




Brines from industrial water recycling: new ways to resource recovery

Malena Kieselbach, Tobias Hogen, Sven-Uwe Geißen , Thomas Track , Dennis Becker , Hans-Jürgen Rapp, Joachim Koschikowski, Joachim Went, Harald Horn, Florencia Saravia, Annika Bauer, Rebecca Schwantes, Daniel Pfeifle, Nicolas Heyn, Miriam Weissroth and Bernd Fitzke

ABSTRACT

Stricter environmental regulation policies and freshwater as an increasingly valuable resource have led to global growth of zero liquid discharge (ZLD) processes in recent years. During this development, in addition to water, the recovery of recyclable materials, e.g. salts, from industrial wastewater and brines is considered more frequently. Within the framework of the HighCon research project, the subject of this study, a new ZLD process with the goal of pure single-salt recovery from industrial wastewater has been developed and investigated in a demonstrational setup at an industrial site. With regard to pure salts recovery, separating organic components is of great importance during the treatment of the concentrate arising from used water recycling. The removal of COD and of ions responsible for scaling worked very well using nanofiltration. The nanofiltration permeate containing the monovalent ions was pre-concentrated using electro dialysis and membrane distillation before selective crystallization for single-salt recovery was performed. An example economic case study for the newly developed ZLD process – based on demonstration results and considering optimization measures for a full-scale design – indicates that the costs are equal to those of a conventional ZLD process, which, however, does not provide *inter alia* the aforementioned benefit of single-salt recovery.


Key words | brine management, cost analysis, industrial wastewater, resource recovery, water reuse, zero liquid discharge



HIGHLIGHTS

- Stricter environmental regulation policies and freshwater as an increasingly valuable resource are leading to a global growth of zero liquid discharge (ZLD) processes in recent years.
- In the study, the results of a demonstrational setup at an industrial site for a newly developed concentrate treatment process are presented. This new ZLD process, named HighCon, has the goal of pure single-salt recovery from industrial wastewater.
- The demonstration results show that separating organic components and monovalent ions worked out very well with nanofiltration in the HighCon process and recovering an organic-free

This is an Open Access article distributed under the terms of the Creative Commons Attribution Licence (CC BY-NC-ND 4.0), which permits copying and redistribution for non-commercial purposes with no derivatives, provided the original work is properly cited (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

doi: 10.2166/wrd.2020.033

Malena Kieselbach
Tobias Hogen
Sven-Uwe Geißen  (corresponding author)
 Technische Universität Berlin,
 Department of Environmental Technology, Chair of
 Environmental Process Engineering, Secr. KF 2,
 Straße des 17. Juni 135, 10623 Berlin,
 Germany
 E-mail: sven.geissen@tu-berlin.de

Thomas Track 
Dennis Becker 
 DECHEMA – Gesellschaft für Chemische Technik
 und Biotechnologie e.V.,
 Forschungsförderung und Tagungen, Theodor-
 Heuss-Allee 25, 60486 Frankfurt am Main,
 Germany

Hans-Jürgen Rapp
 DEUKUM GmbH,
 Maybachstraße 5, 72636 Frickenhausen,
 Germany

Joachim Koschikowski
Joachim Went
 Fraunhofer Institute for Solar Energy Systems ISE,
 Heidenhofstr. 2, 79110 Freiburg,
 Germany

Harald Horn
Florencia Saravia
Annika Bauer
 DVGW-Research Center at the Engler-Bunte-
 Institut, Water Chemistry and Water Technology,
 Karlsruhe Institute of Technology,
 Engler-Bunte-Ring 9a, 76131 Karlsruhe,
 Germany

Rebecca Schwantes
Daniel Pfeifle
 SolarSpring GmbH, Christaweg 40, 79114 Freiburg,
 Germany

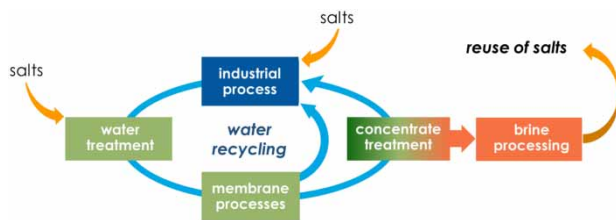
Nicolas Heyn
 Terrawater GmbH,
 Wischhofstraße 1-3, Gebäude 11, 24148 Kiel,
 Germany

salt mixture or – using selective crystallization – the separation of an organic-free single salt with >90% purity has been enabled.

Miriam Weissroth
Bernd Fitzke
WEHRLE Umwelt GmbH,
Bismarckstr. 1-11, 79312 Emmendingen,
Germany

- In a cost analysis, the total specific costs have been calculated for the newly developed HighCon process and a comparable ZLD process. With approximately 4 €/m³, the results show that the specific costs are in the same range for both processes.
- The HighCon process has the advantage of pure (single-)salt recovery over conventional ZLD generating the mixture of solid wastes. Recovery of resources is becoming increasingly important – economically and with regard to the closing of recoverable substance cycles.

GRAPHICAL ABSTRACT



NOMENCLATURE

AAS	Atomic absorption spectroscopy	MEH	Multi-effect humidification
AEM	Anion exchange membrane	MWCO	Molecular weight cut-off
AIC	Annual investment costs	NF	Nanofiltration
CAPEX	Capital expenditure	OC	Operating costs
CEM	Cation exchange membrane	OPEX	Operational expenditure
COD	Chemical oxygen demand	PF	Plate and frame module for feed gap air gap
CRF	Capital recovery factor	FGAGMD	Membrane distillation
Cryst.	Crystallization	PV	Pressure vessel
ED	Electrodialysis	RO	Reverse osmosis
EDR	Electrodialysis reversal	RR	Recovery ratio
Evap.	Evaporation	SW AGMD	Spiral wound module for air gap membrane distillation
FC	Frequency control	TC	Total costs
FO	Forward osmosis	TIC	Total inorganic carbon
GOR	Gained output ratio	TMP	Transmembrane pressure
HP	High-pressure pump	TNb	Total nitrogen bound
IC	Ion chromatography	TOC	Total organic carbon
ICP OES	Inductively coupled plasma optical emission spectroscopy	TRL	Technology readiness level
IX	Ion exchange	TS	Total solids
KPI	Key performance indicator	UF	Ultrafiltration
MBR	Membrane bioreactor	XRD	X-ray diffractometer
MD	Membrane distillation	ZLD	Zero liquid discharge

INTRODUCTION

Freshwater is one of our most important resources. This applies not only to agricultural and potable uses but also to industrial production (Götz *et al.* 2019) in which water is required for cooling and as a solvent. Therefore, in many industrial sectors, water recycling plants have been in operation for decades. Conventional recycling processes are often limited by the discharge options and the costs of disposing of residual streams. For this reason, water recycling rates are often kept artificially low at only 20–50%.

Due to water scarcity and the protection of water bodies, wastewater, and residual streams (e.g. brines from membrane processes) of industrial processes have received more and more attention worldwide (Yaqub & Lee 2019). Increased public environmental awareness and increasingly strict environmental regulation policies are resulting in a change in industrial wastewater treatment; the discussion about wastewater-free industrial production has gained considerable momentum in recent years, and zero liquid discharge (ZLD) has become a serious alternative to conventional systems for wastewater treatment and water recycling (Tong & Elimelech 2016; Götz *et al.* 2019). Furthermore, the increasing value of freshwater – not least due to the globally increasing freshwater scarcity – and the rising cost of wastewater disposal is driving ZLD forward as an attractive strategy for used water management (Tong & Elimelech 2016; Yaqub & Lee 2019). Even where there is no regulatory or financial pressure, companies are striving for ZLD to obtain recognized seals of approval or awards confirming resource-efficient and sustainable production (green labeling) (Götz *et al.* 2019).

During the last decade, there has been a tremendous development of ZLD systems, particularly in North America, Europe, and Asia (Götz *et al.* 2019). According to MarketsandMarkets (2019), the ZLD market was estimated at USD 5.4 billion in 2018. With a compound annual growth rate of 8.3%, the ZLD market is projected to reach USD 8.1 billion by 2023 (MarketsandMarkets 2019).

Although ZLD is becoming increasingly important in industrial wastewater treatment, it is still associated with increased energy consumption and additional costs for investment and operation. Conventional ZLD systems

consist of a series of thermal processes alone or, more common recently, combined with a reverse osmosis (RO) system for a pre-concentration. To decrease the energy demand and therefore the operational costs, further enhanced pre-concentration with a lower energy consumption than conventional brine concentrators is targeted (Tong & Elimelech 2016). Applications such as electro dialysis (ED) or electro dialysis reversal (EDR), forward osmosis (FO) and membrane distillation (MD) are emerging as alternative ZLD technologies to further concentrate used water, e.g. after the RO stage (Tong & Elimelech 2016; Pramanik *et al.* 2017; Yaqub & Lee 2019). Since membrane fouling/scaling is a limiting factor in all membrane-based processes, pre-treatment, e.g. for reducing organic components or softening, can enable a further concentration as well. Semblante *et al.* (2018) suggest a wide range of methods/technologies, such as chemical precipitation and coagulation, electrocoagulation, ion exchange (IX), nanofiltration (NF), adsorption, or advanced oxidation, as potential pre-treatment for ZLD. Currently, a change is taking place in the design of ZLD processes; instead of focusing exclusively on volume minimization with well-established technologies – often accepting high energy consumption – innovative technologies or process designs are being considered for an optimized ZLD process.

