Influence of magnesium hydroxide content and fineness on the carbonation of calcium hydroxide

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HIGHLIGHTS

- Magnesium and calcium are widespread in nature.
- Mineral carbonation is becoming a effective method in reusing waste mineral.
- Calcium to magnesium mole ratio is a key parameter in this study.
- Thermogravimetric analysis has been used in this study.
- Thermogravimetric analysis is an useful method on the calculation of carbonation efficiency.

ARTICLE INFO

ABSTRACT

Accelerated carbonation material is a kind of air hardening cementitious materials. The influence of magnesium content on the properties of carbonate binder, such as compressive strength, CO_2 mass gain degree and products morphology, were investigated. Solid state carbonation method that low water to solid ratio (W/S) of 0.10 was performed in this study. The samples were prepared at a range of compaction pressures (0 MPa–8.0 MPa). And then the samples were exposed at a constant CO_2 gas pressure (0.2 MPa) for different carbonation time. The result showed that different calcium to magnesium mole (C/M) ratios has a significant impact on compressive strength and CO_2 mass gain degree of samples. The CO_2 mass gain degree increased at first, reached the maximum, and then decreased with the increasing C/M ratio. The C/M ratio of that CO_2 mass gain degree reached the maximum was 5. The compressive strength not only changed by magnesium content but also influenced by the fineness of magnesium hydroxide, more finer practical size more higher compressive strength. SEM photographs showed that the morphology of carbonated products changed by different compaction pressures and content of magnesium hydroxide.

1. Introduction

Calcium hydroxide is a kind of air hardening inorganic binding material and carbonate binder has a long history that as a kind of cementitious materials in ancient China [1]. With the developing of portland cement technology, the carbonate binder has been neglected by us. However, recently, carbon sequestration [2–4] and bio-mineralization [5,6] were attracting more attention. Therefore, carbonate binder has a great potential to use for building and construction materials in the future.

Environmental pollution has become a serious and global problem with the development of industry. Cement plants are emission about 5% CO_2 occupied the whole human production [7,8], and about the CO_2 emission in iron and steel industry were widely observed [9–11]. Moreover, steel slag has become one major type

industrial waste and utilization was low because of low hydration and poor soundness [12,13], although it could regard as a kind of cementitious [14]. Apparently, magnesium was a main chemical component of steel slag that C/M ratios were ranged from 0.8 to 428.5 [15,16], but they are mainly concentrated in the range of 2–10. Moreover, the role of Mg^{2+} as an impurity composition in calcium carbonate have been wildly investigated [17–19]. Although many literatures has mentioned before were illustrated that Mg^{2+} inhibited calcium carbonate crystal growth in the solution, the behavior of it might be different in the solid carbonation comparison to in the solution. There was scarcely researched with respect to Mg^{2+} in solid carbonation.

2. Experimental

2.1. Materials

In order to avoid other impurity ions influence, the analytical reagents calcium hydroxide and magnesium hydroxide, high concentration CO_2, which mass fraction reached 99.9%, and distill water were used.

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Table 1
Mix formulations of the different C/M ratios.

Sample	C_1M	C_3M	C_5M	C_7M	C_9M	$C_{12}M$	$C_{13}M$	CH	MH
Ca/Mg mole ratio (M_r)	1	3	5	7	9	11	13	Pure $Ca(OH)_2$	Pure $Mg(OH)_2$

Table 2
Different carbonation time and compaction pressures on the optimum mix proportions.

Sample No.	Parameters				Variable parameter
	Carbonation time (h)	C/M ratios (M_r)	Type of $Mg(OH)_2$	Compaction pressure (MPa)	
CH^3	3	0	–	2, 8	Compaction pressure
CH^{12}	12	0	–	2, 8	
C_5M^{c3}	3	Optimum	Coarse	2, 8	
C_5M^{c12}	12	Optimum	Coarse	2, 8	
C_5M^{f3}	3	Optimum	Fine	2, 8	
C_5M^{f12}	12	Optimum	Fine	2, 8	

2.2. Methods

This study focus on the influence of magnesium content on properties of carbonate binder, such as compressive strength, CO_2 mass gain degree and products morphology with a solid carbonation method. The C/M ratios were ranged from 0 to 13. Table 1 is the mix formulations of carbonated compacts. The C/M ratios (M_r) were 0 (MH, pure $Mg(OH)_2$), 1 (C_1M), 3 (C_3M), 5 (C_5M), 7 (C_7M), 9 (C_9M), 11 ($C_{11}M$), 13 ($C_{13}M$) and pure $Ca(OH)_2$ (CH) by means of changing the ratio of calcium hydroxide and magnesium hydroxide. Table 2 is the experimental design of the optimum C/M ratio under different test conditions.

The samples were prepared at W/S ratio of 0.15. Firstly, two chemical reagents were stirred in dry condition and then adding water into mixture. Next, molding them under the set compaction pressures and keeping constant pressure for 30 s when reached the maximum pressure. Finally the compacts were put into the sealed carbonation reactor. After carbonation, the compacts were dried under the 105 °C for 24 h.

