Microstructure changes of waste hydrated cement paste induced by accelerated carbonation

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HIGHLIGHTS

- Products with excellent property were produced by carbonation of waste cement.
- The competitive carbonation of different minerals was analyzed using QXRD and TG.
- Compressive strength-to-CO_2 uptake value of different carbonation stage is defined.

ARTICLE INFO

ABSTRACT

From the perspective of effective utilization of resources and environmental preservation, accelerated carbonation of waste cement paste is a promising and environmentally beneficial application. Greenhouse gas CO_2 can be captured, waste hydrated cement can be reused, and building materials with excellent performance can be produced. In this study, samples were exposed to high CO_2 concentration (99.9 wt%, 0.2 MPa) for accelerated carbonation. The compacts with water/solid ratio of 0.15 absorbed 19.8 wt% CO_2 after carbonated for 2 h, and the compressive strength was 28.6 MPa. The total pore volume decreased from 0.41 cm^3/g to 0.26 cm^3/g due to the precipitation of calcium carbonate and silica gel. Rietveld refinement quantitative phase analysis and TG analysis showed calcium carbonate are mainly from $Ca(OH)_2$ and C–S–H, accounting for about 70–80% of the total calcium carbonate. $Ca(OH)_2$ has superiority in the early carbonation period, and the carbonated compacts has a relative higher "compressive strength-to-CO_2 uptake" value, corresponding. When the carbonation degree of C–S–H and other carbonation phase exceed $Ca(OH)_2$ in the later stage, the compressive strength has a slower gain tendency.

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1. Introduction

Waste hydrated cement paste (abbr. WHCP) is generated as a by-product of aggregate recycling processes where waste concrete is pulverized and classified to separate the aggregate from WHCP. The quantity of WHCP generated in aggregate recycling processes can be as high as 1/3 the mass of the waste concrete [1]. With the demolition and construction of large-scale urban civil and public buildings, municipal facilities, the quantity of construction wastes has been increasing rapidly in recent years, accounting for about 30–40% of the whole city solid wastes [2]. Indeed, approximately 200 million tons of waste concrete are currently produced annually in China, the quantity of waste concrete will be 638 million metric tones in 2020 and the amount will increase by over 8% every year [3,4]. However, China is building massive

amounts of infrastructure, huge consumption of cement and concrete materials will be needed. So it is necessary that an effective and promising treatment process of the waste concrete to be proposed.
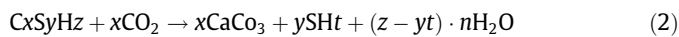
The most common use of waste concrete is to recycle coarse aggregates for recycling aggregate concrete, many studies have been focused on the mechanical property, durability and structural performance of recycling aggregate concrete [5]. But at the same time, WHCP is a large-multi by-product of aggregate recycling processes. At the present, most of the waste cement paste has been either used as roadbed materials or directly sent to landfill. Many investigations have indicated that WHCP after high temperature can regain hydration activity [6,7], according to which Korean researchers have produced recycling cement with waste concrete successfully. However, generally speaking, the utilization of WHCP is still limited due to its unsatisfactory performance.

At the same time, cement industry is one of the largest CO_2 emitters, generating 5% of global CO_2 emissions [8,9]. Since the

mineral carbonation was first proposed to alleviate the greenhouse effect [10], there has been increasing interest in CO_2 sequestration through mineral carbonation. Many researchers have found alkaline solid wastes, rich in calcium (magnesium) oxides and hydroxides, are desirable candidate materials for carbon capture and storage, such as steel slag, WHCP, waste ash [9,11–13]. Previous studies have also proved that calcium silicate hydrates (C–S–H) and calcium hydroxide, the major constituents of hydrated cement paste, are prone to be carbonated and calcite and highly polymerized silica gel formed along carbonation reaction proceeded Eqs. (1) and (2) [14].

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \tag{1}$$

$$CxSyHz + xCO_2 \rightarrow xCaCo_3 + ySHt + (z - yt) \cdot nH_2O \tag{2}$$

So it makes carbonation of WHCP a promising and environmentally beneficial application, where calcium carbonate from WHCP can either be used as raw material for cement production or preparing for new building materials [1,15,16]. Carbonation of WHCP can be viewed as either a CO_2 sequestration process or a waste recycling process. But most studies have been focused on the feasibility, CO_2 uptake and chemical change of WHCP carbonation [13], there has been a long lack of studies on the mechanism of carbonation process and microstructure changes, which is crucial for the application of building material. The solid phase dissolution and precipitation and the changes in the microstructure are not yet well understood [17]. In fact, $Ca(OH)_2$, C–S–H gel, AFt, AFm and unhydrated clinkers (mainly C_3S, C_2S) all can be carbonated. The aim of this paper is to provide improved understanding of the effects of accelerated carbonation on the microstructure and competitive carbonation of carbonation phases in the whole carbonation procedure.

2. Materials and methods

2.1. Characters of raw material

To eliminate the influence of aggregate, cement paste with a water/cement ratio of 0.5 was prepared and hydrated for 28 d. Rapid hardening ordinary Portland cement was used (P.O 42.5R). The chemical composition was determined by X-ray Fluorescence (XRF) spectrometry and is presented in Table 1. After hydration for 28 d, the cement paste was crushed, milled and sieved at 80 μm for accelerated carbonation.

Mineral phases of cement and hydrated cement were determined by quantitative X-ray diffraction (QXRD) analysis (Fig. 1). 10% ZnO was added as internal standard to determine the amorphous content of hydrated cement paste. The diffraction data was recorded with D8 advance powder diffraction with Cu K_α radiation (λ = 0.15406 nm, 40 kV and 40 mA, scan interval 10–60° 2θ, 0.01° and 0.5 s per step). Phase identification was carried out using Diffract EVA software and Rietveld refinement quantitative phase analysis was performed using TOPAS4.2 software. The Rietveld refinement strategy consisted of emission profile, background, instrument factors and zero error.

