



## Potential applications of quarry dolomite for post treatment of desalinated water

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### ABSTRACT

Recent WHO publications recommend a minimum concentration of 10 mg Mg/L in desalinated water. Dolomite dissolution was investigated as means of adding magnesium ions to desalinated water at the post treatment stage, in addition to  $\text{Ca}^{2+}$  ions and carbonate alkalinity. The results show that dolomite dissolution *per se* is not feasible for post treatment purposes, because dolomite stops dissolving at a relatively low pH, rendering the alkalinity and Calcium Carbonate Precipitation Potential values very low and negative, respectively. To overcome this problem three combined dolomite-calcite dissolution alternatives were investigated. The results show that the most promising method is to dissolve dolomite and then use the  $\text{CO}_{2(\text{aq})}$ -rich effluent to further dissolve calcite. Applying such in-series dissolution, it is possible to produce water with the following quality criteria: alkalinity = 75 mg/L as  $\text{CaCO}_3$ ,  $[\text{Mg}^{2+}] = 12.4$  mg/L,  $[\text{Ca}^{2+}] = 120$  mg/L as  $\text{CaCO}_3$ , pH 8.17. However, the resultant total hardness value is high (170 mg/L as  $\text{CaCO}_3$ ). The operational costs of this alternative were approximated at 0.042 \$  $\text{m}^{-3}$  product water.

**Keywords:** Dolomite dissolution; Post treatment; Desalination; Calcite dissolution; Magnesium

### 1. Introduction

Desalinated water is providing an increasing portion of the total fresh water supply in a growing number of countries. At present, seawater desalination provides ~1% of the world's drinking water and production is increasing at an annual rate of up to 25% [1]. Notwithstanding that desalinated water is of superior quality, it is widely accepted that soft waters supplied with low alkalinity concentrations are characterized by low buffering capacity and thus may be aggressive to water distribution systems, resulting in metal corrosion and red water events [2]. In addition, constant consumption of water that contains low concentrations of calcium and magnesium ions has been associated with a variety of human health disorders. Finally, water low in minerals may damage agricultural crops [1].

To partly overcome these drawbacks, explicit quantitative criteria have been proposed in Israel to address the

required quality of desalinated water, following the post treatment stage. The criteria, adopted in 2006 by the Israeli Ministry of Health, are: alkalinity  $>80$ ,  $80 < [\text{Ca}^{2+}] < 120$ , calcium carbonate precipitation potential (CCPP)  $>3$  and  $<10$  (all concentrations in mg/L as  $\text{CaCO}_3$ ), and pH  $<8.5$ . The reason for this specific choice of parameters and the decision regarding the explicit range of concentrations is covered in detail in Lahav and Birnhack [3] and Birnhack et al. [4]. It is noted that in the bid published for the new Hadera desalination plant (100 million  $\text{m}^3/\text{y}$ , currently under construction), the Israeli Water Authority adopted the above criteria; however, the requirement for  $\text{Ca}^{2+}$  was replaced by a more stringent requirement for total hardness (i.e.,  $80 < \text{total hardness} < 120$  mg/L as  $\text{CaCO}_3$ ).

#### 1.1. The need for $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ in drinking water

According to the WHO, the two most important ionic components required in drinking water (health-wise) are  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  [5]. In desalinated water the dissolved  $\text{Ca}^{2+}$  concentration is typically restricted by a maximum and a

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minimum concentration values. The minimal value, attributed mainly to prevention of cardiovascular diseases (CVD) in humans, has been typically set at 50 to 60 mg/L as  $\text{CaCO}_3$  [6–9]. However, in most cases the  $\text{Ca}^{2+}$  concentration that is required to stabilize the water chemically exceeds this value. On the other hand, the maximum  $\text{Ca}^{2+}$  value is typically decided upon based on economic reasons attributed to the need to supply water that is not excessively hard. In Israel this value was set at 120 mg/L as  $\text{CaCO}_3$ , as mentioned above [3]. Note that the quality criteria for desalinated water in Israel were set under the assumption that the water would be mainly used for domestic use. In case the water is planned to be used for both domestic and agricultural irrigation, an extended set of criteria was recommended [1]. The most noticeable change between the two criteria sets was the inclusion of  $\text{Mg}^{2+}$  at a concentration of between 12 and 18 mg/L in the latter criteria set.

$\text{Mg}^{2+}$  ions, despite not being included in the current Israeli quality criteria, are welcome in desalinated water for both agricultural [1,10] and human health reasons [5,7,9,11]. In a recent WHO meeting of experts (held in Washington D.C. in April 2006) on the possible protective effect of hard water against cardiovascular disease, it was reported that low magnesium status in humans had been implicated in a variety of diseases including hypertension, coronary heart disease, type 2 diabetes mellitus and the metabolic syndrome. The importance of  $\text{Mg}^{2+}$  in drinking water was emphasized and it was stated that recent studies indicate that the benefits of magnesium in water level off at a concentration of about 10 mg  $\text{Mg}^{2+}$ /L [9]. Another recommendation that emerged from this meeting was that desalination stabilization practices should ensure that the overall process does not significantly reduce total intake of nutrients such as calcium and magnesium [9]. Monarca et al. [11], who reviewed epidemiological studies on the relation between drinking water hardness and CVD, concluded that recent available information supports the hypothesis that low intake of magnesium from drinking water increases the risk of dying from, and possibly developing CVD or stroke. They stated that increased magnesium intake from water used for drinking and cooking may be beneficial especially in populations with insufficient dietary intake and would be a relatively easy way for maintaining a sufficient Mg level for the entire population. In other words, the benefit in increasing magnesium content of drinking water is considerable, because of the large population that is affected [11]. A national survey among US adults found that 68% consume less than the recommended dietary allowance (RDA) of magnesium [12]. Two liters of water reaching in magnesium (40 mg/L) can provide about 25% of the RDA, and magnesium may be more bioavailable in drinking water than in food [11].

