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Development of an additional step to current CO_2-based $CaCO_{3(s)}$ dissolution post-treatment processes for cost-effective Mg^{2+} supply to desalinated water

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ABSTRACT

New water quality standards, specific for desalinated water, have been recently approved in Israel. To satisfy the new quality criteria a novel post-treatment process has been developed, aimed at cost-effectively meeting the new standards as well as supplying Mg^{2+} ions, required for both health and agricultural reasons. The paper introduces a modification to the original process. In the modified process calcite is dissolved using CO_2 (instead of H_2SO_4, as in the original process), and/or a combination of CO_2 and H_2SO_4. An additional presented feature is the option to elevate product water pH by CO_2 stripping rather than NaOH dosage. The modified process can be implemented as an add-on to existing CO_2-based calcite dissolution post-treatment systems or in cases where a restriction is posed on the total hardness value in the product water, since the modification extends the flexibility in the product water quality, with respect to the ratio attained between total hardness and alkalinity concentrations.

Cost estimation reveals that upgrading a conventional post-treatment process based on CO_2 dissolution of $CaCO_3$ to the modified process for attaining $[Mg^{2+}]$ of 10 mg/l, can result in an increase in the operational costs of between 0.15 and 0.69 \$cents per m^3 of product water, depending on the cost of chemicals.

1. Introduction

As the volume of desalinated water introduced into distribution systems increases continuously, the development of new water quality standards is becoming a priority. Specific standards for desalinated water have already been approved in Israel [1,2], including five parameters: (1) CCPP > 3 mg/l as $CaCO_3$ and < 10 mg/l as $CaCO_3$; (2) Alk > 80 mg/l as $CaCO_3$; (3) $[Ca^{2+}]$ > 80 mg/l as $CaCO_3$ (32 mg/l as Ca^{2+}) and <120 mg/l as $CaCO_3$; (4) pH < 8.5; (5) turbidity < 0.5 NTU. The addition of a sixth quality parameter, i.e. a minimum Mg^{2+} concentration (between 10 and 20 mgMg/l—the precise value has not yet been decided) is being currently considered by the Israeli Ministry of Health.

A novel, cost-effective SW desalination post-treatment process is being developed by the writers under the assumption that a certain Mg^{2+} threshold will be required in desalinated water in the near future. The process goal is to supply water that complies with these new criteria, along with the addition of a desired Mg^{2+} concentration. As an example for a required Mg^{2+} threshold in drinking water the WHO has recently recommended a minimum concentration of 10 mgMg/l in all drinking waters, with special emphasis on desalinated water [3]. This recommendation is based on recent publications which stress the role of Mg^{2+} in drinking water on the human body and the possible implications of Mg^{2+} deficiency on the public health [4–8]. Mg^{2+} requirement in desalinated water for irrigation purposes has been set at 12–18 mgMg/l [9]. The new process, shown schematically in Fig. 1, is based on dissolving quarry $CaCO_{3(s)}$ (calcite or "limestone") to supply Alk and Ca^{2+} ions and subsequently replacing a part of the Ca^{2+} concentration with Mg^{2+} ions that originate from SW. Separating Mg^{2+} from SW is carried out using a specific IX resin. A detailed description of the process and results from pilot-scale operation are given elsewhere [10–12]. This paper presents a modification to the process. The main operational difference between the modified process and the original version is the type of acid that is used to allow for significant calcite dissolution. While in the original process a strong acid (H_2SO_4) was applied (see Eqs. (1) and (2)), in the modified version, $CO_{2(g)}$ (see Eq. (3)), or a combination of $CO_{2(g)}$ and H_2SO_4 is used, as depicted in Fig. 1. In both processes a fraction of the Ca^{2+} ions released to the water in the calcite dissolution step is exchanged for Mg^{2+} ions, using a specific cation exchange resin, as shown in Fig. 1. The IX step is divided into three sequential steps: an "exchange" step, in which Mg^{2+} loaded resin is brought to contact with water that contains a high Ca^{+2} concentration and virtually no Mg^{2+}. As a result, Mg^{+2} ions are released to the water; a "load" step, in which Mg^{2+} ions are preferentially separated from SW onto the resin; and a "drain" step, in which SW which remains in the resin's pores at the end of the load step, is drained from the bed, using pressurized air. This way, the volume of residual SW that remains in the bed and is consequently mixed with the desalinated water (introduced to the bed

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Nomenclature

Acd	acidity (CO_3^{2-}) = $2[H_2CO_3^*] + [HCO_3^-] + [H^+] - [OH^-]$
Alk	alkalinity ($H_2CO_3^*$) = $2[CO_3^{2-}] + [HCO_3^-] + [OH^-] - [H^+]$
BV	bed volume
CCDP	calcium carbonate dissolution potential
CCPP	calcium carbonate precipitation potential
C_T	sum of the carbonate species concentrations
HRT	hydraulic retention time
IX	ion exchange
SW	seawater
TH	total hardness
WHO	World Health Organization

in the following exchange step) is negligibly low:

$$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-} \tag{1}$$

$$H^+ + CaCO_{3(s)} \leftrightarrow Ca^{2+} + HCO_3^- \tag{2}$$

$$CO_{2(aq)} + H_2O + CaCO_{3(s)} \leftrightarrow Ca^{2+} + 2HCO_3^- \tag{3}$$

The modified process is designated to be implemented either in already-operative desalination plants in which a post-treatment process based on calcite dissolution using $CO_{2(g)}$ is already installed or in cases where a strict restriction is posed on the TH (i.e. the combined concentration of $[Ca^{2+}] + [Mg^{2+}]$ in the case of desalinated water) value of the product water. As explained in the following paragraph, the use of $CO_{2(g)}$ as the acidic substance for calcite dissolution results in a much lower ratio between TH and alkalinity in the product water, thereby allowing for a lower TH value for a given alkalinity concentration requirement.

1.1. *Calcite dissolution*

There are two main chemical differences between a process that is based on dissolving calcite using a strong acid (i.e. H_2SO_4) and a process in which $CO_{2(aq)}$, a weak-acid, is used: (1) less calcite can be dissolved in the latter case for a given acid dosage (in equivalent acidity terms) and (2) the Ca^{2+} to Alk concentration ratio in the product water differs significantly between the two alternatives. As a result, the acidic substance that is used to enhance calcite dissolution has an effect on both the product water quality and the required size of the post-treatment reactors.

