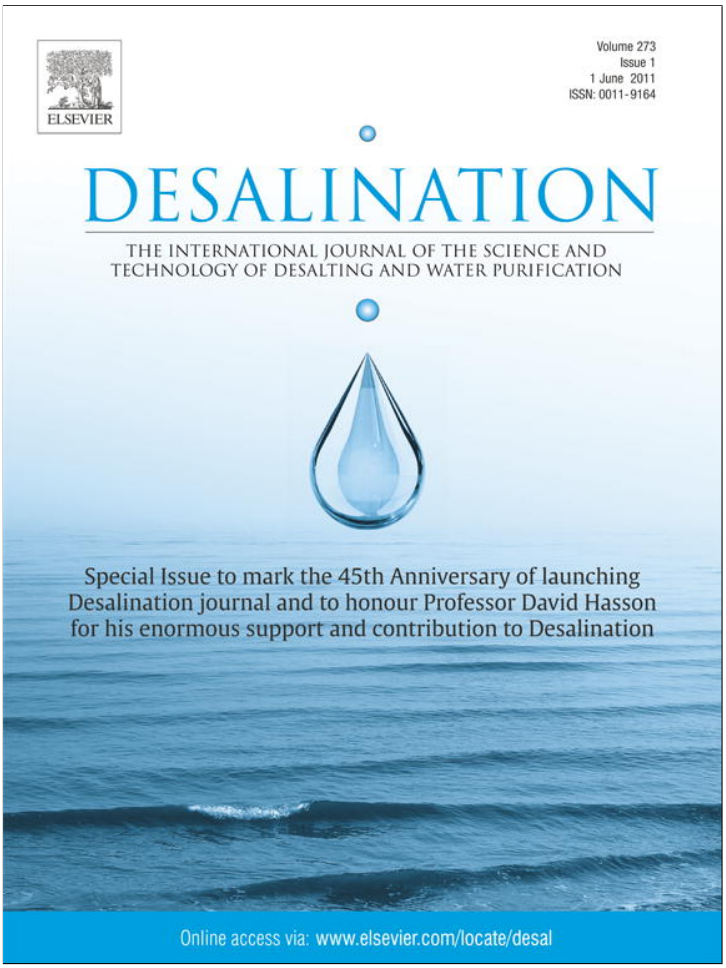

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Fundamental chemistry and engineering aspects of post-treatment processes for desalinated water—A review

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ABSTRACT

The quality with which water is released from desalination plants is continuously increasing. Since desalination permeates are slightly acidic, contain very low buffering capacity and are very soft, post-treatment is always required. This paper reviews the knowledge accumulated in the last decades on desalination post-treatment processes. It covers fundamental chemistry aspects, required water quality criteria, advantages and disadvantages of currently applied processes, engineering and cost considerations, recent full-scale project experience and up-to-date research trends.

Contents

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Nomenclature

AI	Aggressiveness Index
Acd	CO_3^{2-} acidity
Alk	$H_2CO_3^*$ alkalinity
AWWA	American Water Works Association
BW	Brackish Water
CCPP	Calcium Carbonate Precipitation Potential (mg/l as $CaCO_3$)
C_T	Total inorganic Carbon
DFI	Driving Force Index
DO	Dissolved Oxygen
HRT	Hydraulic Retention Time
EC	Electrical Conductivity
IX	Ion Exchange
LSI	Langelier Saturation Index
LR	Larson Ratio
NTU	Nephelometric Turbidity Units
PT	Post-Treatment
RCI	Riddick Corrosion Index
SAR	Sodium Adsorption Ratio
SW	Seawater
TDS	Total Dissolved Solids (mg/l)
TH	Total Hardness
WHO	World Health Organization

1. Introduction

In the last decades, the worldwide production of desalinated water has increased dramatically [1]. In certain locations desalinated water constitutes a significant percentage of overall fresh water consumption. In Israel, for example, desalinated water capacity has risen from 25 Mm^3/y to 315 Mm^3/y (corresponding to >20% of the fresh water supply) between 2005 and the end of 2009, and it is planned to grow to 650 Mm^3/y in the year 2013. Countries in the Persian Gulf have been long relying on desalinated water. Nonetheless, the percentages of desalinated water (out of the total fresh water supply) in these countries have recently also increased significantly: i.e. from 54% to 94% and from 63% to 98% in Bahrain and in the United Arab Emirates, respectively [2]. Similarly, municipalities in remote arid locations in Australia are now receiving most of their water supply through desalination [3].

From this description it is clear that an increasing fraction of the world population is consuming desalinated water, either blended with other water sources, or as a main or sole water source. This trend is expected to continue and even increase in the foreseeable future. Desalinated water is currently used mostly for domestic consumption but in some locations it also serves for irrigation purposes [1,4].

The quality of unconditioned desalinated water can differ significantly, depending both on the type of desalination technology used for salt separation (Reverse Osmosis (RO) membrane or thermal desalination) and on the specific design and operation of the desalination process [5]. For example, permeate produced by a single-pass RO system typically has higher total dissolved solids (TDS) concentration than permeate of two-pass RO system. However, in all cases, desalination permeates are slightly acidic, contain very low buffering capacity and are very soft (i.e., contain very low calcium and magnesium hardness). Water with such quality cannot be supplied directly for either domestic consumption and/or irrigation, for a variety of reasons [6]. Delivery of unconditioned desalinated water to the consumers may result in unwanted outcomes throughout the usage cycle: in the distribution system, to the consumers, to downstream wastewater treatment facilities and in some locations also to consumers who reuse the downstream treated wastewater for agriculture. For these reasons, post-treatment (PT) must be applied to adjust the water quality, as required according to local considerations and potential uses.

Surveying the relevant literature reveals that (a) water quality standards, specific for desalinated water, which take into account the abovementioned issues, have been set thus far only in Israel [7]. Consequently, practiced PT processes around the world result in a

varying product water qualities, which frequently, are inadequate to meet final user needs (i.e., protect human health related objectives and agricultural crop yields). For example, in Finland, post-treatment is aimed at raising the alkalinity (Alk) and pH values, and at reducing the dissolved carbon dioxide (CO_2) concentration in desalinated water [8]. The calcium concentration appears not to be addressed at all, and consequently, so is any $CaCO_3$ precipitation index, which is essential for corrosion control, nor is the issue of a minimum Ca^{2+} concentration required for public health reasons, addressed. In this respect, there are many examples that demonstrate that the causes for red water episodes and corrosion of metal pipes are not yet clear [9–11] and so are issues related to the blending of a several water sources in water distribution systems [12]. Moreover, $CaCO_3$– precipitation indices for water's corrosivity potential are frequently used incorrectly, due to what appears to be misunderstanding of the fundamental principles by which these indices should be implemented and also misinterpretation of their limitations [13]; (b) The various differences between the alternative PT methods have been rarely properly addressed [14]. A survey of the literature that discusses PT reveals that the importance of the subject of conditioning of desalinated water was emphasized mainly when the first large desalination plants were built in the 1980s. However, this subject has received very limited attention thereafter, as shown in Fig. 1, which presents the number of publications dedicated to PT of desalinated water as a function of time. The water treatment industry has grown significantly since the 1980s. Unfortunately, this growth has not led to a corresponding advancement of PT methods, since most of the research to-date has mainly focused on the desalination processes per se. Pre-treatment methods have also received very limited attention until recently [6]. Scientific publications dedicated specifically to PT are rare, relative to the available publications addressing other aspects of desalination, such as the salt-separation method itself or related energy saving issues. An approximate estimate of the number of publications dealing with subjects relevant to desalination in the last 20 years revealed the following: the majority of the publications (~95%) address the desalination process itself (>85% and >10% focus on membrane technologies and on thermal desalination, respectively). The number of papers on pretreatment is more than twice higher than the number of publications focusing on post-treatment (>1%, ~0.5%, respectively). In addition, more publications (~0.7%) focus on the subject of brine disposal than on post-treatment. (c) Finally, in addition to the gaps in knowledge (i.e. the required water quality and the methods for attaining it), even the already existing knowledge in these fields is often misused or misunderstood, as mentioned, for example in the context of corrosion control strategies, by Seacord et al. [13].

The limited understanding of the alternatives available for post-treatment of desalinated water and the general lack of knowledge in this field has often led to unfavorable results. Examples include corrosion and other product water quality related problems in a number of projects worldwide e.g. Israel [15], Boston [10], Florida [16], Cyprus [17]; Sweden [18]; Arizona [19].

The aim of the current review is to provide a detailed overview of existing knowledge on PT processes, including theoretical background, advantages/disadvantages and main challenges of commonly practiced PT processes, newly developed water conditioning technologies, and recent research trends.

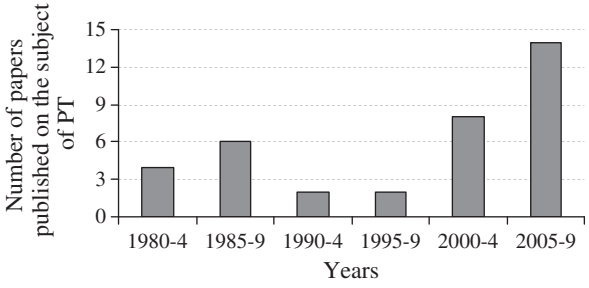

Fig. 1. Number of publications focusing on PT issues in the last three decades.

1.1. Considerations associated with desalinated water quality

In order to determine the required quality of desalinated water (following PT) for a given use, the following aspects should be considered:

1.1.1. Interaction with the distribution system

The need to stabilize the water so that it would not enhance metal corrosion and concrete dissolution has been recognized for decades. Corrosion of system pipes is associated with health hazards due to unwanted release of metal ions such as lead, copper and zinc into the drinking water [13,20–25]. In addition, corrosion-related problems are associated with distribution system integrity, longevity and maintenance costs [24,26–30]. In 1999, for example, the AWWA estimated that it would cost US water utilities $325 billion over the following 20 years to upgrade damaged water distribution systems [28]. This may perhaps be used to explain why most PT technologies and scientific research focus primarily on controlling the corrosivity of desalinated water (by chemically stabilizing it), while often overlooking other important water quality aspects. "Red water" events (sudden detachment of corrosion products from the pipe sidewall and its release to the water) are a byproduct of corrosion. However, it should be referred to as a separate problem, which is the outcome of a combination of conditions and which results in different problems than "crawling" corrosion [24,31].

1.1.2. Public health

Two water quality aspects may be directly related to the consumer's health: (1) Bio-stability of the water in the distribution system, or in other words the efficiency of disinfection, as well as minimization of bacterial re-growth in the distribution system. (2) Lack of important minerals, such as calcium and magnesium ions: an important issue, with a potential to directly affect consumers' health. Calcium and magnesium ions are minerals of key importance for human health and agricultural and horticultural water uses. These minerals are practically absent from the unconditioned desalinated water.

1.1.3. Possible detrimental effects on downstream wastewater treatment plants

This issue is related to the biological wastewater treatment for ammonia and nitrate removal, and has been recognized only recently. If a complete removal of nitrogen compounds is required, then high alkalinity in the wastewater is necessary in order to restrain the pH drop and maintain biological process stability [7,32]. The minimum amount of alkalinity needed in the wastewater to sustain stable nitrification process may not be available if water with a too low alkalinity is released by the desalination plant and distributed without proper conditioning [32].

