air is lower than the saturation vapour pressure of water corresponding to its temperature, the water will evaporate. The enthalpy of vaporisation that is required for the liquid-gas phase change is supplied by the heated air or by the heated water or by both.

The system undergoes a phase transition and strives toward phase equilibrium. Thus, water particles (molecules) are transferred from one phase to the other until equilibrium is attained. From a thermodynamic point of view, the Gibbs energy, which depends on the temperature, the pressure and the number of particles of each component in the two phases, decreases and the system moves toward a stable state. The Gibbs energy reaches its minimum at equilibrium, i.e. the infinitesimal change of the Gibbs energy will be zero, which is characterised by a uniform chemical potential. Particles tend to move from higher chemical potential to lower chemical potential because this reduces the Gibbs energy. The equilibrium state between the two phases implies that the pressure and the temperature of both phases are equal and the chemical potential of

each component is the same in both phases. Thus, the **chemical potential difference** is the **driving force** for the transfer of particles between the phases which is **triggered by heating (initiator)** [3, 4].

Separation Principle

The separation of water from salt is based on the large vapour pressure difference between water and salt. Water has a low boiling point and can readily change from a liquid state to a gas state with high vapour pressure, whereas salt has a negligibly small vapour pressure and is considered as non-volatile. The water changes from a liquid state to a vapour state leaving behind the salts. Thus, the gas phase is composed of water vapour and air. The water vapour is subsequently condensed and the condensate is collected. Hence, the **selective vaporisation of water due to the large vapour pressure difference between water and salt** represents the fundamental separation principle.

Process

A process scheme of the Spray Evaporation process is shown in Figure 1. The saline water is heated by the condensing water vapour. Then the saline water is broken up into small droplets through spray nozzles and sprayed into an evaporator chamber. Ambient air is heated by an external heating source and conveyed into the evaporator chamber by an air blower. If the partial pressure of water vapour in the air is lower than the saturation vapour pressure of water corresponding to its temperature, the water will evaporate. The small droplets provide a large phase interface area for heat and mass transfer.

When the water evaporates, the concentrations of the dissolved salts in the droplets increase and the solubility limits may be exceeded. Thus, the salts may precipitate and a salt slurry is formed which must be separated from the water vapour. The mixture of suspended solids and water vapour is filtered to remove and collect the salts [2]. Hou et al. [5] also described that the water in the small droplets can be fully evaporated leaving behind salt particles which are separated by a cyclone, as shown in Figure 1.

The water vapour carried away by the air is condensed and the condensate (desalinated water) is collected. The enthalpy of condensation is transferred to the saline feed water which serves as cooling water and is preheated.

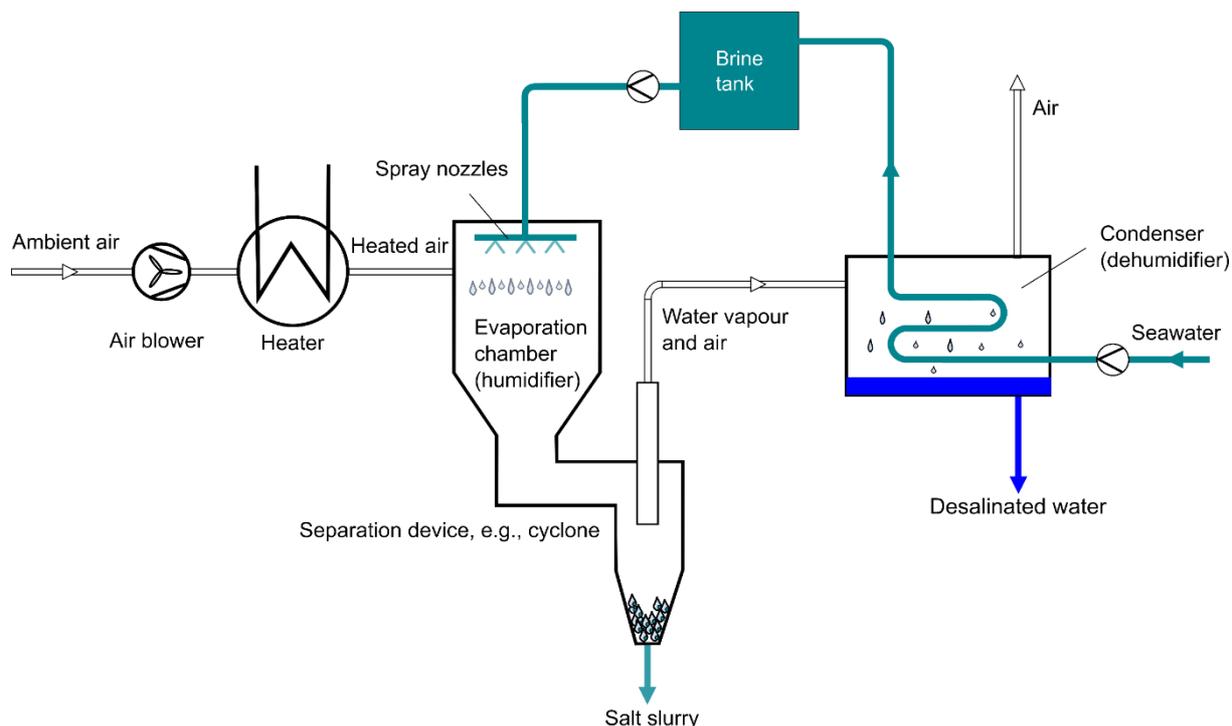


Fig. 1. Process scheme of Spray Evaporation (based on [5]).

Instead of heating the ambient air, as shown in Figure 1, the saline water can be heated by the external heating source before it is sprayed into the evaporation chamber. Depending on the state of the air and the saline water entering the evaporation chamber, the enthalpy of vaporisation that is required for the liquid-gas phase change is supplied by the air or by the water or by both.

For the atomisation of the feed water, single-fluid nozzles [2] and two fluid-nozzles using compressed air [5] are described. Hou et al. [5] used a water-cooled nozzle in order to prevent scale formation in the nozzle.

Motivation of Use

All Spray Evaporation plants are still lab-scale or pilot plants. The advantage claimed for the Spray Evaporation process is that a high ratio of desalinated water to feed water (i.e., recovery ratio) above 90 % can be achieved [2, 5] and, thus, the brine volume can be reduced, leading to a lower environmental impact of brine discharge and to a reduction of desalination costs especially when the salt is a profitable by-product [5]. It is proposed to combine the Spray Evaporation process with other traditional desalination processes in order to enhance the recovery ratio and to reduce the brine discharge.

Furthermore, 'low grade' or 'waste' heat at a low temperature level can be used as thermal energy source. Thus, a particular benefit is the possibility to drive SE processes with solar irradiation or waste heat.

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4.2.4 Membrane Distillation (MD)

Dr. Markus Spinnler

Separation Principle

Membrane Distillation (MD) imitates the natural rain cycle in an artificial environment. In the natural rain cycle, only pure water evaporates from the surface of the oceans, while the salt ions remain in the seawater. The separation of pure water and salt is due to a substantially lower **vapour pressure** of salt compared to water, see Annex 1. Thus, at a given temperature, pure water will evaporate while the salt ions remain dissolved in the liquid brine.

MD systems use the principle of evaporation of pure water in a feed channel, diffusion of water vapour across a porous membrane and subsequent condensation of the water vapour at a condenser [1-3]. The role of the MD membrane is to contain and stabilise the feed water channel. Due to its open pores, it provides a free evaporation surface, but it is not involved in the separation process itself [4].

Driving Force and Initiator

The fundamental driver of MD systems is the establishment of a difference in partial vapour pressure between the water in the saline feed water, the water vapour in the adjacent air, i.e. in the membrane pores, and the saturation vapour pressure of the condensate. As vapour pressure is an exponential function of temperature, the required vapour pressure differences are established by building up a temperature difference between the feed water channel and the condenser. This is mostly done by heating the feed water itself, sometimes also by heating the feed water channel. Therefore, **heating** can be identified as main initiator for driving MD processes.

Different from vaporisation-based techniques, a large majority of MD systems evaporates water to humid air. Hence, MD is classified as a purely **evaporative** process. One exception is Vacuum MD (VMD), which is a vaporisation process. In the present classification approach, VMD is therefore filed as a stand-alone desalination technique.

Process

Figure 1 is illustrating the basic principle of an Air Gap MD system (AGMD). In an AGMD cell, feed water is flowing through a channel with a solid, non-permeable boundary on the left and a porous, hydrophobic MD membrane on the right side. In consequence, the liquid feed water is held back in the feed channel. The voids formed by the air-filled membrane pores provide a free evaporation surface. Therefore, only water vapour is passing through the pores and hence across the membrane. In MD, the feed channel or the feed water itself is heated in order to establish the required temperature and thus vapour pressure difference between feed water and condensate. Furthermore, heating provides the necessary heat of evaporation. Similar to HD systems, the Top Brine Temperature (*TBT*) can be up to 85 °C.

Through the pores of the membrane, the feed channel releases pure water molecules from the feed water to the humid air in the pores. Due to the vapour pressure, temperature and concentration gradient the water vapour is diffusing through pores and air gap and reaches the condenser surface.

Here, the warm, humid air is cooled down to temperatures lower than the dew point temperature. In consequence, the water vapour molecules are condensing and the condensate is captured in a condensate film. The heat of condensation is released and can be recovered for preheating the feed water. Note that the mass flow of pure water molecules is always following the gradient from high to low vapour pressure or in other words from high temperature in the feed water to low temperature in the condensate. Note also that in MD, the condensate is commonly called “permeate”, as in Reverse Osmosis (RO). Even though MD is mainly a thermally driven process, MD nomenclature is based on membrane systems.

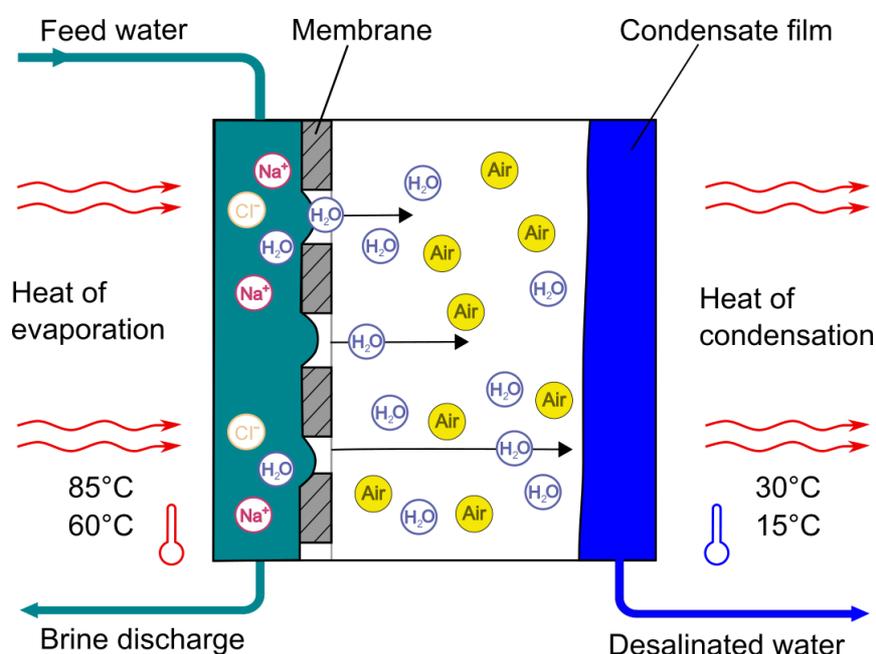


Fig. 1. Principle of water mass transfer in AGMD systems with air as carrier medium.

Besides temperature, the partial vapour pressure of water in aqueous solutions is also a function of salinity. Increasing salinity means decreasing the concentration of water in the solution and hence decreasing the partial vapour pressure of water. Especially in applications with high salinity, for example in Zero Liquid Discharge (ZLD) applications, the temperature-induced vapour pressure increase has to overcome the salinity-induced vapour pressure reduction, which demands high feed water operation temperatures. With increasing salinity, this leads to an increasing Specific Energy Consumption (SEC).

So far, the basic mechanisms are similar to the Humidification-Dehumidification (HD) process. The main difference is that HD is evaporating water vapour from a free surface – the liquid feed water film in the humidifier – whereas MD is evaporating from a surface which is fixed by the porous membrane.

However, one of the main advantages of MD over HD lies in the thermodynamic limitations of exchangers involving both heat and mass transfer. In HD, the humidifier and in MD the feed channel with porous membrane would represent such a heat and mass exchanger. The goal of humidification is to enrich humid air with water vapour. On the other hand, this leads to a highly unstable heat capacity flow in the humidifier and in consequence to significant thermodynamic losses. These losses increase with increasing temperature difference between feed water in- and outlet. One solution to overcome these limitations is to multistage the humidifier in order to reduce this temperature difference. [5-6]

In HD this can be realised at the cost of high plant complexity (e.g. [5, 7-9]), whereas in MD the solution is already part of the system: each single pore of an MD membrane forms a complete HD unit with infinitesimal temperature drop of the feed water. Thus, MD can be considered to be a Mega-Multistage HD system. This advantage applies specifically to Direct Contact Membrane Distillation (DCMD), but other disadvantages of DCMD limit the described effect, see description of Figure 2.

In order to stabilise the liquid water film on the feed side of the membrane, it is very important to use a hydrophobic membrane. Hydrophobicity prevents the feed water from entering the pores (= Membrane Wetting) and from leaking through the membrane. MD membranes have a pore size from 0.1 to 0.45 microns and are mostly manufactured from PTFE (Teflon), more seldom from PVDF (Polyvinylidenfluorid) or PP (Polypropylene). For most MD applications, Ultrafiltration (UF) membranes can be used [10]. Subconsciously, a majority of the readers has an almost daily access to MD membranes, as nearly everybody is familiar with the blessings of waterproof and breathable fabrics for outdoor clothing. MD membranes have the same properties – they repel liquid water (waterproof) and are permeable for water vapour (breathable). Indeed, MD membranes were carrying and do still carry the big brand names also found in “functional textiles” [11].

In Figure 2, a coarse overview on four different MD configurations is shown [12]. In Direct Contact MD (DCMD) feed water and condensate are only separated by the air-filled membrane pores. DCMD is the simplest setup and, in theory, would suffer the least from the thermodynamic losses described above. However, its main problem is a low thermal resistance over the separating layer between feed and permeate channel. This leads to a reduction of the driving temperature and thereby vapour pressure gradient. By introducing an Air Gap (AGMD) which forms a thermal insulation layer, these issues are solved at the cost of higher membrane complexity and problems with Non-Condensable Gases (NCG). In Sweep Gas MD (SGMD), a dried gaseous carrier medium is used instead of air. The sweep gas brings advantages in heat- and mass transfer but causes a high system complexity. Therefore, SGMD is mainly used in special applications like the separation of volatile components [13]. In Vacuum MD (VMD), NCG issues can be avoided which allows an optimisation of the heat and mass transfer characteristics. The resulting advantages enhance the performance by approximately 30 %, but again at the cost of a high plant complexity [14].

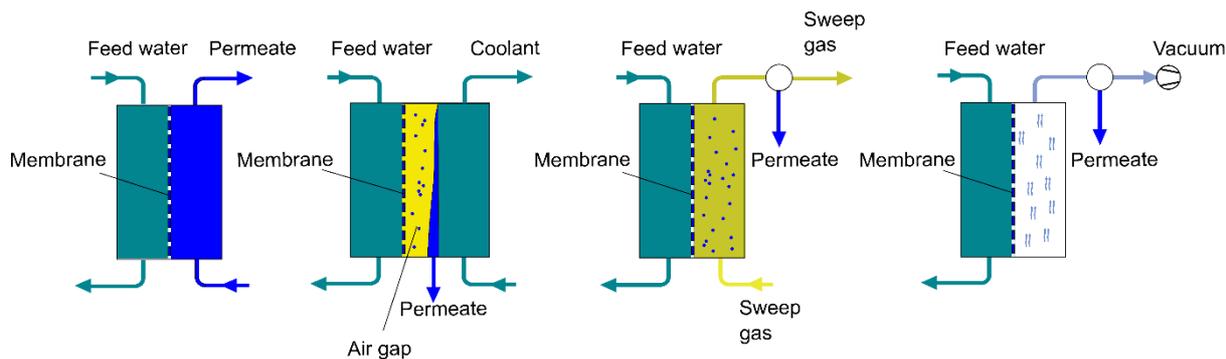


Fig. 2. MD arrangements (from left to right) with Direct Contact MD (DCMD), Air Gap MD (AGMD), Sweep Gas MD (SGMD) and Vacuum MD (VMD). Adapted from [15].

Motivation of Use

A major advantage of the MD process is that it can be operated with thermal energy at a low temperature level (60 °C – 85 °C). Thus, one particular benefit is the possibility to drive MD processes with solar irradiation or waste heat. Another key advantage is its robustness towards the feed water quality and its suitability for Zero Liquid Discharge (ZLD) applications, e.g. [16 - 17]. The plant sizes of MD plants are relatively small in the range of 1 – 50 m³/day installed capacity but can be modularly extended up to 10'000 m³/day [10]. Compared to HD, MD has a slightly higher Performance Ratio *PR* and a much lower need for installation space whereas HD plants usually have a lower complexity and a higher tolerance to problematic feed waters. Strongly depending on the plant configuration and its operation parameters, *PR*s between *PR* = 1.8 ... 8 have been reported [16 - 18]. However, as the upper limits are determined theoretically it would be more realistic to assume *PR* = 4 (*SEC* = 160 kWh/m³) for a commercial MD plant [15]. In MD, the use of chemicals is very limited [17].

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4.3. Selective Crystal Formation

4.3.1 Gas Hydrate Desalination (GHD)

Detlef Taprogge

Gas Hydrate Desalination is a technique to separate water from salt by

- forming a gas hydrate slurry by bringing saline water into direct contact with a gas hydrate forming gas, and
- subsequent (spontaneous) liquid to solid phase change of the gas hydrate slurry into gas hydrate (clathrate) solids **initiated by pressure elevation**, and
- subsequent physical separation (washing) of gas (clathrate) hydrate solids from brine, and
- subsequent decomposing of gas hydrates (clathrate) solids by phase change into desalted water and clathrate forming gas by addition of heat.

Before getting to the details of desalination by use of gas hydrates (clathrates), some introductory comments on the nature of clathrate hydrates may be helpful to better understand the concept of desalination by way of clathrates.

