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Use of the desalination brines in the saturation of membrane electrolysis feed

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ABSTRACT

Seawater desalination by reverse osmosis (RO) invokes the necessity of brine disposal. On the other hand, the chlor-alkali industry requires saturated brine with a low content of calcium and magnesium contaminations. This paper describes a preliminary study exploring the possibility of the application of RO, nanofiltration–reverse osmosis, and nanofiltration–reverse osmosis–multieffect distillation seawater desalination brines as a sodium chloride source for membrane electrolysis. A concept has been proposed in which electrodialysis with univalent permselective membranes is used to enrich chlor-alkali lean brine with sodium chloride, and simultaneously desalinate discharge brine. The experiments with an electrodialyzer equipped with Neosepta® ACS and CMS membranes of 42 cm effective length have shown that the desired concentration of membrane electrolysis feed (above 300 g/L as NaCl) can be achieved. At the same time, the concentrations of both calcium and magnesium are decreased, the latter to a greater extent, that facilitates the successive brine purification step.

Keywords: Electrodialysis; Chlor-alkali brines; Brine reuse; Membrane electrolysis feed; Univalent permselective membranes; Calcium and magnesium transport

1. Introduction

The increasing interest in seawater reverse osmosis (RO) desalination causes problems with the discharge of salinated RO brines, which are environmentally unfriendly. In the literature, a few conceptions how to solve a waste water disposal problem have been described. Ahmed et al. [1] proposed an integrated process for the sequential extraction of dissolved compounds from inorganic saline waters in the form of valuable chemical products in crystalline, slurry, and liquid forms. Van der Bruggen et al. [2] pointed out several methods for the minimization of brackish and seawater RO brine volume: evaporation, multi-stage flash evaporation (MSF), multi-effect distillation (MED), electrodialysis (ED), and electrodialysis reversal (EDR). The MED and ED were said to be the most promising methods, especially given high recovery during the ED and the synergetic effect of distillation and RO (the preheating the RO feed by using it as a distillation cooling medium).

Comparison of MED and ED as possible methods for obtaining concentrated brine from seawater RO (SWRO) retentate shows that MED may offer lower energy consumption and lower unit costs. In the case of MED plants, as reported in a survey by Al-Shammiri and Safar [3], the evaporator electric consumption can be as low as 1 kWh/m^3 of distillate (three plants in UAE), while thermal energy consumption is of

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5.5 kWh/m^3 (Trapani ME) or below 5 kWh/m^3 (Curacao LT-ME-TVC).

Another advantage is that MED is more suitable for obtaining brines close to NaCl saturation. The MED effectiveness at high salt concentration is only slightly lower than that at the seawater concentration level, which is caused by lowering the water vapor pressure. The ED on the other hand has to cope with back-diffusion and water pumping, both phenomena being responsible for lower electric efficiency and difficulties in obtaining NaCl solutions close to saturation, because of the concentrate stream dilution by water transported from the diluate compartment. The latter disadvantage can be overcome by the application of high current density. However, energy consumption is further increased. One advantage of ED results from the application of univalent permselective membranes. In this case, NaCl to Ca^{2+}, Mg^{2+}, and SO_4^{2-} concentration ratios increase with increasing brine concentration. The higher corrosion rate of construction materials when working with highly concentrated brine may be recognized as another MED disadvantage; however, it is relatively easy to overcome by the application of modern, corrosion-resistant materials.

