New desalinated drinking water regulations are met by an innovative post-treatment process for improved public health

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ABSTRACT

The recent supply of large volumes of seawater desalinated water in Israel prompted both the development of new water quality standards and the development of a novel post treatment process, designed to comply with the new standards at a cost effective price. The new process is designed to supply water with alkalinity, Ca²⁺ and calcium carbonate precipitation potential values as required in the new criteria, along with the addition of a threshold Mg²⁺ concentration recently recommended by the WHO. The current paper describes the process in general, and focuses in particular on attaining these criteria while maintaining a low total hardness concentration (120 mg/L as CaCO₃). The process is based on dissolving calcite using H₂SO₄ and replacing the excess calcium ions generated in this process by Mg²⁺ ions (using a specific cation exchange resin—Amberlite) and by Na⁺ (using a second cation exchange resin—chabazite, from the zeolite group). Once exhausted the resins are re-loaded with Mg²⁺ and Na⁺ by the brine generated in the RO process, thus no unwanted brines are generated. A case study is presented for which operational costs were approximated at 0.034 $US/m³ product water.

Key words | desalinated water, magnesium deficiency, post treatment, quality criteria

INTRODUCTION

In 2012 a large portion of the urban population in Israel will be drinking water produced by two-pass seawater reverse osmosis processes, which virtually remove all soluble minerals. Recent studies by the World Health Organization (WHO 2005, 2006, 2009; Cotruvo 2006) concluded that drinking-water may be important as a partial source of daily dietary nutrition of calcium and magnesium. Studies have shown that populations consuming hard water have been associated with reduced ischemic cardiac mortality. In industrialized countries the daily intake of magnesium of many people often does not reach the recommended daily allowance (RDA), and magnesium deficiencies are common. For example, a national survey among US adults found that 68% consume less than the RDA of magnesium (King et al. 2005) and in about 23% the measured magnesium serum concentrations were defined as hypomagnesaemia (Ford 1999). Drinking water supplies up to 50% of the daily Mg requirement (Churina et al. 1999). It has been claimed that the benefit of increasing magnesium content in drinking water is considerable because of the large population that is affected (Monarca et al. 2006).

This paper presents new drinking water quality regulations recently developed in Israel to cope with potential problems that may result from demineralization and from interaction of desalinated water with water distribution systems and a novel, cost effective Mg-Ca re-mineralization process developed to meet the described requirements plus the addition of Mg²⁺ ions to the water. In particular, this paper describes an additional step to the process, aimed at preventing the production of water with an excessive total hardness concentration.

Newly developed standards for desalinated water in Israel

In 2005 the Israeli Ministry of Health appointed the so-called “Israeli Drinking Water Standards Update Committee” (Adin & Halperin 2007). One of the committee’s tasks was to develop new criteria for desalinated water. At the time no such criteria existed anywhere in the world.

Most of the committee’s discussions addressed issues related to the interaction between desalinated water and the distribution system. Desalinated water streams in Israel are planned to be mixed with other local water sources, either surface water originating from Lake Kinneret at the north of the country (mixed to some extent with groundwater on the way) and/or various groundwater sources. “Red water” is one phenomenon that has occurred in the past as a result of mixing surface waters with other water sources. Continuous slow-rate corrosion of metal pipes within the distribution system is another well-known phenomenon. Since the desalinated product water (following membrane separation) is usually slightly acidic and has no buffering capacity, it is corrosive to metal pipes, and thus should be adjusted for pH, Ca\(^{2+}\), and alkalinity before being piped off-site. The compatibility of the desalinated supply with existing potable supplies may also affect taste and odor and disinfection efficiency. The primary goal of the newly developed criteria was to minimize corrosion and red water effects due to the addition of desalinated water into the distribution system and to minimize bacteria re-growth.