The term “clathrate” is derived from the Latin word “clat(h)ratus”, meaning “with bars, latticed” [1] or “caged”. Broadly defined, clathrates are “inclusion compounds” in which the “guest molecule” is in a cage formed by the “host molecule” or by a lattice of host molecules.” [2-3]

More specifically, clathrates (or clathrate hydrates or gas hydrates or hydrate clathrates) are crystalline compounds in which the cage forming host molecule is water and the entrapped guest molecule is typically gas (or a liquid). Water molecules represent the majority component, gas molecule(s) represent the minority component. Without the support of the trapped molecules, the lattice structure of hydrate clathrates would collapse into conventional ice crystal structure or liquid water [2].

Figure 1 depicts the structure of a gas hydrate (clathrate) compound.

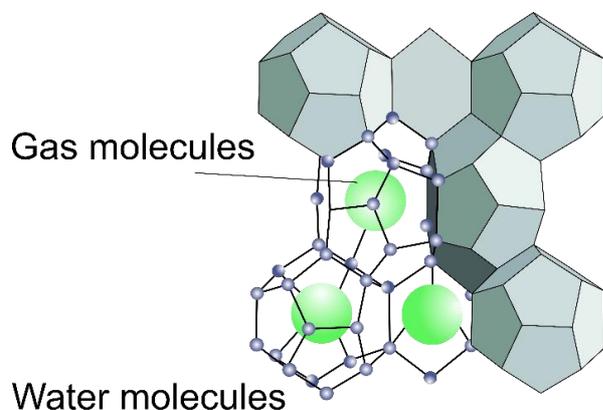


Fig. 1. Gas hydrate (Clathrate) structure adapted from [4]

Hydrogen bonding is the primary mechanism of interaction between the water molecules while van der Waals forces are responsible for the stabilisation of the guest molecules. After occupation of a sufficient number of cages, a thermodynamically stable crystalline unit cell structure is formed. Note well that clathrate hydrates are not “chemical” compounds, as the “enclathrated” guest molecules are never bonded to the lattice [2, 5].

Clathrate hydrates physically resemble ice-like solids, in which small non-polar molecules (typically gas molecules) are trapped in cages of hydrogen bonded frozen water molecules. On a mole basis, methane gas hydrate consists of 85.7 % water and 14.3 % methane. Due to the presence of such a large amount of water in the hydrates, the physical (i.e., density, refractive index) and thermal (specific heat) properties are similar to ice (with some exceptions) [6].

As illustrated in Figure 2, clathrate hydrates exist in three types of crystalline structures, Type I, Type II and Type H. [2, 7] Each of the structures contains cage-like sub-structures that are formed by water molecules and “enclathrate” the guest molecule [2, 8].

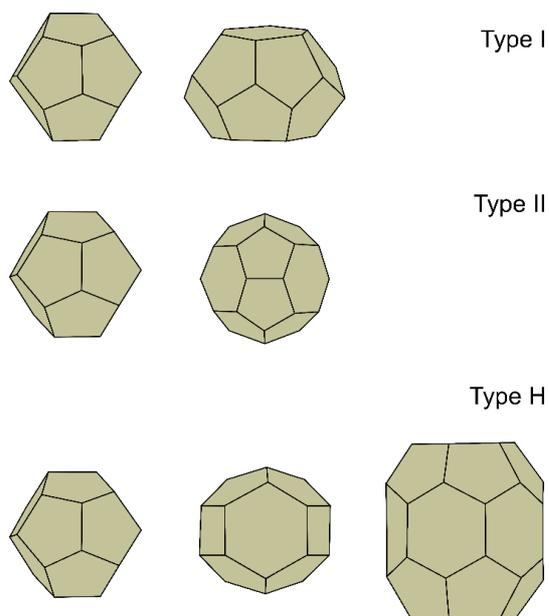


Fig. 2. Crystalline structure of different gas (clathrate) hydrate types.

Type I clathrates consist of 48 water molecules, Type II clathrates of 146 water molecules. Both types form small and large cages. Typical guests forming Type I hydrates are CO_2 in carbon dioxide clathrate and CH_4 in methane clathrate. Type II hydrates are formed by gases like O_2 and N_2 . A Type H clathrate cell consists of 34 water molecules, forming three types of cages – two small ones of different types, and one “huge”. The formation of Type H requires the cooperation of two guest gases (large and small) to be stable. It is the large cavity that allows structure H hydrates to fit in large molecules, e.g. C_4H_{10} (butane) or hydrocarbons, given the presence of other smaller help gases to fill and support the remaining cavities [4, 8].

Gas hydrates form spontaneously at specific temperature and pressure conditions which depend on the hydrate-forming gas [2, 7, 9]. The formation and decomposition of clathrate hydrates are phase transitions, not chemical reactions. The detailed

formation and decomposition mechanisms of clathrates on a molecular level, however, are still not well understood [10].

Numerous low molecular weight gases (e.g. O₂, H₂, N₂, CO₂, CH₄, H₂S, C₂H₄, C₂H₆, C₃H₈) are able to form hydrates at suitable temperatures and pressures [2]. Typically, the temperatures at which clathrate hydrates are stable, are slightly above the freezing point of water, although certain guest molecules stabilise hydrates at nearly ambient temperature [2].

Bridging now from the above introductory comments on clathrates to the idea of desalination of saline water via clathrates, the conceptual background of Gas Hydrate Desalination (GHD) is very similar to Freezing Desalination (FD); first, a phase change into solid clathrates is brought about, and, subsequently decomposed again into gas hydrate forming gas and desalinated water. The rejection of salts which occurs as a natural phenomenon when converting water to ice, also occurs when clathrates are formed. Particularly the idea of converting saline water into stable, ice-like clathrate solids at temperatures above the freezing point (or even at ambient temperatures), is a compelling idea as it offers the chance to lower the cost of freezing compared to ice formation by conventional freezing of water.

At the same time, though, it should be noted that each clathrate forming gas will only create stable, above freezing point temperature clathrate conditions, if a pressure level unique to each clathrate forming gas was exercised simultaneously. Therefore, only a certain range of temperature–pressure combinations specific to the individual clathrate forming gas is necessary to create and maintain stable clathrate conditions. Typically, gas hydrates form at low temperature (T), typically $T < 20$ °C, and high pressure (P), typically $P > 30$ bar, conditions. For example, the hydrate formation conditions (T and P) required for propane (C₃H₈) and CO₂ hydrate are lower than most of the commonly used guest molecules to form hydrates [6]. As another example, at 50 bar, a methane-water solution solidifies around 8 °C [11].

Driving Force and Initiator

What exactly triggers and drives clathrate desalination? As may be derived from the above, gas hydrate desalination is **initiated by the elevation of pressure**, typically, and depending on the specific gas hydrate forming gas, pressures > 30 bar. It should be noted that the pressure elevation may need to be accompanied by a temperature correction (typically cooling/refrigeration) in order to adjust the temperature to a level that – for the specific gas hydrate forming gas – secures stability for the clathrates that have formed at the pressure level chosen.

Upon process **initiation by pressure elevation** the saline water that has been mixed with a specific gas hydrate forming gas undergoes a phase change from liquid gas hydrate slurry to solid gas hydrates. The **pressure increase (Initiator)** must be supplied to the system from an external source. The pressure elevation will bring the prevailing equilibrium of the system out of balance and, in response, the system will strive towards a new equilibrium between liquid slurry and solid gas hydrate phase (ice like crystals) by letting certain molecules of the system undergo a phase transition. The **driving force** for the transfer of molecules of the gas hydrate slurry between liquid phase and solid gas hydrate phase is the **chemical potential difference** (or the

difference in Gibbs energy) of all participating molecules in each phase. The Gibbs energy, which depends on temperature, pressure and number of molecules of each component in the two phases, decreases as the system moves toward a new stable state. The driving force of the process stops, when the Gibbs energy reaches its minimum at equilibrium.

Separation Principle

It is the nature of all crystals that impurities are excluded from the crystals' structures as they grow [12]. Just like Freeze Desalination (FD), Gas Hydrate Desalination (GHD) is enabled by a phenomenon of nature: Repelling of foreign particles (here: salt ions) upon formation of ice-like clathrate solids [7,12].

As mentioned above, clathrates - due to their dominant water content - physically resemble ice crystals. Similar to Freeze Desalination, the natural phenomenon of **selective (gas hydrate) crystal formation under rejection of salts** is the **separation principle** of gas hydrate desalination. In other words, a physical phase coupled with an exclusion of ions by the hydrogen bonding of water molecules during hydrate formation is the core of the HBD process [7, 9, 13].

Process

Figure 3 illustrates an exemplary gas hydrate desalination process in which liquid water is transformed into solid hydrates while repelling dissolved salts from the liquid phase.

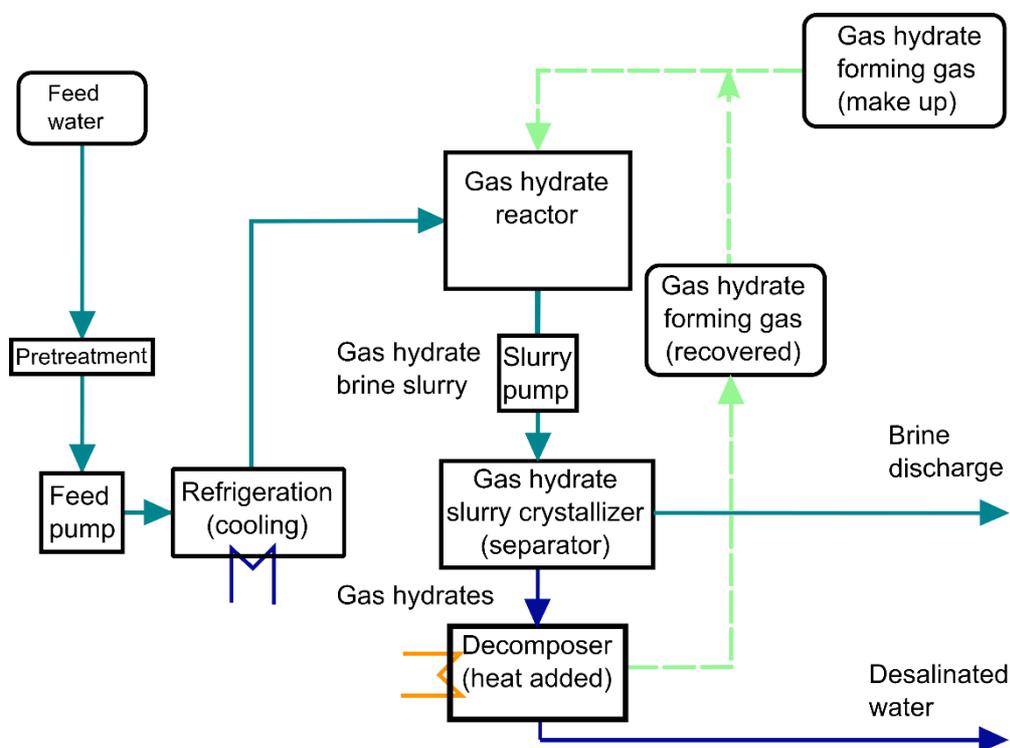


Fig. 3. Gas Hydrate Process

A gas hydrate desalination process can be considered being much like a direct contact freeze desalination process, in which the hydrate forming gas is brought into direct contact with saline water. As shown in Figure 3, a gas hydrate desalination process involves – in principle – the following steps [6]:

- gas hydrate slurry crystallization by establishing a pressure (and temperature) condition specific to the chosen gas hydrate forming gas
- separation of gas hydrates from brine by washing, and
- decomposition of gas hydrates into desalinated water and hydrate forming gas
- hydrate forming gas recovery

Before entering the saline water into the gas hydrate reactor, the saline water is pretreated and the heat content of the saline water may need to be removed by a heat exchanger, unless the process works with a gas that can generate stable clathrate conditions at ambient temperatures. As a further input, a specific gas hydrate forming gas is supplied to the reactor. Saline water (the host) and the “guest” gas are then thoroughly mixed in the gas hydrate reactor. A stirrer is used in the reactor to generate a good bonding between the water and gas molecules at the pressure and temperature conditions specific to the gas used [6, 14].

Low temperature and high pressure conditions are maintained in the reactor for given gas hydrate system. After the formation of hydrate slurry, it is transferred to the gas hydrate crystallizer via a hydrate slurry pump. In the crystallizer, this hydrate slurry is converted into crystalline solid structure gas hydrates with salt ions being repelled forming a concentrated brine. The concentrated brine is drained out from the crystallizer, while the crystalline solid structure of gas hydrates is transferred to a decomposer. In the decomposer the gas hydrate decomposes into gas and desalinated water by adding heat. The recovered gas is then added to the make-up flow of fresh gas hydrate forming gas; they jointly feed the process again [6, 14].

Motivation of Use

The motivation to use HBD for desalination is straightforward: the energy required to freeze water should be higher than to desalinate by gas hydrates, as it is not necessary (if at all) to refrigerate the saline water down to as much as freezing temperature; therefore, energy savings are the fundamental motivation. Also, low maintenance needs may be expected compared with other existing desalination techniques.

Nevertheless, HBD has not found its way into the desalination market as of today. Gas hydrate desalination encounters similar problems in practice as Freeze Desalination. In particular, separating hydrate crystals from the concentrated brine and the deletion of dissolved hydrate forming gas from the desalinated water are still a struggle [13]. Furthermore, salt removal efficiencies need further improvement to compete with other desalination techniques. As an example, it was observed that CO₂ as a gas hydrate forming gas is more suitable than CH₄ for the HBD process. In a CO₂ based gas hydrate process, 71 % – 94 % of each cation was removed and 73 % – 83 % of each anion was removed. In any case, Gas Hydrate Desalination would be more economic if operated in colder regions of the world. Gas hydrates may also play a bigger role in the future as a means of gas storage in the form of clathrates, and, thus, may become an interesting alternative energy source [11].

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4.3.2 Freeze Desalination (FD)

Detlef Taprogge

Freeze Desalination (FD) is a technique to separate water from salts

- by partial liquid to solid phase change initiated by the withdrawal of heat (cooling to freezing point), and
- subsequent physical separation of solids (ice crystals) from liquid (brine), and
- further phase change of solids (ice crystals) to liquid stage (desalted water) by “thawing” or “melting” (addition of energy) [1-2].

It should be noted that only a fraction of the salt water - typically less than 15 % - is transformed to ice at a time, reason for which we refer to a „partial“ liquid to solid phase change; the remaining, non-frozen liquid takes up the salt ions and will enrich the brine in as much as new ice crystals are formed.

It should also be noted that “thawing” and “melting” are not identical terms, even though in both cases heat needs to be supplied to revert from solid to liquid stage. In the case of “thawing”, energy is added by heat exchange with the environment, in the case of “melting”, heat is actively added.

Driving Force and Initiator

Freeze Desalination is **initiated by the withdrawal of heat**. The **initiator** of the FD process, therefore, is a **temperature change (cooling to freezing point)**. Interestingly, and as can be seen from Figure 1, the phase change of water to ice requires significantly less energy (enthalpy of freezing) than the phase change of water to steam (heat of vaporisation). More precisely, the energy consumptions differ by a factor of 6,7, letting freeze desalination appear – ceteris paribus – to be a very attractive alternative of desalination in terms of energy cost. This does not mean, however, that Freeze Desalination is a thermodynamically more efficient technique; it only means that the energetic cost in phase transfer, given by the thermodynamic laws, are lower in the freezing case [3].

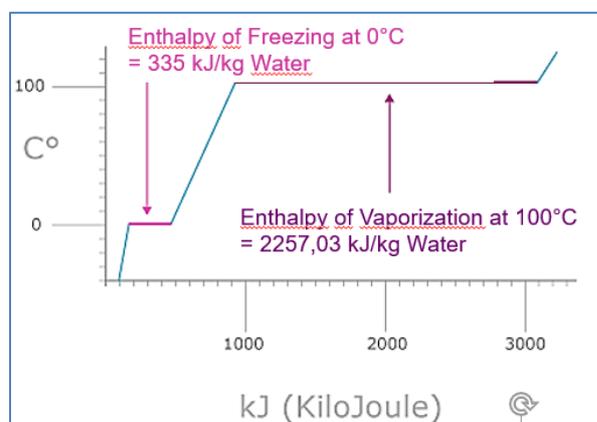


Fig. 1. Pure water properties – enthalpy of vaporisation and freezing

There is one more important phenomenon when considering saline water instead of pure water, which is known as “Freezing Point Depression”, i.e. a drop in the freezing temperature of a substance to be frozen which occurs when another non-volatile compound (e.g. salt) is added. As shown in Figure 2, the solution then has a lower freezing point than that of the pure solvent.

While pure water freezes at 0 °C, conventional seawater with 35.000 ppm (3.5 % salinity) for example, will only begin freezing at -1.9 °C. Thus, for any freeze desalination process, in order to recover 50 % as pure water from seawater, refrigeration to -3.8 °C is required to initiate the process [3].

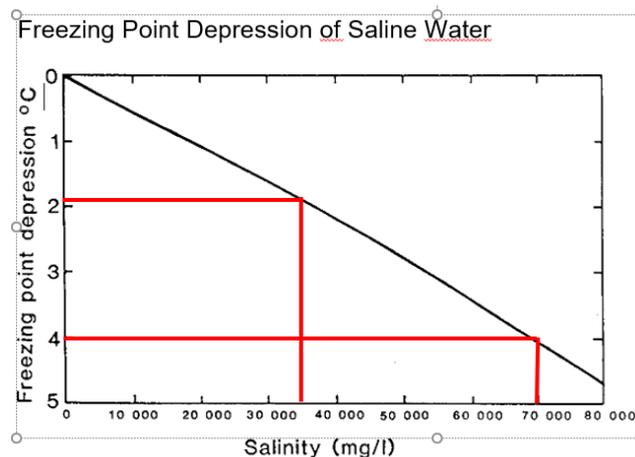


Fig. 2. Saline water - freezing point depression [3]

Upon **process initiation** by creating a **temperature difference (Initiator)** the saline water – being a mixture of water (as the solvent) and soluble salts (solutes) – is cooled to its freezing temperature and then freezes at constant pressure and temperature. The heat of freezing must be supplied to the system from an external source. The withdrawal of heat (cooling) has brought the prevailing equilibrium of the system out of balance and, in response, the system strives towards a new equilibrium between fluid (water) and solid phase (ice) by certain molecules of the system undergoing a phase transition. The **driving force** for the transfer of molecules of each constituent of the solution between the water phase and the ice phase is the **chemical potential difference** (or the **difference in Gibbs energy**) of the constituents’ molecules in each phase. The Gibbs energy, which depends on temperature, pressure and number of molecules of each component in the two phases, decreases as the system moves toward a new stable state. The driving force of the process comes to an end when the Gibbs energy reaches its minimum at equilibrium.

