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ABSTRACT

This work introduces a novel method for the development of nearly zero CO₂ cementitious composites, by adding a CaCO₃ nanofiller produced via innovative recovery systems of carbon dioxide in cement manufacturing. This novel process of CO₂ reconversion makes it possible to obtain calcium carbonate with a high degree of purity and useful features e.g. morphology, particle size distribution or crystal phase that make it suitable for use as a nanofiller in cement-based composites. In this study, synthesized nanoCaCO₃ particles were incorporated into the cementitious composites with different percentages according to the weight of the cement, in order to understand their behaviour within the cement matrix. Mechanical properties were investigated through three point bending and compression tests, both at 7 and 28 days and results show a promising improvement in strength and toughness. This study is a first step towards developing a CO₂ circular economy in cement and concrete technology.

Keywords: CO₂, calcium carbonate, cementitious composites, circular economy.

1. INTRODUCTION

Cement production generally emits 0.65 – 0.95 tonnes CO₂ per tonne cement ^[1].

In recent years, concrete technology is increasingly turning to environmentally sustainable approaches and is studying new materials which can decrease and/or replace the amount of cement used in the production of concrete.

In particular, nanomaterials can enhance performance of cement-based material given their physical effect (filling and nucleation effects) as well as their chemical reactivity ^[2]. Nano-silica (nano-SiO₂) ^[3], nano-alumina (nano- Al₂O₃) ^[4], nano-titanium oxide (nano-TiO₂) ^[5], nanotubes ^{[6][7]}, carbon-based nanoparticles ^{[8][9][10][11]} and nano-CaCO₃ ^[12] are some of the nanomaterials that have been studied for use in cement-based materials.

Although CaCO₃ was first considered as a filler, some studies indicate that it reacts chemically and accelerates the cement hydration process, thus increasing the early-age strength of conventional cementitious materials, because of the additional quantity of C-S-H gel produced ^{[13],[14]}.

This paper describes a novel method to improve the quality of cementitious composites.

To the best of our knowledge, this is the first study to develop CO₂ recovery systems derived from the production process of cement in order to obtain CaCO₃ nanofiller in cement-based composites. The present investigation can be an important step towards a CO₂ circular economy.

Calcium carbonate nanoparticles are synthesized via a carbonation route^{[15],[16]} and have a wide range of applications. They are widely used as filler materials and, because of their porosity, non-toxicity and biocompatibility, they are also used in the biomedical and food industry^[17]. Several process variables have been investigated, including the pH of the solution, the concentration of the calcium ion, the concentration ratio of [HCO₃]⁻ / [CO₂]^{[18],[19]}, and the gas liquid mixing mode^[20]. During the carbonation process, once the CO₂ is absorbed, the CaCO₃ precipitation takes place and its driving force is supersaturation, determined by the product of the ionic concentration of calcium and carbonate ions. Precipitation involves four steps: (i) dissolution of CaO, (ii) mass transfer between the CO₂ phase and the water phase and the formation of carbonate ions, (iii) a chemical reaction, and (iv) crystal growth which results in higher absorption rates in water compared to other similar compounds.

In this study, a packed bed reactor is proposed to obtain CaCO₃ nanoparticles via carbonation. This apparatus can provide a good mixing gas-liquid and control the CO₂ absorption step. The particles obtained through this method were tested according to a standard European procedure to determine their effect as a cement filler.

2. EXPERIMENTAL PROCEDURE

2.1. Materials and methods

The CaCO₃ particles were synthesized through a carbonation route in packed bed reactor. This reactor was constructed from a light polyvinyl chloride (PVC) pipe and filled with <10 mm industrial produced monolith. The synthesis was carried out in continuous conditions, starting from a CaO slurry (0.015 M) in an experimental setup. The slurry and the gas stream were flowed to the bottom of the PBR, where contacted in a T-mixer. The precipitated particles were rapidly filtered by vacuum and dried at 60 °C overnight.

The dried powder was re-dispersed in isopropanol (1g/L) and about 1 mL of sample was put into a UV cuvette and size distribution were measured by dynamic light scattering (DLS) method with a particle size analyzer (Malvern nano ZS model). The phase purity of the samples was examined by X-ray diffraction. Morphological characterization was obtained using scanning and transmission electron microscopy (ZEISS MERLIN FE-SEM operated at 3 kV).

Surface area was determined from N₂ adsorption and desorption isotherms, measured at the temperature of liquid N₂ (Quantachrome Autosorb-1). The surface area was calculated from the Brunauer-Emmet-Teller (BET) equations. All samples were outgassed at 120 °C overnight prior to measurement.