With respect to addition of nutrients, the Israeli Committee has decided to recommend the introduction of a minimum calcium dose to desalinated water. The value chosen, based on recent WHO recommendations, was 25 mg/L as Ca\(^{2+}\). As a rule, the committee’s approach was that in populations that are marginal for nutrition for a particular mineral, supplementing that mineral with the drinking-water may be crucial. The WHO assumes a daily water intake of 2 L/day. This would provide an extra 50 mg Ca/day which is about 5% of the Recommended Daily Allowance (RDA) value of between 1,000 and 1,200 mg Ca/day. The committee believed that it was important to achieve a suitable balance between protection against adverse effects and potential beneficial effects, with respect to essential minerals (Adin et al. 2006). Note that because of chemical stability considerations (positive CaCO\(_3\) precipitation potential) the recommended minimum Ca\(^{2+}\) concentration was higher than the required health recommendation (see below). Considering Ca/Mg optimum ratio, the Committee recommended long-term medical monitoring (bone density and cardiovascular phenomena) of populations that consume desalinated water versus populations that are supplied with natural water rich in Ca and Mg. No standard has been yet recommended for magnesium concentration in desalinated water.

The Israeli committee focused on control strategies and water stabilization means aimed at minimizing detrimental effects in distribution systems. A calcification process was selected as a mandatory post-treatment stage with specific five quality standards to be met (Adin et al. 2006; Lahav & Birnhack 2007):

1. Calcium Carbonate Precipitation Potential (CCPP) higher than 3 mg/L as CaCO\(_3\) and lower than 10 mg/L as CaCO\(_3\).
2. H\(_2\)CO\(_3\) alkalinity higher than 80 mg/L as CaCO\(_3\).
3. \([\text{Ca}^{2+}]\) higher than 80 mg/L as CaCO\(_3\) (32 mg/L as Ca\(^{2+}\)) and lower than 120 mg/L as CaCO\(_3\).
4. pH lower than 8.5.
5. Turbidity lower than 0.5 NTU.

These standards are compatible with the nutrition requirement set for calcium, and are intended to provide reasonably high buffering capacity and stability against pipe attack and release of problematic substances that might affect human health. It is noted that the Israeli Water Authority has added a new restriction to the criteria in a bid subsequently published for the new Hadera desalination plant (100,000,000 m\(^3\)/y, expected to start delivering water in November 2009). In this bid the Israeli Water Authority required that the maximum total hardness, rather than the Ca\(^{2+}\) concentration, would not exceed 120 mg/L as CaCO\(_3\). This restriction means, in practical terms, that if the target for magnesium concentration is \(\sim 10 \text{ mg Mg/L}\), the Ca\(^{2+}\) concentration should not exceed a value of 80 mg/L as CaCO\(_3\) (32 mg Ca/L).

Post treatment options

The choice of the post-treatment process in desalination plants is determined both by the quality of water required and by economic considerations. For calcium and alkalinity...
supply calcite (CaCO$_3$$_{aq}$) dissolution processes are recognized to be the most cost effective in most places (Delion et al. 2004; Hasson & Bendrihem 2006). Two acidic substances are typically used to lower the pH to enhance calcite dissolution kinetics: H$_2$SO$_4$ and CO$_2$$g$. H$_2$SO$_4$ based processes are advantageous from economic and engineering aspects (Lahav & Birnhack 2007) and therefore more commonly applied in Israel. However, these processes are bound to yield a ratio of approximately 2 to 1 between the Ca$^{2+}$ and alkalinity concentrations in the water, and often even a higher ratio (both parameters in units of mg/L as CaCO$_3$). As a consequence, 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 is below the recommended value.

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 (Yermiyahu et al. 2007) and human health reasons, as explained earlier. Post treatment processes that are based on calcite dissolution cannot, naturally, supply Mg$^{2+}$ ions. Other options such as dolomite rock (MgCa(CO$_3$)$_2$) dissolution or direct chemical dosage are expensive and either result in a high, unwanted counter anion concentration (direct chemical dosage) or in a high hardness concentration (dolomite dissolution) (Birnhack et al. 2009).

A novel post treatment process for meeting the new quality criteria plus supply of 10 mg Mg$^{2+}$/L while restricting the total hardness value to 120 mg/L as CaCO$_3$

A new, cost effective and promising post-treatment method for desalinated water has been recently developed. The approach makes use of the H$_2$SO$_4$ based calcite dissolution post-treatment process for alkalinity and Ca$^{2+}$ supply, but at the same time results in a significant concentration of dissolved Mg$^{2+}$ in the water, while fully conforming to the other required criteria. A detailed description of the process is provided in Birnhack & Lahav (2007) and Birnhack et al. (2008). In the current paper a new process feature is introduced: the ability to conform to a restriction on the total hardness value in addition to compliance with the other requirements.

