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Salt recovery from brine generated by large-scale seawater desalination plants

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ABSTRACT

Water shortages in the Middle East and North Africa (MENA) region countries mandate the installation of large-scale desalination plants. Concentrate management requires properly operated cost-effective technologies to reduce the environmental impacts arising from brine discharge. Significant improvement in economics may be obtained by the recovery of chemicals from brines. This study addresses the management of modular brine streams generated from large-scale reverse osmosis desalination plants with microfiltration and nanofiltration (NF) as pretreatment stages. Appropriate salt recovery schemes have been identified and analyzed from the performance and environmental points of view. The economics of salt recovery schemes from NF and reverse osmosis (RO) brine based on evaporation ponds, brine evaporator and membrane crystallizer (MCr) are analyzed and compared. Phased application of the salt recovery program is considered. The results indicate that using NF as pretreatment and adopting salt recovery schemes provide higher water recovery in addition to producing valuable products. The adoption of MCr has high prospects for application in salt recovery from desalination brine. Increasing the capacities of salt recovery systems offers both technical and economic merits.

Keywords: Salt recovery; Brine; Desalination; Membrane crystallizer; Evaporator; Techno-economics

1. Introduction

Brine generated from reverse osmosis (RO) desalination systems, currently, represents an environmental nuisance. Hybrid membrane desalination systems comprising MF/NF/RO (microfiltration/nanofiltration/reverse osmosis) have been technically and economically analyzed in previous works [1,2]. The use of NF is justified by the softening ability of the membrane via reducing calcium and magnesium ions from the permeate. Thus, the NF permeate contains mainly monovalent ions with minimum divalent ions [3], while the NF brine is practically divalent ions constituting an additional advantage for magnesium or calcium recovery [4]. Moreover, the RO brine is of higher quality and contains mostly sodium chloride

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which permits marketing of this high-value purified product.

Although direct discharge through outfalls or deep well injection is commonly adopted for brine disposal, efforts have been dedicated to adopt conventional/tailored systems for recovery of fractionated salts from brine. Drioli et al. [5], introduced membrane distillation (MD) to treat the RO brine in order to enhance the recovery factor of RO. The preliminary experimental results of using MF/UF + RO + MD confirmed the possibility of reaching a seawater recovery factor of 87%. A near-zero liquid discharge (ZLD) integrated system for concentrate management which increase the recovery of water to 90% has been proposed by Ohya et al. [6].

Salt recovery methods conventionally employ solar evaporation and/or thermal/mechanical evaporation [7,8]. Another integrated system (NF + RO + MCr) was suggested by Drioli et al. [9] where the presence of the NF in this integration allowed an increase in the water recovery of the RO unit up to 50%. Moreover, an introduction of a membrane crystallizer (MCr) led to a 100% recovery and elimination of the brine disposal problem, where pure crystals are produced as valuable products [2,10].

MCr is a relatively new and promising technology for salt recovery. This technology has been analyzed through the development of MD/crystallizer which contributes to the efficient removal/recovery of target salts with a rather small footprint [11,12].

It is worth mentioning that very recently, salinity gradient technologies have been proposed for facing the brine disposal problem, by producing energy from brines and seawater [13].

This paper addresses salt recovery schemes and related financial issues to propose some of the best management practices for the production of water and salt.

2. Brine management practices

Table 1 presents brine salinities of some seawater RO desalination plants generated at SWRO plants with feed water of typical composition presented in Table 2. Brine characteristics are related to feed and operating parameter of a given desalting plant.

Management of the concentrate produced by desalination processes has become an increasingly difficult challenge due to several factors that include the following: growing size of plants which limits disposal options, increased number of plants in a region such that the cumulative effect on receiving waters is becoming a limiting factor, increased regulation of discharges that makes disposal more difficult and slows the permitting process, increased public concern with environmental issues that plays a role in the permitting process, and increased desalination plants in semi-arid regions where conventional disposal options are limited.

