- Technical Paper -

ARAGONITE PRECIPITATION AND MICROSTRUCTURAL DEVELOPMENT IN RECYCLED CONCRETE FINES (RCFs)-BASED CALCIUM CARBONATE CONCRETE (CCC)

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ABSTRACT

A calcium carbonate concrete (CCC) was made based on recycled concrete fines (RCFs) and CO_2. Results showed that the hardening mechanism of RCFs-based CCC is due to the entangled aragonite crystals generated at the contacting areas of particles. A dual precipitation process happened in the CCC-making process, while the hardening mechanism is ascribed to the precipitation from the $Ca(HCO_3)_2$ solution. The RCFs with a cement paste layer structure tend to have a higher affinity for combining the precipitated aragonite crystals.

Keywords: demolished concrete, heterogeneous precipitation, Ca extraction, wet carbonation, binder distribution

1. INTRODUCTION

Cement-based concrete, next to the water, is the largest consumed raw material for the building and construction industry [1]; however, producing the necessary volume of cement for buildings and construction consumes a large amount of limestone, which is a natural resource that cannot be regenerated [1]. More importantly, CO_2 emissions, generated by the calcination of limestone in the cement manufacturing process, have become a serious problem during the past decades as CO_2 is a greenhouse gas that can cause the serious global warming issue [1], it has been reported that the cement industry is responsible for 5-8% man-made CO_2 emissions [2]. It had also been reported that only the year 2018 produced approximately 2.4 million tons of cement globally, and it is predicted that the figure will rise to 4.8 million tons in 2030 [3]. Hence, it can be foreseen that the limestone resource will probably be in severe shortage, and the greenhouse effect and global warming issue will become much more obvious.

Meanwhile, with the rapid development of urbanization, Construction and Demolition (C&D) wastes have been accumulated in many countries, which have also developed into a global concern since it can pose great threats to the environment, society and economy. There were approximately 2.4 billion and over 35 million tons of C&D wastes, respectively, being generated in China and South Korea annually over the past decades [4], [5]. Only the year 2015 witnessed that more than 500 million tons of C&D waste were produced in the USA [6]. Another aspect is that among the countries producing a large amount of C&D wastes, China has a relatively lower recycling rate (less than 5% [7], [8]), in comparison to some developed economies, such as the UK and Denmark, with recycling rates of 75% and 94% [8], respectively. Besides, the average recycling rate (48%), evaluated from the statistical data organized by Vieira and Pereira (2015) [8], indicates that over 50% of C&D wastes in the world have been receiving unreasonable disposal.

Many efforts, aiming at realizing a sustainable and economic society, have been dedicated to making the most of the C&D wastes and reducing cement manufacturing production [9], [10]. One promising method is that the C&D wastes can be used to replace the natural aggregate in concrete, which forms recycled aggregate concrete (RAC) [11]; however, the applications of RAC by far mainly concentrate on the pavements and roads, since it has an unsatisfactory mechanical property and durability performance, in comparison to ordinary Portland cement concrete [12], [13], and the replacement rates are always limited within 50%. Some industrial byproducts, such as fly ash, slag powder, and silica fume, can be adopted to partially replace the cement in concrete or mix with alkaline activators, producing concrete with mineral admixtures or geopolymer concrete [14], [15], which can, to some extent, reduce the cement production and CO_2 emissions.

Calcium Carbonate Concrete (CCC) is a novel building material, which can be manufactured by precipitating $CaCO_3$ crystals between substrates. It contains two different raw materials, i.e., concrete waste demolished from construction and CO_2 in the air, and the CCC blocks can realize 100% recycled aggregate replacement rate and zero new added cement.

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The fundamental theory is that the Ca in CCC can be reused for many times for capturing CO_2 without too much energy, which is an excellent recyclable process.

This study intends to provide some evidence for the hardening mechanism of CCC made from recycled concrete fines (RCFs).

2. MATERIALS AND METHODS

2.1 Materials

The RCFs were prepared from the laboratory-tested concrete components (Fig. 1), which has been placed in the ambient environment for more than 1 year. It should be noted that, in actual projects, the demolished concrete will be hydrated for more than 50 years (if considering the service life of constructions). Therefore, the cement could have a relatively higher hydration degree, in comparison to that shown here. However, for simulating the demolished concrete in actual projects, the concrete which has been hydrated for more than 1 year will have an almost comparable hydration degree with that in actual projects. The original material was from the commercialized concrete.

Fig. 1 Laboratory-tested concrete components

Table 1 shows the mixture proportions of original concrete components.

