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RO brine treatment and disposal methods

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ABSTRACT

More than 50 percent of countries in the world will likely face water stress or water shortages by 2025, and by 2050, as much as 75 percent of the world's population could face water scarcity. Desalination technologies, particularly the reverse osmosis (RO) process, have increasingly been adopted to produce freshwater from alternative sources such as seawater and brackish water due to water scarcity. However, desalination applications have always been limited by the disposal costs of RO brine and the adverse impact of brine on the receiving environment. The scope of this paper is to identify technically and commercially RO brine disposal and treatment methods such as deep well injection, discharge into the sea, sanitary sewers, evaporation ponds, forward osmosis (FO), vacuum membrane distillation (VMD), vacuum-enhanced direct contact membrane distillation (VEDCMD), RO–NF Integrated system, bipolar membrane electrodialysis (BMED), electrodialysis (ED), Electrodialysis reversal (EDR), vibratory shear enhanced processing (VSEP), capacitive deionisation (CDI) and so on. In this paper, as a part of our desalination research package, to achieve profitable and environmental solutions, we assess advantages and disadvantages of mentioned methods through a comprehensive review of worldwide laboratory, pilot and industrial scale experiments.

Keywords: Reverse osmosis; Brine; Water treatment

1. Introduction

With rising population and water sources becoming stretched, increasing attention is being paid on how water is used and reused. Industry, agriculture, and domestic water users are all competing for this most precious natural resource [1]. More than 50 percent of countries in the world will likely face water stress or water shortages by 2025, and by 2050, as much as 75 percent of the world's population could face water scarcity [2]. Desalination of seawater has become an important and growing industry due to the present water shortage in many countries [3].

Desalination technologies, particularly the reverse osmosis (RO) process, have increasingly been adopted to produce freshwater from alternative sources such as seawater and brackish water due to water scarcity and according to Fritzmann et al., the capacity of RO desalination industry today is around 20 million m^3/d [4–9]. However, desalination applications have always been limited by the disposal costs of the produced concentrated waste brine (also referred to as membrane concentrate, reject brine or wastewater; the main components of which are inorganic compounds) and the adverse impact of brine on the receiving environment [10–17].

The scope of this paper is to identify technically and commercially RO brine disposal and treatment methods

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such as deep well injection, discharge into the sea, sanitary sewers, evaporation ponds, forward osmosis (FO), vacuum membrane distillation (VMD), vacuum-enhanced direct contact membrane distillation (VEDCMD), RO–NF Integrated system, bipolar membrane electrodialysis (BMED), electrodialysis (ED), electrodialysis reversal (EDR), vibratory shear enhanced processing (VSEP), capacitive deionisation (CDI) and so on. In this paper, as a part of our desalination research package, to achieve profitable and environmental solutions, we assess advantages and disadvantages of mentioned methods through a comprehensive review of worldwide laboratory, pilot and industrial scale experiments.

2. RO brine treatment methods

2.1. Forward osmosis (FO)

FO is a novel water treatment process that potentially can be used as an alternative for both traditional desalination and brine disposal technologies due to its smaller energy requirement. In the FO process, a solution of considerably high concentration (known as draw solution) is utilized to generate a hydrostatic osmotic pressure gradient across a semipermeable membrane to extract freshwater from a feed solution (such as seawater or brine), which is on the other side of the membrane. Since this process capitalizes the phenomenon of natural osmosis, little energy and thus, little cost is required as compared to traditional technologies [18]. The history of study on FO can be traced back to as early as 1965. However, few publications have been released until in recent years, during which FO has been better understood and further developed [19].

Martinetti et al. investigated FO for water recovery enhancement in desalination of brackish water [3]. In this research two RO brine streams with total dissolved solid concentrations averaging 7500 and 17,500 mg/l were further desalinated by FO. In the mentioned process, high water recoveries were achieved; however, recoveries were limited by precipitation of inorganic salts on the membrane surface. Various cleaning techniques were able to remove the scale layer from the membrane and restore water flux to almost initial levels. FO achieved water recoveries up to 90% from the brines. Addition of a scale inhibitor during process was effective at maintaining high water flux for extended time. The total water recovery (the recovery from the RO processes combined with the batch recovery from the FO process), achieved was greater than 98% total was achieved for the two different brine streams [3].

Tang and Ng assessed the viability of applying the FO process for concentration of brine produced from brackish or seawater desalination plants through laboratory-scale experiments [20]. They have reported that concentrating brine could be potentially achieved by the FO process. The dense selective layer of the CA membrane performed about 1.5 times better than the FO membrane in the FO process due to a thinner membrane with similar hydrophilicity that minimized both internal and external concentration polarization. This study suggested the viability of developing an ideal FO membrane using a highly hydrophilic material with only a thin dense selective layer that can facilitate water transport in the FO process to be used for brine concentration. Using the FO process for concentrating brine with the draw concentration being maintained at a consistently high value (i.e., 5 M fructose), a relatively high and steady osmotic driving pressure could be maintained. As a result, water fluxes could be achieved consistently at a relatively high level. When 1 M brine was used as the feed solution, the dense selective layer of the CA membrane achieved a water flux from a high initial value 8.9 GFD (4.2 μm/s or 15.0 l/m^2 h) declining to 6.0 GFD (2.8 μm/s or 15.0 l/m^2 h) at the end of 18 running hours. In this case, about 76% of brine volume was reduced, which greatly simplified the disposal process.

2.2. VMD

Vacuum membrane distillation (VMD) is a hybrid technology using transmembrane pressure difference between feed partial vapor pressure on one side of a hydrophobic micro-porous membrane and a vacuum or low pressure applied on the other side. When a salty solution is introduced into the feed, water evaporates from the feed side of the membrane and vapor goes through membranes pores whereas salts stay in this feed [21].

Mericq et al. study has shown a global recovery factor of 89% can be obtained by coupling RO and VMD [22]. On the basis of simulation and experiments at bench-scale, VMD has proved to be very interesting when integrated in a seawater treatment line as a complementary process to SWRO [22]. It was necessary to note that the water recoveries were limited by fouling [21].

