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A new, energy-efficient approach for boron removal from SWRO plants

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ABSTRACT

A different approach for the operation of seawater reverse osmosis desalination plants, in which the boron concentration in the product water should not exceed 0.3 mgB/L, was recently introduced. The new approach is based on strong acid (either H_2SO_4 or HCl) dosage to the feed seawater to attain pH ~ 4.3, followed by almost complete CO_2 stripping and subsequently strong base addition to pH 9.0–9.25. At this high pH range, a high *B* removal efficiency can be attained even by the new generation of ultra-low energy (high-flux) membranes. This paper addresses the energy saving potential stemming from the elimination or size reduction of the 2nd reverse osmosis (RO) pass and from the use of high-flux elements, both made possible by the new approach. Additionally, total dissolved solids removal from the 1st RO pass permeate can be obtained by operating a smaller, more energy efficient, 2nd RO pass.

Keywords: Boron removal; SWRO; Desalination; Post treatment; Stripping towers

1. Introduction

Increasing water scarcity in arid and semiarid countries is promoting seawater reverse osmosis (SWRO) desalination projects in growing numbers, worldwide. It is safe to assume that in the foreseeable future, more and more cities in such regions will rely entirely (or almost entirely) on desalinated seawater for their urban water supply. Moreover, desalinated water is increasingly being used directly for agricultural purposes or indirectly via reclamation of treated municipal wastewater for irrigation, for which the lower salinity of the water makes the treated effluents from desalination origin very welcome. As a result, product water quality requirements from large desalination projects, and specifically the boron and total dissolved solids (TDS) product water criteria, are becoming more and more stringent. Low *B* concentration is required for irrigation due to the negative effect this element has on some crops at concentrations higher than 0.5 mg/L [1]. Wastewater reclamation also requires a low TDS background in the desalinated water to minimize soil salting and structure degradation due to the relatively large addition of sodium to the water due to domestic and industrial uses. In Israel, where over 50% of the irrigation water is reclaimed wastewater, large SWRO projects are contracted to produce water with $B < 0.3$ mg/L and TDS < 200 mg/L. A good example of direct use of

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desalinated water for irrigation is the 210,000 m^3/d SWRO plant in Aguilas–Murcia Spain, which is currently under construction. This plant was designed for $B < 0.5$ mg/L and TDS < 400 mg/L in the product water. Bearing in mind that between 100 and 150 mg/L TDS are added in the post-treatment step, reverse osmosis (RO) permeate TDS is required to be 100 mg/L in the former example and 250–300 mg/L in the latter. The permeate of the 1st SWRO pass cannot meet these criteria at the conventional recovery ratios applied and thus has to be further treated by applying a second RO pass. The conventional methods for *B* removal are either high-pH 2nd RO pass, which also results in efficient TDS removal, or an ion exchange step commonly termed as boron-specific resin [1]. Economic works comparing the two methods show the IX cost to be the lower of the two alternatives [2,3]. However, since even 300 mg/L TDS is difficult to obtain in a single RO pass, a 2nd RO pass has become the preferred strategy in recent SWRO designs. A new approach for single pass *B* removal was recently introduced by the authors [4], under which low target *B* concentrations can be attained using a single RO pass. The suggested process, depicted in Fig. 1, begins with acidification of the feed seawater to eliminate all the carbonate alkalinity in the water (i.e. to pH ~ 4.3). This step is followed by CO_2 stripping, designed to remove 90–95% of the inorganic carbon concentration (C_T). A strong base is then added to obtain high pH (pH 8.8—pH 9.25) prior to the 1st SWRO pass. At this high pH, *B* is effectively removed, while $CaCO_3$ scaling is prevented by the lack of inorganic carbon (C_T) in the feed water. The 20–30% of stripped CO_2 is transferred to the re-mineralization step for calcite or lime dissolution. Nir et al. [4] showed this approach to be feasible and cost competitive. In the current paper, the potential of using ultra-low energy SWRO membranes for *B* removal as well as the application of a partial 2nd pass to meet the water quality demands detailed above are discussed in the context of the new approach.

