Precipitation of $MgCO_3 \cdot 3H_2O$ from aqueous solutions: the role of $Mg^{2+}:CO_3^{2-}$ concentration ratio, pH and temperature

Vasilios Skliros[1], Panagiotis Papazotos[1], Filio Daskalaki[1], Petros Tsakiridis[1], Maria Perraki[1]

(1) National Technical University of Athens, School of Mining and Metallurgical Engineering, 9 Heroon Politechniou St., 15780, Zografou (Athens), Greece, sklirosbill@metal.ntua.gr

Synthetic nesquehonite ($MgCO_3 \cdot 3H_2O$), a promising building material (Glasser *et al.*, 2016), as recently gained interest as mineralization product of carbon capture and storage (CCS). The main advantage of nesquehonite in being a potential permanent storage solution for CO_2 emissions is that at least 30% of its structure consist of CO_3^{2-} (Ferrini *et al.*, 2009).

PHREEQC geochemical software has been recently proposed to be a useful tool in modeling CCS mineralization products (Liu *et al.*, 2019).

The aim of this study is to investigate the thermodynamic kinetics of CO_2 mineralization and to determine the precipitation of nesquehonite in the MgO-CO_2-H_2O system applying the geochemical software PHREEQC (Parkhurst & Appelo, 1999, v. 3), and using data from laboratorial experiments. Nesquehonite was synthesized herein by mixing a rich in Mg^{2+} aqueous solution with a rich in CO_3^{2-} one, at a temperature of 25 °C and pH 9.3, according to the following reaction:

$$Mg^{2+} + CO_{2\,(g)} + 4H_2O \rightarrow MgCO_3 \cdot 3H_2O_{\,(s)} + 2H^+ \quad (1)$$

Since during the reaction, pH was continuously decreasing, an additional input of alkaline solution (NH_3) was required to keep pH in alkaline values (Ferrini *et al.*, 2009).

An important controlling factor of the amount of Magnesium (Mg)-carbonate minerals crystallized and precipitated by CO_2 mineralization is the CO_3^{2-} concentration in the solution reactant (Ferrini *et al.*, 2009).

For simulating the nesquehonite synthesis experiments with the geochemical software PHREEQC, Minteqv4 thermodynamic database (Allison *et al.*, 1991) was used. Saturation Index (SI) of $MgCO_3 \cdot 3H_2O$ was calculated under different thermodynamic conditions in order to better study the precipitation/dissolution reactions of $MgCO_3 \cdot 3H_2O$.

SI of the solution is given by the equation:

$$SI = \text{Log}\,(IAP / K_{SP}),$$

where IAP is the ion activity product; K_{SP} is the equilibrium constant. When SI value is 0 the solution is in equilibrium with the mineral phase; when the SI value is >0 the solution is oversaturated, resulting in mineral precipitation, and when SI value is <0, the solution is undersaturated indicating that dissolution is required to reach equilibrium.
The parameters evaluated herein were $Mg^{2+}:CO_3^{2-}$ concentration ratio, pH and temperature. The precipitation/dissolution reaction of $MgCO_3 \cdot 3H_2O$ was investigated in a range of pH from slightly acidic to strong alkaline pH values (5-14) (Figure 1) and temperature values from 10°C to 80°C (Figure 2). Calculations were performed for 1.5M solution of Mg^{2+}.

