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INFLUENCE OF HYDRATION TIME ON THE HYDRATION OF MgO IN WATER AND IN A MAGNESIUM ACETATE SOLUTION

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The time required for maximum hydration of MgO obtained from the calcination of magnesite was determined. The MgO samples were hydrated for different time intervals in both water and magnesium acetate. A thermogravimetric analysis (TG) method was used to determine the degree of hydration to $Mg(OH)_2$. Increasing the hydration time, the degree of hydration of MgO and surface area of the formed $Mg(OH)_2$ increased. A leveling effect was observed on the percentage $Mg(OH)_2$ obtained from hydration in magnesium acetate, and an optimum amount of 85% was obtained after 500 min. For the hydration in water, the leveling effect was only observed after 800 min giving a maximum of 65% $Mg(OH)_2$.

Keywords: *calcination, hydration, magnesium acetate, magnesium hydroxide, magnesium oxide, TG*

Introduction

Previous studies on the hydration of magnesium oxide to form magnesium hydroxide range from the mechanism of magnesia hydration in magnesium acetate solutions [1], the effect of surface area and pore structure of the calcined magnesite and subsequent hydration of MgO produced [2, 3], hydration of calcined magnesite [3–7], to the effect of magnesium acetate concentrations, hydration time, amount of MgO and hydration solution temperature [8]. Recently, the effect of different hydrating agents on magnesia hydration to $Mg(OH)_2$ was investigated [9].

The use of magnesium hydroxide as a flame retardant and smoke-suppressor in polymeric materials is well-known. Magnesium hydroxide has been reported to be superior to flame retardants based on antimony metals or halogenated (chlorinated and brominated) compounds. As it contains no halogens or heavy metals, it is environmentally more friendly than these compounds. The decomposition products of the halogenated compounds are known to cause environmental concerns, as there is a risk of release of corrosive vapors [10]. Aluminium trihydrate ($Al(OH)_3$) has also been applied as a flame retardant in many polymeric materials, but as a result of its low decomposition temperature (approximately 180°C), its application has been limited since most polymers are processed at higher temperatures. Due to magnesium hydroxide's higher decomposition temperature (350°C), it is now the mineral flame retardant most often used [11]. Calcium hydroxide, $Ca(OH)_2$, can also be used since when heated, a highly endothermic dehydration reaction is observed. However, it may act as an efficient combustion promoter when combined with organic materials, and due to its high decomposition temperature, it was found to be not suitable as a flame retardant additive [12].

$Mg(OH)_2$ can be formed through the hydration of MgO, which is usually produced industrially from the calcination of the mineral magnesite (mainly $MgCO_3$). The duration and temperature of the calcination process dramatically affects the reactivity of the MgO formed, where the reactivity of MgO refers to the extent and the rate of hydration thereof to $Mg(OH)_2$ on exposure to water and moisture [3, 5, 8].

Raw magnesite is mined at Chamotte Holdings SA, and heated in rotary kilns to produce magnesium oxide, which is subsequently upgraded and then processed to produced hydrotalcite, magnesium hydroxide and magnesium carbonate. These products are then used as flame retardant additives in plastics and they are intended to replace toxic heavy metal salts currently being used as heat stabilizers. Flame retardants are essential additives to numerous plastics, including polyolefin found in products such as pipe, containers, bags and bottles. They are also essential in PVC (polyvinyl chloride) processing such as extrusion and injection molding to remove the hydrochloric acid that forms during heating. The hydrochloric acid causes degradation of the plastic.

The effect of calcination temperature and time on the hydration of industrially obtained MgO has been studied before [13]. The percentages indicated

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refer to the amount of $Mg(OH)_2$ formed from the calcined MgO after treatment for 30 min at 80°C in a magnesium acetate solution. It was shown that up to 60% $Mg(OH)_2$ (rehydrated MgO) can be obtained using calcination temperatures up to 1000°C. When calcined at 1200°C, the influence of the calcination time becomes more significant and the results have shown that a maximum amount of 40% of $Mg(OH)_2$ can be obtained after 1 h of calcining, while only 14% could be obtained after 4 h of calcining at 1200°C.

For the present study, the aim was to investigate whether an increased degree of hydration of MgO, calcined at different temperatures with subsequent different reactivities, can be obtained by elongating the hydration time in both water and magnesium acetate solutions.

