

Quality criteria for desalinated water and introduction of a novel, cost effective and advantageous post treatment process

Liat Birnhack, Roni Penn, Ori Lahav*

*Faculty of Civil and Environmental Engineering, Technion, Haifa 32000, Israel
Tel. +972 4 9292191; Fax +972 4 8228898; email: agori@tx.technion.ac.il*

Received 7 January 2007; accepted 15 January 2007

Abstract

In many places desalinated water is becoming a significant component of the overall water supply. Notwithstanding its superior quality, un-stabilized desalinated water may be corrosive to water distribution systems, and mixing such water with other water sources in the distribution system can result in corrosion of metallic constituents and in “red water” events. To date, no explicit quality criteria for desalinated water can be found in the literature. In this work, such criteria are discussed from various perspectives, including chemical stability, bio-stability, effect on wastewater treatment, water palatability, health and economic effects, and post-treatment engineering considerations. The first part of the work was carried out for the Committee for the Update of Water Quality Standards, appointed in 2005 by the Israeli Ministry of Health. As a result of the study, the following set of quality criteria was proposed and approved: Alkalinity > 80, $80 < [\text{Ca}^{2+}] < 120$, $3 < \text{CCPP} < 10$ (all concentrations in mg/L as CaCO_3), and $\text{pH} < 8.5$.

The second part of the paper focuses on the implications of the new criteria on the post treatment process. A comparison between existing alternative post treatment processes is presented, and a novel, cost effective and unique post treatment process is introduced. The new process was developed not only to comply with the new criteria in a cost effective way, but also to result in a supply of Mg^{2+} ions, which are required in desalinated water for both health and agricultural reasons.

Keywords: Desalination post treatment; Quality criteria; Chemical stability; Bio-stability; Ion exchange; Mg^{2+} addition

1. Introduction

In September 2005 a 100-million $\text{m}^3 \text{y}^{-1}$ sea-water desalination plant started to supply water

to the southern coastal region of Israel, near the city of Ashkelon. By the end of the decade three more desalination plants are expected to become operative, bringing the total annual volume of desalinated water to around 250 million m^3 , which is over 20% of Israel’s annual fresh water

*Corresponding author.

Presented at the conference on Desalination and the Environment. Sponsored by the European Desalination Society and Center for Research and Technology Hellas (CERTH), Sani Resort, Halkidiki, Greece, April 22–25, 2007.

supply. Because desalination is cost effective only when operated continuously, the desalinated water is planned to be the base water resource for supply, while other resources (ground and surface waters) are added only at peak demand. In most cases the desalinated water is planned to be pumped directly into the distribution system, without being first mixed with other water sources, as is typically the case in other places [1,2]. Within the distribution system the water will be at times blended with other water sources (ground water or a mixture of surface water and ground water), however in areas adjacent to desalination plants the desalinated water is expected to constitute the major water source, most of the time. From this description it is clear that the distribution system will receive at times desalinated water with its specific chemical characteristics, and at other times varying water qualities, depending on both the quality and the percentage of mixing of each of the other sources pumped into the distribution system. Many works exist that describe the potential problems that may occur when waters that have different chemical characteristics are supplied intermittently into distribution systems [3–10]. The most problematic occurrence is the phenomenon of “red water”, which describes a situation where a layer of (mostly) iron oxides is detached from the internal surface of metal pipes into the water and arrives at the consumer’s tap with a characteristic yellow–brown–red color. On top of red water related nuisances, there are a few other quality related factors that need to be taken into account when considering the overall required quality of desalinated water. These factors include the chemical and biological stability of the water and its interaction with the distribution system; minimal concentrations of certain elements required due to human health and agricultural irrigation considerations; water palatability and minimization of consumer complaints; and possible effects of the water quality on downstream wastewater treatment plants. In the work presented here each of these factors is discussed, while

taking into consideration conflicting effects. Based on all considerations, a set of quality criteria was proposed. The suggested criteria-set has been approved by the committee for the update of water quality standards, appointed in 2005 by the Israeli Ministry of Health. The second part of the paper focuses on the effect of prescribed sets of quality criteria on the choice of the post-treatment technology. A comparison is presented between conventional post treatment approaches, and advantages and disadvantages of these are presented. Following this, a new post-treatment process is introduced. The advantages of the new process are its ability to comply with the new criteria at a reasonable cost, along with the ability of supplying Mg^{2+} ions to the water, required for both human health and irrigation purposes.

2. Addressed criteria

2.1. Chemical stability

The need to stabilize the water so that it would not enhance metal corrosion and concrete dissolution has been recognized for decades. The most problematic phenomenon in urban distribution systems is related to the release of dissolved metal ions to the water (mostly iron ions but also Zn^{2+} , Pb^{2+} and Cu^{2+} ions). Solid elemental iron tends to donate electrons and transform into Fe(II) and Fe(III), with dissolved oxygen being the most common electron acceptor in distribution systems. Depending on specific conditions, corrosion reactions on the pipe’s surface may result in a continuous release of metal ions into the water, or may give rise to precipitation of minerals on the active electro-chemical sites on the pipe’s internal surface. The latter occurrence may cause the formation of a “passivation layer”, which, depending on its properties (width, density, species composition), can serve as a protection layer which reduces the diffusion of dissolved oxygen and ions to the surface of the pipe and thus reduces the rate of corrosion. On the other hand, the sudden collapse/dissolution of this layer may

cause the release of a large amount of iron (and other) species into the water which may cause the known phenomenon of “red water” to occur.

Conventionally, three parameters are considered to control the chemical stability of drinking water: (1) the buffering capacity of the water, i.e. the ability of the water to withstand substantial changes in pH when a strong base or a strong acid are added to it; (2) the propensity of the water to precipitate CaCO_3 ; and (3) the concentration of soluble Ca^{2+} ions in the water. The fourth relevant parameter, pH, is a dependant parameter that is determined by the values of the previous three.