The size of the reactors in the post-treatment process is a result of the fraction of treated (and untreated) water streams (see Fig. 1). There are two parameters that should be taken into account when calculating this fraction: (1) the capability of the water entering the calcite reactor to dissolve $CaCO_{3(s)}$, which is determined by its CCDP. The CCDP index can be used to quantify the potential of the water to dissolve $CaCO_{3(s)}$ [13,14]. (2) The second parameter is the required product water quality. In other words, based on the required TH and maximal CCDP (i.e. the most negative CCPP) that can be gained at the influent of the calcite dissolution reactor, one can calculate the minimum %split flow by dividing the TH by maximal CCDP. Given a required product water quality, the fraction of water that bypasses the treatment train is a direct result of the calcite reactor influent's CCDP. The decision on the fraction of treated water is primarily economic (i.e. it has practically no effect on the water quality).

All the following calculations were conducted under the assumption that the product water should comply with the new Israeli standards (specified above), however, the process can be considered general in the respect that is can result in almost any required water quality.

1.2. *[Ca^{2+}] to Alk ratio as a result of the chosen calcite dissolution process*

The dosage of H_2SO_4 to the water acts to decrease the Alk value since protons (H^+ ions) are released to the water (see Eq. (1)). Thus, the water that flows into the calcite dissolution reactor is characterized by a negative Alk value. Conversely, the dosage of CO_2 does not affect the Alk value of the water. Moreover, the dosage of both acids to desalinated water add no Ca^{2+} and thus the Ca^{2+} concentration in the water flowing into the calcite reactor is practically zero. Thus, in the latter case (CO_2 dosage), at the entrance to the calcite dissolution reactor, both Alk and Ca^{2+} concentrations are zero. Dissolution of 1 mole of calcite (in either process) increases both the dissolved calcium and the Alk concentrations in 2 equivalents. This can be explained by observation at Eqs. (2) and (3). According to Eq. (2), describing the H_2SO_4 dissolution process, it is apparent that altogether the Alk is increased by 2 equivalent through the consumption of 1 equivalent of protons, and the release of 1 equivalent of bicarbonate. According to Eq. (3) describing the CO_2 dissolution process, the Alk is also increased by 2 equivalents through the release of 2 equivalents of bicarbonate. Therefore, CO_2-based calcite dissolution processes result in a Ca^{2+} to Alk concentration

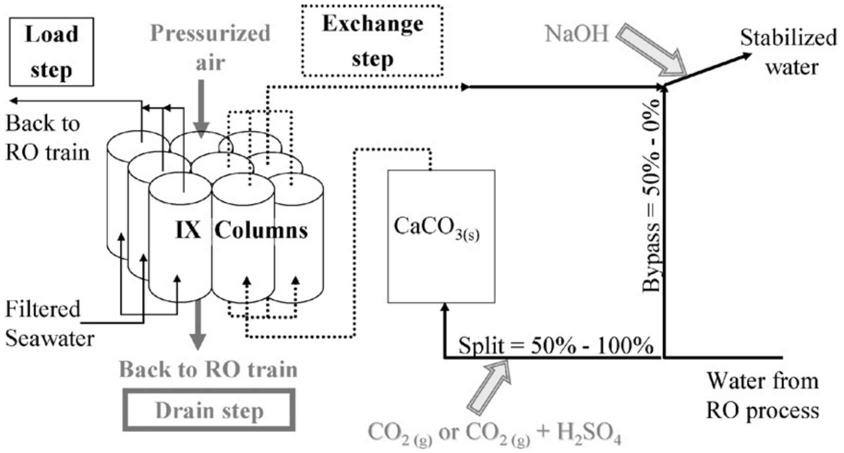

Fig. 1. Schematic of the proposed post-treatment process based on CO_2 (or CO_2/H_2SO_4) calcite dissolution.

Table 1
Comparison of water qualities attained in the calcite dissolution stage as a result of different acid dosages, assuming $T = 20\,^{\circ}C$ and initial TDS is 50 mg/l.

CO_2 dosage		H_2SO_4 dosage		Calcite reactor influent			Calcite reactor outlet	Split flow
mg/l	mequiv./l	mg/l	mequiv./l	CCPP (mg/l as $CaCO_3$)	Alk (mg/l as $CaCO_3$)	Practical CCDP[a] (mg/l as $CaCO_3$)	TH/Alk (equiv./equiv.)	%
–	–	784	16.0	−1150	−800	1100	3.7[b]	15[c]
–	–	392	8.0	−642	−400	590	3.1[b]	29[c]
176	8.0	–	–	−278	0	228	1.0	75[d]
88	4.0	–	–	−169	0	120	1.0	100[d]
25	1.1	294	6.0	−530	−300	480	2.7[b]	30[d]
65	3.0	98	2.0	−290	−100	240	1.7[b]	50[d]

[a] Calculated based on the assumptions of CCDP of 50 at the reactor outlet.

[b] Further addition of NaOH is required, thus the final TH/Alk ratio is lower.

[c] Calculated according to a final TH of 170 mg/l as $CaCO_3$.

[d] Calculated according to a final TH of 120 mg/l as $CaCO_3$.

ratio of 1 to 1 (in equivalent units) or slightly lower if NaOH is further dosed to the water after it flows out of the calcite reactor. On the other hand, H_2SO_4-based calcite dissolution processes result in a ratio that is always close to 2 to 1 in case the pH of the product water (after the addition of NaOH) approaches pH 8.3. The alteration in the Alk can be explained as follows: the product water Alk (denoted Alk_f) equals: $Alk_f = CaCO_3$ dosage + NaOH dosage − H_2SO_4 dosage (all components in units of equivalent per m^3 of product water). Similarly, the product water acidity (Acd_f) equals: $Acd_f = H_2SO_4$ dosage − NaOH dosage. Clearly, the product water Ca^{2+} is $[Ca^{2+}]_f = CaCO_3$ dosage. Taking into account the well known fact that at pH 8.3 Alk = Acd, and the terms developed for Alk_f and Acd_f one gets that H_2SO_4 dosage − NaOH dosage = $CaCO_3$ dosage. Substituting this in the expression for Alk_f one gets that indeed $Alk_f = 0.5[Ca^{2+}]_f$.