Experimental

Samples

Pure magnesium acetate ($Mg(CH_3COO)_2{\cdot}4H_2O$) was obtained from Merck, South Africa. The MgO sample was obtained by the calcination of natural magnesite (mainly $MgCO_3$), obtained from Chamotte Holdings, S.A.

Sample preparation and procedure

The magnesite samples were calcined in the laboratory at 650, 1000 and 1200°C for 2 h. The samples were milled and sieved to a particle size of less than 75 μm before hydration. BET surface area analyses and thermogravimetric analyses were performed on the raw material, the calcined material and the products obtained after hydration. XRD and XRF analyses were performed on the raw and calcined material.

The hydration reactions were performed in a 250 mL glass beaker immersed in a thermostated water bath. A 10 g portion of the calcined and sieved MgO sample was poured into a 250 mL glass beaker containing 100 mL of a 0.1 M magnesium acetate solution or water at 80°C, and the slurry was continuously stirred at a constant rate of 250 rpm for different time intervals. The reaction temperature was held constant at 80°C. The products were then filtered under vacuum, dried in an oven at 200°C for 2 h and stored in a desiccator.

TG analyses

A Q500 TGA (TA Instruments) was used to perform the thermogravimetric analysis on all the products. A heating rate of 10°C min^{-1} was used in a nitrogen atmosphere. Platinum pans were used, and the sample masses were pre-weighed to approximately 10 mg. The percentage $Mg(OH)_2$ in the products were obtained from the curves of mass loss (%) and derivative mass (% $°C^{-1}$) *vs.* temperature (°C), as described earlier by the authors [14].

BET surface area analyses

A NOVA 1000^e Surface Area and Pore Size Analyzer from Quantachrome Instruments, using nitrogen gas as an adsorbent, was used to determine the surface areas of the products.

XRD analyses

X-ray powder diffraction analyses were performed on an automated Siemens D501 XRD spectrometer with a 40-position sample changer and monochromatic CuK_α radiation. The results were analyzed with the use of the International Center of Diffraction PDF database sets.

XRF analyses

For the X-ray Fluorescence analysis, the MgO sample was ground to <75 μm in a Tungsten Carbide milling vessel and roasted at 1000°C to determine the loss on ignition value (LOI). The milled MgO sample (1 g) was then mixed with 9 g $Li_2B_4O_7$ and fused into a glass bead. Major element analysis was executed on the fused bead using an ARL9400XP+ spectrometer.

Results and discussion

The XRD analyses indicated that the phases present in the sample before calcination mainly are periclase (cubic MgO), with some $MgCO_3$, SiO_2, $Mg(OH)_2$ and CaO or $CaCO_3$. After calcination of the sample at the respective temperatures, XRD analyses confirmed that most of the $MgCO_3$ and $Mg(OH)_2$ were converted to MgO. Table 1 gives the chemical composition of the raw material, as determined by XRF analysis. This result confirmed the results obtained by XRD, indicating that the sample consisted mainly of Mg-containing phases, with small amounts of Si-, Al- and Ca-containing phases present.

Table 2 presents some of the physical properties of the raw and calcined material. The surface area of the raw material increases from 10.98 $m^2\ g^{-1}$ to 21.17 $m^2\ g^{-1}$ after calcining at 650°C, the temperature at which all the moisture is removed and all the $Mg(OH)_2$ and $MgCO_3$ is decomposed to MgO. The surface area then decreases again with an increase in calcining temperature, due to the effect of sintering. As expected, the loss on ignition value was

Table 1 XRF analysis of the raw material obtained from Chamotte Holdings

Composition	Mass/%
MgO	85.00
SiO_2	1.74
Al_2O_3	0.44
CaO	0.87
Fe_2O_3	0.07
Other oxides	0.83
LOI	11.00
Total	99.95

Table 2 The physical properties of MgO under different calcination conditions

Properties	Raw material	Calcined material		
		650°C	1000°C	1200°C
Loss on ignition/%	11.00	<0.01	<0.01	<0.01
Surf. area/ $m^2\ g^{-1}$	10.98	21.17	11.72	4.32
Particle size/μm	>75	<75	<75	<75

