

# **Evaluation of the Effect of Steam Concentration in Flue Gas, on Carbonation of Magnesium Hydroxide for Mineral CO<sub>2</sub> Sequestration**

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**Abstract.** Mineral sequestration is known as one of the most appealing technologies to reduce CO<sub>2</sub> emission from combustion sources such as power generation stations and chemical plants. This process is suitable for widely available raw materials such as natural minerals and industrial wastes and brings the advantage of permanently storing CO<sub>2</sub> in the form of thermodynamically stable carbonates. However, it greatly suffers from a slow kinetics and a large energy penalty. A lot of strategies have been so far accomplished to enhance the kinetics of mineral carbonation process. Indirect carbonation has been suggested as the most effective approach. Through an indirect approach, carbonation process is divided into two separate sections. For example, during an indirect well-investigated Mg-silicate minerals carbonation, at the first stage the reactive compound such as Mg(OH)<sub>2</sub> is extracted from the raw Mg-silicate and, during the second level, carbonation is performed on the extracted compound. In order to improve the efficiency of indirect carbonation process, Mg(OH)<sub>2</sub> carbonation factors needs to be well-controlled and the energy release should be quantified. Carbonation efficiency of Mg(OH)<sub>2</sub> could be greatly enhanced under water steam including carbonation condition. In this study the concrete investigation on effects of steam concentration on Mg(OH)<sub>2</sub> carbonation is performed and the determinant effect of Mg(OH)<sub>2</sub> dihydroxylation has been discussed. Carbonation process is evaluated in the isothermal conditions of 200 °C, 250 °C and 325 °C under the atmosphere of Ar-CO<sub>2</sub>-H<sub>2</sub>O mixture. H<sub>2</sub>O concentrations of 0, 10 and 15% are tested and the effective concentration range of H<sub>2</sub>O is suggested based on the proposed carbonation mechanism. The results clearly support the enhancing effect of water steam on the kinetics of Mg(OH)<sub>2</sub> dry carbonation process. However, the exact effect of water steam on kinetics of Mg(OH)<sub>2</sub> dry carbonation is strongly dependent upon the dihydroxylation ability of Mg(OH)<sub>2</sub> feedstock. Finally, with the careful consideration of water steam effect on dihydroxylation and carbonation Mg(OH)<sub>2</sub>, the concentration of 10% water steam is addressed as an optimal concentration among those tried, resulting in the most enhanced kinetics of Mg(OH)<sub>2</sub> dry carbonation.

**Keywords:** Mineral sequestration, indirect dry carbonation, steam concentration effect.

## **1. Introduction**

Fossil fuels are still the primary energy source and are considered as a source of more than 80% total world energy [1]-[3]. Besides all advantages of fossil fuels, it is facing very important global challenges in regard with CO<sub>2</sub> emission. ICCP has reported atmospheric CO<sub>2</sub> concentration of almost 380 PPMV in 2007 [4] and 402.5 PPMV, in January 2016 at the Manua Loa, USA [5]. Several strategies have been already suggested for reduction of CO<sub>2</sub> emission in atmosphere. However CO<sub>2</sub> capture and sequestration in geological formation via carbon mineralization is still among the most trustable approaches to reduce CO<sub>2</sub> concentration in atmosphere through CO<sub>2</sub> storage in the form of thermodynamically stable products, with no chance of later leakage [3]. Carbon mineralization is defined as sequestration of CO<sub>2</sub> by reducing divalent

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cation containing minerals with CO<sub>2</sub> to form stable carbonates [6]. Mineral carbonation has been advanced in different routes by the researchers, while indirect/dry mineral carbonation has attracted a lot of attention, by providing the possibility of controlling carbonation parameters and storing exothermic released heat of carbonation reaction to compensate for other required energies in the flow of carbonation such as feedstock material activation [7]. In indirect carbonation, the whole process is divided into two critical stages, i.e., extraction of more reactive compounds such as Mg(OH)<sub>2</sub> from the original feedstock and later carbonation of extracted material. For this purpose, enhancement of Mg(OH)<sub>2</sub> carbonation rate has attracted a lot of attention, in order to optimizing mineral carbonation process. So far, a number of studies have been performed on carbonation of Mg(OH)<sub>2</sub> in dry atmosphere, although addition of water steam has been suggested to improve the efficiency and kinetics of Mg(OH)<sub>2</sub> carbonation [8]-[13], the optimal amount of water steam for enhancement of Mg(OH)<sub>2</sub> carbonation, via considering an effective carbonation mechanism among different suggested mechanisms, is still unclear. In this research, the effects of water steam addition to CO<sub>2</sub> are quantitatively characterized for carbonation of Mg(OH)<sub>2</sub> under different thermal conditions and in all cases the effects are discussed based on the possible proposed mechanisms.