Table 1 Mixture proportions of original concrete

Material	Cement	water	Coarse aggregate	Fine aggregate
Content (kg/m^3)	296	191	880	865

The demolished concrete was crushed and sieved into four parts, i.e., (1) when the concrete components were crushed, the first part of RCFs could be obtained by sieving, and (2) after that, the collected aggregates would be further crushed into ca. 5 mm, ca. 2.3mm, and ca. 1 mm, the other three parts could be obtained. It can be predicted that the four parts will contain different amounts of fine/coarse aggregates. Here, due to that the crushing and sieving process was time-consuming for small particles (less than 150 um), the particles will be carbonated under ambient temperature and relative humidity, the properties of final products will be measured. This research was based on the third part of RCFs. The selected third part of RCFs was further crushed into target sizes (<25 um, 25-53 um, 53-75 um, 75-100 um, 100-150 um, 150-212 um, and 212-300 um), and then, the sieved fine aggregates were mixed in a digital roller at 60 rpm for 2 hours. After that, the aggregates for making 10 mm-diameter and 20 mm-height CCC specimen could be obtained, which were stored in a desiccator before being used.

According to the quantitative X-ray diffraction results, the RCFs phases are mainly quartz (18.1%), granite (Analbite and Microcline (19.4%)), calcium carbonate (Vaterite and Calcite (total 12.1%)), and the amorphous phase (27%), according to the thermal gravimetric analysis, the amorphous calcium carbonate (Cc) also generated in the RCFs preparation process, the total amount of amorphous Cc and crystalline Cc was 16.28 g/100 g-RCFs, the content of calcium hydroxide (CH) was 1.19 g/100 g-RCFs.

Fig. 2 shows the particle size distribution of aggregates for making CCC.

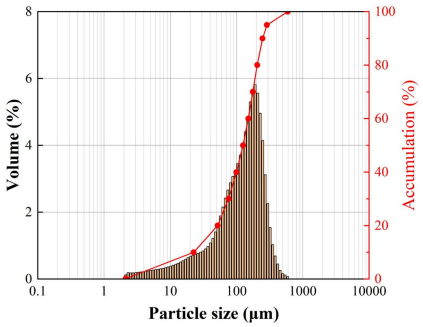


Fig. 2 Particle size distribution of aggregates for making CCC

2.2 Methods

2.2.1 Calcium bicarbonate solution-making process

A calcium bicarbonate ($Ca(HCO_3)_2$) solution was prepared to precipitate Cc between aggregates, the RCFs from the same demolished concrete with a particle size less than 75 um were used to make the solution. A water-solid ratio of 20 was accepted. The solution temperature was controlled as 5 °C. CO_2 gas was bubbled through the solution, and the flowing rate was controlled at 0.1 L/min. An automatic stirrer with a speed of 1000 rpm was used to make the solids fully in contact with the water containing CO_2. After mixing for 48 hours, the solution in the upper part was pumped into a container and further filtered through 50 um and 10 um filters. After the solution was obtained, the concentrated CO_2 gas was continuously bubbled through the solution to avoid precipitation of Cc before the CCC-making process. Here, one wet carbonation trial under the same condition was also performed to determine the Ca element extraction potential of real RCFs.

2.2.2 CCC-making procedure

The CCC making process followed the same procedure described in [16]. Fig. 3 illustrates the CCC-making process. The prepared $Ca(HCO_3)_2$ solution was pumped through the mold containing aggregates. In the meantime, the mold was heated to 70 °C to make precipitation of Cc between aggregates.

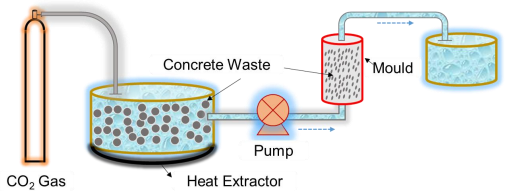


Fig. 3 CCC-making process

Here, RCFs was used to make CCC with a geometry of 10 mm-diameter and 20-mm height. After 48 hour-precipitation, the specimen was demolded and dried under 80 ℃ until constant mass was achieved. Fig. 4 shows the hardened RCFs-based CCC specimens.

Fig. 4 Hardened RCFs-based CCC specimens

2.2.3 X-ray diffraction

X-ray diffraction (XRD) was accepted to analyze the crystalline phases of RCFs and CCC, the experiment was performed in the Rigaku-Mini Flex 600 X-ray diffractometer. CuKa X-rays ranging from 5°-70° 2θ at a step size of 0.02° with a scanning rate of 2°/min were adopted. The dried powders were sieved through 75 um sieve, 10 mass% of a-corundum was manually mixed in an agate mortar for 10 mins with 90 % of powders for quantitative XRD (QXRD) analysis.