1.1.4. Effect on the quality of reclaimed water used for agricultural irrigation

Reclaimed water (i.e., highly treated secondary or tertiary effluent from wastewater treatment plants) is often used for agricultural irrigation in the same location where desalinated water is a major source of freshwater. Certain quality characteristics of the reclaimed water are directly dependent on the quality of the desalinated water. The most disturbing problem appears to be the high to very high Sodium Adsorption Ratio (SAR) values expected to develop in wastewaters generated from pure desalinated water origin. SAR, a quantitative indicator for soil sodicity hazards, should, according to recent Israeli legislation, not exceed a value of 5 $(meq/l)^{0.5}$, however in the vicinity of the Ashkelon desalination plant values as high as 10

have been recently recorded [33]. From this aspect and others, it appears advantageous to enrich the desalinated water with Ca^{2+}, Mg^{2+}, SO_4^{2-} ions and in some cases also with alkalinity [33].

1.2. Water quality parameters

The following parameters are usually used to determine the required water quality of soft waters: [Ca^{2+}], alkalinity, pH, TDS and Calcium Carbonate Precipitation Potential (CCPP) (or another $CaCO_3$ precipitation related index). Clearly, different threshold concentrations of these parameters can and have been required in different locations, depending on the local conditions, e.g. the quality of other water sources with which the desalinated water is blended; the portion of desalinated water in the overall water supply; the average daily Ca and Mg intake from food, etc. Between 2005 and 2007, a comprehensive work was carried out in Israel, with the aim of determining a set of target water quality criteria, specific for desalinated water. The work was carried out for the Committee for the Update of Water Quality Standards, appointed by the Israeli ministry of Health. It relied partly on various worldwide water quality standards and guidelines for corrosion control of naturally occurring soft waters. Based on this work the following specific water quality criteria for desalinated water are now enforced by the Israeli Ministry of Health: Alk>80 mg/l as $CaCO_3$; 80<[Ca^{2+}]<120 mg/l as $CaCO_3$; 3<CCPP<120 mg/l as $CaCO_3$; and pH<8.5. The considerations that led to the establishment of these new criteria are summarized in the following paragraphs [7]:

- *[Ca^{2+}]*—The minimum Ca^{2+} concentration required for adequate protection of human health is 50 to 60 mg/l as $CaCO_3$ [34]. The upper recommended value was set in these criteria due to economic reasons attributed to the need to supply water that is not excessively hard. Combined with the calcium concentration required for establishing a positive CCPP value at pH close to 8, the recommended Ca^{2+} concentration in the product water was in the range 80 to 120 mg/l as $CaCO_3$.
- *$H_2CO_{3\,alkalinity}^{*}$*—it is widely accepted that high Alk values are advantageous in desalinated water for various reasons including increased water buffer capacity (e.g.[13]); prevention of metal ion release in the water (e.g. [35,36]), i.e. for the minimization of corrosion and red water events (except when lead and copper form a part of the water distribution systems [13]; for minimizing the potential negative effects of blending of desalinated water with other water sources within the distribution system [37]. In case the desalinated water is used for agricultural irrigation, a relatively high alkalinity value may be needed for maintaining a stable pH when acidic or basic fertilizers are added through the irrigation system. Finally, a target minimum content of alkalinity in the drinking water may be needed to allow for stable operation of downstream wastewater treatment plant, as already mentioned.
- *$CaCO_{3(s)}$ precipitation index*—CCPP is the quantitative measure of the precise potential of a solution to precipitate (or dissolve) $CaCO_{3(s)}$. As such it constitutes an unambiguous parameter that can be used in the context of guidelines or regulations without invoking misunderstanding [13]. Maintaining a high CCPP has been associated with a decrease in the rate of corrosion and potential for red water events occurrence. However, an upper CCPP value should also be set in order to prevent possible buildup of excessive $CaCO_3$ scales on pipes and pumping stations [13]. Note that if desalinated water is supplied only to nearby agricultural areas and its retention time in the distribution system is relatively short, a less stringent minimum threshold of CCPP can be imposed.
- *pH*—within the range of pH values attained after PT (between ~6 and ~8) a lower pH value results in a higher chlorine disinfection efficiency [38,39] and higher buffer capacity. Maintaining an appropriate buffering capacity in potable water is essential because several processes (either deliberate or not) that occur in the distribution system can potentially affect the pH value, possibly resulting in changing the CCPP value from positive to negative. Examples of deliberate water treatment processes that result in a decrease in the pH value are disinfection with Cl_2 gas [13] and dosage of fluorine by the addition of H_2SiF_6 (fluorosilicic acid). Unintentional processes include nitrification of ammonia present due to chloramination practices and iron oxidation and precipitation.
- *[Mg^{2+}]*—a threshold value for Mg^{2+} concentration has not yet been included in the Israeli criteria [7]. Nevertheless, in 2009 the Israeli Ministry of Health decided to add a minimum requirement of 10 mg Mg/l to the criteria due to the acknowledged importance that Mg^{2+} ions have on both crop irrigation [15] and the public health [20,25,34,40–42]. It is stressed that in spite of the recent recommendations by the World Health Organization (WHO), the issue related to potential health benefits of Mg^{2+} in drinking water is still under intense debate. As an example to an opposing view, Morris et al. [43] stated that high magnesium intake does not appreciably protect against cardiovascular disease and coronary heart disease. On the other hand, Catling et al. and Monarca et al. [41,42], among many others, concluded that there is significant evidence for statistically significant inverse association between Mg^{2+} concentrations in drinking water and cardiovascular mortality. Despite the lack of unanimous agreement on this issue, the 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" [40]. The WHO has thus recommended in its recent publications to maintain a minimum Mg^{2+} concentration in all drinking waters [20,40].

1.3. Chemicals used for corrosion minimization in water distribution systems

Addition of corrosion inhibitors (e.g. poly-phosphates, mono-phosphates, zinc orthophosphate and silicates) is a common technique for conditioning of soft and low buffering capacity waters. It is typically used in addition to post-treatment but sometimes it is practiced as a stand-alone corrosion protection alternative [12,22,28,44–46]. The recognition of the harmful effect of zinc loading on wastewater treatment plants has curtailed the usage of zinc-phosphate [28]. Numerous studies claim that dosing polyphosphate and silicates to the water have the potential to reduce iron release and visible appearance of iron particles [20,47]. Thus, they are considered to reduce corrosion and red water events. However, the interaction between iron scales and these chemicals is still very much unclear [12,28,44]. Moreover, the use of corrosion inhibitors has often been criticized because of their apparent environmental adverse effects and also because of some inaccuracies appearing in the reported studies. For example: (a) the difference between corrosion and red water is sometimes overlooked; (b) The analysis of the results is frequently improper, which might lead to wrong conclusions. Such is the case when the concentration of dissolved iron is measured instead of total iron (dissolved and suspended). This difference is essential, since in the presence of inhibitors, iron is released to the water in the form of stabilized particles [28]. Thus, when measuring the concentration of dissolved iron, it might be mistakenly concluded that the iron release (and hence also corrosion rate) has decreased (e.g. in [47]), while total iron measurement may lead to an opposite conclusion. (c) It has been shown that the some corrosion inhibitors had adverse effects related to lead release. (d) It has been shown that even small phosphorus dosages are correlated with an increase in the total microbial count in water from drinking water distribution systems [48,49], however this issue is still under debate. (e) There are several pathways by which phosphorous added to drinking water can be reduced to toxic PH_3 [50]. In addition, there are ample indications that

reduced phosphorous can in fact enhance iron corrosion in drinking water systems.

To conclude, it is possible that phosphate inhibitors actually enhance iron corrosion rate, as shown in several studies (e.g. [20,28,50]) and this application has been associated with further adverse outcomes. Thus, in some locations this application was stopped and corrosion control is now maintained by adjusting the water quality with respect to Alk, Ca^{2+} and CCPP concentrations.

1.4. The need for post-treatment

The apparent conclusion that arises from the discussion in Sections 1.1 and 1.2 is that the chemical characteristics of raw desalinated water (or any other soft water, for that matter) must be modified, particularly with respect to buffering capacity; content of total hardness (TH) components (Ca^{2+} and Mg^{2+}) and corrosion-related parameters (e.g. CCPP). In order to achieve such improvements, the water has to be post-treated.

Researches and engineers have reached this conclusion several decades ago (e.g. [46,51,52]). However, comprehensive understanding of the various considerations that lead to the choice of the most appropriate target water quality has been lacking, until recently [13].

1.4.1. Post-treatment nomenclature

PT processes are sometimes termed re-carbonation-, re-mineralization- or potabilization-processes. Re-carbonation can be defined as "the elevation of the C_T (total inorganic carbon) concentration of the water" while "re-mineralization" can be defined as the introduction of minerals to the water [5]. Most PT processes are aimed at both re-carbonizing and re-mineralizing the water. Indeed, some re-carbonation techniques also re-mineralize the water, resulting in an unavoidable dependency between the mineral content of the water and its carbonate alkalinity concentration. On the other hand, supplementation of certain chemicals can result in re-mineralization of the water without its re-carbonation, e.g. $MgCl_2$ and $Ca(OH)_2$ dosage. "Potabilization" is the process by which the water becomes suitable for drinking. In desalination plants it usually refers to enriching the water with minerals, stabilizing it (i.e. re-carbonating it), and also disinfecting it [53]. It should be noted, though, that this terms are often used interchangeably. In this paper the expression "post-treatment" is used to describe the method by which the quality of the desalination process product is improved, in order to comply with drinking water regulatory requirements in terms of alkalinity, TH and corrosivity.

1.5. Subjects not included in the scope of this review: disinfection, fluoridation, boron removal and aeration

Disinfection, fluoridation, boron removal and aeration are occasionally referred to as part of the PT process. However, these issues are not discussed in the current review, which solely addresses PT processes designed to control water's buffering capacity, TH (i.e. Ca^{2+} and Mg^{2+} concentrations) and corrosivity. Nevertheless, these issues are not completely ignored in this review, and indirect influences of the PT process on them are discussed and explained.

2. Basic chemical principles

2.1. The carbonate system

The carbonate system is the main (usually even the only) weak acid system in natural fresh waters, hence it is also the only weak acid system present in desalinated product waters. The carbonate system is a di-protic weak acid system, comprising three species: $H_2CO_3^*$, HCO_3^- and CO_3^{2-}. The sum of the concentrations of the species is often denoted C_T or TIC (total inorganic carbon concentration).

In actual fact, there are four carbonate species present in the aqueous pase since $H_2CO_3^*$ is a fictitious species, representing the sum of two "real" species: H_2CO_3 and $CO_{2(aq)}$, which are in equilibrium according to the following reaction:

$$CO_{2(aq)} + H_2O \leftrightarrow H_2CO_{3(aq)} \qquad K = 1.7\cdot 10^{-3} \tag{1}$$

Note that according to the equilibrium constant of Eq. (1) the concentration of the species $CO_{2(aq)}$ is three orders of magnitude greater than the concentration of the species $H_2CO_{3(aq)}$.

Each of these species can release a proton to the water according to its own equilibrium constant. However, for the sake of simplicity, the sum of the concentration of the two species, i.e. $H_2CO_3^* = CO_{2(aq)} + H_2CO_3$, is usually considered instead of the individual concentrations. A theoretical equilibrium constant $K_{H_2CO_3^*/HCO_3^-} = 10^{-6.35}$ was established to describe the tendency of the virtual species $H_2CO_3^*$ to release a proton:

$$H_2CO_3^* \leftrightarrow HCO_3^- + H^+ \qquad K_{c1} = 10^{-6.35} \tag{2}$$

The second protonation reaction of the carbonate system is:

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \qquad K_{c2} = 10^{-10.33} \tag{3}$$

Fig. 2 describes the distribution of the carbonate system species as a function of pH, according to the quoted equilibrium constants. Note that at pH values below 5, the dominant species is $H_2CO_3^*$. Such pH values prevail at the entrance to calcite ($CaCO_3$) dissolution reactors, for example. Similarly, at $7.5 < pH < 9.5$ the dominant species is HCO_3^-. This is usually the case in the product water of a PT plant.