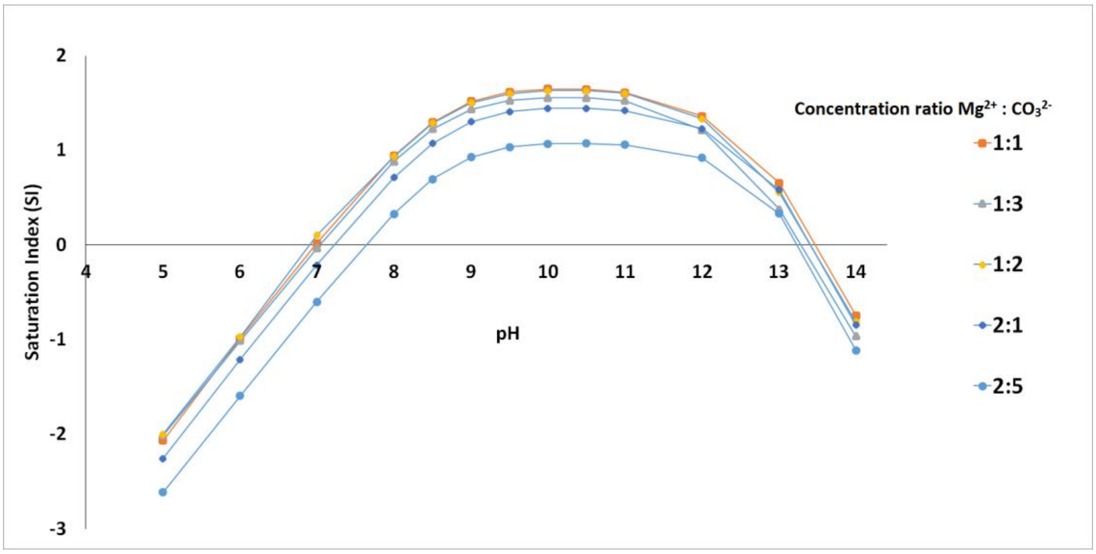

Figure 1. Saturation Index of $MgCO_3 \cdot 3H_2O$ in various pH (T=25°C) and concentrations of Mg^{2+} and CO_3^{2-}.

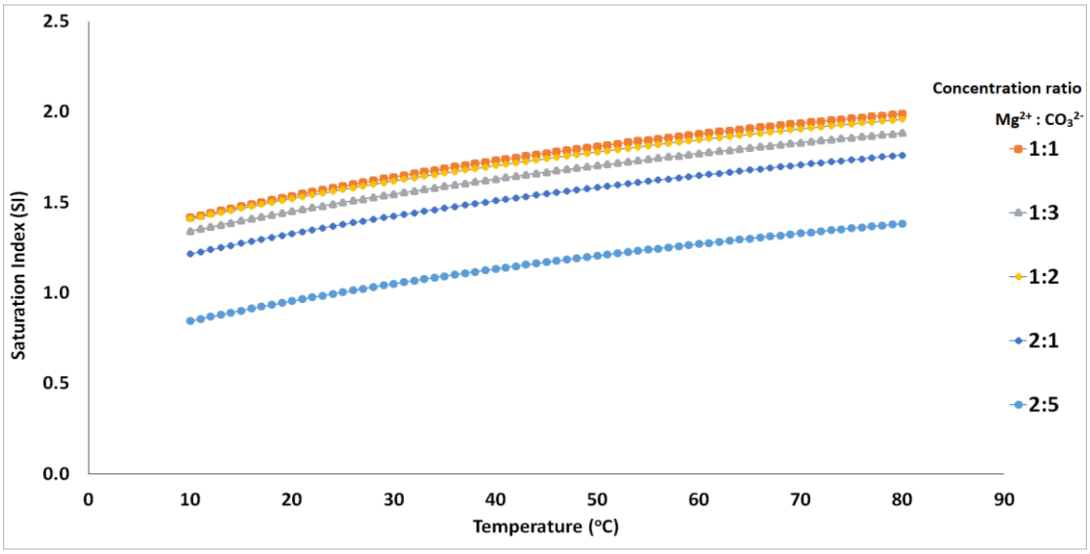

Figure 2. Saturation Index of $MgCO_3·3H_2O$ in various temperatures (pH 9.3) and concentrations of Mg^{2+} and CO_3^{2-}.

$MgCO_3·3H_2O$ precipitation may potentially take place in a range of thermodynamic conditions (Figures 1, 2) under different ratio concentrations of Mg^{2+} and CO_3^{2-}. $MgCO_3·3H_2O$ precipitation occurs from pH 7 to pH 13 in a temperature range from 10ºC to 80ºC, under different Mg^{2+}:CO_3^{2-} concentration ratio.

The higher the Mg^{2+}:CO_3^{2-} concentration ratio of the initial solution is, the higher SI is. SI exhibits the highest value in slightly alkaline to alkaline pH conditions (pH 9.5-10). SI values in slightly acid to neutral (pH<7) and strong alkaline (pH>13.5) pH conditions are <0 indicating dissolution of nesquehonite (Figure 1). SI exhibits an upward inclined trend line with temperature increase (Figure 2) since K_{SP} is highly dependent on temperature. As shown, the effect of temperature is less significant compared to the effect of pH.

PHREEQC modeling of nesquehonite synthesis indicates that $MgCO_3·3H_2O$ precipitation might occur in higher pH and temperature conditions than those referred to in previous studies.

References

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