## 1.2. Post treatment alternatives for desalinated water

The current methods applied for post treatment of reverse osmosis (RO) desalination plants focus on supplying required concentrations of  $\text{Ca}^{2+}$  and alkalinity and adjusting the  $\text{CaCO}_3$  stability index (LSI or CCPP). To the best of the writers' knowledge,  $\text{Mg}^{2+}$  addition is not practiced, except for one desalination plant in Cyprus where  $\text{MgSO}_4$  is being added to the water. Three main groups of post treatment processes currently exist: (1) processes that are based on direct dosage of chemicals (e.g. dosage of  $\text{Ca}(\text{OH})_2$  followed by  $\text{CO}_{2(\text{g})}$ ) [13,14]; (2) processes that are based on mixing desalinated water with other water sources, with or without further adjustment of water quality parameters [15]; and (3) processes that center around dissolving  $\text{CaCO}_{3(\text{s})}$  (typically calcite) for alkalinity and  $\text{Ca}^{2+}$  supply, followed by pH (and CCPP) adjustment using NaOH [16,17].

The first two process groups are less commonly practiced because (a) direct dosage of chemicals is usually more expensive than limestone ( $\text{CaCO}_{3(\text{s})}$ ) dissolution, in places where limestone is encountered in nature and can be easily excavated (despite the fact that the capital costs associated with methods that are based on direct dosage of chemicals are much lower), and (b) when desalinated water is diluted with other water sources further chemical addition is usually unavoidable, if all criteria are to be met [13–15]. Consequently, dissolution of  $\text{CaCO}_{3(\text{s})}$ , using either  $\text{H}_2\text{SO}_4$  or  $\text{CO}_{2(\text{g})}$  is often the most cost-effective choice.

Three alternative processes have been proposed for the addition of  $\text{Mg}^{2+}$  to desalinated (or soft) water: (1) direct dosage of a chemical ( $\text{MgCl}_2$  or  $\text{MgSO}_4$ ) to the water (e.g. [2]); (2)  $\text{H}_2\text{SO}_4$ -based calcite dissolution followed by an ion exchange reactor, in which excess  $\text{Ca}^{2+}$  ions are exchanged with  $\text{Mg}^{2+}$  ions originating from seawater streams fed to the RO plant [18]; and (3) dissolution of dolomite minerals.

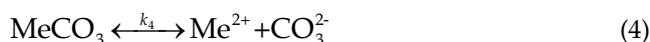
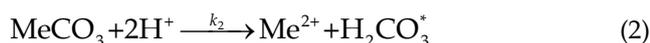
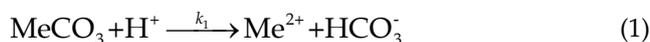
Direct chemical dosage is a very expensive alternative that also results in a high concentration of unwanted counter anions (typically chloride ions) to the water. Calcite dissolution followed by ion exchange has been shown cost effective [4,18]. The third alternative group, i.e. dolomite dissolution, is a method that has not been characterized quantitatively to-date in connection with post treatment of desalinated water. Accordingly, no design data are available, and there has been neither an attempt to determine the resultant water quality nor the costs associated with this process.

This paper describes the results of experiments aimed at characterizing the water quality that can be attained from dissolving dolomite (with or without calcite) using four different alternatives, along with the estimated cost of the chosen alternative.

## 2. Dissolution of carbonate rocks

The term “dolomite” refers in the literature both to a natural carbonate rock and to the pure mineral. The dolomite rock is composed mainly of the dolomite mineral (i.e. more than 90% magnesium calcium carbonate,  $\text{CaMg}(\text{CO}_3)_2$ , on weight basis), [19,20]. However, in nature dolomite is often inter-bedded with limestone, and in some places the thickness of the bed of the rocks is less than one meter, and therefore excavated dolomite frequently contains a significant amount of calcite ( $\text{CaCO}_3$ ) [19]. In this paper the term “dolomite” is used to describe the quarry, non-homogeneous mineral, while the pure mineral is referred to as “dolomite mineral”.

Generally speaking, the dissolution of metal carbonates can be described by four parallel reactions that occur at the solid/water interface [21]:



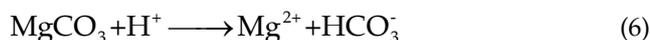
where  $\text{Me}=\text{Ca, Mg}$ ;  $\text{Me}^{2+}$ ,  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  represent total dissolved species (free ions plus ion pairs).

Investigation into the influence of pH on the rate of dissolution of calcite ( $\text{CaCO}_3$ ) and dolomite in near  $\text{CO}_2$  absence and far from equilibrium shows that below pH 5 the rate of dissolution is strictly proportional to the activity of  $\text{H}^+$ , and the rate becomes independent of pH above this value [22,23]. In other words, Eqs. (1) and (2) are dominant under acidic conditions, whereas at higher pH values (pH>5) Eq. (3)—and to a lesser extent Eq. (4)—determine the dissolution kinetics. Dissolved carbon dioxide (depicted by  $\text{H}_2\text{CO}_3^*$ ) was shown to contribute markedly to the dissolution process under high  $P_{\text{CO}_2}$  conditions, according to Eq. (3).

Busenberg and Plummer [22] suggested that the dissolution of the mineral dolomite under acidic conditions (pH <5) is a two-step process, the first step described by Eq. (5):



The second step, which is the slower and thus rate limiting, is described by Eq. (6):



Clearly, the stoichiometric addition of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $C_T$  (total inorganic carbon concentration) to the water as a result of dissolution of dolomite mineral is at a ratio of 1:1:2. However, if the excavated dolomite rock contains a certain amount of calcite (as often is the case) the ratio of  $\text{Ca}^{2+}$  to  $\text{Mg}^{2+}$  added to the water would be higher than 1:1. Moreover, according to Busenberg and Plummer [22] the ratio of  $\text{Ca}^{2+}$  to  $\text{Mg}^{2+}$  released to the water during dolomite dissolution fluctuates between <1 and >1. The observations were explained by the dissolution mechanism described in Eqs. (5) and (6).