The modified process, shown schematically in Figure 1, hinges around replacing the excessive Ca$^{2+}$ ions generated in the H$_2$SO$_4$ based calcite dissolution process by Mg$^{2+}$ and Na$^+$ ions originating from seawater. Mg$^{2+}$ concentration in seawater is over five times higher than that of Ca$^{2+}$ (approximately 105 meq Mg$^{2+}$/L vs. 20 meq Ca$^{2+}$/L). The Na$^+$ concentration is much higher, around 500 meq Na$^+$/L. In typical seawater RO brines these concentrations are approximately doubled.

The process uses two specific ion exchangers (Resin #1 and Resin #2 in Figure 1) to separate Mg$^{2+}$ and Na$^+$ respectively from seawater. Resin #1 is characterized by a very high affinity towards divalent ions and an extremely low affinity towards monovalent ions (namely Na$^+$). Resin #2 has a reasonably high affinity towards Na$^+$ and Ca$^{2+}$ and a very low affinity toward Mg$^{2+}$. Following the ion exchange loading step, water rich in Ca$^{2+}$ (generated by a H$_2$SO$_4$-based calcite dissolution process) is brought in contact with the Mg$^{2+}$ and Na$^+$ loaded resins, and excess Ca$^{2+}$ ions are exchanged to release Mg$^{2+}$ and Na$^+$ to the water. The process is stopped at a predetermined Ca$^{2+}$ and Mg$^{2+}$ (and consequently Na$^+$) concentrations, and then the operation of the ion exchange columns is switched back to the loading step. In previous publications only the exchange of Ca$^{2+}$ with Mg$^{2+}$, using one ion exchange resin, was described. In this paper the combination of two resins is described, with the aim of attaining both the required Ca$^{2+}$
and Mg$^{2+}$ concentrations, but also to satisfy the requirement of total hardness concentration $\leq 120$ mg/L as CaCO$_3$.

All the water streams used in the process are internal streams generated in the RO process. The RO process in Ashkelon includes four stages (Redondo et al. 2003). Either seawater after pretreatment or the brine of the 1st pass of the Ashkelon process (which is basically seawater concentrated by a factor of about 2.2) can be used to load the resins with magnesium and sodium (Resin #1 and Resin #2, respectively). The brine generated in the so called 4th stage in the Ashkelon process is characterized by low TDS concentration and hence can be utilized for rinsing the resin before switching between seawater and freshwater streams.

In the Results and Discussion section a case study is shown, designed to attain the following quality criteria in the product water: Alkalinity = 85, [Ca$^{2+}$] = 80, CCPP = 3 (all concentrations in mg/L as CaCO$_3$), [Mg$^{2+}$] = 9.7 mg/L (40 mg/L as CaCO$_3$) and Total hardness = 120 mg/L as CaCO$_3$.

**METHODS**

**Ion exchange simulation runs**

A 13.6 meq/L Ca$^{2+}$ solution was used in the Ca$^{2+}$-Mg$^{2+}$ and Ca$^{2+}$-Na$^{+}$ exchange steps. The 1st brine from the Ashkelon plant was used for loading the resins. Distilled water was used to simulate the wash step. Experiments were carried out in two 25.2-mm internal-diameter PVC columns, each filled with a different resin. A peristaltic pump was used to ensure constant 30 BV/h flow-rate to both columns.

**Analyses**

Mg$^{2+}$, Ca$^{2+}$, K$^+$ and Na$^+$ were analyzed by inductively coupled plasma (ICP) emission spectrometry, Optima 3,000 DV, Perkin Elmer.

**RESULTS AND DISCUSSION**

**Choice of resins**

As previously reported in Birnhack & Lahav (2007) Amberlite IRC747 (Rohm & Haas, INC) was found suitable for use as Resin #1 within the process (exchange of Ca$^{2+}$ by Mg$^{2+}$). For resin #2 (exchange of Ca$^{2+}$ with Na$^+$), chabazite, a natural zeolite, was chosen. When brought to equilibrium with seawater, chabazite absorbed mainly Na$^+$ (66.8% of the total capacity) while Ca$^{2+}$ was hardly absorbed (3.6%).

