

Assessing the reactivity of magnesium oxide calcinated at different temperatures for understanding its role in degradation processes

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Motivation

In Tyrol, Austria, dolomite rock was commonly used as raw material for the production of historic mortars and plasters [1]. During calcination of dolomite rock, almost equal amounts of calcium oxide (CaO) and magnesium oxide (MgO) are produced, which later will be wet slaked.

While CaO hydrated rapidly, historic mortars occasionally contain non-hydrated MgO suggesting incomplete slaking. Over a large time span, these relicts of MgO react slowly with water to magnesium hydroxide. The associated volume expansion of about 118% takes place after the solidification of the binder leading to local spalling.

The goal of this study is to assess the influence of the calcination temperature on the reactivity of MgO during wet slaking (= degree of MgO hydration).

The gained insights are believed to be beneficial for a deeper understanding of hydration kinetics of dolomitic quicklime that can be later helpful for the use of light-calcinated dolomite rock as supplementary cementitious material (SCM) [2,3].

Approach

The present study assess the reactivity of magnesium oxide calcinated at different temperatures by recording the wet slaking curves.

For minimising the influence of e.g. impurities or particle size on the calcination process, very fine powder of reagent-grade heavy magnesium carbonate basic (calcium <0.75% according to certificate of analysis) supplied by Sigma-Aldrich was used.

The magnesium oxide was calcinated in steps of 100°C from 600 to 1000°C, subsequently quenched in air and characterised using X-ray diffraction (XRD) analysis.

The wet slaking process was performed in a cylindrical dewar under continuous stirring (as proposed by [4]) and constant monitoring of the temperature. The degree of hydration was estimated XRD analysis and thermogravimetric analysis (TGA).

Experimental Setup

Calcination of the raw material for one hour was done in a laboratory electric muffle furnace (Nabatherm) with a heating-rate of 15 K/min.

Wet slaking was performed with a MgO to water ratio of 1:4 (25 g MgO, 100 g deionised water) under constant mechanical stirring (500 rpm) in a cylindrical dewar (KGW-ISOTHERM) at ~20°C. The changes in temperature were recorded every 60 sec over a total time span of 72 h.

XRD analyses were performed with the help of powder diffractometer Empyrean (Panalytical) working with Cu-K α radiation generated at 40 kV and 40 mA. Spectra were taken from 5 to 70° 2 theta with a step size of 0.013° and a counting time of 40 sec/step.

Thermogravimetric analyses (TGA) was performed using Netzsch 449 F5 Jupiter from 25 to 1000°C with a temperature gradient of 10°C in a static air atmosphere (specimens dried at 105 °C before analyses).

Raw Material

First, the mineralogical characterisation of the reagent-grade basic magnesium carbonate with the help of XRD revealed hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$) as the main mineral phase (see Fig. 1).

According to TGA results, the dehydroxylation and decarbonation of hydromagnesite is completed at 575°C confirming 600°C as the lowest possible calcination temperature.

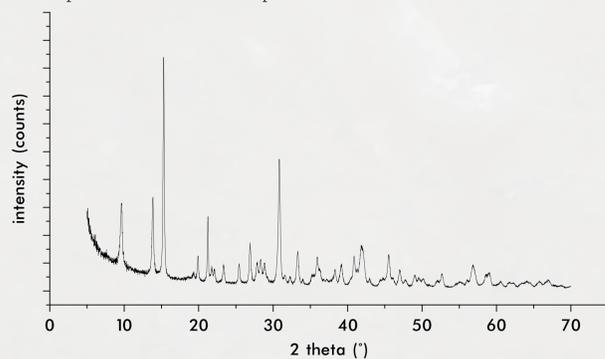


Figure 1: X-ray diffraction pattern of the used hydromagnesite (reference code: 01-070-0361).

Calcination

Second, the characterisation of the calcination products using X-ray diffraction revealed periclase (MgO) as the main mineral phases confirming complete thermal decomposition of the raw material (see Fig. 2).

The periclase peaks are observed to increase in height (intensity) and to become narrower with increasing calcination temperature. The differences in peak width are attributed to different crystallite size. Hence, with the help of the Scherrer method approximate crystallite sizes were calculated. The so-obtained results are listed in Table 1 and confirmed the increase in crystallite size with increasing calcination temperature.

In summary, the calcination process leads to the decomposition of the investigated basic magnesium carbonate (hydromagnesite) by releasing H_2O and CO_2 . This process is assumed to create porous structures made up of agglomerates of many MgO microcrystals (pseudomorphs [5]). With increasing calcination temperature, these MgO crystals undergo sintering leading to the observed increase in crystallite size. As reported by [5,6], this process can reduce specific surface area and internal porosity.