Within this development, the recovery of recyclable materials from RO concentrates is also being considered more frequently. Considering that the storage or disposal of the solid waste mixed salts generated by conventional ZLD processes can have negative impacts on the environment, other options, such as the recovery of several high-purity salts in ZLD applications, are increasingly becoming an objective (Yaqub & Lee 2019). According to Kim (2011), salt recovery is realized most commonly by evaporation and cooling, but membrane separation processes have become more and more attractive as well. In contrast to salt recovery from brackish water or seawater, the separation of organic and inorganic substances can be of particular importance for salt recovery during industrial wastewater treatment. For this reason, NF has been applied, e.g. in the textile industry to separate dyes and salts (Dasgupta *et al.* 2015). NF has also been investigated for recovering NaCl from a regeneration effluent for ion exchange at a sugar decolorization plant (Wadley *et al.*

1995) and for separating NaCl and lactic acid (Freger *et al.* 2000), as well as retaining organic solutes (glucose) affected by NaCl in a highly concentrated solution (Luo & Wan 2011). In a recent study, Linden *et al.* (2020) investigated the separation of natural organic matter and NaCl by NF, but also by ED and IX in RO brine from a ZLD process in the petrochemical industry.

Since salts and recalcitrant organics are released into wastewater not only through production processes but also through water treatment (coagulants, flocculants, biocides, antiscalants, etc.), an integrative approach and optimization are of great importance. If, for example, water chemicals or substances added in the production process could be substituted or completely omitted, this would have a major impact on concentrate treatment.

The HighCon research project aims to develop a holistic solution for concentrates arising from industrial wastewater reuse (Figure 1) while taking into account the various technical possibilities, production-integrated measures, and the energy efficiency and sustainability of concentrate treatment processes.

In this study, the results of one selected process from one of the demonstration sites within the HighCon project are presented. This includes experimental results of the pilot demonstration as well as an example economic case study for the newly developed concentrate treatment process.

MATERIALS AND METHODS

Demonstration site

The demonstration plant developed within the HighCon project was piloted at two industrial production sites. The results from the food industry site are presented in this study.

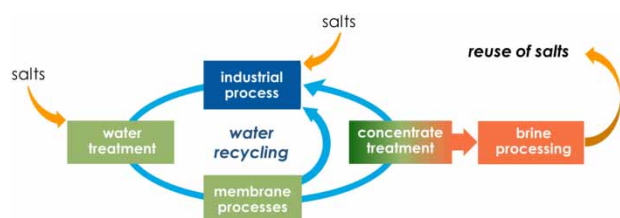


Figure 1 | Scheme of the HighCon concept for concentrate treatment.

The DEK Deutsche Extrakt Kaffee GmbH produces a range of instant coffee products and liquid coffee extracts at their manufacturing facility in Berlin. Here, along with other steps, the roasting, extraction, drying, and agglomeration are carried out. During these process steps and, especially, the system cleaning, process wastewater with high organic contamination accumulates. Apart from good biodegradable substances, this used water contains coffee components that are hardly or non-biodegradable and inorganic salts, e.g. Na⁺ and Cl⁻, from the cleaning processes. The existing wastewater treatment on-site consists of a mechanical pre-treatment and a membrane bioreactor (MBR) with submerged ultrafiltration (UF) membranes. As process water recycling at the site of DEK Berlin can only be realized when the accumulated concentrate is treated as well, the company participated in the HighCon research project to find new solutions for concentrate handling.

Demonstration plant

Besides the investigation of the overall process combination, one focus was on the separation of organic and inorganic components in the RO concentrate by NF. A second focus was on the further development of single innovative technologies, such as an MD module with a novel channel configuration.

The UF permeate from the DEK's MBR served as influent for the HighCon demonstration plant. The demonstration plant consists of an RO system for investigating water recycling and the following subsequent technologies for further processing the RO concentrate:

- NF for separating organic components and polyvalent ions in NF concentrate, and monovalent ions in the NF permeate;
- ED; and
- MD, both for further concentration of NF permeate near to saturation limits.

The final steps to ZLD, evaporation and crystallization (Evap. & Cryst.) were investigated at lab-scale at TU Berlin. A simplified process flow sheet of the full-scale wastewater treatment plant and the HighCon demonstration plant for water recycling and RO concentrate treatment is shown in Figure 2.

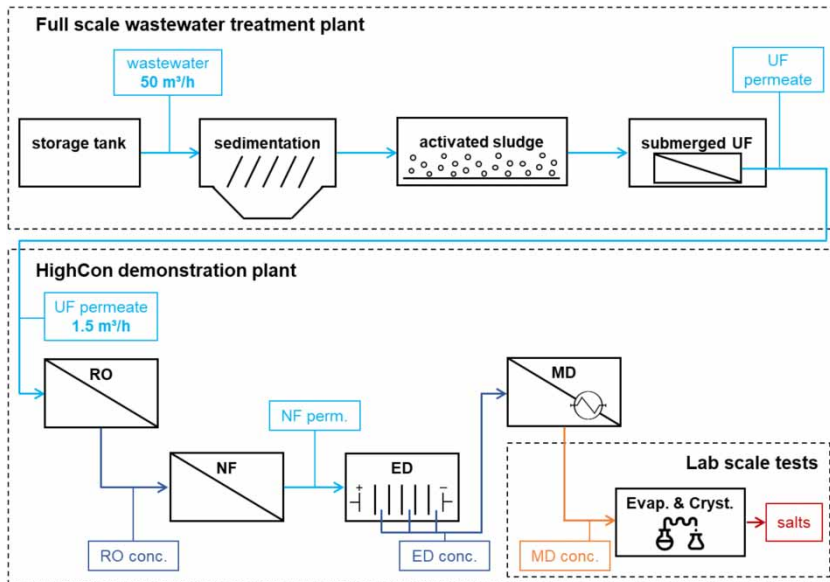


Figure 2 | Simplified process scheme of full scale and demonstration plant at the site of DEK Berlin.

The UF permeate was temporarily stored in a 1 m³ intermediate bulk container (IBC) before entering the RO system. To protect the membranes in all the following steps, a pre-filter was inserted between the storage tank and the RO plant. RO, NF, and ED were operated for approximately 6–10 h/d, 5 days a week. The MD was operated 24 h/d if required. All plants were shut down over the weekend. System cleaning was carried out at the end of the week, either with clear tap water, distillate, or, if necessary, with cleaning agents. The lab-scale experiments for salt recovery by evaporation and selective crystallization were performed in a batch mode with samples collected from the demonstration plant.

Sampling

During operation days, random samples of all demonstration process flows were taken at least once throughout the day. After sampling, the following parameters were analyzed immediately on-site at the DEK: chemical oxygen demand (COD), total solids (TS), pH, conductivity, and temperature. As these parameters were intended for process monitoring of the single technologies, they were taken at different times. Once a week, samples for analyzing the total organic and inorganic carbon (TOC and TIC), total

nitrogen bound (TNb), and ions/elements were taken contemporaneously in the flows of all demonstration plants. The samples were preserved if necessary and stored at 8 °C until analyses had been finalized. These measurements form the data basis for evaluating the HighCon process.

Analytical methods

The following parameters were analyzed to characterize process water flows from the DEK Berlin demonstration site and/or feed, permeate and concentrate samples during demonstrational experiments: pH, conductivity, TS, COD, TOC, TIC, TNb, and a variety of relevant ions respectively.

Conductivity and pH were measured by using a FiveGo Mettler Toledo conductivity meter, Switzerland conductivity F3 with the corresponding measuring sensor Mettler Toledo LE703, and pH meter FiveGo Mettler Toledo pH F2 with the pH electrode LE438-IP67, respectively. COD measurements were achieved using cuvette tests LCK 014, LCK 514, and LCK 1414; a thermostat LT 200; and a UV-VIS spectrophotometer DR 5000 (all HACH LANGE, Germany) according to standard methods (DIN ISO 15705:2003-01). TS was measured using a DBS 60-3 Moisture analyzer (KERN & SOHN, Germany). These parameters were measured

directly after sampling at DEK Berlin. Additionally, depending on the level of automatization of the demonstration technology, the pH, conductivity, and temperature were recorded continuously.

The analyses of TOC, TIC, and TNb were performed at TU Berlin using an Analytik Jena, Germany TOC analyzer multi N/C 3100 according to standard methods (DIN EN 1484:1997-08).