Since the IX process replaces Ca^{2+} by Mg^{2+} on an equivalent basis, the TH concentration in the water that leaves the calcite reactor remains constant throughout the IX process. Thus, instead of referring to the Ca^{2+} to Alk ratio in the product water, one might refer to the TH to Alk ratio. Considering water that corresponds to the minimal requirements presented by the new Israeli criteria, i.e. $[Mg^{2+}] = 10$ mg/l, $[Ca^{2+}]$ = alkalinity = 80 mg/l as $CaCO_3$, it is clear that the TH to Alk ratio should be ~1.5 (the combined Mg^{2+} and Ca^{2+} concentration is ~120 mg/l as $CaCO_3$). However, as explained above, the use of CO_2 to dissolve $CaCO_3$ results in a TH to alkalinity ratio that is not higher than 1 to 1 while the use of H_2SO_4 to dissolve $CaCO_3$ results in ratio of at least 2 to 1.

There are two options to overcome this problem: (a) to increase the CO_2 dosage and dissolve more calcite, resulting in the dissolution of at least 2.42 mequiv./l Ca^{2+}, out of which 0.82 mequiv./l will be further exchanged with Mg^{2+}. In this case, after the exchange step and the dilution with the untreated water, the water will have a Ca^{2+} concentration of 1.6 mequiv./l (i.e. 80 mg/l as $CaCO_3$) along with a Mg^{2+} concentration of 10 mg/l, as required. Note that since the ratio between Alk and Ca^{2+} at the outlet of the calcite reactor in this alternative is 1 to 1 (equivalent to equivalent), the Alk value of the water prior to the addition of NaOH (which will further raise the Alk value) will also be 2.42 mequiv./l (126 mg/l as $CaCO_3$), which is much higher than the minimum required value.

The major drawback associated with this alternative is that this high final Alk requires a high NaOH dosage to attain the required CCPP value (i.e. >3 mg/l as $CaCO_3$). However, since the IX effluent is highly supersaturated with respect to CO_2 it may be feasible to attain the required CCPP by stripping CO_2 using air rather than by NaOH dosage. Super-saturation with respect to atmospheric CO_2 in the water leaving the dissolution reactor is a result of the incomplete consumption of the injected CO_2 by the dissolution reaction. The CO_2 stripping alternative is potentially cheaper and results in a lower Na^+ concentration in the water. (b) To dissolve calcite using a combination of CO_2 and H_2SO_4, as described in the following section.

1.3. H_2SO_4-based calcite dissolution processes

Water introduced into the calcite dissolution reactor from the membrane separation step has (in practical terms) a zero Ca^{2+} concentration. In case H_2SO_4 is used as the acidifying agent, the water's C_T (which corresponds in desalinated water to the $CO_{2(aq)}$ concentration of the water) also tends towards zero (this statement applies in most of the SW desalination applications). The pH value, however, can be very low and correspondingly, the CCPP value can be very negative. In practical terms the CCPP can be set as low as −1400 mg/l as $CaCO_3$. Note that the pH value can be lowered to almost any desired value. However, low pH is typically achieved by a high dosage of H_2SO_4 (i.e. high concentration of $SO_4{}^{2-}$, see Eq. (1)), and as a result the concentration of dissolved Ca^{2+} may also be very high. Combined high concentrations of $SO_4{}^{2-}$ and Ca^{2+} can lead to unwanted gypsum precipitation, as shown in Eq. (4) [15]. In the current study it was calculated that in order to avoid gypsum precipitation under the conditions prevailing in the calcite dissolution reactor (considering the ionic strength and the concentration of potential Ca-ligand complexed species) the H_2SO_4 dosage must be lower than 1040 mgH_2SO_4/l, applying a margin of safety. As mentioned before, such a high concentration of acid enables dissolving a high calcite concentration and consequently treating a small fraction of water, which in turn facilitates the design and operation of relatively small reactors.

$$CaSO_{4(s)} \leftrightarrow Ca^{2+}_{aq} + SO^{2-}_{4aq}, \quad K_{sp} = 10^{-4.38} \tag{4}$$

1.4. $CO_{2(g)}$-based calcite dissolution processes

$CO_{2(aq)}$ is the most acidic of the three species of the carbonate weak-acid system ($pK(H_2CO_3{}^*/HCO_3{}^-) = 6.3$). The pH of desalinated water acidified by $CO_{2(g)}$ cannot be lowered below the $H_2CO_3{}^*$ equivalence point. The concentration of $CO_{2(aq)}$ in the water is determined according to Henry's law, thus a pressurized system is required and the practical lowest pH due to $CO_{2(aq)}$ dosage is around pH 4.3.

Table 1 summarizes the water qualities that can be attained in calcite dissolution post-treatment processes using several acidification alternatives. The acid dosages are reported in units of mg of chemical per liter of treated water, i.e. the water that is introduced to the calcite reactor. Comparing the CCPP as a result of, for example, a dosage of 8 mequiv./l H_2SO_4 or CO_2 it becomes apparent that a greater fraction of the desalinated water must be treated (i.e. smaller bypass flow rate and greater split flow, see definitions in Fig. 1) in order to achieve a similar TH concentration in the product

