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HYDRATION OF MEDIUM REACTIVE MAGNESIUM OXIDE USING HYDRATION AGENTS

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Water, magnesium acetate, magnesium chloride, acetic acid and hydrochloric acid were used as hydrating agents for an industrially obtained MgO sample. The influence of these different hydrating agents on the pH of the hydrating solution, degree of hydration to $Mg(OH)_2$, and product surface area was studied as a function of the temperature of hydration. When compared to the hydration in water, all hydrating agents improved the degree of hydration between 5 and 50% at all temperatures. $MgCl_2$ and a mixture of HCl and $Mg(CH_3COO)_2$ seemed to be the most effective hydrating agents below 60°C, while at temperatures above 60°C $Mg(CH_3COO)_2$ formed the largest percentage $Mg(OH)_2$. $Mg(CH_3COO)_2$ was the hydrating agent that showed the strongest temperature dependence. The mechanism of the hydration reaction seems to be dependent of the availability of Mg^{2+} ions and the increased formation of $Mg(OH)_2$ as temperature increases.

Keywords: *acetic acid, hydration, hydrochloric acid, magnesium acetate, magnesium chloride, magnesium oxide, pH, temperature*

Introduction

Recently, there has been growing interest in the utilisation of magnesium hydroxide as flame retardant and smoke-suppressing additive to produce polymers [1, 2]. Magnesium hydroxide is usually obtained through the hydration of MgO:

$$MgO(s)+H_2O(l)\rightarrow Mg(OH)_2(s)$$

Literature indicated that the reaction mechanism of the hydration reaction comprises steps of MgO dissolution followed by $Mg(OH)_2$ precipitation [3]. Rocha *et al.* suggested that the reaction is controlled by the oxide dissolution, and that the mechanism consist of the following steps [3]:

- Water adsorbs at the surface of MgO and diffuses inside porous particles,
- MgO dissolution occurs within the particles, changing the porosity with time and
- supersaturation, nucleation and growth of $Mg(OH)_2$ on the surface of MgO takes place.

They also suggested two distinct processes during hydration, depending on the temperature. At high temperatures, the hydration seems to be initially governed by the dissolution of MgO (chemical control), but as the reaction progresses, both the surface and pores of the MgO particles are progressively covered by the $Mg(OH)_2$ produced. As a result, the diffusion of water is hindered inside the particles thus reducing the overall reaction rate (diffusion controlled). At low temperatures, the hydration is purely chemical controlled because conversion is relatively low.

Filippou *et al.* [4] studied the kinetics of MgO hydration in diluted magnesium acetate solutions at temperatures ranging between 60 to 90°C, and found that high-quality $Mg(OH)_2$ can be produced. They also suggested that the hydration process is a dissolution–precipitation process controlled by the dissolution of MgO. Their proposed mechanism for hydration in the presence of acetate ions is as follows:

- Magnesium acetate dissociation:

$$Mg(CH_3COO)_2(aq)\leftrightarrow CH_3COO^-(aq)+Mg^{2+}(aq)$$

- MgO dissolution by complexation:

$$MgO(s)+CH_3COO^-(aq)+H_2O(l)\rightarrow Mg(CH_3COO)^+(aq)+2OH^-(aq)$$

or even by direct attack by acetic acid which is formed in the bulk of the solution:

$$CH_3COO^-(aq)+H_2O(l)\rightarrow CH_3COOH(aq)+OH^-(aq)$$
$$MgO(s)+CH_3COOH(aq)\rightarrow Mg(CH_3COO)^+(aq)+OH^-(aq)$$

- Dissociation of magnesium complexes and magnesium hydroxide precipitation in the bulk of the solution due to supersaturation:

$$Mg(CH_3COO)^+(aq)\rightarrow CH_3COO^-(aq)+Mg^{2+}(aq)$$
$$Mg^{2+}(aq)+2OH^-(aq)\rightarrow Mg(OH)_2(s)$$

The mechanisms described by Rocha *et al*. [3] and Filippou *et al*. [4] both incorporate the precipita-

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tion of $Mg(OH)_2$ due to supersaturation as a final step. It seems therefore important to take into account the stability of $Mg(OH)_2$ over a range of temperatures. Because the species $MgOH^+$ only becomes significant at pH values higher than 11, it is negligible under the experimental conditions used in this study [5]. According to McGee and Hostetler [6], the activity product constant for the dissolution of $Mg(OH)_2$

$$Mg(OH)_2\ (s) \leftrightarrow Mg^{2+}(aq) + 2OH^-(aq)$$

is described by $K_B=[Mg^{2+}][OH^-]^2$ where the brackets indicate activities. Since the concentrations of these species are very low, the activity can be assumed equal to the concentration. They have determined the temperature dependence of the activity constant to be $-\log K_B=10.91-0.00304T+0.0000563T^2$. The temperature is measured in ºC.

