Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2018.22475

115 (2018) 194–198
May

Dolomite dissolution is not an attractive alternative for meeting Ca^{2+}, Mg^{2+} and alkalinity criteria in desalination plants' post treatment step

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Received 19 March 2018; Accepted 5 May 2018

ABSTRACT

Dolomite dissolution is often mentioned as an option for post-treatment of desalinated water for supplying calcium, magnesium and alkalinity to the product water and comply with non-aggressiveness criteria. This paper uses reliable literature-based dolomite dissolution data to compute and discuss various options for utilizing this process to meet two common sets of desalinated water quality criteria. Alkalinity mass-balance was performed to corroborate literature-data correctness. Discussion shows that CO_2-enhanced dolomite dissolution is impractical due to slow dissolution rates encountered at the relatively high pH values induced by the CO_2 dosage, resulting in low Mg^{2+} concentrations at reasonable retention time. In the H_2SO_4-enhanced dolomite dissolution the main difficulty arises from the low alkalinity value attained in the water following its blending with raw desalinated water. This, in turn, necessitates very high NaOH dosages to meet required alkalinity and LSI. At relatively low H_2SO_4 dosages, the post-dilution alkalinity value can be increased, but at the expense of treating the majority of the desalination plant flow, resulting in excessively-high dissolution-reactor volumes. The overall conclusion is that dolomite dissolution is markedly inferior (cost- and quality-wise) to competing Mg^{2+} addition alternatives, including simple dissolution of off-the-shelf chemicals, such as $MgSO_4$.

Keywords: Dolomite dissolution; Post treatment; Desalination; Water quality criteria; Magnesium

1. Introduction

The rise in the interest in the health effects associated with magnesium deficiency in desalinated water and the development of practical methods for supplying a reasonable Mg^{2+} concentration (10–20 mg Mg/L) with the product water supplied by desalination plants, is apparent in the many recent papers published on the topic [1–15]. The issue of magnesium deficiency in drinking water and its adverse relation to human health is not new [16–17].

In essence, three main approaches should be considered for Mg^{2+} addition to desalinated water. The first is to simply dissolve food grade chemicals, namely $MgCl_2$ or $MgSO_4$ into the water. This option is viable and easily executed, however it is relatively costly (\$ 0.035–\$ 0.05/m^3 of product water for supplying 20 mg Mg/L) and in the case of $MgCl_2$ it also releases to the water a relatively high concentration of unwanted Cl^- ions.

Another approach is to selectively separate Mg^{2+} from raw seawater or seawater reverse osmosis (SWRO) brine. Such methods are being developed mostly by our research group throughout the last decade [11,14,18,19] and are not discussed here, apart from noticing that the cost of replenishing 1 m^3 of desalinated water with 20 mg/L of Mg^{2+} using these methods has been shown to range from ~\$ 0.01 to ~\$ 0.03, and that the latter two approaches, which are based on nano filtration as the means of selective separation of the magnesium ions, operate on top of the post treatment method applied in the plant, and not as part of it.

A third approach that is mentioned in the literature focuses on dissolving quarry dolomite (i.e. impure Ca $Mg(CO_3)_2$) beads in a manner similar to dissolving calcite ($CaCO_3$) beads, in the post treatment stage of the desalina-

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tion plant. Despite it being repeatedly mentioned as a feasible option, this approach has inherent deficiencies that render it unreasonable for this purpose. The purpose of this paper is to demonstrate that this approach is not feasible *per se*, due to slow kinetics at close-to-neutral pH, resulting in insufficiently high Mg^{2+} concentration (when CO_2 is the dissolving acid) on the one hand, and mainly due to very low alkalinity values obtained in the water when a strong acid (H_2SO_4, HCl) is used to enhance the dissolution, on the other.

Several recent papers [20–22] addressed the issue of dolomite dissolution with respect to remineralization of desalinated waters and provide meaningful data that can be used for proving the arguments of this paper. In this regard we chose to use the excellent data presented by [21]. Tables 1 and 2 in [21] list the results obtained by these authors from dissolving an impure quarry dolomite (Ca to Mg molar ratio ~ 1.15) into desalinated water under various operational conditions, using either CO_2 or H_2SO_4 as the dissolution enhancing agent. It is noted that quarry "dolomite" products differ much from each other in their composition, and the results presented in this paper are based on a specific type of rock, in which the ratio between Ca^{2+} and Mg^{2+} is relatively close to 1, i.e. to the ratio expected in pure dolomite.