Tanaka et al. [4] have modeled SWRO discharge brines concentration by ED in the salt manufacturing plant. They defined the term "saturation current density"—the current density value required for the concentrate solution to reach saturation level in the ED and established a method for its estimation [5]. The saturation current density value was found to be equal to 510 A/m^2 for seawater and applied ED parameters (4 cm/s linear flow velocity and 0.75 mm spacer) [6]. Turek et al. examined ED for the desalination of brackish water, seawater, and coal-mine brines with simultaneous obtaining of concentrated brines. Electrodialytic desalination/concentration of brackish water (TDS ca. 10 g/L) in an integrated ED—thermal desalination system was examined. The ED unit stacks geometry and the ED system arrangement and operating conditions were optimized to identify minimum desalination/concentration costs. The ED stacks with relatively low 0.19 mm membrane to membrane distance, and three stages ED system arrangement was investigated to identify optimum process parameters. The minimum total desalination/concentration cost was found at 255 g/L NaCl concentrate content. When ED alone was applied for desalination, concentration up to TDS of 300 g/L (close to NaCl saturation level) relatively low value of energy consumption, equal to 275 kWh/t of salt, was observed at optimum conditions [7]. When ED–EDR concentration of coal-mine brine of salinity ca 58 g/L up to 140 g/L was considered, the energy consumption found, at 0.19 mm membrane to membrane distance, was equal to 200 kWh/t of salt produced while electrodialytic concentration up to saturation consumed ca 350 kWh/t [8].

Another problem related to RO brine concentration is the risk of scaling due to the presence of sparingly soluble salts in the feed. In order to increase the water recovery rate, the ED should aim for the high concentration in the concentrate stream. Unfortunately, this increases the scaling tendencies. Scaling problems in the ED process have been widely studied. Korngold et al. [9] have examined the possibility of ED application for the concentration of RO brines and proposed a high recovery RO–ED desalination process. In order to prevent gypsum crystallization on ion-exchange membranes, the ED concentrate was recirculated through the gypsum precipitator with $CaSO_4$ seeds. A pilot studie of brackish water RO–EDR system with continuous crystallization [10] has shown that such solution can be economically competitive to conventional RO. Zhang et al. [11] have studied the possibility of electrodialytic concentration of RO brines. To reduce the carbonate scaling potential, ED solutions pH was adjusted with HCl; although acidification decreases the carbonate scaling potential, it would be more expedient to minimize the amount of additives such as acids or antiscalants, because it increases the desalination costs and creates problems with further crystallization of sparingly soluble salts if zero liquid discharge technology is considered. That is why in our previous research [12–14], we have proposed a different approach to scaling problem, combining crystallization kinetics and ED hydrodynamic conditions to perform a single-pass ED without antiscalants in such a manner, that supersaturated solution will leave the concentrate compartment before the crystallization can be macroscopically observed. This approach was allowed to achieve very high supersaturation of calcium sulfate solution (up to 368%) and Langelier saturation index (LSI) up to 2.12 [12].

The production of chlorine and sodium hydroxide in the chlor-alkali industry requires the saturated brine which is free of calcium and magnesium impurities. The chlorine production by membrane electrolysis, a technology which was concluded to be a BAT for the chlor-alkali industry by the European Commission JRC [15], requires the 182 g/L as Cl^- (300 g/L as NaCl) feed with sum of magnesium and calcium content less than 20 μg/L and sulfate concentration less than 7 g/L [16]. Typically, the lean brine, the brine leaving the anode compartment of the membrane electrolysis cell with lowered concentration of sodium chloride, is resaturated with solid sodium chloride and recirculated. The membrane electrolysis feed typically require two-stage pretreatment [15]: in the first stage, sodium carbonate and sodium hydroxide are added to precipitate calcium carbonate and magnesium hydroxide. The precipitates are removed by sedimentation or filtration. The second stage is ion-exchange with chelating resins. The lean brine is typically resaturated with solid sodium chloride (vacuum-crystallized salt from solution-mined brine, rock salt, or solar salt [15]), although chlor-alkali industry can utilize different chloride sources, i.e. coal mine waters [17]. Because the addition of solid salt is costly, a cheaper source of sodium chloride is needed. Desalination brines could be of use in this case; however, they usually contain not only sodium chloride, but also other salts, which are considered as impurities in the membrane electrolysis process. The direct addition of desalination brines into electrolysis lean brine would increase the load on further sedimentation/ion-exchange pretreatment before electrolyzer. Moreover, the direct addition of desalination brines (concentration at most 300 g/L as NaCl, but usually much lower) to lean brine leaving the membrane electrolysis (ca. 210–250 g/L as NaCl) will not create the saturated brine of sodium chloride concentration more than 300 g/L. Therefore, there is a need for a method of selective transport of sodium chloride from the desalination brines to the membrane electrolysis feed.