2.2.4 Thermal gravimetric analysis

Thermal gravimetric (TG) analysis was used to determine the Cc content in the original particles and CCC, about 20 mg samples were prepared, the samples were heated from 25 ℃ to 950 ℃ at a rate of 10 ℃/min. The phase content was calculated by the tangential method [17].

2.2.5 EDTA titration method

EDTA titration method was accepted to determine the Ca^{2+} concentration in the solution:

(1) Mixing 10 mL solution with 2 mL 8 mol/L Potassium Hydroxide solution.
(2) Adding ca. 1 mL NN solution, mixing by hand, the color is red.
(3) Adding EDTA-2Na till the color becomes blue.

According to the method, the Ca ion concentration was calculated as 549.33 (±30.02) ppm (mg/L).

2.2.6 Scanning electron microscopy (SEM) coupled with energy dispersive spectrometry (EDS)

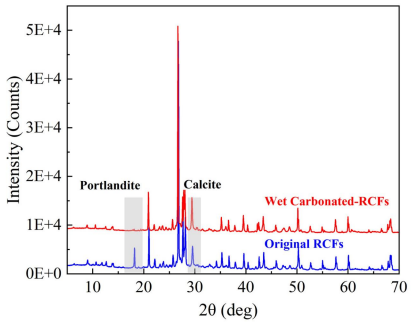
Scanning electron microscopy (SEM) coupled with energy dispersive spectrometry (EDS) mapping was used to check the binder (precipitated crystals) distribution in CCC, the accelerating voltage was 15 keV and 600 pA, backscattered scanning electron (BSE) was selected in this study. The working distance was 10 mm. The samples were cut along two directions, i.e., horizontal and vertical directions, and then were dried under 105 ℃ for one day. After that, the samples were immersed in epoxy resin and hardened for 24 hours. Finally, the samples were well polished in a MA-200 precise polishing machine.

3. RESULTS AND DISCUSSION

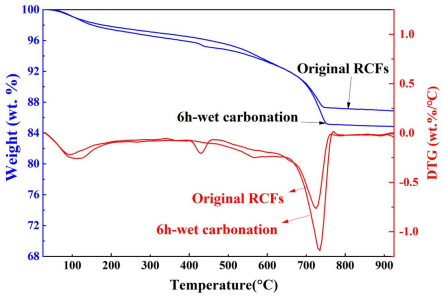
3.1 Ca extraction potential of real RCFs

Here, the Ca extraction potential is defined as the maximum content of Cc contained in the RCFs. Fig. 5 depicts the Ca extraction potential of real RCFs through XRD (Fig. 5(a)) and TG (Fig. 5(b)) analyses. Portlandite was depleted in the wet carbonation, and calcite crystals were formed during the wet carbonation process, which is a common result in wet carbonation process [18]. Calcium-silicate-hydrates (C-S-H) was consumed in the carbonation process, some gel-based substances existed in the carbonation products. According to the calculation, the Cc content in original RCFs of this test was 13.52 (±0.54) g/100 g-RCFs, after 6h–wet carbonation, the Cc content was 21.64 (±0.60) g/100 g-RCFs. CH original was 1.26 (±0.30) g/100 g-RCFs, after wet carbonation, CH was not observed in the results. When considering the dissolution of Cc under the low temperature (5 ℃), the Ca extraction potential of real RCFs in this test could be larger than the Cc amount generated through 6-h wet carbonation.

Hence, the demolished concrete in actual projects possesses a large potential for Ca elements extraction, which further provides some potentials for the CCC-making strategy.



(a) XRD pattern of CCC and RCFs



(b) TG results of original RCFs before and after 6 h-wet carbonation

Fig. 5 Ca extraction potential of real RCFs

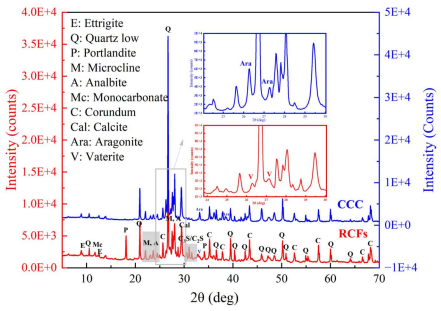
3.2 Phase assemblage of CCC

Fig. 6 illustrates the phase assemblage of CCC after the precipitation process. As depicted by Fig. 6(a), due to the 70 ℃ heating temperature, aragonite crystals