Ions and elements were measured by the DVGW Research Center at the Engler-Bunte-Institute (DVGW-EBI), Karlsruhe. Ion chromatography (IC) was used to quantify the amount of selected anions (Metrohm 790 Personal System, Germany). Cations and elements were analyzed with an ICP-OES (inductively coupled plasma optical emission spectroscopy) spectrometer (Agilent Technologies, Germany ICP-OES 5110). Due to high salinity contents of feed and concentrate samples, dilutions up to 1:1000 were applied to perform IC and ICP-OES measurements properly. Ions or elements present in small amounts might be underestimated, caused by the required dilutions.

Solid matter fractions produced in the crystallization tests were analyzed at TU Berlin via Rigaku, Germany SmartLab 3 kW X-ray diffractometer (XRD). The corresponding ion analyses were performed using atomic absorption spectroscopy (AAS, Perkin Elmer, Germany PinAAcleTM) and a Metrohm, Germany 790 Personal IC fed with resolved sample solutions.

Experimental procedure

RO for water recovery and concentrate production at demonstration scale

The RO pilot plant was equipped with four spiral wound membrane modules FilmTec™ BW30-4040, USA, connected in series. The operating pressure was applied using a high-pressure pump, which was designed for a maximum operating pressure of 40 bar at 1.5 m³/h. In addition, a recirculation pump was installed to ensure a sufficient cross-flow velocity.

For investigations of the concentrate treatment, the RO should be operated continuously and at a maximum possible permeate recovery rate. Therefore, the permeate flux was kept constant (as far as possible due to changes in the wastewater composition) at an average value of 33 L/(m² h). As

the RO was run in a single-pass operation, the corresponding permeate recovery rate was nearly constant at about 65%, on average. To keep the flux and recovery rates constant, the transmembrane pressure (TMP) was adjusted within the 21–34 bar range. The average TMP was 26 bar.

The temperature during demonstration ranged between 14 and 43 °C. This temperature range also applies to the operation of the other demonstration plants.

Treatment of RO concentrate by nanofiltration

The RO concentrate was subsequently treated by an NF pilot plant. The main task for the NF was rejecting the organic compounds and, thus, preventing fouling in the downstream processes ED/MD. The secondary goal was to achieve a maximum passage of salts to optimize salt recovery.

The NF pilot plant's design is identical to that of a full-sized NF and operated in a 'feed-and-bleed' mode. It is designed to treat between 200 and 800 L/h, with the actual feed volume being regulated via frequency control (FC) of the high-pressure pump (HP). The NF's HP is a Grundfos, Denmark multi-stage centrifugal pump with a nominal pressure head of about 20 bar. There are two pressure vessels (PVs), one 4" and one 8", both of which can hold one membrane element each. The different PVs are required to ensure the plant's optimal performance under varying feed flows and/or filtration rates. During the DEK-trial, the NF was operated using DOW-FilmTec™ NF270 elements, USA, first a 4"-element (7.6 m²), and later, as feed increased, an 8"-element (37 m²). Feed temperatures ranged between 14 and 43 °C, with an average of 27 °C. The average pH in the feed was 8.3 and the average conductivity was about 5.2 mS/cm. Since hardness and concentrations of multivalent ions, in general, were expected to be very low, no acid dosing was provided during the DEK-trial. This proved to be disadvantageous because the hardness/scaling potential of the effluent was higher than expected, and consequently, the plant suffered from scaling. Yet despite the problems with scaling, the average flux ranged at approximately 18 L/(m² h). The yield varied between 30 and 90%, depending on the tested process conditions.

Further concentration of nanofiltration permeate by ED and MD

Electrodialysis. The ED was designed with four fluid cycles, one for the electrode rinsing, which was operated with a 0.1 mol/L Na₂SO₄ solution, the second for the feed, and two cycles for different concentrates. The membrane module itself consists of a membrane stack in the characteristic plate and frame design by the company DEUKUM, Germany. The flow channels were equipped with a special spacer layer with integrated sealing. The membrane module consisted of 40 cells, respective pairs of anion and cation exchange membranes (CEM and AEM). The channel thickness was 270 μm and the average flow velocity in the channels was approximately 2.5 cm/s. The active membrane area was 14.17 m² (number of all membranes (CEM and AEM), 51 cm width × 51 cm length). Mono-selective ASV and CSO membranes made by Asahi Glass Co., Japan, and standard ion-exchange membranes FAS and FKS from FUMATECH BWT GmbH, Germany, were used in the module.

The unit was operated in a ‘feed-and-bleed’ mode on the concentrate side and ‘batch’ operation on the feed side. The ED module was operated at a constant 15 VDC. A batch started with the conductivity of the NF permeate and 4.2 A and ended at 1.0 mS/cm (2.2 A) in the diluate. Each batch was about 33 L. The conductivity of the concentrate was controlled at a constant value of approximately 20 mS/cm via ‘feed-and-bleed’ operation by adding deionized water. No classic polarity reversal was applied during operation. Polarity reversal was only used for back-flush while refilling the feed tank.

Membrane distillation. The MD pilot system has been designed and constructed by SolarSpring (Germany) and consists of a module pair with a combined membrane area of 16 m². In MD, water vapor passes through a hydrophobic membrane due to a vapor pressure difference across the membrane. This vapor pressure difference is induced by applying a temperature difference in a heating and a cooling channel. In the HighCon MD pilot system, a novel channel configuration was implemented that enabled a much higher recovery ratio (RR) of distillate per single pass than previously possible. A depiction of the pilot system with tanks

and a control unit is given in Figure 3. Details on the new configuration and other typical MD channel setups can be found in Schwantes et al. (2019).

Due to the fully automated control system and onboard thermal energy supply of the plant, flexible system operation could be implemented according to the requirements of the upstream processes. Typically, however, the permeate flow from the system was between 13 and 27 kg/h depending on the salinity of the feed solution. The resulting RR was between 30 and 92%, again depending on the feed solution composition. Flux ranged between ~1 and 2 kg/(m² h) depending on the operational setting and feed salinity.

Selective crystallization of MD concentrates at lab-scale

The selective crystallization investigations were conducted at lab-scale using a rotational evaporator (BÜCHI, Switzerland Rotavapor R-300). The feed solution (MD concentrate) was evaporated at a 60 °C heating bath temperature while manually adjusting the operational pressure (in a range of <200 mbar) to maintain smooth boiling. After 90% evaporated, the residue mixture of precipitate and saturated brine was filtered at 60 °C using a glass microfiber filter in a pressurized, heated cartouche. The filtration residue was washed with acetone and subsequently dried at room temperature. The gained solid matter was named ‘Fraction I’ of the selective crystallization step. The filtrate was fed to a second evaporation step at 60 °C which was stopped after a sample weight change was no longer detected. The sample was

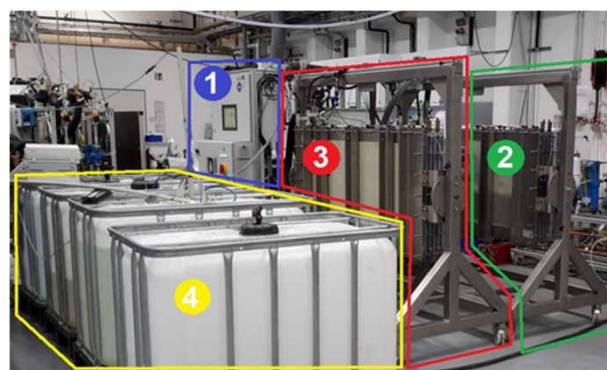


Figure 3 | Perspective view of the MD pilot system and modules: (1) Rig with pumps, valves, and controls; (2) Module 1; (3) Module 2; (4) Feed, concentrate, and distillate tanks (Schwantes et al. 2019).

then dried for 24 h at 60 °C; the resulting solid matter was named 'Fraction II'. The testing parameters had previously been assessed using PHREEQC software applying the provided Pitzer-Model database (USGS 2017) to simulate solid-liquid equilibria with regard to the different salt solubilities.

Based on the model assessment, Fraction I was assumed to comprise a big share of sodium hydrogen carbonate with a low percentage of chlorides or nitrates. Fraction II was assumed to contain all dissolved solids of the feed solution that were not present in Fraction I. The solid matter fractions were analyzed according to the section 'Analytical methods'. In this test sequence, dissolved organic solids were neglected due to their low mass share of <0.2% compared to the inorganic solids.

RESULTS AND DISCUSSION

Main influencing factors of the concentrate treatment process

Reverse osmosis

RO permeate and concentrate flow have a huge impact on the entire HighCon process. The RO permeate is decisive for water recycling due to its major part in recovery, and the concentrate determines the design of the entire following concentrate process chain. The characteristic parameters of these two flows during the demonstration are shown in Table 1. Ammonia was not analyzed due to its low concentration.

As expected, the RO membrane rejected organic components >99.5% for COD and TOC, as well as all analyzed cations >99.0%. Anions and TIC passed the membrane somewhat better, at a rejection of 99.0% for Cl⁻, 98.5% for SO₄²⁻, and 97.1% for NO₃⁻, which represents the lowest rejection of all measured parameters.