Separation Principle

There is a striking difference between liquid water and ice in terms of salt solubilities. On one hand, water is an excellent solvent which is capable to dissolve inorganic salts like NaCl. On the other hand, salts are almost insoluble in ice [4]. In fact, it is the nature of all crystals that impurities are excluded from the crystals’ structures as they grow [2]. Freeze Desalination is, therefore, made possible by an important phenomenon of nature: Repelling of foreign particles upon formation of ice crystals [2]. The natural

phenomenon of **selective (or fractional) ice formation under rejection of salts** is the **separation principle** of Freeze Desalination. For temperatures above the eutectic point of a salt, e.g. $-21.1\text{ }^{\circ}\text{C}$ for NaCl, the solutions freeze as neat ice with salt ions being rejected into the unfrozen part of the system. As the freezing process progresses, a salt concentration gradient as well as a temperature gradient establish across the freezing front. This leads to macroscopic instabilities due to which an originally planar freezing front becomes corrugated and eventually collapses, leaving behind pockets of unfrozen concentrated brine. Still, a large amount of salts is rejected from the ice region [4].

Process

Freezing of salt water can be carried out in many ways. As shown in Figure 3, any Freeze Desalination process involves in principle three discrete steps:

- ice formation/crystallization by heat removal (freezing) from saline water,
- separation of ice from the brine (by washing), and
- melting of the ice [2].

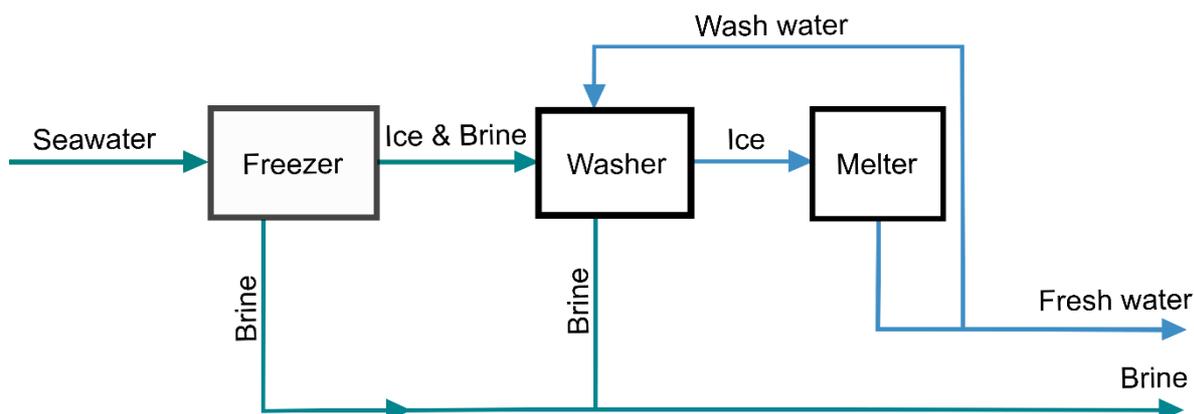


Fig. 3. Diagram of basic freeze desalination process [5]

As only a fraction of the incoming saline water is transformed in the freezer to ice at a time, remaining brine will be released from the freezer. Also, brine will be separated from ice in the washer. After melting the ice in the melter, a fraction of the fresh water gained will be branched off for reuse in the washer.

Literature describes two major variants of Freeze Desalination [2]:

- **Direct contact freezing**, whereby a liquid refrigerant such as butane, which will not mix with water, is brought into direct contact with saline water and is vaporised. In the freezer, the liquid refrigerant, which is initially maintained at high pressure, is dispersed into the seawater by spraying nozzles. The refrigerant then evaporates due to the lower pressure in the freezer (and expansion through the nozzle) and the evaporation of the refrigerant cools the seawater to below its freezing point and causes the formation of ice crystals. The ice-brine slurry formed is then pumped to a washer, where the ice is separated and cleaned by the wash water and then transported to the melter as shown in Figure 4. The

refrigerant vapour formed in the freezer is compressed and thus increases the temperature. This elevated temperature vapour is then used to melt the ice in the melter. Any refrigerant vapour which remains is then compressed and condensed to high pressure and is recycled to the freezer to start the process again. Figure 4 also shows how cooled water and brine is used for cooling the incoming saline water for partial heat recovery.

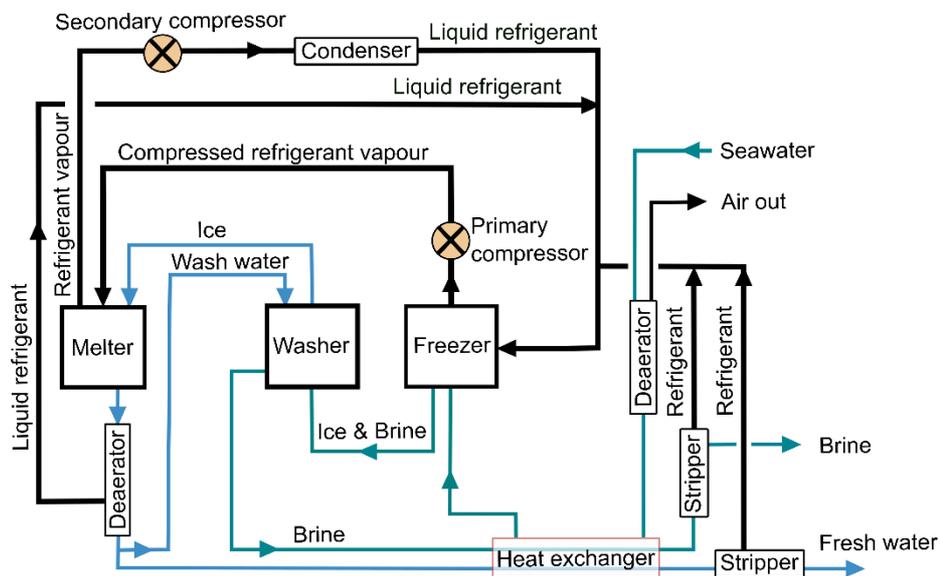


Fig. 4. Direct FD process [6]

Operating at around $-5\text{ }^{\circ}\text{C}$, this method has low energy cost and is compact, however requires a precise refrigerant with a normal boiling temperature (at ambient pressure) below $-4\text{ }^{\circ}\text{C}$ [5] and which is immiscible, non-toxic, chemically stable and inexpensive.

- **Indirect contact freezing**, whereby the saline water does not come into contact with the refrigerant directly; the ice is formed on a surface by refrigeration or other methods [2]. The saline water is first transported through a heat exchanger to reduce its temperature and then enters the freezer for fractional crystallization. The ice-brine slurry is transported to the melter where ice is melted by the heat released from condensation of the compressed refrigerant. A small portion of the product water is bypassed to the wash brine contamination from the ice crystals and the main portion is passed to the heat exchanger to cool down the feed saline water. The brine from the washer is returned to the heat exchanger to cool the feed saline water and is then discarded.

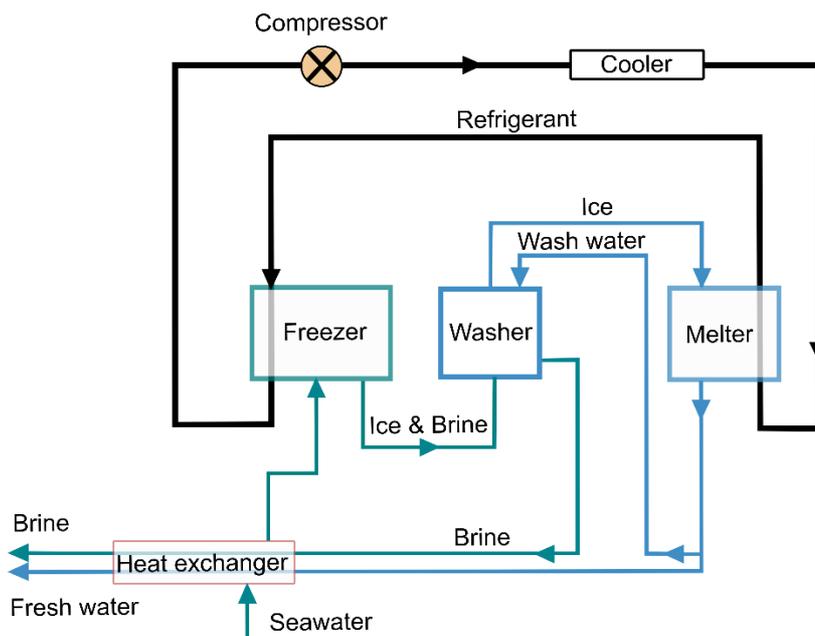


Fig. 5. Indirect FD Process [2]

Despite its simple process, this variant of desalination has an unfavorable energy consumption compared with the direct FD process. This is due to the lower heat exchange surface and the resistances of the metallic heat transfer surface between refrigerant and saline water which also leads to higher capital expenditure.

Motivation of Use

At first sight, the motivation to use the Freeze Desalination technique (FD) for desalination is simple, but compelling: the energy required to freeze water is (in theory) about 6 to 7 times lower than the energy required for vaporising saline water.

Also, the low operating temperature support a lower degree of fouling and scaling issues compared with other thermal or membrane desalination techniques, thus limiting intensive pretreatment and chemical consumption. An interesting side aspect of FD is the possibility of exploiting the low operating temperatures of this technique for cooling purposes.

However, FD has not found its way into the desalination market as of today. Literature contributes this to the complexity of the Freeze Desalination process. In particular the difficulties of separating ice crystals from brine generate mechanical complexity and operational cost which are not competitive with state-of-the-art desalination techniques [1, 6]. Freeze Desalination technique has, however, found particular applicational ground in the beverage industry for the purpose of concentrating liquids [1].

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4.4. Selective Membrane Permeability

4.4.1 Reverse Osmosis (RO)

Dr. Markus Spinnler

Separation Principle

Reverse Osmosis (RO) is a technique that uses a **semipermeable membrane** to remove pure water from saline solutions. The term “semipermeable” describes a selective permeability for water molecules (high permeability) and for dissolved salt ions (low permeability). In simple terms: by applying favourable boundary conditions, pure water will pass across an RO membrane, while the majority of salt ions will be held back.

Driving Force and Initiator

In order to tap into the operation principle of osmotic processes, it is crucial to understand their universal driving force, which is the difference in chemical potential across a membrane. The chemical potential is basically depending on three parameters: it will decrease with rising *salinity* and *temperature*, and it will increase with enhancing *pressure*. Following the difference in chemical potential from high to low, pure water starts to pass across the membrane. With this knowledge, it becomes possible to adapt the chemical potential to the needs of the application on hand by adjusting salinity (like in “Engineered” or “Forward” Osmosis EO) or pressure (like in Reverse Osmosis RO). [1-3]

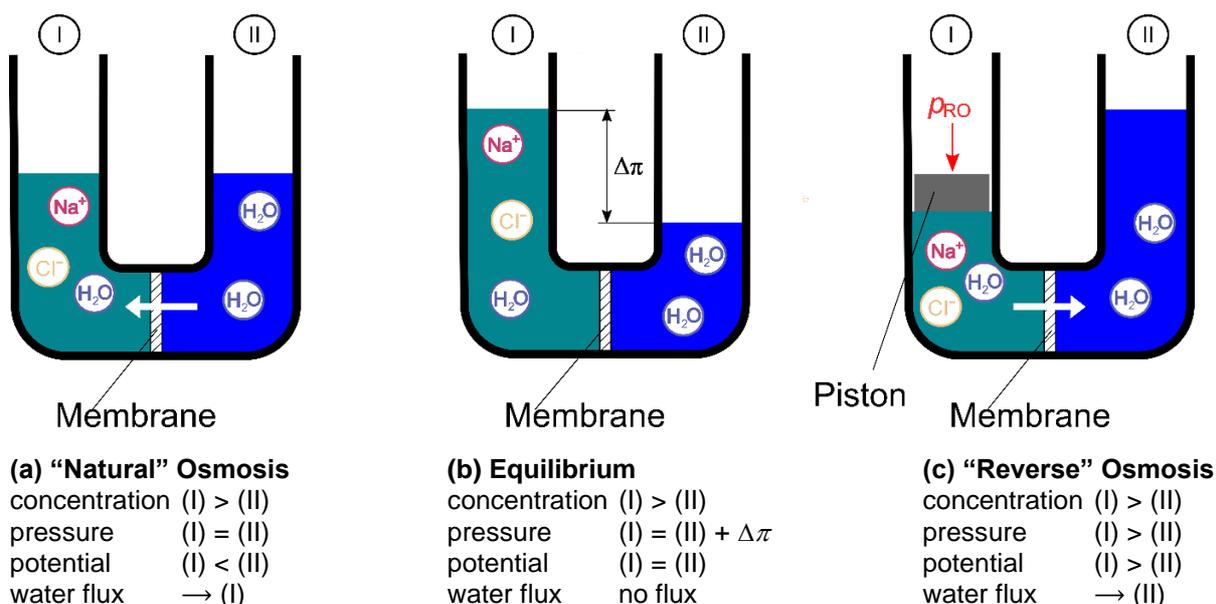


Fig. 1. Osmotic Cell with (a) “Natural” Osmosis, (b) Osmotic “Equilibrium” and (c) “Reverse” Osmosis. Adapted from [3].

Figure 1 illustrates the fundamental principle of trimming the chemical potential. In Figure 1a, the salinity of the solution on side (I) of the membrane is higher than that on side (II). As a result, the chemical potential on side (I) is lower than that on side (II) and a pure water flux towards side (I) is building up. As this effect can be observed in numerous examples in nature, it is called “Natural” Osmosis. For instance, in food conservation, adding salt will dehydrate fish or meat, making them more durable. In the example on hand, the rising water column on side (I) is establishing two effects: first, a static pressure difference between sides (I) and (II) is arising and second, the solution on side (I) is being diluted. Both effects are increasing the chemical potential on side (I), until an equilibrium between (I) and (II) is reached. This phenomenon is shown in Figure 1b, where the static pressure difference between sides (I) and (II) equals the so-called “Osmotic Pressure” difference $\Delta\pi$.

As illustrated in Figure 1c, the chemical potential as well as the “natural” osmotic process can be reversed by applying an external pressure to side (I). The essential prerequisite is to overcome the osmotic pressure difference $\Delta\pi$ across the membrane. The chemical potential on side (I) is now higher than that on side (II). “Reversing” the chemical potential by applying a high pressure on side (I) results in building up a pure water flux from side (I) – the feed water – to side (II) – the permeate.

In RO, the application of a sufficient pressure difference across the membrane with **pressure elevation** on the feed side can therefore be identified as the main initiator establishing a pure water mass flux from feed to permeate. In membrane-based techniques, permeate denotes the desalinated water which is the product in standard desalination applications.

RO systems are operated isothermally with equal temperatures on both sides of the membrane, thus temperature effects are negligible. However, it is important to mention that in reality, RO membranes are not ideally semipermeable. Besides the required water flux, there will always be a comparably small salt flux across the membrane. While the water flux is pressure-driven, the salt flux is concentration-driven. Hence, it will build up independently of the applied feed pressure and spoil the permeate quality. As a result, special attention has to be paid when aiming for ultra-pure water generation, in low part load conditions or after shutdown of an RO plant. In conventional seawater desalination, the product water salinity will always be higher than in evaporation/vaporisation-based systems. [1, 3-4]

Please note, that against a widespread perception, RO is by no means a filtration technique but is commonly treated as a diffusion process through the closed active layer of a semi-permeable membrane [1, 4-5].

Process

The general setup of a medium- to large-sized RO plant consists of basically four main components, as is illustrated in Figure 2.

(1st) In order to protect the vulnerable RO membranes and to guarantee a tolerable permeate quality, a pretreatment step is needed. Depending on the feed water quality, solids and colloids (filters, coagulation, flocculation) as well as toxics like Boron are removed, biofouling is mitigated (biocides, UV exposure, Micro- or Ultrafiltration) and anti-scalants are added. [6-9]

(2nd) The pressure and hence chemical potential difference is applied by a series of electrically driven high-pressure pumps on the feed side. To overcome the osmotic pressure difference and pressure losses of the hydraulic system, a feed pressure of about 6'000 kPa is necessary for conventional seawater desalination. The pressurised feed water is passed over the membranes and a pure water flux across the membrane is established. The pressurised brine at the feed water outlet contains a considerable amount of potential energy, which is recovered by an Energy Recovery Device (ERD). The ERD can be an Energy Conversion System, a Pressure Exchanger or Intensifier or a Pressure Storage. In order to supply the required feed inlet pressure and depending on its characteristics, it is combined with a low-pressure feed or high-pressure booster pump, as shown in Figure 2. The permeate side remains pressureless. [3, 10-12]

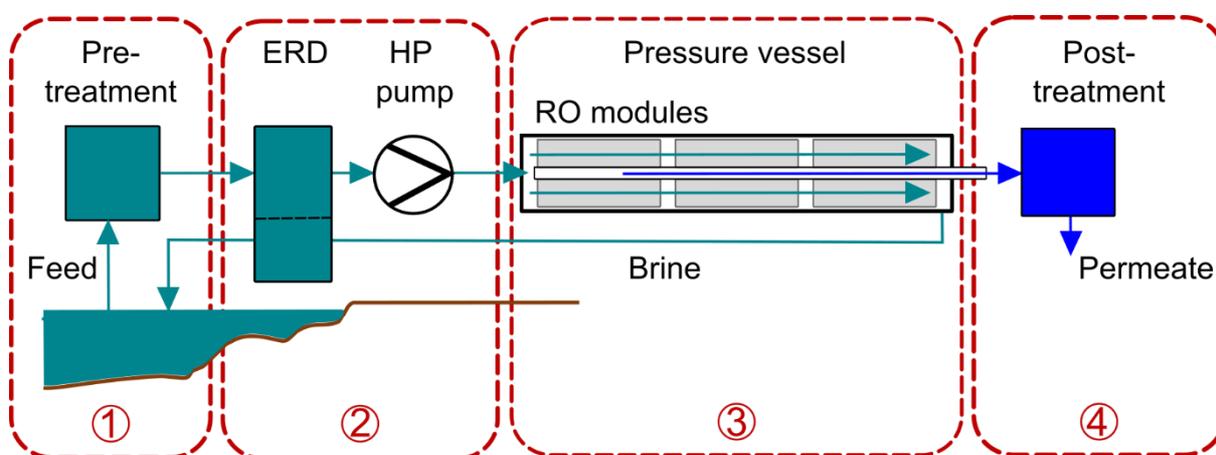


Fig. 2. General setup of a medium- to large-sized RO plant with four main components. Adapted from [3].