Similarly, Brown *et al.* [5] found the temperature dependence of the formation constant, β, for the hydrolysis of $Mg(OH)_2$

$$Mg^{2+}(aq)+2H_2O(l) \leftrightarrow Mg(OH)_2(s)+2H^+(aq)$$

to be $\log \beta=2.49-5847/T$ at zero ionic strength, with the temperature measured in K. This formation constant,

$$\beta=\frac{[H^+]^2}{[Mg^{2+}]}$$

is the inverse of the activity product described by McGee and Hostetler, and is related to the activity product by

$$\beta=\frac{K_w^2}{K_B}$$

where K_w is the dissociation constant of water.

Van der Merwe *et al.* [7] studied the influence of the concentration of magnesium acetate, solution temperature, solid to liquid ratio of MgO to magnesium acetate and hydration time on the hydration of a medium reactive MgO. Nakanishi *et al.* [8] have studied the hydration of magnesia clinker in magnesium acetate and magnesium chloride solutions. Strydom *et al.* [9] and Maryška [10] have studied the effect of calcining temperature and calcining time on the hydration of industrially obtained MgO. Both found that the degree of hydration is influenced significantly by calcining temperature and time.

In this study, the effect of selected hydrating agents on the hydration of MgO will be studied at hydrating temperatures ranging between 30 and 80ºC. The aim will be to evaluate the influence of hydration temperature and hydrating agent on the pH of the hydrating solution, the degree of hydration of MgO and the surface areas of the products.

Experimental

Sample preparation

Pure chemicals were obtained from Merck. Industrial MgO was obtained from Chamotte Holdings, South Africa.

The bulk industrially obtained magnesium oxide sample was hand milled and then screened to –75 μm. The following procedure was then followed to study the influence of pH on hydration of the MgO.

To remove the moisture, 20 g of MgO was calcined at 500°C for 1 h. Then 10 g of the calcined sample was stirred at a constant rate of 200 rpm in a 100 mL solution of the hydrating agent, while the temperature was controlled by performing the reaction in a water bath at temperatures ranging between 30 and 80°C. The hydrating agents used were H_2O, 0.1 M $Mg(CH_3COO)_2$, 0.1 M CH_3COOH, 0.1 M HCl, 0.1 M $MgCl_2$ and a mixture of $Mg(CH_3COO)_2$ and HCl of which the final concentration of both was 0.1 M. The pH and temperature of the slurry was measured every minute. After 30 min, the sample was filtered and dried for 1 h at 200°C. The percentage $Mg(OH)_2$ in the samples was determined by TG analysis [11].

Methods

Instrumentation

Thermogravimetric analyses were performed on a Netzsch STA 409 simultaneous TG/DSC instrument. A heating rate of 10°C min^{-1} was used in an air atmosphere. Platinum pans were used, and the sample masses were approximately 20 mg.

A NOVA 1000^e Surface Area and Pore Size Analyser, using nitrogen gas as an adsorbate, was used to determine the surface areas of the products.

An ARL9400XP+spectrometer was used to perform the XRF analysis. The sample was ground to –75 μm in a tungsten carbide milling vessel, and was then roasted to 1000°C to determine its loss on ignition value. 1 g of sample was then added to 6 g of $Li_6B_4O_7$ and was fused into a glass bead, after which the major element analysis was performed.

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. Samples were prepared using standard Siemens sample holders and the powdered samples were pressed into the holder using a glass slide.

Citric acid reactivity test

The reactivity of the MgO samples was determined by making use of the citric acid method of determination of powder reactivity. In this method, an 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 at 30ºC, with phenolphthalein as indicator, until the colour changed from white to pink. The time needed to completely neutralize the acid is then reported as the citric acid reactivity.