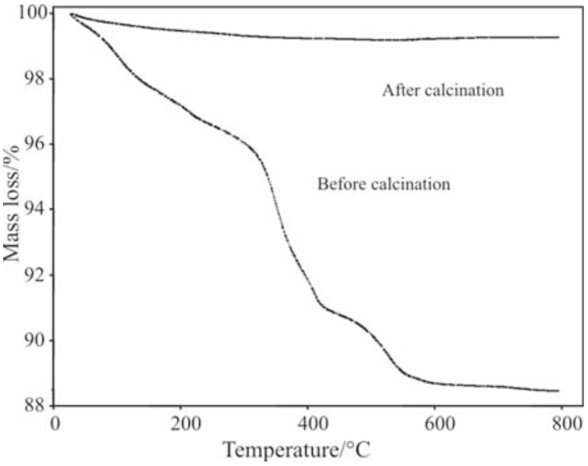

Fig. 1 TG analysis of raw magnesite (solid line) and calcined magnesite (dotted line)

reduced to close to zero after calcining. A particle size of <75 μm was obtained by milling and sieving.

Figure 1 shows an example of the thermogravimetric analysis (TG) curves obtained for the raw and calcined samples. The TG curve of the raw material exhibits a number of mass loss steps up to a temperature of 600°C. These steps can be ascribed to moisture loss (between 50 and 200°C), $Mg(OH)_2$ decomposition to MgO (between 200 and 450°C) and $MgCO_3$ decomposition to MgO (between 450 and 600°C). The calcined sample, with a mass loss percentage of less than 1%, has a good thermal stability over the temperature range, indicating that the sample consisted mainly of MgO. Therefore thermogravimetric (TG) analyses confirmed that the $Mg(OH)_2$ and $MgCO_3$ were decomposed to MgO after calcination of the samples at the respective temperatures.

Figures 2 and 3 present the TG curves showing the effect of increasing the hydration time on the percentage $Mg(OH)_2$ obtained from MgO calcined at 1200°C after hydration in magnesium acetate and water. It can clearly be seen that the amount of magnesium hydroxide starts to level off after 210 min when hydrated in magnesium acetate. TG results for MgO calcined at 650 and 1000°C and hydrated show similar tendencies for the two hydrating agents.

Figure 4 summarizes the results obtained for the percentage of $Mg(OH)_2$ produced from MgO calcined at the different temperatures, following hydration in magnesium acetate and water. The percentage magne-

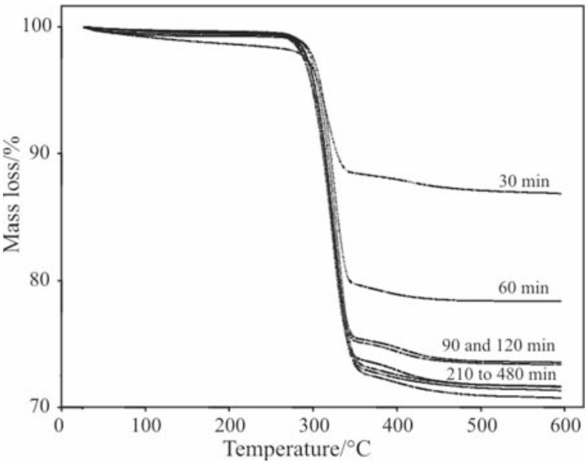

Fig. 2 TG curves showing the effect of increasing hydration time on percentage $Mg(OH)_2$ obtained in magnesium acetate after calcination at 1200°C

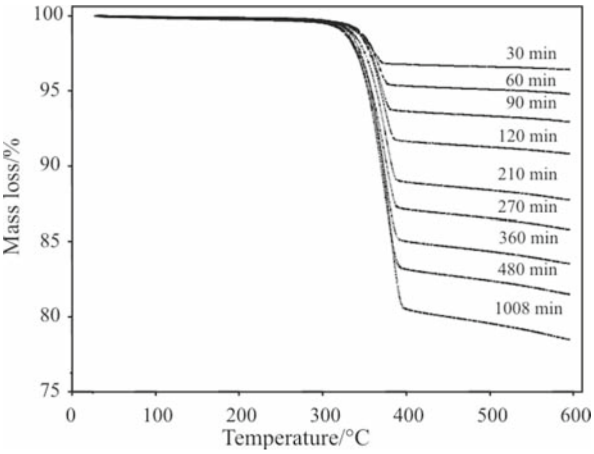

Fig. 3 TG curves showing the effect of increasing hydration time on percentage $Mg(OH)_2$ obtained in water after calcination at 1200°C