## 2. Experimental Study

Magnesium hydroxide (Mg(OH)<sub>2</sub>) powders, produced by Fluka analytical (purity > 99%) and supplied by Sigma Aldrich (Germany), was utilized. The carbonation process and thermogravimetry analyses were performed in a NETZSCH STA 429 thermal analyser coupled with a water vapour generation furnace. To evaluate the effects of water steam concentration on carbonation process of Mg(OH)<sub>2</sub>, carbonation was performed under three different gas mixture concentrations with the total gas pressure of 1 atm, namely, (100%CO<sub>2</sub>), (80%CO<sub>2</sub>-10%H<sub>2</sub>O-10%Ar) and (80%CO<sub>2</sub>-15%H<sub>2</sub>O-5%Ar). Isothermal conditions of 200, 250 and 325 °C were applied for the duration of 600 min.

## 3. Results and Discussion

Carbonation of Mg(OH)<sub>2</sub> powders was investigated under three different steam concentration conditions (0%, 10% and 15% water steam) under varied isothermal conditions. Sample mass variation during thermogravimetry analysis (TGA) is presented as Fig. 1.

TGA graphs were studied to reveal the conversion percentage of carbonation as Eq.(1).

$$\text{Conversion\%} = (\text{Actual amount of carbonation} / \text{Maximum theoretically possible amount of carbonation}) * 100 \quad \text{Eq.(1)}$$

The maximum theoretically possible amount of carbonation could be calculated based on the maximum possible mass change percentage, during Mg(OH)<sub>2</sub> carbonation process (Eq.(2)).



Considering the amount of mass change percentage in Eq.(2), the maximum theoretically possible mass gain during Mg(OH)<sub>2</sub> carbonation is about 44%. On the other side, the maximum theoretically possible mass loss could be occurred as a result of pure Mg(OH)<sub>2</sub> dihydroxylation (without carbonation), based on Eq.(3).



In the same way, the maximum theoretically possible mass loss is about -31%, based on Eq.(3).

In all cases the amount of conversion % is calculated considering these upper and lower mass change limits, using lever rule, to address carbonation contribution, during a combined dihydroxylation/carbonation process. Fig. 2 shows the variation of conversion % under varying temperature and steam concentration conditions.