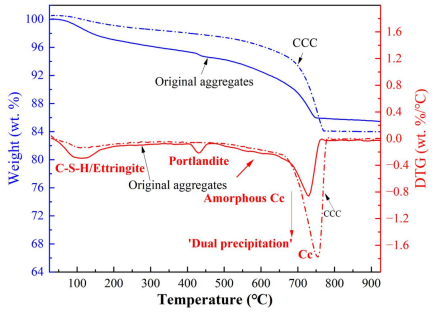
generated in this CCC-making process [19]. Portlandite, unreacted cement clinkers, amorphous (C-S-H) were also wet carbonated during CCC-making process, probably due to (1) the redissolution of CO_2 into the solution, and (2) the supersaturated $Ca(HCO_3)_2$ solution with respect to the CO_2. (QXRD of CCC: Aragonite: 17.0%, Calcite: 11.9%, Vaterite: 0.64%, Amorphous: 13%; QXRD of original materials: Aragonite: 0%, Calcite: 5.1%, Vaterite: 7.0%, Amorphous: 27%). Besides, it seems that during the precipitation process, most of the vaterite disappeared, these vaterite crystals could be transformed into calcite and aragonite, as demonstrated by XRD results. The most important phenomenon is that two precipitation (dual precipitation) processes generated in the CCC-hardening procedure, i.e., (1) precipitation from the calcium bicarbonate solution, and (2) dissolution and precipitation of hydrates/unreacted cement clinkers. The dissolution and precipitation process could be resulted from the wet carbonation process generated from the solution containing dissolved CO_2.

However, further research about the wet carbonation under 70 ℃ is needed to confirm the Cc crystalline phase.

The Cc content calculated by TG (Fig. 6(b)) was 27.24 g/100g-sample, which was in accordance with QXRD results shown before. The TG analysis further confirmed the discussion above, i.e., the dissolution-precipitation also happened in the CCC-hardening process. Hence, the strength development mechanism of CCC should consider the dual precipitation mechanisms, which make it more complex.



(a) XRD pattern of CCC and original RCFs



(b) TG results of CCC and original RCFs

Fig. 6 Phase assemblage of CCC

3.3 Binder distribution in the RCFs-based CCC system

3.3.1 Horizontal direction

Fig. 7 illustrates the aragonite crystals distribution in the RCFs-based CCC system, the aragonite crystals mainly generated around the surfaces of carbonated cement paste, and it seems that around the fine/coarse aggregate surfaces, only a small amount of Cc crystals can be visible.

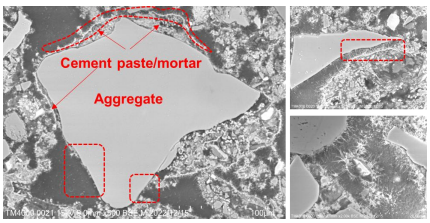


Fig. 7 Aragonite crystals distribution in the RCFs-based CCC system

As shown in Fig. 8, it can be seen clearly that the needle-like aragonite crystals entangled with each other, forming a network along the horizontal direction.

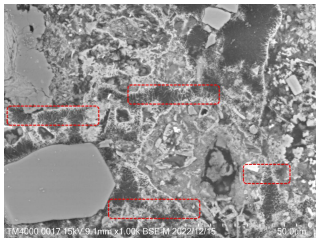


Fig. 8 The entangled aragonite crystals

3.3.2 Vertical direction

Fig. 9 shows the binder distribution in the RCFs-based CCC system, through the vertical direction (the solution-flowing direction), the positions were randomly chosen from the sample height to illustrate the general phenomenon through the sample vertical direction. It gets more obvious that the needle-like aragonite crystals formed mainly around the surfaces of RCFs, and at the contacting area, the enhanced aragonite network formed, which is a general phenomenon through the whole vertical direction. These entangled aragonite crystals are the actual binder in the CCC system.

Fig. 10 shows the typical entangled aragonite crystals in the RCFs-based CCC specimen, it can be inferred that the bonding performance is related to the density of the entangled aragonite network.