The recovered water can be reused as cooling water, for rinsing purposes, or as boiler feed water (after ion-exchange

polishing). Potentially, further processing would be required. In any case, the RO permeate has a higher purity than the used tap water, so the process water pre-treatment can be reduced or even eliminated.

Nanofiltration

The main goal of the NF, the removal of the COD, was successfully achieved; the average COD-removal rate was 99.5% with a standard deviation of 0.33%. With an average COD of 2,400 mg/L in the feed and a COD of usually <10 mg/L in the permeate, the original treatment target value of 100 mg/L COD was reliably reached (Figure 4).

The excellent COD-removal rate can be explained by the composition of the refractory COD, which was mainly complex, color-giving molecules, the so-called melanoidins that arise during coffee roasting. These have high molecular weights of 1,000–100,000 Da, so that their rejection by NF270 (molecular weight cutoff (MWCO) by 200–400 Da) is nearly perfect.

The salt passage was good to excellent for the monovalent ions and poor to very poor for the multivalent ions (Figure 5 and Table 2). In this respect, the pilot system confirmed all expectations with regard to the performance of an NF membrane. Only the rather high passage of silicon was surprising, the concentration in the permeate being about 65% of that in the feed.

The following average concentrations were determined in the NF feed and permeate during the demonstration:

However, although the salt passage was acceptable, the overall salt recovery was unsatisfactory during the trial period because the water yield was only ~50% and much lower than expected. This was a result of the missing acid dosing (see Section 'Experimental procedure') and the constant scaling on the NF, which could not be prevented by antiscalant dosing alone.

To assess the potential total recovery of the most interesting ions – Cl⁻, Na⁺, and K⁺ – the data from a 3-week period

Table 1 | Characteristic composition of RO permeate and concentrate at a 65% water recovery rate

	pH	Cond. (mS/cm)	COD (mg/L)	TOC	TIC	Ca ²⁺	Na ⁺	K ⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Si
Permeate	5.8	0.02	<5	<0.5	3.4	<0.05	2.7	0.7	1.3	3.3	0.5	<0.05
Concentrate	8.0	6.5	2,957	1,035	605	86	888	184	323	298	104	18

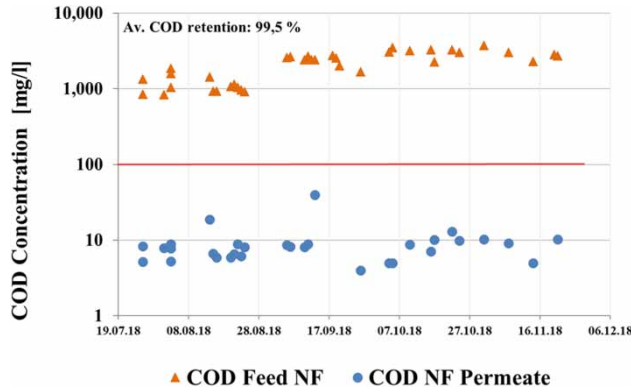


Figure 4 | COD of feed and permeate; permeate target value of 100 mg COD/L.

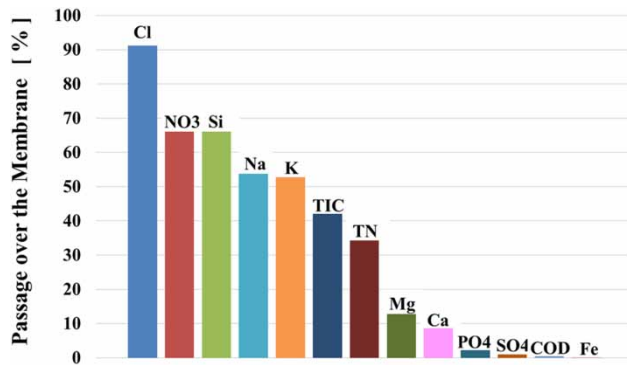


Figure 5 | Average passage of ions over the membrane, expressed as % of feed concentration.

with an ~80% yield were examined more closely. During this period, an average of 40% of K^+ , 51% of Na^+ , and ~61% of Cl^- were recovered with the NF permeate (Figure 6).

For the cations K^+ and Na^+ , the expected and the measured recovery were in good accordance. For Cl^- , however, the measured recovery was remarkably lower than expected (61% instead of ~70%). This is caused by a lower passage of chloride during this 3-week period trial compared to the average passage during the complete trial. This was most likely caused by the relatively high concentration and the retention of the divalent anions (Donnan effect). SO_4^{2-} ,

in particular, seems to have an influence, since high SO_4^{2-} -concentrate and Cl^- -permeate concentration correspond. Thus, the passage or retention of chloride is governed by the anion concentration in the concentrate.

In conclusion, the rejection of COD and polyvalent ions responsible for scaling was very good. This is very favorable as COD as well as these ions can impact the process stability of the subsequent ED and MD. Unfortunately, this advantage for process operation is a disadvantage in salt recovery since the polyvalent ions end up together with the organic components in the NF concentrate and cannot currently be reused. Further investigations are necessary for NF concentrate treatment. Additionally, monovalent ions recovery was not optimal during the demonstration phase because the plant operation had not yet been optimized (pH control, choice of antiscalant). But these conditions can be enhanced effortlessly in future plant operations.

Electrodialysis and membrane distillation

Electrodialysis. Figure 7 shows the current over conductivity for the ED system at the end of the demonstration phase in different states of cleanliness. The relationship in this value range is almost linear. It is measured with pure NaCl solutions of different concentrations as feeds and a constant 15 VDC. The initial value of 4.2 A at 2 mS/cm could not be restored, even after intensive cleaning. Significant degradation of performance already occurred after 3 days of operation with the NF permeate as feed.

At low diluate conductivities, the electrical resistance rises. Batch operation at the feed respectively diluate side was chosen to utilize the high conductivity periods and reduce the periods of low conductivity. Concerning specific energy consumption, the reference parameter has to be selected carefully. Usually, in desalination, the energy demand is linked to the production of desalinated water. However, the diluate flow with ~1 mS/cm is not really

Table 2 | Average NF feed and permeate concentration

	pH	Cond. (mS/cm)	COD (mg/L)	TOC	TIC	Ca^{2+}	Na^+	K^+	Cl^-	NO_3^-	SO_4^{2-}	Si
Feed	8.3	5.2	2,355	815	588	72	663	154	194	233	82	19
Permeate	7.9	3.0	8.1	1.8	238	6.4	333	98	160	161	1.1	13

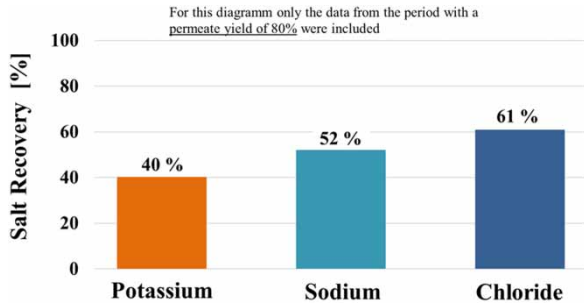


Figure 6 | K^+ , Na^+ , and Cl^- recovery in the permeate; mass in the permeate compared to the NF feed for 3 weeks.

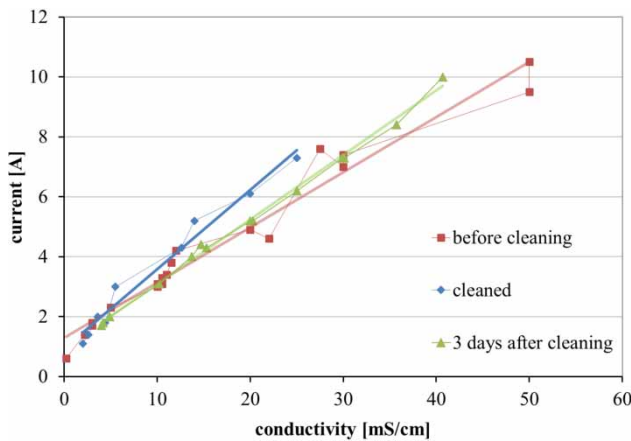


Figure 7 | Characteristic desalination performance of ED system.

desalinated water and must be further treated, e.g. with RO. Diluate and feed flow are almost the same since the transmembrane water flux is low. The specific energy demand is related to the inlet flow. The operation of the four pumps and the blower had an energy demand of 430 W. Together with all consumers in the control box, the peripheral devices required 460 W of standby power. During a batch process, the direct current energy demand started at 63 W and ended at 33 W. An average total energy demand of 520 W was measured. This corresponds to an average measured feed flow rate of 55 L/h resulting in a specific energy demand of 9.45 Wh/L for this ED system. The peripheral devices make up more than 85% of the energy demand for this small-scale device. This fraction can be significantly reduced in a production scale ED unit, so 2–4 kWh/m³ can be used as a realistic assumption.

During the demonstration experiments, some potential for optimization was found as necessary with regard to a

real operation. First, as in NF operation, the concentration factor can be significantly improved with an optimized pH adjustment and antiscalant dosage. Furthermore, thicker channels in the ED membrane module can avoid the high sensitivity of the system to organic fouling and calcite scaling.