2. Methods

Average ionic composition and pH values measured in the feed (Mediterranean Sea) water are shown in Table 1. Single pass *B* removal experiments were carried out using a pilot-scale seawater desalination unit comprising one 4´´ spiral-wound RO module. The experimental system included two pumps, a booster pump and a heat exchanger for maintaining a constant 25 ± 2°C temperature. In addition, the system

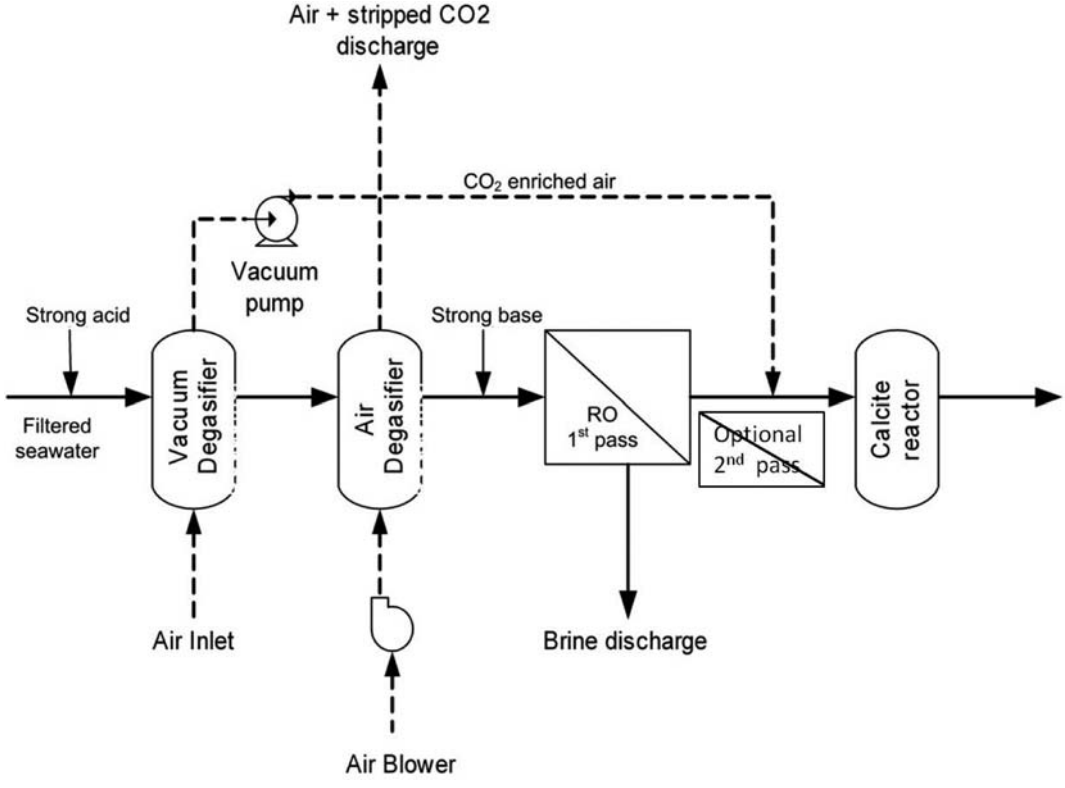

Fig. 1. Schematic of the proposed process (source: Nir et al. [4]).

Table 1
Seawater feed composition used in the 1st pass experiments (before the decarbonation step) and for the computer projections. Concentrations appear in mg/L

Cl^-	Na^+	Ca^{2+}	Mg^{2+}	K^+	SO_4^-	HCO_3^-	B_T
21,950	12,656	433	1,306	466	3,344	140	5