2.3. VEDCMD

Direct contact membrane distillation (DCMD) is a thermally driven separation process involving the evaporation of water through the pores of a hydrophobic, microporous membrane and direct condensation of that water vapor into a cold water stream flowing on the support side of the membrane [23]. In DCMD, warmer feed water is in contact with the active side of the membrane and a cooler water stream is in direct contact with the support side. The driving force for mass transfer in DCMD is the vapor pressure difference across the membrane induced by the temperature difference across the membrane. Because the partial vapor pressure of water is only minimally affected by increased concentrations of dissolved salts, DCMD has the potential to be an ideal treatment method for highly saline feeds. The performance of DCMD can be improved in different ways. High-temperature DCMD (e.g., DCMD with the same temperature difference, but at higher temperatures) can achieve higher water fluxes than low-temperature DCMD [24]. This is because vapor pressure increases exponentially with increasing water temperature. In another configuration, vacuum enhanced DCMD (VEDCMD), the cooler water stream flows under negative pressure (vacuum). Under specific operating conditions, VEDCMD has been shown to increase flux by up to 85% compared to the conventional DCMD configuration [24].

Martinetti et al. have studied VEDCMD for water recovery enhancement in desalination of brackish water [3]. In this research two RO brine streams with total dissolved solids concentrations averaging 7500 and 17,500 mg/l were further desalinated by VEDCMD. In the mentioned process, high water recoveries were achieved; however, recoveries were limited by precipitation of inorganic salts on the membrane surface. Various cleaning techniques were able to remove the scale layer from the membrane and restore water flux to almost initial levels. VEDCMD achieved water recoveries up to 81% from the brines. Addition of a scale inhibitor during process was effective at maintaining high water flux for extended time. The total water recovery (the recovery from the RO processes combined with the batch recovery from the VEDCMD process), achieved was greater than 96% total was achieved for the two different brine streams [3].

2.4. BMED

Bipolar membrane electrodialysis (BMED) is a membrane based electrochemical process, which uses bipolar membranes for separation of ionic species from a salt to produce the respective acid and base. This process has been used in the food industry to produce organic acids like lactic acid, ascorbic acid and salicylic acid with a reasonable amount of success [25,26]. It has also been applied to pure NaCl solutions to produce HCl and NaOH [27]. RO concentrate is mostly made of Na$^+$ and Cl$^-$ ions with substantial amounts of divalent ions. However, proper pretreatment of the RO concentrate stream is required for beneficial reuse of this stream for production of mixed acids and bases. Phosphorus removal from wastewater has been studied in detail as wastewater containing phosphorus that is discharged to surface streams can cause major environmental impacts [28].

Several water treatment plants have been switching to onsite chlorine generation as a disinfectant source due to operational safety concerns and ease of implementation. Conceptually, commercial hypochlorite generators split by NaCl using an electrolytic cell to produce hypochlorite. Again, since RO concentrate contains significant amounts of Na$^+$ and Cl$^-$ ions, this stream could be beneficially reused through production of hypochlorite [29].

MWH and Sandia National Laboratories have conducted a proof of concept study looking at the above innovative beneficial reuse alternative for the RO concentrate using bench scale testing [29].

In Hilal et al.'s research several preliminary tests were conducted with synthetic solutions of salt (NaCl) at high and low concentrations followed by tests with mixed salt solutions representing pretreated RO concentrate and finally with actual pretreated RO concentrate from two sources [29]. These tests were used to select the operating conditions for tests with pretreated concentrate. During tests with pretreated concentrate it was intended to design the tests with actual concentrate to show complete desalination in 8–10 h so the batch volume was adjusted accordingly. The tests were conducted with RO concentrate from two sources. Results are presented here from one source. These results shown in Fig. 1 were obtained with RO concentrate which is from an IMS (integrated membrane system) system operating on raw wastewater after appropriate pretreatment. The current utilized density was optimized after testing various current densities. These figures show that close to complete desalination of the RO concentrate feed stream is possible in 8 h. Additionally acid and base concentrations of 0.2 N or higher were obtained. The acid and base concentrations are highly dependent on the volume of the concentrate. Therefore, higher concentrations could be expected in the treatment of larger batches of concentrate and when longer run times are utilized. The water quality composition of the product shows that TDS and other major ions except silica concentration were in low levels. Therefore, after production of acid and bases, the product water can be treated again with RO

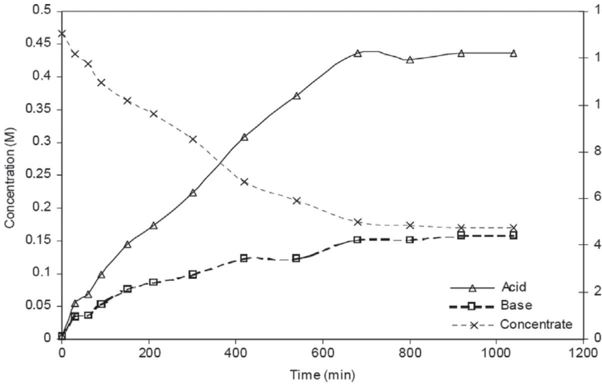

Fig. 1. BMED Results on Softened RO concentrate [29].

further minimizing the concentrate volume. So the Bipolar Membrane Electrodialysis process was shown to be technically feasible for producing mixed acids and bases of reusable quality from RO concentrate. Mentioned process will be able to achieve overall water recovery up to 85% [29].

2.5. ED

Electrodialysis (ED) is one of the two common membrane processes in desalination. ED is based on selective movement of ions in solutions. ED uses a direct electric current to transfer ions through a membrane that possesses fixed ionic groups chemically bound to the membrane structure. ED is primarily used in desalting brackish waters. Electric energy is consumed in proportion to the quantity of salts to be removed [30].