However, irrespective of the exact composition of the dolomite rock, the ratio between the  $C_T$  added to the water and the sum of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  should always tend toward 1:1 (excluding impurities).

Kinetics wise, the overall dissolution rate of carbonate minerals was described by [21] as follows:

$$r_{\text{dissolution}} = k_{1,2}a_{\text{H}^+}^n + k_3a_{\text{H}_2\text{CO}_3} + k_4 \quad (7)$$

where  $r_{\text{dissolution}}$  is the dissolution rate;  $k_i$  is the rate constant of reaction  $i$  and  $a_x$  is the activity of  $x$ .

The first term in Eq. (7) corresponds to protonation under acidic conditions described by Eqs. (1) and (2) (or Eqs. (5) and (6) for the case of dolomite) and the second to surface carbonation at high  $P_{\text{CO}_2}$ , as described in Eq. (3). The third term corresponds to simple hydration of the surface and detachment of  $\text{Me}^{2+}$  and  $\text{CO}_3^{2-}$  ions, as described in Eq. (4). In natural environments the dominant process is better described by Eq. (4) [24], whereas in reactors aimed at supplying alkalinity and  $\text{Ca}^{2+}$ , where acidic conditions prevail and  $\text{CO}_{2(\text{aq})}$  concentration is high, the reactions described in Eqs. (1)–(3) and (5) and (6), dominate.

To conclude, the dissolution rate of calcite and dolomite does not depend exclusively on pH, but it is rather a more complex function of pH and  $C_T$ . A high  $C_T$  contributes to the dissolution capacity of the water in two ways: first, higher  $C_T$  at a given pH corresponds to a higher  $\text{CO}_{2(\text{aq})}$  concentration, which results in a faster dissolution rate [second term in Eq. (6)]; and second, a higher  $C_T$  value results in a higher buffering capacity that decreases the extent of the increase in pH as a result of the release of  $\text{CO}_3^{2-}$  during dissolution, allowing for further dissolution.

### 2.1. Dolomite dissolution

Several problems have been encountered when attempting to dissolve dolomite rocks for water treatment purposes: the most noticeable drawback is related to the dissolution kinetics, which is much slower than that of calcite [24–26]. For example, Liu et al. [26] 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. A 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 [27–29]. In these applications dolomite was used to raise the pH to above pH6 using a retention time of several days. For this application the slow kinetics of the process was not considered disadvantageous. Rooklidge and Ketchum [30] showed that a thin layer of crushed dolomite media can be placed within a slow sand filter to improve downstream corrosion control.

Beyond these reports the information on dolomite dissolution within water treatment works is very limited, and does not provide useful data with respect to operational parameters required for design of post treatment processes. For example, one cannot conclude from the literature what would be the  $\text{Ca}^{2+}$  to  $\text{Mg}^{2+}$  ratio released to the water at a given pH range, in case the dolomite rock contains a  $\text{Ca}^{2+}$  to  $\text{Mg}^{2+}$  ratio higher than 1:1. More importantly, because the dissolution kinetics of dolomite rocks under the conditions which prevail in dissolution reactors is not well quantified, one cannot conclude what would be the final pH (and alkalinity) of acidified water after it is brought to contact with dolomite for a short retention time (in the order of minutes, as required in desalination plants). These uncertainties are exacerbated because quarry products tend to slightly differ in composition and in dissolution characteristics.

## 2.2. Dissolution of quarry dolomite for post treatment of desalinated waters

Considering that reasonable dolomite dissolution kinetics can be attained only at a relatively low pH, it was hypothesized in this work that dissolving dolomite per se cannot result in water that meets all the required criteria at a cost effective price. Therefore, in addition to investigating dolomite dissolution, three further alternatives were examined: (1) parallel dissolution of dolomite and calcite in separate reactors and combining the effluent streams to attain the final product; (2) dissolution of a predetermined mixture of dolomite and calcite in a single reactor; and (3) dissolution of dolomite and calcite one after the other (in-series operation). In all four options strong acid ( $\text{H}_2\text{SO}_4$ ) was added to the water prior to dissolution in order to reduce pH and expedite dissolution kinetics. Following the dissolution step NaOH dosage, required to raise alkalinity, CCPP and pH, was calculated for chosen water quality scenarios. Since the usage of a strong acid ( $\text{H}_2\text{SO}_4$ ) enables reducing pH to

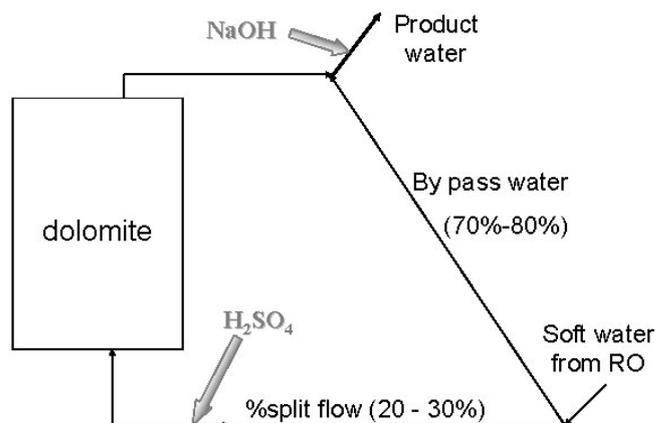


Fig. 1. Schematic of alternative #1: dolomite dissolution as means of post treatment of desalinated water.

practically any required value, not all the water needs to be treated, and a "split flow" strategy can be applied (see Fig. 1).