included flow meters for permeate and brine streams. The RO element used was SWC6–4040, manufactured by Hydranautics Ltd. The membrane was conditioned before use by circulating seawater at 60 bars for 2 h. Pretreated seawater was collected from the Palmachim desalination plant (Israel). Seawater feed (150 L) was acidified by sulfuric acid (98%) and thereafter exposed to air bubbling overnight to obtain > 90% CO_2 degasification. The pH of the feed water was raised before each run using 5 M NaOH solution. Four experiments (1 for each pH value) were performed, in which the concentrate was continuously recycled back to the feed tank and permeate was collected in a separate tank until 43.3% recovery ratio was attained. Samples were taken from the permeate tank (after stirring) at six points of accumulated permeate volume, representing six recovery ratio values. The working pressure was 65–66 bars; feed temperature was 25 ± 2° C; and feed flow rate was 2,000 ± 150 l/h. A more detailed description of the experimental system, including schematics, can be found in [4]. Computer projections were conducted with IMSDesign 2011, provided by Hydranautics Ltd, using the ion composition shown in Table 1. The only exception was that the boron concentration was set at 5 mg/L and HCO_3^- concentration was set at 5 mg/L in the high pH scenarios. Membrane age was set at 3 years. Flux decline and salt passage increase were 7 and 10% per year, respectively. Pump and motor efficiency was set at 83 and 93%, respectively. A pressure exchanger was included in the simulations with the default settings of the software. Input parameters which varied between scenarios are shown in Fig. 4. The PHREEQC software package was used to calculate the required chemical dosages to the seawater. Activity coefficients were calculated by using the Pitzer approach, which is integrated in the software's database.

3. Results and discussion

The results of two types of SWRO membranes were used to simulate the performance of the 1st pass in the presented approach. The first was SW30-HRLE (DOW), which is commonly used in large seawater desalination plants and is known to be a good compromise between relatively high *B* rejection and low energy demand. The second was SWC6 (Hydranautics), a membrane categorized by ultra-low energy demand (or alternatively, a high-flux membrane).

The results of *B* removal by the SW30HRLE element also appear in [4] and are presented here for the purpose of comparison between the two SWRO elements. The permeate flux of SWC6 can be expected to be 22% higher than that of the HRLE membrane, according to data reported by the manufacturers, obtained under standard test conditions. In this work, the average time for reaching recovery of 43.33% was 18% shorter when SWC6 was used under similar conditions, implying permeate flux that is 18% higher (both membranes have similar active areas). This result may enable the decrease of either the size or the energy requirements in the 1st pass. However, the standard trade-off for the higher flux is lower rejection for *B* (Fig. 2) and TDS (Fig. 3). Indeed, when the feed water pH was 8.0, which is the typical pH value in SWRO applications, 60 and 78% of total *B* rejections were observed with SWC6 and SW30HRLE, respectively (Fig. 3). Permeate TDS (approximately the sum of Cl^- and Na^+ concentrations plus 5–10 mg/L contributed by other solutes) was unaffected by pH, yielding ~370 and ~210 mg/L for SWC6 and SW30HRLE, respectively (Fig. 3). Higher *B* and TDS permeation is probably one of the main reasons why this type of high flux membranes have hardly been applied in large SWRO plants, although they have been available from several manufacturers for a few years now.

Bartels et al. [5] used computer simulations to show that placing ultra-high-flux elements in the rear positions of the 1st pass pressure vessel can save 5–10% of the energy required for this pass. This approach, termed "hybrid element design" or "internally staged design," solves in an elegant fashion the flux distribution problems (causing fouling hazards in the lead element and improper hydraulics in the rear elements) associated with high-flux elements [6]. In a later work, dedicated to *B* removal, these authors showed however that the higher *B* passage caused by the high flux hybrid design requires a larger 2nd pass, which consumes more energy and chemicals and eventually results in a higher product water cost [7]. Significantly, higher *B* rejection during the 1st pass

can be obtained by elevating the pH of the feed to pH > 9. This holds true for both membranes, as shown by the results presented in Fig. 2. However, feed pH elevation is limited by $CaCO_3$ scaling propensity, as antiscalants are largely ineffective at high pH values. Additionally, large amounts of expensive strong base would be required to overcome the buffer capacity, attributed mainly to the carbonate system (the apparent second dissociation constant in seawater is ~8.9, in pK terms).