To tackle the question of the ability/inability of this method to attain a reasonable water quality we consider in this paper two already applied quality criteria sets: the one is the set currently implemented in Israel and Cyprus [23,24] to which a requirement of 20 mg/L of Mg^{2+} is added; and the other is a much less stringent quality criteria, which is required in many plants worldwide, and also in the Ashkelon desalination plant in Israel, to which the WHO recommendation for Mg^{2+} concentration of 10 mg Mg/L was added [25]. The two sets are shown in Table 1. It is noted that the Israeli quality requirements employed in most desalination plants in Israel also disallow surpassing Na^+ concentration of 30 mg/L is the product water.

Table 2 lists representative empirical data reported in [21]. The data appears to be very reliable and should the experiments be repeated with the same operational conditions we are positive that the results would come out almost identical. The following paragraphs detail the practical conclusions arising from these results. All calculations shown in the paper were conducted with the PHREEQC software (Wateq4f database), assuming temperature of 25°C.

We wish now to discuss the results in Table 2 in light of the quality criteria defined in Table 1. Let us start from the option of CO_2 enhanced dissolution (first six lines in Table 2). The requirement for 10 and 20 mg/L of magnesium translate into 0.41 and 0.82 mM, respectively. The highest Mg^{2+} concentration listed in Table 2 for the CO_2 runs is 0.46 mM (Run #22). Thus, attaining 20 mg Mg/L, i.e. 0.82 mM

Table 1
Two sets of desalinated water quality criteria considered in this paper

Parameter	[1]Alkalinity mg/L as $CaCO_3$	$[Ca^{2+}]$ mg/L as $CaCO_3$	pH	LSI/CCPP (-) / mg/L as $CaCO_3$	[2] $[Mg^{2+}]$ mg Mg/L
Approved criteria in Israel	>80	80 < and < 120	<8.5	>0; 3–10	20
Ashkelon (Israel) desalination plant bid	Not specified	>60	7.5–8.5	>0; >0	10

[1] The term "Alkalinity" refers to alkalinity with respect to H_2CO_3* as reference species

[2] The Israeli requirement for Mg^{2+} concentration (between 20 mg/L and 30 mg/L) is conditional on "a pilot study". WHO criteria of 10 mg Mg/L is defined as a recommendation.

Table 2
Results of dolomite dissolution obtained from [21]. In bold: the scenarios disscussed in this paper

Run # in [21]	CO_2 inlet (mM)	H_2SO_4 inlet (mM)	EBCT (min)	pH in product water	$[Ca^{2+}]$ in product (mM)	$[Mg^{2+}]$ in product (mM)	Alkalinity in product (meq/L)
7	4.7		12.8	6.00	0.35	0.28	1.26
5	9.4		12.8	5.90	0.47	0.37	1.68
9	2.5		6.4	6.14	0.26	0.19	0.99
22	**10.0**		**6.4**	**5.70**	**0.49**	**0.46**	**1.90**
10	1.8		4.3	5.92	0.20	0.16	0.79
23	10.3		4.3	5.77	0.41	0.37	1.40
29		**4.9**	**12.8**	**5.62**	**2.86**	**2.54**	**0.92**
32		9.9	12.8	5.33	6.04	5.37	1.32
39		4.7	6.4	5.58	2.72	2.46	0.80
33		**10.6**	**6.4**	**5.04**	**5.81**	**5.15**	**0.68**
36		4.8	4.3	5.31	2.84	2.44	1.30
34		**9.9**	**4.3**	**5.12**	**5.55**	**5.03**	**1.10**

(the Israeli criteria) is ruled out. According to Table 2, for attaining 10 mg/L (0.41 mM) one has to apply 10 mM of CO_2 and the Ca^{2+} concentration that is attained is 0.49 mM (i.e. 19.6 mg Ca/L or 49 mg/L as $CaCO_3$). The pH of the product water is pH 5.70. To attain a slightly positive LSI one should either add NaOH (the requirement in this case is 332 mg/L) or strip CO_2 out to the atmosphere. Both options are clearly very expensive and impractical from the environmental standpoint. The unequivocal conclusion from this data is that dissolving dolomite using CO_2 is unfavorable for attaining both quality criteria considered in Table 1.

Let us now focus on the alternative of dissolving dolomite with a strong acid (H_2SO_4). To describe the main limitation of this method with respect to meeting the quality criteria, one should perform a mass balance on the alkalinity value attained in the dissolution process. Alkalinity with $H_2CO_3^*$ as reference species is defined mathematically in Eq. (1):

$$Alk\left(H_2CO_3^*\right) = 2\left[CO_3^{2-}\right] + \left[HCO_3^-\right] + \left[OH^-\right] - \left[H^+\right] \tag{1}$$

where the brackets stand for molar concentrations and the alkalinity appears in eq/L units.