To decrease the discharge volume from desalination plants, we have proposed in the previous work [18] an integrated system consisting of ultrafiltration, nanofiltration (NF), RO, thermal process (MED/MSF), and evaporated salt obtained by crystallization. The integrated system offered low desalination unit costs (\$0.5 at 50,000 m^3/d capacity) and very high water recovery (78.2%). The brine from the integrated system can be further reused; the proposed concept is to enrich the lean brine from membrane electrolysis with the sodium chloride originating from the discharges from various steps of the above-mentioned integrated system and recycle the enriched brine back to the electrolysis loop. To minimize the amount of calcium and magnesium being passed to the electrolysis loop, the proposed solution is the ED with the univalent permselective membranes. Although commercially available membranes have bivalent ions transport numbers of ca. 0.1, some calcium and magnesium ions will still pass through the membranes, so the membrane electrolysis feed is usually subjected to the alkalization and ion-exchange pretreatment (see Fig. 1). Casas et al. [16] have modeled a pilot ED plant for SWRO brine concentrations. Based on the Nernst–Planck equation and mass balance equations, they have developed a model describing the plant performance with respect to the transport of sodium chloride; however, calcium and magnesium transport was neglected. Although the desired chlor-alkali feed concentration of 300 g/L as NaCl was not reached in the experiments because current density was not high enough, the model predicted that such concentrations should be reached in the investigated plant at ca. 600–700 A/m^2 after 25–28 h of operation (inlet concentration ca. 65 g/L as NaCl).

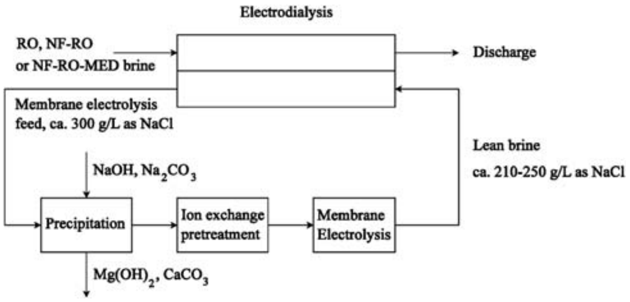

Fig. 1. A proposed system for saturation of membrane electrolysis lean brine.

2. Experimental

The electrodialyzer consisted of platinum-covered titanium electrodes, electrolytic compartment spacers, Neosepta® CMS and ACS univalent permselective membranes, and 0.26 mm woven spacers constructed based on the previous research [12,13]. The densely packed membrane abutments allowed working with high current density, with different linear flow velocities without risk of membrane bulging. The spacers also allowed for work in counter-current mode, which lowered the concentration gradient between diluate and concentrate compartments. The back-diffusion from the concentrate to the diluate compartment was thus lowered and higher concentration in the concentrate compartment might be reached. The membrane stack consisted of four cation-exchange and anion-exchange membrane pairs, with an effective membrane length (the fraction of membrane length that actually takes place in the mass transfer) of 42 cm and an effective membrane area of 84 cm^2. The voltage drop on the membrane stack was a mean value of voltages measured by wire probes placed inside outer compartments along the electrodialyzer. The current was measured by the ammeters connected to the electrode. The electrolytic solution was sodium sulfate (100 g/L) which, together with the proper design of the electrolytic compartment spacer (an open mesh one) and a linear flow velocity of ca. 3.5 cm/s for each experiment, lowered the gas accumulation and allowed for work at high current densities (up to 620 A/m^2). The electrodialyzer worked in a single-pass mode in the diluate and concentrate compartments, while the electrolytic solution was recirculated, mixing the anolyte and catholyte streams in an open tank. A set of three pumps allowed the regulation of linear flow velocity in the concentrate, diluate, and electrode compartments.