Membrane distillation. For interpreting the operational results from the MD pilot stage within the HighCon system, the following key performance indicators (KPIs) are introduced:

Flux is a well-known value for the evaluation of distillate/permeate production per m² of active membrane surface in membrane technologies. It is calculated by dividing the distillate output \dot{m}_d by the membrane surface A , as shown below:

$$j_d = \frac{\dot{m}_d}{A} \text{ (kg/m}^2\text{h)} \quad (1)$$

Gained output ratio (GOR) provides a dimensionless coefficient for evaluating the heat recovery inside the MD module by giving a relationship between the thermal energy amount needed for the evaporation process of the distillate (numerator) and the amount of heat introduced externally (denominator).

In Equation (2), $\dot{m}_{H/C}$ (kg/h) is the mass flow rate of the heating and cooling solution, $c_{p,H/C}$ (kJ/kg K) is the specific heat capacity of the heating and cooling solution, T_{hi} is the heating inlet temperature, and T_{co} is the cooling outlet temperature. h_v (kJ/kg) is the specific evaporation enthalpy

$$\text{GOR} = \frac{\dot{m}_d \times \Delta h_v}{\dot{m}_{H/C} \times c_p \times (T_{hi} - T_{co})} \quad (2)$$

Thermal efficiency η_{th} is a percentage value for the ratio of latent heat used for the phase change, to the total heat transported through the membrane, and is shown in Equation (3). T_{ho} is the heating outlet temperature.

RR (Equation (4)) is the quotient of the distillate mass flow rate and H/C flow rate:

$$\eta_{th} = \frac{\dot{m}_d \times h_v}{\dot{m}_{H/C} \times c_{p,H/C} \times (T_{hi} - T_{ho})} \times 100 \text{ (}\%) \quad (3)$$

$$\text{RR} = \frac{\dot{m}_d}{\dot{m}_f} \times 100 \text{ (}\%) \quad (4)$$

Figures 8 and 9 can be analyzed with these KPIs. During the piloting phases, an array of different parameter settings were applied to evaluate and characterize the novel MD system to gain reliable data for cost calculations and upscale the pilot system. A detailed analysis is given in Schwantes et al. (2019). Since MD is primarily used for concentrating feed solutions that are of higher salinity than other technologies are capable of treating, the performance of a selected analysis in correlation with salinity increase is presented. The general trend in both graphs and for all values of flux, GOR, RR, and η_{th} is a decreasing one. This effect can be assigned to the fact that as more salt ions are present in the feed solution, more thermal energy will be required to evaporate the same amount of distillate due to the decrease

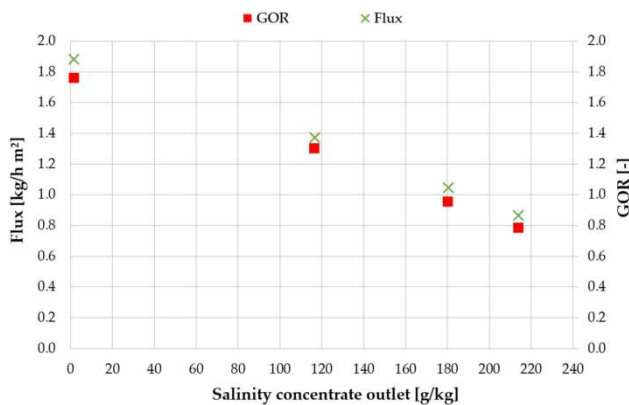


Figure 8 | Influence of concentrate salinity on flux and GOR; MD1 + MD2 combined; feed inlet salinity 0.3/55/95/143 g NaCl/kg; $\dot{V}_f = 40$ kg/h, $\dot{V}_{H/C} = 600$ L/h, $T_{hi\ 1/2} = 80$ °C, $T_{cl\ 1/2} = 25$ °C (Schwantes et al. 2019).

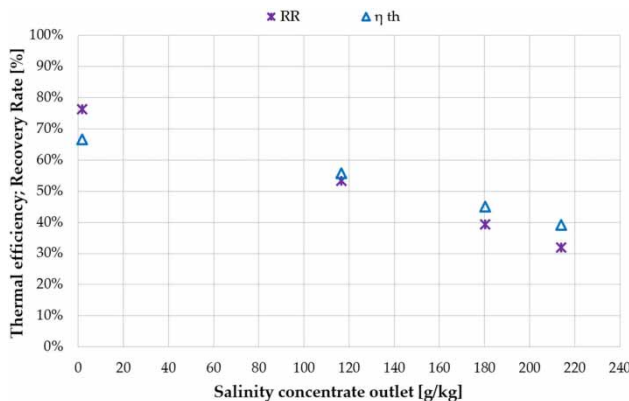


Figure 9 | Influence of concentrate salinity on RR and thermal efficiency η_{th} ; MD1 + MD2 combined; feed inlet salinity 0.3/55/95/143 g NaCl/kg; $\dot{V}_f = 40$ kg/h, $\dot{V}_{H/C} = 600$ L/h, $T_{hi\ 1/2} = 80$ °C, $T_{cl\ 1/2} = 25$ °C (Schwantes et al. 2019).

in vapor pressure. Thus, under the same operating conditions, the flux will reduce with increasing salinity in the feed solution, as seen in Figure 8. As an indicator of internal heat recovery, which is coupled to the distillate production, GOR values will decrease correspondingly.

Thermal efficiency η_{th} , which is shown together with RR in Figure 9, is also affected by the increase in salinity. The effective driving force available for the actual evaporation is reduced with the increase in salt ions in the solution. Alongside this reduction, the fraction of total heat used for evaporation is subsequently also reduced, which can be seen in the η_{th} trend. In comparison to 67% at tap water salinity, only 39% of the incoming thermal energy is used to bring about the phase change when reaching a 214 g/kg salinity. Since one of the main design goals of the novel MD module was a significant increase in RR compared to previous module concepts, the analysis of RR is of specific interest. Although the decrease in RR is high from 76 to 32%, the absolute value is a huge improvement in comparison to earlier MD modules used in high salinity applications. Table 3 provides a comparison of KPIs from the novel plate and frame module (PF FGAGMD) and the previous configuration, an Air Gap MD spiral wound module (SW AGMD; Schwantes et al. 2018). At a typical average conductivity for an MD concentration stage of 155 mS/cm, the RR in the novel module type was 15× higher (45%) than in the spiral wound module (3%). The flux was similar, the thermal efficiency was slightly higher, and the GOR was lower by 0.3. The reduced GOR can be explained by the suboptimal flow regime in the first-generation plate and frame prototype in which the main construction focus was more upon general functionality than optimal heat transfer. It is expected that equal or higher GOR values can be achieved after one iteration of the internal flow geometry redesign.

Table 3 | Average KPI values for plate and frame FGAGMD and spiral wound AGMD module, mean concentrate salinity ~ 155 mS/cm; $\dot{V}_f = 40$ kg/h, $\dot{V}_{H/C} = 300$ L/h per module; $\dot{V}_{sw} = 300$ L/h; $T_{hi\ 1/2} = 80$ °C; $T_{cl\ 1/2} = 25$ °C

	Flux (kg/m ² h)	GOR (-)	RR (%)	η_{th} (%)
PF FGAGMD	1.2	1.1	45	50
SW AGMD	1.1	1.4	3	46

Thus, the performance of the MD pilot stage was successful with regard to the desired goals.

Selective crystallization

Figure 10 displays the mineral compositions of Fraction I and Fraction II gathered from the selective crystallization test. The minerals were assessed on ion mass shares, stoichiometric balances, and simulated saturation indices; the respective values can be taken from Table 4.

Table 5 shows the quantitative results of the detected crystalline minerals mass share by XRD.

When comparing the results of ion analyses and XRD, it must be noted that the XRD analysis does not identify the stoichiometry of the amorphous solid matter; thus, this method does not deliver a full ion mass balance. Nevertheless, both results prove the feasibility of using selective crystallization to separate sodium hydrogen carbonate into a new solid, Fraction I, from other dissolved solids with a lab-scale purity of approximately 90%. Other (previously

dissolved) solids end up in Fraction II. The occurrence of a remarkable share of NaCl and KNO₃ in Fraction I is not plausible compared to their low saturation in the feed solution. It is assumed that these precipitates are the result of local effects due to an inhomogeneous temperature and concentration distribution through the sample in the reaction flask; near the sample surface, the flask wall was moistened by a thin liquid film that is supposed to deviate from the theoretical perfectly stirred sample in the bulk solution.

The prediction of the formed phases in Fraction II is still subject to improvement. The XRD measurement shows a formation of sodium carbonate (Na₂CO₃) instead of sodium hydrogen carbonate, which had not been predicted by the PHREEQC simulation. Two aspects have been identified as the main influencing factors for the deviation. On the one hand, the high ion strength occurring in the final evaporation process of Fraction II leads to inaccuracies in the simulation model. On the other hand, the ternary system Na⁺-CO₃²⁻-H₂O provides numerous stable solid phases, also hydrated, that are quite close with regard to equilibrium activities (Wegscheider & Mehl 1928). In addition, the conducted assessments covering steady-state equilibria had not considered kinetics or possible hydrate conversions during cool-down.