A comprehensive literature survey was conducted by the authors [11] to reveal the various water quality recommendations that exist worldwide to control corrosion propensity of water. Based on the survey it was concluded that there is a general agreement on the main parameters that should be used for chemical-stability control: alkalinity, Ca^{2+} and calcium carbonate precipitation potential (CCPP) concentrations (at times replaced by the qualitative parameter LSI). In the following paragraphs the effect of the three parameters is discussed.

2.1.1. Alkalinity

The commonly used term “alkalinity” in natural waters refers to the value of H_2CO_3^* alkalinity, defined as the proton accepting capacity of the water with respect to H_2CO_3^* as a reference specie [12]. The mathematical expression of this value is given in Eq. (1), where square brackets stand for molar concentrations and the alkalinity is expressed in eq/L. The value of H_2CO_3^* alkalinity is typically measured by strong acid titration to a pH value close to 4.5 (i.e. close to the H_2CO_3^* equivalence point), or by applying the Gran titration technique [13].

$$\text{Alkalinity}_{(\text{H}_2\text{CO}_3^*)} = 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{OH}^-] - [\text{H}^+] \quad (1)$$

From the knowledge of the alkalinity value and pH one can calculate the value of the buffering capacity of the water. For a given pH value, the higher the alkalinity concentration, the higher the buffering capacity is. Minimization of local pH variations has been shown to promote a denser scale structure on the pipe’s wall, thereby decreasing the chance for red water events to occur [14]. A comprehensive pilot study conducted recently on red water prevention concluded that maintaining the alkalinity concentration above 80 mg/L as CaCO_3 is the most important individual parameter for preventing the release of metal ions to the water [4].

2.1.2. Calcium carbonate precipitation potential

CCPP is the quantitative measure of the precise potential of a solution to precipitate (or dissolve) $\text{CaCO}_{3(s)}$. As such it constitutes an unambiguous parameter that can be used in the context of guidelines or regulations without invoking misunderstanding. In the review conducted by the authors [11] it was noticed that only small differences exist worldwide between recommended ranges for CCPP values.

Choosing the recommended CCPP range is based on the following considerations: although a higher CCPP value increases the potential for the formation of a denser, more effective passivation layer, an upper CCPP value should be set in order to prevent the buildup of excessive CaCO_3 scales on pipes and pumping stations. When setting the lower limit of CCPP it should be noted that a high CCPP value (for given Ca^{2+} and alkalinity values) is attained at a higher pH value, which results in less effective chlorine disinfection.

2.1.3. $[\text{Ca}^{2+}]$

The dissolved Ca^{2+} concentration in the water is restricted by a maximum and minimum concentration values not directly related to chemical stability. The minimal value is required for health

reasons and has been typically set at 50 to 60 mg/L as CaCO_3 [15,16]. The maximum value is set due to economic reasons attributed to the need to supply water that is not excessively hard. Accordingly the range for Ca^{2+} values can be safely assumed to lie between 50 and 120 mg/L as CaCO_3 .

2.1.4. pH

Once the alkalinity, Ca^{2+} and CCPP concentrations are set, pH is a dependant value (whose exact value depends also on the ionic strength and temperature). However, there is logic in providing a maximum value for pH, mainly because of its effect on disinfection efficiency. In addition, pH (along with the alkalinity value) also determines the buffering capacity of the water: within the typical pH range of 7.5–8.4, a higher pH results in a lower buffering capacity (for a given alkalinity value), thus from this perspective too a lower pH is advantageous.

2.1.5. Effect of other relevant parameters: ionic strength, temperature and the ratio between $[\text{HCO}_3^-]$ and $([\text{SO}_4^{2-}] + [\text{Cl}^-])$

As a rule, the apparent $\text{CaCO}_{3(s)}$ equilibrium constant becomes lower as the temperature increases and the ionic strength decreases, i.e. at these conditions the water tends to precipitate more $\text{CaCO}_{3(s)}$ at given Ca^{2+} pH and alkalinity concentrations. The criterion $[\text{HCO}_3^-]$ to $([\text{SO}_4^{2-}] + [\text{Cl}^-])$ (all concentrations in eq/L) is commonly termed “Larson index”, and its value has been recommended at >5 for the purpose of minimizing corrosion rates [17–19].

2.1.6. The importance of “buffering capacity”

Buffer capacity is defined as the slope of a strong acid (or strong base) titration curve at a particular pH, or in other words the concentration of strong acid or base required to bring about a change of one unit in pH.

Several processes (either deliberate or not) that may occur after desalinated water has left the plant have the potential to affect the alkalinity concentration and thus the pH value. As examples of deliberate processes one can consider disinfection with Cl_2 and dosage of fluorine by the addition of H_2SiF_6 (fluorosilicic acid). Unplanned processes that affect pH include in-line nitrification and iron oxidation and precipitation. Clearly, water that has a high buffering capacity would be less susceptible to changes in pH (and thus in CCPP) due to either deliberate or unintentional processes. With regard to deliberate processes it is imperative that the water supplier will be responsible for returning the alkalinity to its initial value prior to the process. High buffer capacity is also beneficial from the chemical stability standpoint of in-line water blends [11].

2.2. Biological stability

Two types of disinfectants are typically used in urban water distribution systems: chlorine gas or its derivatives (HOCl and OCl^-) and chloroamines. Both types are known to be more effective as bactericides at lower pH values. The common recommendation is to maintain pH values lower than about pH 8.0 [20,21]. With respect to desalinated water quality, this consideration leads to an upper limit for pH, which should be as close as possible to pH 8.0.

2.3. Possible effect of the alkalinity concentration in desalinated water on downstream wastewater treatment plants

In places where desalinated water is planned to constitute the major water source for prolonged periods of time, the quality of the influent to the wastewater treatment plant will be directly affected by the quality of the desalinated water. With respect to the effect of desalinated water quality on wastewater treatment processes, the most important water quality parameter is alkalinity.

The alkalinity concentration in wastewater is important in the widespread cases where full nitrogen species removal is planned, a process which releases approximately 1 meq of acidity (H^+ ions) for each mmol of NH_4^+ transformed to 0.5 mmol of N_2 . In cases when nitrate is not fully reduced, alkalinity consumption as a result of nitrification/denitrification is even higher (because denitrification is an alkalinity supplying process). Alkalinity consumption results in both lower buffering capacity and lower water pH. In raw wastewaters low in alkalinity (resulting from unblended desalinated water) this phenomenon might have a disruptive effect on the nitrification process, since nitrifying bacteria are extremely pH-sensitive.