Table 1
Brine characteristics from coastal SWRO desalination plants

Feed TDS ppm	Brine concentration ppm	Recovery	References
35,000	87,000	40% first stage 20% second stage	[14]
35,000	58,000	40%	[15]
46,400	81,316	38%	[16]
15,000–28,000	22,500	35–50%	[17]
42,000	67,000	55%	[17]
40,500	60,750	50%	[17]
38,795	71,509	43% two stages	[18]
40,000	78,900	50% first stage 78% second stage	[19]
44,000	63,609	31%	[20]

Table 2
Seawater composition [20]

Parameters	Concentration
Cl (mg/l)	19,345
Mg (mg/l)	1,295
Ca (mg/l)	416
Na (mg/l)	10,752
TDS	35,000

As a result of these trends, it is becoming more and more challenging to find a technically, environmentally, and financially viable method of dealing with the concentrate. The concentrate management challenge is particularly acute in the arid areas where frequent disposal to surface water and sewer are not viable options for plants above a small size.

The selection of a cost-effective salt recovery system may incorporate multiple unit operations to achieve the specified recovery targets. The development of beneficial salt reuse options and specific salt separation methods are also important for the cost reduction of the overall process [12,21]. Some examples of beneficial reuse of the solid product include the extraction of gypsum and sodium chloride by means of selective precipitation. However, the economic viability of beneficial reuse of desalination by-product salts depends on finding local markets to avoid high transportation costs [22].

The increasing tendency for salt recovery aims at mitigation of disposal and also maximum resource recovery. Analysis of brine management practices are compiled in Table 3.

3. Approach and methodology

Large-scale desalination (150,000 m^3/d) by MF/NF/RO has been techno-economically analyzed, and optimum conditions have been identified in previous work by the authors [1]. The present work aims at analyzing emerging salt recovery schemes to identify prospects for improving economic and environmental aspects of seawater desalination adopting membrane systems. The adopted methodology includes the following:

- Identifying emerging salt recovery modules and analyzing their technical and financial aspects for a base case (1,000 m^3/d for NF brine and 300 m^3/d for RO brine).
- Formulating appropriate integrated schemes for the recovery of selected salts from NF and RO brines, respectively.
- Investigating technical and financial aspects of proposed integrated schemes to come up with recommended scheme(s) for salt recovery.
- Exploring the effect of increasing the capacity of the recommended salt recovery scheme on the financial indicators.

4. Proposed salt recovery systems

4.1. Technical considerations

Numerous salt recovery processes recognized from commercial practices and results of emerging technologies and applications are compiled in Table 3, which also summarizes comparative technical and environmental indicators of these systems.

In this paper, three modules have been technically and economically analyzed to formulate four integrated optional schemes for salt recovery from brine generated from NF and/or RO systems. These modules are briefly outlined below.

Table 3
Comparison between different discharge/recovery methods of desalination brine

Items	Max capacity used	Benefits and constraints	Land requirements	Region appropriateness	Reference
Discharge to surface water	Unlimited	Low capital and OM costs	Small	Any where	[7]
Deep well injection	Unlimited	Economy of scale is required, high capital cost	Land requirements for injection wells	Depend on local geology	[7]
Land application	Dilute brine according to land application	As a backup disposal method	Depend on local needs	Depend on use and environmental regulations	[7]
Evaporation/ solar pond	1.5 MGD	Very reliable, little technical equipment required, feasible for small scale	Large	Dry climate characterized by high evaporation rate Large areas are available at low cost	[23,24]
MD/crystallizer	Still in laboratory development stage, high salinity limits mass transfer, which reduces flux through the system; no-full-scale performance data are available			Used anywhere	[25,26]
Capacitive deionization	Still in laboratory development stage, no-full-scale performance data are available			Used anywhere	[27]

4.1.1. Modules for salt recovery

4.1.1.1. Evaporation ponds. Pond systems are reliable and simple to operate. The solar pond evaporation method has high capital costs primarily due to the land acquisition costs due to the large surface areas required and the costs of impermeable liners, if needed. For example, assuming a relatively high evaporation rate of $0.1\,L/h/m^2$, the typical capital cost of an evaporation pond is reported to be U.S.$ 40 million for a concentrate flow of $3{,}800\,m^3/d$ (1 MGD) [28].