(3rd) the very heart of an RO plant. In the majority of technical applications, the RO unit is built out of so-called “spiral wound” membrane modules, that basically consist of several membrane envelopes wrapped around a central permeate pipe. Typically, several RO membrane modules are installed in a pressure vessel, which in turn can be interconnected serially and/or parallelly in a modular system. In standard seawater desalination, the so-called “fir-tree” arrangement is the preferred option. Here, a diminishing number of parallel pressure vessels forms stages which are connected in series. [1, 13]

(4th) In the case of potable water production, the post-treatment basically removes harmful contaminants like Boron in the permeate, adjusts the pH-level, re-mineralises the desalinated water (if needed) and disinfects the permeate mainly due to possible contamination from the hydraulic system. [3, 14]

Motivation of Use

The main advantage of the RO technique is its extremely low Specific Energy Consumption (SEC) of 2.2 – 5 kWh/m³ permeate (for seawater desalination), which is so far unrivalled by any other commercially available desalination technique [10, 12].

A further advantage is its very versatile and flexible applicability to a large variety of water treatment and desalination tasks.

The design of RO plants is based on pre-manufactured RO membrane modules, which can be built up from very small (a few litres per day for emergency purposes, for instance in life rafts e.g. [15]) to very large (several hundred thousand cubic metres per day in central water works, e.g. [16]). Due to its low *SEC*, the mass manufacturing of membrane modules and the applicability of standardised braces and pumps, RO is comparatively cost-efficient [17]. Since 2010, RO is the most commonly applied technology in the global desalination market [18].

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4.4.2 Pervaporation (PV)

Dr. Markus Spinnler

Separation Principle

The main peculiarity of the Pervaporation (PV) technique is a superposition of two separation principles: 1st, it uses a semipermeable membrane and 2nd, the permeate is selectively vaporised [1-3]. The term “semipermeable” describes for instance a selective permeability for water molecules (high permeability) and for dissolved salt ions (low permeability). In simple terms: by applying favourable boundary conditions, pure water will pass across a PV membrane, while the majority of salt ions will be held back. The subsequent separation of pure water and the remaining salt ions is due to a substantially lower vapour pressure of salt compared to water, see Annex 1. Thus, at a given temperature and pressure, pure water will vaporise while the salt ions remain dissolved in the liquid brine.

With this background, it can be said that PV is a combination of *permeation* and *vaporisation*. Due to the double separation step, a very good separation result can be achieved [2, 4].

As the initial separation process is due to the selectivity of a membrane, PV is classified under the category of **selective membrane permeability**. Selective vaporisation plays an important but nevertheless secondary role [1].

Driving Force and Initiator

The fundamental driver of PV systems is the establishment of (1st) a difference in chemical potential of the required component across the membrane and (2nd) a difference in vapour pressures of the required component in the permeate and near the condenser [1-2]. Therefore, it can be said that the permeating component of PV is working analogously to systems relying on solution-diffusion membranes like in Reverse Osmosis (RO) and Engineered (e.g. Forward) Osmosis (EO) [1, 4].

However, solving the equations for the chemical potential of the required component in the PV case, it becomes obvious that the ratio of the saturation vapour pressure on the feed side and the partial vapour pressure on the permeate side plays a decisive role. Hence, especially for PV, the chemical potential difference is triggered by a difference in vapour pressures across the membrane [1-2]. For a detailed explanation of vapour pressures please refer to Annex 1.

The influencing factors for building up the required vapour pressure difference are: reducing the feed *salinity*, increasing the feed *temperature* and finally reducing the permeate *pressure*. According to [1-2], the main initiator driving permeation in PV systems is a **pressure reduction** on the permeate side. Heating or pressurising the feed water can only help to maintain favourable operation conditions.

Different from RO and EO, selective vaporisation is setting in on the permeate side of the membrane. However, this is a similarity to Membrane Distillation (MD, VMD): the feed side is working in the liquid phase, while the permeate side is gaseous (even

though in MD/VMD evaporation/vaporisation happens on the feed side and the gaseous phase is passing across the membrane).

In desalination applications, the required component is pure water. Due to the absence of Non-Condensable Gases (NCG), the separation process on the permeate side can be classified as **vaporisation**.

Process

Figure 1 is showing the principal set-up of a PV system. As was already described, the permeate flux is forced across the membrane by an applied vapour pressure gradient or in other terms by a difference in chemical potential.

Reaching the permeate side of the membrane, the required component is instantaneously vaporising. Due to the difference in the vapour pressure near the membrane and the saturation vapour pressure at condensation temperature, it will diffuse towards the condenser, where it is liquefied and collected. The heat of condensation can be recovered e.g. for preheating the feed water.

In most applications, the required heat of vaporisation on the backside of the membrane is provided by heating the feed water [1]. Note, that heating the feed water is not the driving force of the process, but merely a method to stabilise the feed temperature and thereby to maintain the process-initiating vapour pressure gradient. Furthermore, it has to be noted that the low pressure on the permeate side is established by the water vapour uptake of the condenser. The pressure level is defined by the condensation temperature and the corresponding saturation vapour pressure. An additional vacuum pump is only needed to remove NCG, which might be set free from the permeate and which drastically reduce the condensation efficiency [5].

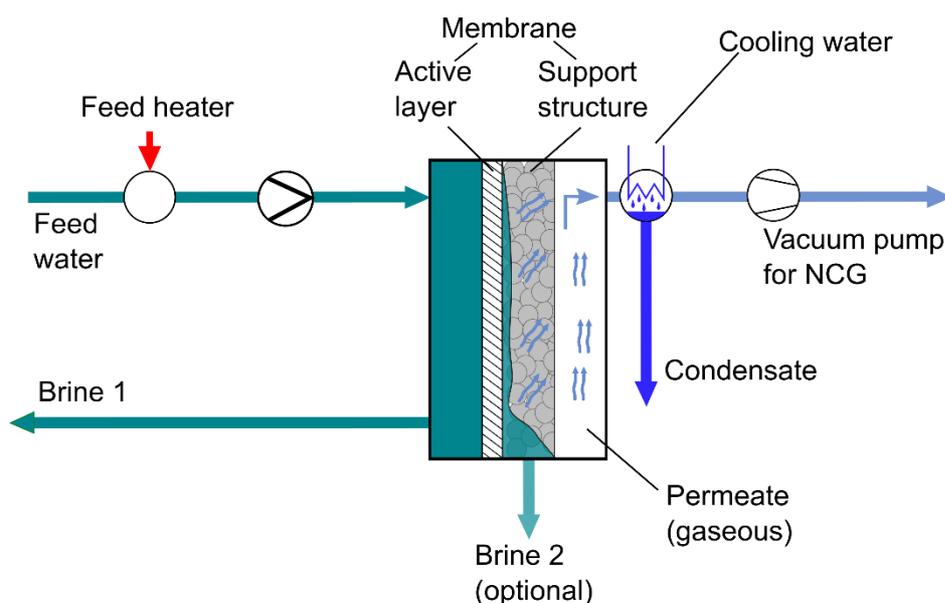


Fig. 1. Schematic set-up of a PV system, adapted from [1].

As in RO and EO, PV membranes have a closed active layer and are working on the principles of solution and diffusion of the permeate. Several membrane materials have been evaluated for the PV process. The main representatives are hydrophilic Polyvinyl Alcohol (PVA), hybrid PVA maleic acid and silica membranes [4]. Hybrid membranes show a high water flux and up to 99.9 % salt rejection [6]. Today, most of the PV applications are built up from flat-plate stainless steel membrane stacks. Similar to RO and EO membranes, the PV membrane performance suffers from both concentration and temperature polarisation effects [1].

Even though RO and PV are showing equal separation potential, the concentration and thereby the Recovery Ratio (RR) in PV can be substantially higher. On the one hand, PV avoids the problem of osmotic pressure. On the other hand, this comes at the cost of providing the heat of vaporisation and to remove it at a much lower temperature level, yielding difficulties in heat recovery [1].

Motivation of Use

Due to the double separation process, PV is an ideal method for partitioning volatile components of the feed water. A further main application is the treatment of azeotropic mixtures, where the saturation vapour pressure is gliding with decreasing concentration and which cannot be separated by conventional distillation processes [1]. In desalination applications with difficult feed water qualities, nearly 100 % salt rejection can be achieved [6 - 7]. PV has also been implemented for irrigation where a network of subsurface tubular membrane pipes is filled with saline water. Thus, water vapour can diffuse through the pipe walls, while the contaminants are retained within the pipes [8].

The major advantages of PV are that no substantial pressure has to be applied and that it offers a high rejection capacity even for RR near 100 %. Compared to other thermally driven desalination systems, lower operating temperatures can be realised and no limitation on feed water concentration is reported up to now [1, 6]. Due to pressure reduction as driving force, extremely low values for Specific Energy Consumption of down to 2 kWh/m³ are reported [9], however this strongly depends on application and process design.

The main disadvantage of the process is the low achievable water flux [9]. The feed water temperature is a crucial parameter due to the increase in diffusivity and reduction in viscosity with temperature [4]. In addition, membrane thickness and permeability are important parameters determining the performance. Up to now, only few pilot-scale data have been published, so PV is still considered to be one of the emerging desalination techniques [6].

Neither MD nor PV technique has any commercial application in desalination, although PV has been commercially used in solvent dehydration and the removal of organics from water. The availability of high-performance commercial membranes is the most important constraint in the development and application of PV. On the other hand, MD is limited by the membrane wetting issue and the module and engineering design in a scaled up application [4].

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4.4.3 Engineered Osmosis (EO) as a collective term for Forward Osmosis (FO), Direct Osmotic Concentration (DOC), Osmotic Dilution (OD) and Pressure Retarded Osmosis (PRO)

Dr. Markus Spinnler

As the well-known Forward Osmosis (FO) process is only one representative of a whole family of related technologies (FO, OD, DOC and PRO), the term “Engineered Osmosis” (EO) as introduced by Mc Cucheon and Huang [1] will be used as an umbrella in the following discussion.

Before diving into the separation and operation principles of EO, it is important to point out that EO does not represent a stand-alone desalination technique but is merely a pretreatment step for a subsequent desalination stage. The main targets of applying EO are to reduce the Specific Energy Consumption (SEC) of the desalination system by Osmotic Dilution (OD) of the feed water or to ensure an optimal separation result when dealing with problematic feed water qualities (FO). Other EO technologies like Direct Osmotic Concentration (DOC) are mainly applied in process engineering. Pressure Retarded Osmosis (PRO) aims at electrical power generation in a stand-alone power plant or to build up pressure in Reverse Osmosis (RO) set-ups. [1-2]

Thus, it could be said that in providing information on EO, the authors deviate from their original goal to focus just on the core of desalination processes, see Section 2.1.2. Nevertheless, for the sake of comprehensiveness and to reflect the growing awareness for EO applications in the desalination community, some core aspects of EO shall be discussed here.

Separation Principle

EO is a “natural” osmosis process working in an artificially created environment. It uses a **semipermeable membrane** to transfer pure water between two saline solutions. The term “semipermeable” describes a selective permeability of the membrane for water molecules (high permeability) and for dissolved salt ions (low permeability). In simple terms: by applying favourable boundary conditions, pure water will pass across an EO membrane, while the majority of salt ions will be held back.

Driving Force and Initiator

The universal driving force of EO processes is the application of a chemical potential difference across a semi-permeable membrane. The chemical potential difference is established by employing two different solutions with either different concentrations or different chemical properties of the solute. Following the chemical potential gradient, a pure water flux across the membrane will set in from high (feed solution) to low chemical potential (draw solution).

The chemical potential is basically depending on three parameters: it will decrease with rising *activity*, and it will increase with rising *temperature* and rising *pressure*. Note that *activity* is a summary parameter for considering the influence of concentration (in our case: *salinity*) and the chemical properties of the *solute*. In other words, the chemical potential of the solution will decrease with increasing *salinity* and/or with the application of an alternative *solute*. With this knowledge, it becomes possible to adapt the chemical potential to the needs of the application on hand by adjusting salinity or solute as in EO, whereas in RO it can be adapted by adjusting pressure. [2-5]

Figure 1 illustrates the fundamental principle. In Figure 1 (left), the salinity of solution (I) is higher than that of solution (II). As a result, the activity and thereby the chemical potential on side (I) is lower than that on side (II) and a pure water flux towards side (I) is building up. This corresponds to the set-up of an FO process. Figure 1 (centre) is basically showing the same set-up but with a different application. Pure water is flowing from high (II) to low chemical potential (I). Depending on the target, the product is either the dilution of solution (I) – an OD process – or the concentration of solution (II) – a DOC process. Due to the rising water column on side (I), a static pressure difference is building up, see Figure 1 (right). The chemical potential on side (I) is increasing due to rising pressure and falling concentration and that on side (II) is decreasing due to the opposite effects until an equilibrium is reached. The equilibrium pressure difference between (I) and (II) is called “Osmotic Pressure Difference” Dp and can be used e.g. for hydropower generation. [2-5]

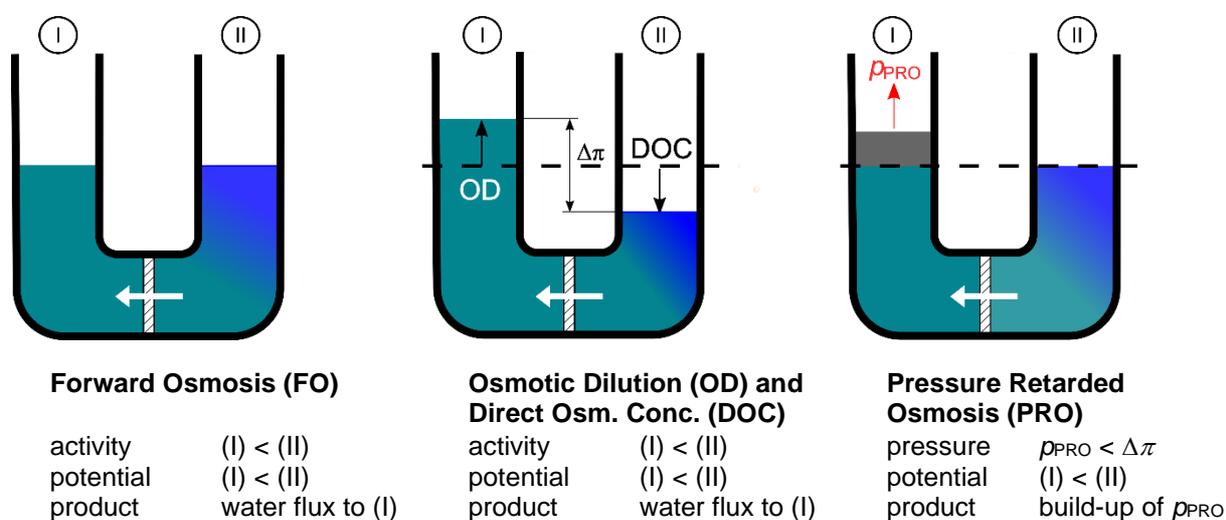


Fig. 1. Osmotic cell in Forward Osmosis (left), Osmotic Dilution / Direct Osmotic Concentration (centre) and Pressure Retarded Osmosis (right) mode. Adapted from [5].

By playing with either choice of solute or higher solute concentration in solution (I) or (II), the chemical potential difference and thus the osmotic pressure difference can be adapted to the application on hand. Like this, the pure water flux can be forced in one or the other direction. Finally, it can be said that in EO systems being operated isothermally with equal temperatures on both sides of the membrane, temperature effects are negligible.

As a result of these considerations please note that in the case of EO and RO the difference in chemical potential which is the universal driving force of almost all desalination techniques can be expressed as Osmotic Pressure Difference Dp [3]. As all desalination techniques working with selective membrane permeability are making use of pressure differences, it appeared reasonable to the authors to determine the **Osmotic Pressure Difference** as main initiator driving the pure water mass flux in EO.

Process

As was already pointed out, EO includes a bunch of technologies [1] which can be summarised as:

- (1) Forward Osmosis (FO) → where the water flux can be a purified water stream,
- (2) Direct Osmotic Concentration (DOC) → where the flux is discarded as waste,
- (3) Osmotic Dilution (OD) → where the diluted form of the draw solution is utilised directly,
- (4) Pressure Retarded Osmosis (PRO) → where the target is to build up kinetic or potential energy with the water flux.

In FO, saline water is the feed stream and an artificial draw solution is used on the other side of the membrane. Figure 2 (left) shows the basic set-up. Pure water moves from the feed into the draw solution, while the semi-permeable membrane retains the main part of solutes on both feed and draw side. Thus, pure water is separated from the feed solution without expending any energy except for feeding the water to the membrane at low pressure.

While the FO stage must be regarded as a pure pretreatment measure, the next step constitutes the actual desalination process. The now diluted draw solution has to be recovered in a secondary separation stage, whose energetic and economic cost is the main driver of process economics. That's why the choice of draw solute requires serious consideration [2, 6]. However, for applications with high fouling feeds, FO has the potential for a lower fouling and scaling propensity [7-9]. Thus, one popular strategy is to use domestic wastewater as FO feed to dilute seawater as feed for an RO system. In RO, a reduced feed salinity will drastically reduce the *SEC*. Anyway, the application of closed-cycle FO in seawater desalination has to be seen critically. Even with optimised draw solutions and the benefit of reduced fouling propensity, it is unlikely that FO-RO combinations can approach the *SEC* of direct seawater RO [10].

Being close relatives to FO, DOC and OD are more common in process engineering applications like food processing. In DOC, the concentrated feed solution is the product (cured meat and dried cod can be considered as original forms of DOC), while OD is e.g. used to prepare emergency provisions for military, expedition or humanitarian aid purposes. [11]

As is shown in Figure 2 (right), PRO harnesses the chemical potential difference caused by naturally occurring or engineered salinity gradients and converts it into electricity using a hydraulic pressure intermediate. Therefore, saline water is pressurised

to a level below its osmotic pressure by a pressure exchanger (PX). Like this, the osmotic flow is retarded and creates a resistance to generate work. The subsequent expansion of the diluted draw solution through a hydroturbine with generator set produces electricity. As an alternative, the elevated draw pressure can be directly used on the feed side of an RO plant. PRO systems can be arranged in an open (as shown in Figure 2) or closed cycle, where the draw solution would have to be recovered.

