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THE EFFECT OF CALCINING CONDITIONS ON THE REHYDRATION OF DEAD BURNT MAGNESIUM OXIDE USING MAGNESIUM ACETATE AS A HYDRATING AGENT

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Magnesium oxide was produced through calcination of magnesite ore. A rehydration percentage of MgO to $Mg(OH)_2$ of higher than 60% is obtained using calcination temperatures of 1000°C and below. At these temperatures medium reactive MgO was formed. The extend to which dead burnt MgO (obtained after calcination at 1200°C and higher) may be rehydrated is dependent on the calcination time, but even after 1 h and using magnesium acetate as a hydrating agent only 40% of the initial product has rehydrated to $Mg(OH)_2$. After 4 and more hours of calcinations at 1200°C, a maximum of approximately 14% of the initial MgO is rehydrated back to $Mg(OH)_2$. Thermogravimetric analysis was performed on the various compounds to determine the amounts of $Mg(OH)_2$ that formed.

Keywords: *calcination, magnesium oxide, reactivity, rehydration, rehydration agent*

Introduction

Magnesite ore from a mine in the northern parts of South Africa is calcined and then use in the production of various magnesium containing compounds, such as magnesium hydroxide, magnesium talcite and magnesium hydroxycarbonates. Polyvinyl chloride (PVC) is one of the five major thermoplastic materials used in the world. Heat stabilizers and flame retardants are essential for the processing and use of PVC and other polymeric materials. The metals in the common compounds used include lead, barium, aluminium and to some extent cadmium [1, 2]. These metals are toxic and pose a health hazard.

Magnesium hydroxide is the only magnesium compound currently used as smoke and flame retardant in organic polymeric materials [2]. The production of magnesium talcite and magnesium hydroxycarbonates from the calcined magnesium ores provides possible alternatives for the toxic compounds. The calcined magnesium ore, however needs to be reactive enough to obtain usable production percentages of the required compounds. The influence of calcining on the reactivity of the produces magnesium oxide is thus of utmost importance.

Magnesite ores are calcined at temperatures varying between 600 and 1400°C, resulting in MgO with different reactivities [3, 4]. Reactivity of MgO refers to the extend and rate of hydration to $Mg(OH)_2$ on exposure of it to water and moisture. Hard and medium burnt MgO reacts slowly and incompletely with available water to form $Mg(OH)_2$, while soft burnt MgO reacts fast and completely.

Magnesium acetate can be used to increase the rate of hydration of MgO. The extents 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 before [3]. 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 to define 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 effect of magnesite calcining conditions on magnesia hydration have been studied by Birchall *et al.* [4], who have shown that temperature was the main variable affecting surface area and reactivity. They also found that the acid activity test should be used with caution as its suitability to predict the hydration behaviour of MgO depends on the sample's characteristics and the conditions under which hydration will take place.

In this study, the effect of calcining temperature and calcining time on the hydration of industrially obtained MgO was studied.

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Experimental

Samples

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

Instrumentation

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

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

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, 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. This method is used as a standard in the lime industry. The time needed by the magnesium hydroxide to completely neutralize the acid is then reported as the citric acid reactivity. The amount of magnesium hydroxide in the sample determines the extent of the exothermic neutralization reaction and thus the temperature increase.

Sample preparation

To study the effect of calcining temperature on the hydration of industrially obtained magnesium hydroxide, samples were calcined for 4 h at 650, 800, 1000, 1200 and 1400°C, respectively. The samples were then milled and screened to <38 μm. Before hydration, the MgO sample was calcined again for an hour at its initial calcining temperature. To hydrate the MgO, 10 g of the calcined samples were stirred at a constant rate of 200 rpm in a solution of 0.1 M magnesium acetate of which the volume were kept constant at 100 mL. The temperature was held constant at 80°C by performing the reaction in a water bath for 30 min. The samples were then filtered and dried for 2 h at 200°C.

To study the effect of calcining time on the hydration of MgO, samples were calcined for 1, 2, 4 and 6 h at 1200°C, and were then hand milled and screened to <75 μm. The hydration of the MgO samples was performed in the same way as described above.

The percentage $Mg(OH)_2$ in the samples was determined by TG analysis. Curves of mass loss (%) and derivative mass (% $°C^{-1}$) *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 between 200 and 370°C was taken as due to the decomposition of $Mg(OH)_2$, while all other steps (between 350 and 540°C) were due to the decomposition of $Mg(CH_3COO)_2$ [3–5]. The percentage mass losses due the decomposition of $Mg(OH)_2$ and $Mg(CH_3COO)_2$ were then determined by using the minimum of the derivative mass *vs*. temperature curve as previously described [6].

Results and discussion

Effect of calcining temperature

The effect of calcining temperature on the surface area and reactivity of industrially obtained MgO is summarised in Table 1. As expected, an increase in time was observed (and thus decrease in reactivity) with an increase in the calcining temperature. The citric acid reactivity times increased slowly up to 1000°C, after which a considerable increase was observed at 1200°C. The surface area results for the calcined MgO samples confirmed the results obtained from citric acid reactivity studies, with a decrease in surface area (thus decrease in reactivity) with an increase in the calcining temperature.