Zhang et al.'s experiments on real RO concentrates using the nonselective anion SA and cation SK membranes were performed to evaluate the separation of salts from organic solutes by electrodialysis in a realistic matrix [31]. Figs. (2 and 3) show the concentration decrease of Cl$^-$, SO$_4^{2-}$ and TOC in diluate of a real RO concentrate stream by electrodialysis. It can be seen from Figs. 2 and 3 also show that the concentration decrease of salts (i.e., Cl$^-$ and SO$_4^{2-}$) is similar, however, the concentration decrease of TOC is very slow and most (over 85%) of the organic fraction was retained at the feed side. This can be explained: most of the organic solutes in the real RO concentrates can be assumed to have a large size, be zwitterions, or be uncharged. Thus, by the SA membrane in electrodialysis, salts can be successfully separated to the concentrate compartment while keeping the organic fraction at the feed side. The fact that more than 85% of the organic fraction in the real RO concentrate was kept at the feed side strongly suggests that the separation of salts from organics by electrodialysis is feasible [31].

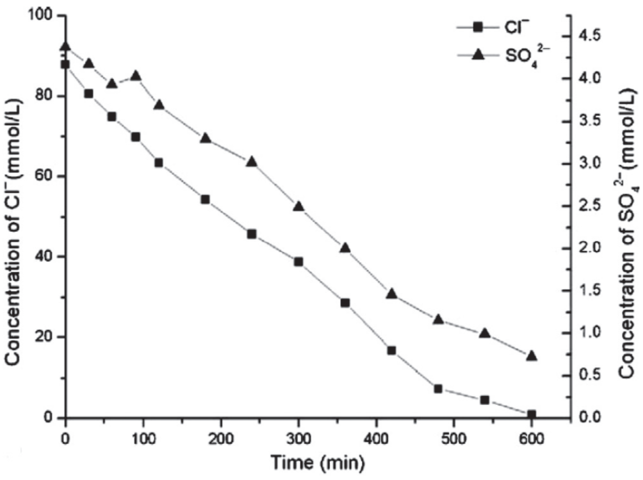

Fig. 2. Concentration decrease of Cl$^-$, SO$_4^{2-}$ in diluate of real RO concentrate stream by electrodialysis [31].

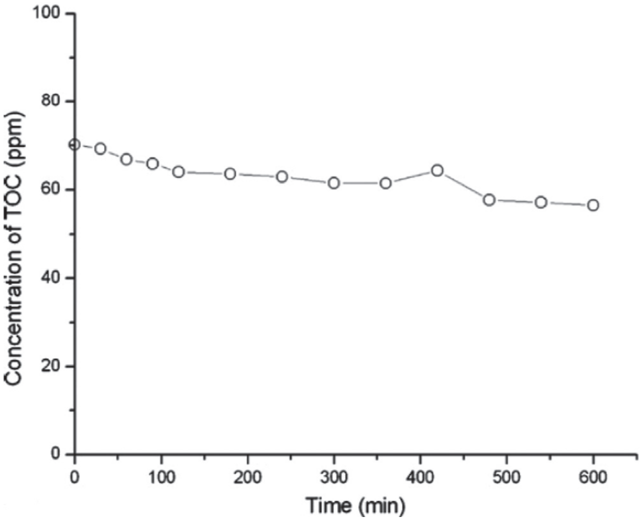

Fig. 3. Concentration decrease of TOC in diluate of real RO concentrate stream by electrodialysis [31].

Korngold et al.'s research shows ED can be used to increase the concentration of RO brine solution from 1.5% to 10% at an energy requirement of 7.0–8.0 kWh/m^3 [32]. The concentration of the RO brine was reduced to 18–20 mN by electrodialysis, and it can be mixed with RO permeate. A recovery of 97–98% was obtained [32].

2.6. EDR

The electrodialysis reversal (EDR) process is based on the same principles of electrochemistry as ED. The fundamental difference in operation is the periodic automated reversal of polarity and cell function. This change is typically done three to four times per hour to reverse the flow of ions across the membrane [30].

In Turek et al.'s research electrodialysis reversal (EDR) treatment of inland brackish water reverse osmosis concentrate was examined [33]. The resistance to CaSO$_4$ and CaCO$_3$ scaling in their single-pass and low residence time EDR is better than in the one that was originally developed by Ionics. Their approach is as follows. The RO concentrate of CaSO$_4$ and CaCO$_3$ content being close to the saturation level (or slightly supersaturated) is concentrated by EDR 4–5 times. This enables the concentrate volume to decrease and, probably, its disposal cost to the same extent. Assuming brackish water composition as follows (mg/l): Mg^{2+}: 95.4; Ca^{2+}: 208.4; Cl$^-$: 1166; SO$_4^{2-}$: 868.8; HCO$_3^-$:170.8; NO$_3^{-1}$:79.8 and 60% RO recovery, concentrate composition was calculated using Dow Chemical Co. RO system analysis (ROSA) software. Simulated RO concentrate containing (mg/l): Mg^{2+}:237.7; Ca^{2+}:519.2; Cl$^-$:2886;

SO_4^{2-}:2164; HCO_3^-:414.4; NO_3^-:424.3 was then treated in a laboratory EDR stand at 79.1% diluate recovery. The overall RO–EDR water recovery was equal to 91.6% despite the high scaling potential of the investigated water. The expected cost of EDR was found to be promising, especially as compared to evaporation e.g. the RCC vapor compression evaporation (turned out to be useful for treatment of $CaSO_4$ containing brine) energy consumption was equal to ca. 20 kWh/m^3 while their EDR laboratory test showed the demand (in similar salinity range) of ca. 3 kWh/m^3 at the estimated unit EDR cost \$0.30/m^3. EDR has an especially high potential in the case of waters containing calcium sulfate and calcium bicarbonate as the dominant solutes. Thus, $CaSO_4$ and $CaCO_3$ may be crystallized in the EDR concentrate and disposed. This will allow zero-discharge technology to develop.