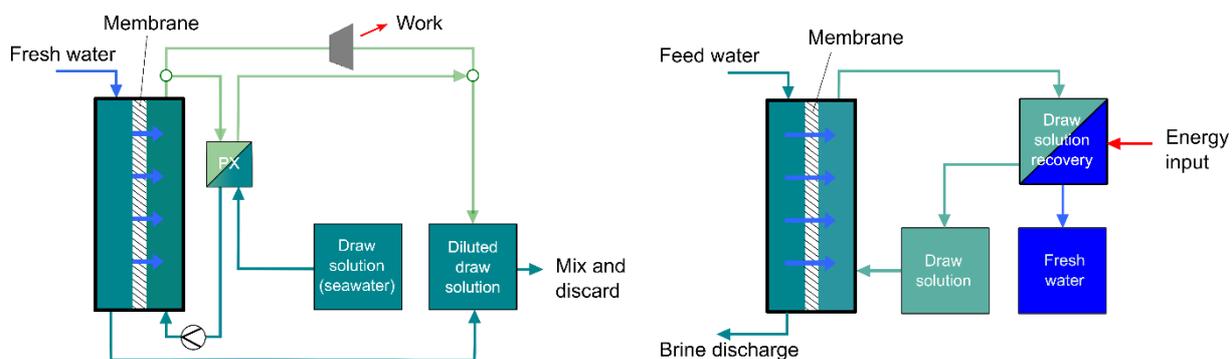


Fig. 2. General setup of an FO system (left) and an open-cycle PRO plant (right). Adapted from [1].

One of the difficulties in designing EO processes is the choice of an appropriate draw solution. The solute's function is not only to effectively drive the water across the membrane. It should also be chemically inert, show a minimal membrane crossover, be removable and recyclable and non-toxic. Depending on the application, suitable draw solute types can be inorganic or organic solutes (commonly inorganic salts), functionalised macromolecules like dendrimers, switchable polarity solvents, hydrophilic magnetic nanoparticles or polyelectrolytes. [1]

EO membranes are widely similar to RO membranes [2, 6]. As in RO, EO composite membranes consist of a support structure to withstand upcoming pressure differences and a closed, thin active layer to perform the separation process itself. A main difference is, that in EO (except PRO) no hydraulic pressure is applied and the support structure only has to withstand some minor system pressure losses of up to 1 bar. For this reason, EO support structures can be realised much thinner than in RO [7]. It is also important to recall, that the osmotic process through the non-porous active layer of the membrane is of purely diffusive nature – EO is by no means a filtration technology!

Finally, it should be mentioned, that due to the elevated solute concentration on both sides of the membrane, concentration polarisation (CP) issues are much more severe as in RO. Due to the fact that in EO, CP can also occur in the porous support structure of the membrane, the active layer should be oriented towards the side with the higher concentration or the higher fouling propensity. [1, 7]

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4.5. Selective Movement of Ions

4.5.1 Electrodialysis (ED) and Electrodialysis Reversal (EDR)

Detlef Taprogge

Separation Principle

Electrodialysis (ED) is a technique to separate salt ions from saline water whereby - under the influence of an electric field - ions are transferred through ion exchange membranes thereby creating two separate streams: an ion depleted stream (product water or dilute) and an ion concentrated stream (brine or concentrate). The process is initiated by applying an electric potential (voltage) difference to the saline solution [1-3].

For a deeper understanding of the fundamental principles of this desalination technique, it is helpful to take a closer look at the electrochemical impact on salt ions in a saline solution when exposed to an electric field:

Saline water contains positively charged ions (cations, e.g. Na^+) and negatively charged ions (anions, e.g. Cl^-). When a pair of electrodes is inserted into the saline water (see Figure 1) and an **electric potential difference** is applied (**Initiator**), an electric field is formed which lets the cations migrate towards the cathode and the anions in the opposite direction towards the anode. This phenomenon, i.e. **the selective movement of ions according to their charge** leading to a separation of salt ions from water is also referred to as **electrophoresis** or **electrophoretic mobility**, and represents the **fundamental separation principle** of ED and EDR [4].

This **separation principle** of salt ions and water is based on the capability of ions to move selectively according to their charge; in other words: positively (Na^+) and negatively charged salt ions (Cl^-) in aqueous solutions migrate towards electrodes of opposite charge.

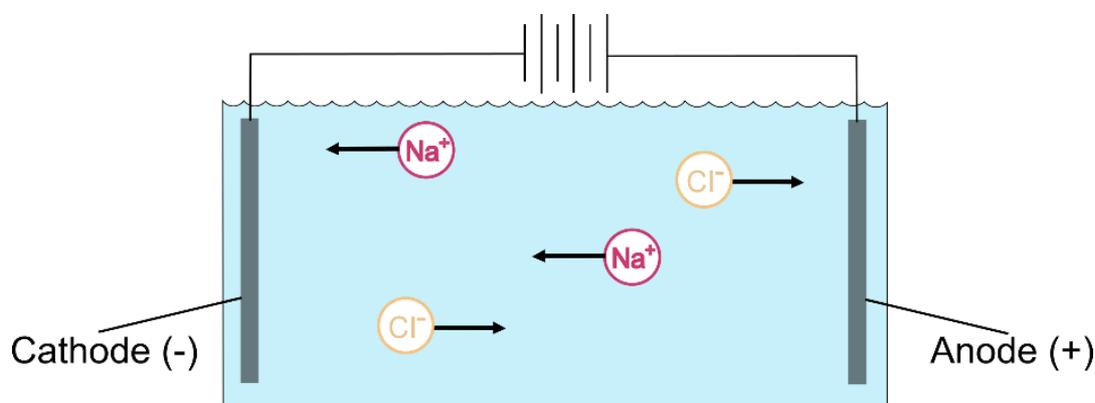


Fig. 1. Principle of electrophoresis

Driving Force

The driving force of the process is a **difference in electrochemical potential** which has been initiated by the application of an **electrical potential (voltage) difference (Initiator)** to the saline solution [4-6] The migration of ions to the electrode of opposite charge will continue until all constituents of the system have come to a new electrochemical equilibrium.

Apart from the initiating electrical field, an ED cell incorporates ion exchange membranes as a functional characteristic. The membranes can also be “permselective”, which means that only specific ions can move through the membrane [2]. As illustrated in Figure 2, there are two types of ion exchange membranes positioned in an alternating fashion between the anode and electrode:

- Anion permeable (or exchange) membranes (marked “A” in Figure 2), which are electrically conductive membranes that are water impermeable and allow only negatively charged ions (anions) to pass through, and
- Cation permeable (or exchange) membranes (marked “C” in Figure 2), which are electrically conductive membranes that are water impermeable and allow only positively charged ions (cations) to pass through.

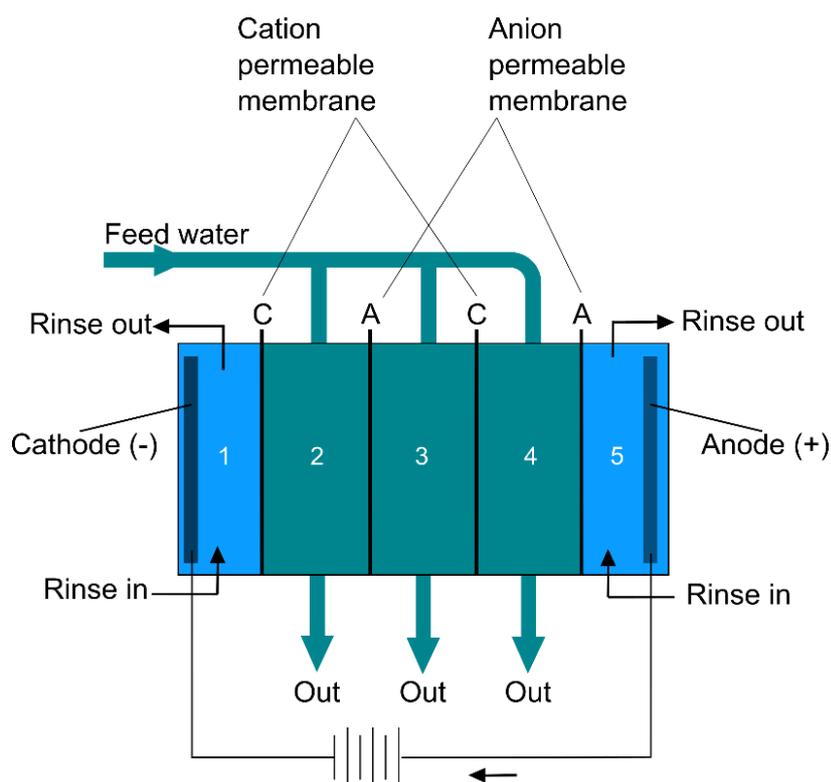


Fig. 2. ED Cell Structure

The spaces enclosed by a pair of neighboring membranes form watertight compartments (ED cells). In practice, however, there are a few hundred of such compartments adjacently positioned and separated from each other by alternating anion and cation exchange membranes forming a stacked structure (ED-stack) [3].

ED Process

In the simplified ED cell arrangement illustrated in Figure 2 and 3, the saline feedwater will be fed to the middle compartments 2 - 4. Compartments 1 and 5 do not participate in the desalination process. They are equipped with means of rinsing to avoid depositions on anode and cathode.

Figure 3 illustrates the movement of ions when an electric potential difference is applied to the ED cell.

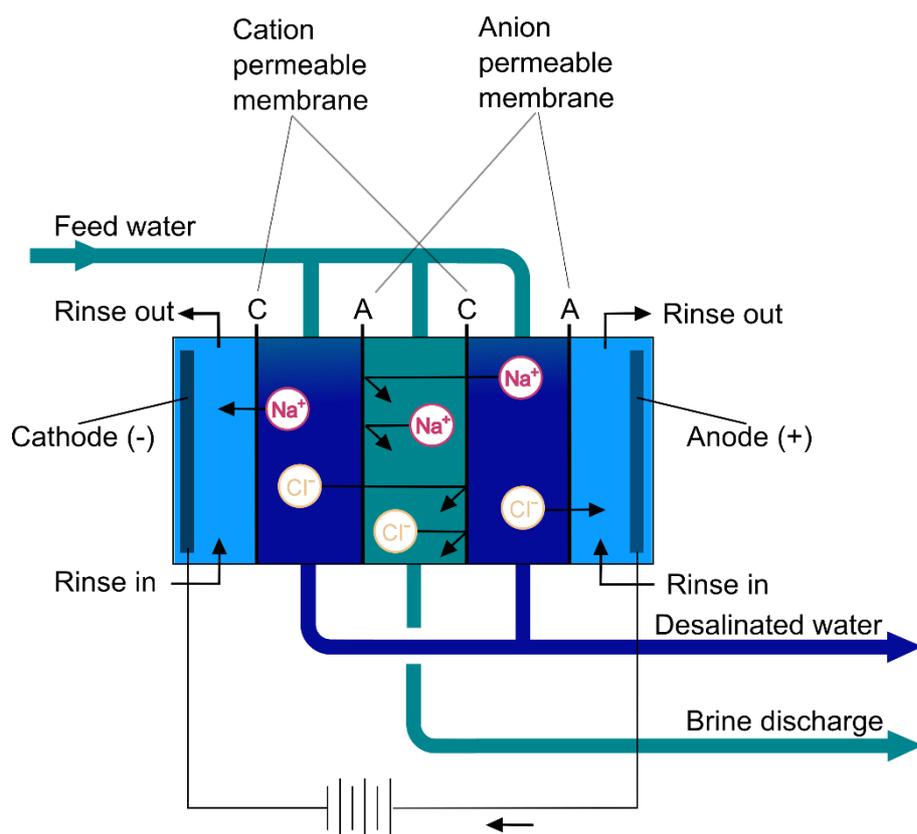


Fig. 3. ED Process adapted from [1]

As elaborated above, the ED process is initiated by applying an electrical voltage difference (**Initiator**). **Electrophoresis supported by the presence of ion exchange membranes** constitutes the **separation principle** of ED. The process of desalination is driven by an **electrochemical potential difference** which keeps ions transferring through those ion exchange membranes that permit ion transfer; only cations can pass through cation exchange membranes, and only anions can pass through anion exchange membranes [4].

As feed water is continuously pumped into the concentrating and the purifying compartments of the ED cell, these water streams remain constantly separated from each other. Consequently, ions migrate and concentrate in the concentrating compartments, from where they leave the ED cell as concentrated brine. Conversely, water leaving the neighboring departments which are depleted of ions will finally leave the ED cell as product water (also referred to as "dilute") [1]. The functional incorporation of ion-exchange membranes in ED cells enhances the fundamental separation mechanism of ED and leads ions selectively according to their charge into

the compartments that will finally discharge their flow as brine (concentrate), while other compartments will be depleted of ions and discharge their flow as product water.

As a result of the process, compartments 2 and 4 will be depleted from Na⁺ and Cl⁻ ions, the effluent of which thus becoming desalted product water (also called dilute), while compartment 3 continuously accumulates Na⁺ and Cl⁻ ions, the effluent of which thus becoming a brine stream with elevated salt concentration (also called brine or concentrate) [4].

EDR Process

Electrodialysis reversal (EDR) is a mode of operation of electrodialysis, in which periodically the direction of the hydraulic flows and the polarity of the electric field is reversed. EDR works the same way as ED, except that the electric flow is reversed, typically two to four times per hour or when a minimum conductivity is reached in one of the compartments [1, 7].

The reversal of the electric field also reverses the ion flux. The periodic reversal of the direction of electric current through the membrane stack helps prevent on membrane scaling and fouling [1] thus improving stack performance.

Motivation of Use

The natural electrical conductivity of water allows ED and EDR processes to be applied to a wide range of water treatment objectives [1, 8]. Like Reverse Osmosis (RO), reduction of TDS to meet drinking water standards is the most common application. In both RO and EDR systems, the energy required to concentrate brine is dependent on the TDS. The more dissolved salts are present in the water, the more expensive water treatment operations become. However, this cost will scale much more rapidly in EDR systems, due to the impact that a change in TDS has on capital and operating cost. For this reason, RO tends to be more cost-effective when significant reductions in TDS are required, and EDR may be more cost-effective when selective ion removal is required, or smaller TDS reductions are necessary [9].

ED and EDR are also capable of controlling specific inorganic constituents or ionised contaminants in saline solutions (e.g. sodium, chloride, fluoride, or sulphate) and thereby contribute to complying with applicable water standards. Furthermore, ED is a functional working element applied in other electrochemical desalination techniques, e.g. EDI [1, 8]

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4.5.2. Electrodeionisation (EDI) also known as Continuous Electrodeionisation (CEDI)

Detlef Taprogge

Separation Principle

EDI - also referred to as “Continuous Electrodeionisation” (CEDI) - is a technique to remove salt ions from saline water by applying a combination of **Electrodialysis (ED)** and **Ion Exchange (IX)**. Because of the combination of two techniques it is also labelled a “hybrid” desalination technique [1-2].

To better understand the fundamental separation principle of this demineralisation technique, a closer look at the electrochemical impact on salt ions in a saline solution when exposed to an electric field is helpful:

Saline water contains positively charged ions (cations, e.g. Na^+) and negatively charged ions (anions, e.g. Cl^-). When a pair of electrodes is inserted into the saline water (see Figure 1) and an electric voltage is applied, an electric field is formed, which drives the cations towards the cathode and the anions in the opposite direction towards the anode. This phenomenon, i.e. the **capability of ions to migrate selectively according to their charge** represents the **fundamental separation principle** in EDI (incl. CEDI) [1]. In different words: positively (Na^+) and negatively charged salt ions (Cl^-) in aqueous solutions migrate towards electrodes of opposite charge. The migration of ions according to their charge under the influence of an electric field is **also known as electrophoresis** [3].

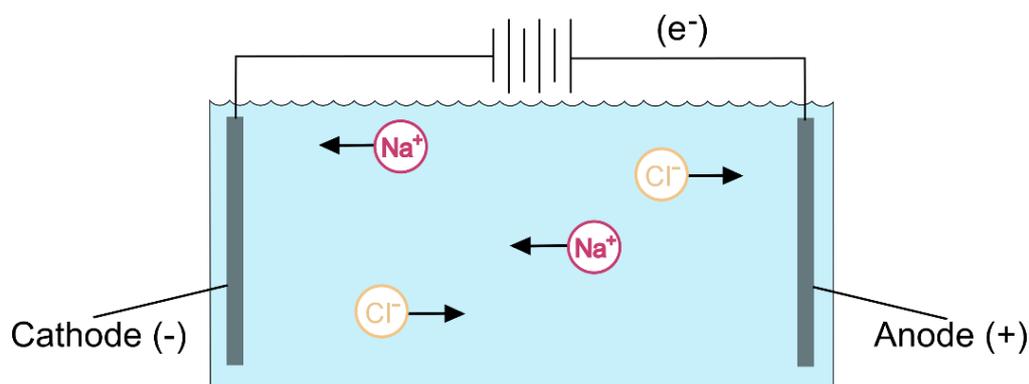


Fig. 1. Principle of electrophoresis, adapted from [4]

Driving Force and Initiator

The driving force of the process is a **difference in electrochemical potential** which is **triggered by the application of an electrical potential difference (Initiator)** to the saline solution. The migration of ions to the electrode of opposite charge will continue until all constituents of the system have come to a new electrochemical equilibrium [1, 3].

Apart from the initiating electrical field, an ED cell, being an integral functional element of an EDI cell, also provides (permselective) ion exchange membranes positioned in an alternating fashion between the anode and electrode and forming watertight compartments as shown in Figure 2. The membranes alternate between two types of ion exchange membranes:

- anion transfer (or exchange) membranes (marked “A” in Figure 2), which are electrically conductive membranes that are water impermeable and allow only negatively charged ions (anions) to pass through, and
- cation transfer (or exchange) membranes (marked “C” in Figure 2), which are electrically conductive membranes that are water impermeable and allow only positively charged ions (cations) to pass through [4].

Figure 2 illustrates the movement of ions when an electric potential difference is applied to the ED cell. As a result of the process, compartments 2 and 4 will be depleted from Na^+ and Cl^- ions, the effluent of which thus becoming desalted product water, while compartments 3 and 5 continuously add Na^+ and Cl^- ions, the effluent of which thus becoming a brine stream with elevated salt concentration [4].

