# Mild desalination of various raw water streams

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## ABSTRACT

For chemical industries, fresh water availability is a pre-requisite for sustainable operation. However, in many delta areas around the world, fresh water is scarce. Therefore, the E4Water project (www.e4water.eu) comprises a case study at the Dow site in Terneuzen, The Netherlands, which is designed to develop commercial applications for mild desalination of brackish raw water streams from various origins to enable reuse in industry or agriculture. This study describes an effective two-stage work process, which was used to narrow down a broad spectrum of desalination technologies to a selection of the most promising techniques for a demonstration pilot at 2–4 m³/hour. Through literature study, laboratory experiments and multi-criteria analysis, nanofiltration and electrodialysis reversal were selected, both having the potential to attain the objectives of E4Water at full scale.

**Key words** | desalination, E4Water, raw water, reuse

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## INTRODUCTION

As a chemical site, Dow Benelux in Terneuzen, The Netherlands, has a significant demand for fresh water with major applications in cooling and heating (via producing steam) to run its processes (UN 2009). Situated at the river Scheldt estuary, this region suffers from an intrinsic lack of fresh water. Consequently, Dow and Evides have already realized large-scale reuse of both industrial and municipal wastewater effluent (Groot *et al.* 2007). To further align demand and supply within the region, a consortium of several regional stakeholders has been formed to develop a strategy that maximizes the usage of recycle water, thereby assuring fresh water availability for each user at affordable cost.

Within the E4Water project (www.e4water.eu), a specific case study is defined to treat three brackish water streams (both industrial and surface water) with a 'mild desalination' step to produce water for use in industry or agriculture. Typically, many applications in both sectors require water with a salinity of <1 mS/cm electrical conductivity. The objective is to reach a production cost of a maximum €0.4/m³ at a volume of 3–4 million m³/year of potential reuse water.

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This work describes a two-stage evaluation process. Through an extensive literature search, the first step resulted in a pre-selection from a broad spectrum of technologies to a set of technologies with the potential to attain the mild desalination objectives. Subsequently, experimental work at laboratory scale and a multi-criteria analysis lead to the final selection of the most promising technologies to be tested at a demo-scale of 2–4 m³/hour at the Evides-Dow pilot location.

## MATERIAL AND METHODS

Raw water stream characteristics, which were investigated in this study, include inorganic and organic constituents, seasonal stability (especially with the collected rainwater streams), bio-degradability and fouling potential. All streams were sampled and analysed on a bi-weekly basis.

The pre-selection of technologies was carried out as a desk study evaluating a total of nine desalination techniques covering three main categories of desalination concepts (Figure 1).

The second-stage evaluation was carried out as follows. Desalination techniques were tested at the laboratories of TU Delft (electrodialysis, capacitative deionization) (Heidekamp 2013) and TNO (membrane distillation). Reverse osmosis/nanofiltration (RO/NF) membrane performance and fouling sensitivity were evaluated at Evides and VITO by means of existing software models and by FHNW and TNO by experimental analysis. Ion Exchange (IEX) was used as a reference desalination technique. Practical performance data provided by Evides were used to simulate IEX performance on the water types under investigation. Pre-treatment requirements were investigated at FHNW (University of Applied Sciences and Arts North Western Switzerland), focusing on using ultrafiltration (UF), activated carbon (AC), and coagulation as generic pre-treatment for all raw waters (Löwenberg *et al.* 2014). A more detailed description of laboratory tests can be found in the specified references.

## RESULTS AND DISCUSSION

Characteristics of the different raw water streams are summarized in Table 1. Seasonal variations (biological parameters, temperature, nitrate levels for farm land run-off, etc.) were significant, especially for collected rainwater, and may have a substantial impact on the performance of certain desalination techniques.

The reuse potential in industrial and agricultural applications comprises specific sets of quality criteria. A generic water quality that is broadly applicable in these sectors requires minimum quantities of salt, total organic carbon (TOC), phosphate, and suspended solids (target levels for each are specified in Table 2, first column). Using these criteria, fact sheets were established for each technology, comprising the expected product quality, cost effectiveness, and robustness. In Table 3, factsheet summary results are presented for the broad selection of desalination technologies.

Hence, the following five technologies were selected for the second stage evaluation: RO/NF, electro dialysis reversal (EDR), capacitative deionization (CDI), and membrane distillation (MD), while using IEX as a reference technology. Table 4 provides an overview of the desalination technologies tested for the different raw water streams.

Table 5 provides an overview of the strengths and weaknesses of the pre-selected technologies. The second-stage activities, including laboratory trials, are focused on addressing the disadvantages and developing solution paths to mitigate the possible negative effects.