Understanding the characteristics of the carbonate system forms the basis for understanding the terms alkalinity, CCPP and buffer capacity, and obviously also for the design of most PT processes. Such understanding appears sometimes to be lacking. For example: a fairly highly used calcite dissolution kinetic model developed by Yamauchi et al. [54] is based on the premise that as water flows through a CO_2 based calcite dissolution reactor, the CO_2 concentration is reduced proportionally to the concentration of the calcite that has dissolved. This assumption appears to disregard the fact that calcite dissolution results in an increase in the values of Alk, C_T and pH, thus, based on the nonlinear mathematical relations between these parameters, the CO_2 concentration has to change nonlinearly as a function of the dissolved calcite concentration.

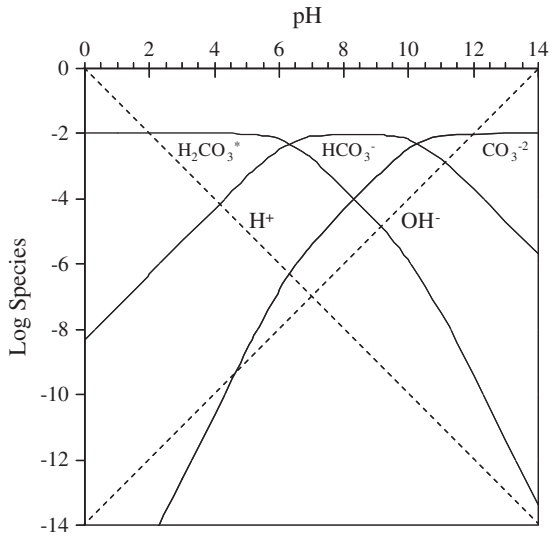

Fig. 2. pH log species representation of the carbonate system. $C_T = 10^{-2}$ M. the concentration of the species H^+ and OH^- appears in dashed lines.

2.2. Aqueous–gaseous phase interaction (CO_2 saturation state)

The carbonate system has an important component in gaseous phase—carbon dioxide ($CO_{2(g)}$). $CO_{2(g)}$ diffuses into (or out of) the aqueous phase to attain equilibrium with dissolved carbon dioxide ($CO_{2(aq)}$), which is the main (~99.7%) constituent of the species $H_2CO_3^*$ (see Eq. (1)). The equilibrium between the gaseous and dissolved species is described by Henry's law:

$$CO_{2(aq)} \leftrightarrow CO_{2(g)} \quad H = \frac{P_{CO_2(g)}}{(CO_{2(aq)})} \tag{4}$$

Where H is Henry's constant for CO_2 (30.2 bar M^{-1}); $P_{CO2(g)}$ stands for the partial pressure of $CO_{2(g)}$ (bar); and ( ) stands for activity (M).

The partial pressure of $CO_{2(g)}$ in the atmosphere is constant and equals $3.7 \cdot 10^{-4}$ bar. Thus, according to Henry's law, if equilibrium between the two phases is attained, then the concentration of $CO_{2(aq)}$ would also be constant and would equal 0.54 mg/l at 25 °C, according to:

$$\left(CO_{2(aq)}\right) = \frac{P_{CO_2(g)}}{H_{CO_2}} \cdot M_{WCO_2} = \frac{3.7 \cdot 10^{-4} bar}{30.2\left(\frac{bar \cdot L}{mol}\right)} \cdot 44,000 \frac{mgCO_2}{mol} = 0.54 \frac{mgCO_2}{L} \tag{5}$$

When the water is in contact with the atmosphere, from the practical point of view there are two initial water qualities of interest: (1) water characterized by a dissolved CO_2 concentration greater than 0.54 mg/l, i.e. oversaturated with regard to atmospheric CO_2. Such waters will therefore, tend to release CO_2 gas; and (2) The dissolved CO_2 concentration is below 0.54 mg/l. Hence, the solution is undersaturated with regard to atmospheric CO_2. Consequently, CO_2 will tend to be absorbed from the gaseous phase to the solution.

When CO_2 is released from solution, the pH value increases and the C_T concentration decreases. Similarly, absorption of CO_2 into solution decreases pH and increases C_T. The Alk ($H_2CO^*_{3\,alk}$) concentration remains constant when CO_2 is released or absorbed into solution (see Section 2.3).

Several steps in the PT processes can include deliberate or unintentional emission/absorption of CO_2. Thus, understanding these processes is essential for making the right decisions in designing and operating a PT process.

2.3. $H_2CO^*_{3\,alkalinity}$

The term "Alkalinity" in drinking water typically refers to the value of $H_2CO_3^*$ alkalinity, which is defined as the proton accepting capacity of the water with respect to $H_2CO_3^*$ as reference species ([55]). Such alkalinity value is typically determined by strong acid titration to a pH value close to 4.5 (i.e. close to the $H_2CO_3^*$ equivalence point, where all the proton accepting species are converted to $H_2CO_3^*$, see Fig. 2), or, more accurately, by applying the Gran titration technique [56]. The mathematical expression of this value is given in Eq. (6):

$$\text{Alkalinity}_{(H_2CO_3^*)} = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] - [H^+] \tag{6}$$

Where alkalinity is expressed in units of meq/l, and [ ] stands for concentrations in mmol/l.

The concentration of each of the species of the carbonate system is a function of C_T, pH and the equilibrium constants of the carbonate system: K_{c1} and K_{c2} (see Eqs. (2) and (3)). Therefore, Alk is a function of C_T and pH. For a given pH value a higher C_T value results in a higher Alk concentration. Out of the advantages gained from maintaining a high Alk value, attaining a sufficient buffer capacity and CCPP values are the most significant, as mentioned before.

Note that the Alk concentration of a given solution (Eq. (6)) is unrelated to its TH value and these terms should not be used interchangeably. Seacord et al., [13] for example, incorrectly states that "calcium hardness may assist in buffering pH", while TH obviously does not contribute to the buffer capacity).

2.4. Buffer capacity

Buffer capacity is defined as the ability of water to withstand changes in pH when a strong base or a strong acid are added to it. The Buffer capacity, β, of natural water can be calculated from the knowledge of the alkalinity value (or C_T) and the pH using Eq. (7):

$$\beta = \frac{dC_b}{dpH} = \frac{2.303 C_T K_{C1}(H^+)}{(K_{C1} + (H^+))^2} + \frac{2.303 C_T K_{C2}(H^+)}{(K_{C2} + (H^+))^2} + 2.303\left(\left(H^+\right) + \left(OH^-\right)\right) \tag{7}$$

Where dC_b = differential quantity of strong base or strong acid added to the solution and dpH = differential change in pH due to the addition of a dC_b amount of strong base or strong acid.

From Eq. (7) it can be seen that for a given C_T value, a higher buffer capacity is attained when the pH is close to the pK of the system, i.e. at pH of 6.3 and 10.3, in the case of the carbonate system. In addition, for a given pH, a higher C_T value (corresponding to a higher alkalinity value) results in higher buffer capacity. Despite this relationship, it should be pointed out that Alk and buffer capacity are, naturally, not similar parameter, contrary to the way they are, sometimes, incorrectly referred to (e.g. [8]).

When a strong acid, for example, is dosed to a water containing a weak acid (e.g. the carbonate system), the proton accepting species of the weak acid (i.e. CO_3^{-2} or HCO_3^-, in this case), reacts with the protons to form the more acidic species of the weak acid system (Eq. (2) and (3)), thus the extent of pH drop is decreased. Similarly, when strong base is dosed to such a solution, pH elevation is minimized by the reaction of the proton donating species ($H_2CO_3^*$ and HCO_3^-) with the hydroxide ions.

Supplying well buffered water ensures that the pH value remains fairly constant, regardless of processes the water might be subjected to in water treatment facilities, in the distribution system, and in downstream wastewater treatment plants. Examples of its importance include the fact that high buffer capacity inhibits potential pH drop in distribution systems as a result of chlorination and fluoridation. In the context of PT, buffer capacity has an important effect on the rate of dissolution of minerals such as dolomite and calcite (see Sections 2.6 and 2.7), as well as on the required dosage of NaOH required for the final pH adjustment in these processes. Again, comprehensive understanding of these principles appears sometimes to be limited. For example, Yamauchi et al. [54] observed that for a higher Alk at the outlet of the calcite dissolution reactor a greater dosage of NaOH is required, in order to attain a given pH. The authors claimed that this was a result of the higher CO_2 concentration [54], while it was clearly the effect of the higher buffer capacity.

2.5. pH

pH, the negative logarithm of the active H^+ concentration, can give a general indication regarding the acidic or basic nature of the solution. However, it should be born in mind that the pH value alone does not provide sufficient information on the acid-base characterization of a given water sample, since having a required pH in combination with very low buffer capacity may often result in a significant pH change due to a variety of downstream chemical reactions. Thus, information on the alkalinity or the C_T concentration in the water, in addition to the value of pH, is essential in order to define the acid-base characteristics of the water.

2.6. $CaCO_3$ solubility

Thermodynamically, the dissolution of metal carbonates can be described by the following parallel reactions, which occur at the solid/water interface [57]:

$$MeCO_3 + H^+ \xrightarrow{k_1} Me^{2+} + HCO_3^- \quad (8)$$

$$MeCO_3 + H_2CO_3^* \xrightarrow{k_3} Me^{2+} + 2HCO_3^- \quad (9)$$

$$MeCO_3 \xleftrightarrow{k_4} Me^{2+} + CO_3^{2-} \quad (10)$$

Where, Me^{2+} represents Ca^{2+} or Mg^{2+}.

Note that as a result of the dissolution process either bicarbonate (as described in Eqs. (8) and (9)) or any other species of the carbonate system can form, as a function of pH and not directly of the dissolution path. In other words, although Eqs. (8) and (9) describe the formation of bicarbonate, however, if solution pH is lower than 6, the dominant species will be $H_2CO_3^*$.

Water is defined as over- or under-saturated with respect to $CaCO_{3\,(s)}$ by comparing the product of Ca^{2+} and carbonate (CO_3^{2-}) activities present in the water (denoted Q) to $K_{sp(CaCO3)}$. In case $Q>K_{sp}$ the water is oversaturated, and in case $Q<K_{sp}$ the water is under-saturated.

In most raw desalinated waters the influence of ionic strength and formation of ion pairs can be neglected and thus analytical concentrations can be used rather than activities. Accordingly, the dissolution/precipitation propensity of $CaCO_3$ (denoted also calcite, limestone or marble, and consists mainly of the calcite mineral) can be considered to be an exclusive function of the concentrations of Ca^{2+} and carbonate (CO_3^{2-}) ions. The concentration of the latter is a function of pH and C_T (or any other two independent parameters, as explained in Section 2.1.). A low pH value corresponds to a high $CaCO_3$ dissolution potential (high Calcium Carbonate Dissolution Potential (CCDP) value), even when the C_T is very low. This can be explained as follows: dissolution of $CaCO_3$ releases Ca^{2+} and CO_3^{2-} to the water. At low pH values (e.g. pH~2), the CO_3^{2-} ions react with H^+ ions (present at a high concentration) to form HCO_3^- and thereafter $H_2CO_3^*$, according to Eqs. (2) and (3) (occurring from right to left), respectively. Thus, only if a sufficiently high amount of $CaCO_3$ is dissolved, the pH increase becomes high enough so that the CO_3^{2-} concentration increases significantly (see Fig. 2), leading to a significant increase in the value of Q resulting in decreased dissolution potential. Therefore, reducing the pH of desalinated water by dosage of a strong acid is a common method for elevating the dissolution propensity of the water with respect to $CaCO_3$. Another option for enhancing $CaCO_3$ dissolution is by dissolving $CO_{2(g)}$ in the water. In this alternative, the pH is also lowered, but to less acidic values relative to strong acid addition. On the other hand, since the dissolution of CO_2 elevates C_T, this, in turn, contributes to the dissolution capacity of the water because a higher C_T value results in a higher buffering capacity. Thus, a significant amount of $CaCO_3$ may be dissolved, before pH and consequently the concentration of CO_3^{2-}, are increased and dissolution potential exhausted.

