



# Design model for magnesium ions re-mineralization of desalinated water by dissolution of magnesia pellets



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## HIGHLIGHTS

- Modeling of magnesia pellet dissolution for Mg remineralization of desalinated water
- Model confirmation by experimental data of magnesia dissolution with CO<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub>
- Comparison of Mg concentrations obtained by CO<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> magnesia dissolutions
- Analysis of the effect of acid strength on the dissolution mass transfer coefficient

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## ABSTRACT

Re-mineralization of desalinated water with magnesium ions is currently under consideration. A simple easily controlled technique for adding magnesium ions to desalinated water consists of dissolution of magnesia pellets in a packed bed by feed water slightly acidified with either carbon dioxide or sulfuric acid. A design model is presented describing magnesia pellets dissolution in a fixed bed as a mass transfer controlled process. The model is confirmed by experimental data covering a range of acid concentrations and contact times. A striking difference was observed between dissolution with the weak carbonic acid and with the strong sulfuric acid. Dissolution of magnesia with dilute sulfuric acid of 1 to 5 mM at very short contact times around 2 min provided virtual equilibrium concentration of magnesium ions whereas the magnesium ion concentrations obtained with CO<sub>2</sub> at the same acid concentrations and contact times were far from equilibrium. Mass transfer coefficients extracted from the dissolution data of the weak carbonic acid were in substantial agreement with literature data whereas coefficients derived from the strong sulfuric acid dissolution data were about 5–6 times higher, probably due to an increased pellet surface generated by a strong acid attack.

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## 1. Introduction

Desalinated water is poor in minerals, making it corrosive and unpalatable. A certain degree of re-mineralization is necessary in order to overcome these drawbacks and to comply with human health concerns [1]. Currently, the two most widely used re-mineralization processes are calcite and lime dissolution by CO<sub>2</sub> acidified desalinated water which introduce calcium ions and carbonate alkalinity to the water. According to a World Health Organization report [2] there is a need to consider dosage of magnesium ions in addition to calcium ions to desalinated water.

The Israel Ministry of Health is considering extending the existing re-mineralization regulations, which specify addition of 32 to 48 mg/L calcium ions, by the requirement of adding also 20 to 30 mg/L of magnesium ions. The issue is controversial due to the lack of agreement on the

necessity of adding magnesium to desalinated water and the concern on the magnitude of the costs involved. This circumstance has evoked interest to examine viable processes appropriate for re-mineralizing desalinated water with magnesium ions. The present paper describes development of a design model for dissolution of magnesia pellets in a packed bed with acidified desalinated water.

Most magnesia (MgO) dissolution literature studies agree that, depending on reaction conditions, the overall dissolution rate is controlled either by diffusion of reactants and products or by surface reaction. Vermilyea [3] investigated rates of acid dissolution of different magnesia powders having a particle size in the range of 10 to 30 μm. Analysis of mechanisms was based on pH measurements. The data indicated that Brucite dissolves by a proton based surface reaction and that dissolution of commercial Mg(OH)<sub>2</sub> is normally diffusion limited. Of special interest to the present study was the conclusion that MgO dissolution starts with a rapid reaction with water to form a Mg(OH)<sub>2</sub> layer on the crystal surface and the dissolution rate is controlled by the rate of Mg(OH)<sub>2</sub> dissolution.

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Several studies examined MgO acid dissolution by the rotating disk technique [4–6]. According to Fruhwirth et al. [4] dissolution rate measurements of MgO crystals in a rotating disk system indicate the following controlling mechanisms; At pH < 5 the dissolution is controlled by proton surface attack:



at pH = 5 the dissolution is controlled by proton diffusion and at pH > 7 the dissolution is controlled by OH<sup>−</sup> attack which discharges surface adsorbed MgOH<sup>+</sup>, followed by Mg<sup>2+</sup> and OH<sup>−</sup> desorption.

Macdonald and Owen [5] investigated the dissolution of sintered MgO pellets by sulfuric acid in a rotating disk at 4 °C and 25 °C. The dissolution process was assumed to be controlled by two proton processes in series: diffusion of protons towards the MgO surface followed by a proton surface reaction. The mass transfer coefficient for the laminar flow on the rotating disk was taken according to the Levich equation [7].

Gušpiel and Riesenkamp [6] also investigated MgO dissolution by sulfuric acid using a rotating disk technique. Dissolution of disk shaped sintered MgO pellets was measured over a temperature range of 0–70 °C and acid concentrations in the range of 0.5 mM to 2.0 M. At low acid concentrations range (<0.5 mM) MgO dissolution was controlled by proton diffusion. Increase of the acid concentration caused a change from diffusion control to activation–diffusion control. In solutions with concentrations exceeding 0.1 M H<sub>2</sub>SO<sub>4</sub> and at sufficiently low temperatures, the dissolution was activation controlled.

Raschman and Fedorocková [8] studied the dissolution kinetics of sintered polycrystalline MgO particles of three sizes (mean diameter of 67, 113 and 335 μm) with dilute hydrochloric acid in a stirred batch vessel. The effect of temperature, particle size, H<sup>+</sup> and Mg<sup>2+</sup> concentrations were investigated. In their evaluation of previous work, they pointed out the following uncertainty. Despite the general agreement between experiment and theory of individual studies, there are cases when the uses of the different theoretical approaches for identical reaction conditions result in different indications regarding the rate controlling steps, with no clear basis for discrimination between these alternatives. Though dissolution rates of the Raschman and Fedorocková [8] study were in good agreement with those measured by other authors, it was similarly concluded the rate-controlling step could not be assigned unambiguously, because the same value of the reaction order for H<sup>+</sup> ions can be predicted by various theories for different rate-determining steps.