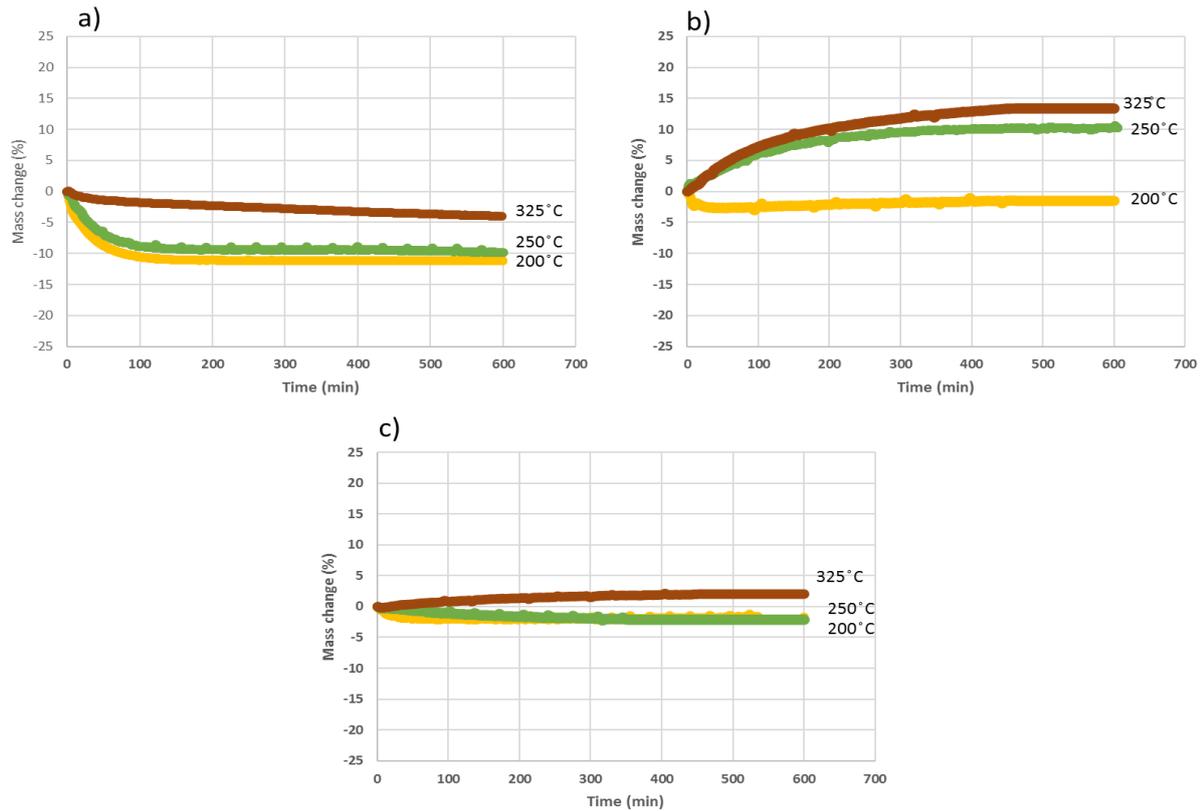


Fig. 1: TGA graphs of Mg(OH)<sub>2</sub> carbonation process, under different steam concentrations. A) Pure CO<sub>2</sub> atmosphere. B) 80% CO<sub>2</sub>-10% H<sub>2</sub>O-10% Ar. C) 80% CO<sub>2</sub>-15% H<sub>2</sub>O-5% Ar.

### 3.1. Thermodynamic stability

Thermodynamic stability must be considered prior to any kinetically and mechanism-based investigation to evaluate the most thermodynamically stable carbonation product. In another word, the possibility of carbonation process and the stable carbonation product is initially evaluated based on thermodynamic stability diagrams under specific applied temperature and steam concentration condition. Thermodynamics stability graphs are plotted by Geochemists Work Bench software (Release11.0.2)(Feb, 2016), using “Therm.com.v8.R6+.tdat” database. Fig. 3 presents thermodynamic stability diagrams at 200 and 250 °C. (available databases supports up to 300 °C). The thermodynamic stability diagram at 325 °C is plotted based on the available thermodynamic data and possible carbonation/dihydroxylation reaction [8], [14]-[18]. As is obvious from Fig. 3, MgCO<sub>3</sub> is the only stable phase under all applied steam concentrations at 200, 250 and 325 °C.

### 3.2. Effect of temperature and steam concentration on kinetics and mechanism of carbonation

As is obvious from the Fig. 2, conversion percentage increases upon increasing steam concentration under pure CO<sub>2</sub> atmosphere. In order to evaluate the possible mechanism involved in the carbonation process of Mg(OH)<sub>2</sub>, dihydroxylation curves of Mg(OH)<sub>2</sub> is plotted as a function of applied temperature and steam concentration. Fig. 4 shows the thermodynamic equilibrium curves of Mg(OH)<sub>2</sub> dihydroxylation [8]. As presented in Fig. 4, in all considered temperatures, Mg(OH)<sub>2</sub> will be dihydroxylated to MgO under pure CO<sub>2</sub> atmosphere. Also, based on the presented TGA graphs as Fig. 1(a) for pure CO<sub>2</sub> atmosphere, both mechanisms of carbonation and dihydroxylation are occurring simultaneously through the carbonation of Mg(OH)<sub>2</sub> and no sharp mass decrease or mass increase is monitored as a result of pure dihydroxylation or carbonation, respectively. This phenomena is also reported by Fricker et.al [11], while studying Mg(OH)<sub>2</sub> carbonation under the atmospheric pressure. On the other hand, MgO which may form as a result of Mg(OH)<sub>2</sub> dihydroxylation is known as a very unreactive compound during carbonation. So, the