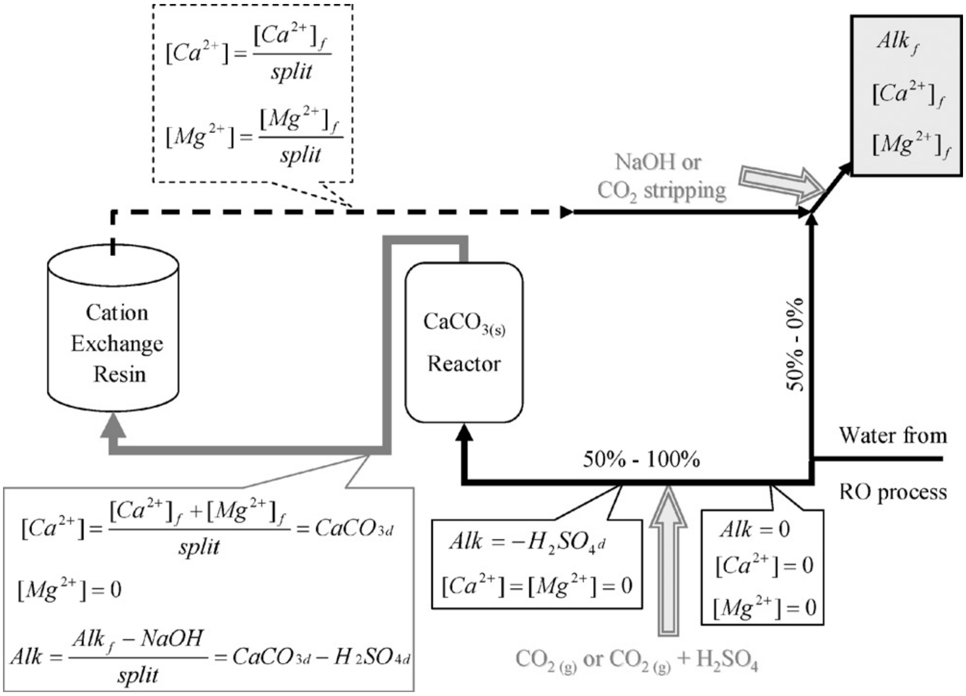

Fig. 2. Alterations in the [Ca^{2+}], [Mg^{2+}] and Alk concentrations throughout the process. The indices *d* and *f* stands for 'dosage' and 'final', i.e. the required quality of the product water. All concentrations appear in equiv./l units.

water when CO_2 is the acidifying agent than when H_2SO_4 is the acidifying agent.

Consequently, the dissolution reactors and the IX reactors in the CO_2-enhanced calcite dissolution alternative have to be much larger.

1.5. Calcite dissolution processes based on a combined dosage of CO_2 and H_2SO_4

In case H_2SO_4 is dosed to the water in combination with $CO_{2(g)}$, the CCPP value (of the influent to the calcite reactor) can be much more negative than the value that can be attained when only CO_2 is added, allowing for a higher $CaCO_3$ dissolution potential. Hence, a combination of the two acids results in an intermediate split flow, as shown in Table 1, and thus also in intermediate reactor sizes. As mentioned before, the ratio between [Ca^{2+}] and Alk concentrations in the product water (after the addition of NaOH) is ~2:1 and ≤1:1 in case H_2SO_4 and CO_2 are applied, respectively. Therefore, the [Ca^{2+}] to Alk ratio will be between ~1:1 and ~2:1 when a combination of the two acids is applied. Consequently, it is possible, for example, to produce calcite reactor effluent with the following characteristics: Alk = 85 and [Ca^{2+}] = 126 mg/l as $CaCO_3$ (i.e. [Ca^{2+}] to Alk ratio of 1.5:1). Following the IX step the corresponding water quality will be: Alk = [Ca^{2+}] = 85 mg/l as $CaCO_3$, and [Mg^{2+}] = 10 mg/l. This specific alternative was studied and is discussed in Section 3.

Fig. 2 shows schematically the changes in the concentrations of [Ca^{2+}], [Mg^{2+}] and Alk throughout the process. Note that each equivalent of strong acid added to the water reduces the Alk value by one equivalent (as shown also in Table 1), whereas each equivalent of NaOH (strong base) added to the water increases the Alk value by one equivalent. NaOH is dosed to the water with the aim of raising the CCPP value (from around −50 to +3 mg/l as $CaCO_3$), but its addition also raises both the pH and Alk values. For example, in case a NaOH dosage of *X* mg/l is required the Alk is increased by 1.25*X* mg/l as $CaCO_3$ due to the NaOH addition, as shown in Eq. (5):

$$\frac{X^{\text{mgNaOH}}/\text{l}}{40^{\text{mgNaOH}}/\text{mequiv.}} \cdot 50\,\text{mgCaCO}_3/\text{mequiv.} = 1.25X\,\text{mgCaCO}_3/\text{l} \tag{5}$$

Eq. (6) shows the relations between [Ca^{2+}] and [Mg^{2+}] at the outlet and inlet of the IX column:

$$[\text{Ca}^{2+}]_{\text{IX inlet}} + [\text{Mg}^{2+}]_{\text{IX inlet}} = [\text{Ca}^{2+}]_{\text{IX inlet}} = [\text{Ca}^{2+}]_{\text{IX outlet}} + [\text{Mg}^{2+}]_{\text{IX outlet}} \tag{6}$$

This paper focuses on the application of the modified process. Theoretical and experimental results of different case studies are shown. The results demonstrate various operational options and the corresponding wide range of water qualities that can potentially be attained. The advantages and disadvantages of the various operational options are discussed, both from the water quality and cost-effectiveness standpoints.

2. Materials and methods

2.1. Theoretical calculations

Theoretical calculations were conducted using the aquatic chemistry software STASOFT4.0 [16].

2.2. IX experiments

Solutions with specific Ca^{2+} concentrations were prepared to simulate the exchange step by dissolving a weighed amount of analytical grade $CaCl_2{\cdot}2H_2O$ in distilled water. Filtered SW 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 (purchased from Rohm & Haas Inc). Resin bed height was measured at rest after a short period of operation, to ensure steady packing of the bed. Resin bed volume was 50 ml. A peristaltic pump was used to attain a constant flow rate into the column (30–34 BV per hour).

2.3. 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 [17]. Occasionally Mg^{2+} and Ca^{2+} were also determined by the EDTA titration method [18].

3. Results and discussion

Three case study groups were examined, differing from each other by: (a) the resulting Ca^{2+} concentration in the water leaving the calcite reactor and (b) the percentage of water that undergoes treatment, out of the overall flow rate (i.e. the split flow). Within each case study three alternatives were considered, differing by the dosages of the acidifying agents used and the method used for final pH elevation. A computer simulation (STASOFT4.0) was performed for each of the nine (sub)case studies, from which the theoretical chemical dosages and resulting water qualities at each stage of the process were predicted. The Ca^{2+} concentration used in the exchange step of the IX laboratory experiments was determined from the results of the theoretical calcite dissolution reactor simulation runs.

3.1. Theoretical calculations

Based on Fig. 2, Eqs. (5) and (6), and the STASOFT4.0 software, it is possible to calculate the chemical dosages (CO_2, H_2SO_4, $CaCO_{3(s)}$ and also the NaOH dosage (or CO_2 stripping)) required for supplying a wide range of water qualities, by applying various split flow scenarios and one of the three acidification options ($CO_{2(g)}$, $CO_{2(g)}+H_2SO_4$ or H_2SO_4). All together, nine optional case studies were studied experimentally and theoretically.