The cement mortars were produced according to the European Standard EN 196-1 “Methods of testing cement - Part 1: Determination of strength”. The proportions by mass are one part of the cement, three parts of CEN Standard sand and one half part of water (water/cement ratio 0.50). Each batch for three test specimens consists of 450 g of cement, 1350 g of sand and 225 g of water and, in the present study, calcium carbonate nano particles were added in different percentages (2%; 3%) according to the weight of cement in a solution with deionized water. The solution was also subjected to ultrasonic bath for 8 minutes to promote a better dispersion of particles. The cement and the solution of deionized water with calcium carbonate were placed into the bowl, taking care to avoid loss of liquid solution or cement powder. As soon as the liquid and the cement were brought into contact, the mixer started at low speed. After 30 s of mixing, the sand was added during the next 30 s. Then the mixer was switched to high speed and continued mixing for an additional 30 s. The mixer was stopped for 90 s to remove the mortar adhering to the wall of the bowl. The mixing then continued at high speed for 60 s. The test specimens (40 mm x 40 mm x 160 mm) were produced by introducing the first of two layers of mortar into each of the mould compartments directly from the mixing bowl. Subsequently, it was compacted using 60 jolts of the jolting apparatus. Then, the second layer was introduced and compacted with a further 60 jolts. The specimens were stored in a humid atmosphere for at least 24 hours, and once unpacked, they were submerged in water at (20.0 ±1.0) ° C for 7 and 28 days curing.

3. RESULTS AND DISCUSSIONS

3.1. Chemical analysis

Through an XRD analysis, the high crystalline nature of the material was determined, and can be seen in the sharpness of the peaks in Figure 1 a. No presence of other CaCO₃ crystalline phases was determined, such as aragonite and vaterite.

In Figure 1 b, quite a wide PSD is shown. This is in good agreement with the FESEM micrograph, since the presence of very small nanoparticles and their aggregates is evident, as shown in Figures 1 c-d. These nanoaggregates are formed by cubic particles, which is the classic morphology of calcite crystals ^{[15],[18]}. With regard to the specific surface area, since the

mean diameter of the particles was about 600 nm, the CaCO_3 powder was expected to have a large specific surface area, but because it has an aggregate form consisting of nano-sized particles, it was only $5 \text{ m}^2/\text{g}$ due to secondary aggregated particles presence.

3.2. Mechanical tests

Results of flexural and compressive strength (figure 2) were calculated according to European Standard EN 196-1.

The experimental specimens characterized by the addition of 2% of CaCO_3 showed good mechanical properties if the ultrasonic bath for water and nanoparticles was included during the preparation of the mortars. At 7 days, the mean value of the maximum force, the flexural and the compressive strength increased (by 10%) in these experimental specimens with respect to sample mortars. By contrast, at 28 days, the mechanical properties decreased in the cement mortar mixtures with calcium carbonate nanoparticles incorporated. The cement mortars prepared without the ultrasonic bath yielded bad results both at 7 and 28 days. Thus, the ultrasonic bath is necessary to promote the dispersion of the nanoparticles in the deionized water and in cement matrix.

The experimental campaign also envisaged incorporating a quantity equal to 3% of nano CaCO_3 in cement mortars, by evaluating the flexural and compression tests results. However, the optimal additional percentage in cement mortars proved to be a 2% addition of nano CaCO_3 . The mean value of the elastic modulus, that represents the slope in σ - ε curves graph, was calculated from Load-Displacement curves (figure 3) obtained from the mechanical tests. At 7 days, the elastic modulus increased with the additional percentages of CaCO_3 equal to 2% and 3% compared to sample mortars (respectively by 29% and 26% in flexural tests and respectively by 11% and 9% in compression tests). By contrast, at 28 days, incorporating calcium carbonate nanoparticles provided no improvements to test results for the elastic modulus.

4. CONCLUSIONS

Cement production has a serious environmental and economic impact. This work investigated the effects of incorporating precipitated calcium carbonate with a high degree of purity by CO_2 recovery derived from cement manufacturing. The production process of the CaCO_3 nanofillers was designed and optimized. Nanosized pure calcite particles were obtained via a carbonation route, by employing a packed bed reactor. The synthesized nano CaCO_3 particles were added

to the cement mortars in different percentages according to the weight of the cement. Results of three point bending and compression tests showed that, after 7 days curing, the mean value of the flexural strength, the compressive strength and the elastic modulus were increased by up to 11%, 11% and 29 % respectively. The optimal additional percentage of nanoCaCO₃ filler into cement mortars was 2%, when using an ultrasonic bath to disperse nanoparticles in deionized water, thus avoiding their agglomeration. To sum up, CaCO₃ increases the early-age strength of conventional cementitious materials, but the experimental campaign showed that at 28 days a decrease of mechanical properties occurred in the specimens with added calcium carbonate. The production of these CaCO₃ particles with appropriate characteristics would make possible their utilization as nanofiller in the cement. Therefore, the results of the present investigation constitute a first step towards achieving a CO₂ circular economy in the cement industry.

CONFLICT OF INTEREST

The authors have no conflict of interest to declare.