The salt recovery yield that is achievable via selective crystallization is dependent on the difference in salts (sub-) saturation in the feed solution. If the saturation of the target salt (in this case sodium hydrogen carbonate) is reached during evaporation and starts to precipitate, the process can be continued until the next salt (in this case sodium chloride) reaches saturation. If the evaporation is continued beyond this concentration point, the yield of the target salt is raised at a trade-off in purity as the next salt starts to precipitate and adds up to the target fraction. The maximum achievable yield rates (precipitate mass divided by the corresponding dissolved solids mass in the feed solution) according to PHREEQC simulation are up to 92% for NaHCO₃ corresponding to 60% of the Na⁺.

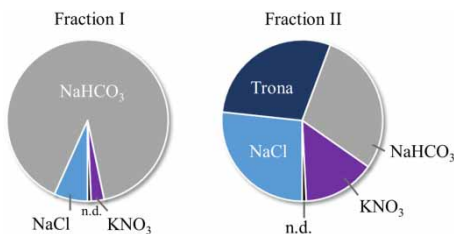


Figure 10 | Solid fractions composition assessment from ion analysis.

Table 4 | Mass share of minerals in Fractions I and II via ion analysis

	Trona	NaHCO ₃	Na ₂ CO ₃	NaCl	KNO ₃	Unknown (n.d.)
Fraction I (%)	0	89.9	0	6.8	2.6	0.7
Fraction II (%)	29.0	29.0	0	26.7	14.5	0.8

Table 5 | Mass share of crystalline minerals in Fractions I and II via XRD

	Trona	NaHCO ₃	Na ₂ CO ₃	NaCl	KNO ₃	Unknown (n.d.)
Fraction I (%)	0	94.0	0	6.0	0	0
Fraction II (%)	27.4	0	13.3	19.8	39.5	0

Full-scale process design based on the demonstration results

Based on the results of the demonstration at the DEK Berlin site, a full-scale process for water recycling via RO and

subsequent concentrate treatment using the HighCon process was designed. In addition to the values determined for flux, rejection, and energy demand, the know-how of the industry partners as experienced plant engineers was drawn upon in developing the full-scale process. The optimization potential identified during the demonstration is also being integrated in this way. The scaling potential was taken into account based on the parameters measured during the demonstration for determining the recovery rates. The following optimizations were considered for the full-scale plant design:

Increasing RO permeate recovery rate: The recovery rate is an important influencing factor for the economic feasibility of the process because all the following technologies in concentrate treatment need to handle smaller volumetric flows. For the overall process design, a high recovery rate of 85% was assumed, but with a lower flux and slightly lower rejection of all components due to the higher concentrations reached. With regard to the energy demand, a lower TMP was calculated, based on an optimized multi-stage RO design instead of the single-pass design and including an optimized antiscalant dosage.

Increasing NF permeate recovery rate: With respect to the salt recovery rate of the whole process, the NF permeate recovery needs to be increased as far as possible. A recovery rate of 80% was estimated to be realistic with optimized additive dosage, thus pH control and optimization of antiscalant.

Increasing recovery rate for ED and MD: To optimize the pre-concentration before entering the evaporation process, the water recovery by ED and MD must be increased as well. Their operation will improve with the optimized additive dosage for the NF due to pH control, but an adapted additive dosing is necessary as well.

Taking these steps into account, a full-scale water recycling and concentrate treatment process was designed for an inflow of 1,100 m³/d UF permeate, as shown in Figure 11.

For the evaporation and crystallization, using multi-effect humidification (MEH) technology was assumed, using the example of technology configuration of the company Terra-water, Germany. In Evap. & Cryst. I (MEH I), a concentrated organic-free salt stream with approximately 10% water content remaining is produced. For the organically loaded residual stream (discharge of MEH II), a remaining water content of approximately 40% was estimated.

Water recovery up to 98% is possible and about 40% of the salts contained in the used water can be recycled without organic contamination. Using a selective crystallization process, about half of this 40% can be recovered as a high-purity single salt (corresponding 20% of the total amount of salts). The other half of the organic-free salts, thus 20% of the total amount of salts, are contained in a salt mixture, e.g. suitable for the use in mine backfilling what is regarded as reuse (according to German waste management enterprises). And 60% of the salts end up in an organic salt mixture arising from evaporating the NF concentrate stream. To utilize the predominantly polyvalent ions, other treatment processes must be considered; promising results have been achieved at the lab-scale, e.g. for electrolysis in an advanced oxidation process for COD reduction. For an application in practice, however, further investigations are required. Nevertheless, in contrast to a conventional ZLD process, 40% of the salts can be recycled. In addition, using energy-optimized technologies reduces the overall energy consumption of the process.

Cost analysis

Based on the process design, costs for water recycling and concentrate treatment were calculated. Investment costs were considered as well as operating costs, such as energy and chemicals used, personnel costs, and costs for residue disposal.

Boundary conditions and database

The cost analysis was carried out for an inflow of 1,100 m³/d for the water recycling and concentrate treatment process.

In accordance with the industry partners, the boundary conditions such as the annual operating hours, amortization, and personnel deployment, and the most important expendables and energy requirements were defined (Table 6). Furthermore, the specific costs for chemicals, personnel, and energy were also determined based on real costs and practical experience (Table 7). The investment costs for the different technologies were estimated by dimensioning with the help of the flux values and the inlet volume flows (Figure 11 and Table 6).

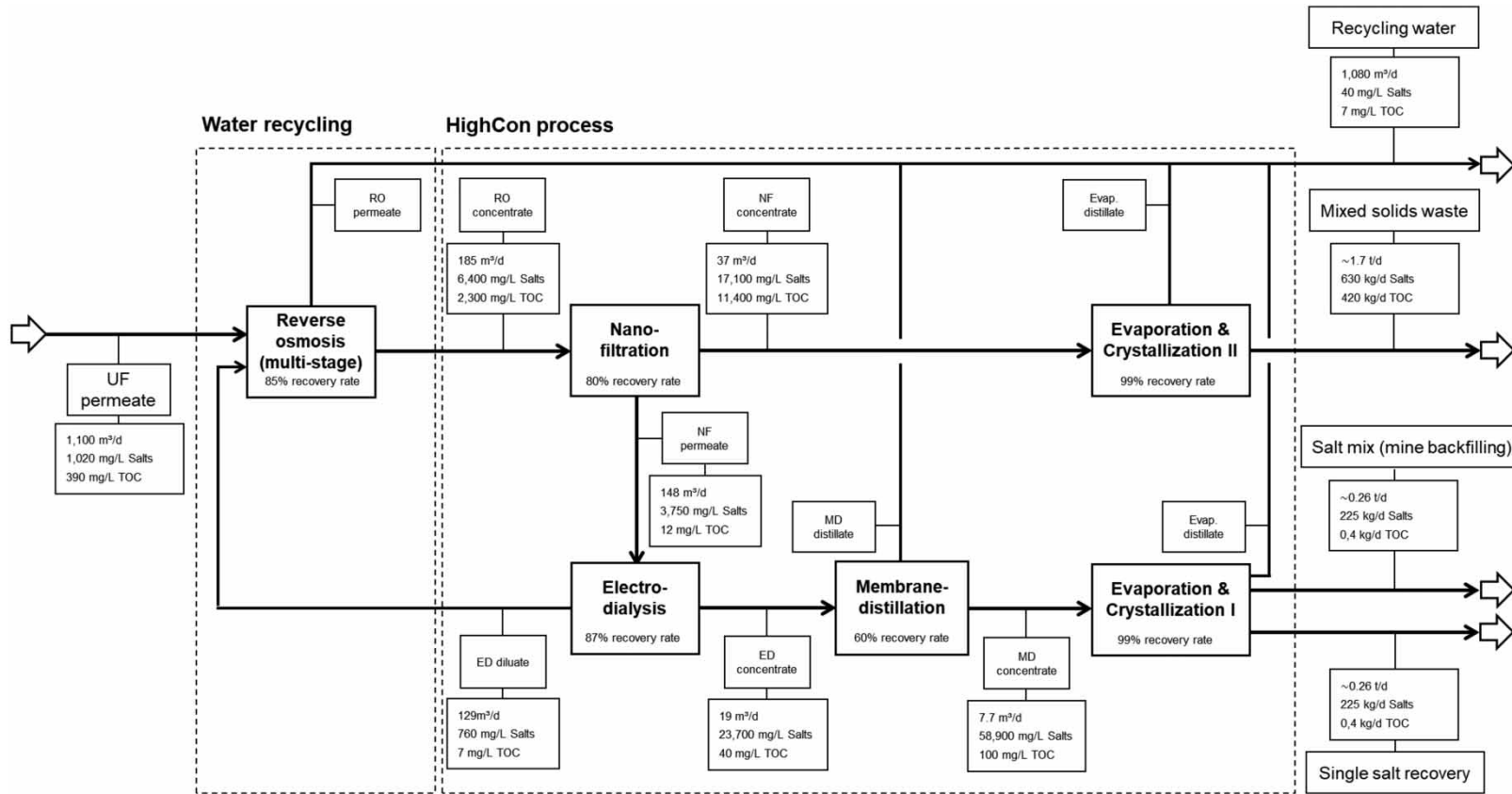


Figure 11 | Simplified process flow sheet for the full-scale water recycling and HighCon concentrate treatment designed for an inflow of 1,100 m³/d MBR UF permeate from coffee production wastewater treatment.