dihydroxylation process of  $Mg(OH)_2$  is suggested to be formed at the same time with carbonation to promote  $Mg(OH)_2$  carbonation process through couple dynamic mechanism[11], [19].

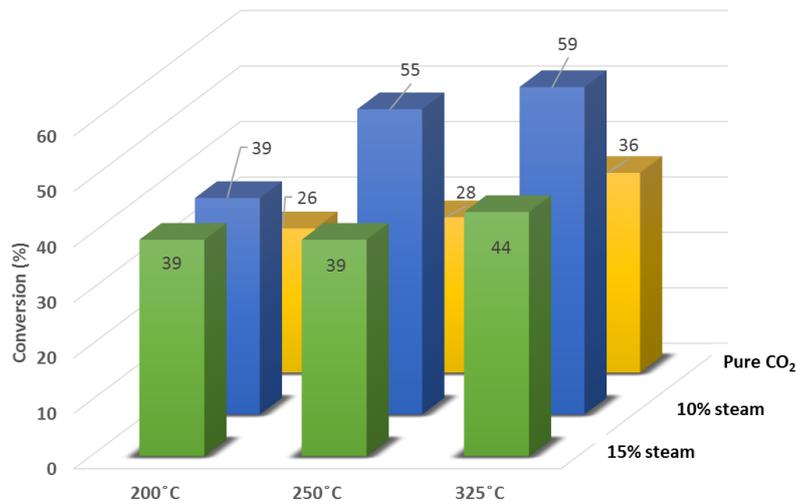


Fig. 2: Conversion percentage variation as a function of carbonation temperature and steam concentration during  $Mg(OH)_2$  indirect dry carbonation. ( $P_{total}=1$  atm).