By the mere definition of the alkalinity concept the dosage to solution of species appearing with a positive sign on the right hand side of Eq. (1) adds to the alkalinity value (i.e. positive alkalinity) while dosage of species that appear with a negative sign in Eq. (1) detracts from the alkalinity value (i.e. negative alkalinity). In the CO_2-based dolomite dissolution process, the addition of $CO_{2(g)}$ to the water does not change the alkalinity concentration (i.e. it remains zero) and thus the dissolution of dolomite contributes an alkalinity value which is roughly double the combined Ca^{2+} and Mg^{2+} molar concentrations (see also results in Table 1 of [21]). However, when H_2SO_4 is used for acidification, each mM of acid added to the water results in dosage of a negative alkalinity value of 2 meq/L (since each molecule of H_2SO_4 releases two H^+ molecules upon dissolving). As a result of this mass balance and the fact that the K_{sp} value of dolomite dictates that the mineral would stop dissolving at a relatively low pH, the final alkalinity value in the water coming off the dolomite dissolution reactor is low and the process cannot be considered attractive.

To exemplify this point let us now calculate the theoretical alkalinity mass balance of Runs #29, #33 and #34 (Table 2). The fundamental assumption in this mass balance is that each mole of Mg^{2+} and Ca^{2+} that dissolves in the water is accompanied by a mole of CO_3^{2-} ion (and 2 equivalents of alkalinity, since CO_3^{2-} is preceded by a factor of 2 eq/mol in the alkalinity equation). Table 3 lists the results of this mass balance and compares these with the measured alkalinity results reported in [21]. As shown, the results of the theoretical and measured alkalinity values are almost identical (see two right hand columns in Table 3), which corroborates the veracity of the empirical results.

Now, in order to attain the quality criteria values listed in Table 1, the three water qualities resulting from the scenarios in Table 3 need to be diluted with raw desalinated water to attain Mg^{2+} concentrations of either 20 or 10 mg/L. Thereafter, an alkalinity containing chemical (invariably NaOH) should be added to increase the alkalinity and pH to meet the demands for both the threshold alkalinity value (if exists) and LSI = 0. In this regard, one encounters difficulties. Take for example the results of Run #29: the Mg^{2+} concentration coming off the dolomite reactor was 2.54 mM. Thus, in order to get 0.82 mM (20 mg Mg/L) the water should be blended with raw desalinated water at a 3.1 to 1 dilution rate (i.e. a very high split-flow ratio of 32.6%). By doing so, the alkalinity value is proportionally diluted, resulting in alkalinity of 0.92/3.1 = 0.296 meq/L (~15 mg/L as $CaCO_3$) when the threshold alkalinity requirement in the product water in this scenario is 80 mg/L as $CaCO_3$. This gap can be bridged only with a NaOH dosage of 52 mg/L. However, such dosage results in a negative LSI value. To also attain LSI slightly higher than zero a NaOH dosage of ~55 mg/L is required, applied on the whole desalination plant's flow. 55 mg/L is approximately twice the NaOH dose required in typical calcite dissolution to attain a similar alkalinity value. At a reasonable food-grade 48% NaOH solution cost of ~$ 500 per ton (or, ~$ 1040 per ton of pure chemical) this step alone corresponds to ~$ 0.057 per m^3 of desalinated water. In fact, merely the gap in the cost of NaOH (which is the most expensive commodity used in the process) between dolomite and calcite dissolution is greater than the cost of adding Mg^{2+} using an external method, such as the ones described in [14] and [15]. Such NaOH dosage would also add ~32 mg/L of Na^+ to the product water, which is disallowed by the Israeli desalination plant bid requirements. It is also possible to apply both $Ca(OH)_2$ and NaOH in the final pH elevation step, instead of only NaOH. Such operation can slightly reduce the process costs, and also the Na^+ concentration. However, $Ca(OH)_2$ dosage often results in elevated water turbidity due to its low solubility and high insoluble matter content. In addition, the $Ca(OH)_2$ dosage is limited to 27 mg/L as $CaCO_3$ (i.e. 0.55 meq/L, or 21 mg/L), due to the upper threshold of Ca^{2+} concentration (see Table 1). The combination of the high portion of water that needs

Table 3
Alkalinity mass balances vs. measured values related to H_2SO_4-based dolomite dissolution runs

Run # in [21]	H_2SO_4 dosage (mM)	Δ Alkalinity from H_2SO_4 (meq/L)	ΔAlkalinity From dolomite dissolution* (meq/L)	Theoretical alkalinity in dolomite reactor water (meq/L)	Measured alkalinity in product (meq/L)
29	4.9	–9.80	+10.80	1.00	0.92
33	10.6	–21.20	+21.92	0.72	0.68
34	9.9	–19.80	+21.16	1.36	1.10

*the molar sum of Ca^{2+} and Mg^{2+} from Table 2, multiplied by 2 to be treated in the dissolution reactors (32.6% of the overall flow) and the high NaOH demand makes this option highly unfavorable, relative to the alternatives, including the alternative to simply dissolve $MgSO_4$ chemical into the water.