2.4. Required range for dissolved calcium concentrations in desalinated water

2.4.1. Minimum values

A certain Ca^{2+} concentration is required in drinking water not only because it induces $CaCO_{3(s)}$ precipitation, but also because of health reasons. Calcium is vital for human growth. Twenty percent of the recommended daily dosage arrives from drinking water [16]. Most guidelines worldwide set the minimum Ca^{2+} concentration value at 20–25 mg Ca^{2+}/L (i.e. 50 to 62.5 mg $Ca-CaCO_3/L$).

2.4.2. Maximum values

When hard waters are supplied, industries are often required to soften the water, and households are faced with damage to boilers, kettles, etc. It appears from economical reasons, thus, that an upper limit of around 100–120 mg/L as $CaCO_3$ should be set for dissolved calcium concentration in desalinated water.

2.5. The effect of desalinated water quality on the palatability of the water

The taste of water is relative and subjective. Various scientific sources link between the

concentration of chloride ions and taste. It appears that very low chloride concentration on the one hand, or $[Cl^-] > 250$ mg/L on the other, promote complaints [22,23]. While the latter is normally not a concern associated with the product of RO desalination plants, the former might be. However, the total dissolved solids (TDS) concentration of desalinated water, following the post treatment stage is typically above 150 mg/L, thus water palatability is not a major issue.

3. Summary of the considerations presented thus far and presentation of the recommended set of quality values

Table 1 summarizes the qualitative conclusions that emanate from the discussion in the previous sections. Because the parameters discussed in Table 1 are in some cases interconnected and in other cases contradictory, the recommendations that appear in Table 1 should be considered in a broad perspective, rather than the value or trend of an individual parameter *per se*. For example, consider the recommendation for Ca^{2+} concentration under the caption “Biostability”: Although it does not directly affect the water’s biostability, the recommendation “highest within the recommended CCPP range” can be explained in the following way: low pH values are beneficial from a biostability standpoint; at a higher Ca^{2+} concentration (for a given alkalinity) the recommended CCPP can be achieved at lower pH values. Therefore, raising the Ca^{2+} concentration within its limits allows lowering the pH and attaining high disinfection efficiency.

4. Effect of the proposed water quality criteria on the choice of the post treatment process

The choice of the post-treatment process to be applied in a desalination plant is determined primarily by the water quality required and economic considerations. Three main groups of post

Table 1

General recommendation for each of the discussed quality parameters with regard to the various water quality effects examined in the paper

Consideration	Chemical stability	Biostability	Health and economic considerations	Wastewater treatment	Water palatability
Water quality Parameter					
Alkalinity	As high as possible	As high as possible	NA	As high as possible	NA
Ca ²⁺	Highest within recommended CCPP range	Highest within recommended CCPP range	50–120 mg/L as CaCO ₃	NA	As similar as possible to other water sources
CCPP (LSI)	>3 and <10	NA	NA	NA	NA
pH	High	Required: pH < 8.5 (preferably pH < 8)	NA	NA	NA
TDS concentration	NA	NA	NA	NA	As similar as possible to other water sources
Larson index $= \frac{[\text{HCO}_3^-]}{[\text{SO}_4^{2-}] + [\text{Cl}^-]}$	>5	NA	NA	NA	NA

treatment processes exist for RO desalination plant streams:

- (1) Processes that center around CaCO_{3(s)} dissolution (typically calcite) for alkalinity and Ca²⁺ supply.
- (2) Processes that are based on direct dosage of chemicals.
- (3) Processes that are based on mixing the desalinated water with other water sources, with or without further adjustment of water quality parameters.

4.1. Calcite dissolution processes

Calcite dissolution processes are cost effective in places where calcite abounds in nature and can be easily extracted (as is the case in Israel). In order to enhance calcite dissolution kinetics, water pH must be reduced before it is introduced

into the calcite reactor. Two acidic substances are typically used to lower the pH: H₂SO₄ and CO_{2(g)}. The advantage of using a strong acid such as H₂SO₄ is that pH can be lowered to any desired value, which results in rapid CaCO₃ dissolution kinetics. As a result, it is possible to pass only a fraction of the water through the calcite column, and blend it with the untreated fraction thereafter. To determine the final pH (and the final CCPP value) NaOH is dosed to the blend prior to its discharge. The process is depicted schematically in Fig. 1 that illustrates a typical calcite-dissolution-based post treatment in which H₂SO₄ is used for pH reduction. Such a post treatment process is currently operated at the 100,000,000 m³/year desalination plant in Ashkelon, Israel.

The main advantage of this method are that it requires a relatively small calcite packed bed reactor, and that the application of the acid is

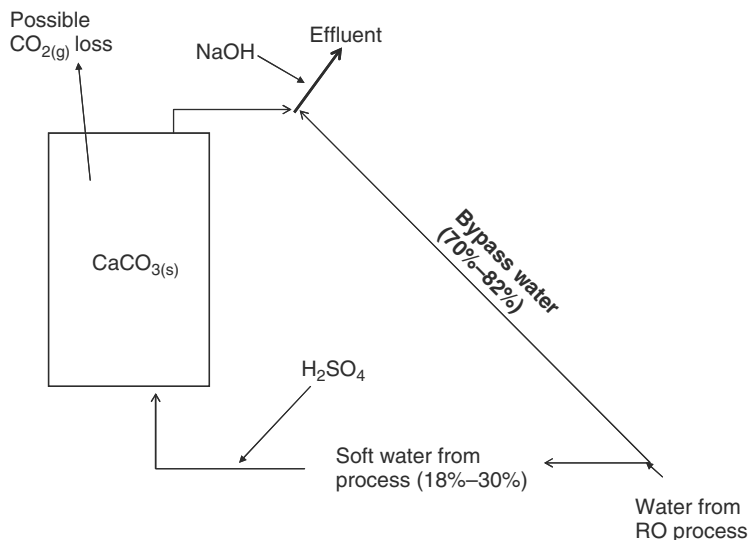


Fig. 1. Schematic representation of a calcite-dissolution based post treatment using H_2SO_4 for pH reduction.