Results and discussion

XRD and XRF

The chemical composition of the raw material, as determined by XRF analysis, is given in Table 1. XRD analyses have confirmed these results, and have indicated that the raw material consisted mainly of MgO, with small amounts of $MgCO_3$, SiO_2 and $CaCO_3$. After calcination at 500°C, most of the $MgCO_3$ has decomposed to MgO. A small amount (0.44%) of Al_2O_3 was observed in the XRF analysis, but was not detected by XRD.

Table 1 Chemical composition of the raw material, as received from Chamotte Holdings, South Africa

	Mass%
SiO_2	2.46
TiO_2	0.01
Al_2O_3	0.44
Fe_2O_3	0.09
MnO	0.01
MgO	91.88
CaO	1.02
Na_2O	0.01
K_2O	0.01
P_2O_5	0.01
Cr_2O_3	0.01
NiO	0.17
V_2O_5	0.01
ZrO_2	0.01
loss on ignition	3.82
total	99.97

XRD spectra of the products after hydration at 80°C were obtained, and indicated that the phases present after hydration were mainly MgO and $Mg(OH)_2$, although a small amount of $MgCO_3$ could also be observed.

Citric acid reactivity test

The reactivity of MgO is measured using the citric acid test, where the time needed for the magnesium oxide sample to neutralize the citric acid solution is measured. Industry uses values of less than 60 s for highly reactive (soft burnt) magnesium oxide. Medium reactive magnesium oxide gives a measurement between 180 and 300 s, while a low reactivity magnesium oxide (hard burnt) gives a value of more than 600 s and dead-burnt magnesium oxide approximately 900+ s.

The citric acid reactivity test was performed on each MgO sample before hydration. The values ranged between 240 and 290 s, indicating a medium reactivity MgO.

Variation of pH with hydration temperature and hydrating agent

The variations of the pH of the hydrating solutions for the hydration of MgO in water and magnesium acetate are given in Figs 1 and 2. The curves obtained using the other hydrating agents were similar to that obtained for magnesium acetate. For all hydrating agents, a decrease in pH was observed when the hydrating temperature was increased. For hydration in water, an increase in pH with time was observed.

Using hydrating agents, the solution pH remains almost constant after 5 min of hydration. In Fig. 3, a summary of the solution pH is presented as a function

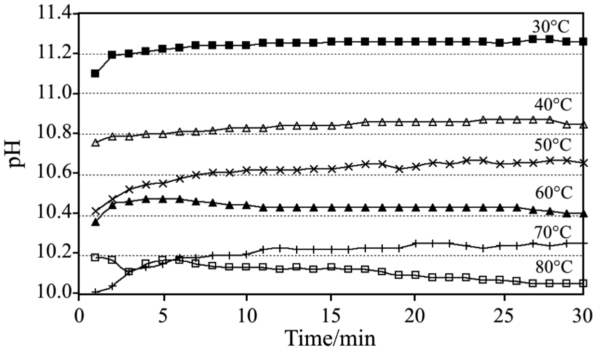

Fig. 1 Variation of pH with time at different temperatures for the hydration of medium reactive MgO in water

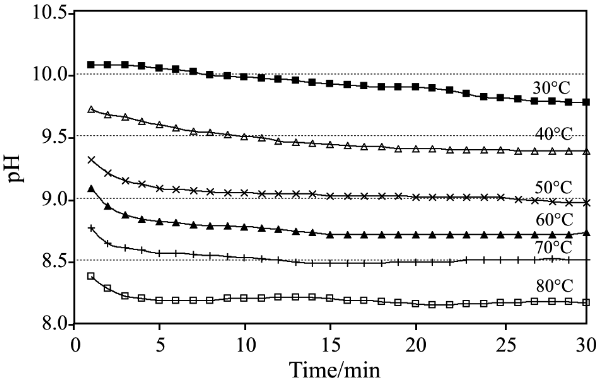

Fig. 2 Variation of pH with time at different temperatures for the hydration of medium reactive MgO in a magnesium acetate solution