A detailed example of the calculations involved in case study #1c is now brought. The considered case study simulated a situation in which all the desalinated water is treated (i.e. bypass flow = 0% or a split flow of 100%) to attain the following product water quality: $[Ca^{2+}] = \text{Alk} = 85$ mg/l as $CaCO_3$ (i.e. 1.7 mequiv./l) and $[Mg^{2+}] = 10$ mgMg/l (0.82 mequiv./l) and CCPP = 3 mg/l as $CaCO_3$. Since the desired ratio between TH and Alk in this scenario was 1.5, a combined dosage of CO_2 and H_2SO_4 had to be applied. The final CCPP was adjusted in this simulation by NaOH dosage.

Based on Fig. 2 and Eq. (6), the Ca^{2+} concentration at the outlet of the calcite reactor, i.e. at the inlet of the IX columns in this case is:

$$\begin{aligned}[Ca^{2+}]_{\text{IX inlet}} &= [Ca^{2+}]_{\text{IX outlet}} + [Mg^{2+}]_{\text{IX outlet}} \\ &= 1.7 + 0.82 = 2.52 \text{ mequiv./l}\end{aligned} \tag{7}$$

Similarly, the Alk concentration at the outlet of the calcite reactor is:

$$\text{Alk}_{\text{IX inlet}} = \frac{\text{Alk}_{\text{final}} - \text{NaOH}}{\%\text{split}} = \frac{1.7 - 0.5}{100\%} = 1.2 \text{ mequiv./l} \tag{8}$$

This difference between $[Ca^{2+}]_{\text{IX inlet}}$ and $\text{Alk}_{\text{IX inlet}}$ concentrations (1.32 mequiv./l) can only result from a dosage of 1.32 mequiv./l of H_2SO_4 that decreases the Alk. Since 2.52 mequiv./l of Ca^{2+} (which correspond to 126 mg $CaCO_3$/l) should be dissolved in the calcite reactor (see Eq. (7)), and assuming that the CCPP at the outlet of the calcite reactor is −50 mg/l as $CaCO_3$ (a reasonable assumption, when the HRT in the dissolution reactor is approximately 10 min. Based on empirical experience) the calculated CCPP at the inlet to the calcite reactor should be:

$$\begin{aligned}\text{CCDP}_{\text{calcite reactor inlet}} &= \text{CCDP}_{\text{calcite reactor outlet}} + CaCO_{3\,\text{dosage}} \\ &= 50 + 126 = 176 \text{ mg/l as } CaCO_3\end{aligned} \tag{9}$$

The dosage of 1.32 mequiv./l of H_2SO_4 to RO water (as required according to the above explanation) acts to decrease the CCPP to −129.7 mg/l as $CaCO_3$. CO_2 should be thus dosed in order to further reduce CCPP to −176 mg/l as $CaCO_3$. Using STASOFT4.0, this requires a further CO_2 dosage of 25 mg/l.

A similar calculation procedure was performed for all the other case studies, and the results are shown in Table 2. The chemical dosages are reported in units of mg of chemical per liter of product water. Each case study is divided into three sub-processes: the first comprises of CO_2 addition as the sole acidifying agent and NaOH dosage for CCPP adjustment; the second combines CO_2 dosage for calcite dissolution and CO_2 stripping for final CCPP adjustment (no NaOH dosage); and the third combines CO_2 and H_2SO_4 for calcite dissolution purposes and NaOH for final CCPP adjustment (the above example relates to this latter sub-process). A fourth alter-

Table 2
Comparison of operational conditions, chemical dosages and resulting water qualities in the tested case studies, assuming $T = 20\,^\circ C$ and initial TDS is 50 mg/l.

Case study	Split flow	Length of exchange step	Chemical dosages					Product water quality[a]	
	%	# of BV	CO_2 (mg/l product water)	H_2SO_4 (mg/l product water)	$CaCO_3$ (mg/l product water)	NaOH (mg/l product water)	CO_2 stripping (mg/l product water)	pH	Alk (mg/l as $CaCO_3$)
1a	100	735	93	–	126	30.5	–	7.79	164
1b			93	–	126	–	−36	7.95	126
1c			18.7	70.9	126	24.7	–	8.25	85
2a	65	505	95	–	126	31.5	–	7.78	165
2b			95	–	126	–	−37.3	7.95	126
2c			18.7	65.7	126	20.7	–	8.25	85
3a	50	350	101	–	126	36.6	–	7.76	172
3b			101	–	126	–	−43.5	7.95	126
3c			18.5	65	126	19.7	–	8.25	84
4	50	–	66	–	85	24.5	–	8.00	116

[a] The product water CCPP, $[Ca^{2+}]$ and $[Mg^{2+}]$ are 3 mg/l as $CaCO_3$, 85 mg/l as $CaCO_3$ and 10 mg/l, respectively, in all case studies, except for case study #4, in which $[Mg^{2+}] = 0$.

native process, relying on a combination of CO_2 and H_2SO_4 as the acidifying agents and adjusting CCPP by CO_2 stripping was found impractical, since the degree of CO_2 super-saturation in this alternative was, in most cases, not high enough.

Note that an identical set of product water requirements was defined for all the tested scenarios. Therefore, the simulated product water concentrations of Ca^{2+} and Mg^{2+} are identical in all cases (85 mg/l as $CaCO_3$ and 10 mg/l, respectively). However, the alkalinity concentration and pH value of the product water in each sub-process (i.e. processes a, b and c) are different, as shown in Table 2.

The explanation for the variations in water qualities and chemical dosages is as follows: the Ca^{2+} and Mg^{2+} concentrations in the product water are determined by a combined effect of the following three parameters: the mass of $CaCO_3$ that was dissolved in the water, the length of the exchange step and the chosen split flow. In order to produce waters with identical TH an identical mass of $CaCO_{3(s)}$ should be dissolved per liter of product water (i.e. $85 + 10/12.15 \times 50 = 126$ mg as $CaCO_3$ in the addressed cases) regardless of the split flow and the acidifying agents used, as shown in Table 2. The reason for the identical required CaCO3 dosage lies in the fact that Ca^{2+} and Mg^{2+} change linearly as a result of chemical dosages and blending actions. Conversely, pH and CCPP are non-linearly altered as a result of these process steps. Their values result from a combined effect of (a) the dosages of the acids applied (CO_2, H_2SO_4 or a combination of both); (b) the dosages of the applied basic species (${CO_3}^{2-}$ from $CaCO_3$ dissolution and OH^- from NaOH dosage); and/or (c) the (optional) emission of acidic species (CO_2 stripping, when this option replaces NaOH dosage).