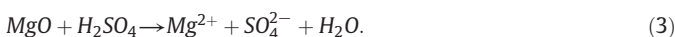
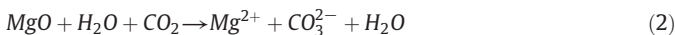
In summary, available magnesia dissolution studies examine powders or single crystals. No practical design model is available for engineering design of MgO dissolution in a packed bed system suitable for desalination post treatment.

## 2. Design model

The design model used in this work adopts the mass transfer control approach which enabled successful correlation of experimental data of dissolution in fixed bed systems of benzoic acid pellets by water [9] and of calcite pellets by acidified desalinated water [10–12]. The model considers dissolution of Mg(OH)<sub>2</sub>, since MgO is known to react instantaneously with water to form magnesium hydroxide [3].

### 2.1. Basic equation

The system investigated is a packed bed column containing magnesia pellets over which desalinated water acidified with either CO<sub>2</sub> or H<sub>2</sub>SO<sub>4</sub> is flowing at a volumetric solution rate of Q (m<sup>3</sup>/s). The overall reactions involved are:



The dissolution driving force is the concentration difference between the equilibrium magnesium ions concentration [Mg<sub>T</sub>]<sub>e</sub> (mol/m<sup>3</sup>) prevailing on the magnesia particles–solution interface and the bulk solution magnesium ions concentration [Mg<sub>T</sub>] (mol/m<sup>3</sup>). The magnesium ions dissolution rate r (mol/m<sup>2</sup> s) along the packed bed length L (m) is proportional to the contact area of the magnesia particles and is given by:

$$r = \frac{Q \cdot d[\text{Mg}_T]}{dS_p} = k\{[\text{Mg}_T]_e - [\text{Mg}]\} \quad (4)$$

where S<sub>p</sub> (m<sup>2</sup>) is the magnesia particles surface area and k (m/s) the mass transfer coefficient. Expressing the particles area in terms of the average particles diameter d<sub>p</sub> (m), the rate of dissolution of the magnesia particles along a bed length L is given by:

$$\frac{d[\text{Mg}_T]}{dL} = \frac{k}{u} \cdot \frac{6}{d_p \cdot \phi} \cdot (1-\varepsilon)\{[\text{Mg}_T]_e - [\text{Mg}]\} \quad (5)$$

where u (m/s) is the flow velocity based on the empty column cross sectional area, [Mg<sub>T</sub>]<sub>e</sub> is the magnesium equilibrium concentration, ε the packed bed porosity fraction and φ the particles shape factor, taken here as unity since the particles investigated were spherical.

The equilibrium concentration [Mg<sub>T</sub>]<sub>e</sub> has a constant value which is governed by the acid concentration fed to the desalinated water, as described below. The magnesium ion concentration profile along the column is then obtained by integration of Eq. (5):

$$\ln \frac{[\text{Mg}_T]_e - [\text{Mg}_T]_L}{[\text{Mg}_T]_e - [\text{Mg}_T]_0} = \frac{6k}{\phi} \cdot \frac{(1-\varepsilon)}{d_p} \cdot \frac{L}{u} = \frac{6k}{\phi} \cdot \frac{(1-\varepsilon)}{d_p} \cdot \tau \quad (6)$$

where [Mg<sub>T</sub>]<sub>0</sub> is the magnesium inlet concentration which in the case of desalinated water is zero and τ is the solution contact time based on the empty bed column volume (the so-called EBCT).

The model predicts that the dissolved magnesium concentration expression  $\ln \frac{[\text{Mg}_T]_e - [\text{Mg}_T]_L}{[\text{Mg}_T]_e - [\text{Mg}_T]_0}$  increases linearly with the packed bed length L. The magnitude of the mass transfer coefficient can be then determined from the slope of this linear relationship.

### 2.2. Equilibrium concentration for CO<sub>2</sub> dissolution

The total equilibrium Mg species at the particle–solution interface is given by:

$$[\text{Mg}_T]_e = [\text{Mg}^{2+}]_e + [\text{MgOH}^+]_e + [\text{MgCO}_3]_e + [\text{MgHCO}_3^+]_e. \quad (7)$$

Values of equilibria constants at room temperatures of the various species involved in the magnesia dissolution system were obtained from the Visual MINTEQ software (v. 3.0).

At the high pH values prevailing at the particles–solution interface, the [MgHCO<sub>3</sub><sup>+</sup>]<sub>e</sub> species can be neglected since equilibria values show that [MgHCO<sub>3</sub><sup>+</sup>]<sub>e</sub>/[MgCO<sub>3</sub>]<sub>e</sub> < 5% at pH > 9.7. The carbonic acid concentration [CO<sub>2</sub>]<sub>0</sub> = [C<sub>T</sub>]<sub>0</sub> (mol/L) injected to the entering desalinated water is distributed in the three pH dependent carbonic species and in the magnesium carbonate species:

$$[\text{C}_T] = [\text{CO}_2]_e + [\text{HCO}_3^-]_e + [\text{CO}_3^{2-}]_e + [\text{MgCO}_3]_e. \quad (8)$$

Using values of the equilibria constants of the various Mg species, Eq. (7) is transformed to an expression relating the total magnesium concentration to the hydroxyl concentration [OH<sup>−</sup>]<sub>e</sub> prevailing on the particles:

$$[\text{Mg}_T]_e = \frac{K_{\text{Mg}(\text{OH})_2}}{[\text{OH}^-]_e^2} + \frac{K_{\text{Mg}(\text{OH})_2}}{[\text{OH}^-]_e K_{\text{MgOH}^+}} + \frac{K_{\text{Mg}(\text{OH})_2} \cdot \text{C}_T[\alpha_2]_e}{[\text{OH}^-]_e^2 \cdot K_{\text{MgCOH}_3}} \quad (9)$$

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