

## Pilot scale evaluation of a novel post-treatment process for desalinated water

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### ABSTRACT

New water quality standards, specific for desalinated water, have been recently approved in Israel. Consequently, a novel post-treatment process was developed, aimed at meeting the new standards in a cost effective way, as well as supplying  $Mg^{2+}$  concentration of at least 10 mg Mg/l, required for both health and agricultural reasons. A pilot plant, capable of post-treating 1600 m<sup>3</sup>/d of desalinated water was operated for ~6 months to optimize economic and engineering aspects of the process. The article presents results from three operational scenarios differing from each other by the percentage of water that undergoes treatment, out of the total flow rate. The results indicate that the required set of water quality parameters can be produced in a stable manner in all the three scenarios tested. All scenarios were found similar with respect to both operational costs and resultant water quality. However, in terms of capital costs, treating a smaller fraction of the total flow rate was found advantageous. The article also introduces a modification to the original process, which was tested at the laboratory scale. In the modified process calcite is dissolved using CO<sub>2(g)</sub> (instead of H<sub>2</sub>SO<sub>4</sub>, as in the original process). The modified process can be implemented as an add-on to existing CO<sub>2</sub>-based calcite dissolution post-treatment systems or in cases where a restriction is posed on the total hardness value in the product water.

**Keywords:** Post treatment; Desalinated water;  $Mg^{2+}$  addition; Ion exchange; Calcite dissolution

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### 1. Introduction

As the volume of desalinated water produced worldwide increases continuously [1], the development of new water quality standards is prompted in many places, and the need for chemical stabilization of the water and re-mineralization becomes apparent [2]. Specific standards for desalinated water have already been approved in Israel [3,4]. A novel post-treatment process has been developed to supply water with alkalinity, Ca<sup>2+</sup>, pH and calcium carbonate precipitation potential (CCPP) values as required by the new criteria, along with the addition of  $Mg^{2+}$  ions to

the water. A minimal  $Mg^{2+}$  concentration, although not included in the current Israeli quality criteria, is very much welcome in desalinated water for both agricultural [5,6] and human health reasons. The presence of  $Mg^{2+}$  in drinking water has been linked with prevention of (mostly) cardio-vascular diseases [7–10]. The health benefits of  $Mg^{2+}$  in drinking water are apparently under debate. For example, Morris et al. [11] suggest that high magnesium intake does not appreciably protect against cardiovascular disease and coronary heart disease. On the other hand, Catling et al. [8] and Monarca et al [9], among many others, concluded that there is a significant evidence of an inverse association between magnesium levels in drinking water and cardiovascular mortality.

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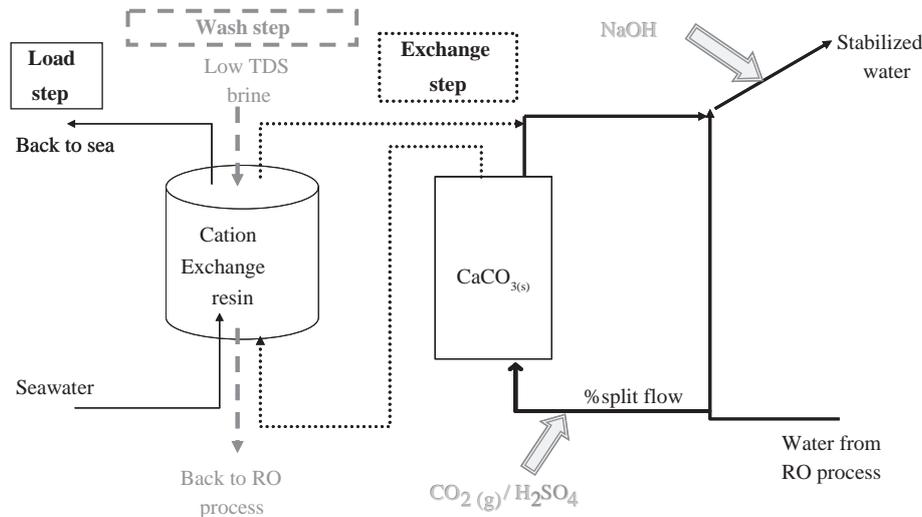


Fig. 1. Schematic of the novel post treatment process.

However, despite this uncertainty, the World Health Organization (WHO) has concluded that “There is a growing consensus among epidemiologists that the epidemiological evidence, along with clinical and nutritional evidence, is already strong enough to suggest that new guidance should be issued” [10]. The WHO thus recommends in its recent publications maintaining a minimum  $Mg^{2+}$  concentration in all drinking water [10,12]. The suggested post treatment process aims at supplying both  $Ca^{2+}$  and  $Mg^{2+}$  at concentrations that meet the most updated WHO requirements.

The process, depicted schematically in Fig. 1, is based on the following treatment sequence, which is applied on a fraction of the total flow rate (denoted %split flow in this article): (a) dissolution of quarry calcite ( $CaCO_{3(s)}$ ) using  $H_2SO_4$  and (b) replacement of a fraction of the  $Ca^{2+}$  ions generated in the dissolution process by  $Mg^{2+}$  ions, using a specific cation exchange resin. Once exhausted the resin is re-loaded with  $Mg^{2+}$  by a seawater stream, originally supplied to the reverse osmosis (RO) plant. For detailed description of the process see [13] and [14]. Since previously conducted laboratory examination had shown promising results [13], a pilot plant was built to optimize economic and engineering aspects of the process. The pilot plant, located in Maagan Michael, Israel, was designed to treat up to  $1600\text{ m}^3\text{ d}^{-1}$ .

