Simple process for hardening desalinated water with Mg^{2+} ions

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ABSTRACT

A simple easily controlled technique for adding Mg^{2+} ions to desalinated water is described. The Israeli Health Authority recommendation of adding of 20–30 mg/L of Mg^{2+} can be readily met by dissolution of magnesia pellets in a packed bed column. Experimental data are presented showing the effects of the specific flow velocity and CO_2 acidification of the inlet desalinated water on the Mg^{2+} concentration in the product stream leaving the column. Acidification of the inlet feed water is shown to enhance considerably the dissolution process. A kinetic expression is presented enabling full design of a dissolution packed column with nonacidified water.

Keywords: Desalinated water; Hardening; Magnesium; Magnesia dissolution; Kinetic model

1. Introduction

The current Israeli regulations specify that the hardening of desalinated water must conform to the following water quality criteria [1]:

- Alkalinity content: above 80 mg/L as $CaCO_3$.
- Calcium ion content: 80–120 mg/L as $CaCO_3$.
- $7.5 < pH < 8.3$.
- Calcium carbonate precipitation potential (CCPP): 3–10 mg/L as $CaCO_3$.
- Turbidity level: less than 0.5 NTU and no more than 1.0.
- Langelier saturation index (LSI) > 0.

There is an ongoing controversy in Israel regarding the need to add Mg ions to the water, as evident from the minutes of the debate held by the Israeli Knesset Committee for Labor, Welfare and Health held on 11 January 2011 [2]. The Ministry of Health supported recommendations for addition of magnesium, which originally specified a level of 5–7.5 mg/L Mg ion and subsequently was raised to the level of 20–30 mg/L. The Israel Water Authority raised strong objections on the grounds that existing evidence did not justify Mg addition to desalinated water. The issue was considered in February 2012 by the government. The high cost penalty led to the decisions to abandon the Health Ministry recommendation to include Mg requirement in desalinated water and to examine also alternative ways for adding magnesium.

So far, the only process suggested for accomplishing the Mg hardening requirement is an ion exchange process [3–7]. The process was developed for incorporation in the sulfuric acid calcite dissolution process in order to add Mg ions and also to rectify a deficiency

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of the H_2SO_4 process with respect to the drinking water criteria. The H_2SO_4 process has the advantage of rapid kinetics which enables saving in the size of the calcite dissolution columns. However, the overall reaction (Eq. 1) of the process yields a ratio of Ca^{2+} to HCO_3^- of 2 to 1 in equivalent units, whereas the water standard calls for a ratio of 1.0–1.5 to 1.0.

$$2CaCO_3 + H_2SO_4 \rightarrow Ca(HCO_3)_2 + CaSO_4 \qquad (1)$$

The excess Ca^{2+} ions can be removed by the rather elaborate magnesium hardening process [3–7] which involves ion exchange operations. Brine generated in the desalination plant is contacted with an ion exchanger that has a high affinity toward Mg^{2+} and Ca^{2+} and a very low affinity toward Na^+. Since the Mg^{2+} concentration in seawater is much higher than that of Ca^{2+}, the resin is enriched with Mg^{2+} ions. The resin is the rinsed with low TDS brine in order to minimize enrichment of product water with sea salts. The last operation consists of contacting the dissolution column effluent with an ion exchanger, which possesses a reasonably high affinity toward Na^+ and Ca^{2+} and a very low affinity toward Mg^{2+}. Excess calcium is removed and replaced by $Ca^{2+}$and Na^+ ions.

The hardening process based on CO_2 dissolution of calcite has the advantage of providing an effluent having the equivalent concentration ratio of Ca^{2+} to HCO_3^- of 1 to 1, which meets the water quality standard.

This paper presents a simple readily controlled technique for addition of Mg^{2+} ions to desalinated water. The technique consists of adding Mg ions by contacting desalinated water in a MgO-pellets column placed in front of calcite hardening column. As shown below (Eq. 2), MgO is sparingly soluble and when contacted with acid-free water it provides a solution of $Mg(OH)_2$ of low Mg content.

$$MgO + H_2O \rightarrow Mg^{2+} + 2OH^- \qquad (2)$$

By acidifying the desalinated water with CO_2, the MgO dissolution rate is considerably enhanced and the column can provide any desired Mg content. The dissolution reaction involved is:

$$MgO + 2CO_2 + H_2O \rightarrow Mg^{2+} + 2HCO_3^- \qquad (3)$$
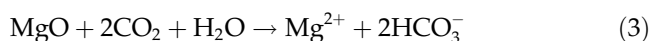
2. Experimental

The dissolution experiments were carried out by continuous flow of distilled water with or without CO_2 dosage, through a 50 mm diameter cylindrical column, 500 mm long, filled with MgO pellets (Fig. 1).