**Simulation of the exchange, load and wash steps**

Continuous experiments were conducted in order to simulate the following operational parameters: 25% of the raw desalinated water was pumped through the calcite dissolution reactor (75% was not treated—see Figure 1). The effluent of the calcite reactor was equally distributed between the two resin columns (i.e. 12.5% of the raw desalinated water flow was passed through each resin column, $Q_1 = Q_2$, see Figure 1). The concentration of each component in the product water is a weighted average of its concentration in the three streams (i.e. effluent from the Amberlite column, the chabazite column and the bypassed desalinated water). Hence, the Na$^+$ concentration in the chabazite column effluent should be eight times higher than the concentration required in the product water. The alkalinity and total hardness in the product water are required to be 85 and less than 120 mg/L as CaCO$_3$ (i.e. 1.7 and $\leq 2.4$ meq/L, respectively). Assuming that 25% of the raw desalinated water is pumped into the calcite reactor, and that the Ca$^{2+}$ to alkalinity ratio at the outlet of the calcite reactor approaches 2:1, as previously explained, the Ca$^{2+}$ concentration (and also the total hardness value) attained at the outlet of the calcite reactor would be 13.6 meq/L (i.e. 1.7 times 4 times 2). In case Ca$^{2+}$ is replaced only with Mg$^{2+}$, the total hardness does not change. Therefore, under such scenario the product water would have a total hardness concentration of 3.4 meq/L, which is above the required value. In order to reduce the total hardness to 2.4 meq/L, as required, 1 meq/L of Ca$^{2+}$ (in the product water) must be replaced with 1 meq/L of Na$^+$. This exchange is carried out in the chabazite column (Resin #2). Therefore, the Na$^+$ concentration at the outlet of the chabazite column should be 8 meq/L.

Figure 2 presents the cumulative cation concentrations (average and standard deviation) in the effluent of the chabazite ($n = 4$) and Amberlite IRC747 ($n = 4$) columns.
during the exchange step, i.e. when the seawater-loaded resins are contacted with a 13.6 meq/L solution. The right hand side of Figure 2 refers to the effluent of the chabazite reactor. It shows that after 69 BV the cumulative concentrations of Ca\(^{2+}\) and Na\(^{+}\) in the effluent were around 5.3 and 8, respectively. At that point (after 69 BV) the Mg\(^{2+}\) concentration was 0.2 meq/L. Considering that the Mg\(^{2+}\) concentration in the product water should be 0.8 meq/L and that each ion exchange column treats one eighth of the raw desalinated water flowrate, it transpires that the required Mg\(^{2+}\) concentration in the effluent of the Amberlite column should be 6.2 meq/L (6.2 meq/L times 0.125 plus 0.2 meq/L times 0.125 = 0.8 meq/L).

The left hand side of Figure 2 presents the average and standard deviation, \(n = 4\) of the cumulative concentrations of Ca\(^{2+}\) and Mg\(^{2+}\) in the effluent of the Amberlite column during the exchange step. This plot shows that after around 61 BVs, the cumulative concentrations of Ca\(^{2+}\) and Mg\(^{2+}\) are around 6.7 and 6.2 meq/L, respectively, the Na\(^{+}\) concentration at this point was 0.3 meq/L. Consequently, the Ca\(^{2+}\) and Mg\(^{2+}\) concentrations in the product water would be 1.6 and 0.8 meq/L, respectively, i.e as required.

Figure 3 shows the number of BVs required to load the chabazite and Amberlite with RO brine taken from the Ashkelon plant (seawater concentration £ 2.2) following the exchange step. Figure 3 shows that the load step of the chabazite and the Amberlite can be practically stopped after 15 and 20 BVs, respectively. These results mean that ~25\% of the Amberlite (i.e. 20/(20 + 61)) and ~18\% (15/(15 + 69)) of the chabazite will be at all times during the work cycle in the load step while 75\% and 82\% respectively will operate at the exchange step.

At the end of the load step, residual brine has to be washed out from the resin’s pores in order to prevent it from mixing with the product water in the subsequent exchange step. The rinsing procedure and the results of

![Figure 2](image1.png)  
**Figure 2** | Results of the exchange step: averaged cumulative concentrations of Ca\(^{2+}\) (gray line), Mg\(^{2+}\) (black line) and Na\(^{+}\) (thick black line), in the effluent of the Amberlite and chabazite columns (left and right hand sides, respectively). (Experimental conditions: resin preloaded with 1st stage brine; inlet water quality: \([\text{Ca}^{2+}] = 13.6\) meq/L and \([\text{Na}^{+}] = [\text{Mg}^{2+}] = 0\)).