From the stoichiometric standpoint, $CaCO_3$ dissolution results in addition of Ca^{2+} and C_T to the water at a 1:1 molar ratio. The ratio between Ca^{2+} and Alk added to the water is also 1 to 1, in meq/l units.

2.7. Dolomite solubility

Busenberg and Plummer [58] suggested that the dissolution of the mineral dolomite under acidic conditions (pH<5) is a two step process, the first step described by Eq. (11):

$$MgCa(CO_3)_2 + H^+ \longrightarrow MgCO_3 + Ca^{2+} + HCO_3^- \quad (11)$$

The second step, which is the slower and thus rate limiting step, is described by Eq. (12):

$$MgCO_3 + H^+ \longrightarrow Mg^{2+} + HCO_3^- \quad (12)$$

The stoichiometric addition of Ca^{2+}, Mg^{2+} and C_T to the water as a result of dissolution of a pure dolomite mineral is at a molar ratio of 1:1:2.

Kinetics wise, at similar water quality and operational conditions, the dissolution of dolomite is much slower than that of calcite [48,59,60]. For example, Liu et al [59] reported that the dissolution rate of dolomite is lower by a factor of 3 to 60 relative to calcite. Due to the slow dissolution kinetics hardly any data exists on the potential use of dolomite in the context of water treatment. The few examples for the use of dolomite in the context of water treatment that appear in the literature include works that describe the application of crushed dolomite to water with the aim of mitigating acidification of streams and lakes [61–63]. In these applications dolomite was used to raise the pH to above pH6 using a retention time of several days. For these quoted applications the slow kinetics of the process was not considered disadvantageous. However, for PT processes, the slow kinetics, which translates into large dissolution reactors, may constitute an economic problem.

Beyond these reports the information on dolomite dissolution within water treatment works is very limited, as further discussed in Section 3.4.

2.8. $CaCO_3$ dissolution indices

As corrosion in distribution systems poses a significant economic and health problem, determining the potential corrosivity of given water is perceived important, as reflected by the large number of aggression-related indices developed over the years. The most commonly used and investigated indices are listed in Table 1.

It is commonly hypothesized that deposition of a thin layer of $CaCO_{3(s)}$ acts to minimize the rate at which metal pipes are corroded [29]. Thus, supplying water that has a slight tendency to precipitate $CaCO_{3(s)}$ is considered a corrosion control strategy. For this reason many of the so-called "aggression indices" or "corrosion indices" are in fact calcite dissolution indices [28]. There are several problems associated with the use of each index, and many studies have shown rather poor correlation between the indices' prediction and actual corrosion rate (e.g. [28,35,64–68]). Moreover, as mentioned by Seacord et al. [13], the indices are too often applied incorrectly, due to what seems to be lack of understanding of the fundamental principles by which they were developed. The AWWA manual on corrosion, for example, states explicitly that the use of Langelier Saturation Index (LSI) should be abandoned [69]. Rossum and Merrill [67] compared a large number of indices. They concluded that CCPP is the best suited index to describe the water's saturation state with respect to calcite; Seacord et al. [13] arrived to a similar conclusion.

Table 1
Important properties of principal water corrosion indices.

Index	$CaCO_{3(s)}$ solubility based on thermodynamics	Other considered parameters	Source
LSI	Yes	Ionic strength and temperature	
CCPP	Yes	Ionic strength and temperature	[29]
Riddick Corrosion Index	No	(Cl^-), (SiO_2), (DO) TH and nitrate	Cited in [35]
Driving Force Index	Yes		Cited in [35]
Aggressiveness Index	No	pH, TH	[93]
Larson Index (LI)	No	(Cl^-), (SiO_2), (HCO_3^-)	Cited in [35]
Singley Index	No	Buffer capacity, EC	[66]

CCPP is the only quantitative $CaCO_{3(s)}$ precipitation index [13,35]. However, it should be kept in mind that CCPP is a pure calcite-related index, and as such it has limited capability in predicting corrosion phenomena unrelated to calcite dissolution. For example, it does not take into account the corrosive nature of high concentrations of Cl^- and SO_4^{2-}.

2.9. Main gaps in knowledge

In the context of PT processes, the kinetics of the dissolution of both calcite and dolomite in packed bed reactors has not yet been sufficiently quantified. Although the dissolution kinetics of these minerals, under the conditions found in nature, is well defined, this data cannot be used directly in the water treatment field because the chemical and hydraulic conditions prevailing in dissolution reactors are completely different than those prevailing in nature. Consequently, the precise water quality at the outlet of the dissolution reactor as a function of the reactor's operational parameters cannot be predicted with reasonable accuracy, to-date [70]. However, it is already well known that the dissolution rate of calcite is much more rapid than that of dolomite. Therefore, the use of calcite to dissolve Ca^{2+} and alkalinity to the water is much more common than the use of dolomite. A few theories on the calcite dissolution inside reactors have been developed. However, as also concluded by others, e.g. [8,70,71], the published models are inadequate for predicting the dissolution performance of reactor operation relevant to PT, for several reasons: (1) the models are aimed at predicting the performance of reactors in which the conditions are irrelevant to typical PT needs. (2) Most of the models describe CO_2-based dissolution kinetics, and cannot be used for predicting H_2SO_4 based dissolution. (3) The assumptions on which some of the models are based are chemically inaccurate.

Dolomite dissolution, on the other hand, is less commonly practiced as means of improving water quality. Thus, relevant data on this subject is even scarcer. Water quality attained when dissolving dolomite for the purpose of water de-acidification under several operational conditions is shown and discussed in Birnhack et al. [72]. In addition, it is mentioned in some papers that semi-calcined dolomite ($MgO{\cdot}CaCO_3$) is more suitable than excavated dolomite for water treatment purposes (e.g. [26,64]). There are other aspects relevant to dolomite dissolution, which are not yet fully understood, apart from reaction kinetics. For example, dissolving semi-calcined dolomite appears to be identical to dissolving two pure minerals (calcite and magnesium oxide) at the same time. Since it is practically impossible to attain water that is in equilibrium with the two minerals, a situation can occur in which the water is oversaturated with respect to one of the minerals and under-saturated with respect to the other. As a result, time fluctuations in water quality ($[Ca^{2+}]$, $[Mg^{2+}]$, C_T, pH, etcetera) may be expected to occur, as well as difficulties in reactor operation, as observed by Ginocchio [26].

In addition to these gaps in knowledge, it should be noted, that surveying the published PT literature shows that even the knowledge that is already well established, is often overlooked or misunderstood. The aim of the current review is to bring together all the relevant knowledge including the relevant theoretical background, the advantages and drawbacks of commonly practiced PT processes as well as PT processes which are still under development.

3. State of the art of PT methods

3.1. Direct dosage of chemicals

Direct dosage refers to direct injection of chemicals to the water. The chemicals may be either in a slurry form (usually hydrated lime, $Ca(OH)_2$, as discussed in Sections 3.1.1 and 3.1.2); dissolved in solution (e.g. calcium salts, as detailed for example in Section 3.1.3), or in a condensed, liquid form ($CO_{2(l)}$) that transforms to $CO_{2(g)}$ and dissolves in the water (as discussed in Sections 3.1.1 and 3.1.4). Most direct dosage treatments combine the addition of TH and alkalinity to the water. However, as a function of the required product water quality, in some cases only alkalinity is supplied, as demonstrated in Sections 3.1.7 and 3.1.9). This is, in most likelihood, an outcome of a poor understanding of the inverse impact of supplying soft water.

The main advantages of applying a direct dosage of chemicals are simplicity, the relatively low capital cost and required space, and the flexibility with regard to product water quality, i.e. the wide range of water qualities that can be attained. Table 2 summarizes the chemicals which are usually applied in post-treatment units based on "direct dosage" methods and the associated ions and other water quality parameters (i.e. C_T and Alk) added to the water as a result of the dissolution of 1 mol of each of the chemicals. Clearly, by choosing appropriate chemical dosages, a wide range of water qualities can be achieved. However, the disadvantages of this method include high operational costs due to the high cost of the chemicals and/or their preparation on site [73] and the unavoidable addition of unwanted counter ions. The practical chemical combinations typically dosed to desalinated water and the associate changes in water quality are detailed in Sections 3.1.1 through 3.1.4. Note that direct dosage of each of these chemicals can be applied as a complementary practice to any other PT approach.

3.1.1. $Ca(OH)_2 + CO_2$

Lime ($Ca(OH)_2$) enriches the water with both TH and alkalinity (at a 1:1 ratio, in equivalent units), however, carbonate alkalinity is not added, as shown in Table 2. Thus, this method does not contribute to the (carbonate) buffer capacity of the water. Moreover, in order to efficiently dissolve hydrated lime, the water must be first acidified. Therefore, CO_2 is dissolved into the water prior to the addition of hydrated lime. Hydrated lime is dosed as slurry, and CO_2 is applied in a condensed, liquid form ($CO_{2(l)}$) which transforms to $CO_{2(aq)}$ in the water. Due to these applications' techniques, the method has several drawbacks. For example, the use of hydrated lime slurry is relatively complex from the engineering point of view [5,51,74,75], especially if the permeate is warm, which reduces the solubility of lime [13]. In addition, the approach may raise water turbidity to values higher than 5 Nephelometric Turbidity Units (NTU) [5,13,73,76]. Finally, the method is associated with control problems, i.e. difficulties in maintaining consistent product water pH [5]. On the other hand, in this alternative no unwanted counter ions are added to the water (Table 2). In spite of the its known drawbacks, this method is widely applied [74]. For example, in a survey of approximately 100 Swedish municipalities it was found that 73% used this method [18]. Fig. 3 shows a photo of the lime feed system in the Tampa Bay SW desalination plant.

3.1.2. $Ca(OH)_2 + Na_2CO_3$ or $Ca(OH)_2 + NaHCO_3$

Using Na_2CO_3 or $NaHCO_3$ as the C_T source instead of CO_2 (as in the previous alternative) results in an elevated pH value, since these salts

Table 2
The increase in Na^+, Cl^-, C_T, Alkalinity and Ca^{2+} as a result of the dissolution of 1 mole of each of the chemicals applied via "direct dosage" methods.

Chemical dissolved (1 mol)	Added quantity				
	Na^+	Cl^-	C_T	Alkalinity	Ca^{2+}
	Equiv	Equiv	mol	Equiv	Equiv
CO_2[a]	0	0	1	0	0
$NaHCO_3$	1	0	1	1	0
Na_2CO_3[a]	2	0	1	2	0
$Ca(OH)_2$[a]	0	0	0	2	2
$CaCl_2$[a]	0	2	0	0	2
NaOH	1	0	0	1	0

[a] 1 mol of chemical equals 2 equivalents.

consist of the basic species of the carbonate system. Consequently, the dissolution potential of lime decreases, and more significantly, even at relatively low alkalinity and Ca^{2+} concentrations (~30 mg/l as $CaCO_3$ and ~10 mg/l, respectively) the resulting pH is excessively high (pH>10.5), making this approach impractical. Accordingly, Withers, [5] states that this method is more appropriate to raw waters which contain a certain initial alkalinity and relatively high $CO_{2(aq)}$ concentration, which is naturally characterized by relatively low pH values. In such case, the raw water contains a substantial amount of buffer capacity as compared to seawater RO permeates, and thus and the dissolution capacity of lime is increased. Comparing this combination to the one described in Section 3.1.1 (CO_2 based lime dissolution) shows that attaining the same C_T and Ca^{2+} concentration in both methods would result in lower product water alkalinity if CO_2 is used, as can be concluded from Table 2. Moreover, the methods based on dissolving $NaHCO_3$ and Na_2CO_3 result in unwanted elevated Na^+ concentration in the product water.