As shown previously [13], the required  $Ca^{2+}$  concentration in the water flowing from the calcite reactor to the ion exchange (IX) columns is determined according to the required product-water quality and the percentage of water that undergoes treatment, i.e. the %split flow (Fig. 1). Since the dissolution process

involves the release of both  $Ca^{2+}$  and  $SO_4^{2-}$  to the water, the value of %split flow is limited by the propensity of unwanted gypsum ( $CaSO_3$ ) precipitation inside the calcite dissolution reactor. Considering a  $Ca^{2+}$  requirement of 120 mg/l as  $CaCO_3$  and  $Mg^{2+}$  of 50 mg/l as  $CaCO_3$  concentrations (i.e. 48 mg Ca/l and 12.1 mg Mg/l or 2.4 meq/l Ca and 1 meq/l Mg) it was calculated that a %split flow lower than 9% cannot be practiced, because it would lead to  $CaSO_4$  precipitation. This calculation took into account both the ionic strength of the water and possible formation of relevant ion pairs. Using a safety factor, the lowest fraction of treated water that was tested in the plant was 11.2%. Examination of the effect of changing the %split flow was carried out in the pilot plant by treating flow rates amounting to 11.2%, 15.7% and 22.6% of the overall flow rate. It was found that in order to attain the required product water quality the  $Ca^{2+}$  concentration at the outlet of the calcite dissolution reactor was, in the three scenarios, 30.2 (since  $(2.4\text{ meqCa/l} + 1\text{ meqMg/l})/0.112 = 30.2$ ), 21.6 and 14.7 meq/l, respectively.

This article also introduces an important modification to the process, which was studied at the laboratory scale. The main operational difference between the modified process and the original version is the acidic substance that was used to dissolve the calcite. While in the original process a strong acid ( $H_2SO_4$ ) is used to enable calcite dissolution, in the modified process  $CO_{2(g)}$  is used, as depicted in Fig. 1. The use of  $CO_{2(g)}$  as the acidic substance results in a much lower ratio between total hardness (TH) and alkalinity values in the water, allowing for a lower TH value in the product water for a given alkalinity concentration requirement. The modified process can be implemented in already-

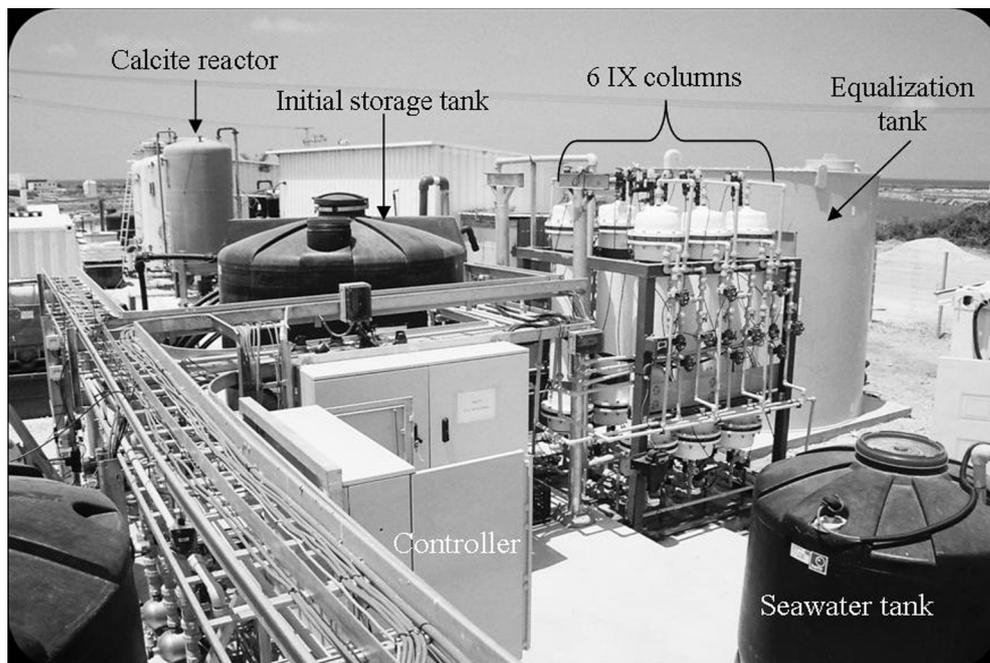


Fig. 2. The Maagan Michael 1600 m<sup>3</sup>/d desalination post-treatment pilot plant.

operative desalination plants whose post-treatment process is based on dissolving calcite using CO<sub>2</sub> or in cases where a strict restriction is posed on the TH value of the product water.