simple and inexpensive. Thus, the process is relatively cheap. Disadvantages include the release of a substantial amount of SO_4^{2-} to the water (may also be considered an advantage if the water is used for agricultural irrigation), the presence of a certain turbidity in the product water and possible gypsum precipitation at the bottom of the calcite reactor. However, the most significant drawback associated with this process is that it is bound to yield a ratio of approximately 2 to 1 between the Ca^{2+} and alkalinity concentrations in the effluent, and sometimes even a higher ratio (both parameters in units of mg/L as CaCO_3). As a result, meeting the demand for an alkalinity concentration of >80 mg/L as CaCO_3 results in a Ca^{2+} concentration that is higher than the upper limit of 120 mg/L as CaCO_3 required by the new criteria. Similarly, if the Ca^{2+} concentration is maintained below the upper limit (i.e. <120 mg CaCO_3/L), the alkalinity concentration in the effluent will be below the recommended value. Consequently, the process depicted in Fig. 1 cannot be implemented to meet the new quality criteria set.

The reason for the approximate 2 (Ca^{2+}) to 1 (alkalinity) ratio is as follows: the ratio between

the concentrations of Ca^{2+} and the total inorganic carbon (C_T) that dissolve into the water is 1 to 1, because the dissolved CaCO_3 is the source of all the calcium and all C_T . Since practically all the C_T at the final pH (pH 8.0 to pH 8.3) is expressed as the monovalent HCO_3^- ion, the Ca^{2+} to Alk ratio in equivalent units is bound to be 2 to 1 and hence also this ratio when it is expressed in units of mg/L as CaCO_3 . More simply put, under these conditions, around 50% of the proton accepting capacity of the CO_3^{2-} that originates from dissolving the calcite solid is used for raising pH from the initial pH value (around 2.3) to a pH value around 4.5 that is typically used as the end point for H_2CO_3^* alkalinity determination. This proton accepting capacity is therefore not accounted for in the alkalinity determination procedure. In full scale H_2SO_4 -based calcite dissolution reactors the Ca^{2+} to alkalinity ratio is often higher than 2 to 1, because of $\text{CO}_{2(g)}$ stripping from the reactors, which are normally not sealed. In the Ashkelon plant, for example, a ratio of 2.3 to 1 has been commonly reported. This ratio was therefore adopted in all the calculations presented in this paper.

In the second calcite dissolution process $\text{CO}_{2(g)}$ is used in order to acidify the water prior to its

introduction into the calcite reactor. The main advantage of the process is that the resultant Ca^{2+} to alkalinity ratio tends towards 1 to 1 (both parameters expressed in mg/L as CaCO_3) and thus both parameters can be attained at similar concentrations, which allows attaining the alkalinity and calcium criteria at the same time. Another possible advantage lies in the fact that no SO_4^{2-} is added to the water, and thus the Larson index can be easily maintained above 5, as recommended for chemical stability. On the other hand, as mentioned before, a certain SO_4^{2-} concentration is imperative from the agricultural irrigation point of view. The main disadvantage of this process is that CO_2 addition can reduce pH to no lower than around pH 4.0, and thus calcite dissolution kinetics are much slower than is the case of H_2SO_4 addition. Moreover, since calcite dissolution practically stops at pH of around 7, less calcite dissolved when the initial pH is around 4 than when it is around 2.3, as is the case with H_2SO_4 based dissolution. Consequently, all (or most of) the water has to be passed through the calcite reactor, and thus much larger reactor volumes are required. Another disadvantage is that the application of $\text{CO}_{2(g)}$ as an acidic substance is more expensive than that of H_2SO_4 . As a result, in terms of cost effectiveness, the operation of the method that uses H_2SO_4 as the acidic substance is considerably cheaper than the method that utilizes $\text{CO}_{2(g)}$. However, as explained before, the process that is depicted in Fig. 1 cannot comply with the required Ca^{2+} to alkalinity ratio, a fact that supports the option of using the $\text{CO}_{2(g)}$ based calcite dissolution process.

Another drawback that is associated with both calcite dissolution processes is that they result in no addition of Mg^{2+} ions to the water. Mg^{2+} ions, although not included in the current Israeli quality criteria, are very much welcome in desalinated water for both agricultural [24] and human health reasons [16,25]. To date, the Israeli water commission office is seeking a cost effective process for adding Mg^{2+} ions into desalinated water. Post

treatment processes that are based on calcite dissolution only, cannot, naturally, supply Mg^{2+} ions.

4.2. Processes that are based on direct dosage of chemicals

These processes are based on a certain combination of chemicals to achieve a specific chemical composition. For example, for stabilizing the water in Cape Town, South Africa, $\text{Ca}(\text{OH})_2$ is dosed to supply alkalinity and Ca^{2+} , followed by $\text{CO}_{2(g)}$ that is bubbled in order to supply inorganic carbon and reduce pH. Other options may include the use of hydrated lime + sodium carbonate, sodium bicarbonate + calcium sulfate or calcium chloride [26]. These processes have the advantage of flexibility, however they tend to be much more expensive, and thus where calcite is available it will invariably be used for post treatment purposes.

4.3. Processes that are based on dilution with other water sources

The alternative of blending brackish water or seawater with desalinated water is based on the fact that saline water contains (apart from higher concentrations of unwanted components such as chlorides) high concentrations of required components, such as calcium, magnesium and alkalinity. When blending desalinated water with another water source, one quality parameter will always limit the dilution fraction of the saline source. It is thus clear that required value of other parameters in the blend will not necessarily be attained. Therefore, further chemical dosage becomes unavoidable. Another disadvantage of this process is the need for a mixing tank, which, in large plants, will be of a considerable size. Moreover, some unwanted components might be added to the final water product as a result of blending. In this context, it is important to emphasize that chloride ion concentration, although not specified explicitly in the new criteria set, should be maintained as low as possible.