If one attempts to attain the second (less stringent) quality criteria (2nd row in Table 1), the dilution required in this case for the water leaving the dolomite reactor in order to attain 10 mg Mg/L is 1 to 6.2, i.e. the alkalinity and [Ca^{2+}] values following the dilution would be ~7.5 mg/L as $CaCO_3$ and ~18.5 mg/L (Ca^{2+} ~ 46 mg/L as $CaCO_3$), respectively. Clearly, both values are not adequate (Ca^{2+} is below the threshold; the alkalinity value is very low and would require very high NaOH dosage). More importantly, the buffer capacity of such water is very low. As a result, the high NaOH dosage (for attaining the minimum alkalinity required) would lead to extremely high pH (>10.3) and LSI (CCPP) values and thus the required criteria set cannot be met.

Let us now apply the same considerations on the results of Run #34. Here, in order to get 0.82 mM of Mg^{2+} (20 mg/L) the dilution ratio should be 1 to 6.1. After the dilution the Mg^{2+}, Ca^{2+} and Alkalinity concentrations would be 20, 36.4 and 9.0 mg/L, respectively (the alkalinity value in units of mg/L as $CaCO_3$) and the pH would be 5.19. Thus, an impractical value of 98 mg/L of NaOH would be required in this case to attain LSI = 0. Alternatively, in case 10 mg/L of Mg^{2+} is required, the required dilution factor is 12.2 and the Ca^{2+} concentration drops to 18.2 (45.5 mg/L as $CaCO_3$), which is below the required threshold.

One can also try to apply lower H_2SO_4 dosing values, such as 3.4 mM and 1.4 mM. Such scenarios would result in somewhat smaller NaOH requirements, but the split ratio would be 46% and 100%, respectively, i.e. a major fraction of the plant's flow rate would have to be treated, making the dolomite reactors gigantic. For example, for the 100% split option the dolomite volume in the dissolution reactors for a 150 Mm^3/y would be ~4200 m^3, assuming 12 min empty bed retention time (EBRT) and 300 annual working days.

To sum up, CO_2-enhanced dolomite dissolution is clearly impractical. H_2SO_4-enhanced dolomite dissolution for complying with the quality criteria can be applied only using a specific combination of operational parameters. However, dissolution of dolomite at such conditions (i.e. run # 29) requires high H_2SO_4 dosage (50% higher than the dosage required for conventional calcite dissolution [18]), approximately doubled costly NaOH dosage and naturally, usage of dolomite which is a more expensive quarry mineral than calcite. In addition, the mass of dolomite dissolved in m^3 of desalinated water should also be approximately twice mass of the calcite used in conventional remineralization. Finally, dissolution reactor sizes are also approximately doubled. Thus, from the cost point of view, considering that calcite dissolution post treatment process costs ~\$ 0.055/m^3 [26,27], it can be objectively assumed that dolomite dissolution would cost at least 70% more, i.e. above additional \$ 0.038/m^3, while the cost of Mg^{2+} addition (20 mg/L) in alternative methods has been assessed at between \$ 0.01 and \$ 0.03/m^3 of desalinated water [14,15,28].

On top of the cost standpoint, the following difficulties should also be borne in mind when dolomite dissolution is planned: treating a higher fraction of the desalinated water in the post treatment step, which manifests itself in much larger reactors, is often impossible in existing desalination plants; the high NaOH dosage would result in excessive Na^+ concentration in the product water; the composition of the quarry dolomite found in the reactor would change with time since the calcite part of it would dissolve more rapidly than the magnesite part; finally, the dolomite rock itself is often non-homogeneous and its Ca to Mg ratio varies even within a given quarry, let alone between different quarries.

The considerations in this paper appear to be general, i.e. not depending on the particular characteristics of the dolomite used (see for example the results in [20] who dissolved a different dolomite rock, but arrived to almost similar conclusions). However, using a dolomite with a higher Ca^{2+} composition for attaining the same Mg^{2+} concentration will result in higher Ca^{2+} and alkalinity values but also in a non-steady operation since the $CaCO_3$ fraction of the rock would dissolve faster than the $MgCO_3$ fraction.

Note

The authors of this paper are developing and commercializing methods for addition of magnesium to desalinated water.

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