Table 1 Effect of calcining temperature on the surface area and reactivity of industrially obtained MgO

Calcining temp./ °C	Citric acid reactivity/ s	Surface area/ $m^2\ g^{-1}$
650	185	17.40
800	202	14.62
1000	327	7.92
1200	1380	2.13
1400	>3000	0.44

The citric acid reactivity results indicated that the samples calcined between 650–1000°C were in the region for medium burnt magnesium oxide, while the samples calcined at 1200 and 1400°C could be classified as dead-burnt.

The results for the citric acid test for reactivity, surface area analyses and extend of hydration of the MgO samples calcined at different temperatures are summarised in Table 2. Although an hour was added to the calcination time, the samples calcined between 650–1000°C were still in the region for medium burnt magnesium oxide, while the samples calcined at tem-

Table 2 Effect of calcining temperature on the hydration of MgO

Calcining temperature/°C	Citric acid reactivity/s	Surface area/m^2 g^{-1}		$Mg(OH)_2$/%
		before hydration	after hydration	after hydration
650	162	17.90	35.77	76.3
800	180	14.54	34.72	73.8
1000	251	11.01	32.91	63.5
1200	1050	3.00	6.71	14.8
1400	>3000	0.66	0.71	0.79

Table 3 Effect of calcining time on the hydration of MgO

Calcining time/h	Citric acid reactivity/s	Surface area/m^2 g^{-1}		$Mg(OH)_2$/%
		before hydration	after hydration	after hydration
1	648	4.41	17.68	40.1
2	937	2.88	7.31	19.1
4	1219	2.38	5.84	13.8
6	1156	2.37	6.82	14.6

peratures more than 1200°C were dead-burnt. The influence of calcining temperature on the reactivity and hydration of MgO is shown in Fig. 1. There was a significant difference in the behaviour between the medium reactive and dead-burnt magnesium oxide samples. Between 63–76% $Mg(OH)_2$ was obtained on hydration of the medium reactive magnesium oxide samples, whereas a significant reduction to 15% was observed for the sample calcined at 1200°C. The sample calcined at 1400°C was almost inactive as its citric acid reactivity time was more than 3000 s, and only 0.8% $Mg(OH)_2$ was formed on hydration. These results were confirmed by the surface area analyses of the calcined and hydrated MgO samples.

Effect of calcining time

The results for the citric acid test for reactivity, surface area analyses and extend of hydration of the MgO samples calcined for different times are summarised in Table 3. As expected the reactivity decreases with increase in calcining time and the surface area decreases with increase in calcining time. It seems that the maximum influence of the calcining time is after 4 h of calcining, whereafter the reactivity and surface areas of the products remain approximately the same. The percentage $Mg(OH)_2$ that formed also dropped from 40% after 1 h; to 19% after 2 h; to approximately 14% for 4 and 6 h of calcining at 1200°C. The effect is at its maximum again after 4 h of calcining.

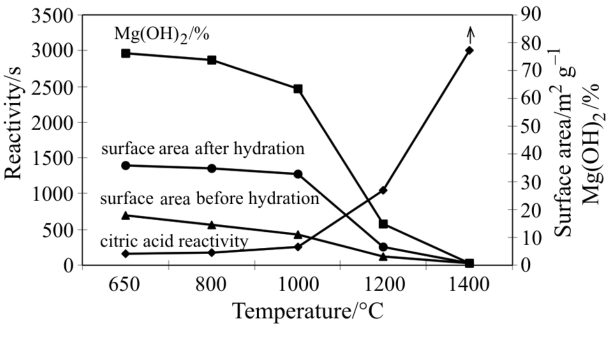

Fig. 1 The influence of calcining temperature on the reactivity and hydration of MgO

Conclusions

The surface areas after hydration are higher than the surface areas before hydration, indicating that during the hydration process, the newly formed $Mg(OH)_2$ crystals arrange in such a way as to increase the surface area of the product. The chemical process through which the magnesium acetate enhances hydration, seems to be due to the differences in solubility of the various magnesium compounds in the slurries [7]. Magnesium acetate is the most soluble of the magnesium compounds in the slurry, giving magnesium and acetate ions. Acetate ions form acetic acid in water, which attack the magnesium oxide, dissolve some of the magnesium oxide, that form magnesium ions, which then reacts with water to form $Mg(OH)_2$.

To obtain a rehydration percentage of higher than 60%, it seems essential to keep the calcination temperature below 1000°C, thus having a medium reactive MgO. The extend to which hard burnt MgO may be rehydrated is dependent on the calcination time, but even after 1 h and using magnesium acetate as a hydrating agent only 40% of the initial product has rehydrated to $Mg(OH)_2$. After 4 and more hours of calcinations at 1200°C, a maximum of approximately 14% of the initial MgO is rehydrated back to $Mg(OH)_2$.

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