The pellets, denoted as "Akdolit Hydrolit Mg grain size II," were supplied by Rheinkalk Akdolit GmbH, Germany and were substantially spherical with diameters in the range of 2–5 mm (Fig. 2). The chemical analysis supplied by the Akdolit Company indicated that the pellets consisted of 70–75% MgO, 4–5% CaO, 3–4% oxides impurity, and 16–20% $H_2O + CO_2$.

The initial efforts were focused on characterization of the dissolution of MgO with pure acid-free desalinated water and development of a design model. Efforts were then devoted to characterization of the dissolution of MgO with CO_2 dosed desalinated water and exploration of the kinetics of this more complex system.

3. Results

3.1. Solubility of MgO in acid-free desalinated water

The equilibrium solubility of the MgO pellets in a closed system (no contact with air) was determined by filling the MgO pellets column with desalinated water and analyzing the solution composition after 80 h. Table 1 presents results of the analysis of the equilibrated solution at a temperature of about 28°C.

At high pH conditions, magnesium ions exist in two forms: Mg^{2+} and $MgOH^+$. The solubility products of these ions can be calculated from the following mass balance and electrical balance relations:

$$Mg_{tot} = [Mg^{2+}] + [MgOH^+] \qquad (4)$$

$$[MgOH^+] + [2Mg^{2+}] = [OH^-] \qquad (5)$$

These relations show that the Mg species concentrations in the saturated solution were $[Mg^{2+}]$ = 0.26 mmol/L and $[MgOH^+]$ = 1.11 mmol/L and the solubility products are:

$$Ksp_{(MgOH)} = (MgOH^+) \times (OH^-) = 1.73 \times 10^{-6} (mole/L)^2,$$
$$Ksp_{Mg(OH)^2} = (Mg^{2+}) \times (OH^-)^2 = 5.01 \times 10^{-10} (mole/L)^3$$

Visual Minteq software V. 3.0 [8] gives a solubility product value of 6.22×10^{-10} for active magnesia at a temperature of 25°C, indicating that the MgO pellets consisted of active magnesia.

3.2. Kinetics of dissolution of MgO in acid-free desalinated water

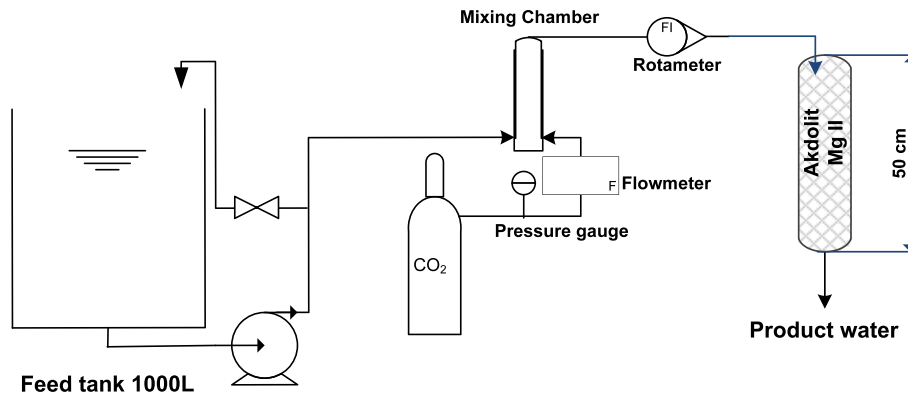The kinetics of simple dissolution of solid pellets in a packed bed column is treated as a mass transfer

Fig. 1. Experimental system.

Fig. 2. Akdolit hydrolit Mg grain size II pellets.

Table 1
Analysis of the equilibrium MgO solution

pH	10.6
Mg_{tot}	1.38 mmol/L (33.5 mg/L)
$[OH]^-$	1.64 mmol/L

process [9]. In the case of magnesia dissolution with pure water, the dissolution rate is given by:

$$\frac{C_2}{C_S} = 1 - \exp\left(-\frac{K \cdot a \cdot Z}{L}\right) \tag{6}$$

where C_2 is the exit concentration (mol/L) of Mg in the effluent leaving the packed bed column, C_S is the equilibrium solubility (mol/L) of the MgO pellets, K is the mass transfer coefficient (mol Mg/s m^2 particle surface per mol Mg/L), a is the pellets specific surface (m^2 per m^3 of total packed bed volume), Z is the bed height (m), and L is the mass flow velocity of the water in the column (kg/s m^2). The mass transfer coefficient is a function of the Reynolds number $Re = \frac{D_p \cdot L}{\mu}$, where D_p is the average particle diameter and μ is the water viscosity.