Table 6 | Boundary conditions and cost design parameters for the technologies of water recycling and the HighCon concentrate treatment process

		RO	NF	ED	MD	MEH I	MEH II
Annual operating hours	(h/a)				8,000		
Real interest rate	(-)				0.03		
Amortization period	(a)				7		
Personnel deployment	(h/a)	440	220	200	200	120	600
Membrane lifetime	(a)	2	3	5	2.5	-	-
Specific consumption electric energy	(kWh/m ³)	5.0	2.5	3.0	0.7	24	32
Specific consumption thermal energy	(kWh/m ³)	-	-	-	250	400	540

Table 7 | Real costs and experience values for selected positions of the water recycling and concentrate treatment process

		RO	NF	ED	MD	MEH I	MEH II
Investment costs	(€)	2,670,000	340,000	350,000	300,000	400,000	1,910,000
Specific costs membrane	(€/m ²)	20	22	100	100	-	-
Chemical costs per feed	(€/m ³)	0.35	0.35	1.00	1.00	1.00	1.00
Personnel hour	(€/h)			50			
Electric energy	(€/kWh)			0.1			
Thermal energy	(€/kWh)			0.02			

Table 8 | Costs for freshwater supply, wastewater, and residual waste disposal

		Costs
Freshwater	(€/d)	1.813 (€/m ³) · Q (m ³ /d) + 19.26 (€/d)
Wastewater discharge (to municipal sewage treatment plant)	(€/d)	2.21 (€/m ³) · Q (m ³ /d) + 18 (€/d)
Landfill disposal	(€/t)	300
Mine backfill disposal	(€/t)	100

The costs for freshwater, wastewater, and especially the landfill or mine backfill disposal of residue streams are given in Table 8.

Calculation of costs

From the investment costs and the various operating costs, the annual costs for water recycling and concentrate treatment were calculated as follows.

The annual costs incurred by investment in the plants or their depreciation were calculated using the method of the

German federal states' working group on water issues (LAWA) (DWA 2012).

In accordance with this approach, a capital recovery factor (CRF) was calculated from a real interest rate i and an assumed amortization period n using the following equation:

$$CRF(i, n) = \frac{i(1+i)^n}{(1+i)^n - 1} \quad (5)$$

All operating costs, such as energy and chemicals used, and personnel costs for operation and maintenance are summarized in the operating costs (OC) and added to the annual share of the investment costs (AIC). This results in the following definition for the total annual costs (TC):

$$TC = AIC \cdot CRF + OC \text{ (/a)} \quad (6)$$

The results for the total annual costs of the whole water recycling and concentrate treatment process are shown in Table 9. For comparison, the costs for the indirect discharge of the UF permeate to the municipal sewage treatment plant

Table 9 | Results for the annual costs of the HighCon process and indirect discharge

		Indirect discharge	Conventional ZLD	HighCon process
Total annual costs TC	(€/a)	820,000	1,590,000	1,410,000
Total specific costs	(€/m ³)	2.2	4.3	3.8
Disposal costs	(€/m ³)	2.2	0.7	0.5
OPEX ^a	(€/m ³)	–	1.2	0.6
CAPEX	(€/m ³)	–	2.4	2.7

^aExcluding disposal costs.

and the costs for a conventional ZLD process are presented alongside.

For the conventional ZLD process, a multi-stage RO, a conventional evaporator, and a second evaporation step with crystallization were assumed. The cost calculation was carried out using the method presented above. As with the organically loaded discharge of the HighCon process, the residual stream of the second evaporation step and crystallization contains about 40% water. Thus, the water recovery is comparable to the HighCon process, with up to 98%. Since only non-selective technologies are used in the conventional ZLD, an organic salt mixture is produced, containing 420 kg/d organic components and about 1,360 kg/d mixed salts. For calculating the disposal costs, landfill disposal was assumed since the waste mixture cannot be utilized. In contrast, in the HighCon process, only 60% of the residuals are not suitable for reuse, and therefore, landfill disposal was assumed. 20% of the salt content can be recovered as a reusable single salt without organic contamination. Therefore, no disposal costs were calculated. The remaining organic-free mixed salts are useable for mine backfilling.

The results of the economic analyses indicate that both ZLD procedures result in comparable total specific costs of about 4 €/m³. While disposal costs are approximately 30% lower in the HighCon process, the capital expenditure (CAPEX) is slightly higher due to the additional technological effort of the specialized process. The major difference is in the operating costs (disposal costs not included) since the operation of the new technologies like ED and MD is less expensive compared to the conventional thermal processes; pre-concentration before entering the evaporator reduces operational

expenditure (OPEX) drastically. Whether in the HighCon process or conventional ZLD, an extensive volume reduction before entering the evaporation process is the key to economic feasibility.

Furthermore, the results show that indirect discharge is significantly low-priced, with total specific costs of about 2 €/m³ instead of 4 €/m³. However, it requires sufficient capacity of the municipal sewage treatment system, does not reduce the discharge of recalcitrant substances into water bodies, and does not lead to a reduction of fresh-water use. The savings of thermal energy related to recycling warm water are an additional benefit. By using recycled water with a temperature 20 °C above that of the replaced tap water, savings up to 20.000 kWh_{th} per day could be possible.

The costs presented in this study can only give an indication, as the following limitations apply to their calculation:

- The costs were determined by extrapolating pilot plant results in a full-scale process. Operation optimizations were not fully investigated; their impact has been estimated by the industry partners as experienced plant engineers and based on demonstration results.
- Generally, it must be considered that cost analyses are not directly transferable since location-dependent cost factors, such as the water price or disposal costs, are included in the calculation.
- The different technology readiness levels (TRLs) must be considered. For emerging technologies, such as ED or MD, investment and membrane costs can be comparably high at the present moment, but they will decrease in the future with the growing application.

Comparison of conventional ZLD and the HighCon process

The separation of dissolved inorganic salts is a challenge but also an important process step in concentrate treatment. On the one hand, this is the only way to prevent their entry into natural water bodies. Loads of salts and organic components, which are non- or hardly biodegradable, enter the (municipal) wastewater treatment plant and subsequently the receiving waterbody. On the other hand, resource recovery is becoming increasingly important both economically

and with regard to the closing of recoverable substance cycles.

The yield of recycled water is also increased by concentrate treatment. Both conventional ZLD and the HighCon ZLD process are estimated to generate residual product streams with 10% water. Hence, the water recycling rate is up to 98% for both processes. Water recycling enables cost savings for freshwater withdrawal and wastewater charges. Above all, the industrial site gains independence with regard to its water supply and wastewater discharge. Overall, ZLD processes cause new costs due to operation and disposal of residuals, so there must be other drivers than just costs savings.

The main advantage of the HighCon process is the separation of organic components in one stream and monovalent ions in another. Combined with selective crystallization, pure salt recovery is possible even for organically highly loaded used water. The HighCon process is applicable for salt recovery where conventional ZLD would result in a waste solid mixture unsuitable for reuse. Thus, disposal quantities are reduced, and disposal safety can be increased by separating the different fractions.

Resource recovery by the HighCon process

The selective crystallization tests demonstrated that it is possible to separate single salts as solid crystals from a complex wastewater matrix resulting from industrial water recycling RO brines. In the first step of the lab-scale experiments, using the concentrate from the DEK demonstration site, sodium hydrogen carbonate salts could be produced with a purity of 90%. As the simple experiments have not yet exploited influence factors like kinetics or volume effects, there is much room for optimization left. It appears probable that technical quality requirements for reusing the recovered salts for defined industrial applications could be met. Another reuse chance could be blending recovered salts with crude material for further processing.

As described in the section 'Full-scale process design based on the demonstration results', the final HighCon process design aims to maximize RO and NF recovery rates, which implies pH adjustment via acidification. This leads to a notable change in the ion concentrations impinging the selective crystallization.

For example, acidic electrolytes will add to the anions, e.g. NO_3^- , when nitric acid is applied. Additionally, along with lower pH, dissolved carbonates will associate, leading to a higher super-saturation of carbonic acid. This leads to CO_2 degassing in the evaporator device, where the specific contact surface of solution and air is maximized for heat and mass transfer efficiency.

The influence of a pH reduction from 8 to 6.5 by nitric acid addition upstream of the RO on the solid-liquid equilibria in the crystallization was assessed for the DEK demonstration site. The NO_3^- would be raised by <1%. Thus, its effect on selective crystallization can be neglected. Nevertheless, the influence on carbonate dissociation cannot be disregarded. Speciation calculations indicate that (compared to the conducted demonstration) approximately 50% of the carbonates could be lost to gaseous CO_2 and, in consequence, will not be available for resource recovery.