The electrodialyzer and spacers were designed to give a narrow residence time distribution (RTD) of the particles leaving the diluate and concentrate compartments by a reduction of stagnant regions [13]. The solubility of calcium sulfate increases in the presence of chloride ions, because the ionic strength is increased. During the ED, in the diluate compartment the chloride ions migrate through the membrane and leave the compartment, while most of the calcium and sulfate ions stay in the diluate compartment due to the membranes permselectivity. Given that water passes to the concentrate compartment due to the osmosis and electroosmosis, the concentration of calcium and sulfate ions increases along with decreasing solubility, creating the risk of membrane scaling in the diluate compartment. The short mean residence time and narrow RTD decrease the scaling risk, since theoretically no calcium sulfate nuclei stays in the diluate compartment long enough to observe macroscopic crystallization. The model solutions of RO, nanofiltration–reverse osmosis (NF–RO) and nanofiltration–reverse osmosis–multieffect distillation (NF–RO–MED) brines were prepared by dissolving appropriate amounts of chemically pure sodium chloride, calcium chloride, and magnesium chloride in the demineralized water of conductivity less than 0.066 μS/cm. The lean brine model solution was prepared by dissolving chemically pure sodium chloride in distilled water; however, used reagent had traces of calcium and magnesium. The chloride concentration was determined by argentometric titration using Fajans method (volumetric titration with standardized silver nitrate(V) solution with fluorescein ethanol–water solution as indicator) and the calcium and magnesium concentrations were determined by complexometric titration (calcium: titration with standardized EDTA solution at pH 13 with sodium chloride–calmagite powder as indicator and sum of calcium and magnesium: titration with standardized EDTA solution at pH 10 with eriochrome black T as indicator). The results of ions concentration analysis in the feeds are presented in Table 1. The NF–RO and NF–RO–MED brines were modeled after different stages of integrated desalination system [18], whereas RO brine was prepared to simulate typical SWRO brine, assuming typical seawater composition [19] of 99% rejection and 48% recovery. The lean brine concentration was modeled after typical membrane electrolysis outlet stream, which is usually 210–250 g/L as NaCl [15].

Table 1
Concentrations of chloride, magnesium, and calcium ions in the model solutions

Solution	Cl^- [g/L]	Mg^{2+} [g/L]	Ca^{2+} [g/L]
Lean brine	137.6	0.0054	0.0012
RO brine	36.2	2.35	0.68
NF–RO brine	51.4	1.20	0.62
NF–RO–MED brine	185.5	4.18	2.24

The experimental conditions are presented in Table 2. In order to reach desired brine saturation, the linear flow velocities were kept at extremely low level. Very low linear flow velocities suggest that a longer electrodialyzer (possibly with membrane effective length of 1 m) or the cascade of electrodialyzers is required. The applied current densities are higher than the typical values used in ED, but are necessary in order to reach the desired sodium chloride concentration level. The necessity of high current density was confirmed by Casas et al. [16] and Tanaka et al. [6]. The high current density may cause the local overheating and chemical damage problems [20]. We have not observed the membrane failure during the experiments, but it is possible that membranes used for saturation of membrane electrolysis feed would have lower life time.

3. Results

The ion concentrations in the diluate and concentrate outlet streams are presented in Table 3. For each feed, it was possible to find such experimental conditions that the saturation level required by the membrane electrolysis was reached (see experiments No. 2, 3, and 5 in Table 3). The experiment No. 1 showed that the concentration in the concentrate stream was decreasing, contrary to what would be expected for ED. This can be explained by high osmotic and electroosmotic water transport that was not overcame by ion migration, because the linear flow velocity was too high for given membrane length and current density. In the case of experiments with NF–RO–MED brines, the initially established current density of ca. 600 A/m^2 resulted in salt crystallization inside the module, so the appropriate current density was established with trial and error method. The results show that it is possible to reach desired sodium chloride concentration of 300 g/L using single-pass ED. The applied intermembrane spacer of 0.26 mm thickness was shown to cause good mass transfer conditions, despite ridiculously low linear flow velocities.