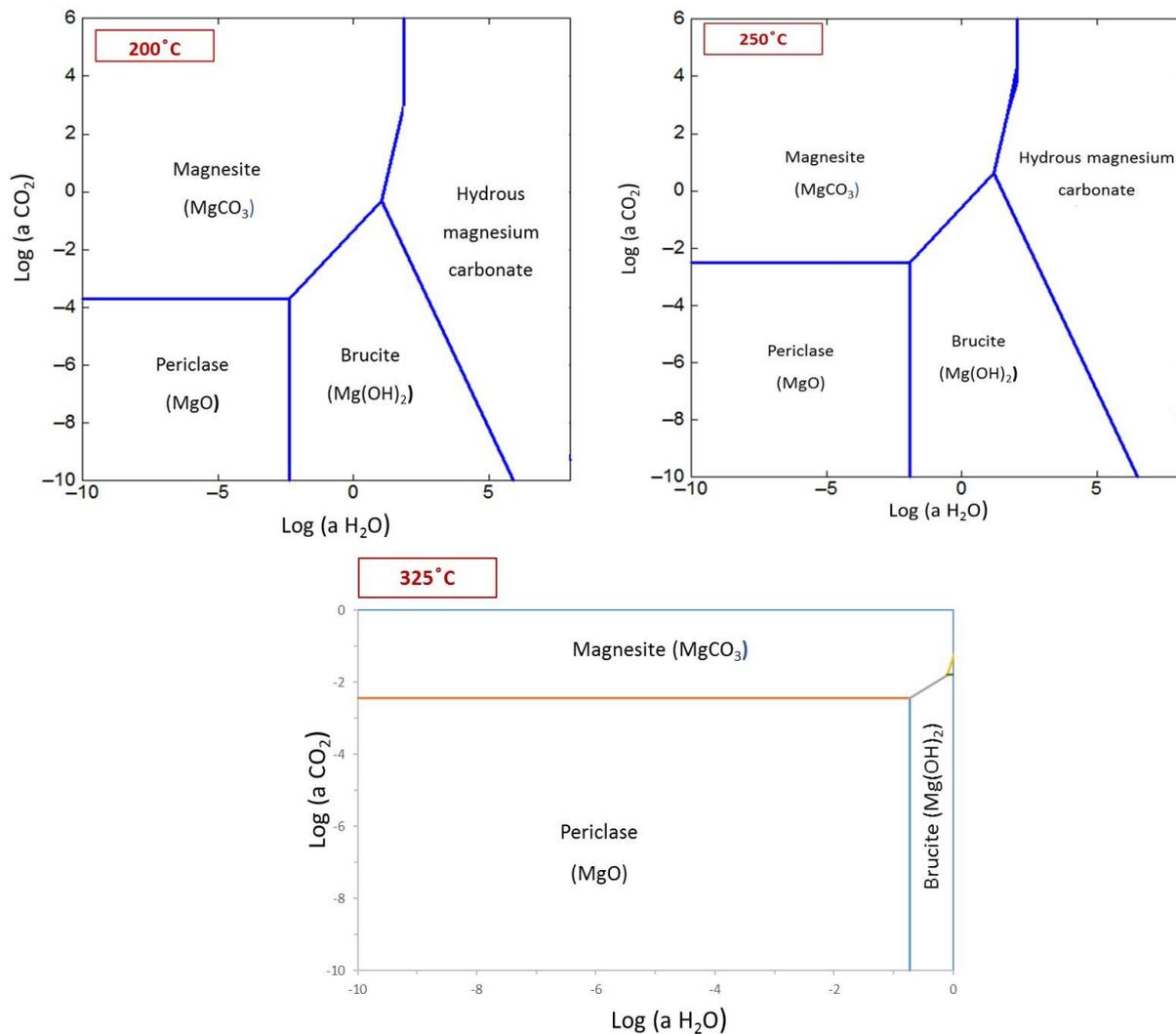


Fig. 3: Thermodynamic stability diagram plotted using Geochemists Work Bench software (Release11.0.2)(Feb, 2016).  
a) 200 °C. b) 250 °C. c) 325 °C.

TGA results of Fig. 1. (a) could be explained, considering the so far proposed mechanisms on  $\text{Mg}(\text{OH})_2$  carbonation by Fagerlund et al. [8], saying that, dihydroxylation of  $\text{Mg}(\text{OH})_2$  would result in the outward transferring of water molecules from inner  $\text{Mg}(\text{OH})_2$  to surface and carbonation reaction will occur on the surface upon surficial dissolution of Mg in the formed layer and reaction with  $\text{CO}_2$ .

However, the formation of surficial  $\text{MgCO}_3$  layer, acts as a diffusion barrier and would prohibit the continuation of carbonation process. In this way, dihydroxylation of  $\text{Mg}(\text{OH})_2$  and consequent water steam outward transferring could be also referred as a promoting factor, which results in the breakage of  $\text{MgCO}_3$  barrier layer as a result of structural water loss and preparation of fresh reactive compound for carbonation.

With this hypothesis, higher temperature can enhance the kinetics of  $\text{Mg}(\text{OH})_2$  carbonation under pure  $\text{CO}_2$  atmosphere upon speeding up the dihydroxylation of  $\text{Mg}(\text{OH})_2$  to  $\text{MgO}$ .

As the water steam concentration increases to 10%, the carbonation conversion percentage will increase dramatically, as presented in Fig. 2. The enhancing effect of water steam on carbonation of  $\text{Mg}(\text{OH})_2$  could be attributed mostly to formation of surficial water shell by external water available in the system, that lessens the impact of outward transferring of structural water.

To confirm this theory, the equilibrium curve of  $\text{Mg}(\text{OH})_2$  dihydroxylation in Fig. 4 could be addressed. Based on the offered trend of equilibrium dihydroxylation temperature, dihydroxylation temperature of  $\text{Mg}(\text{OH})_2$  increases noticeably as a function of available water steam and hence, the thermodynamic tendency of  $\text{Mg}(\text{OH})_2$  dihydroxylation under 10% steam condition would be less than that of pure  $\text{CO}_2$  atmosphere. So, if the carbonation of  $\text{Mg}(\text{OH})_2$  under steam involving atmosphere is still dependant upon outward structural water steam transferring, steam condition would be even a destructive factor in regard with kinetics of process.

