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HYDRATION OF MEDIUM REACTIVE INDUSTRIAL MAGNESIUM OXIDE WITH MAGNESIUM ACETATE
Thermogravimetric study

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Abstract

Medium reactive magnesium oxide reacts incompletely with available water to form magnesium hydroxide. To enhance the hydration of medium reactive magnesium oxide, the effect of magnesium acetate as hydrating agent was studied. The extent to which different parameters (concentration of magnesium acetate, solution temperature and solid to liquid ratio of MgO to magnesium acetate) influence the hydration rate of a medium reactive industrial sample of magnesium oxide were evaluated. The degree of rehydration measured as percentage $Mg(OH)_2$ being formed, increases from approximately 56% using 0.5 M magnesium acetate solutions at 25°C to 64% at 50°C, to more than 70% at 70°C. The major part of rehydration of the medium reactive MgO sample occurs within the first few minutes of the reaction for all three temperatures studied.

Keywords: magnesium acetate, MgO, rehydration, TG

Introduction

Magnesium hydroxide has many industrial applications, one of them as a mineral flame retardant additive in polymers [1, 2]. It can be found naturally as a mineral, can be produced synthetically from seawater or brines, or from the hydration of magnesium oxide. The rate of hydration of magnesium oxide influences the size of the magnesium hydroxide aggregates that form. Rapid hydration of magnesium oxide results in the formation of hydroxide aggregates with a high surface area [3].

Magnesium oxide is usually obtained through heating of the various forms of magnesium carbonate. The temperature and duration of heat treatment of the magnesium compounds during the production of magnesium oxide determine the reactivity of the magnesium oxide. The reactivity of magnesium oxide determines the rate and extent of rehydration of the magnesium oxide sample, when exposed to water. Literature shows that thermogravimetric analysis can be used to study the reactivity of solids [4].

The reactivity is measured industrially by using the citric acid test (as described in the experimental part of this paper), where the time needed for the magnesium ox-

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ide sample to neutralize the citric acid solution is measured. Industry uses values of less than 60 s for highly reactive magnesium oxide. Medium reactive magnesium oxide gives a measurement between 180 and 300 s for the standardized test. A low reactivity magnesium oxide gives a value of more than 600 s and 'dead burnt' magnesium oxide approximately 900 s.

As it seems that the formation of magnesium hydroxide in the magnesium oxide slurry occurs through a solution-dissolution process, various other ions in solution may influence the rate of formation of the hydroxide [5]. In this study, the influence of the addition of low concentrations of magnesium acetate on the hydration of a medium reactive industrial magnesium oxide sample was studied.

Experimental

Samples

Pure $Mg(CH_3COO)_2 \cdot 4H_2O$ was obtained from Merck. Medium reactive MgO was obtained from Chamotte Holdings, South Africa. The magnesium oxide sample was heated at 650°C for 2 h before use.

Instrumentation

A Q500 TGA (TA Instruments) was used to perform the thermogravimetric analysis. A heating rate of 10°C min^{-1} was used in an air atmosphere. Platinum pans were used, and the sample masses were approximately 10 mg.

A Micromeritics Flowsorb II 2300 BET instrument, using nitrogen gas as an adsorbant, was used to determine the surface areas of the products.

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

X-ray powder diffraction analyses were done on an automated Siemens D501 XRD spectrometer with a 40-position sample changer and monochromated CuK_α radiation. The results were analysed with the use of the International Centre of Diffraction for PDF database sets.

Citric acid reactivity test

The activity of the MgO sample, obtained from Chamotte Holdings (South Africa) was determined after the sample was dried for 2 h at 650°C. The citric acid method of determination of powder activity was used. In this method, a 0.40 N citric acid solution was prepared, and a slurry of 2.0 g of powdered MgO in 100 mL of the 0.4 N citric acid solution was shaken, with phenolphthalein as indicator, until the colour changed from white to pink. The time it takes for the slurry to change colour is then reported as the citric acid reactivity.

Effect of varying the magnesium acetate concentration

The influence of the concentration of magnesium acetate on the degree of hydration of MgO was studied. 15 g MgO in 100 mL of magnesium acetate solutions ranging between 0.005 M and 1.0 M was stirred for 20 min at a constant stirring rate of 250 rpm. The reaction temperature was held constant at 25°C by performing the hydration reaction in a water bath. The products were filtered and dried for 2 h at 200°C.