3.1.3. $CaCl_2 + NaHCO_3$

This process is based on simple dissolution of chemicals, and no handling of slurries or gases is required. Hence, from the engineering point of view, it is simpler than the first two options discussed in Sections 3.1.1 and 3.1.2. However, $CaCl_2$ is often a more expensive source of Ca^{2+} than lime and the method involves the introduction of unwanted Cl^- and Na^+ ions to the water. Withers, [5] stated that further pH adjustment is often required when applying this alternative. This statement is puzzling, since dissolution of $NaHCO_3$ results in a pH value around 8.3 (the HCO_3^- equivalent point), and the addition of $CaCl_2$ can lead to practically any required CCPP value. It is correct however, that at low Ca^{2+} concentrations (Ca^{2+}<80 mg/l as $CaCO_3$) pH elevation is required to attain positive CCPP (or LSI).

Note that in the scientific literature the following combinations are also mentioned: $CaCl_2 + Na_2CO_3$ and $CaCl_2 + NaHCO_3 + Na_2CO_3$ [6]. However, to the writers' understanding, these methods are impractical since the combined addition of bicarbonate and carbonate ions render product water pH (and thus also CCPP) excessively high.

3.1.4. $Na_2CO_3 + CO_2$ or $NaOH + CO_2$

These alternatives are also mentioned in the literature and even practiced in a few desalination plants, although they do not involve the addition of Ca^{2+} or TH to the water, and thus, no $CaCO_3$ dissolution index can be satisfied. Accordingly, these alternatives can be considered only for elevating the carbonate alkalinity and the pH value of acidic water. Nevertheless, Berghult et al., [18] for example, stated that 9% of the Swedish municipalities used this method as means of corrosion control, although the natural Ca^{2+} content in the water was very low. Another example is given by Sung et al. [10], who described the treatment procedure in the Massachusetts Water Resource Authority, which supplies water to 43 communities: the raw water, which is very low in hardness (13 mg/l as $CaCO_3$) and alkalinity (5 mg/l as $CaCO_3$), is treated with NaOH and CO_2 as means of corrosion control.

3.2. Blending

Blending of SW or BW may be considered a low-cost method to increase the concentration of some desired ions in desalinated water, but it invariably adds other, undesired species, to the water. The concentrations of all the introduced salts are a function of the blended water composition and the dilution fraction. Thus, control over product water quality is limited. Consequently, blending is not recommended for water intended for domestic use [73] or agricultural use [77]. When desalinated water is destined for irrigation, blending with seawater (SW) or brackish water has both negative environmental and economic implications such as elevation in the concentrations of boron, chlorides and sodium ions. Nevertheless, the scientific literature continues to address the option of blending either as a sole re-mineralization technique, e.g. when groundwater is blended with permeate [14,78–80], or as a complementary alternative [14,51]. Since it is often recognized that blending alone introduces mainly TH and TDS to the water, in case blending is practiced as a PT approach, it is in many cases followed by pH correction. For example, in the City of Abu Dhabi, which receives practically all its water from a desalination plant, the PT approach is to blend the permeate with SW at a ratio of 1:500 followed by final pH elevation by NaOH dose [64].

3.3. Calcite dissolution

Unlike direct dosage, calcite and also dolomite dissolution processes are conducted in reactors, in which the retention time is in the order of minutes (typically <15 min). These reactors are often mistakenly termed "filter beds" although their exclusive purpose is the introduction of Ca^{2+} and CO_3^{2-} (and also Mg^{2+} in case dolomite is dissolved) to the water through dissolution, and not filtration. In order to enable rapid dissolution of a high $CaCO_3$concentration, the pH must be reduced before desalinated water is introduced into the dissolution reactor (as explained in Section 2.6). It should also be stressed that in any dissolution reactors thermodynamic equilibrium is in practice not attained, due to kinetic limitations. In other words, the CCPP of the water leaving the calcite dissolution reactor is always slightly negative. Thus, although the dissolution of $CaCO_3$ results in elevated pH (pH~6.5) it must be further increased, both for achieving a more appropriate pH value for drinking water and mainly for elevating the $CaCO_3$ precipitation potential above zero i.e. to produce water that is chemically stable within the distribution system. Fig. 4

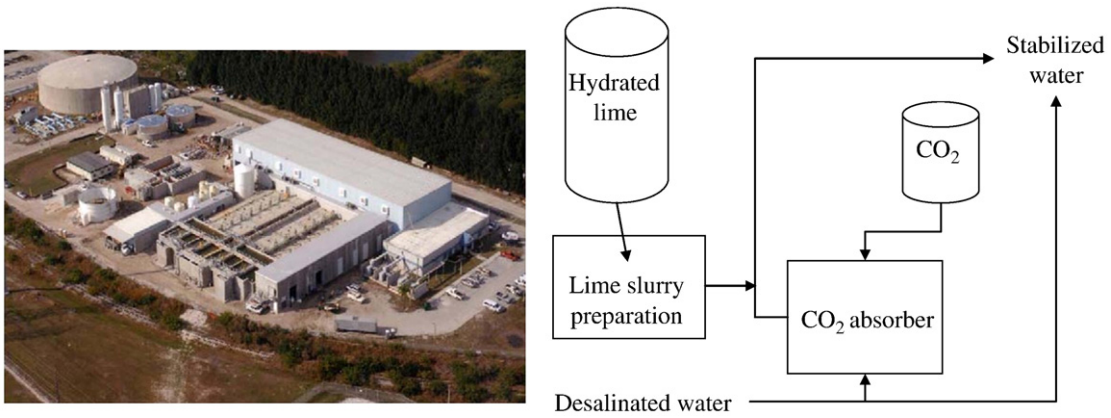

Fig. 3. Tampa Bay Seawater Desalination Plant (Left hand side, lime feed system shown in upper left corner); right hand side: schematic of the CO_2 and lime direct dosage process.

shows the calcite addition system in the Ashkelon SW desalination plant in Israel.

3.3.1. Acidifying agents used to enhance calcite dissolution

Two acidic substances are typically used to lower pH: H_2SO_4 and $CO_{2(g)}$. Unless an unconventional low-cost source of CO_2 is available (such as treated power station exhaust gas), using a strong acid such as H_2SO_4 is a less costly and simpler practice. Therefore, this approach was chosen, for example, as the PT method in the Ashkelon (130 Mm^3/y) and Palmachim (45 Mm^3/y) desalination plants in Israel. The main advantage of this approach is that, due to the high CCDP values that can be attained when a strong acid is introduced to the water and the rapid dissolution rate of calcite under these conditions, it is possible to dissolve a significant amount of calcite in the water that passes through the reactor, and let the majority of the flow (between ~70% and ~85% of the total flow rate of the plant, in case the product water alkalinity should be ~80 mg/l as $CaCO_3$), bypass the reactor, a fact that renders the reactor considerably less costly [81]. The percentage of treated water out of the total desalinated water flow rate is denoted "% split flow" in this review (see Fig. 5).

From the water quality standpoint, the main difference between applying H_2SO_4 and CO_2 is that the H_2SO_4-based calcite dissolution process results in dissolved calcium to alkalinity concentration ratio that is always equal to or higher than 2 to 1 (in equivalent units) while the alternative process, i.e. CO_2-based calcite dissolution, results in a ratio of approximately 1 to 1. This statement is corroborated by the characteristics of the product water produced in PT plants that apply this method [79,82,83]. The obtained ratios are discussed in detail in [7]. The 2 to 1 ratio can be explained by the data shown in Table 3, which presents the alterations in alkalinity, acidity (Acd) and Ca^{2+} concentrations as a result of applying the H_2SO_4-based calcite dissolution process (acidity in this context is defined as the hydroxide ions accepting capacity of a solution with respect to the species CO_3^{2-}, i.e. Acd = acidity $(CO_3^{2-}) = 2[H_2CO_3^*] + [HCO_3^-] + [H^+] - [OH^-]$). The process ends when the pH is raised (by NaOH addition) to around 8.3, i.e. close to the HCO_3^- equivalent point. At this point the Alk value exactly equals the Acd value. Substituting the expressions for the final Alk and Acd (given in the last row of Table 3) yields:

$$Alk_{final} = Acd_{final} \quad \Rightarrow \quad y + z - x = x - z$$

Thus,

$$y = 2(x - z)$$

and thus:

$$Alk_f = y - (x - z) = 0.5y, \text{ i.e. exactly half the } Ca^{2+} \text{ concentration.}$$

The 1:1 ratio attained in the CO_2 based process can be simply derived from the data given in the first row of Table 2 and the second row of Table 3.

Note that the dissolution rate of calcite at pH<5.5 is significantly faster than the rate observed at higher pH values (or in other words at lower CCDP values). As a result, in H_2SO_4 based dissolution reactors, ~75% of the calcite is dissolved in the first ~15 cm of the reactor. At this point (i.e. after the water has passed ~15 cm in the reactor), once the majority of calcite had dissolved, and pH has been raised to between pH4.5 and pH6, the $CO_{2(aq)}$ concentration may become very high, and in fact, acid/base conditions closely resemble those prevailing in a the entrance to a CO_2-based dissolution reactor.

Calcite dissolution enhanced by a combined dosage of CO_2 and H_2SO_4 is also theoretically possible. In this case the resultant water quality (e.g. from the Alk to Ca^{2+} ratio and the CO_2 concentration perspectives) will fall in between the qualities obtained when either CO_2 or H_2SO_4 are applied as the sole acidifying agent.

3.3.2. Final pH adjustment

As mentioned, calcite dissolution results in pH values slightly lower than pH7.0. Arriving at the final pH value in drinking water applications typically involves controlled addition of NaOH. However, in some cases it can also be carried out by controlled CO_2 stripping. pH elevation by CO_2 stripping can be practiced only in cases in which the solution coming out of the dissolution reactor is significantly supersaturated with respect to atmospheric $CO_{2(g)}$, since this technique it is based on emitting excess CO_2 and approaching aqueous–gas phase equilibrium with respect to CO_2. As a result, this approach can be applied only when CO_2 is used as the acidifying agent. The maximal final pH value that can be theoretically achieved in this method is primarily a function of the extent of super-saturation, i.e. the concentration of CO_2 that can be emitted before equilibrium is approached. In practice, thermodynamic equilibrium can never be attained because of kinetic limitations. However, the final distance from equilibrium can be controlled by engineered parameters, such as the applied air flow rate, the hydraulic retention time and the average air bubbles size.

Often, following the stripping step, the pH and CCPP values are still not sufficiently high. In such cases further pH elevation is realized by NaOH dosage, as practiced, for example, in Kuwait [82] and Qatar [83].