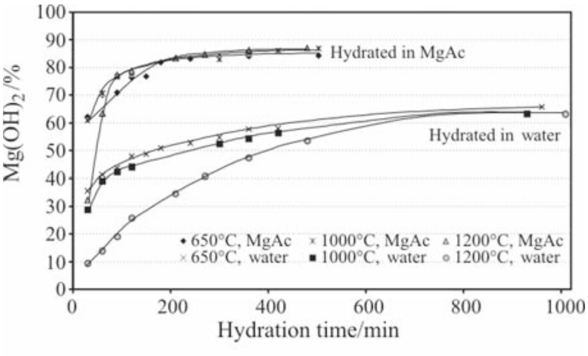

Fig. 4 The effect of increasing the hydration time of the sample calcined at different temperatures on the percentage of $Mg(OH)_2$ obtained in both magnesium acetate and water

sium hydroxide obtained after hydration in both solutions increases with time for both agents. The results obtained for the percentage of $Mg(OH)_2$ produced from hydration of the sample calcined at 650°C in magnesium acetate starts to level off after 180 min and a maximum amount of 84% $Mg(OH)_2$ was obtained after approximately 503 min.

Similar results were obtained when the same experiments were performed using water as a hydrating reagent. After 960 min of hydration, 66% $Mg(OH)_2$ was obtained for MgO calcined at 650°C in water. These results clearly demonstrate that magnesium acetate is a better hydrating agent when compared to water under these reaction conditions.

Performing the hydration experiments using MgO calcined at 1000°C, approximately the same results were obtained for both the water and magnesium acetate as hydrating agents. The maximum hydration time was 503 min in the magnesium acetate solution, where 87% $Mg(OH)_2$ was obtained. After 930 min in water, the degree of hydration for MgO calcined at 1000°C is 63%.

The calcination of magnesite at 1200°C results in a MgO product with low reactivity and a small degree of hydration after 30 min exposure to hydration agents [12]; however, results obtained indicate that by increasing the reaction time, the amount of magnesium hydroxide is increased dramatically. The hydration of MgO calcined at 1200°C gives only 9% $Mg(OH)_2$ in water and 32% in magnesium acetate solutions after 30 min of hydration. 87% $Mg(OH)_2$ was obtained after 480 min of hydration in a magnesium acetate solution, and 63% $Mg(OH)_2$ after 1008 min in water, giving the same results as for the maximum hydration for the previous two cases of MgO calcined at 650 and 1000°C. The same maximum percentage $Mg(OH)_2$ is thus obtained regardless of the calcination temperature of MgO.

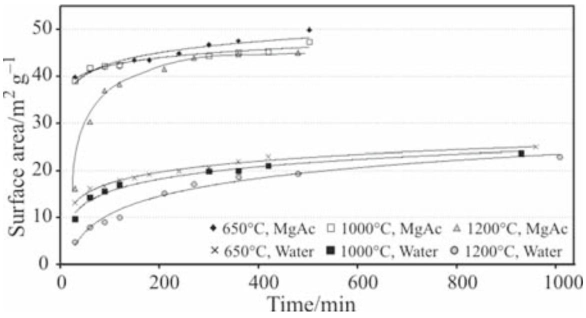

Fig. 5 Variation of the surface area of $Mg(OH)_2$ formed with hydration time obtained from the samples calcined at different temperatures after hydration in magnesium acetate and water

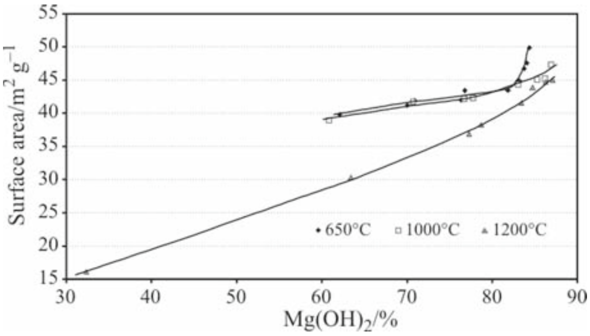

Fig. 6 The surface area of $Mg(OH)_2$ formed *vs*. % $Mg(OH)_2$ obtained from the samples calcined at different temperatures after hydration in a magnesium acetate solution

Considering the rate of MgO hydration to $Mg(OH)_2$, the hydration of MgO calcined at 1200°C is slow within the first few minutes. Comparing the results obtained for the hydration of MgO calcined at 650 and 1000°C in magnesium acetate, an average percentage $Mg(OH)_2$ of 61% was obtained after 30 min in comparison to 32% $Mg(OH)_2$ obtained from MgO calcined at 1200°C after 30 min of hydration. The results obtained during the hydration of MgO calcined at 650 and 1000°C in water gave an average percentage $Mg(OH)_2$ of 46% after 2 h, and only 25% $Mg(OH)_2$ was obtained from MgO calcined at 1200°C after the same hydration time.