The approach suggested in this work eliminates both problems by removing all the carbonate species prior to dosing the base and treating the water in the 1st RO pass. A substantial mass of strong acid (2.5 eq/m^3) is needed to convert all C_T to CO_2, but strong acid is generally much cheaper than strong base. The use of H_2SO_4 adds less than 5% to the sulfate concentration of seawater, which does not induce $CaSO_4$ precipitation in the concentrate (i.e. the brine remains undersaturated with respect to gypsum). $Mg(OH)_2$ solid, another potential scaling agent, is undersaturated at below pH 9.45 as shown in [4]. With enhanced *B* removal in the 1st pass, the hybrid elements design comprising ultra-low and low energy elements can be attractive, while at the same time, the 2nd pass can be smaller. As can be easily seen from Figs. 2 and 3, for attaining $B < 0.5$ mg/L TDS < 400 mg/L, a 2nd pass is not required if

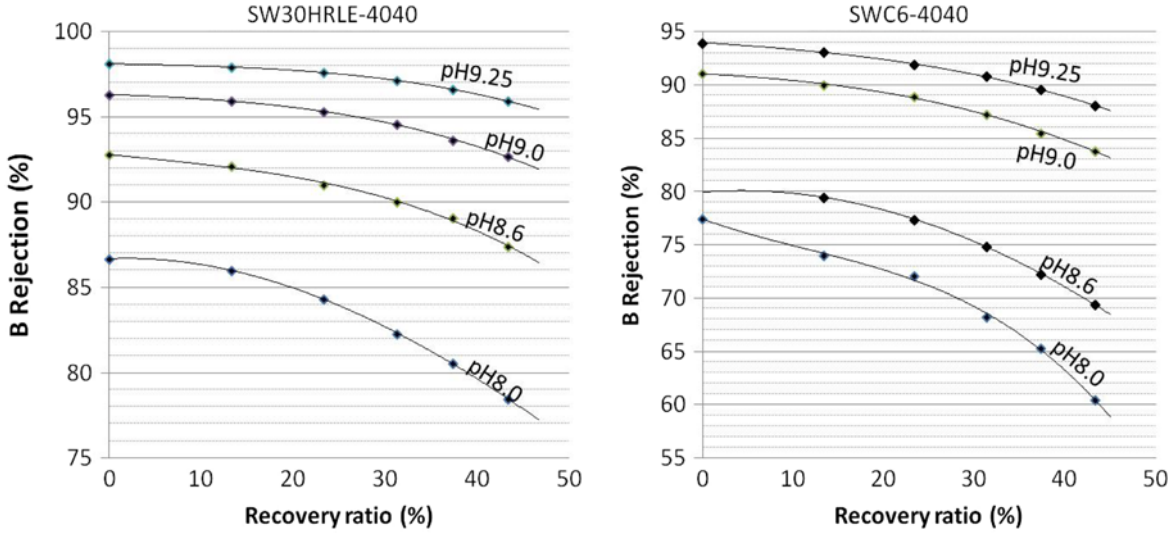

Fig. 2. Overall *B* rejection by two types of SWRO elements plotted vs. recovery ratio at 4 feed pH values.

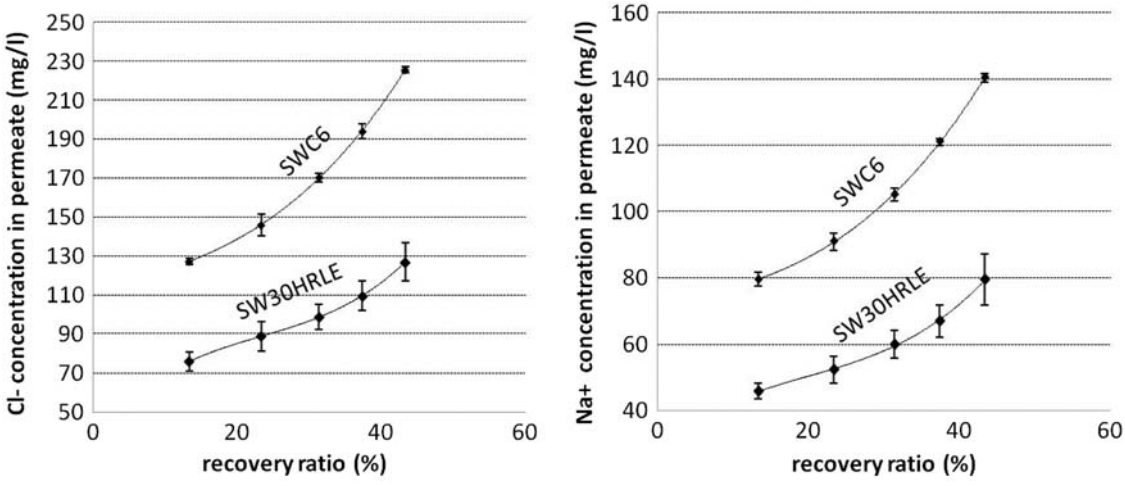

Fig. 3. Average Cl^- and Na^+ concentrations in SWRO permeate vs. recovery for two types of membrane elements ($n = 8$ for SW30HRLE and $n = 3$ for SWC6).