Evaporation under environmental conditions (''natural evaporation'') has the disadvantage of requiring large earth extensions, since the productivity of the process is quite low (around $4\,L/m^2/d^1$). This drawback can be overcome by using wet surfaces (capillaries or clothes) exposed to wind action, so surface density would be high enough to generate a proper evaporation flow with minimum energy consumption. Hence, the surfaces of the system would wet by means of capillarity and the water would evaporate while the salts of the brine would crystallize on the surfaces [29].

In SAL-PROC technology, evaporation ponds are used for volume reduction of waste stream, and also evaporation pond can be used before brine concentrator to raise the salinity to an appropriate level for the brine concentrator to achieve the required recovery [7]. Wind-aided intensified evaporation ponds (WAIV) is a type of evaporation ponds that is constructed with hydrophilic materials and wetting methods to increase the evaporative capacity per area by a factor of 10 or more [30,31].

The costs for a lower evaporation rate would be proportionally higher (e.g. four times as much for a rate of $0.025\,L/h/m^2$). These costs exclude any solids disposal or seepage monitoring options. Solar ponds require an all-year solar exposure, large volumes of brine, as well as an adequate source of "fresher" water, cheap flat land of low permeability, and high thermal and structural stability to be located away from shallow aquifers and consistent electricity demand [32].

4.1.1.2. Membrane crystallizer. MCr is relatively simple in operation; a heated, aqueous feed solution is brought into contact with the feed side of a hydrophobic membrane. The nature of the membrane prevents the penetration of the aqueous solution into the pores, resulting in a vapor–liquid interface at each pore entrance. The driving force is linked to both the partial pressure gradient and the thermal gradient between the two membrane sides. When the feed is water-containing salts as seawater, the solvent will be vaporized at the liquid/vapor interface and then passes as vapor through the membrane pores. The feed solution will be concentrated above its saturation limit, thus achieving a meta-stable state in which crystals may nucleate and grow [33].

The potentialities of MCr as an advanced technique for crystals recovery have been previously analyzed [9,12,34]. This membrane system is an emerging technology and is subject to extensive R&D. The success of the R&D results motivated progress toward production of MCr for commercial applications [35].

4.1.1.3. Mechanical evaporators. Mechanical evaporators (brine concentrator) are a proven technology for the reduction of concentrate volume in many industrial applications and can handle a range of feed water compositions. According to scale control, "Patented brine distributors" that ensure a smooth flow of brine, avoiding scale formation. Total recovery of water across the brine concentrator ranges from 90 to 99% depending on water chemistry. The distillate has a concentration of 5–10 mg/l, making it an excellent source of water [36,37]. The NF retentate stream is passed to an evaporator (brine concentrator), in which the recovery reaches 95%. The RO retentate stream, before introduction to the brine concentrator should be passed to the evaporation pond to raise the TDS up to 75,000 mg/l, to enhance the evaporator (brine concentrator) efficiency, for the recovery to reach 95% [30,38].

4.1.2. Integrated schemes

The above technologies have been studied with respect to four alternative integrated schemes for salt recovery from NF and/or RO brines. These are NF retentate/MCr, NF retentate/evaporator, RO retentate/evaporation pond/evaporator, and RO retentate/evaporation pond/MCr.

Brine from NF retentate or RO retentate from MF/NF/RO desalination system is fed to the alternative schemes as shown in Fig. 1. It is assumed that the system base case has a capacity of $1{,}000\,m^3/d$ for NF brine retentate and $300\,m^3/d$ for RO retentate. The seawater analysis used in the study is presented in Table 2. The material balance for this base case has been developed based on experimental published results and on the assumed performance presented in Table 4. Purge stream presented in Figs. 1–4 may be further processed to an evaporation pond or recycled with feed stream.

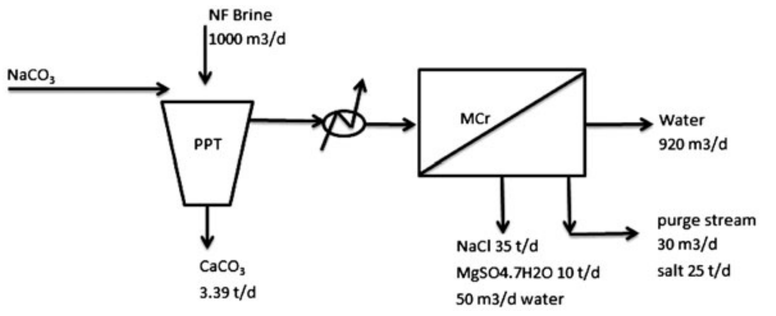

Fig. 1. Flow sheet of scheme 1: NF retentate/MCr.