Figure 5 shows the variation of the surface area of $Mg(OH)_2$ formed with hydration time obtained for the samples calcined at different temperatures after hydration in magnesium acetate and water. Surface area changes follow a similar trend with change in temperature as the degree of hydration with temperature (Fig. 4).

Conclusions

Increasing the hydration time of MgO in water or magnesium acetate solutions increases the degree of hydration. A maximum amount of 84% of theoretically possible Mg(OH) can be obtained upon hydration of MgO calcined at 650°C in magnesium acetate after 180 min of hydration, while 66% $Mg(OH)_2$ formed after approximately 600 min of hydration in water. Similar results were obtained for the hydration of MgO calcined at 1000°C in both water and magnesium acetate.

Despite the fact that the MgO calcined at 1200°C resulted in a hard burnt and a low reactivity sample, the degree of hydration increased considerably by increasing the hydration time. Again, as for 650 or 1000°C, approximately 87% $Mg(OH)_2$ was obtained after 210 min of hydration in magnesium acetate while only 63% $Mg(OH)_2$ was obtained in water after 1000 min of hydration.

Khangaonkar *et al.* [15] reported that the particle size of MgO and the formed $Mg(OH)_2$ during hydration decreases continuously in spite of the increase in the mass due to hydration and reduction in density, both involving an increase in volume. It seems that the process taking place is breaking up of the solids due to the hydration reaction, with the product layer of magnesium hydroxide causing stress leading to breakage, instead of continued growth of the $Mg(OH)_2$ layer. This breakage then causes a fresh MgO surface to be made available for further rapid hydration and breakage. The repetitive cycle then leads to a rise in the number of particles and surface area of $Mg(OH)_2$, particularly in the later stages of the hydration. As the hydration time increases, more breakage results and more MgO surface sites are available, leading to faster hydration of MgO, and subsequently more $Mg(OH)_2$ is formed.

Figure 6 shows the results of the percentage $Mg(OH)_2$ obtained from MgO hydrated in magnesium acetate *vs*. the surface area obtained for the present study. The surface area of the product rises as the percentage $Mg(OH)_2$ increases with longer hydration times. Similar observations were also made for MgO hydration in water. This observation can be used to confirm the hydration mechanism offered by Khangaonkar *et al.* [15], and indicates that a decrease in particle size (with subsequent increase in surface area) was obtained with an increase in the degree of hydration.

During calcination of MgO, the decrease in MgO reactivity with an increase in calcination temperature seems to be due to structural changes. Maryska and Blaha [16] have reported that the influence on the hydration rate of MgO is exhibited by the degree of crystallization and sintering of MgO. As the calcination temperature is raised, the surface area of MgO decreases due to sintering, resulting in a decrease in available surface sites for reaction and thus a decrease in the hydration rate of MgO. A smaller surface area implies less Mg^{2+} ions to go into solution to react to form $Mg(OH)_2$, however, as the hydration time is increased, with time more Mg^{2+} ions become available to form $Mg(OH)_2$. At 1200°C, there is more sintered MgO (with a very low surface area) as compared to MgO calcined between 650 and 1000°C, and therefore, hydration of MgO calcined at 1200°C, will result in a lower rate of hydration. However, the same maximum hydration as obtained from the hydration of MgO calcined at 650 and 1000°C is eventually obtained.

The same maximum degree of hydration for different reactivity MgO samples was obtained and depends on the hydration agent; however the time needed for maximum hydration differ for the hydration agents. The rate of hydration of different reactivity magnesium oxides (or different surface areas) is influenced by the calcination conditions and thus the reactivity of the samples. The initial rate of hydration seems to be dependent on the reactivity of the calcined MgO.

These results indicate that the MgO hydration process proceeds with a physical step as the rate determining mechanism. Sintering seems to be the main contributing kinetic parameter, influencing the availability of reaction sites on the MgO surface. Nan [17] have studied the sintering of aggregated MgO powder, and has found that the pores in the MgO aggregate almost disappear at temperatures as low as 1200°C. This will cause a lower surface area of the MgO to be available for hydration, with a subsequent lower initial degree of hydration.

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