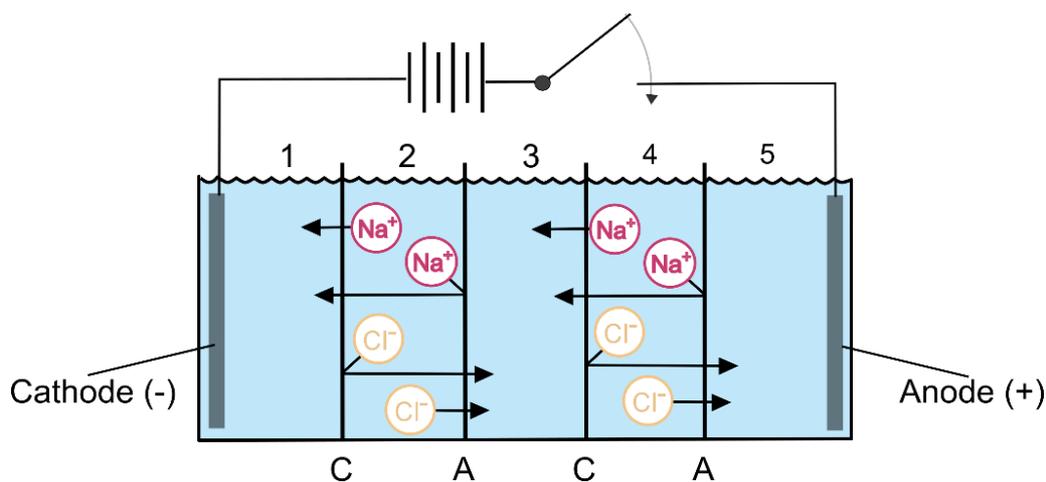


Fig. 2. Principles of ED cell structure and operation (electric potential applied) adapted from [4]

As an EDI cell incorporates ion exchange membranes as a functional characteristic just as an ED cell, it can be said that also in EDI, the fundamental separation mechanism (electrophoresis), is enhanced by use of ion exchange membranes which lead ions selectively according to their charge into compartments that will finally discharge their flow as brine (concentrate), while other compartments will be depleted of ions and discharge their flow as product water. In this fashion, concentrated brine is neatly separated from product water [1].

As stated earlier, EDI incorporates elements of ED (in particular ion exchange membranes positioned between electrodes) as well as IX resins. The step from an ED cell in Figure 2 to an EDI cell demonstrated in Figure 3 is simply achieved by incorporating ion exchange resin into the ED cell. The EDI compartments separated from one another to the right and the left by an anion and a cation exchange membrane are filled with ion exchange resin (beads) to enhance demineralisation performance [2]. Figure 3 illustrates a simple EDI cell with said compartments and flows.

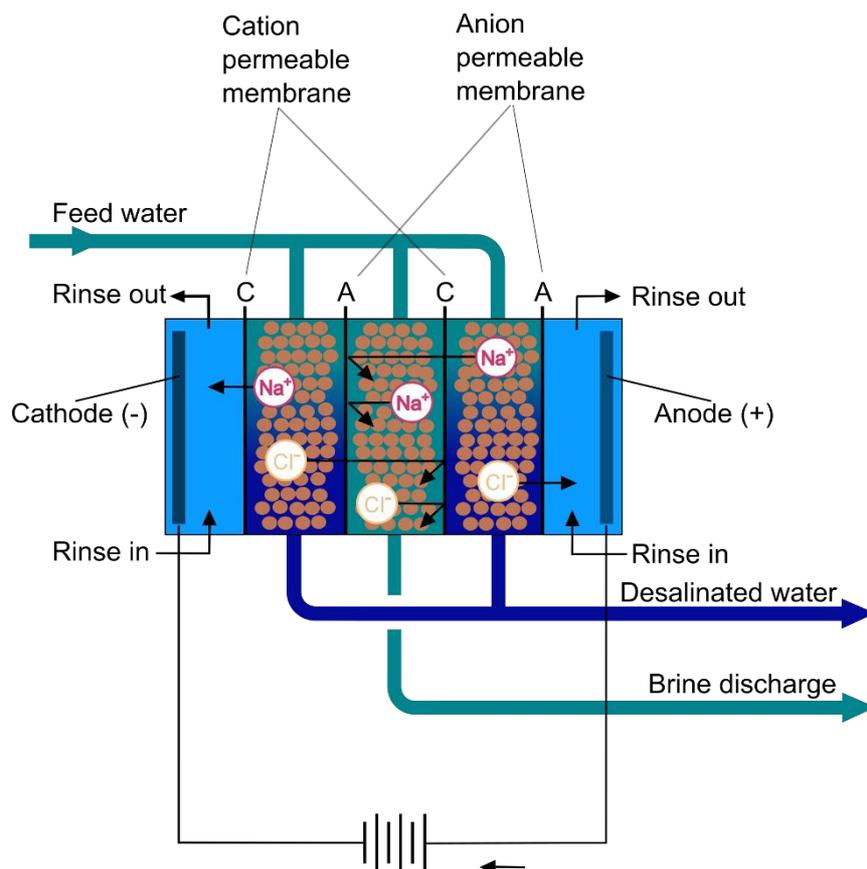


Fig.3. Basic EDI cell (with two anion and two cation exchange membrane only)

In practice, however, there are a few hundred of such compartments adjacently positioned and separated from each other by alternating anion and cation exchange membranes.

Process

Like Electrodialysis (ED), the EDI process is initiated by applying an electrical voltage difference (**Initiator**). As elaborated above, electrophoresis enhanced by the presence of ion exchange membranes constitute the **separation principle** of EDI. The process of deionisation is driven by an electrochemical potential difference which keeps ions transferring through those ion exchange membranes that permit ion transfer; only cations can pass through cation exchange membranes, and only anions can pass through anion exchange membranes.

Different for ED, though, the compartments of EDI cells are filled with Ion Exchange (IX) resin. The reason for this specific EDI design feature is the fact that the movement of ions in an ED cell (i.e. without IX resin filling) is fairly slow, and, as the compartment being more and more deprived of ions (product water compartment) and, thus, getting more and more pure, the lowering conductivity of this water impedes the ion removal. To avoid this phenomenon and to enhance ion transfer performance, IX resins are sandwiched between a pair of anion and cation exchange membranes. The large surface area offered by resin beads acts as a conductive path and lets ions bridge that path through IX membranes faster than moving in water alone. Ion-exchange resins increase the conductivity in the diluted cells, and hence the EDI stack resistance is

significantly lowered, which leads to lower energy consumption [4]. In consequence, the IX filling effectively eliminates the ion diffusion resistance as it allows ions to move freely, even when very pure water conditions have been achieved [2, 4-5].

As feed water is continuously pumped into the concentrating and the purifying compartments of the EDI cell, these water streams remain constantly separated from each other. Consequently, ions migrate and concentrate in the concentrating compartments, from where they leave the EDI cell as concentrated reject flow. Conversely, water leaving the neighboring departments which are depleted of ions will finally leave the EDI cell as desalinated water (also referred to as “dilute”) [4].

Looking at Figure 3 showing a feed flow from the top, it should be noted that at the top of the purification compartment the ion concentration is highest; it continues to decrease from top to bottom as more and more ions migrate to the neighboring concentration compartments. At the bottom of the purification compartment, the electric field becomes concentrated between the resin beads and the surrounding water. When this localised voltage potential exceeds a certain voltage, an electrochemical reaction occurs, whereby water molecules are split into hydrogen and hydroxide ions. In particular, a water dissociation reaction takes place which produces **hydrogen (H⁺)** and **hydroxyl ions (OH⁻)**. These produced ions continuously **regenerate** the ion exchange resins electrochemically without using chemicals [1].

These hydrogen and hydroxide ions function as acid (H⁺) and caustic (OH⁻), i.e. just like the acidic and caustic regeneration chemicals conventionally used to regenerate deionisation systems like e.g. IX resins.

Different from conventional ion exchange, in EDI the IX resins are continuously regenerated (explaining the origin of the term “Continuous Electrodeionisation” (CEDI)) without the need of adding regeneration chemicals, an important ecological advantage. This is all achieved by the electric potential difference; the electric current regenerates the resin mass continuously. As a further benefit, the lifetime to the IX resins is extended.

Motivation of Use

EDI is a widely known desalination technique, typically used for feed water with low salinity for polishing applications (with conductivity below 0,1 µS/cm), e.g. after a Reverse Osmosis (RO) process (polishing function) and/or to generate ultrapure water with very low conductivity and with minimal recovery losses [1]. Typical industrial applications include post-RO ultrapure water generation in semiconductor plants, EDI is capable of segregating almost completely any ionic species from dilute solutions.

EDI combines the advantage of ED and IX. It enhances ED performance by integration of IX resins [1]. Compared to IX, EDI does not generate chemical regeneration residues; Different from IX, IX beads in EDI stacks are regenerated by the EDI process itself; also, unlike IX, EDI operates continuously and without interruption for IX resin regeneration.

Due to being electrically controlled, good part-load adaptability can be achieved. Different from RO, EDI moves ions only, and not water molecules. The system-inherent losses are, therefore, smaller [2].

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4.5.3. Capacitive Deionisation (CDI) and Membrane Capacitive Deionisation (MCDI) also known as Electrochemical Demineralisation or Electrosorption

Detlef Taprogge

Separation Principle, Driving Force and Initiator

Capacitive Deionisation (CDI) is a technique for removing salt ions from water by applying an electrical voltage difference between two porous carbon electrodes in which the ions will be temporarily stored [1].

The driving force of the process is a difference in electrochemical potential which has been initiated by the application of an **electrical potential (voltage) difference (Initiator)** [2]; the **separation principle** of salts from water is based on the **capability of ions to move selectively according to their charge**; in different words: positively and negatively charged salt ions in aqueous solutions migrate towards electrodes of opposite charge.

Literature has traditionally classified CDI by its nature as an electrochemical technique, however, recent research [1] suggests that the most fundamental underlying principle of CDI is “capacitive ion storage”, a phenomenon based on the formation of a so called “electrical double layer” (EDL). In simple words, upon applying an electrical charge, ions are captured electrostatically and stored capacitively (analogous to electrical charge being stored in an electrical condenser / “capacitor”) in a diffuse layer formed next to the carbon surface. Ideally, pure physical accumulation of ions (sorption) dominates the process, not chemical (faradaic) reactions. The process is, therefore, easily reversible. Congruently, CDI may also be viewed as a process of ion sorption and desorption on electrically charged surfaces; CDI is, therefore, also named “Electrosorption” [1].

Following the above explanations, CDI is a desalination technique that operates by adsorbing ions in an EDL formed in the proximity of electrodes by the application of an electrical potential difference. These electrodes are made of porous carbons optimised for high (ion) salt storage capacity and for good ion and electron transport [1].

Process

The basic mechanism underlying CDI is schematically shown in Figure 1. It depicts a single CDI cell. In practice, multiple CDI cells are stacked on top of each other to form a stack; several stacks are packed together to form a CDI module. The process of CDI comprises three steps:

Step 1 – Purification (Ion Electrosorption) (see Figure 1A)

Upon applying a direct current (DC) voltage difference (typically between 1.2 and 1.5 V) between two porous carbon electrodes (typically attached to metallic current collectors) ions are attracted to the respective electrodes, i.e. cations (ions with positive charge, here, for example, Na^+) to the negatively charged electrode, and anions (ions with negative charge, here, for example, Cl^-) to the positively charged electrode. During this first “ion electrosorption” step, ions are stored in each of the two porous carbon

electrodes. As a result, the saline feed water gets more and more deprived of the salt ions and, thus, is desalinated [1].

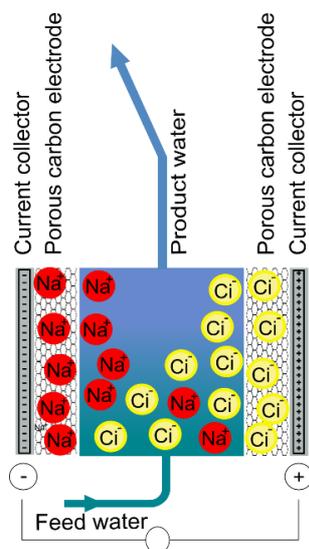


Fig. 1 A.
CDI purification step

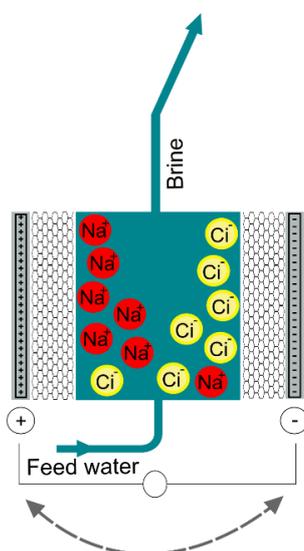


Fig. 1 B.
CDI regeneration step

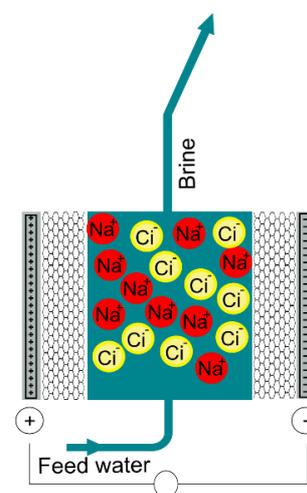


Fig. 1 C.
CDI flushing step

Step 2 – Regeneration Step (Ion Desorption) (see Figure 1 B)

As the electrodes become saturated with ions electroadsorbed into the porous carbon, the electrodes require regeneration after some time. For regeneration purpose, the potential difference is reduced to zero (or reversed) and, in consequence, ions are desorbed from the electrodes and released back into the water stream [1] for the purpose of subsequent flushing them out with the bulk fluid as brine.

Step 3 – Flushing Step (see Figure 1 C)

As a 3rd step (or combined with the 2nd step), the desorbed ions are released into the water stream and flushed out of the CDI cell as brine. A further desalination cycle can restart hereafter [3].

To separate desalinated water from intermittent brine flushing, corresponding flow separation needs to be procured in the system's piping arrangement.

A disadvantage of this CDI design is that - when reversing the electrical potential difference - ions may be driven to the electrode on the opposite side of the feed water channel. Once the electric potential difference is reversed, the adsorbed ions will be desorbed; at the same time, however, oppositely charged ions from the bulk fluid will be attracted and adsorbed. Therefore, ion desorption and adsorption occur simultaneously during this step.

To avoid this drawback, a modification of CDI exists using specific membranes which is generally referred to as "Membrane Capacitive Deionisation" (MCDI).

Process Description MCDI

To enhance desalination performance, traditional CDI cells are modified by integration of ion selective membranes. This design is known as **Membrane Capacitive Deionisation (MCDI)** (see Figure 2 A – B).

In MCDI, ion selective membranes (ion exchange membranes) are applied as thin films (typically 50 – 200 μm thickness) or coated (typically 20 μm thickness) directly to each of the two carbon electrodes, i.e. a cation exchange membrane to the cathode and an anion exchange membrane to the anode [1]. Cations can pass cation exchange membranes freely, anions are repelled; vice versa, anions can move freely through anion exchange membranes, cations cannot.

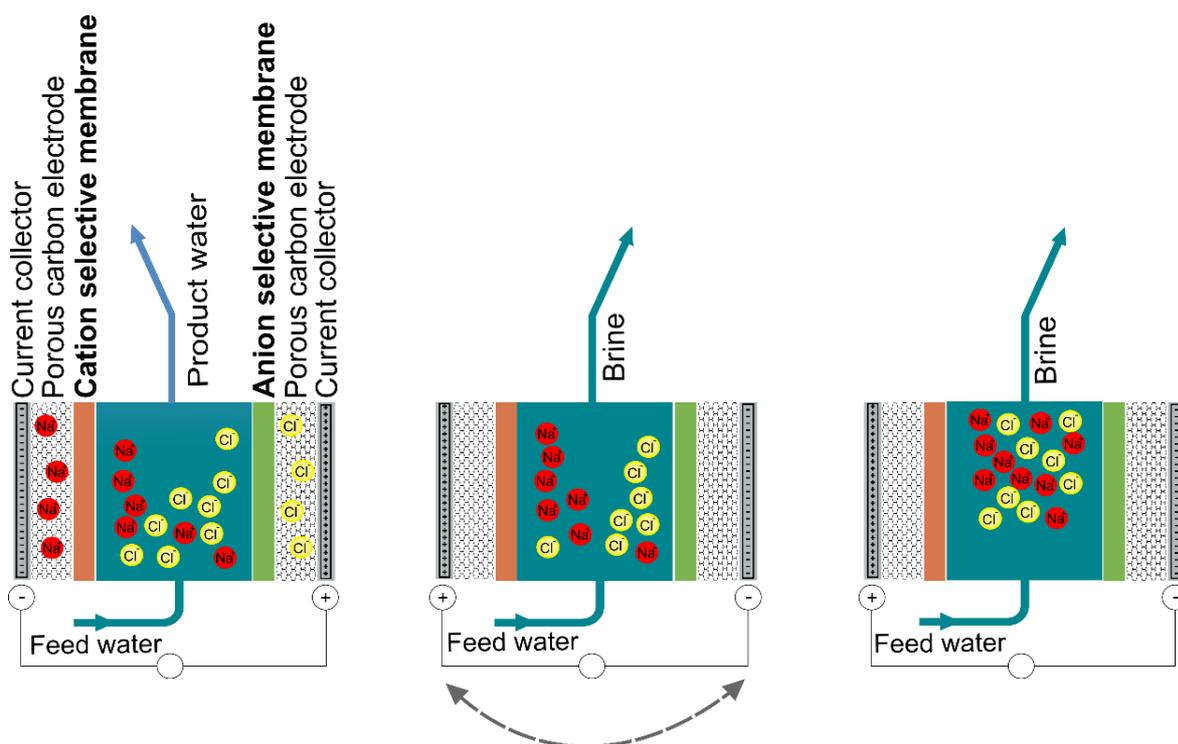


Fig. 2 A.
MCDI purification step

Fig. 2 B.
MCDI regeneration step

Fig. 2 C.
MCDI flushing step

As a particular advantage of MCDI, the ion selective membranes attached to the respective electrodes hinder salt ions to get electroadsorbed by the opposite electrode when switching the potential difference during the regeneration step [4].

Motivation of Use

(M)CDI has been developed as a non-polluting, energy-efficient and cost-effective alternative to desalination technologies such as Reverse Osmosis (RO) and Electrodialysis (ED) [5] or Ion Exchange (IX).

Preferred uses are in brackish water desalination (energy efficient below 4,000 ppm feed water *TDS*) [6], in point-of-entry & point-of-use water softening, horticulture, treatment of cooling tower make-up water and in applications with operating temperatures too high for RO, but manageable for CDI (e.g, commercial laundry waste water deionisation).

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4.5.4. Microbial Desalination (MDC)

Detlef Taprogge

Driving Force and Initiator

Microbial Desalination is a technique to remove salt ions from saline water (deionise saline water). The **driving force** of the process is a **difference in electrochemical potential** which is initiated by electric current (electric potential difference) generated by the metabolic activity of “exoelectrogenic” microorganisms, i.e. **initiated by a “bio-electric” potential difference**. Triggered by such bio-electric potential difference, ions are transported through ion selective membranes, thus generating ion-enriched streams and an ion-depleted stream (desalinated water). Ion transport is effected in proportion to the electric current being generated by these microorganisms [1-3]. The transport of ions to the electrode of opposite charge will continue until all constituents of the system have come to a new electrochemical equilibrium.