Hydration of MgO

A specific amount of the MgO sample was stirred at a constant rate of 200 rpm in a solution of water or magnesium acetate, while the temperature was held constant by performing the reaction in a water bath. After a specific time period, the sample was filtered and dried for 2 h at 200°C.

The different experimental parameters are given in Table 1. The actual temperature of samples stirred in the 50°C water bath was between 48 and 49°C, while those in the 70°C bath was between 66 and 68°C.

Table 1 Experimental parameters for the hydration of MgO in water and $Mg(CH_3COO)_2{\cdot}4H_2O$ solutions

Temperature	25, 50 and 70°C
$Mg(CH_3COO)_2{\cdot}4\ H_2O$ concentration	0, 0.2 and 0.5 M
Amount of MgO	10 and 15 g per 100 mL
Reaction time	0, 1, 5, 10, 20, 30 and 60 min

The percentage $Mg(OH)_2$ in the samples was determined by TG analysis [2]. Curves of mass (%) and derivative mass (%/°C) *vs.* temperature (°C) up to a temperature of 600°C were obtained. The percentage mass loss due to water of crystallization and surface water was subtracted from the mass of the sample. The first mass loss above 200°C was taken as due to the decomposition of $Mg(OH)_2$, while all other steps was considered due to the decomposition of $Mg(CH_3COO)_2$.The percentage mass loss due the decomposition of $Mg(OH)_2$ and $Mg(CH_3COO)_2$ was then determined by using the minimum of the derivative mass *vs.* temperature curve as previously described [6].

TG analyses were performed on all products, while BET surface area analyses were only performed on selected products. The surface areas were measured after the products were dried at 200°C for 2 h.

Results and discussion

XRF and XRD results

The results of the XRF analysis of the MgO sample, as obtained from Chamotte Holdings, are given in Table 2. It is clear from the LOI value that the sample was rehydrated to some extent. It was decided to heat all samples at 650°C for 2 h before

further testing and use. XRD analyses confirmed that the sample consisted mainly of periclase (cubic MgO), with some $MgCO_3$, SiO_2, $Mg(OH)_2$ and CaO or $CaCO_3$. Upon drying the sample at 650°C for 2 h, the $MgCO_3$ and $Mg(OH)_2$ was converted to MgO (confirmed by XRD analysis).

Table 2 XRF analysis of medium reactive MgO, obtained from Chamotte Holdings, before drying at 650°C

Element	%
SiO_2	0.85
TiO_2	<0.01
Al_2O_3	0.14
Fe_2O_3	0.06
MnO	<0.01
MgO	62.5
CaO	1.47
Na_2O	<0.01
K_2O	<0.01
P_2O_5	0.02
Cr_2O_3	<0.01
NiO	0.08
V_2O_5	<0.01
ZrO_2	<0.01
SO_3	0.21
LOI	33.92
Total	99.32

Reactivity tests

The citric acid test for reactivity of the MgO sample after heat treatment at 650°C for 2 h gives a reactivity value of 213 s, which corresponds to the values given for a medium reactive sample.

Effect of magnesium acetate concentration on rehydration of MgO at 25°C

The effect of varying the concentration of magnesium acetate on the degree of hydration of MgO is shown in Table 3. It was clear that the degree of hydration increased with an increase in the magnesium acetate concentration, up to a concentration of 0.5 mol L^{-1}. Magnesium acetate concentrations up to 0.010 mol L^{-1} did not play a significant role in increasing the degree of hydration. It was decided to investigate the influence of concentrations of magnesium acetate of 0, 0.2 and 0.5 mol L^{-1} at different reaction temperatures, for different reaction times and for different solid MgO to liquid magnesium acetate solution ratios.

Table 3 Influence of magnesium acetate concentration on the degree of hydration of MgO

$Mg(CH_3COO)_2 \cdot 4H_2O$ concentration/mol L^{-1}	$Mg(OH)_2$ / %
Untreated MgO	2
0	29
0.005	30
0.010	31
0.050	36
0.100	42
0.150	47
0.200	49
0.500	54
1.000	47

Rehydration at 25°C

Figure 1 summarises the results obtained for rehydration of slurries of 5, 10 or 15 g MgO in 100 mL of 0, 0.2, 0.5 and 1.0 mol L^{-1} magnesium acetate solutions. From these values it is clear that using 5 g MgO per 100 mL pure water or magnesium acetate solution resulted in lower amounts of magnesium hydroxide being formed than for the 10 and 15 g MgO/100 mL slurries. Using 10 or 15 g MgO per 100 mL water or magnesium acetate solution gave approximately the same results. An optimum magnesium oxide slurry content of 10 g per 100 mL is thus proposed.