The chemical dosages were calculated in the simulations in such a way that the final product water CCPP value would, in all scenarios, be +3 mg/l as $CaCO_3$. Therefore, the CCPP value is constant in all the presented scenarios, while the chemical dosages, and also the values of pH and alkalinity, differ.

Comparing the chemical dosages of the three splits of the first sub-process (i.e. alternatives #1a, #2a and #3a) it is apparent that as the CO_2 dosage is increased, more NaOH needs to be dosed in order to attain a given CCPP (i.e. 3 mg/l as $CaCO_3$). This is explained by the fact that a greater dosage of CO_2 results in a higher C_T and a slightly lower pH value, both making the buffering capacity of the product water higher.

Comparing the chemical dosages of the three splits tested within the second sub-process (i.e. alternatives #1b, #2b and #3b) it can be observed that when a higher CO_2 dosage is applied, more CO_2 mass needs to be stripped to attain the required CCPP value. By subtracting the mass of CO_2 stripped from the mass of CO_2 dosed, in all the tested scenarios, it can be shown that an equal net amount of CO_2 is added to the water in all cases. This explains why the resultant product water quality is identical in the discussed three sub-cases.

Comparison of the chemical dosages required in the three splits considered within the third sub-process (i.e. alternatives #1c, #2c and #3c) shows that higher H_2SO_4 dosages result in a higher NaOH demand to attain a given CCPP value. This phenomenon emanates from the fact that a greater dosage of H_2SO_4 results in a lower pH value at the outlet of the calcite dissolution reactor and thus the water is characterized by higher buffering capacity (effluent pH approaches pH 6.3, i.e. close to the 1st pK value of the carbonate system, where the buffering capacity is the highest). Not surprisingly, in order to elevate pH to a given value, needed for attaining a given CCPP, the NaOH dosage increases with an increase in the buffer capacity of the water.

Note that for each case study only one dosage combination is shown in Table 2. In reality, however, an infinite number of chemical dosage combinations are possible, and accordingly an infinite number of product water qualities and associated costs.

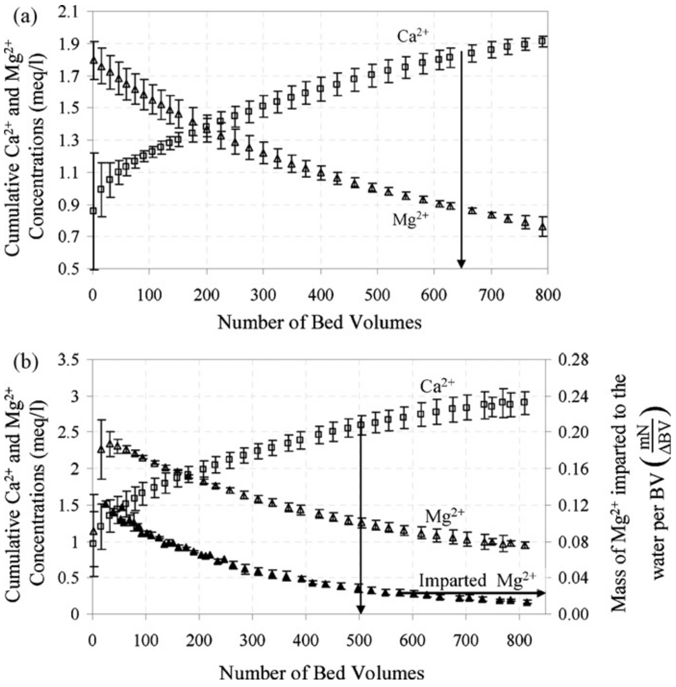

Fig. 3. Cumulative Ca^{2+} (squares) and Mg^{2+} (triangles) concentrations at the outlet of the IX column, simulating the exchange step of case studies #1 and #2 (a and b, respectively), and the mass of Mg^{2+} imparted to the water per BV in case study #2 (full triangles in b).

3.2. Results of IX experiments

Laboratory experiments were conducted to determine the exact number of BVs that should be passed through the IX column during the load and exchange steps in order to attain the required water quality in all the investigated scenarios. In all case studies the column was filled with the resin Amberlite IRC747, which is characterized by a very high affinity towards divalent cations. The considerations leading to the choice of this resin are detailed in Ref. [10].

The exchange step of case studies #1, #2 and #3 (corresponding to split = 100%, 63% and 50%, respectively, see Table 2) was investigated (four repetitions) in a continuous IX experiment, in which the inlet Ca^{2+} concentrations were 2.52, 3.86 and 5.04 mequiv./l, respectively. The results of the exchange steps are summarized in Table 2. Fig. 3 shows the average ($n = 4$) of the cumulative $[Ca^{2+}]$ and $[Mg^{2+}]$ at the outlet of the IX column in the experiments that examine case study #1 and #2. It can be seen that the exchange steps of case study #1 and #2 can be stopped after 650 and 505 BV, respectively, since at these points the cumulative $[Ca^{2+}]$ concentrations were 1.7 and 2.6 mequiv./l, respectively, while the cumulative $[Mg^{2+}]$ concentrations were 0.82 and 1.26 mequiv./l, respectively, i.e. as desired. Similarly, case study #3 was stopped after 350 BV, when the cumulative $[Ca^{2+}]$ and $[Mg^{2+}]$ were 3.4 and 1.64 mequiv./l, respectively, again as required (results not shown graphically).

Fig. 3b also shows the mass of Mg^{2+} released to the water per BV in the course of the exchange step. Clearly, as the exchange step proceeds less Mg^{2+} is released to the water since the ratio between Ca^{2+} and Mg^{2+} absorbed on the resin increases during the exchange step, and therefore the mass of Mg^{2+} that is released from the resin to satisfy the equilibrium reaction between the two phases is reduced.