If steady-state operation is attained, the  $\text{Ca}^{2+}:\text{Mg}^{2+}$  concentration ratio in the effluent of the dolomite dissolution reactor should tend towards the ratio in the dolomite rock. Two operational parameters have to be adjusted in order to attain the required concentrations in the product water: the pH at the inlet of the dissolution reactor and the fraction of the flow that is pumped through the reactor (see Fig. 1). The inlet pH determines the extent of dissolution (i.e. the nominal parameters concentrations at the outlet of the reactor); the "split flow" determines the dilution ratio. The "split flow" is therefore controlled in order to attain a required concentration of one of the species in the effluent (e.g.  $\text{Mg}^{2+}$ ), while the other species ( $\text{Ca}^{2+}$ , alkalinity, CCPP) are dependent, and may need to be adjusted by further chemical dosage.

The following discusses the theoretical advantages and disadvantages of the four alternatives.

- Alternative #1: Direct dissolution of quarry dolomite: The main drawback of alternative #1 is that, as shown in the Results and Discussion section, the dolomite part in the dolomite rock practically stops dissolving at pH ~5.5, thus the water at the outlet of the dolomite reactor is characterized by low pH and alkalinity values. NaOH can be theoretically dosed in order to adjust water quality, but such an approach is neither technically nor economically feasible.
- Alternative #2: Parallel operation of dolomite and calcite dissolution reactors: Alternative #2 assumes parallel operation of several reactors for dolomite dissolution and several reactors for calcite dissolution, followed by NaOH dosage to the blended stream in order to adjust either alkalinity, or pH or CCPP, as shown in Fig. 2a. The alkalinity mass supplied by dolomite dissolution is lower than that supplied by the

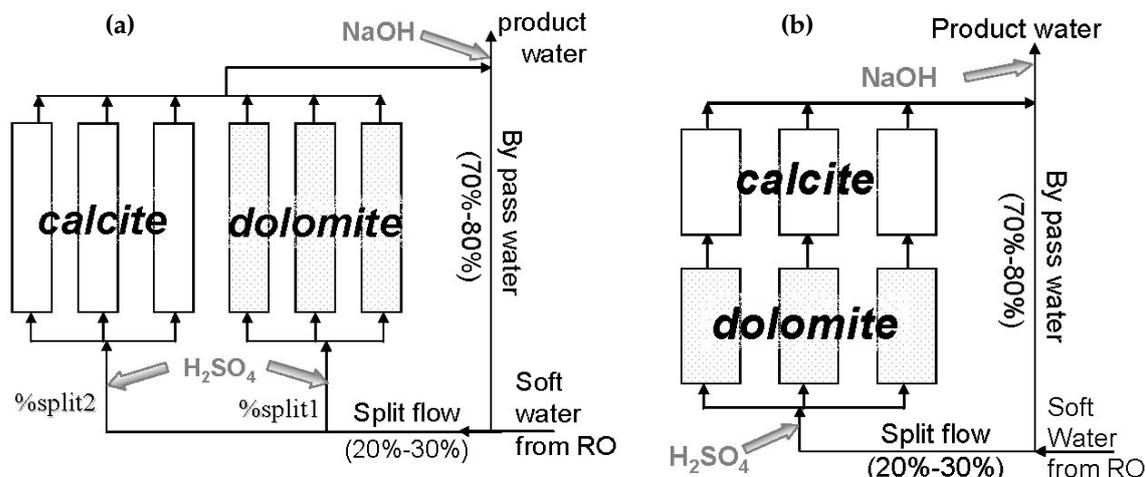


Fig. 2. Schematics of alternatives #2 and #4: (a) parallel operation; (b) operation in series.

calcite dissolution because dolomite stops dissolving at a much lower pH value. Therefore, it was hypothesized that this alternative may result in a better and more flexible water quality than that attained by alternative #1. The ratio between alkalinity and dissolved calcium and magnesium can be controlled (to a certain degree) by changing the relative flow rate pumped to the calcite and dolomite reactors. The main shortcoming of this alternative relates to the fact that the effluent of the dolomite reactors has a low pH value, and consequently low alkalinity and CCPP values, and thus a high base dosage is unavoidably required in the product water.

- Alternative #3: Dissolution of a mixture of dolomite and calcite rocks in a single reactor: In this alternative a reactor is filled with a pre-prepared mixture of the two rocks according to the  $Ca^{2+}:Mg^{2+}$  ratio required in the product water. On top of the additional cost associated with mixing the rocks prior to application, this alternative was expected to result in a low  $Mg^{2+}$  concentration for a given initial pH applied, because the kinetics of  $CaCO_3$  dissolution is much faster than that of dolomite. Moreover, it was assumed that controlling the Ca:Mg ratio in the effluent would be difficult due to the different dissolution kinetics of the two minerals. Nevertheless, this alternative was also examined, in order to cover all contingencies.
- Alternative #4: In-series operation of dolomite and calcite reactors: In this alternative the acidified water is pumped through dolomite and calcite reactors in series, as illustrated in Fig. 2b. As in the other alternatives,  $NaOH$  is dosed to the treated water for adjustment of alkalinity, pH or CCPP. The high  $CO_{2(aq)}$  concentration at the outlet of the dolomite reactor is used in order to dissolve the calcite, thereby higher alkalinity and CCPP concentrations are expected in the product water along with a lower  $NaOH$  requirement.

In other words, the same amount of acid dosage is used to dissolve both dolomite and calcite, while in the other alternatives it is used to dissolve either calcite or dolomite. Therefore, this option was hypothesized from the onset to be the most promising alternative.

### 3. Materials and methods

Two to four mm crushed dolomite (from the Even Vasid Har Dragot quarry) was used in all experiments following rinse with distilled water.

Two types of experiments were conducted: dolomite was first dissolved at batch conditions to verify its stoichiometric composition, and second, dolomite and calcite packed bed reactors were operated to simulate the four operational alternatives at steady state operation.