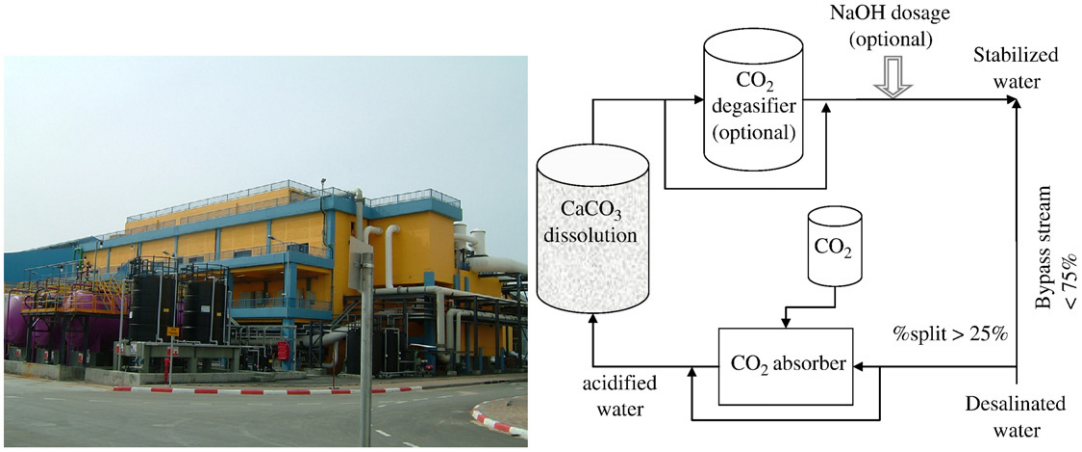

Fig. 4. Calcite contact tanks for the Ashkelon SWRO Plant in Israel (left hand side); Schematic of the CO_2 based calcite dissolution process (right hand side), as applied in the Hadera desalination plant in Israel . Final pH adjustment can be achieved either by CO_2 stripping or by NaOH dosage.

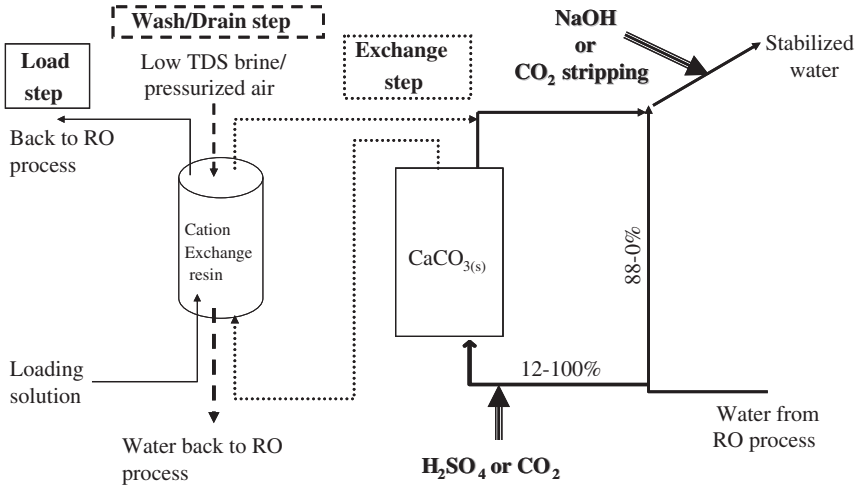

Fig. 5. Schematic of the post-treatment process based on calcite dissolution followed by IX.

3.3.3. Unintentional $CO_{2(g)}$ emission

CO_2 based $CaCO_3$ dissolution reactors are normally operated at pressures higher than atmospheric (i.e. sealed reactors). Obviously, loss of CO_2 to the atmosphere is minimal in these reactors. On the other hand, H_2SO_4 based $CaCO_3$ dissolution reactors are often open to the atmosphere, since unsealed reactors are less costly and easier to maintain. In such reactors, after a significant amount of calcite has dissolved, the water is characterized by low pH values (~pH5) and a relatively high C_T concentration, which is comprised almost entirely of $CO_{2(aq)}$. In other words, the water is highly supersaturated with respect to atmospheric CO_2. At the outlet of the reactor, the C_T concentration is higher, but the pH is also higher. Consequently, the dissolved CO_2 concentration is lower (see Fig. 2). Nevertheless, super-saturation still prevails. According to this description, it is clear that either up-flow or down-flow operation of H_2SO_4 based $CaCO_3$ dissolution open reactors can result in CO_2 loss to the atmosphere. It is worthy to note that CO_2 emission does not affect the calcium or Alk concentrations; on the other hand, it reduces the Acd value, and elevates pH. As a result, a decreased dosage of NaOH is required in order to reach the same final pH (~8.3), and thus the elevation of the Alk concentration as a result of NaOH dosage is also lower. In this case, the ratio between dissolved calcium and alkalinity concentrations in the product water is higher than 2, as observed in the water quality produced, for example, in the Ashkelon plant: Alk = 45–50 mg/l as $CaCO_3$ and $[Ca^{2+}]$ = 90–110 mg/l as $CaCO_3$ [79].

3.4. Dolomite dissolution

Dissolution of quarry dolomite ($CaMg(CO_3)_2$) as means of supplying carbonate alkalinity, Mg^{2+} and Ca^{2+} ions to the water as part of the PT step suffers from several drawbacks: (1) The dissolution rate of dolomite is slow relative to that of calcite, thus, the required reactors' volume is large, as compared with equivalent calcite dissolution reactors. (2) Dolomite dissolution practically stops at low pH values (the magnesium part of the rock stops dissolving at ~pH5.5) and low alkalinity concentrations [72]. Consequently, the water leaving the dissolution reactor has a highly negative CCPP value (i.e. high CCDP value) and low buffer capacity. Consequently, the increase in pH due to NaOH dosage is steep, and excessively high pH values may be obtained at relatively low Alk values. (3) The composition of quarry dolomite (i.e. the percentage of calcite within the excavated rock) varies from location to location and often also within the same quarry. Thus, the Ca^{2+} and Mg^{2+} concentrations in the product water are expected to vary in somewhat uncontrolled manner. (4) Engineering know-how related to dissolving dolomite for water re-mineralization purposes is lacking. (5) Problems associated with parallel dissolution of two minerals. These include both time fluctuation in water quality ($[Ca^{2+}]$, $[Mg^{2+}]$, pH and the Alk concentration) and operational difficulties. Because of these negative aspects of dolomite dissolution it was concluded that it is probably impossible to generate water quality that complies (for example) with the Israeli criteria for desalinated water, using this alternative. Evidently, this approach is very rarely used. However, similarly to the blending method, it is also widely mentioned in the scientific literature as a PT alternative (e.g. [26,46,51,64,84]). According to reports dolomite dissolution is practiced for soft waters stabilization by ~9% of the Swedish municipalities [18].

Table 3
Alterations in water quality parameters as a result of the H_2SO_4-based calcite dissolution process steps.

Chemical added in the process	Dosage	Alteration in component value		
		Alk	Acd	$[Ca^{2+}]$
	eq/L	eq/L	eq/L	eq/L
H_2SO_4	x	−x	+x	0
$CaCO_3$	y	+y	0	+y
NaOH to ~pH 8.3	z	z	−z	0
Product water		y+z−x	x−z	Y

3.5. Combination of PT methods

High flexibility and efficiency (with respect to water quality, process costs, engineering aspects and more) may be attained through combining two or more of the treatment approaches introduced above. A few examples of such combinations are described below:

1. Calcite dissolution followed by direct dosage of $Ca(OH)_2$, as practiced in the 130 Mm^3/y Hadera desalination plant, Israel, where calcite is dissolved using CO_2 [79].
2. CO_2 calcite dissolution and BW blending, as practiced in Eilat, Israel [78], or SW blending.
3. Application of a direct dosage method combined with SW or BW blending.
4. CO_2-based calcite dissolution, followed by pH adjustment using $NaHCO_3$ or Na_2CO_3 (i.e. direct dosage); and finally, blending the

treated water with SW at a range of less than 1%. As suggested by Gabbrielli [51].

5. CO_2 dissolution of semi-calcined dolomite, complemented by blending with SW at a 0.5% ratio, so that only 100 mg/l and 60 mg/l of Cl^- and Na^+, respectively, are introduced to the product water. This option was suggested by Gabbrielli [51] for cases in which carbonate rocks are not available for the post-treatment stage. No direct dosage is required in this process scheme.

4. New and innovative post-treatment processes

Two parallel trends led to recent development of new PT methods: (1) the increasing acknowledgment for the need for efficient PT solutions capable of producing water complying with new and more stringent quality criteria; and (2) the recently accumulated evidence on the importance of Ca^{2+} and Mg^{2+} in drinking water (e.g. [34,42,85,86]), in water used for agricultural irrigation [15] as well as in aquaculture.

In Section 3 the currently applied PT methods are described. From this evaluation it is clear that hitherto no PT is available that supplies Mg^{2+} in a cost-effective manner, and which also results in low addition of unwanted components to the water. The two newly developed PT methods are aimed at addressing these issues.

4.1. Calcite dissolution combined with an ion exchange step (IX) (The calcite dissolution-IX process)

The method is shown schematically in Fig. 5. It is based on dissolving $CaCO_3$ to supply carbonate alkalinity and Ca^{2+} ions and subsequently replacing a part of the dissolved Ca^{2+} concentration with Mg^{2+} ions which originate from the raw water supplied to the desalination plant (either SW or BW), or from BWRO brine. The Mg^{2+} rich solution is denoted in this process "loading solution" since it is used for loading an IX resin with Mg^{2+}. Separating the Mg^{2+} ions from the loading solution is performed by a specific cationic IX resin, characterized by a high affinity toward Mg^{2+} and Ca^{2+} and a very low affinity toward Na^+ ions. A detailed description of the process and pilot-scale operation results can be found elsewhere (e.g. [81,87,88]).

The calcite dissolution-IX process can be operated with either SW or BW as the loading solution. In case SW is available, it is preferred over BW, since both the Mg^{2+} concentration and the Mg^{2+} to Ca^{2+} concentration ratio are higher, resulting in higher efficiency of the Load step, which manifests itself in lower costs and higher flexibility, especially with respect to the product water Mg^{2+} concentration. A detailed description of the application of this alternative is given in Birnhack and Lahav [87]. Alternatively, when SW is not available (i.e. inland locations) BW can be used. However, the use of BW characterized by Mg^{2+} to Ca^{2+} concentration ratio lower than 1:1 was found impractical, in case H_2SO_4 is the acidifying agent [89]. The reason for this was that the mass of Mg^{2+} that could be uploaded on the resin was not sufficiently high, making the subsequent exchange step too short and the process less economically favorable.

The use of different loading solutions and different acidification alternatives i.e., CO_2, H_2SO_4 or combination of both acids (resulting in different possible %split flow values—see Fig. 5) determines the length of the exchange and load steps, for a given required Mg^{2+} concentration. Since there is a minimum practical ratio between the length of the exchange step and the load step, applying operational conditions that increase this ratio (e.g. using CO_2 as the acidifying agent or SW as the loading solution), enables supplying higher a Mg^{2+} concentration.

The use of a combination of resins may be needed in case a stringent restriction on the TH is imposed in addition to a demand for a substantial SO_4^{2-} concentration (required for agricultural uses). Under such water quality requirements, the use of CO_2 is not possible, since it results in a zero SO_4^{2-} concentration, while the use of H_2SO_4 is not a viable solution because of the high resultant TH to Alk ratio. The use of a combination of the acids may produce water that complies with the criteria. However, a combined requirement of low TH and high SO_4^{2-} concentration cannot be achieved in this way. An alternative solution is to use two different IX resins: the first resin is aimed at replacing the excess Ca^{2+} ions by Mg^{2+} ions and the second one is aimed at replacing Ca^{2+} with Na^+ [90].

4.2. Dolomite dissolution combined with calcite dissolution

As mentioned in Section 3.4, dolomite dissolution is not feasible as a sole PT method. Birnhack et al. [72] described a new process based on dolomite and calcite dissolution in series, which is capable of producing water able to meet almost any required quality criteria.