2.7. VSEP

To reduce scaling potential and increase recovery, New Logic Research, Inc. has developed an alternative method for producing intense shear waves on the face of a membrane known as vibratory shear enhanced processing (VSEP). This process, like EDR, would decrease the amount of concentrate needing to be disposed. However, an ultimate disposal mechanism such as crystallization/landfill would still be required to completely dispose of the concentrate. In a VSEP system, shear cleaning action is created by vigorously vibrating the leaf elements in a direction tangent to the faces of the membranes. The vibration helps reduce the level of concentration at the surface of the membrane, a phenomenon known as concentration polarization (CP). In addition to cutting down on the flux performance of the membrane, the CP layer acts as a secondary membrane reducing the native design selectivity of the membrane in use. The shear waves produced by the vibration of the membrane cause potential foulants to be lifted off the membrane surface and remixed with the bulk material flowing through the membrane stack. This high-shear processing exposes the membrane pores for maximum throughput that is typically between 3 and 10 times the throughput of conventional cross-flow systems [34].

Johnson et al. used VSEP treatment of RO reject from brackish well water [1]. Table 1 shows the complete analytical results from grab samples collected during the pilot trails. The purpose of testing was to confirm compliance with primary and secondary EPA drinking water standards related to health issues and aesthetic considerations.

Table 1
RO reject VSEP analytical results [1]

Analyte		EPA limit	VSEP feed	VSEP permeate	VSEP reject	Reporting limit
Aluminum	Al	0.050 mg/l	0.600	ND	27.550	0.100
Arsenic	As	0.010 mg/l	0.008	ND	0.253	0.005
Barium	Ba	2.000 mg/l	0.120	ND	5.706	0.010
Cadmium	Cd	0.005 mg/l	ND	ND	–	0.005
Calcium	Ca	none	45.00	ND	2,235.0	0.500
Chromium	Cr	0.100 mg/l	0.038	ND	1.557	0.010
Copper	Cu	1.000 mg/l	0.029	ND	1.107	0.010
Iron	Fe	0.300 mg/l	2.300	ND	112.55	0.100
Lead	Pb	0.015 mg/l	ND	ND	–	0.003
Magnesium	Mg	none	3.200	ND	147.75	0.500
Selenium	Se	0.050 mg/l	0.008	ND	0.302	0.005
Silver	Ag	0.100 mg/l	ND	ND	–	0.005
Zinc	Zn	5.000 mg/l	0.180	ND	8.510	0.020
Cyanide	CN	0.200 mg/l	ND	ND	–	0.010
Silica	SiO_2	none	23.00	5.300	890.3	1.000
Chloride	Cl	250 mg/l	50.00	8.300	2,093.3	0.200
Fluoride	F	2.000 mg/l	1.500	0.200	65.20	0.100
Sulfate	SO_4	250 mg/l	120.0	1.800	5,911.8	0.500
Total dissolved solids	TDS	500 mg/l	2,340	82.0	112,982	10.0
Color		15 color units	13,000	ND	–	5.0

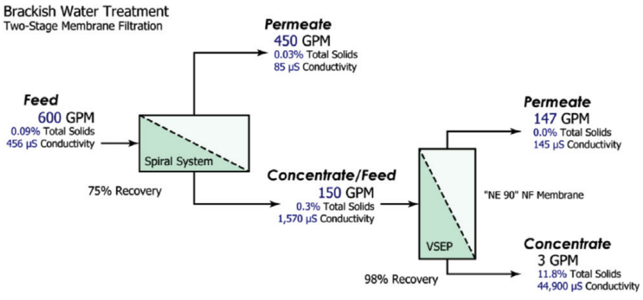

Fig. 4. Process schematic of VSEP to treat RO brine [1].

Mentioned configuration (Fig. 4) will be able to achieve 98% recovery of treated water, leaving only 2% of the volume to be disposed of as reject (Fig. 4) [1].

Shi and Benjamin showed that vibration of RO membranes in an L-mode VSEP system reduced fouling in treatment of both a brackish solution and brine [35]. For a given TMP, vibration reduced the rates at which the permeate flux and hydraulic permeability declined, increased the practical water recovery, and greatly reduced the resistance attributable to fouling. RO treatment in the absence of vibration rejected 70–88% of major ions in both solutions, whereas treatment with vibration led to rejections of >95% for most ions in the brackish solution and >90% for most ions in the brine. The lower salt concentration in the permeates of the systems with vibration appeared to be coupled with the reduction in membrane fouling, which resulted in a higher water flux but either a lower (for the brackish water) or similar (for the brine) flux of ions through the membrane.

2.8. CDI

In RECLAIM WATER, brine treatment was tested with capacitive deionisation (CDI). Piloting CDI confirmed its capacity to remove ions to a degree allowing to recycle the treated brines back to the dual membrane treatment and thus increasing the total water yield from 75% to >95% [36].

In Tao et al.'s study, pilot scale investigation onsite on a NEWater production plant to treat and recover RO brine with a CDI unit of up to 5,000 m^3/d treatment capacity was conducted (Fig. 5 In Singapore, NEWater is the product of a multiple barrier water reclamation process from secondary treated domestic effluent using MF/UF-RO and UV technologies) [37]. The study elucidated various operational issues with the objective of achieving sustainable operation of the RO brine treatment process. The results show that ion concentrations in the CDI product were low, except SiO_2, when compared with RO feed water. RO permeate (CDI product as feed) was of good quality including low SiO_2 when compared with NEWater. It could be beneficial to use a dedicated RO operated at optimum conditions with better performance to recover the water. The observation was made that that the type of pretreatment, the feed water chemistry and the cleaning technique and chemicals played an important role in sustainable operation. Enhanced pretreatment and lowering pH could minimize the fouling. The CDI pressure increased faster with high TOC feed. The biological activated carbon (BAC) as pretreatment was able to achieve 15–27% TOC removal of RO brine; about 40% of TOC removal could be achieved when combined with membrane filtration. To control the organic fouling of CDI cells, 60% TOC removal could be the setting point for activated carbon regeneration or replacement. CDI had a water recovery of at least 80%, so CDI based RO brine treatment could improve overall water recovery of NEWater production to over 90%. The CDI cells had energy consumption about 0.7 kWh/m^3. Organic fouling was the major cause of CDI pressure increase. Sustainable operation especially organic fouling control and effective cleaning should be further studied.