![Figure 3](image2.png)  
**Figure 3** | Loading step results: averaged concentrations of Ca\(^{2+}\) (gray line), Mg\(^{2+}\) (black line) and Na\(^{+}\) (thick black line) in the effluent of the Amberlite and chabazite columns (left and right hand side, respectively). Experimental conditions: resin composition as attained as a result of the previous exchange step depicted in Figure 2; loading solution: Ashkelon desalination plant’s 1st-stage brine.
applying it on a column filled with Amberlite are described elsewhere (Birnhack & Lahav 2007). Similar results were observed when this procedure was applied to a column filled with chabazite (results not shown). In both cases (Amberlite and chabazite) three to four BVs were required for rinsing.

At the end of the rinsing step, the solution was gravitationally drained out of the column. The volume of the rinsing solution that remained in the Amberlite and chabazite beds was empirically approximated at 0.11 BV and 0.34 BV, respectively. In case low TDS brine from the RO process is available for rinsing, the enrichment of the product water with salts from the rinsing brine can be calculated according to the volume of the brine that remains after drainage and the number of BVs in the subsequent exchange step. For example, TDS and boron concentrations in the 4th stage brine in the Ashkelon desalination plant are 1,250 and 80 mg/L, respectively. Therefore, the TDS and boron concentrations added to the product water from washing the Amberlite column are 0.28 mg TDS/L and 0.02 mg B/L, respectively. The TDS and boron concentrations added to the water from rinsing the chabazite column using this technique are 0.77 and 0.05 mg/L, respectively (see detailed calculation in Birnhack & Lahav 2007). The overall TDS and boron concentrations added to the product water from applying this procedure would be approximately 1.05 and 0.07 mg/L, respectively.

**CONCLUSIONS**

1. An improved two-step post-treatment process for desalinated water was introduced. The process enables meeting quality criteria for a balanced combination of pH, CCPP, alkalinity, Ca$^{2+}$, Mg$^{2+}$, SO$_4^{2-}$ and total hardness concentrations. The process is based on exchanging excess Ca$^{2+}$ ions generated in the common H$_2$SO$_4$-based calcite dissolution post-treatment process by Mg$^{2+}$ and Na$^+$ ions that originate from seawater, using two specific cation exchange resins.

2. A significant improvement to the process, i.e. the reduction in the total hardness concentration in the product water was achieved by an additional resin used to exchange a fraction of the excess Ca$^{2+}$ with Na$^+$. Under the described case study, chabazite and Amberlite resins were shown to operate for 69 BVs and 61 BVs, respectively in the exchange step before being switched to the load step, in which Na$^+$ and Mg$^{2+}$ were reloaded on the resins, using RO brine. 15 and 20 BVs were required to load either resin, suggesting that the time in which each resin would spend in the load step is approximately one sixth and one fourth of the overall time of the ion exchange cycle, respectively.

3. The number of BVs required for rinsing both resins was found to be between three and four BV. The volume of the rinsing solution that remains in the Amberlite and chabazite beds after gravity draining is approximately 0.11 BV and 0.34 BV, respectively. Under such conditions the total TDS and boron added to the product water as a result of the rinsing solution remaining in the beds are 1.05 and 0.07 mg/L, respectively.

4. The approximated total volume of resin required for applying the process in the 100-million m$^3$/y Ashkelon plant is 80 m$^3$ for the Amberlite and 69 m$^3$ for the chabazite (assuming that each resin treats 1/8 of the overall flowrate and that 18% to 25% of the time the resins are in the loading step, as discussed above and assuming a flow rate of 50 BV/h through the resins).

5. The operational cost of the described post treatment process was approximated at US$0.034 per m$^3$ of product water (applying the cost analysis technique shown in Birnhack & Lahav 2007). The following chemical cost list was used ($/ton): H$_2$SO$_4$ (98%) = 225, CaCO$_3$$_{s_v}$ = 35, NaOH = 500, Amberlite = 12,000 $/m^3$ and chabazite = 300 $/m^3$.

6. Post-treatment regulations for desalinated water can be met effectively and economically without threatening the use of seawater as a major water resource.

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