The CO_2 mass gain of carbonation is a very important parameter for the ability of carbon sequestration and it can be calculated by Eq. (1) [20]:

$$\text{Mass gain } (\%) = [(\text{Mass}_{\text{after carbonation}} + \text{Water}_{\text{lost}}) - \text{Mass}_{\text{before carbonation}}]/\text{Mass}_{\text{dry binder}}$$
$$= \Delta\text{Mass}/\text{Mass}_{\text{dry binder}} \qquad (1)$$

The CO_2 contents of the carbonated compacts were carried out on the thermal analysis instrument (TGA, Mettler Toledo TGA/DSC1) with a heating rate of 10 °C/min in the range from 50 to 1000 °C. The powder X-ray diffraction patterns were recorded using a diffractometer (XRD, Rigaku D/max-2400) with Cu radiation and the two-theta angles was between 5 to 60°, with a resolution of 0.02°. Samples microstructure was characterized by scanning electron microscopy (SEM, FEI Quanta 450) that in conjunction with energy dispersive spectroscopy (EDS, Oxford X-Max). The electronic universal testing machine (WDW-50) for compressive strength test and sealed carbonation reactor was used. The porosity of compacts was determined by mercury intrusion porosimeter (MIP, AutoPore IV 9500).

3. Results

3.1. CO_2 mass gain degree of the carbonation

At the beginning, in order to achieve optimum C/M ratio, the compacts of different C/M ratios that prepared at 1 MPa compaction pressure 0.3 MPa CO_2 gas pressure and 0.10 W/S were carbonated. Fig. 1 shows the CO_2 mass gain degree at different C/M ratios, which indicates with the magnesium content increased, the CO_2 mass gain degree increased firstly and then decreased. After the carbonation, the CO_2 mass gain degree of MH (specific surface areas is 40.62 m²/kg) was 10.00%, C_5M was 23.75% and CH was 21.33%, which indicates C_5M is the optimum and MH was difficult be carbonated [21].

Fig. 2 is the CO_2 mass gain degree of C_5M that performed with different compaction pressures, carbonation time and the different fineness of magnesium hydroxide. We can see that the CO_2 mass gain degree increased with carbonation time and the CH's are exceeded by the C_5M. Moreover, the CO_2 mass gain degree of
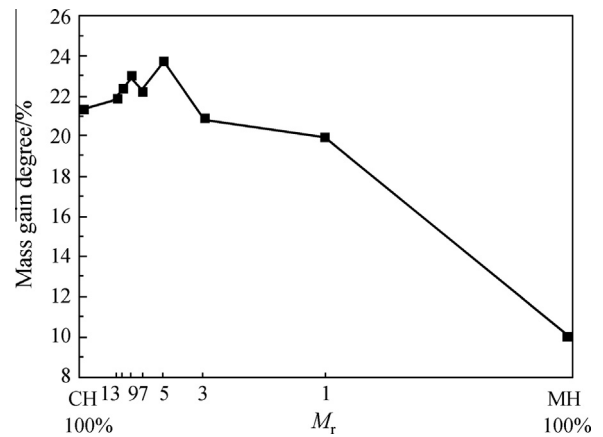
Fig. 1. Effect of M_r on CO_2 mass gain degree.

compacts that mixed with fine $Mg(OH)_2$ were higher than that of mixed with coarse $Mg(OH)_2$ and the specific surface areas of coarse and fine $Mg(OH)_2$ were 40.62 m²/kg and 1500.00 m²/kg, respectively. In order to make sure that fine $Mg(OH)_2$ can improve CO_2 mass gain degree of $Ca(OH)_2$ greater, the pure fine and coarse $Mg(OH)_2$ were carbonated, and their CO_2 mass gain were 8.20% and 11.05% (carbonated conditions: 3 h; 0.2 MPa gas pressure; 8 MPa compaction pressure), respectively.

3.2. Compressive strength

The compressive strength of carbonated C_5M with different compaction pressures and carbonation time were list in Fig. 3. It shows that the increase of compressive strength was very little when carbonation time was over 3 h. From Fig. 3 we can also find that 2 MPa compaction pressure have a higher increase in compressive strength, indicates that the compaction pressure has a significant influence on the compressive strength. The compressive strength of compacts that under 2 MPa and 8 MPa compaction pressure (CH^3, C_5M^{c3} and C_5M^{f3}) were 5.03 MPa, 5.80 MPa, 5.25 MPa, 22.75 MPa, 26.63 MPa and 35.50 MPa, respectively. And the compressive strength of CH^{12}, C_5M^{c12} and C_5M^{f12} were 5.38 MPa, 6.75 MPa, 8.75 MPa, 23.58 MPa, 28.25 MPa and 36.00 MPa, respectively. Therefore, although the increase of compressive strength was very little when carbonation time over 3 h, $Mg(OH)_2$ was still enhanced the compressive strength of compacts whether or not how much compaction pressure was applied.