The practice of dissolving calcite using CO<sub>2</sub>, a weak acid, differs from using a strong acid (H<sub>2</sub>SO<sub>4</sub>) by two main aspects: (1) The practical ability to dissolve calcite is lower [15,16], therefore an increased fraction of the water should undergo treatment (i.e. %split flow of at least 50%), and thus larger reactors (both calcite dissolution and IX) are required; and (2) The concentration ratio between dissolved calcium and alkalinity ([Ca<sup>2+</sup>]: Alkalinity) in the effluent of the calcite reactor is 1:1 (rather than > 2:1 in the H<sub>2</sub>SO<sub>4</sub>-based dissolution) [4]. Thus, for a given alkalinity requirement the Ca<sup>2+</sup> concentration in the water leaving the calcite dissolution reactor is much lower and the driving force for the Ca–Mg exchange reaction is reduced.

Since in the IX stage Ca<sup>2+</sup> ions are exclusively exchanged for Mg<sup>2+</sup> ions, the [Ca<sup>2+</sup>] to alkalinity ratio in the effluent of the calcite reactor is identical to the TH to alkalinity ratio in the water leaving the IX reactors. Exclusive use of CO<sub>2(g)</sub> in the dissolution stage will result in a TH : alkalinity ratio of 1:1 (or slightly lower when NaOH is dosed to the water after the IX stage), while the sole use of H<sub>2</sub>SO<sub>4</sub> will result in a ratio of 2:1 or slightly higher. To conclude, the ability to use either CO<sub>2(g)</sub> or H<sub>2</sub>SO<sub>4</sub> in the dissolution stage extends the product water quality especially with respect to the TH to alkalinity ratio.

## 2. Materials and methods

### 2.1. Pilot plant performance evaluation

A photograph of the Maagan Michael pilot plant is shown in Fig. 2. The pilot plant consists of a main storage tank which receives raw desalinated water from a nearby desalination plant. Water leaving the tank is divided into two streams: the main stream bypasses the treatment train and is mixed with the treated stream at the end of the process, as depicted in Fig. 1. The smaller stream (less than 25% of the flow rate) is acidified using H<sub>2</sub>SO<sub>4</sub> 98% and then fed into a calcite dissolution reactor. From the calcite reactor the water is introduced into five out of six installed IX columns, filled with Amberlite IRC747 (purchased from Rohm & Haas Inc). The IRC747 resin is characterized by a very high affinity towards divalent cations. The considerations that led to the choice of this specific resin are detailed in [13]. There is a constant time gap between the inception times of the Exchange step (and thus also of the Load and Wash steps) of each column, i.e. at every given moment in time, five columns are in different phases of the Exchange step and one is in the Load or Wash step. An effluent equalization tank is located downstream the IX columns. The equalization tank is required because the Ca<sup>2+</sup> and Mg<sup>2+</sup> concentrations in the effluent of the Exchange step change with time; its purpose is to minimize fluctuations in product water quality. The water collected from the outlet of the five IX columns is mixed with the bypass stream (untreated RO water) and dosed with NaOH before it is fed into the equalization tank.

The plant consists also of an ultra-filtration (UF) system used to treat seawater before it is pumped into the IX columns in the Load step (the step in which  $Mg^{2+}$  is absorbed onto the resin, see detailed description in [13]).

Samples were routinely taken from the outlet of the calcite reactor and the six IX columns and also from the outlet of the effluent equalization tank. The concentrations measured in the samples from the outlet of the IX column represent momentary concentrations, while the samples from the equalization tank represent cumulative and averaged concentrations. The term “cumulative and averaged” deserves explanation: “cumulative” means that water leaving each single IX column operated in the Exchange step accumulates in the equalization tank; “averaged” means that the outlets of the five columns operating in the Exchange step at the same time are combined and their cumulative concentrations are blended in the equalization tank. From a practical standpoint, the momentary concentrations were used to calculate the theoretical cumulative concentrations.

## 2.2. Continuous ion exchange experiments for lab scale simulation of the modified process

A solution with specific  $Ca^{2+}$  concentration was prepared to simulate the Exchange step by dissolving a weighed amount of analytical grade  $CaCl_2 \cdot 2H_2O$  in distilled water. Filtered seawater was used to simulate the Load step.

Adsorption and desorption experiments of  $Ca^{2+}$  and  $Mg^{2+}$ , used to simulate the Load and Exchange steps, were carried out using a 25.2 mm internal diameter PVC column, filled with Amberlite IRC747. Resin bed height was measured (at rest) after a short period of operation, to ensure steady packing of the bed. The resin bed volume (BV) was 50 ml. A peristaltic pump was used to attain a constant flow rate into the column (between 30 and 34 BV per h).

Continuous laboratory experiments were conducted to determine the exact number of BV that should be passed through the IX column during the Exchange step and the antecedent Load step in order to attain the required water quality. In this article we present results from one investigated scenario, corresponding to %split flow of 70%.

### Theoretical calculations

The software STASOFT4.0 [17] was used to calculate CCPP values and also to simulate the overall process, i.e. to determine chemical dosages and alkalinity,

pH and CCPP following blend with untreated desalinated water.

### Analyses

$Mg^{2+}$ ,  $Ca^{2+}$ ,  $K^+$  and  $Na^+$  concentrations were analyzed by inductively coupled plasma (ICP) emission spectrometry, Optima 3000 DV, Perkin Elmer. Alkalinity was determined by the Gran titration method [18].