Note that the actual TH of the experiment which simulated the 100% split flow (case study #1) was (inadvertently) a bit higher (by 8.7%) than planned, thus the results were treated theoretically to correspond to a 92% split flow. The outcome of this error was that

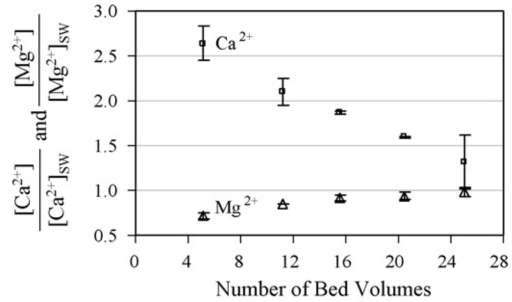

Fig. 4. Momentary Ca^{2+} (squares) and Mg^{2+} (triangles) concentrations at the outlet of the IX column in experiments simulating the load step. All concentrations are shown relative to their concentrations in the Mediterranean SW (i.e. $[Mg^{2+}]_{SW}$ = 1530 mg/l and $[Ca^{2+}]_{SW}$ = 499 mg/l).

the exchange step was stopped when the concentrations of $[Ca^{2+}]$ and $[Mg^{2+}]$ were slightly higher than the desired values, i.e. 1.85 and 0.89 mequiv./l, respectively.

Fig. 4 shows the change in the Ca^{2+} and Mg^{2+} concentrations in the course of a typical load step. The concentrations in Fig. 4 are presented relative to their concentrations in SW from the Mediterranean. Fig. 4 shows that after 25 BVs the Ca^{2+} and Mg^{2+} concentrations at the outlet of the IX column are almost identical to the concentrations at the inlet (i.e. the Mediterranean SW concentration). Thus, it can be concluded that the number of BVs required for loading the resin using SW is approximately 25. Note that Fig. 4 shows the concentrations during the load steps that followed the exchange steps in case study #1, the load steps that followed the other case studies were similar, i.e. they were also completed after 25 BV. The reason for this similarity lies in the fact that the same mass of Mg^{2+} was released from the resin to the exchange solution in all the experiments, regardless of the split flow, as shown in Eq. (10):

$$\text{Mass of } Mg^{2+} = \frac{[Mg^{2+}]_{\text{required}}}{\%\text{split}} \times Q_{\text{tot}} \cdot \%\text{split} \tag{10}$$

Another important outcome of the fact that the same mass of Mg^{2+} is released from the resin during the exchange step (or absorbed during the load step) is the linear relations between the length of the exchange step and the %split, as shown in Fig. 5. Fig. 5 shows the length of six case studies, simulating six different split flows, and given the same required Mg^{2+} concentration (the data of the lower split flow case studies were taken from Ref. [10]). A larger split flow implies that the driving force for the exchange step is reduced, since the concentration of Ca^{2+} in the water entering the IX column is reduced, see Fig. 1. A smaller driving force results in a longer exchange step.

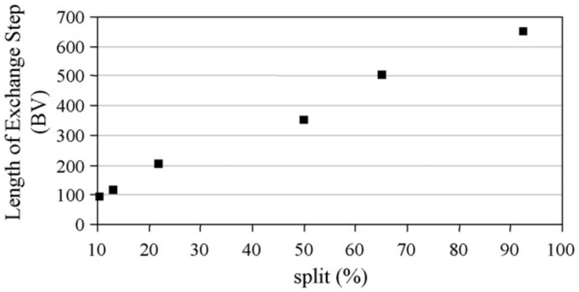

Fig. 5. Lengths of exchange steps versus % split flow. The load step of all case studies was carried out using SW. The required product water Mg^{2+} was 10 mg/l.

3.3. *Example of a general design for a 100 Mm^3/year desalination plant*

The new 100 Mm^3/year Hadera desalination plant (Israel) became operative in November 2009. The product water of this plant is required to comply with the existing Israeli quality criteria (i.e. excluding Mg^{2+}). There are many ways to achieve the required water quality. To name a few alternatives, it is possible to apply the CO_2-based calcite dissolution process followed by NaOH addition or CO_2 stripping; it is also possible to combine direct dosage of CO_2 and $Ca(OH)_2$ followed by calcite dissolution, etc.

To exemplify the application of the proposed Mg^{2+} addition process as an "add-on" to an existing post-treatment plant, a commonly applied post-treatment was assumed for attaining the required water quality in the Hadera plant was assumed. Under this assumed alternative (denoted #4 in Table 2) 50% of the overall flow rate is treated by CO_2-based calcite dissolution, this step being followed by NaOH dosage, to attain the required CCPP value. Out of the nine considered case studies presented in Table 2, case study #3b is the most similar, in terms of the post-treatment scheme, to case study #4, except, of course, the additional IX step applied in case study #3c. Note, that case study #3c can be applied as an add-on to process #4, since the same flow rate flows through the treatment train and it involves less CO_2 and NaOH dosages, and thus requires only the addition of H_2SO_4 dosing pumps and the installation of the IX treatment component. In addition, larger calcite reactors are required because 50% more calcite should be dissolved.

The following calculations simulate the application of the proposed process as an add-on to the chosen post-treatment alternative for a 100 Mm^3/year desalination plant. Case studies #3 and #4 overall design flow rate was assumed to be 14,000 m^3/h, out of which 50% was designed to be treated (i.e. flow through the calcite reactor and IX columns, see Figs. 1 and 2). For simplicity purposes a flow rate of 35 BV/h (HRT of ~2 min) was assumed in calculating the resin volume required in the exchange step ($\not{V}_{IX}$):

$$\not{V}_{IX} = \frac{14,000\ m^3_{\text{total}}/h \cdot 0.5\, m^3_{\text{treated}}/m^3_{\text{total}}}{35\ BV/h} = 200\, m^3_{\text{treated}}/BV \tag{11}$$

The volume of resin required in the load and drain steps together amounts to around 8% of the amount in the exchange step (25 BV + 4 BV in the load and drain steps, respectively, versus 350 BV in the exchange step), thus a total volume ($\not{V}_{IX\ \text{total}}$) of approximately 217 m^3 resin is required in the process.