Table 4
Performance of suggested systems for salt recovery

Mass balance of the proposed systems	Feed (m^3/d)	Recovery (%)	NaCl (ton/d)	$CaCO_3$ (ton/d)	$MgSO_4.7H_2O$ (ton/d)	Water (m^3/d)
NF brine stream						
Scheme 1, MCr	1,000	92	35	3.39	10	920
Scheme 2, evaporator	1,000	95	73			950
RO brine stream						
Scheme 3, pond/evaporator	300/255	95	19			242.25
Scheme 4, pond/MCr	300/255	92	9	0.8	2.55	234.6

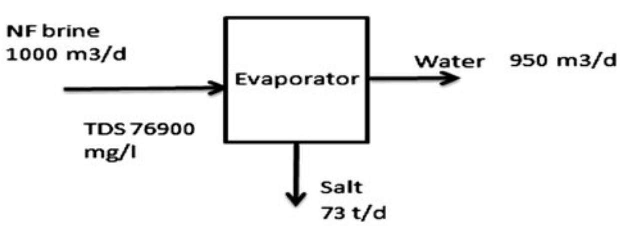

Fig. 2. Flow sheet of scheme 2: NF retentate/evaporator.

4.2. Financial aspects of water and salt production from the proposed schemes

The financial objective of the concentrate management is realized when sales revenues exceed total annual costs. This section is dedicated to the cost analysis of the proposed modules and integrated schemes to come up with selection guidelines and relevant indicators.

4.2.1. Basis of estimates for the base case

Basis of estimates are outlined below:

- Capital and operating costs for seawater the desalting systems are estimated using previously reported WTCostII, which is a well known computer software program, has been developed by the US Bureau of Reclamation and Moch and Associates for the evaluation and comparison of water treatment processes [1].
- The calculations of the principal components of the MCr are also based on previous work [9]. MCr is a rather recently recommended process and is newly developed technology, and thus, our costs are based on reported data.
- The service life of the MCr is assumed to be 15 years and for MCr module five years.

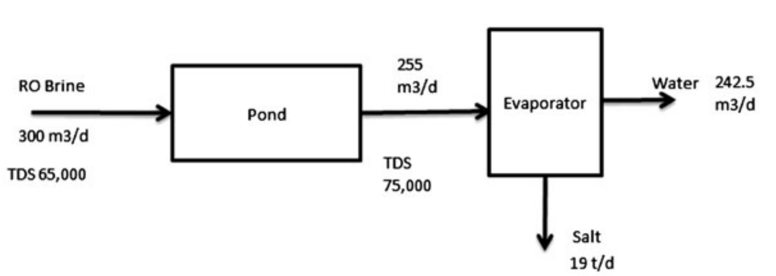

Fig. 3. Flow sheet of scheme 3: Retentate/evaporation pond/evaporator.

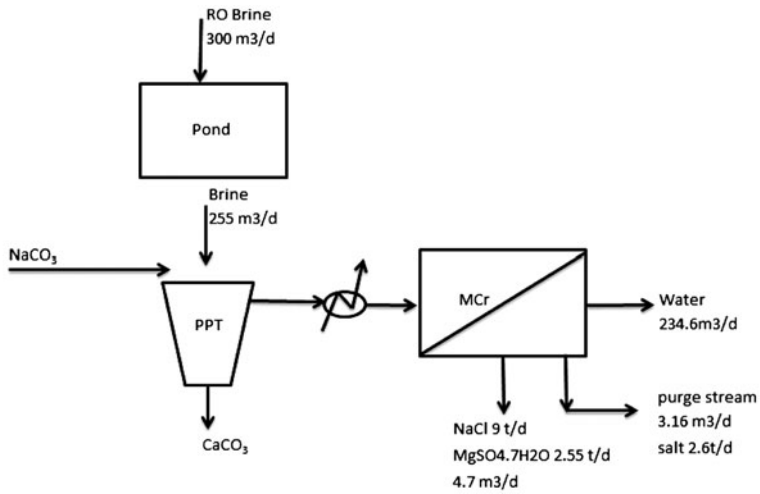

Fig. 4. Flow sheet of scheme 4: RO retentate/evaporation pond/MCr.