Conclusion: the consequence of the suggested criteria set is that the post treatment process that is based on calcite dissolution using H_2SO_4 becomes unfeasible because it does not supply the desired ratio between alkalinity and Ca^{2+} concentrations. Calcite dissolution with CO_2 and direct dosage of chemicals are both acceptable alternatives, as well as any other approach that is capable of meeting the required criteria.

5. Introduction of an alternative process for Mg^{2+} addition

Practical alternative processes for the addition of Mg^{2+} ions to desalinated water include direct chemical dosage and dissolution of dolomite minerals. Direct chemical dosage is an expensive alternative that results in a high concentration of unwanted counter anions (typically chloride ions). Dolomite dissolution is, in terms of reactor configuration, similar to the calcite dissolution process. However, several problems are encountered when dissolving dolomite rocks ($\text{MgCa}(\text{CO}_3)_2$): the most distinct drawback is related to dissolution kinetics, which is much slower than the calcite dissolution kinetics [27]. As a result, much larger reactor volumes are required in order to dissolve an adequate amount of Mg^{2+} ions. Alternatively, higher dissolution kinetics can be achieved by maintaining a low pH value throughout the dissolution process. The effluent of such an approach would have an adequate concentration of Mg^{2+} ions, but also a low pH and hence the alkalinity value would be much lower than required. Therefore, a high NaOH concentration would be required to elevate alkalinity and CCPV values, and often the limit for pH (i.e. pH 8.5) would be exceeded. Moreover, NaOH is the most expensive chemical used in the stabilization process, and a high requirement of this chemical is highly unwanted. Moreover, dolomite dissolution has not been widely applied in engineered systems and therefore full understanding of the mechanisms controlling

the dissolution is lacking [28,29]. Such understanding is not only important with regard to Mg^{2+} supply — it rather also affects process operation and the resultant water quality. For example, there is a lack of knowledge regarding the Ca^{2+} to Mg^{2+} ratio released during the process [30], and also regarding the dependence of the dissolution kinetics on pH [28]. Finally, when dissolving a pure dolomite rock ($\text{MgCa}(\text{CO}_3)_2$) the flexibility of the ratio between calcium and magnesium concentrations is limited: For example, if a magnesium concentration of 12 mg/L is required (~ 1 meq/L) the resulting Ca^{2+} concentration is bound to be 50 mg/L as CaCO_3 .

5.1. Development of a H_2SO_4 -based calcite dissolution process coupled with ion exchange for magnesium ions supply

A process which provides a new and unique post treatment alternative to be used after water desalination is introduced. The approach makes use of the most cost-effective post-treatment process (i.e. calcite dissolution using H_2SO_4) for alkalinity and Ca^{2+} supply, but at the same time results in a Ca^{2+} concentration that complies with the new water criteria regulations, and also in a significant concentration of dissolved Mg^{2+} in the water, while fully conforming to the other required criteria.

The proposed process hinges around replacing the excessive Ca^{2+} ions generated in the H_2SO_4 based calcite dissolution process by Mg^{2+} ions originating from seawater. Mg^{2+} concentration in seawater is over five times higher than that of Ca^{2+} (approximately 105 and 20 meq/L respectively in the Mediterranean Sea). In the first step of the proposed method (termed “Load step”, see Fig. 2), Mg^{2+} ions are preferentially separated from seawater by means of an ion exchange resin that has a high affinity towards divalent cations (Mg^{2+} and Ca^{2+}) and an extremely low affinity towards monovalent cations (namely Na^+ and K^+). Subsequently, the resin is washed and disinfected

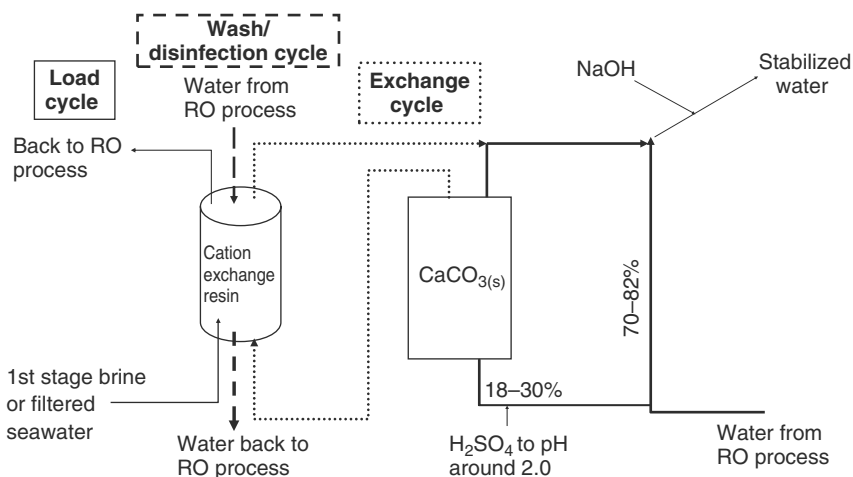


Fig. 2. Schematic of a H_2SO_4 calcite-dissolution-based desalination post treatment process operating in parallel to a set of ion exchange columns.

to prevent product water contamination. Finally, the Mg^{2+} loaded resin is contacted with the effluent of the calcite reactor (the “Exchange step”). In this step Mg^{2+} and Ca^{2+} are exchanged. As a result, the Ca^{2+} concentration in the desalinated water decreases while the Mg^{2+} concentration increases to comply with the required quality criteria. All the water streams used in the ion exchange process are internal streams that are a part of the desalination plant sequence irrespective of the additional ion exchange process. For example, the stream used to load the resin with Mg^{2+} ions may be either filtered seawater before it enters the RO process or the brine of the 1st desalination step. The water that is used to load the resin returns back to the container from where it was taken (closed loop).

The process can be carried out in either a batch mode (multiple reactors) as illustrated in Fig. 2 or in a continuous mode. Batch mode operation, (which is by definition a non steady state operation), may be preferred in cases where the desalinated water is stored in a sufficiently large downstream storage tank prior to discharge, where the product water is mixed. Alternatively, when no storage exists, the preference may be to apply a continuous ion exchange process (i.e. steady

state operation) that allows for the discharge of water with quality parameters that do not change with time.