3.4. *Cost estimation*

Table 2 can be used to assess the cost of chemicals, used in the proposed process for a given set of chemical costs. The following chemical costs were used in a preliminary operational cost analysis (all prices are in units of \$ per ton of pure chemical): H_2SO_4, 120; CO_2, 150; $CaCO_3$, 30; NaOH, 400. Using these values one can easily calculate the cost of each chemical by multiplying the chemical cost by the dosage. In order to assess the overall operational cost, the cost of energy consumption for pumping the water through the reactors and cost of amortized resin replacement were calculated using Eqs. (12) and (13), respectively. Both parameters were calculated in units of \$m^3 product water:

$$\text{Energy cost} = \frac{\gamma Q_{\text{treated}} H}{\eta Q_{\text{tot}}} 24\ \text{h/day} \cdot 365\ \text{days/year} \cdot \text{Electricity cost} \tag{12}$$

where $\gamma = \rho g$ (kg m^{-2} s^{-2}); Q_{treated} and Q_{tot} represent the treated water flow rate (m^3 s^{-1}) and the total product water flow rate (m^3 year^{-1}), respectively; H represents the total head imparted to the water by the pumps (assumed to be 12 m); η represents the pumps efficiency (assumed to be 0.75); and the electricity cost was assumed to be 0.0001$/Wh. Multiplying by 24 and 365 is required in order to correct the units of the energy required for pumping.

$$\text{Resin replacement cost} = \frac{\text{ARRR} \cdot \not{V}_{\text{IX tot}} - \text{resin price}}{Q_{\text{tot}}} \qquad (13)$$

where the annual resin replacement rate (ARRR) was assumed to be 10% and the resin price was assumed to be $8 per liter. Note, that unlike the chemical dosages (and hence also the chemical costs), the costs of energy consumption and resin replacement are strongly influenced by the %split flow, this can be explained as follows: as more water is treated the needed energy is increased proportionally (Eq. (12)); similarly, according to Eqs. (11) and (13) a higher %split flow results in a proportional increase in the total required volume of resin, and in the required cost of resin replacement. However, calculation of the chemical costs (based on average prices), the energy consumption cost and the resin replacement cost of all investigated cases, revealed that the chemical costs comprise the major operational cost component (i.e. above 80%). A similar conclusion was found in other post-treatment processes [19].

Based on the above-mentioned chemical prices, and Eqs. (11)–(13) the additional operational cost associated with upgrading process #4 to process #3c can be easily evaluated. For example, process #3c requires 66–18.5 = 47.5 g/m^3 less CO_2 than process #4, thus the cost of CO_2 is reduced by 0.81 to 0.71 $cents per m^3 of product water (based on the minimum and maximum prices). The required NaOH dosage is also reduced while the dosages of calcite and H_2SO_4 are higher. Thus, the total additional cost of chemicals is similar in the two case studies. The additional costs associated with energy consumption cost and the resin replacement cost are 0.11 and 0.17 $cents per m^3 of product water, respectively, assuming that the head the water should be given in case there is no IX component is only 6 m. The overall operational costs are thus increased by between 0.15 and 0.69 $cents per m^3 of product water based on the minimum and maximum prices, respectively. Note that the additional cost of the proposed process is a function of the chosen applied scenario and the chemical costs, which can differ significantly in time. In case the maximum H_2SO_4 price increases by 30%, the application of process #3c results in an additional operational cost of 1.08 $cents per m^3 of product water.

4. Conclusions

The paper describes a modified two-step post-treatment process for desalinated water. The presented process enables meeting quality criteria for a balanced combination of pH, CCPP, alkalinity, Ca^{2+}, Mg^{2+}, $SO_4{}^{2-}$ and TH concentrations. The modified process is based on exchanging Ca^{2+} ions generated in a CO_2-based calcite dissolution post-treatment process (unlike the original process, where calcite dissolution results from H_2SO_4 dosage). The Ca^{2+} ions are exchanged with Mg^{2+} ions that originate from SW, using a specific cation exchange resin.

It was shown that two additional features can be feasibly installed in conventional post-treatment processes: (a) combined controlled dosage of two acids (H_2SO_4 and CO_2) to enhance $CaCO_{3(s)}$ dissolution and (b) pH elevation by CO_2 stripping rather than NaOH dosage to attain a required CCPP value. Comparing the results of possible alternative sub-processes indicates that: (1) the highest alkalinity value in the product water is attained when H_2SO_4 is not dosed at all (sub-scenarios “a” and “b” in Table 2); (2) NaOH dosage acts to further increase the Alk value; (3) a higher Alk value corresponds to a higher buffering capacity, therefore the pH value in sub-scenarios “a” was the lowest for attaining a CCPP value of +3 mg/l as $CaCO_3$.

The two main advantages of the presented modification(s) are: (I) higher flexibility for attaining a required ratio between TH and Alk concentrations in the product water. As shown in Table 2, the TH to Alk concentrations ratio can be as low as 0.73: 1 (case study #3a) and (II) the ability to upgrade existing desalination post-treatment processes that are based on CO_2 dissolution to supply Mg^{2+} ions simply by adding a relatively cheap IX stage to the treatment scheme. Note that the proposed IX step is unique in the sense that it results in no brine generation and in the feature that the regeneration solution (~2% of the flow rate of SW introduced into the desalination plant) is supplied at a very low cost.

Under the described three split flow scenarios, the Amberlite resin column was shown to operate for 650, 505 and 350 BVs, respectively, in the exchange step before it should be switched to the load step. 25 BVs were required to load the resin, suggesting that the time in which the resin would spend in the load step is approximately 3.7%, 4.7% and 6.6% of the total operation time in scenarios #1, #2 and #3, respectively.

The results indicate that regulations for desalinated water can be met effectively and economically using the proposed process. In addition, it is possible to produce water with a wide range of water qualities, and a wide range of percentages of treated water. More specifically, the addition of Mg^{2+} in the proposed process will result in water that is more healthy to humans and acceptable by the agricultural community.

It was shown that considering the same required Mg^{2+} concentration and split flows ranging between 22 and 100%, an approximate linear relationship exists between the length of the exchange step and the %split.

The approximated total volume of resin required for applying the process in the 100 million m^3/year Hadera plant under the assumed conditions is 217 m^3.

It was shown that the addition of Mg^{2+} to the water by applying process #3c as an add-on to process #4, results in a very small change in the operational costs. The minimum and maximum additions of operational costs are 0.15 and 0.42 $cent per m^3 of product water, respectively, for the following set of chemical cost ranges: H_2SO_4: between 100 and 200; CO_2: between 150 and 170; $CaCO_3$: between 25 and 35; NaOH: between 350 and 450, all prices in units of $ per ton of pure chemical.

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