- Evaporator (brine concentrator) costs are based on USBR [7] report.
- Evaporation pond costs are based on data in Desalting handbook for planners [39]. The cost of the pond does not include land costs.
- All capital costs have been updated to 2010 using Marshall&Swift Cost Index.
- Operating costs include depreciation, steam cost, labor, maintenance, chemicals, and others.
- The revenues are estimated according to reported prices of salts as given in Table 5. These prices are expected to vary based on sales, purity, and market conditions.

Construction cost trends of the principal salt recovery modules are given in Table 6. The costs of the salt vary according to purity, form and use which is mentioned in the references of each cost. Since this work is theoretical and purity is not clearly defined, it is presumed that adding a lower and upper limit for magnesium sulfate could reflect the effect of salt prices on the financial analysis of the optional processes.

4.2.2. Results for the base case

Based on the aforementioned assumptions and estimates, the revenues from the sales of water and salts are presented for the modules and integrated schemes in Tables 7 and 8, respectively.

It is noted that the actual water produced exceeds the nominal capacity of the desalination system, due to the excess water recovered from the brine treatment system. Table 8 depicts the base case production cost.

Table 5
Reported prices of some salts

Product	Chemical composition	Price, US $	References
Gypsum-magnesium hydroxide	$CaSO_4{\cdot}2H_2O + Mg(OH)_2$	150/t	[40]
Magnesium hydroxide	$Mg(OH)_2$	400/t	[35]
		238–250/t	[7]
Sodium chloride	NaCl	70/t	[40]
Calcium carbonate	$CaCO_3$	300–900/t	[40]
		50/t	[6]
		60–350/t	[7]
Sodium sulfate	$NaSO_4$	170–200/t	[40]
		115–130/t	[7]
Calcium chloride	$CaCl_2$	220/t	[40]
		132–354/t	[7]
Epsomite	$MgSO_4{\cdot}7H_2O$	570/t	[41]
		150	[42]

Table 6
Capital cost of modules and unit cost on water production basis

	Capacity (m^3/d)	Total capital cost US ($)	Unit cost US ($/$m^3$) on water production basis
MF/NF/RO desalting system	150,000	206,000,000	0.8
Evaporator*	255	3,483,957	14
Evaporator*a	1,000	8,585,317	9
MCr*	255	463,286	0.77
MCr*a	1,000	1,205,788	0.65
Pond*	300	159291.4	

*For RO brine. *aFor NF brine.

Table 7
Revenues from salt and water produced from the proposed schemes

Salt and water revenues	Selling price US ($/t)	NaCl US ($/y)	Selling price US ($/t)	$MgSO_4.7H_2O$ US ($/y)	Price US ($/t)	$CaCO_3$ US ($/y)	Water US ($/y)
Scheme 1, Mcr*	90	265,680	570	476,748	62	16,268	61,559
Scheme 2, Evaporator*a	30	718,320		–		–	249,280
Scheme 3, Evaporator*	30	186,960		–		–	63566.4
Scheme 4, MCr*a	90	1,042,056	570	1,869,600	62	68,939	241,408

*RO retentate stream. *aNF retentate stream.

Table 8
Revenues of salt and water produced from the proposed schemes

	System	Total annual cost US ($/y)*	Annual revenues US ($/y)	Profit US ($/y)	Simple rate of return (%)
NF brine stream	Scheme 1: MCr	201,785	3,222,003	3020217.8	250.5
	Scheme 2: Evaporator	2,738,101	967,600	−1,770,501	
RO brine stream	Scheme 3: Pond/evaporator	111,132	250,526	139,393	3.8
	Scheme 4: Pond/MCr	61,842	820255.8	758413.4	121.8

*Depreciation: 6.67% of capital costs, steam, membrane replacement, others (labor, chemicals, overheads) $ 0.24, $ 0.125, $ 0.025, per m^3 of produced water, respectively.