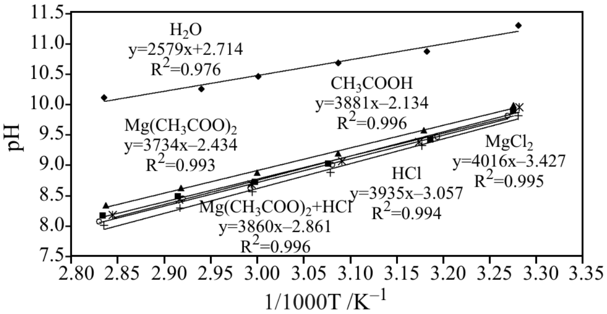

Fig. 3 The variation of pH with the inverse of the hydration temperature for the different hydrating agents; ◆ – H_2O, ■ – $Mg(CH_3COO)_2$, ▲ – CH_3COOH, ∗ – HCl, + – $MgCl_2$, ○ – $HCl+Mg(CH_3COO)_2$

of the inverse of the average solution temperature, both calculated as the average between 5 and 30 min of hydration. The variation of pH with the inverse of temperature followed a linear relationship for all hydrating agents. The average pH for the hydration performed in water was about 1.5 pH units higher than the hydrations performed in the other solutions.

Variation of degree of hydration with hydration temperature and hydrating agent

In Fig. 4, the percentage $Mg(OH)_2$ formed during hydration is given as a function of the average hydration temperature. A reasonably good linear fit was obtained for all hydrating agents ($R^2 \approx 0.98$). When compared to the hydration in water, all hydrating agents improved the degree of hydration between 5 and 50% at all temperatures.

The hydrations done in CH_3COOH and HCl followed a similar trend, and more $Mg(OH)_2$ is formed than those performed in $Mg(CH_3COO)_2$ below 40°C. The hydrations performed in $MgCl_2$ and the mixture of HCl and $Mg(CH_3COO)_2$ also followed a similar trend, and seemed to be the most effective hydrating agents below 60°C. At temperatures above 60°C $Mg(CH_3COO)_2$ formed the largest percentage $Mg(OH)_2$.

Comparing the slopes of the linear fits, it seems that temperature enhances the hydration performed in $Mg(CH_3COO)_2$ more than for any of the other hydrating agents, and that the hydration performed in water was the least temperature dependent. This could indicate that the solubility of the various compounds plays an important role in the mechanism of the process.

Surface area

Figure 5 summarises the surface areas of the rehydrated MgO samples after 30 min of reaction time. The surface area of the raw MgO sample after milling and screening was 11.0 m^2 g^{-1}, and after calcination at 500°C it ranged between 23 and 26 m^2 g^{-1}. The products obtained from hydration in water, HCl and $MgCl_2$ had similar surface areas (in the region of 13 to 20 m^2 g^{-1}) over the temperature range studied, with those formed in HCl slightly higher than those in water and $MgCl_2$. Upon hydration in CH_3COOH, a product with slightly higher surface area was obtained for temperatures up to 40°C (~24 m^2 g^{-1}). Surface areas between 28 and 30 m^2 g^{-1} for hydration performed from 50°C and higher were observed using solutions containing the acetate ions.

Again, $Mg(CH_3COO)_2$ was the hydrating agent used that showed the strongest temperature dependence, with a constant increase in product surface area with increasing temperature, ranging from 24 m^2 g^{-1} at 30°C to 42 m^2 g^{-1} at 80°C. The products obtained from hydrations performed in the mixture of $Mg(CH_3COO)_2$ and HCl also showed an increase in surface area with an increase in hydrating temperature, with product surface areas of approximately 5 m^2 g^{-1} lower than those formed in $Mg(CH_3COO)_2$.

According to Fillipou *et al.* [3], rapid hydration of MgO will result in the formation of relatively large hydroxide aggregates with high surface areas. This can explain the higher surface areas of products formed from the hydration in magnesium acetate. It seemed