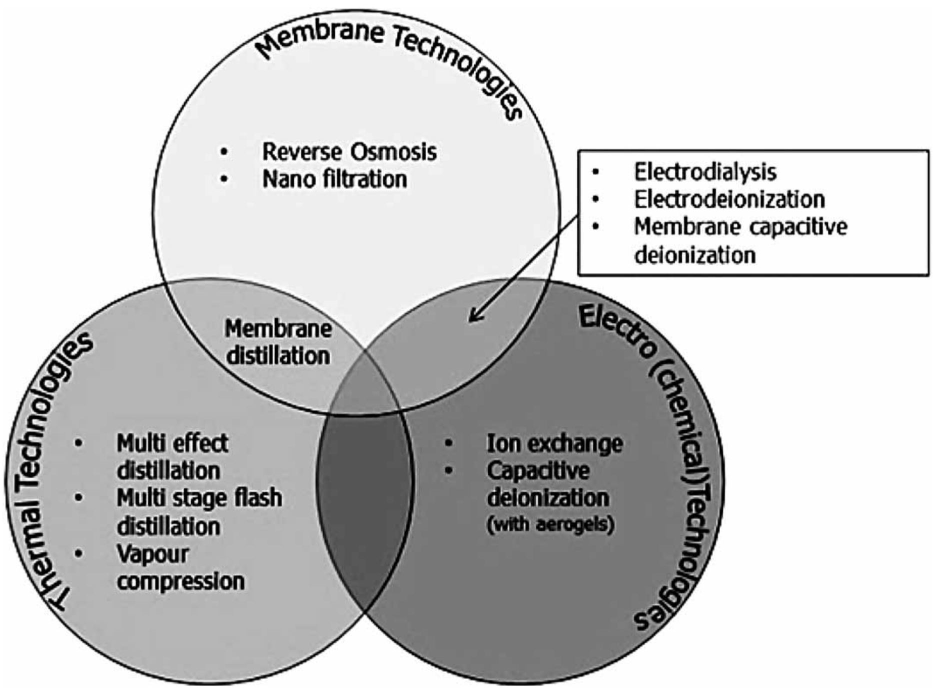


**Figure 1** | Classification of desalination techniques.

**Table 1** | Raw water quality of three selected Dow water streams

| Water quality/Water source | | 1. Dow wastewater effluent | 2. Rainwater collected | 3. Cooling tower blow down |
|---|---|---|---|---|
| Volume | $m^3$/yr | 1,500,000 | 500,000 | 1,000,000 |
| Chloride | mg/l | 75–200 | 300–400 | 400–600 |
| Electrical conductivity | μS/cm | 1,000–1,500 | 1,500–3,000 | 3,500–4,500 |
| TSS | mg/l | 5–20 | 10–25 | <15 |
| TOC | mg/l | 10–20 | 8–20 | 40–60 |
| Nitrate | mg/l | 5–10 | 0–2 | 50–100 |
| Phosphate | mg/l | 0–5 | 0–2 | 5–15 |
| $HCO_3^-$ | mg/l | 80–160 | 10–15 | 30–60 |
| Ca (total) | mg/l | 60–70 | 80–240 | 350–600 |
| Mg (total) | mg/l | 5–20 | | 40–80 |
| Iron, dissolved | mg/l | 0.1–0.3 | 0–1 | <0.2 |
| Chlorophyll A | μg/l | | 50–200 | <2 |
| pH | | 7–8 | 7.5–8.5 | 7.5–8.5 |
| Temperature | °C | 20–35 | 5–25 (ambient) | 20–30 |

**Table 2** | Overview of desalination technology criteria assessment for treating cooling tower blow down water

| Pre-treatment | Target | Nanofiltration UF | Electrodialysis reversal multi media filtration (MMF) | Capacitative deionization MMF | MD MMF |
|---|---|---|---|---|---|
| Product quality (mS/cm) | <1 | 0.4 | 0.7 | 1.0 | 0.04 |
| Recovery (%) | | 64 | 81 | 71 | 76 |
| Critical parameters | | | | | |
| Phosphate (mg/l) | <1 | <0.2 | 1.4 | 1.4 | <1 |
| Susp. solids (mg/l) | <1 | <0.1 | <1 | <1 | <1 |
| TOC (mg/l) | <15 | <10 | 51 | 51 | <1 |
| Normalized costs per $m^3$ of produced water (vs. NF desalination) | | | | | |
| Pre-treatment | | 0.73 | 0.31 | 0.35 | 0.33 |
| Desalination | | 1 | 1.7 | 2.3 | 2.5 |
| Potential show stoppers | | Pre-treatment | Phosphate<br>TOC<br>Asset availability | Phosphate<br>TOC<br>Asset availability<br>Maturity<br>Component lifetime | Maturity<br>Asset availability |

The basis for critical criteria selection has been set in the technology pre-selection process. Obviously, those criteria are also valid for the final screening. However, the present case study is fairly complex, as the raw waters of interest substantially differentiate and, moreover, have their own characteristics in seasonal variance (volumetric availability, quality trends). Also, final product use can ultimately vary anywhere between a relatively low quality application (water for flushing or fire fighting) and high purity demand (demineralized water for steam production). As a result, there is a dynamic interaction in the overall process ranging from raw water supply, pre-treatment, and desalination technology to the final product. None of these steps or unit operations can be seen independently from the others.