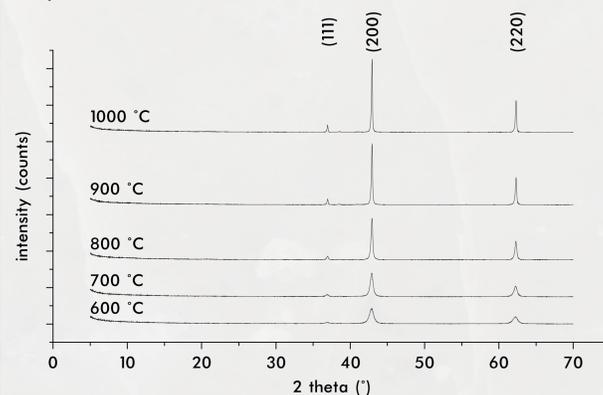


Figure 2: X-ray diffraction patterns of periclase (MgO) obtained through calcination of hydromagnesite at 600, 700, 800, 900 and 1000 °C showing an increase in peak heights and a decrease in peak widths with increasing calcination temperature.

| 600°C | 700°C | 800°C | 900°C | 1000°C |
|-------|---------|-------|-------|--------|
| 20 nm | no data | 41 nm | 51 nm | 85 nm |

Wet Slaking

Finally, the reactivity of the different MgO was assessed with the help of wet slaking curves.

The changes in temperature resulting from the exothermic character of the hydration reaction over time are plotted in Fig. 3. It can be seen that the maximum temperature spike and the time when the maximal temperature was reached varied between the individual MgO. The highest temperature and shortest time span were reached by MgO calcinated at 600°C, while the maximal temperature decreases as well as the time span increases with increasing calcination temperature.

The degree of hydration after 72h was assessed with the help of TGA by estimating of the dehydroxylation of the brucite ($Mg(OH)_2$) formed. The results revealed that the highest degree of hydration was obtained for MgO calcinated at 600°C (see Table 2). Thus, MgO that resulted from the calcination in the range 600 – 800 °C showed a high reactivity and can be described as 'light-burnt'. Whereas MgO formed in the range of 900 and 1000 °C showed a lower reactivity ('hard-burnt') that increase the risk of the associated volume expansion taking place after solidification of the binder.

Besides the magnesium oxide properties, the hydration process is affected by many factors, such as external force environment, hydration temperature, and nucleation site.

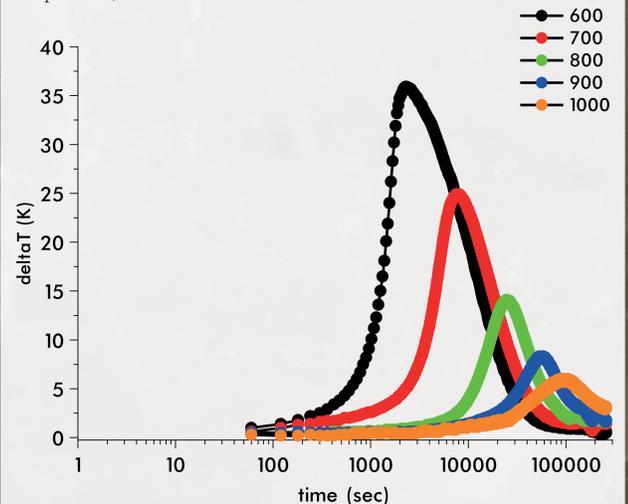


Figure 3: Wet slaking curves (T/t curves) showing differences in the hydration kinetics of magnesium oxide obtained from calcination at different temperatures.

Table 2: Degree of hydration of MgO estimated with the help of TGA in the temperature range of 320 - 480°C and the calculated amount of MgO that was reactive.

| 600°C | 700°C | 800°C | 900°C | 1000°C |
|-------|---------|-------|-------|--------|
| 87.7% | no data | 87.0% | 80.2% | 78.8% |

Conclusion

The aim of the present study was to investigate the effect of the calcination temperature on the reactivity of the so-obtained MgO during the wet slaking process.

The results revealed that the calcination temperature influences the degree of hydration. For the used experimental setup (permanent stirring at 500 rpm), the highest degree of hydration was achieved for calcination temperatures of 600 to 800 °C. For calcination temperatures of 900 and 1000 °C, sintering of MgO occurred, which is assumed to reduce, both, the internal porosity and the specific surface area resulting in lower reactivities (= lower degree of hydration).

A low reactivity can increase the risk of non-hydrated MgO relicts that induce damaging due to delayed expansion. This might limit the use of MgO obtained from light-burnt dolomite rock as SCM. At this point, it should be noted that these preliminary results were obtained using reagent-grade magnesium carbonate basic as raw material and, thus, further work on the reactivity of 'natural' MgO is required.

Outlook

Next steps comprises the hydration of MgO obtained from calcination of natural dolomite rock. Besides the presented experimental methods, scanning electron microscopy (SEM) will be employed to study morphological characteristics of the so-obtained MgO.

The gained insights will be a first step to assess the use of light-burnt dolomite rock as SCM. Later, accelerated carbonation experiments will be carried out to examine the conversion of hydrated MgO (brucite) into magnesium carbonate hydrate phases.

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