The rehydration in the magnesium acetate solutions resulted in approximately double the amount of magnesium hydroxide being formed in comparison to pure water solutions, as is clear from Fig. 1. All samples show a fast rehydration within the

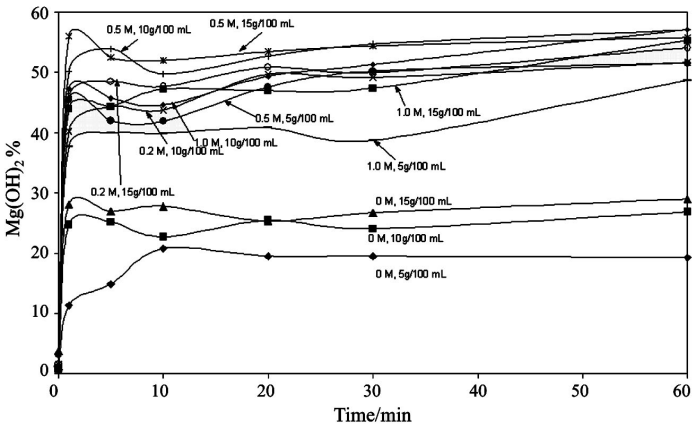

Fig. 1 The effect of solid to liquid ratio and magnesium acetate concentration on the rehydration of medium reactive MgO at 25°C

first minute of exposure to water, the rehydration then levels off and only increases slowly with time. Considering the 10 g MgO/100 mL slurries, the solution containing 0.5 M magnesium acetate solution gave the best rehydration results, although the percentages $Mg(OH)_2$ formed after 60 min is the same for the 0.5 and 1.0 M magnesium acetate solutions. Considering the cost of the chemical, it is proposed that a 0.5 M magnesium acetate solution is used to increase the rehydration of MgO. The rehydration of the medium reactive MgO at 25°C approximately doubles using a 10 g MgO per 100 mL 0.5 M magnesium acetate solution when compared to the rehydration in pure water, even after 1 min of exposure to the solution.

It is clear that the rehydration increases only slightly after 30 min, and a reaction time of between 20 and 30 min is proposed.

Rehydration at 50°C

Due to the fact that a 5 g MgO solution resulted in lower amounts of $Mg(OH)_2$ to be formed and a 1.0 M magnesium acetate solution did not result in a higher degree of rehydration than 0.5 M, these conditions were not investigated at 50 and 70°C. Figure 2 clearly indicates that the rate and degree of rehydration of this sample of medium reactive MgO more than doubles using 0.2 or 0.5 M solutions of magnesium acetate when compared to rehydration in pure water (0 M) solutions. Results for the 0.2 and 0.5 M magnesium acetate solutions are similar within experimental error, resulting in approximately 50% $Mg(OH)_2$ that formed after 1 min of reaction, with a slow increase to approximately 63% after 60 min of reaction. At a temperature of approximately 50°C, it seems that the 0.2 M magnesium acetate solution gave high enough concentrations of the ions to obtain an optimum value.

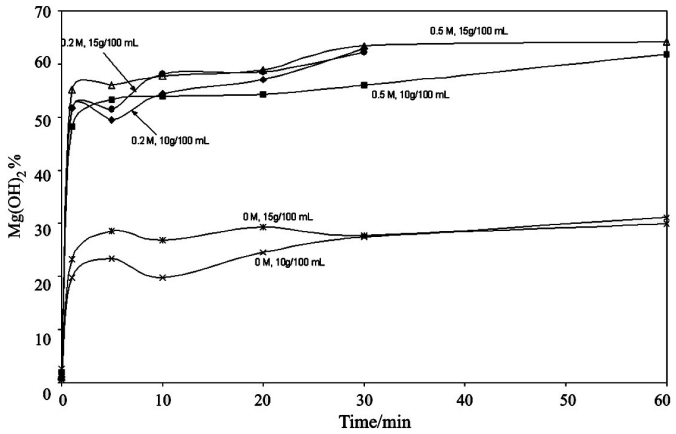

Fig. 2 The effect of solid to liquid ratio and magnesium acetate concentration on the rehydration of medium reactive MgO at 50°C