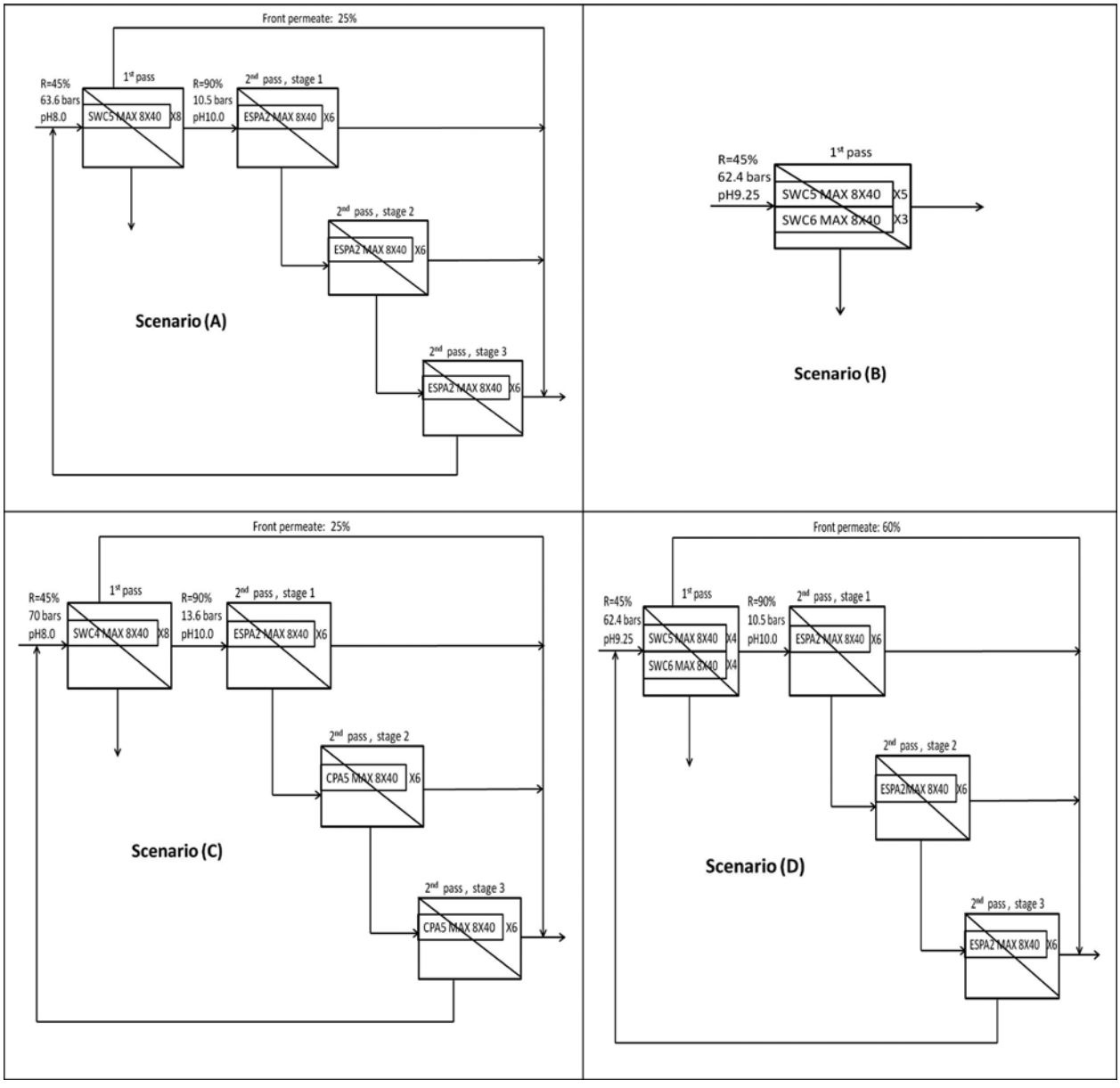

Fig. 4. Designs and operational conditions used as input for the computer projections in the different scenarios tested.