As mentioned before, the effluent of a dolomite dissolution reactor is characterized by low pH, very negative CCPP but also by a high $CO_{2\ (aq)}$ concentration and a high buffering capacity. The logic behind the new alternative is that the water leaving the dolomite reactor can be used to further dissolve calcite to increase alkalinity, pH and CCPP. Such a strategy is superior over NaOH dosage from both water quality and cost standpoints. Birnhack et al. [72] showed that the pH and C_T values in the effluent of the dolomite reactor, which were found unsuitable for further dolomite dissolution, were indeed appropriate for dissolving further several meq/l of calcite. Thus, the alkalinity and pH values obtained in the product water in this alternative were significantly higher than those obtained when the dolomite was dissolved alone. Using this method, it was possible to produce water characterized by an alkalinity value that is slightly lower than the required threshold in the Israeli criteria (i.e. 75 instead of 80 mg/l as $CaCO_3$), but the CCPP, pH value and Ca^{2+} concentration complied with the criteria, and in addition 12.4 mg Mg/l were supplied. On the down side, the use of this alternative resulted in relatively high TH concentration in the product water.

5. Comparison between PT methods

In this section, the engineering, water quality and economic aspects of several PT processes are compared. The PTs investigated in this comparison are direct dosage, calcite dissolution (CO_2-based, H_2SO_4 based, or based on a combination of the acids), blending, in series operation of dolomite and calcite dissolution reactors; and calcite dissolution followed by IX.

5.1. Water quality

The water qualities attained in the various PT processes are similar in the sense that they are all characterized by a certain Ca^{2+} and carbonate alkalinity concentrations (in the following comparison it was assumed that all the methods aim at reaching a similar Ca^{2+} concentration). However, they differ from each other in terms of other parameters. The following evaluation focuses on the key differences between the discussed PT processes with respect to six parameters. Explanation on the importance of each of the parameters is given in Section 1.4.

5.1.1. Addition of unwanted ionic compounds

Attaining a Ca^{2+} concentration of 30 mg/l through blending SW with the desalinated water will result in the addition of ~2400 mg/l of TDS to the desalinated water, out of which ~1200 mg/l Cl^- and ~700 mg/l Na^+. As a result, blending of RO permeate and pretreated SW cannot be considered a viable method to post-treat desalinated SW. Direct dosage of $CaCl_2$ at a concentration that adds 30 mg/l of Ca^{2+} to the permeate leads to the addition of 50 mg/l Cl^-. Similarly, direct dosage of $NaHCO_3$ and Na_2CO_3 results in an increase of 23 mg/l of Na^+ for each meq/l of alkalinity supplied to the water. Dissolution of limestone or dolomite rocks results in a negligible elevation of the

TDS due to impurities in the rock, and an additional very small elevation in the Na^+ concentration due to final pH adjustment carried out via NaOH dosage (around 10 mg/l). In case CO_2 stripping is applied for final pH adjustment (feasible only in case CO_2 is used as the acidifying agent) the dissolution leads to a negligible amount of unwanted TDS. The novel calcite dissolution-IX process results in a very small increase in TDS. This is the consequence of a very small volume of loading solution (SW, in the worst scenario) that remains in the bed after the drain step and is incorporated in the product water in the following "exchange" step [87].

To conclude, from the point of view of addition of unwanted species, the processes can be graded as follows: blending SW<<direct dosage of $CaCl_2$, $NaHCO_3$ and Na_2CO_3<calcite dissolution followed by IX<calcite/dolomite dissolution.

5.1.2. SO_4^{2-} supply

Any PT that relies on H_2SO_4-based calcite (or dolomite) dissolution results in the addition of SO_4^{2-} to the water. A supply of around 32 mg/l SO_4 as S is attained when H_2SO_4 is used to dissolve around 170 mg/l of calcite (all units are per liter of product water) (e.g. [89]). Such a SO_4^{2-}concentration lies within the recommended concentration for irrigation water [15]. Clearly, the water is not enriched with SO_4^{2-} when CO_2 is used for dissolving calcite. Direct dosage of $MgSO_4$ also results in a considerable concentration of SO_4^{2-}. Finally, blending SW for attaining a required Ca^{2+} concentration of 80 mg/l as $CaCO_3$ results in the addition of more than 60 mg/l SO_4 as S. the amount of SO_4^{2-} added when BW is blended with the permeate depends on the BW composition.

5.1.3. Mg^{2+} supply

As explained before, most of the PT processes do not enrich the water with Mg^{2+}. Nevertheless, a considerable concentration of Mg^{2+} can be supplied by the following alternatives: direct dosage of $MgCl_2$ or $MgSO_4$; dolomite dissolution; blending and calcite dissolution followed by IX.

The concentration of Mg^{2+} added in the direct dosage techniques is almost unlimited; in the dolomite–calcite dissolution process it is a function of the amount of dolomite dissolved, which, in turn, impacts the amount of calcite dissolved and the overall product water quality; in the calcite dissolution followed by IX process, it is a function of (1) the availability of SW, (2) the concentration of Ca^{2+} (and also the alkalinity) since in this process the Mg^{2+} ions are exchanged with Ca^{2+}, which is supplied through calcite dissolution. Thus, there is a certain linkage between the carbonate alkalinity and the Ca^{2+} and Mg^{2+} concentrations.

5.1.4. Buffer capacity

The buffer capacity attained in the water varies significantly between the PT alternatives and also within each PT, depending on the final product water (which can differ within a certain range, for a given PT). Thus, comparing the methods from the buffer capacity perspective is difficult. As stated in the beginning of this section, the baseline water quality of all compared PTs was [Ca^{2+}] of 30 mg/l. however, this constraint is not sufficient for the current evaluation since each PT can result in a variety of buffer capacities, while maintaining the same [Ca^{2+}], which itself has no influence on the buffer capacity. Therefore, another constraint was defined i.e. product water pH ~ 8.2. Under these two constraints, the PT processes can be ranked by the buffer capacity parameter as follows (from the highest to the lowest): (1) CO_2-based calcite dissolution followed by NaOH dosage; (2) CO_2-based calcite dissolution followed by CO_2 stripping; (3) $Ca(OH)_2 + CO_2$; (4) H_2SO_4-based calcite dissolution followed by NaOH dosage; (5) H_2SO_4-based dolomite dissolution followed by NaOH dosage; (6) direct dosage of $CaCl_2 + NaHCO_3$; (7) blending SW; and (8) the lowest buffer capacity is attained when $CaCl_2 + Na_2CO_3$ are dosed, since the addition of Na_2CO_3 elevates the pH dramatically, and consequently, C_T remains very low. Note that the addition of an IX stage to the calcite dissolution processes, under the above mentioned assumptions, results in a higher C_T (because more calcite is dissolved), and thus, also in a higher buffer capacity, as compared with the same dissolution process in the absence of the IX stage.

Note that the addition of lime ($Ca(OH)_2$) for achieving the required Ca^{2+} concentration, results in a very high pH value (>11). Thus, as explained in Section 3.1.2, the combined addition of lime and $NaHCO_3$ or Na_2CO_3 is impractical, since the final pH value is excessively high. Accordingly, this alternative was not further evaluated.

5.1.5. Flexibility

When desalinated water is blended with other water sources (either SW or BW) there is practically no flexibility since it is impossible to attain control over more than one quality parameter. In the other discussed processes flexibility is higher. Nevertheless, there are several restraints on the quality of the water that can practically be attained in each of the processes. Table 4 shows the three main product water quality limitations of the considered processes. Note that in case BW is used to load the resin with Mg^{2+} (PT processes #1a, #2a and #3a) the ratio between the concentrations of Mg^{2+} and Ca^{2+} is limited by the Mg^{2+} to Ca^{2+} ratio in the BW itself. Obviously, supplying a ratio of Mg^{2+} to Ca^{2+} close to that in the BW is not feasible.

5.2. Practical aspects

5.2.1. Percentage of treated water

The percentage of treated water is a significant parameter when comparing PT processes that rely on calcite dissolution. Operating the PT plant in a by-pass mode is favorable from both operating and capital cost points of view [83]. The minimum possible percentage of treated water out of the total desalinated water flow rate (%split flow) is a function of two parameters: (1) the available acid concentration in the influent to the dissolution reactor (either CO_2 or H_2SO_4) and the resultant CCDP. Higher CCDP values enable to treat lower volumes of water, i.e. lower %split flow. (2) The required product water quality, in particular the required Ca^{2+} and alkalinity concentrations. A lower requirement for Ca^{2+} and alkalinity concentrations enables operating the plant with a lower %split flow.

Generally speaking, as the addition of 1 meq/l of CO_2 results in a less negative CCDP than the addition of 1 meq/l H_2SO_4 and higher pressure is needed for the application of CO_2, it can be concluded that H_2SO_4 based calcite dissolution can result in lower %split flow values.

Literature survey on the actual %split flow used in desalination plants resulted in only a handful of examples: A PT plant in Ras Laffan is designed to dissolve 220 mg/l $CaCO_3$ using CO_2 as the acidifying agent [83]. Thus, in order to supply product water that contains >80 mg/l as $CaCO_3$ alkalinity, a split flow of at least 37% must be applied. According to de-Souza et al [74], who also used CO_2 for dissolving 45 mg/l as $CaCO_3$ of alkalinity to the product water, it was feasible to let even 80–90% of the flow rate bypass the treatment plant, i.e. apply a %split flow of 10–20%. Accordingly, for attaining an alkalinity concentration of >80 mg/l as $CaCO_3$ a split flow of around 17–35% would be required. The 130 and 45 million m^3/y Ashkelon and Palmachim plants in Israel use H_2SO_4 as the acidifying agents. Both plants are operated with %Split flow of 18%–25%.

5.2.2. Reliability

Kettunen and Keskitalo [8] state that: "limestone dissolution has been favored in Finland because it provides constant Alk without overdose risk." Moreover, it was shown that under the examined conditions, altering the hydraulic retention time in the calcite dissolution reactor from 0.7 h to 5 h caused only slight differences in the product water pH. Already in 1981 it was recognized that calcite dissolution ensures "particular flexibility and reliability...

Table 4
The resultant water quality of the investigated PTs, with regard to the values or ranges of values of Ca^{2+} to Alk ratio, TH to Alk ratio and Mg^{2+} to Ca^{2+} ratio.

PT process		Ca^{2+} to Alk ratio	TH to Alk ratio	Mg^{2+} to Ca^{2+} ratio
		(eq/eq)	(eq/eq)	(eq/eq)
1	$CO_2 + CaCO_3 + NaOH$	Slightly above 1	Slightly above 1	Not relevant
2	$CO_2 + CaCO_3 + CO_2$ stripping	Precisely 1	Precisely 1	Not relevant
3	$H_2SO_4 + CaCO_3 + NaOH$	~2	~2	Not relevant
4	H_2SO_4 + dolomite + NaOH	Depends on the ratio in the rock (>1)	~2	As the ratio in the rock (<1)
1a	$CO_2 + CaCO_3$ + IX + NaOH	Depends on the IX stage, ≤1	Slightly above 1	Depends on the IX stage, very flexible
2a	$CO_2 + CaCO_3$ + IX + CO_2 stripping	very flexible ≤1	1	(usually <1)
3a	$H_2SO_4 + CaCO_3$ + IX + NaOH	≤2	2	
5	$H_2SO_4 + CaCO_3$ + dolomite + NaOH (in series operation)	Depends on the ratio between dissolved calcite and dolomite. ~2	Depends on the NaOH dosage. >2	Depends on the ratio between dissolved calcite and dolomite. <1
6	$Ca(OH)_2 + Na_2CO_3$[a]	Very flexible	Very flexible	Not relevant
7	$CaCl_2 + NaHCO_3/Na_2CO_3$	Very flexible	Very flexible	Not relevant
8	$CO_2 + Ca(OH)_2$	1	1	Not relevant
9	Blending SW	8	49	5
10	Blending BW	Depends on the BW composition		

[a] This alternative is impractical, (see Section 3.1.1).

Furthermore, the basic parameters characterizing water stability (i.e. calcium, alkalinity and pH) can be adjusted to a safe value" [51]. On the other hand, it was also recognized that lime injection is potentially associated with handling and injecting problems [51].