- Batch experiments: Dolomite rock samples were dissolved using a 37% HCl (pH ~1) acid in order to determine the Ca:Mg ratio in the rock and to quantify presence of metal impurities.
- Continuous packed bed experiments: The experimental apparatus for the dolomite/calcite dissolution consisted of a 200-L inlet solution tank and two packed bed columns (32 mm internal diameter, 148 cm long, filled with crushed rock to the top) operated as a single reactor (the first column was sealed to the atmosphere and its effluent constituted the influent of the second column). The up-flow rate in the columns was adjusted by a peristaltic pump. Fourteen sampling points were positioned along the columns.

A solution at pH 2 (560 mg/L  $H_2SO_4$ , i.e. 0.304 ml  $H_2SO_4$  98% (analytical grade) per liter of distilled water) was used to dissolve the rocks. Metal impurities in the dolomite rock, and calcium and magnesium concentrations were measured using ICP. Alkalinity was

determined using the Gran titration technique [31]. STASOFT4 [32] was used to calculate CCPP values and to simulate the overall process, i.e. to determine chemical dosages and alkalinity, pH and CCPP following blend with untreated desalinated water.

The experimental set-up was slightly adjusted according to the alternative tested. The reactor was either filled up with dolomite and/or calcite or a uniform mixture of the two rocks. Since the aim of the work was to investigate dolomite dissolution (alternative #1) and since the fourth alternative (in-series operation of dolomite and calcite reactors) seemed from the onset to be the most promising, alternatives #1 and #4 were examined under three different flow velocities (4, 7 and 10 m/h). Alternatives #2 and #3 were examined using an up-flow velocity of 7 m/h.

#### 4. Results and discussion

Complete dissolution experiments resulted in  $\text{Ca}^{2+}$ : $\text{Mg}^{2+}$  ratios of between 1.267 and 1.753 (meq/meq) for the specific dolomite rock used in the work (average ratio =  $1.44 \pm 0.13$ ;  $n=12$ ). The weighed average (sum of calcium from all the samples divided by the sum of magnesium from all the samples) was 1.46. Note that the rock's composition was not homogeneous and thus small samples invariably showed different ratios.

No significant heavy metal impurities were encountered in the tested dolomite rock.

##### 4.1. Continuous packed bed experiments

All reported and discussed results correspond to steady-state operation.

###### 4.1.1. Alternative #1: dolomite dissolution

The results of dissolving dolomite rock at three different up-flow velocities are shown in Fig. 3. It is shown that 80% of the total  $\text{Mg}^{2+}$  mass added to the water dissolved in the first few cm of the reactor and 98% of the magnesium dissolved in the first 57 cm when an upflow velocity of 4 m/h was applied, and in the first 90 cm and 120 cm at 7 and 10 m/h, respectively. The pH at which the  $\text{Mg}^{2+}$  concentration leveled out was approximately pH5.5 under all the operational conditions tested. However, although the  $\text{Mg}^{2+}$ -containing part of the rock (i.e. dolomite mineral) stopped dissolving at  $\sim$ pH5.5, the calcite part continued to dissolve at higher pH values. Nevertheless, since calcite constituted only a small fraction of the rock, the  $\text{Ca}^{2+}$  concentration in the water increased relatively gradually. As long as the calcite part of the rock dissolved, the alkalinity value also increased. The pH, on the other hand, increased very gradually in

the upper part of the reactor, not only because the rock dissolved slowly but also because the buffer capacity of the carbonate system at this pH range is high. The alkalinity and pH values obtained in the effluent in this alternative were very low, as also manifested by the very negative CCPP value in the effluent: between  $-200$  mg/L as  $\text{CaCO}_3$  (at 10 m/h) and  $-170$  mg/L as  $\text{CaCO}_3$  (at 4 m/h). The differences between the water qualities obtained with the three flow velocities were not significant. Analyzing the chemicals dosages required for attaining a given water quality it was observed that these were almost identical for the three velocities (results not shown). The same experiments (three upflow velocities) were repeated for the alternative of dissolving dolomite and calcite in series, and a similar conclusion was reached. Thus, although all three up flow velocities were tested, for brevity only the results recorded with the medium velocity (7 m/h) are shown for alternative #4.

Dosage of strong acid (e.g.  $\text{H}_2\text{SO}_4$ ) to the water at the reactor inlet enables reducing the pH to almost any desired value. The practical implications of using a strong acid are first that a large mass of dolomite or calcite can be dissolved into a small fraction of the total flowrate (this fraction is denoted “%split” in the paper). This %split is then blended with the untreated water that bypasses the reactor. The lower the inlet water pH is, the more mineral mass can be dissolved into the water, thus for a given initial pH (a given acid dosage) the value of %split determines the concentrations in the product water (and vice versa, i.e. for a given %split the acid dosage determines the concentrations in the product water). In other words, regardless of the values of %split and the pH at the inlet of the reactor, as long as the acid dosed per  $\text{m}^3$  of product water (see Fig. 1) is identical, the resultant water quality would be the same.

To sum up, the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations in the product water are a combined function of the dolomite rock composition and the  $\text{H}_2\text{SO}_4$  dosage applied per  $\text{m}^3$  product water. For a given pH at the inlet of the reactor, the percentage of the raw water that is pumped to the reactor can be decided-upon according to the required  $\text{Mg}^{2+}$  concentration in the final product water.