## 3. Results and discussion

### 3.1. Evaluation of pilot plant performance – ion exchange step

Fig. 3 shows the cumulative  $Ca^{2+}$  and  $Mg^{2+}$  concentrations attained in the product water of a single IX column at each of the three investigated %split flows. As shown in Fig. 3, the cumulative  $Mg^{2+}$  concentration decreases at the evolution of the Exchange step. Therefore, for attaining a given final  $Mg^{2+}$  concentration for a decreased %split, the Exchange step should be shorter, since the cumulative  $Mg^{2+}$  concentration of the treated water should be higher. This can be explained as follows: the  $Ca^{2+}$ – $Mg^{2+}$  exchange should be stopped when the  $Mg^{2+}$  (and  $Ca^{2+}$ ) concentrations are such that after recombining the treated and untreated water flows (see Fig. 1) the concentrations would be as planned. In order to achieve a similar  $Mg^{2+}$  and  $Ca^{2+}$  concentrations despite of the larger dilution effect, caused by the increased percentage of untreated water, the Exchange step is stopped after the passage of less BV, i.e. when the  $Mg^{2+}$  concentration is higher. For example, the cumulative magnesium concentration at the end of the Exchange of the 23% and 11% split flow case studies should be  $(1 \text{ meq/l}) / (0.23 \text{ treated/total flow}) = 4.34 \text{ meq/l}$  and  $1 / 0.11 = 9.09 \text{ meq/l}$ , respectively, as demonstrated in Fig. 3.

As shown in Fig. 3, stopping the Exchange steps after 175, 105 and 75 BVs, when 23%, 16% and 11% of the water is treated, respectively, resulted in the attainment of the required  $Mg^{2+}$  concentration (12.1 mg  $Mg/l$ ). Conversely, no difference was observed in the required Load step length in the investigated scenarios. This makes sense as the overall amount of  $Mg^{2+}$  released to the water in the Exchange step of each of the three scenarios was similar and thus the loaded  $Mg^{2+}$  mass should also be identical.

### 3.2. Evaluation of pilot plant performance – calcite dissolution step

According to results obtained in the plant, it seems that changing the %split flow also slightly affects the

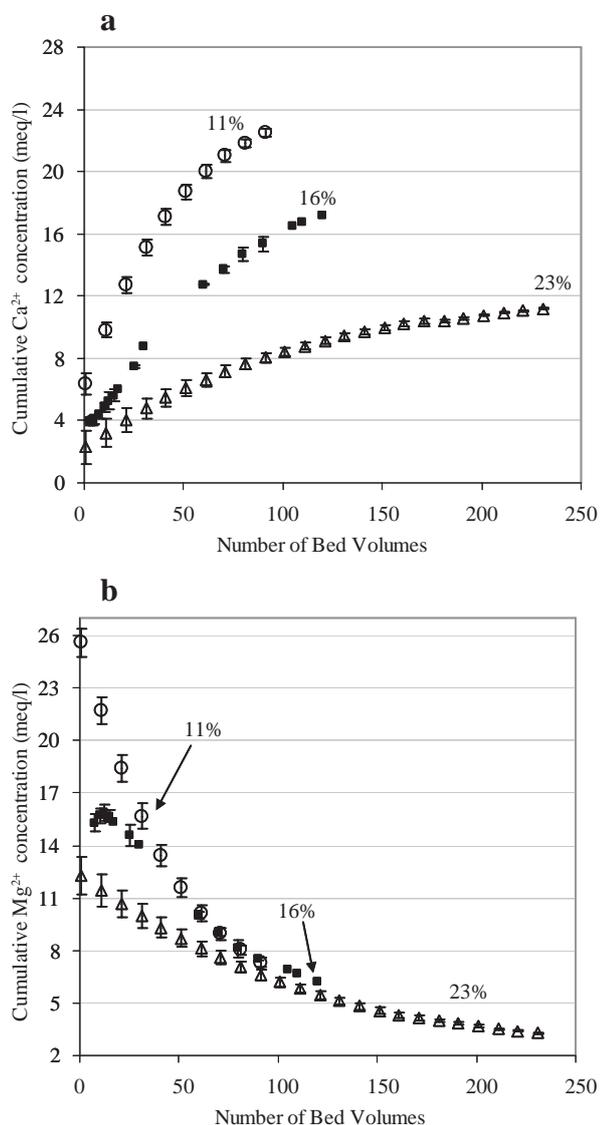


Fig. 3. Average ( $n = 5$ )  $\text{Ca}^{2+}$  (a) and  $\text{Mg}^{2+}$  (b) cumulative concentrations attained in the product water in the three case studies tested during pilot plant operation. %split flows of 23%, 16% and 11% are represented by triangles, squares and circles, respectively; correspondingly, the  $\text{Ca}^{2+}$  concentrations in the inlet solutions were 14.6, 21.6 and 30.2 meq/l.

water quality parameters related to the calcite dissolution step and thus to the required chemical dosages involved. Table 1 summarizes the chemical dosages in the three scenarios. Table 1 also lists the product-water quality in each scenario. The chemical dosages are reported in units of mg of chemical per liter of product water. Decreasing the %split flow must be compensated by an increase in the  $\text{Ca}^{2+}$  concentration in the water leaving the calcite reactor because of the dilution effect caused by the increased percentage of untreated water. This is achieved by an increased

$\text{H}_2\text{SO}_4$  dosage to the reactor influent followed by an increased dissolution of calcite. The increased concentration of calcite dissolved in the reactor is proportional to the split flow. In other words, the mass of dissolved calcite per unit of product water remains constant, regardless of the split flow (see Table 1). However, the increased dosage of  $\text{H}_2\text{SO}_4$  is greater than the proportional increase of %split flow, because the value of CCPP is not linearly influenced by the dosage of  $\text{H}_2\text{SO}_4$ . As a result, the dosage of NaOH is also greater than the proportional increase of the %split flow. Consequently, in the 11% split flow scenario the highest NaOH dosage was required in order to attain the required CCPP value of 3 mg/l as  $\text{CaCO}_3$  (see Table 1).