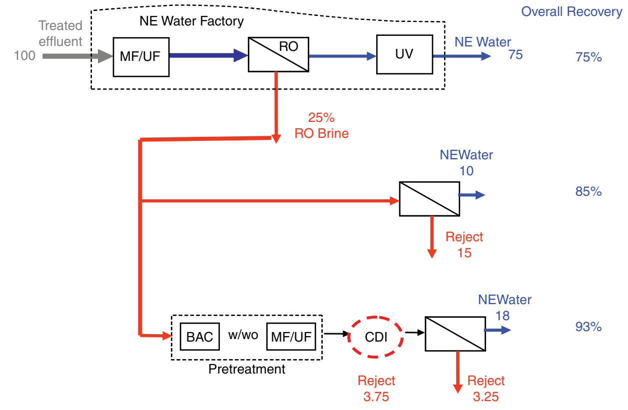

Fig. 5. Increase water recovery over 90% using CDI based process [37].

2.9. ICD

Fig. 6 provides a conceptual schematic of a two-pass RO facility with integrated ICD (chemical demineralization) [38]. The term "chemical demineralization" is a general term for a variety of technologies that have been proposed whereby precursor scalantions are removed from the primary RO concentrate via chemical precipitation. A number of scoping studies using a variety of conceptual process schemes to achieve high-recovery RO desalting via ICD have been conducted [17,39–51]. More recently, Gabelich et al. demonstrated that upwards of 95% total system water recovery was possible for CRW RO desalting using ICD at the pilot and demonstration scales [38,52]. ICD was shown to be effective in reducing the concentrations of Ca^{2+} and other scaling precursors in the primary RO concentrate below saturation or to a metastable super saturation range (i.e., very slow

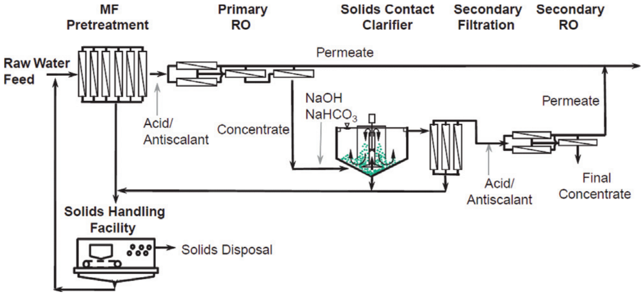

Fig. 6. Conceptual schematic drawing for two-pass RO facility with integrated intermediate chemical demineralization [17].

precipitation kinetics) so as to allow further RO desalting of this concentrate stream.

2.10. VC

The VC (vapor compression) process is well established and is used for seawater desalination as well as treating RO concentrate (i.e., brine concentrator application) in a near-ZLD (zero liquid discharge) application (commercial scale) [17,53–56]. For example, brine concentrators (VC evaporators operating with seed recycle) are used in Australia to treat RO concentrate from cooling tower blowdown to achieve ZLD in power plants. Scaling is still an issue in VC process, and another disadvantage of the thermal technology is high energy consumption.

2.11. MD

Membrane distillation (MD) is an emerging separation process that combines simultaneous mass and heat transfer through a hydrophobic microporous membrane [57–59]. During the treatment of a RO concentrate with high silica concentration, MD could reduce the volume of RO concentrate by 60%, achieving an overall water recovery of 90% through RO–MD (bench scale) [60]. Scaling occurred on the MD membrane surface at high recovery as determined by the saturation indices of mineral sealants. However, the sealants formed in treating RO concentrate did not clog membrane pores and could be removed almost completely by chemical cleaning [17].

2.12. MDC

In recent years, the innovative process of membrane distillation crystallization (MDC) has been investigated for the recovery of valuable salts from nanofiltration brines produced by desalination operations [61]. MDC exploits the excellent ability of membrane distillation (MD) process, a thermally driven operation to concentrate aqueous solutions up to super saturation.

Ji et al. have investigated the performance, in terms of water recovery and NaCl crystallization kinetics, of a MDC bench-scale plant operated on brines discharged from a seawater reverse osmosis (RO) unit [12]. This study confirms the ability of membrane distillation crystallization to concentrate RO brines to achieve a water recovery of greater than 90% with a concomitant reduction in volumetric waste discharged to the environment. Moreover, batch runs carried out on natural RO concentrates resulted in the production of 17 kg/m^3 of NaCl crystals, representing the 34% c.a. of the total content of dissolved solids in the brine.

2.13. RO–NF Integrated system

RO–NF coupling permits treatment of the brine rejected from RO modules by NF membranes. As shown in Fig. 7, this configuration gives a better recovery factor from 37% to 85% (Fig. 8) [62].This kind of RO–NF coupling allows recuperation of the RO reject brine water energy and increases the quantity of produced water. A RO–NF serial configuration has highly increased the

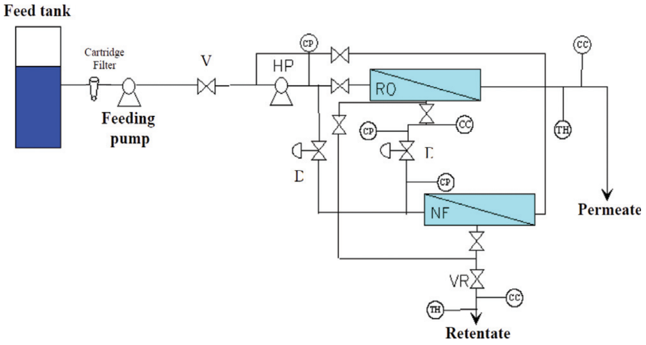

Fig. 7. Experimental set-up. V: valve; VR: reject valve; D: pressure regulator; HP: high-pressure pump; RO: RO module; NF: NF module; CP: pressure vessel; CC: conductivity vessel; TH: temperature vessel [62].