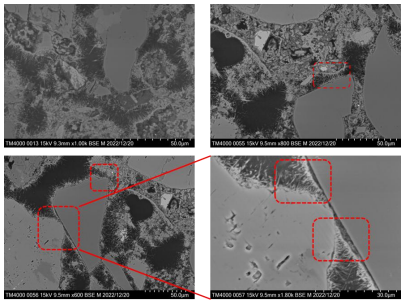


Fig. 9 Binder distribution along the vertical direction of the CCC specimen

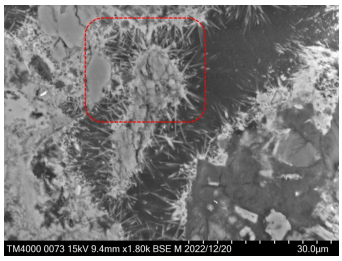


Fig. 10 Entangled aragonite network through the vertical direction

Strong evidence on the crystal distribution around fine/coarse aggregates could be found in Fig. 11, it seems that the fine/coarse aggregates exposed to the voids have a lower affinity for combining aragonite crystals.

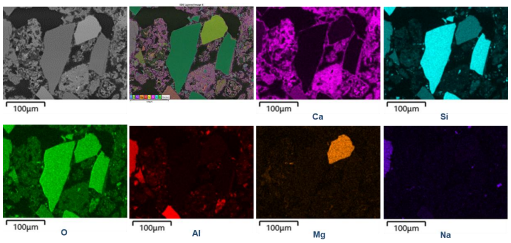


Fig. 11 element distribution around aggregates

3.3.3 Hardening and precipitation mechanisms in the RCFs-based CCC system

Generally, two main types of nucleation theory have been proposed so far, i.e., heterogeneous nucleation and homogeneous nucleation. Homogeneous nucleation mainly occurs in the bulk solution without any foreign particles, and heterogeneous nucleation will be induced when the solution contains foreign components [20]. The kinetics of heterogeneous precipitation contains several consecutive parts [21], i.e., (1) Adsorption of ions onto the surface. (2) Nucleation of crystals on the surface. (3) Growth of crystals (adsorption of ions onto the nucleus lattice) on the surface. The rate of heterogeneous nucleation process sometimes is higher than that of homogeneous nucleation. Combined with the aragonite crystals distribution along the horizontal and vertical directions of the specimen, the precipitation is a kind of heterogeneous precipitation, the crystals will first nucleate on the surface of aggregate and then grow there.

From the SEM results, it can be inferred that the hardening mechanism of CCC is related to the generation of 'aragonite network [22]' in the contact area of particles, which forms a network to realize stress transfer, as further demonstrated by Fig. 12. These entangled aragonite crystals could be the main sources resisting the compressive load. The effective binder in the CCC system are the entangled aragonite crystals [16], [22] distributed around the contacting areas of particles. The aggregates with a hardened cement paste layer structure tend to have a higher affinity for Cc precipitation; however, it is still remained unclear that which phases in cement paste have an affinity for combining Cc [23], further investigations are needed.

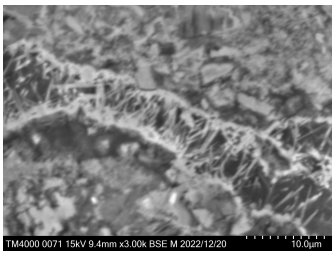


Fig. 12 The 'Micro-frame structure' in CCC

Besides, it seems that when the fine/coarse aggregates surfaces exposed to the voids, very small amount of aragonite could be observed, combined with the BSE results, such kind of surfaces have a lower affinity for combining aragonite crystals; however, these defects generated at the surface of fine/coarse aggregates could provide channels for the flowing of the solution, that is also why in the vertical direction, aragonite crystals could distribute evenly.

4. CONCLUSIONS

In this study, the hardening mechanism of RCFs-based CCC was investigated, based on the test results and discussion, the following conclusions can be drawn:

(1) The hardening mechanism of CCC with no compaction is related to the entangled needle-like aragonite crystals generated at the contacting points/area of particles, the grown aragonite crystals could entangle with each other and form a 3D-network around the contacting area. Also, if the distance between two particles is enough, the entangled aragonite crystals could also be generated.

(2) The binder/aragonite crystals mainly distributed around the (carbonated) cement paste surfaces. At the surfaces of silica sand/coarse aggregates which exposed to the voids, a very small amount of aragonite could be observed, which means in the aggregates for making CCC, (carbonated) cement paste tends to have a higher affinity for combining Cc.

(3) The basic precipitation mechanism in the CCC-making process is a kind of heterogeneous precipitation. From the crystal nucleation theory, the Cc crystals could first nucleate at the surface of aggregates and then grow there.

From the test results, it can be inferred that a dual precipitation process could happen in the CCC hardening process, i.e., 1) dissolution-precipitation of cement hydrates and unreacted cement clinkers, and 2) direct precipitation from the $Ca(HCO_3)_2$ solution. In the RCFs-based CCC system, the direct hardening mechanism could be related to the latter. Further experiments are needed.

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