Table 2
The experimental conditions

No.	Diluate feed	Current density [A/m^2]	Voltage [V]	Linear flow velocity [cm/s]			
				Diluate		Concentrate	
				Inlet	Outlet	Inlet	Outlet
1	RO brine	617	3.38	1.63	1.50	0.20	0.34
2	RO brine	623	2.20	1.64	1.50	0.12	0.26
3	NF–RO brine	613	2.40	1.27	1.16	0.085	0.23
4	NF–RO–MED brine	368	2.00	0.190	0.119	0.079	0.174
5	NF–RO–MED brine	477	3.27	0.191	0.087	0.079	0.210

Table 3
The outlet concentrations

No.	Diluate feed	NaCl [g/L]		Ca^{2+} [g/L]		Mg^{2+} [g/L]	
		Diluate	Concentrate	Diluate	Concentrate	Diluate	Concentrate
1	RO brine	35.3	217.4	0.69	0.21	2.47	0.36
2	RO brine	41.3	313.0	0.70	0.38	2.35	0.71
3	NF–RO brine	66.9	310.1	0.68	0.47	1.11	0.64
4	NF–RO–MED brine	70.1	275.9	1.02	0.51	5.93	0.58
5	NF–RO–MED brine	148.3	323.7	1.52	0.76	3.47	0.95

Table 4
The current efficiencies and energy consumption for the performed experiments

Experiment	1	2	3	4	5
Current efficiency [%]	46	89	85	83	105
Energy consumption [kWh/kg of NaCl transported]	0.84	0.28	0.32	0.27	0.36

4. Discussion

The content of calcium and magnesium in the concentrate outlet stream is unexpectedly high—up to 0.76 g/L of Ca^{2+} and 0.95 g/L of Mg^{2+}. Moreover, the magnesium to calcium ratio was not preserved. In the RO brine it is approximately 3.5:1—see Table 1 (model solution prepared according to the earlier research [18]); it is lower with NF pretreatment (ca. 2:1), which is an expected behavior. In the concentrate, the ratios of magnesium to calcium are 1.7:1–1.9:1 in the case of RO brine (compared to 3.5:1 in the diluate), 1.4:1 in the case of NF–RO brine; and 1:25:1 and 1.14:1 in the case of NF–RO–MED brines—see Table 3. This suggests that the calcium flux across the membrane is higher than magnesium flux. This can be explained as a result of magnesium having higher tendency for hydration than calcium, which causes solvated magnesium ions to be bigger and of smaller mobility than solvated calcium ions. It is hard to explain the differences in magnesium to calcium ratio among each experiment, since there were only five of them and each in the different mass transport conditions, so further studies are going to be conducted in order to describe the bivalent ions transport across univalent permselective membranes. The lower magnesium to calcium ratio is preferable from the point of electrolysis feed pretreatment with sodium hydroxide and sodium carbonate. The alkalization of brine results in obtaining slowly settling magnesium hydroxide suspension, so lowering the magnesium concentration would result in the reduction of both sodium hydroxide consumption and magnesium hydroxide sludge volume. The current efficiencies and energy consumption for each of the experiment have been calculated—see Table 4. The high energy consumption and low current efficiency for experiment No. 1 is a result of high back-diffusion, osmotic, and electroosmotic water transport. In the case of experiments No. 4 and

5, the diluate was more concentrated than concentrate (an unusual case for ED), so the diffusion and osmotic water transport worked in the opposite way, increasing the flux from the diluate to concentrate compartments and thus increasing the current efficiency, which explains the current efficiency above 100%. The energy consumption is higher than the 0.15 kWh/kg of NaCl transport calculated by Tanaka [6]; however, this is only a preliminary research on the possibility of lean brine resaturation with ED and the results are far from optimal.

5. Conclusion

Since this is only a preliminary study, the experimental conditions were not optimized for membrane ED feed concentration or energy consumption. The point was to show that it is in fact possible to use ED with univalent permselective membranes for the saturation of chlor-alkali depleted brines up to the concentration of 300 g/L as NaCl or above. This goal was reached, and the magnesium to calcium ratio was found to be lower in the ED concentrate than it was in the RO, NF–RO, and NF–RO–MED brines, which is beneficial behavior. The matter of transport of divalent ions across the Neosepta® CMS and ACS membranes is the subject of a recently launched study. Further optimization is also required to study the economical viability of the proposed solution.

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