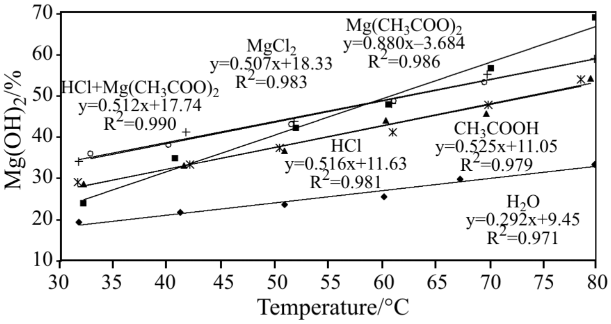

Fig. 4 The degree of hydration as a function of temperature for the different hydrating agents; ◆ – H_2O, ■ – $Mg(CH_3COO)_2$, ▲ – CH_3COOH, ∗ – HCl, + – $MgCl_2$, ○ – $HCl+Mg(CH_3COO)_2$

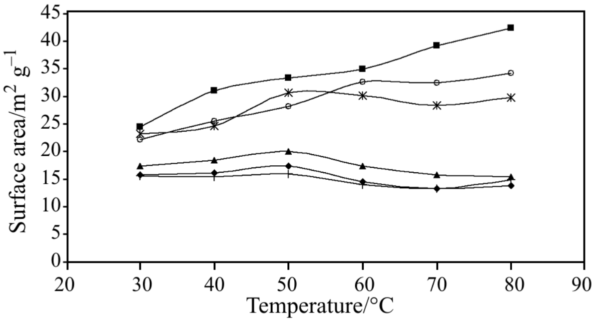

Fig. 5 The variation of product surface area with hydration temperature; ; -◆- – H_2O, -■- – $Mg(CH_3COO)_2$, -▲- – HCl, -∗- – CH_3COOH, -+- – $MgCl_2$, -○- – $Mg(CH_3COO)_2+HCl$

that these products were formed at a rate that decreased the possibility of crystal formation or agglomeration.

The degree of hydration in both magnesium acetate and magnesium chloride was improved significantly when compared to that in water, but when the surface areas of the products are compared a significant difference is observed. The products formed from hydration in magnesium chloride have surface areas close to those obtained for hydration in water, while the products formed from hydration in magnesium acetate have surface areas between 10 and 25 $m^2\ g^{-1}$ higher. Nakanishi *et al.* [8] observed that the morphologies of the products formed from hydration in magnesium acetate and magnesium chloride were different. They reported that in the acetate system the $Mg(OH)_2$ produced was in the form of hexagonal plates of uniform diameter, while elongated hexagonal prisms were obtained in the chloride system.

Conclusions

From the results and literature, it seems that the mechanism of MgO hydration in different hydrating solutions is complex, and depends on the hydrating solution and its pH [12]. The hydration of MgO is a dissolution–precipitation process, controlled by the dissolution of MgO. Although this is the rate-determining step, the degree of hydration will also be determined by the stability of $Mg(OH)_2$ at the temperature of interest.

In aqueous solutions, the activity product constant for the dissolution of $Mg(OH)_2$ decreases with an increase in temperature [6], which indicates that the formation of more $Mg(OH)_2$ with an increase in temperature. The dissolution of MgO also increases with temperature. A decrease in solution pH was observed with an increase in solution temperature, which can also be explained by the decrease in the activity product constant for $Mg(OH)_2$ with increasing temperature.

Using HCl and CH_3COOH as hydrating agents, the degree of hydration was improved by between 10 and 20% when compared to water. It seems that the addition of H^+ plays a role, possibly by increasing the solubility of MgO through the following reaction:

$$MgO(s)+2H^+(aq)\rightarrow Mg^{2+}(aq)+H_2O(l)$$

Jost *et al.* [13] explained the higher degree of hydration of MgO in $MgCl_2$ by an increase in the solubility of MgO in $MgCl_2$ solutions. They reported the solubility of MgO in a 0.1 M $MgCl_2$ solution to be $3.5\cdot10^{-3}$ mol L^{-1}, compared to $1.5\cdot10^{-4}$ mol L^{-1} in an aqueous solution.

The mechanism of hydration in $Mg(CH_3COO)_2$ was described by Filippou [4], and is given in the Introduction of this paper. This mechanism can also describe the increase in degree of hydration when acetic acid was used as hydrating agent. If so, the difference in performance between acetic acid and magnesium acetate as hydrating agents can be ascribed to the additional Mg^{2+} ions that will further increase the degree of hydration in magnesium acetate. The improvement in the degree of hydration when a mixture of $Mg(CH_3COO)_2$ and HCl was used, when compared to that in HCl alone, can be explained similarly.

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