5.2. Results and discussion

Two resins were purchased from Rohm & Haas INC and tested for their suitability to the process by determining their binary separation coefficients for the relevant cations (results not shown). The chosen resin, Amberlite IRC747, has, as required in the process, a high affinity towards divalent cations and an extremely low affinity towards monovalent cations, as shown in Fig. 3.

Continuous column experiments were conducted in order to determine the number of bed volumes (BV) required in the Load and Exchange steps. Assuming that 25% of the raw desalinated water passes through the calcite reactor (see Fig. 2), the concentrations of the effluent of the Exchange step should be four times higher than the concentrations required product water.

Two distinct case studies are shown: the first case study simulates a post treatment process designed to meet the new water criteria regulations. In this case, the water quality at the outlet of the calcite reactor should be $[\text{Ca}^{2+}] = 15.2 \text{ meq/L}$ and

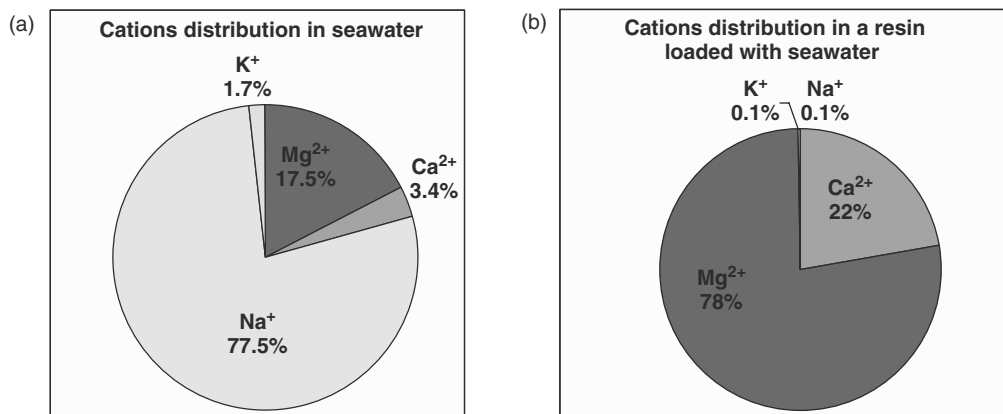


Fig. 3. Distribution of cations in seawater (a) and the distribution of the same cations adsorbed to Amberlite IRC747 at equilibrium with seawater (b).

alkalinity = 6.6 meq/L (2.3 to 1 ratio). Considering that the product water (a mixture of the ion exchange column effluent and the raw desalinated water — see Fig. 2), should have a final dissolved calcium concentration of approximately 2.0 meq/L (100 mg/L as CaCO₃), the dissolved calcium concentration in the water should be reduced during the Exchange step from 15.2 to 8.0 meq/L. The water quality at the end of the Exchange step is therefore [Ca²⁺] = 8.0 meq/L and [Mg²⁺] = 7.2 meq/L (the alkalinity concentration does not change). The number of BV in the Exchange step for the conditions of this case can be derived from Fig. 4a which presents the cumulative

concentrations of Ca²⁺ and Mg²⁺ in the water leaving the ion exchange resin, when a seawater loaded resin is contacted with a 760 mg/L Ca²⁺-CaCO₃ (15.2 meq/L) solution. Fig. 4a shows that after around 60 BVs the cumulative concentrations of Ca²⁺ and Mg²⁺ are around 8 meq/L and 7.2, respectively.

Fig. 4b shows the number of BVs required to load the resin with fresh seawater, after the Exchange step. Assuming that the Load step can be practically stopped after 15 BV, it can be concluded that the time in which the resin is in the Load step is typically 25% of the time in the Exchange step. As mentioned before, loading

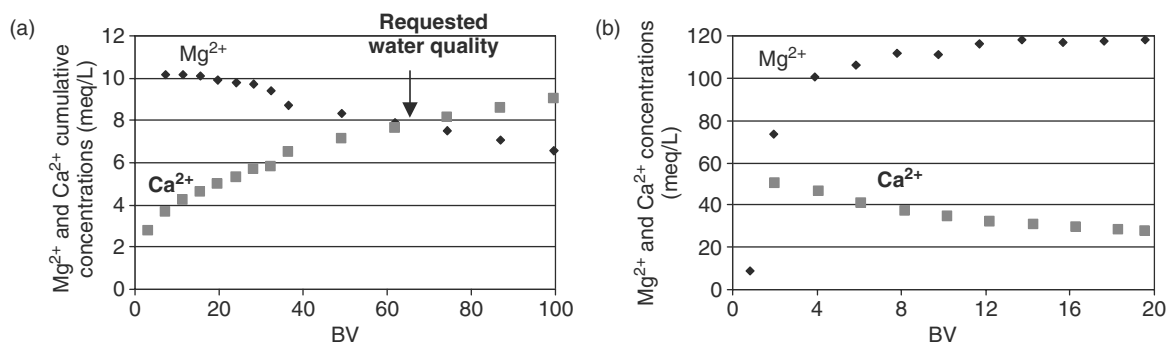


Fig. 4. Results of exchange experiments simulating the first case study. Cumulative Mg²⁺ and Ca²⁺ concentrations in the effluent of the ion exchange column during the Exchange step (a) (inlet water quality: [Mg²⁺] = 0, [Ca²⁺] = 760 mg/L as CaCO₃ (15.2 meq/L)); and Mg²⁺ and Ca²⁺ concentrations in the effluent of the consequent Load step (b).

the resin with Mg^{2+} ions can be carried out also with the RO 1st stage brine (see Fig. 5). The Ca^{2+} and Mg^{2+} concentrations in the 1st stage brine are twice as high as the concentrations in seawater. Using the brine is advantageous from the perspective of the RO process. This can be explained in the following way: In the Load step Mg^{2+} ions from the solution are exchanged with Ca^{2+} ions from the resin. Therefore, the Ca^{2+} concentration of the seawater increases. To save costs, the effluent of the Load step is planned to be further used as the influent to the RO process. In this respect an increase in the Ca^{2+} concentration may be problematic since it leads to an increase in the $CaCO_3$ precipitation potential that will increase the potential for scaling on the membrane surface. Loading the resin with the brine of the first stage, which is thereafter disposed back to the sea, circumvents this problem.