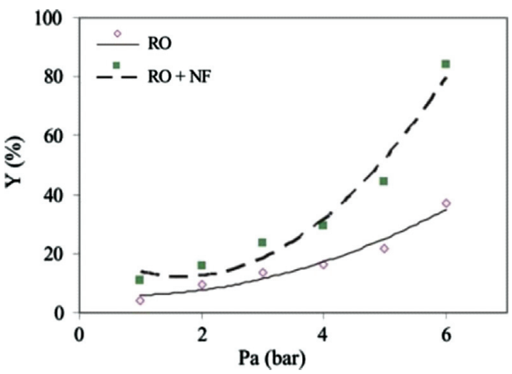

Fig. 8. The recovery factor vs. pressure for RO/NF serial coupling [62].

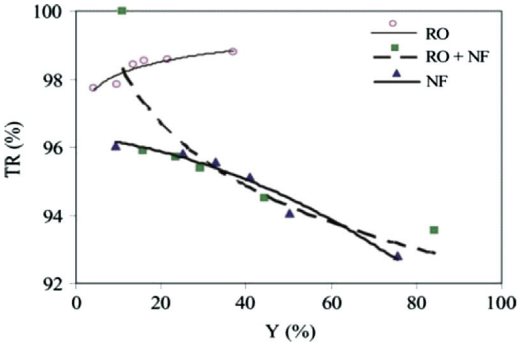

Fig. 9. The rejection rate vs. recovery factor for RO/NF serial coupling [62].

recovery factor (Fig. 9). This rate did not exceed 40% in RO and 80% in the coupled RO–NF.

In principle, integration of the NF unit with RO in water desalination plants makes it possible to improve salt rejection and thus leads to a decrease in the salinity of the water product and consequently the recovery has improved considerably, compared to that obtained in RO alone [63–71].

Pilot scale experience show integration of the NF unit with RO in water desalination plants makes it possible to approach these advantages: (1) preventing RO membrane fouling by the removal of turbidity and bacteria with NF membrane, (2) preventing scaling by removal of scale forming hardness ions with NF membrane, (3) lowering required pressure to operate RO plants by reducing feed flow TDS depending on the type of NF membrane and operating conditions, (4) improving salt rejection and thus leads to decrease in the salinity of water product and consequently the recovery has improved compared to that obtained in RO alone(overall product water recovery up to 96%), (5) producing less entropy (less amount of lost work) per unit mass of water product than RO alone (6) decreasing the total unit cost of desalted water, (7) producing stable permeate water quality, (8) The NF-SWRO process makes it feasible to produce high purity permeate from a single-stage SWRO process without the need for a second desalination stage [72].

2.14. *Eutectic freeze crystallization*

Eutectic freeze crystallization (EFC) is a novel technology that has shown promise in the treatment of brines. Eutectic Freeze Crystallization is an extension of the freeze crystallization process and exploits the density differences between the ice and the salt produced to ensure effective separation. The process is operated at the eutectic point, where both ice and salt crystallize. Thus, the major problems of a mixed salt product can be avoided by the production of many pure salts at their unique crystallization temperatures [73].

Some EFC work focused on the recovery of one salt from a simple binary [74–77] or ternary system [78,79]. These researches showed the feasibility of using EFC technology for the recovery of a wide range of salts which included sodium sulphate, magnesium sulphate, potassium nitrate to name but a few. However, the applicability of using EFC to remove multiple salts from complex multi-component, hypersaline brines has not yet been demonstrated. The sequential removal of individual salts from a multi-component aqueous stream using EFC technology is theoretically possible since each salt crystallizes out at its own unique eutectic temperature. Thus, multiple individual salts can be recovered in their pure form by cooling the system down to the unique eutectic temperature of each salt and sequentially removing it along with ice. The volume of the waste stream can also be significantly reduced if all the possible crystallizing salts are removed together with ice [73].

The use of EFC as a treatment method for aqueous solutions such as brines has shown that the liquid waste obtained from the eMalahleni Water Reclamation Plant can be reduced by 97%. This would potentially take the overall water recovery to 99.9%. Pure calcium sulphate (98.0% purity) and pure sodium sulphate (96.4% purity) were also produced, along with potable water. Novel technologies such as EFC bring the concept of a zero percent waste process closer, especially if used strategically in conjunction with existing technologies [73].

3. RO brine disposal methods

3.1. *Surface water discharge*

Discharge of desalination concentrate to a surface water body (river, lake, lagoon, canal, ocean, etc.) is the most common management practice for brine disposal, primarily because this method frequently has the lowest cost and most plants are located relatively near surface water. Costs for disposal are typically low provided that pipeline conveyance distances are not excessively long and the concentrate is compatible with the environment of the receiving water body. The primary environmental concern is compatibility of the concentrate with the receiving water.

An assessment of salinity or TDS impact as well as those of specific constituents on the receiving stream is undertaken. Rarely can a higher salinity concentrate be discharged into lower salinity water if the resulting salinity is more that 10% higher than the upstream receiving waters. Some facilities address this by dilution of the concentrate with other water such as other surface water or groundwater, WWTP effluent, cooling water, etc. Dissolved gases and lack of oxygen can also be concerns for concentrate disposal. Concentrates from the treatment of most groundwater have very low levels of dissolved oxygen (DO). Prior to discharge, DO levels must be increased to avoid negative impacts on receiving stream biota. If the groundwater contains hydrogen sulfide, hydrogen sulfide in the concentrate must be suitably reduced before its discharge to prevent negative effects. Discharge to surface waters has been used with all sized concentrates [80–83].

3.2. Sewer

Discharge of concentrates to sanitary sewer systems is sometimes feasible if the concentrate mixture is not toxic and does not adversely affect the clarifier settleability or restrict final effluent disposal [84].

Sanitary sewer discharge of a small volume of concentrate usually represents a low cost disposal method with limited permitting requirements. The adequacy of sewer capacity and wastewater treatment plant capacity must be addressed. In addition, wastewater effluent quality will change but must still comply with the wastewater treatment plant's discharge permit. If the concentrate salinity and flow levels are significant, impacts of salinity on the biological efficiency of the wastewater plant should be considered. These capacity and/or quality criteria may limit the amount of RO concentrate discharged to the sewer. Discharge to sewer is used more often with smaller and medium sized plants than larger plants due to the effects of larger volume concentrate on the WWTP system. The WWTP may charge a discharge fee. These are sometimes low, however, the portion of the wastewater treatment plant capacity utilized by the discharge may be considered as a disposal cost. In some situations a one-time 'buy-in' cost has been charged based on this consideration [80–82].