In the current work three final  $\text{Mg}^{2+}$  concentrations were considered in order to calculate the %split flow to the reactor: 12 and 18 mg Mg/L for domestic water supply and 24 mg Mg/L for agricultural applications, according to Yermiyahu et al. [1]. The supplementary NaOH dosage to the final water product was calculated in order to achieve an alkalinity concentration  $>80$  mg/L as  $\text{CaCO}_3$ , as required by the Israeli criteria (for the domestic use alternatives). In case the water is used solely for agricultural purposes the quality does not necessarily have to comply with the domestic use criteria. Nevertheless, acidic water may damage soil and crops and corrosive water

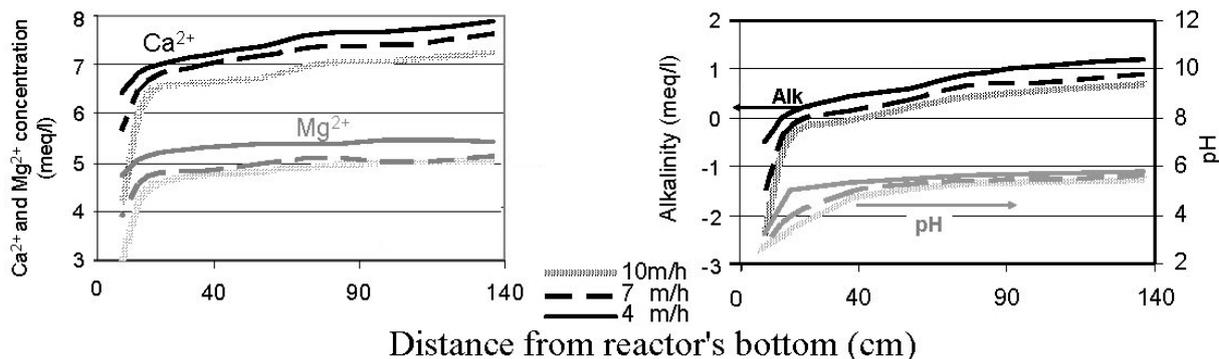


Fig. 3. Results of dolomite dissolution (alternative #1). pH of inlet solution = 2.00. Concentrations of  $\text{Ca}^{2+}$  (black lines),  $\text{Mg}^{2+}$  (gray lines) (left hand graph) and of alkalinity (black lines) and pH (gray lines) (right hand graph), at three flow velocities: 10, 7 and 4 m/h (dotted line, dashed line and continuous line, respectively).

Table 1

NaOH dosage and final water quality of several dolomite dissolution alternatives tested in the work. Value of %split was chosen to attain the  $\text{Mg}^{2+}$  concentration required in each scenario. **In bold**: values that do not conform to the Israeli quality criteria range

|                                            | Alternative number | %split (%)  | NaOH dosage (mg/L) | Final water quality        |                  |              |                |            |             |
|--------------------------------------------|--------------------|-------------|--------------------|----------------------------|------------------|--------------|----------------|------------|-------------|
|                                            |                    |             |                    | $\text{Mg}^{2+}$           | $\text{Ca}^{2+}$ | pH           | Total hardness | Alkalinity | CCPP        |
|                                            |                    |             |                    | (mg/L as $\text{CaCO}_3$ ) |                  |              |                |            |             |
| Dolomite dissolution                       | 1a                 | 20          | 57                 | 12.4                       | 30.6             | <b>10.27</b> | 128            | 80.4       | <b>62.1</b> |
|                                            | 1b                 | 29          | 54                 | 18.0                       | 44.3             | <b>9.42</b>  | 185            | 80.8       | <b>31.2</b> |
|                                            | 1c                 | 38.7        | —                  | 24.0                       | 59.2             | 5.75         | 247            | 17.6       | -113        |
| Parallel calcite & dolomite dissolution    | 2                  | 25          | 46                 | 12.4                       | 47.1             | <b>9.40</b>  | 169            | 80.2       | <b>29.7</b> |
|                                            |                    | %split#1=20 |                    |                            |                  |              |                |            |             |
|                                            |                    | %split#2=5  |                    |                            |                  |              |                |            |             |
| Calcite and dolomite dissolution in series | 4a                 | 20          | 24                 | 12.4                       | <b>47.9</b>      | <b>8.91</b>  | 171            | 81.1       | <b>14.6</b> |
|                                            | 4b                 | 29          | 24.8               | 18.0                       | <b>69.4</b>      | 7.75         | 248            | 105.1      | 3.5         |
|                                            | 4c                 | 38.7        | —                  | 24.1                       | 92.7             | 6.66         | 331            | 98.8       | -54.3       |
|                                            | 4d                 | 20          | 19                 | 12.4                       | 47.9             | 8.17         | 171            | 74.9       | 3.1         |

might harm agricultural infrastructure (pumps, etc.). Limitation on irrigation water quality can therefore be set at either  $\text{pH} > 7$  or positive CCPP or both. However, since no explicit criteria are available for water supplied exclusively to agriculture, any decision on the water quality should be site-specific. For the sake of the ensuing discussion it was assumed that the water should be supplied with a close-to-neutral pH value.

The required NaOH dose for all the examined scenarios, as well as the resultant final water quality, is shown in Table 1. Examining the results listed in Table 1 several conclusions can be drawn with respect to alternative #1: (1) Since the buffer capacity of the effluent under this alternative is low, the addition of NaOH results in a significant pH increase, and the upper pH limit ( $\text{pH} 8.5$ ) is exceeded before the alkalinity threshold (80 mg/L as  $\text{CaCO}_3$ ) is attained; (2) As a result of the previous conclusion, when NaOH is dosed to attain the

alkalinity threshold, the CCPP value becomes excessively high. (3) In case a requirement of 24 mg/L magnesium is set (alternative #1c), no further chemical addition is required. However, the pH and CCPP values of the effluent are very low. If the pH value is to be raised in order to supply water that is not very negative with regard to  $\text{CaCO}_3$  precipitation potential, a very high NaOH dosage would be required.

To sum up this alternative, because quarry dolomite stops dissolving at a relatively low pH value it is practically impossible to generate water that complies with all the criteria using this alternative. As a result, this alternative has to be considered infeasible.