An exoelectrogenic microorganism is a microorganism that has the ability to transfer electrons extracellularly. Exoelectrogenic microorganisms are also referred to as “exoelectrogens”, “electrochemically active bacteria”, “anode respiring bacteria” and “electricigens” [4]. A known species of exoelectrogens is, e.g., *Geobacter sulfur-reducens*.

In a Microbial Desalination Cell (MDC) exoelectrogenic microorganisms serve to generate electric current (electrons) from oxidation of organic matter present, e.g., in wastewater [3] or in artificially created nutritious solutions. The electric potential difference between anode and cathode initiated in such bio-electric way is used to induce ion transport through ion exchange membranes [2, 5], thus desalinating water.

Separation Principle

Saline water contains positively charged ions (cations, e.g. Na^+) and negatively charged ions (anions, e.g. Cl^-). When a pair of electrodes is placed into saline water and an electric or bio-electric potential difference is applied, an electric field is formed which lets cations migrate towards the cathode and anions in the opposite direction towards the anode. This phenomenon, i.e. the **capability of ions to move selectively according to their charge** represents the fundamental **separation principle** of salt ions and water in MDC. In other words: positively (Na^+) and negatively charged salt ions (Cl^-) in aqueous solutions migrate towards electrodes of opposite charge.

MDC is in nature similar to Electrodialysis (ED), yet different from ED because it does not require external electricity [1]. Instead, energy is provided by the exoelectrogenic microorganisms, being an integral part of the MDC.

Process

The first proof of concept of MDC was demonstrated in 2009 by a 3-chamber configuration [1, 6,-7]. This basic Microbial Desalination Cell resembles a fuel cell, containing an anode and a cathode, between which a pair of ion selective membranes is inserted. Figure 1 depicts the basic design of a Microbial Desalination Cell (MDC).

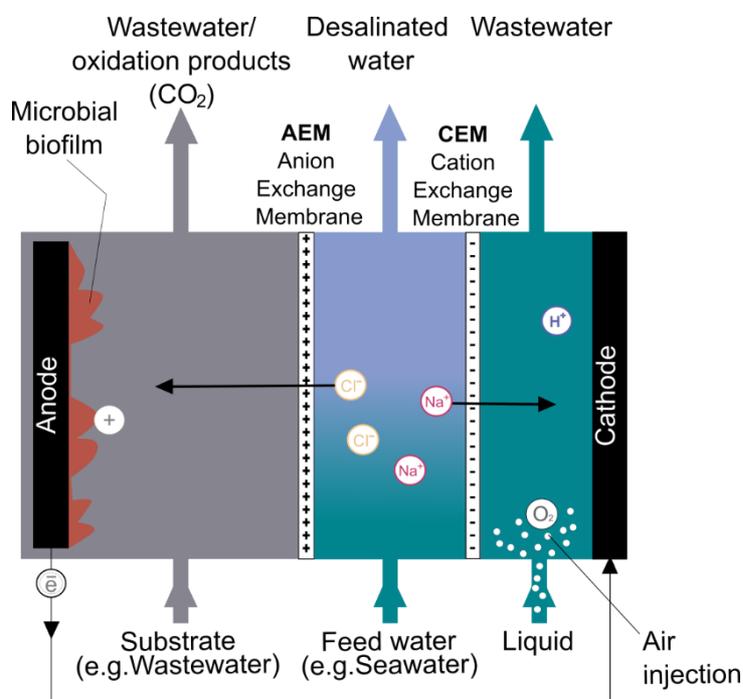


Fig. 1. MDC – basic design

It consists of three chambers:

1. the anode chamber with an anion exchange membrane (AEM). Next to the anode a film of exoelectrogenic microorganisms is attached as a kind of biofilm. The chamber is typically filled with a liquid (e.g. wastewater) which contains nutrition for the exoelectrogenic microorganisms. These exoelectrogenic microorganisms oxidise organic matter, and, in doing so, release protons and electrons.
2. the cathode chamber with a cation exchange membrane (CEM) positioned next to the cathode. This chamber, in which the electrons transferred from the anode are consumed by a chemical reduction reaction (as described below), is typically filled with a liquid that enhances cathode performance (e.g. water + air injection).
3. the middle chamber between the two ion exchange membranes (AEM and CEM) is filled with feed water to be desalinated [1].

The MDC process (here with an air-cathode) is depicted in the following sequence (Figure 2 A. – C.):

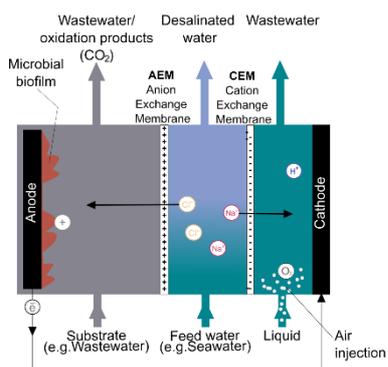


Fig. 2 A. MDC process - anode chamber

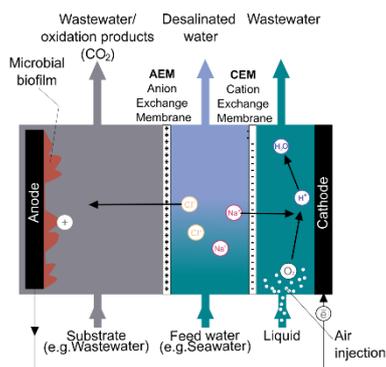


Fig. 2 B. MDC process - cathode chamber

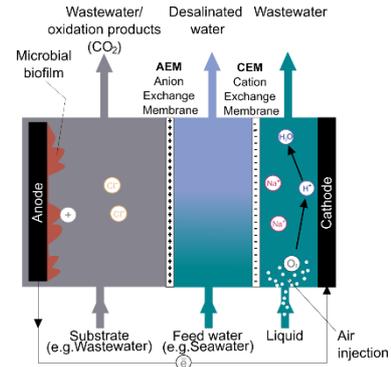


Fig. 2 C. MDC process - middle chamber

Exoelectrogenic microorganisms on the anode oxidise organic matter fed into the anode chamber. In doing so, they release protons (H^+) and electrons (e^-) (see Figure 2 A.). The following equation represents the oxidation reaction at the anode [8]:



The electrons (e^-) leave the **anode chamber** and are transferred as electric current via external wire to the cathode. Protons (H^+) cannot leave the anode chamber, as they are rejected on the anion exchange membrane (AEM). The surplus of positive charge in the anode chamber resulting from protons (H^+) produced, however, desires balancing. The only way of balancing charge is drawing negatively charged ions (Cl^-) through the AEM from the middle chamber into the anode chamber (see Figure 2 A.).

Simultaneously, in the **cathode chamber**, electrons (e^-) are received as electric current (see Figure 2 B.). There they combine, e.g., with the oxygen provided by an air-cathode or by oxygen injection into the cathode chamber. They combine as well with the protons (H^+) drawn from the liquid in the cathode chamber (chemical reduction reaction) to form H_2O . The following equation represents the reduction reaction at the cathode [8]:



The extraction of protons required for the formation of H_2O leaves a deficit of positive charge in the cathode chamber which can only be replenished by attracting positively charged ions (Na^+) from the middle chamber. As only positively charged ions can pass the cation exchange membrane (CEM), Na^+ ions cross the CEM and replenish the protons consumed in the formation of H_2O (see Figure 2 B.).

As a result (see Figure 2 C.), the feed water in the **middle chamber** is depleted of salt ions, i.e. desalinated. Thus, the generation of electric current through oxidation activity of exoelectrogenic microorganisms induces an electric potential difference between anode and cathode, which in turn induces a selective ion transfer through the AEM and CEM, thereby depleting the feed water stream from salt ions.

This depletion of ions in the middle chamber results in water desalination without any water pressurisation or use of draw solutions or externally supplied electrical energy. Instead, energy is generated while water is desalinated, and, as the case may be, organic matter is removed from wastewater while being metabolised by the microorganisms' activity in the anode chamber [1-2, 5-6, 8-10].

While the basic MDC cell containing three chambers forming one stack - as illustrated in Figure 1 above - is indispensable for lab purposes, multiple stack designs are desirable in practice to increase desalination volume and to decrease manufacturing cost. Multiple stack structuring is achieved by repetitive addition of AEM and CEM membrane pairs to the module as illustrated in Figure 3 below, thus creating repeating desalting and concentration cells [7].

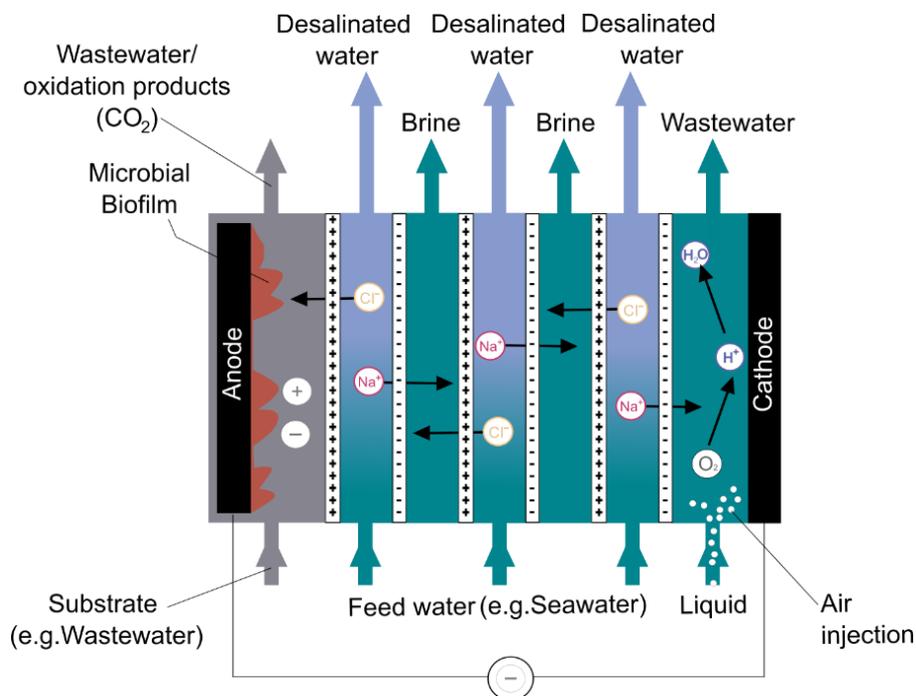


Fig. 3. Stack structure of MDC

Stacking increases the magnitude of ionic separation. In a stacked MDC, a single electron transfer from anode to cathode can separate as many ion pairs as the number of repeated AEM and CEM membrane pairs. For instance, in a three-cell pair stack, a single electron transfer separates three pairs or mono-valent cations and anions by use of an (ideal perm-selective) ion exchange membrane [2, 8].

Motivation of Use

Considering the high relevance of energy cost in water desalination, the particular attraction and benefit of MDC lies in the fact that MDC allows desalination without external electrical energy input. It requires, however, the integration of a further process element, i.e. energy production by exoelectrogens from digesting organic matter. Depending on design, MDC may also integrate a third function. If, for example, wastewater is used to feed the MDC and the organics contained therein serve as a source of nutrients for the microorganisms, then MDC could in the future emerge as a technique to perform three functions simultaneously: energy generation, desalination and wastewater treatment [8].

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4.6. Selective Exchange of Ions - Ion Exchange (IX or IE)

Detlef Taprogge

Separation Principle

Ion Exchange (IX) is a technique for removing salt ions from water by use of an ion exchange “resin” (also referred to as “resin bed”). Ion exchange resins are insoluble, porous materials (“beads”) containing loosely held ions which can be exchanged with other ions in solution.

The exchange takes place between ions of like charge; for instance, a positively charged Na^+ ion may be exchanged against another positively charged ion (e.g. H^+) and a negatively charged ion (e.g. Cl^-) may be exchanged against another negatively charged ion (e.g. OH^-).

The structure of the resin is a polymer on which a fixed ion has been permanently attached. This ion cannot be removed or displaced; it is part of the structure. To preserve the electrical neutrality of the resin, each fixed ion must be neutralised with a counterion. This counterion is mobile and can get into and out of the resin bed.

Each ion going into the resin bed has to be replaced by an ion getting out of the bead, again to preserve electrical neutrality. This is what is called ion exchange.

As mentioned above, only ions of the same electric sign are exchanged; It is not possible to create a resin that can exchange cations as well as anions, because the fixed cations inside the resin beads would neutralise the fixed anions and no exchange with the outside (ions of the saline solution) would be possible. Therefore, separate cation exchange resins and anion exchange resins are required [1-2].

The **fundamental separation principle** of the ion exchange process is the **capability of ion exchange surfaces to (selectively) exchange ions** [3]:

- For seawater desalination, this means: positively charged H^+ ions, contained in a cation exchanger resin are displaced by Na^+ ions from the saline solution, because the cation exchanger resin has a higher affinity for sodium than for hydrogen ions; in simple words: the cation resin is built in a way that it prefers sodium over hydrogen ions.
- Congruently, negatively charged OH^- ions contained in an anion exchanger are displaced by Cl^- ions from the saline solution, because the anion exchanger resin has a higher affinity for chloride than for hydroxide; in simple words: the anion resin is built in a way that it prefers chloride over hydroxide ions.
- The ion exchange capability is “selective” in the sense of being able to target specific salt ions to be removed from the saline solution.

The exchange does not need an external initiator to start the desalination process other than to bring an ion exchange surface into contact with saline water. The fundamental separation capability is **enabled, however**, by the **difference in affinity** of the ion exchange resin towards another ion to be exchanged. The higher the affinity, the more intense the ion exchange. Generally, the affinity is greatest for large ions with high valency [1].

Driving Force and Initiator

When bringing an ion exchange surface into contact with saline water, an initially prevailing equilibrium of the system will get out of balance, as ionic migration is triggered. In response, the system will strive towards a new equilibrium between all ions in the saline water and all ions on the ion exchange surfaces by transfer of ions in-between. The ion exchange process will stay active. The **driving force** for the transfer of ions from the saline solution and those on the ion exchange surfaces is – in most abstract finality – the **electrochemical potential difference** (or the difference in Gibbs energy) of the ions in the saline solution and those on the ion exchange surfaces. A more difficult question, however, in Ion Exchange (IX), is the clear identification of the **initiator of the IX process**. In particular, the typical external Initiator, as found in other desalination techniques initiated by an electric potential difference, appears to be missing. Furthermore, the breadth of IX membranes apparently leaves room for multiple explanations that may serve as Initiators of the IX processes [3-4].

While a precise initiator may not be safely and uniformly identifiable from literature, it has been found opportune to leave the initiator for IX processes unspecified for the purpose of the present paper. However, in the absence of an electric potential (voltage) difference being triggered by an external source, (like e.g. in all other electrically initiated desalination techniques), a **difference in ion concentration** could be regarded as a plausible **initiator** [5-6]: when an ion exchange surface is brought into contact with saline water, the ratio of ions in the saline water to the ions in the IX resin (actual ion concentration) will have become different from its original equilibrium concentration; the initially prevailing equilibrium of the system has then gone out of balance. According to this logic, with temperature and pressure being unchanged, **the Initiator** for the exchange of ions between the saline water and the ion exchange surface could be an in (actual) **ion concentration difference** of the system and its equilibrium concentration. Following this logic, once the actual ion concentration has reached a new equilibrium concentration, the ion exchange process will come to an end [5-6].

Process

As shown in Figure 1, feed water for the IX process is typically pre-treated by filtration to protect the Ion Exchange (IX) bed from particulate contamination (sand or gravel filters). To avoid load reduction of the anion exchanger by carbon dioxide which may be dissolved in the feed water, a degasifier is typically applied. The ions are then exchanged in two separate ion exchanger columns. The product water quality may be monitored by conductivity measurement in order to determine the start of the regeneration process.

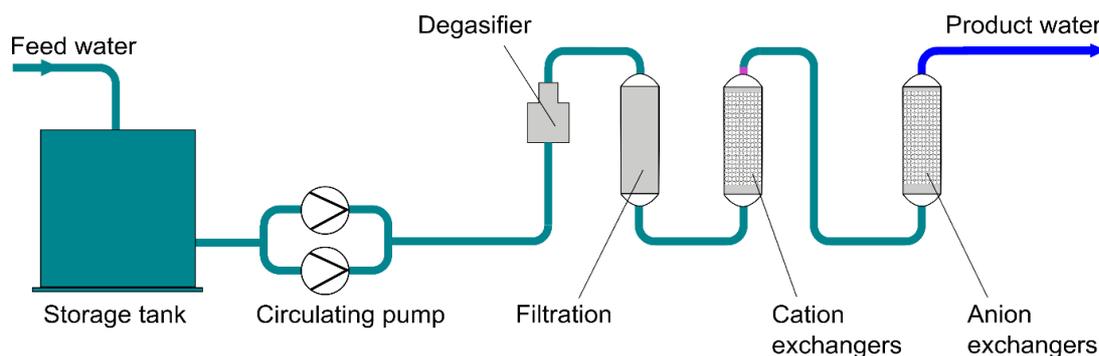


Fig. 1. IX Process chart inspired by [7]

For a better understanding of the IX mechanism, by which salt is separated from water in an IX desalination process, it may be helpful to segregate the IX cycle into fragments, taking NaCl, the most prominent salt in desalination, for the purpose of illustration [1]:

Fragment 1: Cation Exchange

Looking first at the behaviour of positively charged Na^+ ions (cations) of the NaCl salt dissolved in a saline solution, they are attracted by cation exchangers, which exchange H^+ ions from the cation exchanger surface with positively charged ions (cations) like Na^+ ions taken from the saline solution (Figure 2a). As much as Na^+ ions are withdrawn from the solution and attach to surfaces of the cation exchanger, H^+ ions embedded in the cation exchanger matrix start leaving the IX resin into the solution. As a result, Na^+ ions start to accumulate on the surface of the IX resin in exchange for H^+ ions leaving the IX resin.

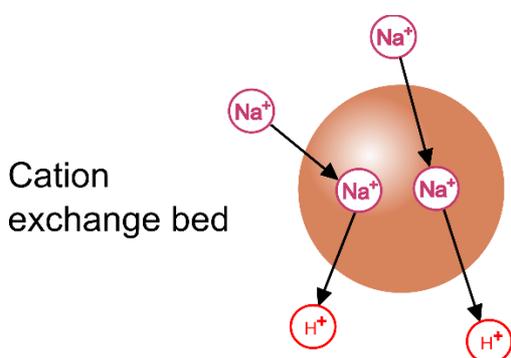


Fig. 2a. Cation exchange - Fragment 1

Fragment 2: Post Cation Exchange

Thereafter, the H^+ ions released from the cation exchanger into the solution will find Cl^- ions in the solution which have become available after the solution has been deprived of Na^+ ions which had been adsorbed by the cation exchanger in Step 2a. Said H^+ ions and Cl^- ions in solution form HCl (hydrochloric acid) in dissociated form (Figure 2b.).