The second case study simulates a situation in which the required water alkalinity is lower than

the new criteria, and is set at 65 mg/L as $CaCO_3$. In such a case the Ca^{2+} concentration expected at the outlet of the calcite reactor is 12 meq/L (again, assuming a 25% split flowing into the calcite reactor, and a Ca^{2+} to alkalinity ratio of 2.3 to 1). The Ca^{2+} concentration during the Exchange step should thus be reduced from 12 to 8 meq/L. The resulting Mg^{2+} concentration under this scenario is 4 meq/L (prior to the mix with the raw desalinated water and 1 meq/L after mixing). Fig. 6 shows the results of a batch experiment that simulates the Exchange step under these conditions. In this case the Exchange step lasts approximately 260 BVs. The Load step is identical for both scenarios. Therefore, in this scenario the ratio between the number of BV in the Exchange step and the Load step is 17 to 1.

After the Load step the resin must be washed to remove residual seawater. Washing is done by passing a low-TDS brine through the resin bed, until the salt concentration of the water in the

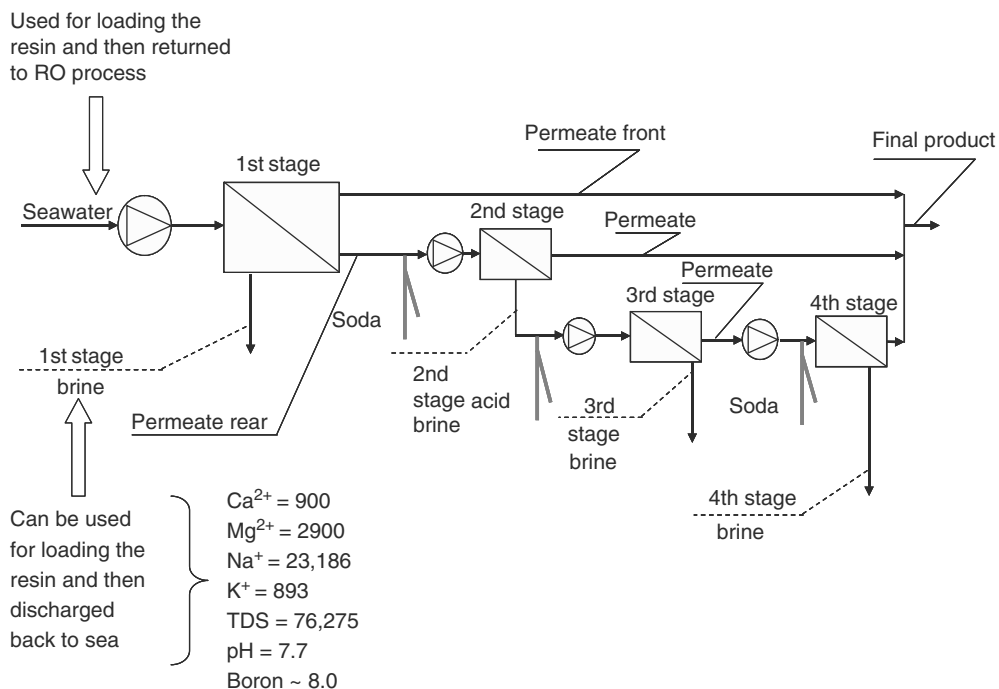


Fig. 5. Schematic of the RO process in Ashkelon, and characterization of the streams used for the Load and Wash steps, all concentrations in mg/L. Original schematic was adopted from [31].

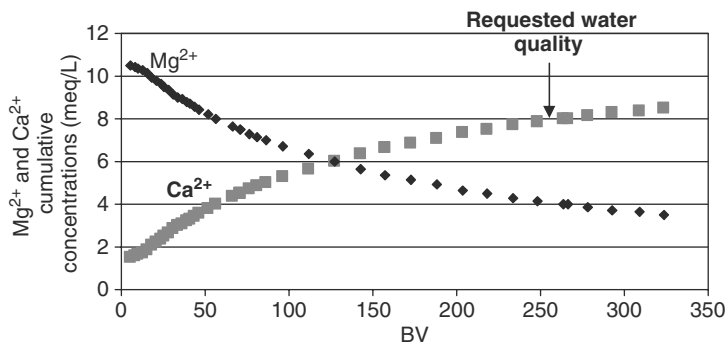


Fig. 6. Results of exchange experiments simulating the 2nd case study. Cumulative Mg^{2+} and Ca^{2+} concentrations in the effluent of the ion exchange column during an Exchange experiment (inlet water quality: $[Mg^{2+}] = 0$, $[Ca^{2+}] = 600$ mg/L as $CaCO_3$).

bed tends towards the salt content of the washing water. Using low-TDS brine for washing is advantageous since the brine comes at a very low cost. An example for such brine is the so-termed 2nd stage brine produced as part of the Ashkelon desalination plant process, shown in Fig. 5. The 2nd stage brine is pumped in the Ashkelon process to a third RO stage, following the dosage of strong acid. In the proposed process, this brine (prior to acid addition) is used to wash the resin and is then pumped back to the RO process with slightly higher salts content. The number of bed volumes required to completely wash the resin is 4 (results not shown). At the end of the Wash step, the resin is allowed to drain so the volume of water (brine #2) that remains in the bed is approximately 0.25 BV. Acknowledging that the TDS and boron concentrations in the brine are 1860 and 10 mg/L respectively one can easily calculate the additional values added to the product water: in the scenario that 80 mg/L of alkalinity is required (60 BV to the end point of the Exchange step) ΔTDS and $\Delta Boron$ will be 1.9 and 0.01 mg/L respectively. In the second scenario (65 mg/L of alkalinity, 260 BV to the end point) the added concentrations drop to 0.45 and 0.002 mg/L respectively. An example to clarify these calculations is given in Eq. (2).