Each process step upstream of the selective crystallization contributes directly or indirectly to the water or solids recovery yield of the whole process. The RO provides 85% of the produced water for direct reuse at a comparably low-energy investment. The achievable RO yield rate is one of the main levers to enable an energy-efficient water recycling process. NF was applied due to its selectivity with regard to organics and multivalent ions. As it rejected >99% of the dissolved organic matter from the main process stream, this technology lays the foundation for subsequent separation of inorganic salts nearly cleaned from organic impurities. The ED provides an indirect contribution to the process of water recovery yield. Due to its technologically inherent minimal required diluate conductivity, this desalinated water stream is not supposed to be reused directly. By recycling it to the RO feed, the ED diluate indirectly adds to the water recycling yield of the process. The thermal processes MD and 'Evaporation/Crystallization I' produce distillate flows at a high quality that allows direct reuse of the produced water. Nevertheless, the share of these distillates in the whole process water yield rate appears quite low with approximately 2% compared to the feed. However, this is reasonable because due to energy efficiency reasons, the process stream is reduced as far as possible before entering the thermal process steps. For full-scale application, an 'Evaporation/Crystallization II' was

postulated to process the NF concentrate (see also Figure 11). The quality of the distillate produced here has not been investigated in this project. Hence, this should be a subject for further investigation.

One side effect of the applied brine processing technologies is the use of additives, e.g. antiscalants or nitric acid that will add to the dissolved matter in the process stream and end up in the produced solid fractions. In a holistic process optimization, the application of additives is reduced to the required minimum (supported, e.g. via automated dosing).

CONCLUSION

- (1) The separation of organic components and monovalent ions worked out very well in the HighCon process and enabled the recovery of an organic-free salt mixture or – using selective crystallization – the separation of an organic-free single salt with >90% purity.
- (2) The recovery of resources is becoming increasingly important both economically and with regard to closing recoverable substance cycles. This refers not only to water recovery but also to other valuable components of industrial wastewater, e.g. salts. With regard to pure salt recovery, the HighCon process, therefore, has an advantage over conventional ZLD. Since additives from the production process and water treatment (e.g. antiscalants) usually end up in the produced solids, holistic process optimization is essential.
- (3) Both conventional ZLD and the HighCon process result in comparable total specific costs of about 4 €/m³. In comparison, indirect discharge is significantly cheaper with total specific costs of about 2 €/m³, but requires sufficient capacity in the municipal sewage treatment system, does not reduce the discharge of recalcitrant substances into water bodies, does not lead to a reduction of freshwater use, and does not recover the thermal energy of the used water. Furthermore, increasingly stricter environmental regulation policies also concern indirect discharges. ZLD processes increase independence with regard to water supply and wastewater discharge for industrial sites.

ACKNOWLEDGEMENTS

The Federal Ministry of Education and Research (BMBF) funded the joint research project ‘Concentrates from Wastewater Reuse (HighCon)’ – the content of this study – from 2016 to 2019 within the funding measure ‘Future-oriented Technologies and Concepts to Increase Water Availability by Water Reuse and Desalination (WavE)’; HighCon funding reference number: 02WAV1406. The company Endress + Hauser supported the HighCon project by supplying various measurement technologies. Dr Stefan Berendts from the Institute of Chemistry, TU Berlin, provided X-ray diffraction crystal analyses for the selective crystallization tests.

DATA AVAILABILITY STATEMENT

Data cannot be made publicly available; readers should contact the corresponding author for details.

REFERENCES

- Dasgupta, J., Sikder, J., Chakraborty, S., Curcio, S. & Drioli, E. 2015 [Remediation of textile effluents by membrane based treatment techniques: a state of the art review](#). *Journal of Environmental Management* **147**, 55–72. doi:10.1016/j.jenvman.2014.08.008.
- DIN EN 1484:1997-08 1997 *Water Analysis – Guidelines for the Determination of Total Organic Carbon (TOC) and Dissolved Organic Carbon (DOC); German Version EN 1484:1997*. Deutsches Institut für Normung e.V. (DIN), Berlin, Germany.
- DIN ISO 15705:2003-01 2003 *German Standard Methods for Water Quality – Determination of the Chemical Oxygen Demand Index (ST-COD) – Small-Scale Sealed Tube Method (ISO 15705:2002)*. Deutsches Institut für Normung e.V. (DIN), Berlin, Germany.
- DWA 2012 *Leitlinien zur Durchführung dynamischer Kostenvergleichsrechnungen (KVR-Leitlinien) (Guidelines for the Performance of Dynamic Cost Comparison Calculations (CCC Guidelines))*, 8th edn. DWA Deutsche Vereinigung für Wasserwirtschaft, Abwasser und Abfall e. V., Hennef, Germany.
- Freger, V., Arnot, T. C. & Howell, J. A. 2000 [Separation of concentrated organic/inorganic salt mixtures by nanofiltration](#). *Journal of Membrane Science* **178**, 185–193.

- Götz, G., Teschke, P., Netzel, L. & Geißen, S.-U. 2019 Zero Liquid Discharge für eine abwasserfreie Industrieproduktion (Zero liquid discharge for a wastewater free industrial production). *Chemie Ingenieur Technik* **91** (10), 1480–1485. doi:10.1002/cite.201900047.
- Kim, D. H. 2011 A review of desalting process techniques and economic analysis of the recovery of salts from retentates. *Desalination* **270**, 1–8. doi:10.1016/j.desal.2010.12.041.
- Linden, N. v., Shang, R., Stockinger, G., Heijman, B. & Spanjers, H. 2020 Separation of natural organic matter and sodium chloride for salt recovery purposes in zero liquid discharge. *Water Resources and Industry* **23**, 1–11. doi:10.1016/j.wri.2019.100117.
- Luo, J. & Wan, Y. 2011 Effect of highly concentrated salt on retention of organic solutes by nanofiltration polymeric membranes. *Journal of Membrane Science* **372**, 145–153. doi:10.1016/j.memsci.2011.01.066.
- MarketsandMarkets 2019 *Zero Liquid Discharge Systems Market (Preview to Market Report, Code: CH 5288) Published Date Feb 2019*. Available from: <https://www.marketsandmarkets.com/Market-Reports/zero-liquid-discharge-system-market> (accessed 11 March 2020).
- Pramanik, B. K., Shu, L. & Jegatheesan, V. 2017 A review of the management and treatment of brine solutions. *Environmental Science: Water Research & Technology* **3**, 625–658. doi:10.1039/c6ew00339g.
- Schwantes, R., Bauer, L., Chavan, K., Dücker, D., Felsmann, C. & Pfaffert, J. 2018 Air gap membrane distillation for hypersaline brine concentration: operational analysis of a full-scale module – new strategies for wetting mitigation. *Desalination* **444**, 13–25. doi:10.1016/j.desal.2018.06.012.
- Schwantes, R., Seger, J., Bauer, L., Winter, D., Hogen, T., Koschikowski, J. & Geißen, S.-U. 2019 Characterization and assessment of a novel plate and frame MD module for single pass wastewater concentration–FEED gap air gap membrane distillation. *Membranes* **9**, 118. doi:10.3390/membranes9090118.
- Semblante, G. U., Lee, J. Z., Lee, L. Y., Ong, S. L. & Ng, H. Y. 2018 Brine pre-treatment technologies for zero liquid discharge systems. *Desalination* **44**, 96–111. doi:10.1016/j.desal.2018.04.006.
- Tong, T. & Elimelech, M. 2016 The global rise of zero liquid discharge for wastewater management: drivers, technologies, and future directions. *Environmental Science & Technology* **50**, 6846–6855. doi:10.1021/acs.est.6b01000.
- USGS 2017 *PHREEQC Interactive 3.3.10.12220 [Software]*. Available from: <https://www.usgs.gov/software/phreeqc-version-3>.
- Wadley, S., Brouckaert, C. J., Baddock, L. A. D. & Buckley, C. A. 1995 Modelling of nanofiltration applied to the recovery of salt from waste brine at a sugar decolourisation plant. *Journal of Membrane Science* **102**, 163–175.
- Wegscheider, R. & Mehl, J. 1928 Über Systeme $\text{Na}_2\text{CO}_3\text{-NaHCO}_3\text{-H}_2\text{O}$ und das Existenzgebiet der Trona (About systems $\text{Na}_2\text{CO}_3\text{-NaHCO}_3\text{-H}_2\text{O}$ and the existence region of Trona). *Monatshft für Chemie* **49**, 283–315. doi:10.1007/BF01518402.
- Yaqub, M. & Lee, W. 2019 Zero-liquid discharge (ZLD) technology for resource recovery from wastewater: a review. *Science of the Total Environment* **681**, 551–563. doi:10.1016/j.scitotenv.2019.05.062.

First received 3 April 2020; accepted in revised form 20 June 2020. Available online 31 August 2020