#### 4.1.2. Alternative #2: parallel dissolution of calcite and dolomite rocks

Calcite dissolution experiments were carried out (results not shown). Under the conditions tested (inlet

pH = 2.00, up-flow velocity = 7 m/h), the effluent of the calcite dissolution reactor had a calcium concentration of 331 mg/L, an alkalinity value of 270 mg/L as  $\text{CaCO}_3$ , a CCPP value of -25 mg/L as  $\text{CaCO}_3$  and pH 6.55. These values remained constant in the upper 100 cm of the reactor indicating that the reactor reached its practical maximum dissolving potential. The values of the parameters at the outlet of the dolomite dissolution reactor are shown in Fig. 3. The overall quality of the product water in alternative #2 depends on the choice of the percentage of the water that is passed through the dolomite and calcite reactors (denoted %split1 and %split2 in Fig. 2a, respectively). %split1 was set according to the required  $\text{Mg}^{2+}$  concentration in the final water product. %split2 was chosen according to the upper required threshold for calcium concentration. Given that 12 mg  $\text{Mg}/\text{L}$  is required in the product water, %split1 was chosen as 20%. Consequently, the calcium concentration in the product water due to dolomite dissolution alone was 30.6 mg/L (see Table 1). 47.1 mg  $\text{Ca}/\text{L}$  was attained in the product water when %split1, %split2 and the untreated water stream were 20%, 5% and 75%, respectively. Thus, if %split2 is >5%,  $[\text{Ca}^{2+}]$  surpassed the allowed limit. In case 18 mg  $\text{Mg}/\text{L}$  is required, the consequent calcium concentration would be 44.3 mg $\text{Ca}/\text{L}$  (see Table 1, alternative #1b). Under this scenario it is impractical to dissolve calcite and still remain within the required  $\text{Ca}^{2+}$  range. The required chemicals dosages and the resultant water quality of this alternative are listed in Table 1. The conclusion is that under this operational alternative it is impossible to produce water that meets all the required criteria at the same time.

#### 4.1.3. Alternative #3: Dissolution of a mixture of dolomite rock and calcite rock in a single reactor

Based on the Ca:Mg ratio in the dolomite rock used in the study, dissolving 0.38 g calcite rock along with 1 g of dolomite rock would result in a Ca:Mg ratio of 2.33 eq/eq in the reactor effluent (under the assumption of steady state conditions). Such a ratio enables meeting both the  $\text{Mg}^{2+}$  criterion (i.e. ~1 meq/L) and the  $\text{Ca}^{2+}$  criterion (i.e. <2.4 meq/L) at the same time. However, it was found that dissolving this mixture resulted in a much higher Ca:Mg ratio (3.10 meq/meq instead of 2.33) in the reactor effluent, a direct result of the different dissolution kinetics of calcite and dolomite. Thus, it was concluded that this alternative is also impractical, and it was abandoned.

#### 4.1.4. Alternative #4: Dolomite dissolution followed by calcite dissolution (in series operation)

It has been shown previously that the effluent of a dolomite dissolution reactor is characterized by low pH, very negative CCPP but also a high  $\text{CO}_{2(\text{aq})}$  concentration. The logic behind alternative #4 is that the high  $\text{CO}_{2(\text{aq})}$

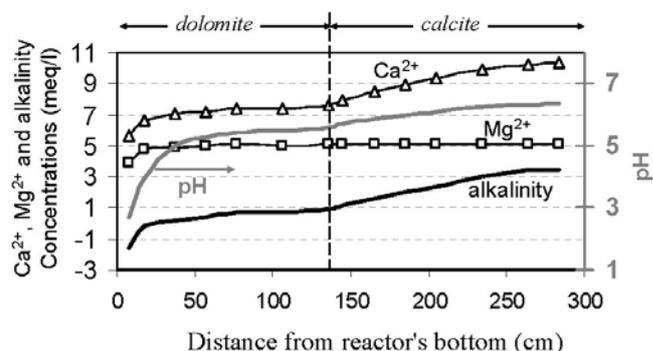


Fig. 4. Dissolution according to alternative #4, pH of inlet solution = 2.00, upflow velocity = 7 m/h. Concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and of alkalinity and pH (triangles, squares, black line and gray line, respectively).

concentration and the low pH and CCPP values can be used to dissolve calcite to increase alkalinity, pH and CCPP. Such a strategy is preferred over NaOH dosage from both water quality and cost effectiveness standpoints.

The results of feeding a calcite reactor with the effluent of a dolomite reactor are shown in Fig. 4. The results show that (1) the pH and  $C_T$  values in the effluent of the dolomite reactor, which were found unsuitable for further dolomite dissolution (Fig. 3), are appropriate for dissolving further several meq/L of calcite; (2) The alkalinity and pH obtained in this alternative were significantly higher than in alternative #1. As a result the CCPP at the outlet of the combined dolomite-calcite reactor was also higher (between -105 mg/L as  $\text{CaCO}_3$  (upflow velocity = 10 m/h) and -50 mg/L as  $\text{CaCO}_3$  (4 m/h) results not shown). To be on the safe side, a further dissolution of ~75 mg/L  $\text{CaCO}_3$  was assumed in all ensuing calculations in order to simulate the results that can be expected in a longer, full scale reactor (i.e. the assumption was that calcite can dissolve at acceptable rates up to a CCPP value of -25 mg/L as  $\text{CaCO}_3$ ). The results of this simulation were used in the calculations of the chemical dosages and the final water quality, as well as in the cost analysis.

Table 1 also lists the required NaOH dosages and the product water quality attained in alternative #4. It can be seen (alternative #4a) that the water quality does not meet all the criteria required for domestic use: for attaining a  $\text{Mg}^{2+}$  concentration of 12 mg/L, the resulting pH and CCPP are excessively high. Moreover, the  $\text{Ca}^{2+}$  concentration is at its upper allowable concentration (120 mg/L as  $\text{CaCO}_3$ ). For 18 mg  $\text{Mg}/\text{L}$  the  $\text{Ca}^{2+}$  concentration becomes excessively high and so does the total hardness value. Since alternative #4a resulted in water quality that does not meet the criteria, an additional scenario (denoted #4d), in which less NaOH dose is added, was considered. In alternative #4d the alkalinity value is slightly lower than the required threshold (i.e. 75 instead of 80 mg/L as