### 3.3. Cost estimation

The cost estimation of the suggested post treatment process comprised the estimation of both capital and operational costs. The following section specifies the assumptions made in the course of the cost analysis, the range of chemical prices on which the analysis was based, and the resultant range of costs for each case study.

Based on the results detailed above, it can be concluded that altering the %split flow has two main monetary impacts on the process: the first impact is related to the size of the reactors and thus to the capital costs of the process, while the second impact relates to the chemical dosages, and thus to the operational costs. Note that the operational costs are primarily composed of the cost of chemicals. Elaboration on these impacts is brought herein.

The first impact is that the required length of the Exchange step for attaining a given final  $\text{Mg}^{2+}$  concentration is shorter when the %split is decreased, i.e., when less water is passed through the calcite dissolution and ion exchange reactors. As mentioned before, the length of the Load step was found to remain constant regardless of the %split flow applied. Clearly, the ratio between the length of the Exchange step and the time required for regeneration (the Load step) decreases as the percentage of treated water decreases. This ratio is important since it determines the fraction of "active" resin (i.e. resin that operates in the Exchange step rather than in the Load or Wash stages). Hence, a higher ratio of resin operating in the Exchange step to resin operating in the Load or Wash steps is advantageous since it results in a lower overall resin volume required in the process. From this perspective, increasing the %split flow is advantageous. On the other hand, a decreased %split flow corresponds to a decreased treated flow rate, and thus a smaller amount

Table 1

Comparison of operational conditions, chemical dosages, resulting water qualities and estimated total costs of the three case studies tested in the pilot plant and in the modified process (bench scale)

Case study	Split flow	Length of Exchange Step	Chemical dosages (pilot plant results)				Product water quality					total cost	
			$\frac{mg}{L \text{ product water}}$				pH	Alk	CCPP	Ca <sup>2+</sup>	Mg <sup>2+</sup>	min	max
			CO <sub>2</sub>	H <sub>2</sub> SO <sub>4</sub>	CaCO <sub>3</sub>	NaOH							
1	23	175	–	115	168	27.7	8.12	82.6	3.0	120	12	3.7	5.7
2	16	105	–	121	167	30.6	8.11	84.2	3.0	120	12	3.7	5.7
3	11	74	–	128	167	38.6	8.11	84.6	3.0	120	12	3.9	6.1
4	70	*409	**93	–	**144	**33.2	7.75	177	3.0	85	12		

\* tested in the laboratory.

\*\* theoretical calculations.

of resin is needed in the Exchange step; similarly, the required calcite reactors are also smaller. Evaluation of these two aspects (i.e. the unwanted reduction in the ratio between the durations of the Exchange step and the Load step and the wanted reduction of required active resin as a result of a decreased %split) leads to the conclusion that an increase in the fraction of the treated water above 12% is disadvantageous as it results in larger IX (and calcite) reactors and thus increased capital costs. On the other hand, decreasing the %split flow below 12% is not advantageous, since it results in larger IX reactors because of the significant reduction in the percentage of “active” resin, i.e. resin operating in the Exchange step. It can be thus concluded that a minimal resin volume is required when 12% of the water are treated. To conclude, from the capital costs point of view the optimal %split flow is 12%.

The second impact of altering the %split flow relates to the required dosages of chemicals, which increase when the %split flow is increased, as explained before. Note that NaOH is the most expensive compound used in the process. Thus, when considering the cost of the chemicals, because of the differences in NaOH (and H<sub>2</sub>SO<sub>4</sub>) dosages between the tested case studies, treating a smaller fraction of the water was less advantageous. On the other hand, it is noted that a smaller treated flow rate results in reduced energy consumption and reduced annual resin amortization. However, as mentioned before, these two factors have a lesser influence on the overall operational cost.

Capital costs were assessed by an external engineering company (BARAN LTD). Their assessment, carried out for a scenario of 25% split flow, showed that the capital cost for erecting the suggested post treatment process for a total RO flow rate of 100Mm<sup>3</sup>/y would

range between \$10M and \$15M. In this article, the capital costs of the examined case studies, i.e. of plants applying 23%, 16% and 11% split flows were considered to be 100%, 90% and 80% of the capital costs calculated for the 25% split flow scenario, respectively. Assuming service life time of 20 years and risk free interest rate of 6%, the capital costs of the plant per m<sup>3</sup> of product water are between \$cent0.7 and \$cent0.9 per m<sup>3</sup> product water, assuming capital costs of \$10M and between \$cent1.0 and \$cent1.3 per m<sup>3</sup> product water assuming capital costs of \$15M.