3.3. Land application

Land application can provide a beneficial reuse of water when membrane concentrates are applied to vegetation, such as irrigation of lawns, parks, or golf courses. Factors associated with land application include the water quality tolerance of target vegetation to salinity, the ability to meet ground water quality standards, the availability and cost of land, percolation rates, and irrigation needs. An assessment of the compatibility with target vegetation is conducted, including assessment of the sodium adsorption ratio (SAR), trace metals uptake, and other vegetative and percolation factors. Regulations governing ground water quality and protection of drinking water aquifers are investigated to confirm the acceptability of this alternative. Usually dilution of the concentrate is required to meet groundwater standards. Where salinity levels are excessive, special salt tolerant species (halophytes) could be considered for irrigation. Land application also includes the use of percolation ponds and rapid infiltration basins. In general, land application is used only for smaller volumes of concentrates. These options are frequently limited by availability of land and/or dilution water. They may also be limited by climate in locations where land application is not possible year around [80–82].

3.4. Deep well injection

Deep well injection is a disposal technology in which liquid wastes are injected through the injection tubing into the well (Fig. 10). Since there is no technical difficulty in injecting desalination waste, it is one of the frequently used methods in disposing waste; however regulations on deep well injection are strict. Also, geology of the plant site is one of the main factors in the decision [85]. Regulatory considerations for deep well injection or other subsurface injection alternatives include the transmissivity and TDS of the receiving aquifer and the presence of a structurally isolating and confining layer between the receiving aquifer and any overlying underground source of drinking water (USDW). A USDW is considered when any water bearing formation contains less than 10,000 mg/l TDS.

Deep wells are not feasible in areas subject to earthquakes or where faults are present that can provide a direct hydraulic connection between the receiving aquifer and an overlying potable aquifer. A tubing and packer design is commonly required to allow monitoring of well integrity. One or more small-bore monitoring wells in proximity to the disposal well are also typically required to confirm that vertical movement of fluid has not occurred. The capital cost for deep well injection is higher than surface water disposal, sewer disposal, and land application in cases where these alternative methods do not require long transmission pipelines. Disposal to deep wells is usually restricted to larger volume

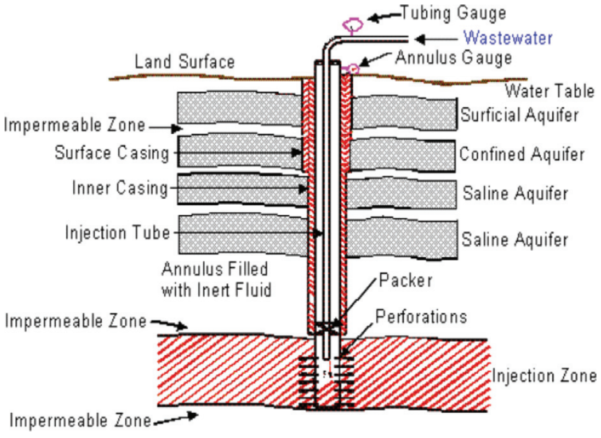

Fig. 10. Typical deep well injection system [85].

concentrates where economies of scale make the disposal option more affordable. Geologic characteristics are not appropriate for deep well injection in many areas of the United States. A backup means of disposal must be available for use during periodic maintenance and testing of the well [80–82].

3.5. Evaporation pond

Solar evaporation is a viable alternative in relatively warm, dry climates with high evaporation rates, level terrain, and low land costs. Regulations typically require an impervious lining and monitoring wells, which will increase costs of evaporation ponds. With little economy of scale, evaporation ponds are usually used only for small volume concentrates. While evaporation ponds are typically designed to accommodate concentrate for the projected life of the demineralization facility, precipitation of salts is expected and must be incorporated into the depth requirements of the pond or provisions must be made for periodic removal and disposal or beneficial use of precipitated salts. In addition, the ultimate fate of the concentrated salts and the future regulatory implications should be considered for any evaporation pond project. Enhanced evaporation systems may increase the evaporation rate and thereby reduce the evaporation area required by a factor of two to six [80–82,86].

The usefulness of surface water discharge, disposal to sewer and land application is usually limited and site-specific. Deep well injection is widely used in the USA, but the risk of contamination of underground drinking water deposits is high [28]. Evaporation ponds/salt processing ponds seem to be a good option especially in dry and hot climate areas; the question of leakages has to be considered. In insufficiently hot regions a large pond surface area is needed. Therefore preliminary volume reduction of saline wastewater might be necessary to maintain pond effectiveness [33,87–91]. Fig. 11 shows the use of the different disposal methods in USA [80,92]. Surface water disposal (106 plants or 45%), disposal to sewer (63, 27%), and disposal via deep well (31, 13%) together account for 85% of the disposal situations.

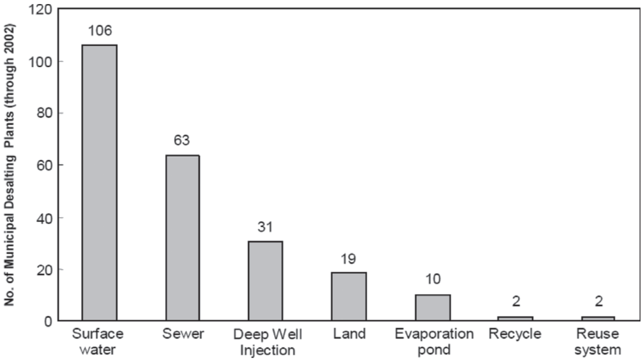

Fig. 11. Number of desalting water treatment plants > 0.025 MGD by disposal method in the USA [80,92].