**Table 3** | Factsheet summary of desalination techniques. (1 = Dow wastewater effluent; 2 = rainwater collected; 3 = cooling tower blow down)

| | Min. influent conductivity (μS/cm) | Max. influent conductivity (μS/cm) | Effluent conductivity possibility (μS/cm) | Literature | Various considerations | Does technology meet main requirements for different streams (1, 2 and 3) |
|---|---|---|---|---|---|---|
| RO | <100 | 25,000 | 0.1–500 | Fritzmann et al. (2007), Greenlee et al. (2009) | Mature technology, used to desalinate SW/BW | Yes (1, 2 and 3) |
| NF | 500 | 25,000 | 500–1,000 | | Mature technology, used to desalinate BW | Yes (1, 2 and 3) |
| ED/ EDR | 1,000 | 8,000 | 100–8,000 | Strathmann (2010) | Mature technology used to desalinate BW | Not as standalone technology |
| MD | <100 | Near crystallization | <10 | Meindersma et al. (2006), Yu et al. (2013), Jansen et al. (2013) | Innovative technology, can treat SW and BW | Yes (1, 2 and 3) |
| MSF | 8,000 | 50,000 | <10 | | Mature technology, generally used for large volumes of SW | No |
| MED | 8,000 | 50,000 | <10 | | Mature technology, generally used for large volumes of SW | No |
| IEX | <100 | 3,000 | <1 | | Mature technology, used as a polishing step | No (3) Yes (1, 2) |
| EDI | <100 | 50 | <1 | Wood et al. (2010) | Innovative technology, used as a polishing step | No |
| CDI | <100 | 8,000 | | Oren (2007), Anderson et al. (2010) | Innovative technology, used to desalinate BW | Doubtful (3) Yes (1, 2) |

**Table 4** | Overview of desalination technologies tested on laboratory scale

| Desalination technology | Wastewater | Rainwater | Cooling tower blow down |
|---|---|---|---|
| Electrodialysis | X | | X |
| Capacitative deionization | X | | X |
| MD | X | X | X |
| Nanofiltration/reverse osmosis* | | | X |
| *Computer modeling (for NF/RO) | | | X |

Therefore, a pragmatic approach has been chosen:

- Average quality characteristics for each of the raw water sources have been defined based on historic data and the extended analysis performed during the laboratory-scale trials.
- Cooling tower blow down water (Table 1, last column) is taken as the reference for evaluating desalination technologies – this stream is the most challenging in terms of salinity and organic constituents, but is fairly consistent in quality and quantity.
- Cooling tower make-up water is taken as the reference for desired product quality, having not only a salinity constraint, but also some more specific target limits for organic and inorganic components (ortho-phosphate < 1 mg/l, chloride < 150 mg/l, TOC < 15 mg/l).
- The desalination technology was assigned to be 'leading' (selected to meet final product specification), whereas pretreatment then ought to be robust as a bridge between raw water quality and desalination technology influent constraints.
- In case a technology provides (by its typical process characteristics) a product quality beyond what is strictly required, a bonus value is calculated based on the quality difference (expressed as an equivalent cost when using IEX technology for that quality difference).
- All flow data are normalized to a production volume of 100 $m^3$ per hour.
- Cost data are normalized to the desalination step using NF technology.