Table 2  
Estimation of chemical dosages and operational costs related to in-series dissolution of dolomite and calcite (alternatives #4a and #4d)

|                                     | Chemical dosed |                                              | Cost of alternative #4d<br>(Alternative #4a) |                                                   |
|-------------------------------------|----------------|----------------------------------------------|----------------------------------------------|---------------------------------------------------|
|                                     | Purity         | Cost <sup>a</sup><br>(\$ ton <sup>-1</sup> ) | Dosage<br>(g/m <sup>3</sup> )                | Cost of<br>product<br>water (\$ m <sup>-3</sup> ) |
| H <sub>2</sub> SO <sub>4</sub>      | 0.98           | 225                                          | 113.0                                        | 0.0252                                            |
| CaCO <sub>3</sub>                   | 1              | 35                                           | 44.5                                         | 0.00156                                           |
| CaMg(CO <sub>3</sub> ) <sub>2</sub> | 1              | 45                                           | 117.5                                        | 0.00528                                           |
| NaOH                                | 1              | 500                                          | 19.0 (24)                                    | 0.0095                                            |
| Energy costs                        |                |                                              |                                              | (0.012)                                           |
| Total operational costs             |                |                                              |                                              | 0.0003                                            |
|                                     |                |                                              |                                              | 0.042 (0.044)                                     |

<sup>a</sup>Represents middle of cost range obtained for H<sub>2</sub>SO<sub>4</sub> (200–250 \$/ton) and NaOH (450–550 \$/ton).

CaCO<sub>3</sub>), but the CCPP and pH value comply with the criteria.

Comparing alternatives #1 and #4 shows that the latter is advantageous because less NaOH is required (for both Mg<sup>2+</sup> concentration scenarios). This is due to the fact that the water leaves the dissolution units with a higher carbonate alkalinity value. On the other hand, because alkalinity supply in this technique is coupled with supply of Ca<sup>2+</sup>, the total hardness concentration attained in alternative #4 was the highest of all the alternatives tested. For 12 mg Mg/L a total hardness of around 150 mg/L as CaCO<sub>3</sub> was attained, and for 18 and 24 mg Mg/L total hardness values of 224 and 300 were recorded, respectively. The high total hardness attained in alternative #4 constitutes a major limitation to the use of this method for post treating desalinated water. As mentioned, in the new desalination plant in Hadera a maximum total hardness concentration of 120 mg/L was set. The results of this study show that dolomite dissolution (either alone or in combination with calcite dissolution) cannot be practiced when stringent (low) total hardness requirements are set.

## 5. Cost estimation

Table 2 shows the operational costs (chemical dosages and energy) per m<sup>3</sup> of product water (in \$ m<sup>-3</sup>) estimated for the two most promising alternatives, i.e. alternatives #4a and #4d. It was shown elsewhere that capital expenses account for only around 5% of the overall cost of post treatment operations [?]. The operational cost for producing 1 m<sup>3</sup> of product water in alternative #4a and #4d was approximated at 0.044 \$ m<sup>-3</sup> and 0.042 \$ m<sup>-3</sup>, respectively. In conclusion, alternative #4d is better than

alternative #4a, both from water quality and cost effectiveness standpoints, but the alkalinity value in this alternative is slightly lower than that required.

As mentioned in the introduction, another method for magnesium re-mineralization was recently proposed by the authors. The method is based on separating Mg<sup>2+</sup> from seawater using specific ion exchange resins [18]. For comparison purposes, the total operational cost of the ion-exchange-based process (using the same cost set for the chemicals and including replacement of the resin at 5% per year) was estimated at 0.036 \$ m<sup>-3</sup> for attaining the following water quality: [Ca<sup>2+</sup>] = 100, alkalinity = 75, CCPP = 1.4 (all concentrations in mg/L as CaCO<sub>3</sub>), [Mg<sup>2+</sup>] = 12.2 mg/L and pH = 8.10.

## 6. Conclusions

The practical aspects of dolomite dissolution as a post treatment method for desalinated water were studied. The straightforward method of dissolving dolomite for post treatment purposes suffers from several drawbacks that make its practice problematic: first, dolomite practically stops dissolving at pH~5.5, resulting in a very low carbonate alkalinity in the effluent. In order to achieve an adequate alkalinity concentration a significant dose of costly NaOH is required, and in many cases the upper required values for pH (pH8.5) and CCPP (10 mg/L as CaCO<sub>3</sub>) are exceeded. Second, process flexibility is limited and only a narrow range of water qualities can be achieved. Within this range it is impossible to supply water that complies with all the criteria required by the Israeli regulations, and at the same time supply 12 mg Mg/L. As a result of the slow dissolution kinetics and the low effluent alkalinity, it may be safely concluded that dissolution of dolomite alone is impractical for post treatment purposes.

Dissolution of dolomite and calcite in parallel reactors and combining the effluents of both reactors results in a better water quality. However, in this alternative too, the carbonate alkalinity in the effluent is relatively low and it is impossible to generate water that simultaneously meets all the quality criteria.

Dissolution of a mixture of dolomite and calcite in a single reactor is impractical because of the difference in the dissolution kinetics of the two minerals. It is practically impossible to control the extent of dissolution of each mineral and it is therefore impractical to achieve a required water quality in a constant fashion.

Out of the four operational alternatives tested, the only alternative that was found feasible was dissolution of dolomite and calcite in series. Applying in-series dissolution, it is possible to achieve water that meets all the criteria except the alkalinity criterion (i.e. 75 instead of >80 mg/L as CaCO<sub>3</sub>). The operational costs of this alternative

were approximated at 0.042 \$ (m<sup>-3</sup> product water). Note that the resultant total hardness value in this alternative is somewhat high (170 mg/L as CaCO<sub>3</sub>).

Theoretically, NaHCO<sub>3</sub> can be dosed to the water at the final treatment stage in addition to NaOH. In case a combined dosage of the two bases is applied, an increase in alkalinity, pH and CCPP values can be carried out to meet all the quality criteria simultaneously. However, this approach is impractical due to the very high cost of the sodium bicarbonate chemical.

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