4. Conclusions

For RO brine treatment methods, above sections illustrate:

- FO achieved water recoveries up to 90% from the brines. Addition of a scale inhibitor during process was effective at maintaining high water flux for extended time. The total water recovery (the recovery from the RO process combined with the FO process), greater than 98% total was achieved.
- The bipolar membrane electrodialysis (BMED) process was shown to be technically feasible for producing mixed acids and bases of reusable quality from RO concentrate.
- VEDCMD achieved water recoveries up to 81% from the brines. Addition of a scale inhibitor during process was effective at maintaining high water flux for extended time. The total water recovery (the recovery from the RO process combined with the VEDCMD process), greater than 96% total was achieved.
- The recovery from the RO process combined with ED was achieved up to 98%.
- The overall RO–EDR water recovery was achieved up to 91%.
- Treatment of RO reject via VSEP will be able to achieve up to 98% recovery of treated water.
- CDI based RO brine treatment could improve overall water recovery over 90%.
- 95% total system water recovery was possible for RO desalting using ICD at the pilot and demonstration scales.
- VC process is well established and is used for treating RO concentrate in a near-ZLD application.
- During the treatment of a RO concentrate with high silica concentration, MD could reduce the volume of RO concentrate by 60%, achieving an overall water recovery of 90% through RO–MD.
- MDC ability to concentrate RO brines is greater than 90%.
- In principle, integration of the NF unit with RO in water desalination plants makes it possible to approach improving salt rejection and thus leads to decrease in the salinity of water product and consequently the recovery has improved considerably, compared to that obtained in RO alone.
- EFC achieved water recoveries up to >95% from the brines.

Key data is summarized in Table 2 for each process.

Table 2
Summary table of RO brine treatment methods

Method	Scale	Recovery combined with RO	Major advantages	Major drawbacks
FO	Bench scale	Up to 98%	High water recoveries, little energy and thus, little cost is required as compared to traditional technologies	Recoveries were limited by precipitation of inorganic salts on the membrane surface
VMD	Bench scale	Up to 89%	High water recoveries	Water recoveries were limited by fouling
VEDCMD	Bench scale	Up to 96%	High water recoveries	Recoveries were limited by precipitation of inorganic salts on the membrane surface
BMED	Bench scale	Up to 85%	High water recoveries, feasible for producing mixed acids and bases of reusable quality from RO concentrate	Fouling
ED	Pilot	Up to 98%	High water recoveries	Fouling
EDR	Laboratory	Up to 91%	High water recoveries	Fouling
VSEP	Pilot	Up to 98%	High water recoveries	Proprietary technology from a single vendor
CDI	Pilot	Up to 95%	High water recoveries	Fouling
ICD	Pilot and demonstration scales	Up to 95%	High water recoveries	Chemical and sludge handling
VC	Commercial	Up to 90%	High water recoveries	Scaling, high energy consumption
MD	Bench scale	Up to 90%	High water recoveries	Scaling, high energy consumption
MDC	Bench scale	Up to 90%	High water recoveries	Scaling, high energy consumption
RO–NF Integrated system	Pilot	Up to 96%	Preventing RO membrane fouling by the removal of turbidity and bacteria with NF membrane, lowering required pressure to operate RO plants by reducing feed flow TDS, improving salt rejection and thus leads to decrease in the salinity of water product and consequently the recovery has improved	–
EFC	Pilot	Up to > 95%	High water recoveries	The applicability of using EFC to remove multiple salts from complex multi-component, hypersaline brines has not yet been demonstrated

And for RO brine disposal methods, above sections show:

- Discharge of desalination concentrate to a surface water body (river, lake, lagoon, canal, ocean, etc.) is the most common management practice for brine disposal.
- Discharge of concentrates to sanitary sewer systems is sometimes feasible if the concentrate mixture is not toxic and does not adversely affect the clarifier settleability or restrict final effluent disposal.
- Land application can provide a beneficial reuse of water when membrane concentrates are applied to vegetation, such as irrigation of lawns, parks, or golf courses. Factors associated with land application include the water quality tolerance of target vegetation to salinity, the ability to meet ground water quality standards, the availability and cost of land, percolation rates, and irrigation needs. In general, land application is used only for smaller volumes of concentrates.
- Deep well injection is a disposal technology which liquid wastes are injected through the injection tubing into the well. Since there is no technical difficulty in injecting desalination waste, it is one of the frequently used methods in disposing waste; however regulations on deep well injection are strict.
- Solar evaporation is a viable alternative in relatively warm, dry climates with high evaporation rates, level terrain, and low land costs. Regulations typically require an impervious lining and monitoring wells, which will increase costs of evaporation ponds. With little economy of scale, evaporation ponds are usually used only for small volume concentrates.

Key data is summarized in Table 3 for each process.

Table 3
Summary table of RO brine disposal methods

Method	Scale	Major advantages	Major drawbacks
Surface water discharge	Commercial	Lowest cost, most plants are located relatively near surface water, discharge to surface waters has been used with all sized concentrates	Environmental effects must be assessed
Sewer	Commercial	Sanitary sewer discharge of a small volume of concentrate usually represents a low cost disposal method (with limited permitting requirements)	This method is not feasible if the concentrate mixture is toxic and does adversely affect the clarifier settleability or restrict final effluent disposal
Land application	Commercial	Land application can provide a beneficial reuse of water when membrane concentrates are applied to vegetation, such as irrigation of lawns, parks, or golf courses	In general, land application is used only for smaller volumes of concentrates. These options are frequently limited by availability of land and/or dilution water. They may also be limited by climate in locations where land application is not possible year around
Deep well injection	Commercial	There is no technical difficulty in injecting desalination waste	Deep wells are not feasible in areas subject to earthquakes or where faults are present that can provide a direct hydraulic connection between the receiving aquifer and an overlying potable aquifer, environmental effects must be assessed
Evaporation pond	Commercial	Solar evaporation is a viable alternative in relatively warm, dry climates with high evaporation rates, level terrain, and low land costs.	With little economy of scale, evaporation ponds are usually used only for small volume concentrates, Regulations typically require an impervious lining and monitoring wells, which will increase costs of evaporation ponds

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