**Table 5** | Advantages and disadvantages of desalination techniques

| Technology | Advantages | Disadvantages |
|---|---|---|
| Reverse osmosis | • Fairly high recovery rates possible<br>• Widely applied on large scale for brackish water desalination<br>• Good TOC removal | • Steady pre-treatment required<br>• Complete desalination – blending required<br>• Operational problems: scaling and bio-fouling<br>• Use of chemicals to control process/clean system |
| Nano filtration | • Fairly high recovery rates possible<br>• Widely applied on large scale for brackish water desalination<br>• Good TOC removal | • Steady pre-treatment required<br>• Complete divalent ion removal<br>• Operational problems: scaling and bio-fouling<br>• Use of chemicals to control process/clean system |
| Electro dialysis | • Limited pre-treatment needed, can treat feed water with fairly high turbidity<br>• Salt removal only<br>• Operational problems limited (robust)<br>• Chemicals only needed for cleaning<br>• High recovery rates possible<br>• Widely applied on large scale for brackish water desalination | • Post- or pre-treatment might be needed before further use (especially for TOC and phosphate)<br>• Low TOC removal, uncharged products are not removed<br>• Electrical energy consumption directly related to the amount of ions removed from feed |
| MD | • Limited pre-treatment needed, can treat feed water with fairly high turbidity<br>• Operational problems limited (robust)<br>• Chemicals only needed for cleaning<br>• Waste heat as energy source | • Complete desalination – blending required<br>• Recovery rates of great influence on operational costs<br>• Technology not yet applied on full scale for desalination<br>• Energy needed to heat water |
| Capacitive deionization | • Limited pre-treatment needed, can treat feed water with fairly high turbidity<br>• Salt removal only<br>• Chemicals only needed for cleaning | • Post-treatment might be needed before further use<br>• Not much known yet on operational problems (fouling/scaling)<br>• Recovery rates still in research<br>• Technology not yet applied on full scale for desalination |

To select the most promising techniques for a demonstration pilot at the desired scale, selection criteria were defined, taking into account a broad range of factors. Special attention was given to the fact that several techniques are already well developed, like RO (Fritzmann *et al.* 2007; Greenlee *et al.* 2009), while others are still premature, like CDI (Anderson *et al.* 2010). It is relatively uncertain how costs for the latter group of technologies will develop in the longer term. Besides using the developed fact sheet information, modeling results and experimental work were carried out, and technology and equipment vendors were involved to provide cost data for capital and operating expenses. Table 2 provides an overview of the technology assessment that was made for the expected worst-case scenario, i.e., treatment of cooling tower blow down water.

These data clearly show some generic trends. All the technologies are able to meet the required product salinity specification, most even go beyond the desired quality of 1 mS/cm. Water recovery, as an overall result of both pre-treatment and desalination, shows quite a variety in performance (or raw water losses). When looking at specific product quality criteria (residual phosphate, TOC and total suspended solids (TSS) levels), only NF and MD are able to meet these limits without further treatment. NF has a major challenge in adjusting the appropriate pre-treatment as UF alone might be inadequate. For both EDR and CDI, an additional treatment is required (either as pre- or as post-treatment) to reach the desired quality with respect to phosphate and TOC. Evaluating the various cost levels, it is clear that overall treatment costs vary substantially, putting the emphasis on optimizing the pre-treatment and desalination combinations. For NF in particular, the pre-treatment step may have a significant overall cost impact (up to 40%). A major drawback for both CDI and MD is the degree of maturity as a commercially available technology – both are emerging technologies and seem to fit in niche application markets thus far. According to vendor information, it is uncertain whether both will develop at sufficient pace to meet large-scale commercialization by 2016. For CDI, the component lifetime is also a major issue – MD membrane surface and energy costs are major hurdles for rapid scale up.

For the trial at the Evides-Dow pilot location, nanofiltration and electrodialysis reversal were selected for demonstration, as pilot units are readily available and the technologies offer good potential to achieve the desired product quality (potentially with additional treatment) at acceptable costs. Although EDR (like CDI and MD) allow MMF as pre-treatment (rather than NF needing UF or better), the pilot will be equipped with a robust pre-treatment fitting both desalination trains. As the project progresses, the pre-treatment will be optimized and tailored to the back-end requirements.

Several supporting activities will be required to provide more back-up for the chosen technologies and to allow future flexibility. More investigation is required with respect to the influence of certain water contaminants on the fouling on NF membranes and feasible measures to reduce these effects. Regular evaluation during the trial process is needed to acquire new insight on the viability of technologies, but also to optimize treatment to meet the overall efficiency targets of the E4Water project.

## CONCLUSIONS

The two-step work process, applied to narrow down a wide variety of desalination technologies to a selection of the two most promising techniques for a demonstration trial, was very successful using commonly accepted selection criteria and a structured evaluation of the pre-selected technologies.

The resulting trials will provide significant insight into the potential reuse of brackish water streams from different origins – the ultimate results with respect to performance and cost will be beneficial for all regions where industries operate close to rural areas, thereby making cross-sector reuse a reality.

The overall outcome of the technology selection can be summarized as follows:

1. Demo trial at the Evides-Dow location will consist of:
   - Two parallel desalination trains
     - Nanofiltration
     - Electrodialysis reversal
   - A preceding robust pre-treatment feeding the two desalination trains.
2. Supporting activities comprising:
   - Enhanced pre-treatment investigation
   - Regular evaluation based on new insights with respect to technologies ready for further evaluation and optimization opportunities to meet the overall E4Water objectives on cost and performance efficiency.

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