3.3. Dissolution experiments with acid-free desalinated water

A series of runs were carried out at five inlet water flow rates in the range of 1–3 L/min. The measured total magnesium concentration was used to calculate from Eq. (6) the values of the mass transfer coefficient K in the various runs. The parameters characterizing the dissolution runs were:

$a = 960 \text{ m}^2/\text{m}^3; Z = 0.5 \text{ m}; C_S = 1.38 \text{ mmol/L};$

$Re = \dfrac{D_p \cdot L}{\mu} = \dfrac{3.5 \times 10^{-3} \text{ (m)} \times L \text{ (kg/s m}^2)}{10^{-3} \text{ (kg/s m)}}; \quad T = 28 \,^\circ\text{C}$

Results are summarized in Table 2.
The linear relationship exhibited in the plot of K as a function of Re (Fig. 3) yields the following mass transfer correlation:

$$K = 4.66 \cdot 10^{-4} \times Re^{0.385} \tag{7}$$

The power index 0.385 measured in the magnesia dissolution runs at Re = 28–90 is in good agreement with the power index 0.31 measured in dissolution of benzoic acid pellets runs at Re = 55–1,500 [9].

The reliability of the design model developed in this study can be observed in Table 3, which compares measured Mg concentrations with values calculated from Eq. 6 for the pure water dissolution runs.

The practical feasibility of obtaining the required Mg concentration by simple contact of the desalinated water in a magnesia pellets column can be exemplified by the following calculation. Typical column dimensions used in hardening of desalinated water are: 2.5 m diameter and 3 m height of packed bed. To achieve suitable Mg hardening, the column is designed using Akdolit magnesia pellets of grain size-I having an average diameter of 1.5 mm which provides a specific pellets area of $a = 2,240$ m^2/m. For an inlet water flow rate $Q = 100$ m^3/h, the specific flow rate is $L = 5.66$ L/m^2 s. The Reynolds number is

Table 2
Measured pH and total magnesium levels and mass transfer coefficient results

Q (L/min)	L (L/m² s)	Re	pH	$C_2 = Mg_{tot}$ (mmol/L)	$C_2 = Mg_{tot}$ (mg/L)	K (mol Mg_{tot}/s m² per mol Mg_{tot}/L)
0.93	7.9	27.7	10.4	0.131	3.2	1.64×10^{-3}
1.45	12.3	43.2	10.3	0.106	2.6	2.06×10^{-3}
1.98	16.8	58.8	10.2	0.095	2.3	1.68×10^{-3}
2.50	21.2	74.3	10.2	0.073	1.7	2.41×10^{-3}
3.02	25.7	89.9	10.1	0.066	1.6	2.63×10^{-3}

Table 3
Comparison of measured Mg concentrations with predicted values

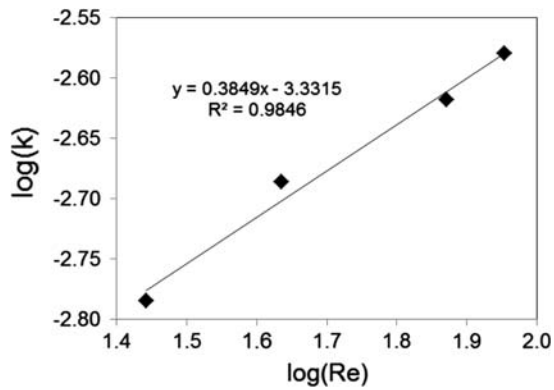| Flow rate-Q (L/min)	Mass velocity-L (kg/m² s)	Measured Mg (mmol/L)	Calculated Mg (mmol/L)	Difference %
0.93	7.90	0.131	0.184	29.0
1.45	12.35	0.106	0.121	12.2
1.98	16.79	0.095	0.090	5.9
2.50	21.23	0.073	0.071	2.2
3.02	25.68	0.066	0.059	11.3

Fig. 3. Effect of the Reynolds number on the mass transfer coefficient.

$Re = 8.5$ and the mass transfer coefficient is $K = 1.06 \times 10^{-3}$ mol Mg/s m^2 s per mol Mg/L. Inserting values into Eq. (6), it is found that the exit Mg concentration obtained from the above column is approximately 1 mmol/L or 24 mg/L, i.e. within the required range.

3.4. Dissolution experiments with CO_2 dosage

The maximum Mg concentration that can be achieved by magnesia dissolution with acid-free desalinated water is limited by its relatively low equilibrium solubility (about 1.38 mmol/L or 34 mg/L). The maximum extent of magnesia dissolution and the rate of its dissolution can be considerably enhanced by acidifying the inlet desalinated water with CO_2. This is evident from the series of runs carried out with inlet CO_2 concentrations of 0.6–4.1 mmol/L and water flow rates in the range of 0.9–3.0 L/min.