The content of C_3S, C_2S, C_4AF, C_3A, $CaSO_4 \cdot 2H_2O$ and $CaCO_3$ were 63.93%, 9.60%, 9.86%, 4.05%, 2.10% and 10.47%, respectively. The high $CaCO_3$ content is due to the use of limestone powder as admixtures. After hydration for 28 d, only C_3S, C_2S still existed. The main hydration products were portlandite, mono-carbonate ($C_3A \cdot CaCO_3 \cdot 11H_2O$) and ill crystallized C–S–H. Limestone cannot only accelerate the hydration process, but also influence the hydrate assemblage of the hydrated Portland cement. Mono-carbonate was more stable than AFm. Lothenbach [18] also indicates that the amount of AFm phases deduced by XRD is certainly underestimated due to its low crystallinity and the fact that it can be amorphous. So, there is no evidence of the presence of AFm.

Table 1
Chemical composition of the cement (wt%).

CaO	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	SO$_3$	MgO	Na$_2$O$_{eq}$
61.13	21.45	5.24	2.89	2.50	2.08	0.77

2.2. Sample preparing and testing method

The water added to the WHCP powder in the molding procedure has an important effect on the carbonation reaction [19], so an optimum water/solid ratio must be obtained where the water/solid ratio ranges from 10% to 25%. A certain amount of water was mixed with waste cement paste powder homogeneously for about 2 min at room temperature. The wet mixture was casted into a cylindrical stainless steel mold and compacted at 8 MPa for 1 min. The specimens obtained were all about Φ 50 mm × 30 mm. Then the compacts were put into a chamber to initiate the carbonation reaction, where CO_2 of 99.9% mass purity was injected into the sealed chamber and the CO_2 pressure was regulated at a constant of 0.2 MPa for 2 h in case of CO_2 starvation. In order to investigate the carbonate procedure of WHCP, samples with the optimum water/solid ratio will be carbonated for 2 min, 5 min, 10 min, 30 min, 1 h, 2 h and 24 h.

CO_2 uptake is an important index of carbon sequestration and mass curve method was used to evaluate the CO_2 uptake, calculated by Eq. (3). The chamber was placed on an electronic balanced with a measurement accuracy of 0.1 g. The electronic balance was connected to a data acquisition system and the balance was zeroed before CO_2 was injected. The total mass change in the carbonation process can be recorded. The CO_2 uptake was corrected by subtracting the mass of CO_2 not participate the carbonation reaction in the chamber. When carbonation reaction finished and the residual CO_2 was vent the mass of residual CO_2 in the chamber can be recorded. The compressive strength measurements of the carbonated cylinders were carried out at the same loading rate of 2 mm/min. Five specimens were used for a statistical average value. A temperature–humidity detector (Rotronic, HC2-IC102) was also used to record the temperature and humidity during the whole procedure. Compressive strength of carbonated WHCP samples were tested after the carbonation treatment finished.

$$CO_2\,uptake(\%) = \frac{CO_{2\,absorbed}}{Mass_{WHCP}} \times 100 \tag{3}$$

To study the effects of accelerated carbonation on the pore structure of WHCP, an automated mercury porosimeter (AUTOPORE IV 9500 series, Micromeritics Instrument Corp, USA), with two low-pressure stations plus one high-pressure station and a maximum pressure of 227.6 MPa for measurements, was used to measure the porosity and the pore size distribution before and after accelerated carbonation. Before test the samples were also dried in vacuum at 60 °C for 24 h to remove the water in pore structure.

Quantitative phase analysis of carbonated samples was also performed using the same method as the WHCP. Simultaneous TG/DSC analysis were performed using a METTLER TOLEDO STARe system under nitrogen atmosphere at a heating rate of 10 °C/min to give the content of calcium carbonate, calcium hydroxide and other hydration products. To avoid the influence of absorbed water samples were dried at 60 °C for 24 h.

3. Results and discussions

3.1. Effects of water content and carbonation time on carbonation

The carbonation reaction can be divided into the following three steps [20]: (1) The diffusion of CO_2 into the pore of WHCP structure. (2) The dissolution of solid $Ca(OH)_2$ and C–S–H from WHCP. (3) The reaction of dissolved CO_2 and Ca^{2+} to form calcium carbonate. The diffusion and dissolution of CO_2 will be affected by the water content. When the water content is relatively high, the diffusion of CO_2 will be blocked by the water in the pore structure. And when the water content is low, not enough CO_2 can be dissolved. Thus, optimal water content must be obtained.

The CO_2 uptake and compressive strength are used as the evaluation indexes of optimum water/solid ratio. From Fig. 2, both compressive strength and CO_2 uptake were influenced by water/solid ratio. Within the giving water/solid ratio range, the compressive strength and CO_2 uptake increases with increasing water/solid ratio, and then decreases after reaches the maximum. 0.15 indicates the highest compressive strength (28.6 MPa) and correspondingly, the amount of CO_2 uptake arrives at the maximum of 19.8 wt%. So to investigate the microstructure of carbonated WHCP, samples of 0.15 water/solid ratio were prepared.

The CO_2 uptake curve and temperature–humidity in carbonation procedure (water/solid ratio of 0.15) are shown in Fig. 3. The CO_2 uptake obtained with the mass curve method is 19.8 wt%. The reaction is rapid in the first 30 min, the CO_2 uptake is 11.3% and it account for 60.8% of the total CO_2 uptake within