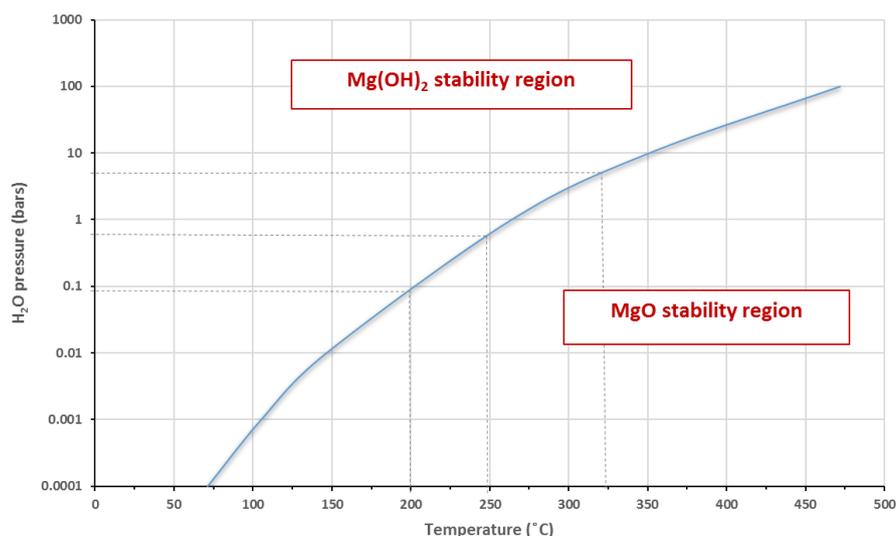


Fig. 4: Thermodynamic equilibrium curve of  $\text{Mg}(\text{OH})_2$  dihydroxylation as a function of temperature and steam concentration [8].

Based on this justification, the enhancing effect of water steam on carbonation of  $\text{Mg}(\text{OH})_2$  is mostly attributed to preparation of a denser water layer to cover the reactive compounds for dissolution of Mg atoms and subsequent carbonation [20], [21]. In another word, in this case, water is provided from externally available steamed atmosphere, and outward transferring of water from  $\text{Mg}(\text{OH})_2$  structural couldn't be a kinetically barrier any more, as is the case for pure  $\text{CO}_2$  atmosphere. However, although the preparation of steam water layer during the carbonation of  $\text{Mg}(\text{OH})_2$  is proposed to be not dependant upon structural water release, under 10% steam condition, dihydroxylation process of  $\text{Mg}(\text{OH})_2$  to  $\text{MgO}$  is still an effective process through the breakage of  $\text{MgCO}_3$  barrier layer which is formed on the surface as a result of carbonation, while releasing and passing the structural water out [22]. As a result of this concept, increasing temperature can promote  $\text{Mg}(\text{OH})_2$  carbonation, through enhancing the dihydroxylation process of  $\text{Mg}(\text{OH})_2$ .

Increasing the amount of water steam to 15% in the system, can not promote  $\text{Mg}(\text{OH})_2$  carbonation conversion %, as shown in Fig. 2. In this case, the external available water steam in the system would be able to form a water shell over the reactive compounds and enhance the dissolution and carbonation of Mg atoms. However a thick layer of water which would be formed might limit the  $\text{CO}_2$  access to the surface, as is reported by Kerisit et al [23] through studying the dynamics of forsterite surface in steam-involved carbonation process. However, in this condition, carbonation could be still promoted by increasing temperature through enhancement of  $\text{Mg}(\text{OH})_2$  dihydroxylation and breakage of surficial  $\text{MgCO}_3$  layer which facilitates an access to reactive core materials. But, the effect of temperature on conversion rate enhancement is much lower than that of 10% steam condition, since in the case of 15% steam system, the availability of  $\text{CO}_2$  on the surface would be suggested to be more controlling compared to the dihydroxylation speed. On the other hand, increasing the level of water steam results in the increment of dihydroxylation temperature (Fig. 4), so that dihydroxylation of  $\text{Mg}(\text{OH})_2$  could be not thermodynamically favorably at  $200^\circ\text{C}$  under 15% steam concentration and this factor could be also added up to the suggested reasons for lower conversion rates under 15% steam concentration compared to 10% steam atmosphere.