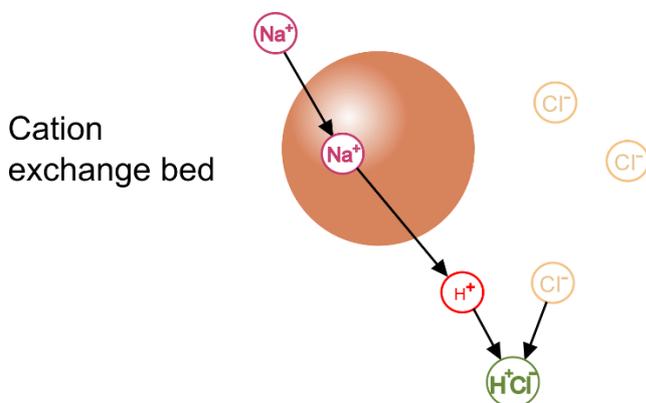


Fig. 2b. Post cation exchange - Fragment 2

Fragment 3: Anion Exchange

With respect to the of H^+ ions and Cl^- ions dissociated in solution (H^+Cl^-), the Cl^- ions will show a behaviour similar to the Na^+ ions described above: the Cl^- ions will be attracted by the anion exchanger which exchange OH^- ions from the anion exchanger surface with negatively charged ions (anions) like Cl^- ions taken from the saline solution (Figure 1c). As much as Cl^- ions are withdrawn from their dissociated existence in solution (H^+Cl^-) and attach to the surfaces of the anion exchanger, OH^- ions so far embedded in the anion exchanger matrix start leaving the IX resin into the solution.

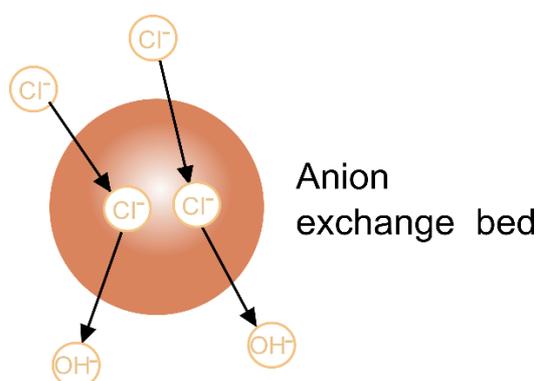


Fig. 2c. Anion exchange – Fragment 3

Fragment 4: Post cation and anion exchange

To complete the IX process, the OH^- ions released to the solution from the anion exchanger will now find an excess of H^+ ions in the solution which has become available after the dissociated solution of H^+ ions and Cl^- ions (H^+Cl^-) has been deprived of the Cl^- ions as they had been adsorbed by the anion exchanger (as seen in Figure 2c). The H^+ ions and the OH^- ions released to the solution form H_2O (water) with covalent bindings (Figure 2d).

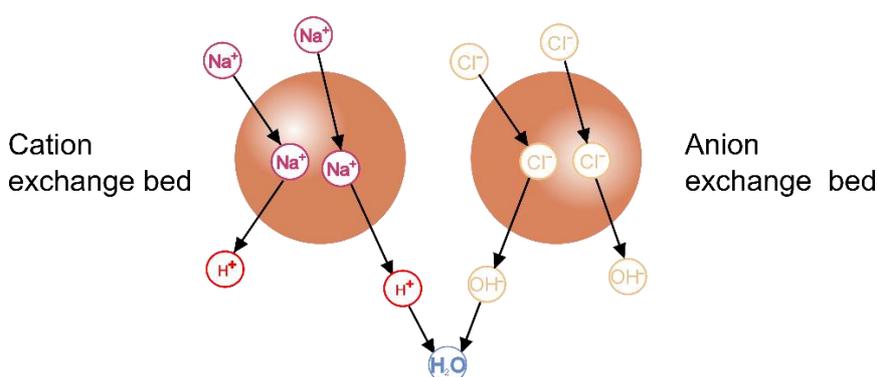


Fig. 2d: Final stage of cation and anion exchange process

It is apparent from the above that the four major process fragments of an IX process differ in nature. While Fragment 2 and Fragment 4 clearly carry the characteristics of chemical processes (Fragment 2 = acid forming reaction and Fragment 4 = covalent bindings reaction to form water), Fragment 1 and 3 resemble “sorption”. However, due to the exchange phenomenon (in and out of ions) as opposed to a simple one-sided ion addition (without replacement), ion exchange is distinctly different from sorption

processes. Ion Exchange is a simultaneous exchange process of ions on surfaces, i.e. a true replacement of coming and leaving ions, whereas in adsorption or absorption there is only an adding of ions (or atoms and molecules) to surfaces without the necessity of other ions (or atoms and molecules) being replaced.

The net result of the complete process chain is the depletion of the NaCl ions from the saline solution. At the end of the exchange process, the resin bed may be loaded with cations and anions from the saline water, i.e. Na^+ on the cation resin, Cl^- on the anion resin), and the salt content of the water processed is reduced.

Once the available ions are exchanged, the resin bed is saturated, and a regeneration process will be required (Figure 3). Regeneration of ion exchange resins is the reversal of the exchange process. For the time of regeneration, the process of ion exchange needs to stop. Cation exchangers may typically be regenerated by hydrochloric or sulphuric acid (HCl or H_2SO_4), anion resins by caustic soda (NaOH) [7].

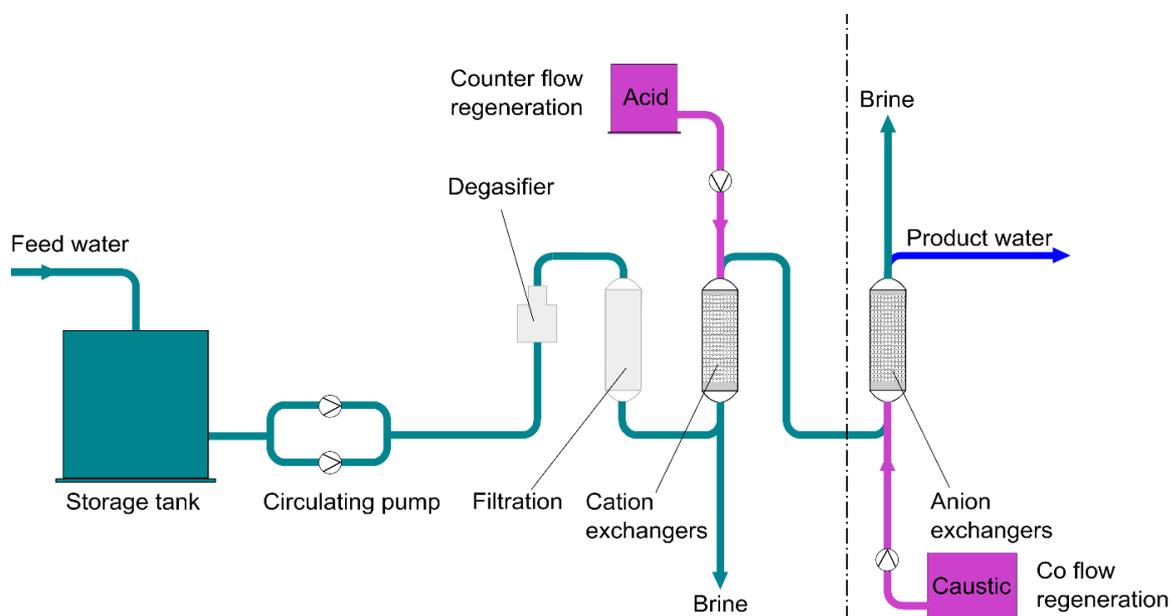


Fig. 3: IX Regeneration options inspired by [7]

Motivation of Use

Ion Exchange (IX) is a very established desalination technique, in particular when salinity levels are low (< 1000 mg/litre), e.g. for polishing applications, e.g. for demineralisation to ultra-pure water quality. Different from Reverse Osmosis, IX is - under special conditions - able to remove single ions selectively from a saline solution. IX is not chemical free due to the regeneration need, for which the IX process needs to be interrupted.

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5. Outlook

Summarising on the benefits and pitfalls of the novel classification maps, it is believed that the newly developed desalination technology maps may have merit in an educational context as a structuring tool with improved consistency in methodological approach and technical language. The classification approach developed in the present paper should, in principle at least, provide a higher level of consistency for long term use. However, the authors acknowledge that there still are challenges remaining, some unavoidable and being linked to clarity in science, some open for alternative classification options depending on judgmental, not scientific priority. The authors invite the interested reader to enriching discussion and advancement on the maps presented.

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Annex 1, Explanatory Note: Notion of Vapour Pressure

In the following Sections the general term “vapour pressure” will be used for any context involving vapour pressure. In connection with desalination techniques, the authors will predominantly speak of the vapour pressure of pure water. However, for a better understanding, the physical background of vapour pressures is briefly summarised in the present Section.

General Definition of “Vapour Pressure”

The general definition of vapour pressure results from the phase equilibrium between liquid and vapour of a pure substance in a thermodynamically isolated system. As is shown in Figure 1a, no heat, work or matter is exchanged across the boundaries and at phase equilibrium, there is no net exchange of heat, work or matter between the liquid and its vapour phase. However, there are equal fluxes of water molecules to and from the liquid-vapour interface (blue arrows) which on the vapour side correspond to the vapour pressure. Considering a closed, stiff vessel at the surrounding temperature and filled with liquid and vaporous water, the pressure measured in this vessel (red arrow) is the vapour pressure of water at this particular temperature. [1, 2]

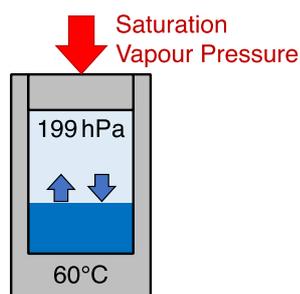


Fig. 1a. Saturation Vapour Pressure of Water at Phase Equilibrium in a Thermodynamically Closed System.

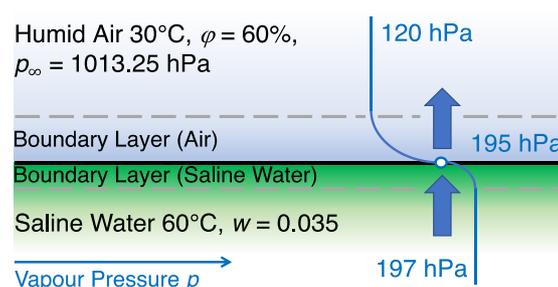


Fig. 1b. Partial Vapour Pressure Profile Across a Phase Boundary between Saline Water and Humid Air. Water Layer Assumed Isothermal, Concentration Polarisation in Water 1.5.

The term “saturation vapour pressure” and “saturation temperature” (= “boiling temperature”) are frequently applied to emphasise the complete attainment of a thermodynamic equilibrium. If, in a thermodynamically open system the saturation vapour pressure exceeds the ambient pressure, the liquid starts to boil. For pure substances, these saturation vapour pressure / saturation temperature curves are approximated by the Antoine, Magnus or Wagner Equation. [1, 3]

The vapour pressure of water increases exponentially with increasing temperature. This can be seen in Figure 2a, where the saturation vapour pressure of water is plotted as a function of the saturation (= boiling) temperature. The blue curve represents the values of pure water with a salt mass fraction of $w = 0 \text{ kg/kg}$. For example, a saturation vapour pressure of 199 hPa corresponds to a boiling point temperature of 60 °C. [4 - 5]

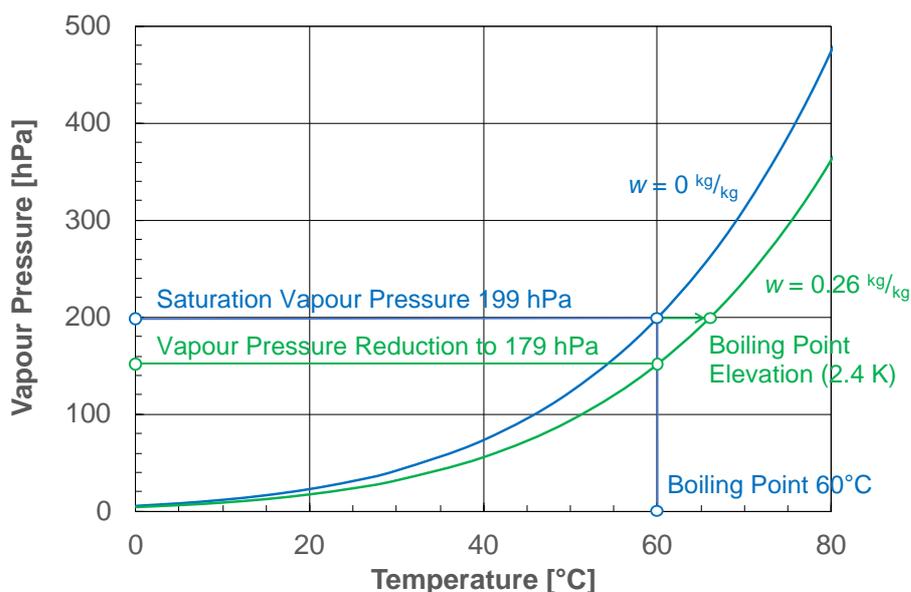


Fig. 2a. Temperature-Dependence of the Saturation Vapour Pressure of Pure Water (blue) and of the Partial Vapour Pressure of Pure Water in a Saline Solution near Crystallisation ($w = 0,26 \text{ kg/kg}$, green).

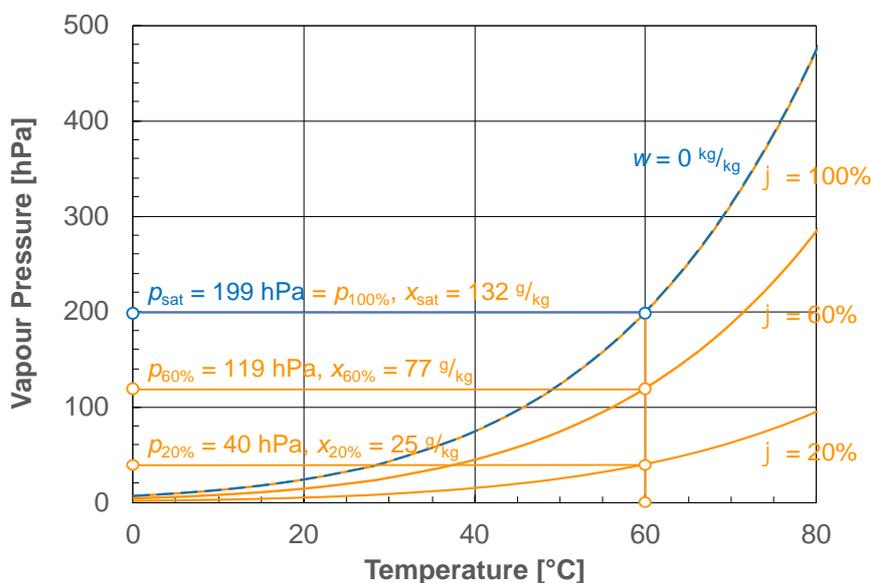


Fig. 2b. Temperature-Dependence of the Saturation Vapour Pressure of Pure Water (blue) and of the Partial Vapour Pressures p of Water Vapour in Air at Different Relative Humidity φ (orange).

Definition of “Partial Vapour Pressure”

The phenomena described up to here relate to pure substances. However, in desalination applications we are dealing with liquid mixtures such as salt water or gaseous mixtures such as the surrounding humid air. In mixtures, the individual vapour pressures of the pure components add up to the overall pressure of the mixture. Being a part of the overall pressure, the vapour pressure of a single component is called “partial vapour pressure”. It relates to the overall pressure by its concentration in the mixture. At a given temperature, the maximum concentration of the component in the mixture is limited by its individual saturation vapour pressure. In ideal, non-reacting gases the summation rule is called Dalton’s Law whereas for ideal liquid mixtures it is referred to as Raoult’s Law. [3, 6, 7]

Talking about desalination, the most important consequence of Raoult's Law is that the vapour pressure of water is not only a function of temperature, but also of salt concentration. At the relevant temperatures, the saturation vapour pressure of sodium chloride is negligible. Filling salt water into the closed, stiff vessel shown in Figure 1a, the resulting vapour pressure will be smaller than that of pure water at the same temperature. Put simply, the vapour pressure of water decreases with increasing salt concentration.

Figure 2a shows the vapour pressure reduction in a saline solution at a salt mass fraction near the crystallisation point ($w_{\text{NaCl}} = 0,26 \text{ kg/kg}$). It can also be seen, that at constant vaporisation pressure, the boiling point of the salt water is elevated (Boiling point Elevation, *BPE*). [5]

The same phenomenon applies for humid air (Dalton's Law): The partial vapour pressures of its components such as nitrogen, oxygen, water vapour etc. add up to the overall pressure. The maximum mass fraction of water vapour in the air (= water vapour saturation), which corresponds to a maximum relative humidity of 100% is defined by the saturation vapour pressure of pure water at air temperature. In general, relative humidity is the ratio between the actual and the maximum partial water vapour pressure for a given temperature. Figure 2b shows the temperature-dependent saturation vapour pressure of pure water (blue dashed line), which equals the maximum partial vapour pressure of water vapour in air (orange line at $\varphi = 100\%$). As an example, the specific water vapour load x [$\text{g}_{\text{H}_2\text{O}}/\text{kg}_{\text{DryAir}}$] for different relative humidity values is given. [7 - 9]

Mass Transfer due to Vapour Pressure Gradients

Desalination techniques based on vaporisation and evaporation work on the basis of local vapour pressure differences occurring at their individual components. Figure 1b shows an example of evaporation from a salt water film to humid air, such as in a Humidification-Dehumidification (HD) evaporator.

The mass transfer of pure water (see the thick blue arrows) from the saline water film into the humid air layer follows the gradient of the local partial vapour pressures. Due to the evaporation of pure water, a combined concentration and temperature boundary layer forms on the salt water side towards the gas-liquid interface. The slightly increased salt concentration and the reduced interface temperature due the accruing heat of evaporation and sensible heat transfer cause a reduced partial vapour pressure of water at the film surface. Similarly, a combined concentration and temperature boundary layer builds up in the adjacent air layer. This leads to an equilibrium vapour pressure of water at the phase boundary. Depending on the flow and operation characteristics, the vapour pressure on the phase boundary lies somewhere in between the two partial vapour pressures in the bulk air and saline water layer.

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