$$\frac{10 \text{ mg B/L}_{(\text{brine})} \cdot \frac{1}{4_{(\text{BV of brine remaining after wash})}}}{60_{(\text{BV during Exchange})} \cdot 4_{(\text{split ratio})}} = 0.01 \text{ mg B/L} \quad (2)$$

5.2.1. Evaluation of overall resin volume required in the two scenarios

Considering the Ashkelon desalination plant conditions, (i.e. a total desalinated water flow rate of 14,000 m^3/h) and a split flow of 25% through the calcite reactor, the constant flow rate through the ion exchange system would be 3500 m^3/h . Assuming a minimum HRT of 1.5 min (i.e. 40 bed volumes per hour, manufacturer's data), the volume of resin required in the Exchange step alone is around 100 m^3 (for both cases). Accordingly, in the first case study a total resin volume of 129 m^3 is required (100 BV continuously in the Exchange step, 25 in the Load and 4 in the Wash/disinfect steps). In the second scenario a total volume of 110 m^3 is required.

6. Conclusion

The ability of the new process to meet the required quality criteria, along with the bonus of an additional Mg^{2+} concentration in the water, has

been shown. Application of the proposed process would eliminate the need to implement the more expensive CO₂-based calcite dissolution process and would result in water that is more healthy to human consumption and also acceptable by the agricultural community. Process development is ongoing: Further research goals include optimization of the Exchange, Wash and Load steps, as well as optimization of the type of resin used, testing combinations of resins to increase the flexibility of the quality of the final water product, and mathematical modeling of the process.

References

- [1] N.M. Fayad, J. Am. Water Works Assoc., 85 (1) (1993) 46–50.
- [2] F. MalAllah and M. Al-Senafy, International Conference on Water Resources Management in Arid Regions, March 23–27, 2002.
- [3] A. Franchi, S. Jousset, T. Brodeur, P. Lowe and M. Prinie, Water Quality Conference and Exhibition, November 10–14, 2002.
- [4] S.A. Imran, J.D. Dietz, G. Mutoti, J.S. Taylor, A.A. Randall and C.D. Cooper, J. Am. Water Works Assoc., 97 (9) (2005) 93–100.
- [5] F. Kumpera, Water Supply, 5 (3–4) (1987) SS12/1-SS12/9.
- [6] V.S. Marangou and K. Savvides, Desalination, 138 (1–3) (2001) 251–258.
- [7] A. Plottu-Pecheux, C. Democrate, B. Houssais, D. Gatel and J. Cavard, Desalination, 138 (1–3) (2001) 237–249.
- [8] A.D. Rodriguez, B. Black, S. Reiber and N.A. Graff, Water Quality Technology Conference, November 2001.
- [9] J. Taylor, J. Dietz, A. Randall and S. Hong, Water Sci. Technol., 51 (6–7) (2005) 285–291.
- [10] S.W. Van der Merwe, Water Supply, 6 (2) (1988) 9–13.
- [11] O. Lahav and L. Birnhack, Desalination, 207 (2007) 286–303.
- [12] O. Lahav, B.E. Morgan and R.E. Loewenthal, Environ. Sci. Technol., 36 (12) (2002) 2736–2741.
- [13] O. Lahav, B.E. Morgan and R.E. Loewenthal, Water Sa., 27 (4) (2001) 423–431.
- [14] P. Sarin, V.L. Snoeyink, D.A. Lytle and W.M. Kriven, J. Environ. Eng. ASCE., 130 (4) (2004) 364–373.
- [15] B. Berghult, T. Hedberg and A.E. Broo, J. Water Supply Res. Technol. Aqua, 48 (2) (1999) 44–52.
- [16] F. Kozisek, Health significance of drinking water calcium and magnesium <http://www.szu.cz/chzp/voda/pdf/hardness.pdf>, 2003.
- [17] N. Delion, G. Mauguin and P. Corsin, Desalination, 165 (1–3) (2004) 323–334.
- [18] R.E. Loewenthal, I. Morrison and M.C. Wentzel, Water Sci. Technol., 49 (2) (2004) 9–18.
- [19] WHO, Guidelines for drinking-water quality – Chapter 8, http://www.who.int/water_sanitation_health/dwq/gdwq3_8.pdf, 2004, p. 52.
- [20] B. Barbeau, D. Huffman, C. Mysore, R. Desjardins and M. Prevost, J. Environ. Eng. Sci., 3 (4) (2004) 255–268.
- [21] L.L. Gyurek, G.R. Finch and M. Belosevic, J. Environ. Eng. Asce., 123 (9) (1997) 865–875.
- [22] H. Glade, J.H. Meyer and S. Will, Desalination, 182 (1–3) (2005) 99–110.
- [23] WHO, Guidelines for drinking-water quality – Chapter 10, http://www.who.int/water_sanitation_health/dwq/gdwq3_10.pdf, 2004, p. 11.
- [24] L.S. Tisdale, W.L. Nelson, J.D. Beaton and J.L. Havlin, Soil Fertility and Fertilizers, 5 edn., Macmillan Publishing Company, New York, 1993.
- [25] WHO, Expert Committee Meeting on Health Effects of Calcium and Magnesium in Drinking-water, 2006, p. 18.
- [26] A. Withers, Desalination, 179 (1–3) (2005) 11–24.
- [27] Z.H. Liu, D.X. Yuan and W. Dreybrodt, Environ. Geol., 49 (2) (2005) 274–279.
- [28] M. Gautelier, E.H. Oelkers and J. Schott, Chem. Geol., 157 (1–2) (1999) 13–26.
- [29] J.W. Morse and R.S. Arvidson, Earth-Science Rev., 58 (1–2) (2002) 51–84.
- [30] L.A. Sherman and P. Barak, Soil Sci. Soc. Am. J., 64 (6) (2000) 1959–1968.
- [31] J. Redondo, M. Busch and J.P. De Witte, Desalination, 156 (1–3) (2003) 229–238.