Operational costs comprise (mainly) of the cost of chemicals, energy and resin replacement. The chemical costs, which constitute the majority of the operational costs, are heavily place and time dependent. However, ranges of operational costs can be calculated based on reasonable ranges of chemical costs (that is, H<sub>2</sub>SO<sub>4</sub>: between 100 and 200; CaCO<sub>3</sub>: between 25 and 35; NaOH: between 350 and 450, all costs in units of \$ per ton of pure chemical). The cost of resin replacement was calculated assuming that the resin cost was \$8/l and that the annual resin replacement was 7%. Energy consumption for pumping the treated water into the reactors was evaluated assuming an electricity cost of 0.1\$/kWh, the efficiency of the pumps was 0.75 and the total head the water were given by the pumps was 12 m. Using these numbers, the operational costs were found to be between \$cent2.8 per m<sup>3</sup> (lowest chemical costs and 23% split flow) to \$cent5.0 per m<sup>3</sup> (highest chemical costs and 11% split flow). It should be noted that the cost of electricity constitutes a negligible fraction of the operational costs. Hence, the electricity cost fluctuation has a negligible effect on the overall operational costs.

Table 1 shows the ranges of the total costs for each case study. The lower values were calculated using the lowest chemical costs and the lowest capital costs,

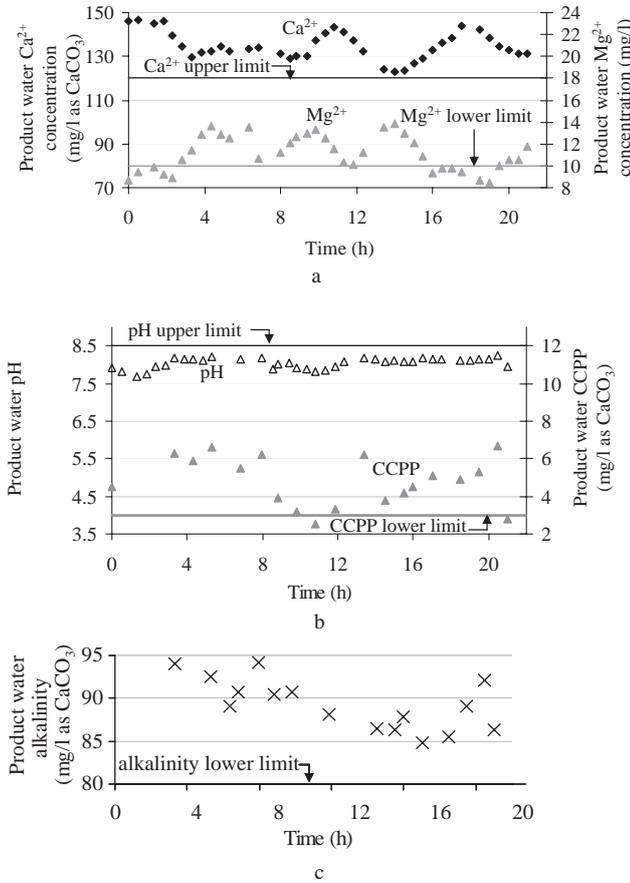


Fig. 4. Product water quality: calcium and magnesium concentrations, (a); pH value and CCPP concentration, (b); and alkalinity concentration, (c), as measured in the equalization tank during a 21 hours full operation. Solid lines represent the threshold values of the five parameters.

while the higher values were calculated based on the highest costs. From Table 1 it can be seen that the total post treatment cost of the three case studies fluctuates within a narrow range. Hence, the decision on the most cost effective %split flow should be taken based on prices relevant to the time and location of the design and future expectations.

In order to consider the economic feasibility of the process, it should be compared with the alternatives. Rygaard et al [2] calculated that supplying untreated desalinated water has a negative total impact of approximately 0.44 EURO per m<sup>3</sup>. In addition, these authors concluded that with remineralization, it is possible to raise the overall impact to a positive value of approximately 0.14 EURO per m<sup>3</sup>. Taking these figures into account, it is clear that the suggested post treatment is economic from a broad point of view. Comparing the IX based post treatment with the option of dissolving dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>) for supplying

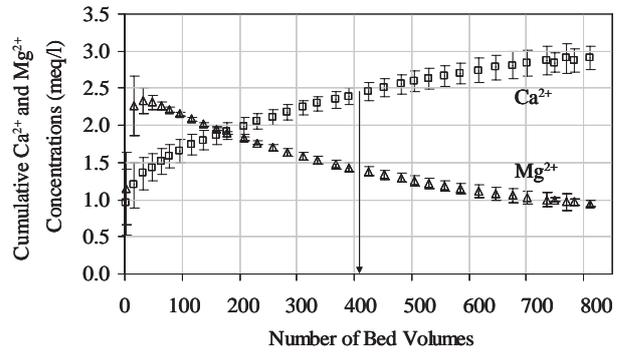


Fig. 5. Simulation of the Exchange step in the modified process using 70% split flow ( $n = 5$ ). Ca<sup>2+</sup> (squares) and Mg<sup>2+</sup> (triangles) are cumulative concentrations at the outlet of a single IX column. The inlet Ca<sup>2+</sup> concentration was 3.86 meq/l.

similar amounts of Ca<sup>2+</sup> and Mg<sup>2+</sup> to the water based on [20] it is concluded that: (a) from the water quality point of view: the alkalinity concentration is more than 10 mg/L lower. Since the flexibility in water quality attained in this process is very low, it is impossible to raise the alkalinity and comply with the other criteria; And (b) from the cost effectiveness point of view, the operational costs of post treating 1m<sup>3</sup> by dissolution of dolomite and calcite in series was approximated at \$0.042, which is similar to the suggested post treatment (operational costs between \$0.003 and \$0.0044 for the higher split flows).