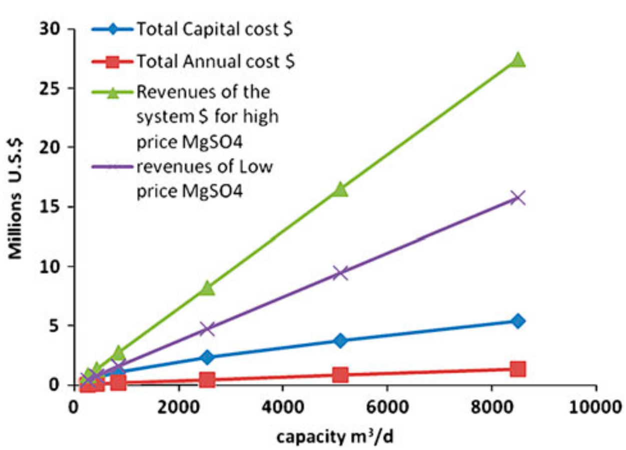

Fig. 5. MCr system increased capacity vs. cost and revenues.

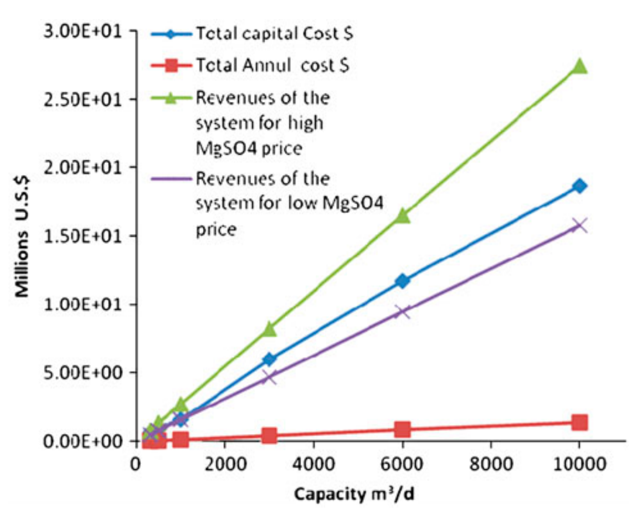

Fig. 6. Pond/MCr system with increased capacity cost vs. revenues.

Table 9
SRR% of different schemes

MCr capacity (m^3/d)		255	425	850	2,550	5,100	8,500
Simple rate of return (%)	MCr system	164.15	192.6	238.8	334.8	413.8	483.4
	MCr with low $MgSO_4$ price	88.3	104.23	130	183.5	227.5	266.3
	Pond/MCr system	122.15	137.5	159.9	128.7	132.9	139.6
	Pond/MCr system for low price $MgSO_4$	65.7	74.4	87	70.5	73	76.9

Results indicate that the schemes involving the emerging MCr technology give the highest revenues and profits, and hence, the highest simple rate of return (SRR%) can be expressed as (net profits/capital costs $\times$ 100). It is therefore recommended that Schemes 1 and 4 be adopted to recover selected salts from NF and RO brines.

4.2.3. *Financial Indicators for increased capacities (1,000–10,000 m^3/d)*

As previously mentioned, salt recovery options are still in early stages of application, and therefore, the base case of the above calculations was for 1,000 m^3/d of NF brine and 300 m^3/d of RO brine. However, for large-scale desalination, larger capacities should be adopted. The effect of increasing the NF brine treatment capacity up to 10,000 m^3/d with a corresponding increase in RO brine capacity for the recommended schemes has been investigated. Also, variation of the price of $MgSO_4$ between lower and upper published estimates, depending on purity, form and application, has been investigated to reflect the estimated effect on the revenues. The results are depicted in Figs. 5 and 6.

The simple rate of return of all the schemes at the increased capacities is presented in Table 9.

5. Conclusions

It is clear that integration of membrane/salt recovery systems improves the unit cost of desalinated water. The results show that the water cost is more competitive when salts are recovered from brines generated from NF and RO systems. It is also clear that including MCr improves the performance, and hence, the economics of seawater desalination processes through higher water recovery in addition to obtaining valuable products.

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