6. Recent full-scale project experience

At present, the most commonly used post-treatment system in desalination plants worldwide is the sequential addition of lime and carbon dioxide. The most frequent challenge with the operation of such re-mineralization systems is maintaining low turbidity in the finished drinking water because lime can cause turbidity increase, often exceeding 5 NTU.

Another re-mineralization process which at present is fairly common for small and medium size plants and is gaining more attention and popularity for larger desalination plants over the past five years is the use of calcite dissolution reactors (often termed "calcite contactors") preceded by addition of carbon dioxide and followed by pH adjustment with sodium hydroxide or controlled CO_2 stripping. Because of the low solubility of calcite at the near-neutral pH of the desalinated water, the addition of adequate calcium concentration requires pH reduction of permeate to usually less than 4.5 (corresponding to CCDP of at least 200 mg/l as $CaCO_3$) before the water enters the contact tanks. As compared to the lime-based post-treatment systems, calcite dissolution systems are usually less costly in terms of both capital and chemical expenditures; require use of less carbon dioxide; and typically produce lower turbidity finished water. However, in many locations worldwide, high-quality food grade calcite is not as readily available as lime, which is one of the main reasons why this technology has not been used as frequently as lime/carbon dioxide conditioning. In addition, the desalination industry has limited experience with the use of calcite contactors for large desalination plants—most of this experience today is in Israel, where all large SWRO desalination plants in operation at present use this technology for permeate conditioning. Outside Israel, the largest operational SWRO plants using calcite contactors are in Barcelona, Spain (200,000 m^3/day) and Larnaka, Cyprus (64,000 m^3/day). In both cases the calcite contractors include gravity-driven concrete contact chambers. Experience at these plants indicates that calcite contactor turbidity is closely related to the type of calcite used and the surface loading rate of the calcite filters [91]. If well washed calcite is used (i.e., calcite that contains less than 1% fines), the product water turbidity is not affected until the surface loading rate on the filters exceeds 14 $m^3/(m^2\,h)$. For calcite with higher content of fine particles (2% or more) the maximum surface loading rate of the filter cells under which the finished water quality is not affected is 11 to 12 $m^3/(m^2\,h)$. The largest thermal SW desalination plant using calcite contactors for PT of desalinated water is located in Bahrain (the 340,000 m^3/day Hidd Phase-1 and -3 plant). This plant employs pressure-driven calcite contactors divided in three parallel treatment trains with 14 contactors per train (42 contactors in total). This plant uses CO_2 to lower the pH of the distillate prior to filtration through the calcite vessels. NaOH is added as a final step of the post-treatment process to adjust the pH of the finished water to the target level. An interesting challenge associated with the operation of this post-treatment system was the relatively high content of organic and particulate residues in the natural limestone used for post-treatment, which resulted in intermittent episodes of increased TOC and turbidity levels of the finished water [92]. Such performance challenges were resolved by using higher quality limestone and modifying the flushing procedures for the calcite contactors.

Most of the existing large SW desalination plants in Australia, the USA, the Middle East, Spain, and North Africa have adopted conditioning of desalinated SW using a combination of lime and carbon dioxide.

7. Cost assessment

The capital costs of lime/carbon dioxide systems vary between US $50 to US$100 per m^3/day of finished desalinated water. For comparison, the capital costs of calcite post-treatment systems producing the same finished water quality is US$30 to US$70 per m^3/day of produced finished water. The capital costs of most other post-treatment systems are in a range of US$80 to US$150 per m^3/day.

The major cost component of post treating desalinated water is the cost of chemicals. Due to nonlinearity of pH and CCPP a reduction in the percentage of treated water leads to elevation in the consumption of acid and base in the calcite dissolution based PT. on the other hand, treating less water results in reduced capital costs expenditure. To conclude, the most cost-effective percentage of treated water is a function of the chosen PT, the cost of chemicals and the required water quality.

Most existing desalination plants with low pH target of the finished water (i.e., pH of 7.5 or less) usually are designed to process 100% of the RO permeate through the calcite filters, especially when the cost of sulfuric acid or carbon dioxide used for permeate acidification before the calcite contactors is relatively high. However, for desalination plants with higher target pH range of the finished water (8.0 to 8.5) the optimum split between RO permeate treated in the limestone contacts and that bypassed for blending is typically 20% to 50%.

7.1. Cost breakdown of a typical lime/carbon dioxide PT system

Breakdown of the capital and O&M costs of a typical lime/carbon dioxide post-treatment system for a hypothetical SWRO desalination plant of fresh water production capacity of 100,000 m^3/day is presented in Table 5. The capital costs included in this table are amortized using capital recovery factor (CRF) estimated for amortization rate of 5% over a period of 20 years (CRF = 12.462).

The lime/carbon post-treatment system for this example uses hydrated lime which is delivered periodically to the plant as powdered lime and stored in two (2) 40-ton lime silos. The lime feed system also includes slurry tanks, mixing and dosing systems and limewater clarifiers. The limewater from the clarifiers is conveyed to a limewater feed tank and from there it is dosed into the SWRO permeate.

Sludge from the limewater clarifiers is removed and processed along with the sludge generated by the spent filter water from the pretreatment filters. Polymer is added to enhance limewater clarification. Carbon dioxide is delivered by 25-ton tankers in liquid form and stored on site in two 50-ton steel storage tanks. This chemical is passed through evaporator and introduced into the lime-conditioned permeate to add alkalinity.

The capital costs presented in Table 5 include the expenditures for all key components of the lime/carbon dioxide post-treatment system along with associated interconnecting piping, fittings, monitoring, instrumentation and control systems and equipment, electrical system, and other service and auxiliary facilities needed for the normal operation of the systems. The dosages and unit costs of the chemicals used for the development of the cost estimate in Table 5 are summarized in Table 6.

The total cost of drinking water production associated with post-treatment (re-mineralization) for protecting human health and the integrity of the distribution system for a hypothetical 100,000 m^3/d plant is estimated at US$0.058/$m^3$ (see Table 5). This cost is approximately 3% to 6% of the total water production cost for a SW desalination plant of this size (US$1.0 m^3 to US$2.0/m^3).

Considering that a conventional facility for feeding magnesium sulfate or magnesium chloride is added to the PT stage, the additional capital cost for such facility would be approximately US$500,000 for a 100,000 m^3/day desalination plant. This expenditure will correspond of additional amortized capital cost of US$0.001/$m^3$.

The additional annual O&M cost for chemical of feed of 10 mg/l Mg^{2+} (by dosing either magnesium sulfate or magnesium chloride) is estimated at US$630,000/y (US$0.017/m^3). As a result, the total additional cost for supplementing post-treated RO permeate with 10 mg/l of magnesium is calculated at US$0.018/$m^3$. This cost would vary depending on the unit cost of magnesium sulfate or chloride used for supplementing magnesium. Similarly, the expenditures for implementing the conventional lime/carbon dioxide system would vary as a function of the costs of conditioning chemicals—lime and carbon dioxide.

It should be pointed out that lime/carbon dioxide conditioning usually is the most costly technology for re-mineralization of desalinated water. For comparison, the capital cost for a post-treatment system for 100,000 m^3/day plant incorporating calcite contact tanks followed by facilities for addition of both calcium and magnesium to the desalinated water would be approximately US $5.0 M (as compared to the capital cost for lime/carbon dioxide system of US$7.09 M—see Table 5). The total cost of re-mineralization desalinated water using calcite/IX system will also be lower than that of lime/carbon dioxide system of the same size (US$0.039/$m^3$ vs. US$0.58/$m^3$ for the same example of 100,000 m^3/d plant). The total costs for most of the other re-mineralization systems described herein will be within the range of US$0.04/$m^3$ to US$0.06/$m^3$ for this size plant and depending on the unit cost of some of the chemicals, it could be outside this range. Re-mineralization costs are very sensitive to the unit costs of chemicals added for conditioning of the desalinated water, which in turn can vary widely from one location to another. Therefore, the cost information provided herein will need to be considered as a guideline rather than as a design or budgeting tool.

Table 5
Capital and O&M costs of lime/carbon dioxide re-mineralization system for 100,000 m^3/day SWRO plant.

Capital costs	Lime/CO_2 system (1000 US$)
Lime silos and slacking system	1100
Lime slurry tanks	400
Lime water clarifiers	1500
Lime water dosing tank	150
Lime feed system	130
Carbon dioxide storage system	940
Carbon dioxide evaporators	130
Carbon dioxide feed system	120
Lime clarifier sludge handling system	100
Other auxiliary and service facilities	470
Land costs	230
Engineering and construction management	850
Start up and commissioning	180
Other costs	790
Total capital costs	7090
Amortized capital costs (US$/$m^3$)	0.016
Operation and maintenance costs	**Lime/CO_2 system (1000 US$/yr)**
Labor	90
Lime	500
Carbon dioxide	195
Polymer for lime clarification	105
Polymer for lime sludge dewatering	45
Lime sludge disposal	80
Maintenance and spare parts	210
Power use	115
Other O&M costs	180
Total annual O&M costs (1000 US$/yr)	1520
Annual O&M costs (US$/$m^3$)	0.042
Total cost of water re-mineralization (US$/$m^3$)	0.058

Table 6
Chemical doses and unit costs used in cost estimate for 100,000 m^3/day desalination plant.

Chemical	Dose (as 100 % concentration)	Unit chemical costs (US$/ton)
Lime	52 mg/l	263
Carbon dioxide	63 mg/l	85
Polymer for lime clarifiers	0.6 mg/l	4800/ton
Polymer for sludge dewatering	2 kg/ton of sludge	1000/ton

7.2. Comparison of costs of alternative chemicals for alkalinity addition to the finished water

Typically, most desalination projects target addition of 80 to 120 mg/l of total alkalinity to the desalinated water. As indicated earlier, alkalinity can be added to the desalinated water using a number of different commercially available chemicals. However, these chemicals add different amounts of alkalinity for the same amount of delivered chemical and their unit costs differ as well. Table 7 presents a summary of the key chemicals used for alkalinity addition and their typical unit prices.

Analysis of Table 7 indicates that calcite is the most cost-effective compound for adding alkalinity to the desalinated water because it has lowest costs per 1 mg/l of $CaCO_3$ added. Use of calcite has the advantage of adding both alkalinity and TH to the finished water. The combination of quicklime (CaO) and carbon dioxide is the most

Table 7
Cost of common chemicals for increase of water alkalinity.

Chemical	Alkalinity addition (as $CaCO_3$) per mg/l of chemical	Unit chemical costs (US$/ton)	Unit costs in US$/ton per 1 mg/l of added alkalinity as $CaCO_3$
Calcite	1.00	30 to 40	30 to 40
Carbon dioxide	1.14	70 to 90	61 to 78
Sulfuric acid	1.02	50 to 80	49 to 78
Quicklime	1.78	120-150	67 to 84
Hydrated lime	1.35	260 to 280	193 to 207
Soda ash	0.94	540 to 580	574 to 617
Sodium hydroxide	1.25	700 to 750	560 to 600
Sodium bicarbonate	0.60	900-950	1500 to 1583

widely used post-treatment method today, although the total costs for this combination of conditioning chemicals is typically one-and-a-half to two times higher than that for calcite and sulfuric acid.

Use of hydrated lime instead of quick lime is usually two to three times more costly for the same amount of alkalinity and TH increase of the desalinated water. Soda ash and sodium bicarbonate are the most costly chemicals for delivery of target alkalinity to the desalinated water. Because in general the cost of soda ash and sodium hydroxide are comparable in terms of unit costs, and because sodium hydroxide is easier to handle, it is more commonly used than soda ash for final pH adjustment of the finished desalinated water.

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