Fig. 5 presents the schematic overview of proposed carbonation mechanisms, discussed at different water steam and carbonation temperatures. The favorability of barrier layer breakdown as a result of dihydroxylation process, is also schematically presented to illustrate a comparative overview dihydroxylation tendency and its effective role during dry  $\text{Mg}(\text{OH})_2$  carbonation process.

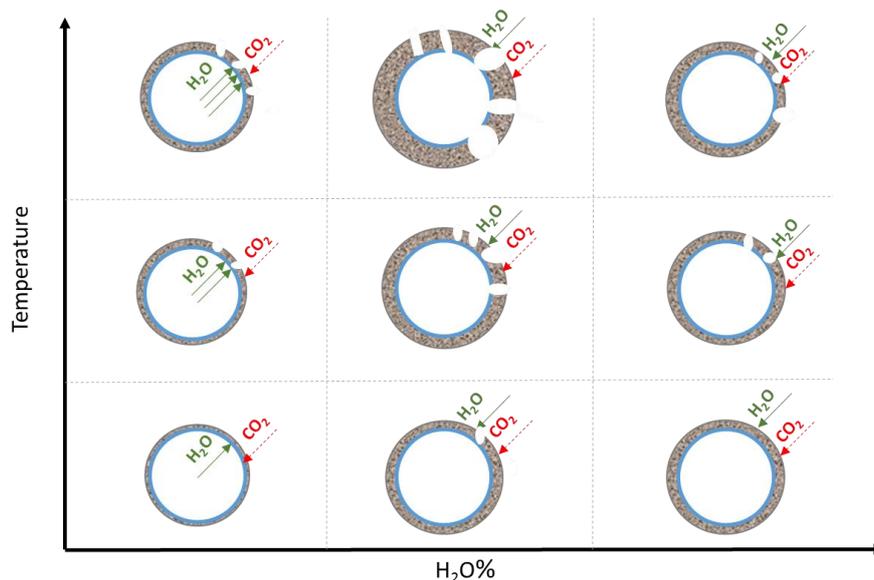


Fig. 5: Schematic overview of  $\text{Mg}(\text{OH})_2$  dry carbonation process over varying temperature and steam concentration.

#### 4. Conclusion

In this study the effect of water steam on enhancing carbonation process of  $\text{Mg}(\text{OH})_2$  has been evaluated. The effective concentration of water steam in flue gas for  $\text{Mg}(\text{OH})_2$  carbonation is investigated through thermogravimetry analyses and the results are discussed based on theoretically possible carbonation mechanisms.

As the results show, availability of external water steam can promote the conversion percentage of  $\text{Mg}(\text{OH})_2$  carbonation through a formation of an externally formed water shell over the reactive compounds, which lessens the dependence of carbonation process to availability of structural water release, as a possible limiting factor. On the other hand, the considerable effect of  $\text{Mg}(\text{OH})_2$  dihydroxylation on breakage of  $\text{MgCO}_3$  diffusion barrier is discussed. Finally, the optimal amount of water steam for enhancement of  $\text{Mg}(\text{OH})_2$  carbonation process is addressed to be around 10% among the evaluated steam concentration range.

However, further research would be suggested with the main focus on analytical methods in order to justify the proposed mechanisms for the dry carbonation of  $\text{Mg}(\text{OH})_2$ . As a sensible recommendation, combined TGA/MS would greatly improve the quality of study through monitoring both mass change (in

TGA) and the type of gas which is responsible for the corresponded mass variation (in mass spectroscopy), simultaneously. In this way, the proposed mechanism would be evaluated truly through monitoring the sequence of reactions that occur during the process of  $\text{Mg}(\text{OH})_2$  carbonation.

## 5. Acknowledgements

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