Experimental results are summarized in Table 4. Comparison with the data relating to nonacidified desalinated water clearly shows that CO_2 acidification enhances dissolution rates and enables control of the Mg content in the effluent to high concentrations. For instance, in the run conducted at a specific flow velocity $L = 7.9$ L/m^2 s ($Q = 0.93$ L/min) and a dosage of 2 mmol/L CO_2, the exit Mg content increased from 3.2 to 44.4 mg/L.

4. Concluding remarks

This paper presents a simple easily controlled technique for adding Mg ions to desalinated water. The current Israeli recommendation of a concentration of 20–30 mg/L can be readily met by dissolution of magnesia pellets without acidification of the desalinated water. The dissolution can be enhanced considerably by acidifying the desalinated water with

Table 4
Dissolved Mg content as a function of inlet CO_2 concentration and water flow rate

$Q_{DI\ water}$ (L/min)	Parameter	[CO_2] (mmol/L)				
		0	0.59	1.06	1.95	4.10
0.93	pH$_{Inlet}$	6.7	5.2	4.6	4.6	4.5
	pH$_{Outlet}$	10.4	7.2	6.7	6.5	6.3
	Mg$_{tot}$ (mg/L)	3.2	17.3	30.4	44.4	49.9
1.45	pH$_{Inlet}$	6.9	5.3	4.8	4.8	4.8
	pH$_{Outlet}$	10.3	6.9	6.5	6.4	6.3
	Mg$_{tot}$ (mg/L)	2.6	11.1	19.0	26.5	31.3
1.98	pH$_{Inlet}$	6.9	2.3	4.9	4.9	4.7
	pH$_{Outlet}$	10.2	5.4	6.4	6.3	6.2
	Mg$_{tot}$ (mg/L)	2.3	6.8	13.6	17.8	19.3
2.50	pH$_{Inlet}$	6.9	5.4	5.1	4.9	4.8
	pH$_{Outlet}$	10.2	6.7	6.3	6.3	6.1
	Mg$_{tot}$ (mg/L)	1.8	5.0	8.8	13.4	14.1
3.02	pH$_{Inlet}$	6.9	5.4	5.2	5.0	4.8
	pH$_{Outlet}$	10.1	6.6	6.3	6.2	6.1
	Mg$_{tot}$ (mg/L)	1.6	4.1	6.0	8.6	10.8

a low CO_2 content. A kinetic expression is presented enabling full design of a dissolution packed column with nonacidified water. The kinetics of dissolution in the presence of CO_2 involves more complex multispecies transport processes. These are currently being investigated aiming to develop a design equation for CO_2 enhanced dissolution.

Acknowledgment

References

[1] Israeli Ministry of Health, Drinking Water Quality Standards, Jan. 2012, pp. 33 (Hebrew text).
[2] Knesset Labor Committee, Social Affairs and Health, Motion following a quick discussion, adding magnesium to desalinated water, 11 January 2011 (Hebrew text).
[3] L. Birnhack, O. Lahav, A new post-treatment process for attaining Ca^{2+}, Mg^{2+}, SO_4^{2-} and alkalinity criteria in desalinated water, Water Res. 41 (2007) 3989–3997.
[4] L. Birnhack, R. Penn, O. Lahav, Quality criteria for desalinated water and introduction of a novel, cost effective and advantageous post treatment process, Desalination 221 (2008) 70–83.
[5] R. Penn, L. Birnhack, A. Adin, O. Lahav, New desalinated drinking water regulations are met by an innovative post-treatment process for improved public health, Water Sci. Technol. Water Supply 9 (2009) 225–231.
[6] L. Birnhack, S. Oren, O. Lehmann, O. Lahav, Development of an additional step to current CO_2-based $CaCO_{3(s)}$ dissolution post-treatment processes for cost-effective Mg^{2+} supply to desalinated water, Chem. Eng. J. 160 (2010) 48–56.
[7] L. Birnhack, R. Penn, S. Oren, O. Lehmann, O. Lahav, Pilot scale evaluation of a novel post-treatment process for desalinated water, Desalin. Water Treat. 13 (2010) 128–136.
[8] Visual Minteq V. 3.0 at www.lwr.kth.se/English/OurSoftware/vminteq (accessed Feb. 2012).
[9] E.J. Wilson, C.J. Geankoplis, Liquid mass transfer at very low Reynolds numbers in packed beds, Ind. Eng. Chem. Fundamen. 5 (1966) 9–14.