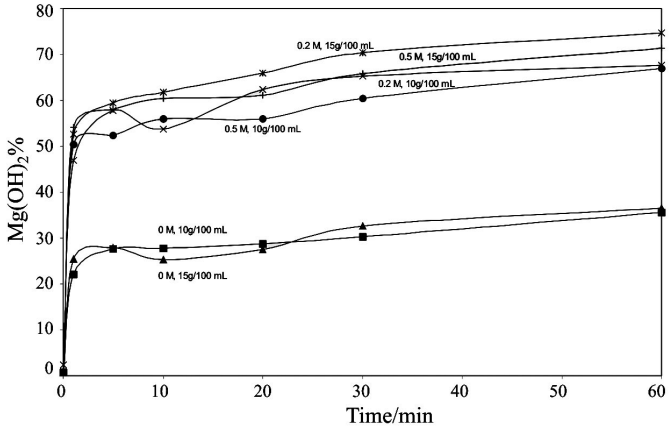

Fig. 3 The effect of solid to liquid ratio and magnesium acetate concentration on the rehydration of medium reactive MgO at 70°C

Rehydration at 70°C

Figure 3 gives the percentages $Mg(OH)_2$ that formed using 10 and 15 g MgO per 100 mL magnesium acetate solutions. As in previous instances, the addition of magnesium acetate approximately doubles the degree of rehydration at this temperature, resulting in a product containing more than 70% $Mg(OH)_2$ for the 15 g 100 mL^{-1} slurry after 60 min. In this case the 15 g 100 mL^{-1} MgO slurry gave approximately 5% higher rehydration values as the 10 g 100 mL^{-1} slurry. This must be due to the better solubility of all the compounds at this higher temperature, indicating that the process occurs via a solution-dissolution process. At this temperature, using a 15 g 100 mL^{-1} MgO slurry in 0.2 M magnesium acetate gave the best rehydration results.

Table 4 BET surface areas of rehydrated MgO samples in $m^2\ g^{-1}$. (Surface area of medium reactive MgO is 16 $m^2\ g^{-1}$)

Magnesium acetate concentration/mol L^{-1}	MgO g per 100 mL $Mg(CH_3COO)_2{\cdot}4H_2O$	Temperature /°C		
		25	50	70
0 M	5	13	14	12
	10	11	10	10
	15	11	10	9
0.2 M	5	n.d.	n.d.	n.d.
	10	21	28	32
	15	20	26	28
0.5 M	5	14	n.d.	n.d.
	10	18	24	28
	15	16	25	29

n.d.: not determined

Surface areas of the formed $Mg(OH)_2$

Table 4 summarizes some of the surface areas of the rehydrated MgO samples after 30 min of reaction time. The untreated medium reactive MgO sample gave a surface area of 16 $m^2\ g^{-1}$. At 25°C, addition of MgO to the magnesium acetate solutions resulted in a product with a higher surface area being formed when compared to products rehydrated in pure water. Increasing the temperature increases the surface area and values between 24 and 32 $m^2\ g^{-1}$ were measured for the products formed at 50 and 70°C.

Conclusions

The major part of rehydration of the medium reactive MgO sample occurs within the first few minutes of the reaction for the temperatures studied between 25 and 70°C. Rehydration levels off after 20 min, using the optimum amounts of 10 and 15 g MgO/100 mL magnesium acetate solutions and only increases with a few more percentages $Mg(OH)_2$ being formed up to 60 min.

The degree of rehydration measured as percentage $Mg(OH)_2$ being formed, increases from approximately 56% using 15 g MgO in 0.5 M magnesium acetate solutions after 60 min reaction time at 25°C to 64% at 50°C, to more than 70% at 70°C. The increase in temperature increases the solubilities of magnesium oxide and magnesium acetate, resulting in a higher concentration magnesium ions in solution, which precipitates out as magnesium hydroxide, being less soluble than magnesium acetate. Solubility of magnesium acetate at 25°C is reported as 39.6 g 100 g^{-1} water, and that of magnesium hydroxide is in the order of 1 x 10^{-4} g 100 g^{-1} water. MgO is reported as being less soluble than magnesium hydroxide.

Industrial considerations and costs will dictate the choice of experimental conditions for the rehydration of medium reactive MgO, as heating costs, desired product surface area and costs of the added chemicals are all factors to take into consideration.

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