### 3.4. Evaluation of pilot plant performance – equalization tank

As shown in Fig. 1, a complete operation of the post treatment process includes the dosage of NaOH and the collection of the water leaving the IX columns (operating in the Exchange step) into the equalization tank, where it is mixed with the untreated flow rate (RO water that bypasses the treatment train). Examination of the performance of the pilot plant under full and continuous operational conditions was carried out twice, as part of the 23% split flow scenario operation: the system was first operated for 21 h and then for 80 h. Fig. 4 shows the pH values and Ca<sup>2+</sup>, Mg<sup>2+</sup>, alkalinity and CCPP concentrations measured in the first continuous operation period. In addition, Fig. 4 indicates the threshold value for each of the monitored parameters. NaOH dosage was aimed at increasing the CCPP value by pH elevation. In order to comply with the minimum CCPP threshold (i.e. 3 mg/l as CaCO<sub>3</sub>) the pH was set to be above 8.2. On the other hand, the regulations also include an upper limit for the pH value (i.e. 8.5). Because of the relatively low buffer capacity of the

water, the pH value was highly affected by the NaOH dosage which made the task of maintaining the pH value within this narrow range difficult with the control measures used in the pilot. Consequently it was also difficult to achieve the required CCPP value at all times. Nevertheless, pH and CCPP values were on average as required, i.e.:  $8.01 \pm 0.14$  and  $4.8 \pm 1.3$  mg/l as  $\text{CaCO}_3$ , respectively. The average alkalinity concentration was  $91.0 \pm 4.2$  mg/l as  $\text{CaCO}_3$ . The calcium and magnesium average concentrations were:  $135 \pm 6$  mg/l as  $\text{CaCO}_3$  and  $11.1 \pm 1.6$  mg/l, respectively. These calcium and magnesium concentrations imply that the Exchange step that was applied was slightly too long, i.e. decreasing the amount of BV passed through the IX would increase the  $\text{Mg}^{2+}$  concentration and decrease the  $\text{Ca}^{2+}$  concentration correspondingly.

### 3.5. Assessment of the performance of the modified process

The Exchange step of the modified process was investigated at the laboratory scale using a continuous IX experiment. The target product water concentrations were:  $\text{Ca}^{2+} = 85$  mg/l as  $\text{CaCO}_3 = 1.7$  meq/l and  $\text{Mg}^{2+} = 12.1$  mg/l = 1 meq/l. The inlet  $\text{Ca}^{2+}$  concentration in this scenario was 3.86 meq/l which corresponds to %split flow of  $(1.7 + 1)/3.86 = 70\%$ . Fig. 5 shows the average ( $n = 5$  repetitions) of the cumulative  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations at the outlet of the IX column. Based on the results shown in Fig. 5 it can be concluded that the Exchange step can be stopped after 409 BV, since at this point the cumulative  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations are 2.44 meq/l and 1.42 meq/l, respectively, as required ( $2.44 \cdot 0.7 = 1.7$  meq Ca/l = 85 mg/l as  $\text{CaCO}_3$  and  $1.42 \cdot 0.7 = 0.99$  meq/l = 12.1 mg Mg/l).

Table 1 (bottom line) shows the chemical dosages and resultant water quality for this scenario. Note that the alkalinity concentration in the product water is much higher when  $\text{CO}_{2(g)}$  is used (i.e. case study #4), as compared with the product water when  $\text{H}_2\text{SO}_4$  is used (i.e. case studies #1–3). As a result a higher NaOH dosage is required to attain a given CCPP value (+3 mg/l as  $\text{CaCO}_3$  in this case) when  $\text{CO}_{2(g)}$  is used instead of  $\text{H}_2\text{SO}_4$ . In addition, the resultant pH is lower. Finally, note that the  $\text{Ca}^{2+}$  concentration (and thus the TH value) is also lower in case  $\text{CO}_{2(g)}$  is used.

## 4. Conclusions

The article presents results obtained from pilot-scale operation of a new post treatment process, under three operational scenarios. Additionally, the article introduces a modification to the process, in which

$\text{CO}_{2(g)}$  is used as the acidic substance for  $\text{CaCO}_3$  dissolution, instead of  $\text{H}_2\text{SO}_4$ . The main conclusions are:

- The original process and the modified version are capable of producing water that complies with the new Israeli water quality criteria for desalinated water while also providing a concentration of  $>10$  mg/l of magnesium ions in the water.
- Full and continuous operation of the pilot showed small fluctuations in the water quality produced. As expected, the pH value and CCPP concentration showed the most significant fluctuations.
- Product water qualities attained in the three scenarios tested in the pilot plant were almost identical.
- Differences in total costs between the three case studies were found minor and resulted mainly from slightly different NaOH and  $\text{H}_2\text{SO}_4$  demands. Thus, it can be safely concluded that the decision on the optimum %split flow is location and time dependent.
- The water quality produced by the modified process was favorable over the quality produced by the original process: While the  $\text{Mg}^{2+}$  concentration was similar in the various case studies, the pH value and the  $\text{Ca}^{2+}$  concentration in the modified process were lower, and the alkalinity concentration higher. Hence, both the chemical and biological stability of the water could be considered better [4]. Therefore, in terms of water quality, this option seems advantageous over the  $\text{H}_2\text{SO}_4$  alternative. Yet, in terms of capital costs, the relatively slow kinetics associated with  $\text{CO}_2$ -based calcite dissolution and the calcite dissolution and the consequently required high %split flow will result in much larger calcite dissolution and IX reactors.
- The presented modification extends the flexibility of the process with regard to the TH to alkalinity concentration ratio in the product water.
- Application of the proposed process will result in water quality that meets the most recent WHO mineral composition requirements and is also more suitable for agricultural irrigation purposes.

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## References

- [1] S. Lattemann and T. Heopner, Environmental impact and impact assessment of seawater desalination, *Desalination*, 220 (2008) 1-15.

- [2] M. Rygaard, E. Arvin and P.J. Binning, The valuation of water quality: effects of mixing different drinking water qualities. *Water Res.*, 43 (2009) 1207-1218.
- [3] A. Adin, R. Reifen, O. Lahav and Brenner, A. Israeli Standards for Calcium in Desalinated Water: Considerations and Recommendations, Proceedings of the International Symposium on Health Aspects of Calcium and Magnesium in Drinking Water, April 24–26, 2006 Baltimore, Maryland, USA.
- [4] O. Lahav and L. Birnhack, Quality criteria for desalinated water following post treatment. *Desalination*, 207 (2007) 286-303.
- [5] L.S. Tisdale, W.L. Nelson, J.D. Beaton and J.L. Havlin, *Soil Fertility and Fertilizers*. 5th ed., Macmillian Publishing Company, New York, 1993.
- [6] U. Yermiyahu A. Tal, A. Ben-Gal, A. Bar-Tal, J. Tarchitzky and O. Lahav, Rethinking desalinated water quality and agriculture, *Science*, 318 (2007) 920-921.
- [7] F. Kozisek, Health significance of drinking water calcium and magnesium. (2003), <http://www.szu.cz/chzp/voda/pdf/hardness.pdf>
- [8] L.A. Catling, I. Abubaker, I.R. Lake, L. Swift and P.R. Hunter, A systematic review of analytical observational studies investigating the association between cardiovascular disease and drinking water hardness. *J. Water Health*, 6 (2008) 433-442.
- [9] S. Monarca, F. Donato, I. Zerbini, R.L. Calderon and G.F. Craun, Review of epidemiological studies on drinking water hardness and cardiovascular diseases. *Eur. J. Cardiovasc. Prev. Rehabil.*, 13 (2006) 495-506.
- [10] World Health Organization, Calcium and magnesium in drinking water: Public health significance, (2009) 180 pp.
- [11] R.W. Morris, M. Walker, L.T. Lennon, A.G. Shaper and P.H. Whincup, Hard drinking water does not protect against cardiovascular disease: new evidence from the British Regional Heart Study, *Eur. J. Cardiovasc. Prev. Rehabil.*, 15(2008) 158-189.
- [12] World Health Organization, Guidelines for Drinking –Water Quality, 2nd addendum to 3rd Ed., vol. 1, 2008, 5 pp. [http://www.who.int/water\\_sanitation\\_health/dwq/secondaddendum20081119.pdf](http://www.who.int/water_sanitation_health/dwq/secondaddendum20081119.pdf)
- [13] L. Birnhack and O. Lahav, A new post treatment process for attaining  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$  and alkalinity criteria in desalinated water, *Water Res.*, 41 (2007) 3989-3997.
- [14] R. Penn, L. Birnhack, A. Adin and O. Lahav, New desalinated drinking water regulations are met by an innovative post-treatment process for improved public health *Water Science and Technology – Water Supply*, 9 (2008) 225-231.
- [15] P.F. de Souza, G.J. du Plessis and G.S. Mackintosh, An evaluation of the suitability of the limestone based sidestream stabilization process for stabilization of waters of the Lesotho highlands scheme, *Water SA – Special Edition, WISA Proceedings*, (2002) 10-15.
- [16] R. Wollast, Rate and mechanism of dissolution of carbonates in the system  $\text{CaCO}_3\text{--MgCO}_3$ . In: W. Stumm (Ed.), *Aquatic Chemical Kinetics*, Wiley, New York, 1990, 431-445.
- [17] R.E. Loewenthal, G.A. Ekama and G.v.R. Marais, STASOFT: a user-friendly interactive computer program for softening and stabilization of municipal waters, *Water SA*, 14 (1988) 159-162.
- [18] G. Gran, Determination of the equivalence point in potentiometric titrations. Part II. *Analyst*, 77 (1952) 661-71.
- [19] L. Birnhack, N. Fridman and O. Lahav, Potential applications of quarry dolomite for post treatment of desalinated water, *Desalination and Water Treatment*, 1 (2009) 58-67.