SW30HRLE or an equivalent membrane (such as SWC4 of Hydranautics, for example) is used. For $B < 0.3$ mg/L and TDS < 200 mg/L requirements, a small 2nd pass will be needed for further TDS removal. In order to estimate the total energy saving potential resulting from the suggested approach, four different SWRO desalination plant designs were tested theoretically using computer simulations, performed with software provided by a membrane manufacturer (IMSDesign of Hydranautics). The flow charts and operation conditions, schematically shown in Fig. 4, were aimed at achieving the distinct water quality criteria mentioned above, assuming both a standard approach (Scenarios A and C in Fig. 4) and the novel approach presented in this paper (Scenarios B and D in Fig. 4). A 0.1 mgB/L safety margin was considered in the simulation for the B concentration in the product water; the pH of the feed to the 2nd pass was limited to pH 10. The predicted energy consumptions are shown in Table 2, along with major chemicals' consumptions. For the $B < 0.5$ mg/L, TDS < 400 quality requirements (Scenarios A and B), 0.48 kWh/m^3 was saved by using the low and ultra-low energy elements and by eliminating the need for the 2nd pass. For the

Table 2
Projected energy consumption, chemicals consumption, and permeate quality for conventional design scenario (A, C) and for the new design suggested in this work (B, D). All consumptions are normalized to product flow rate

Scenario	(A) pH 8.0 $B < 0.5$ TDS < 400	(B) pH 9.25 $B < 0.5$ TDS < 400	(C) pH 8.0 $B < 0.3$ TDS < 200	(D) pH 9.25 $B < 0.3$ TDS < 200
Overall recovery (%)	41.63	45.0	41.63	43.2
Need for 2nd pass	Yes	No	Yes	Yes
Specific energy consumption (kWh/m^3)	3.01	2.53	3.29	2.74
Specific NaOH consumption (g/m^3)	8.5	44.4	7	49.3
Specific H_2SO_4 consumption (g/m^3)	0	272.2	0	283.6
Specific CO_2 consumption (g/m^3)	45	0	45	0
Specific antiscalant consumption (g/m^3)	3.2	0	3.2	0
Permeate quality (mg/L)	$B = 0.39$ TDS = 33.4	$B = 0.4$ TDS = 293	$B = 0.19$ TDS = 24	$B = 0.19$ TDS = 92.3

more strict $B < 0.3$ mg/L, TDS < 200 objectives, the 2nd pass was reduced from 75 to 40% of the flow rate of the 1st pass permeate. By this and by incorporating lower energy elements in the 1st pass, ~0.6 kWh/m^3 was saved. H_2SO_4 and NaOH consumptions increased in the novel approach, while antiscalants and CO_2 (used in the remineralization step) consumptions decreased.

4. Conclusions

The enhancement of B removal in the 1st SWRO pass and the potential for significant energy saving achieved by the novel operational approach were demonstrated by both experimental results and computer simulations. These improvements, however, come at the expense of larger consumption of acid and base chemicals. Eventually, the cost effectiveness of the new design will depend on the balance between energy and chemicals' costs. Nevertheless, the suggested process has several advantages over the conventional alternatives. It was shown, for example, that antiscalants can promote biofouling in membranes application [8]. In the new design, antiscalants are not needed and biofouling is further decreased by the relatively sharp pH diversions. This can increase the membranes lifespan and save capital and energy expenses. Furthermore, since no $CaCO_3$ scaling is expected, it would be likely possible to increase the recovery ratio of the 1st pass to just before the Mg $(OH)_2$ precipitation limit, which, at pH 9.25, is higher than 50% [4]. Increasing the recovery value will reduce the specific consumption of chemicals added to the feed. Finally, while post-treatment requires the use of food-grade chemicals, chemicals used upstream of the RO step can be of lower purity, provided that impurities do not comprise of scaling agents or are environmentally hazardous. If a source of cheap industrial grade acid is available, it can be considered for the feed acidification step, thereby saving much of the expenditure on the chemicals associated with the suggested approach.

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