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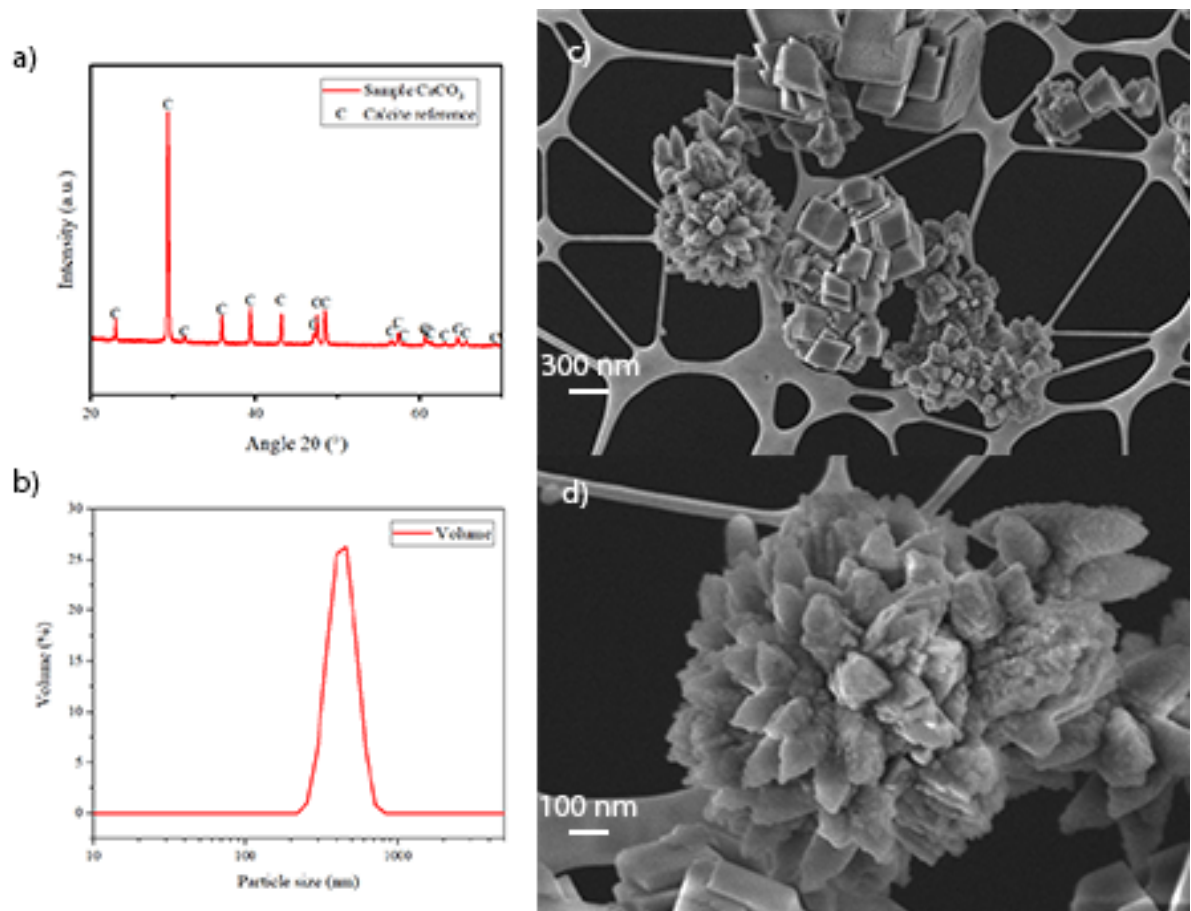


Figure 1. Characterization of CaCO₃ particles: a) XRD spectra - b) Particle size distribution - c-d) FESEM micrographs.

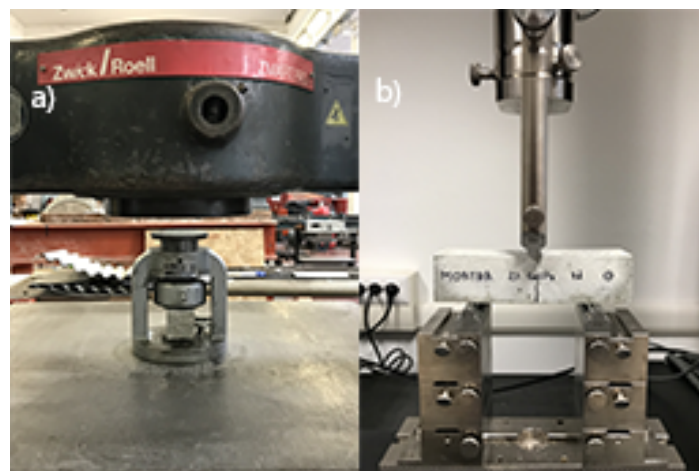


Figure 2. Mechanical tests: a) compression test - b) flexural test

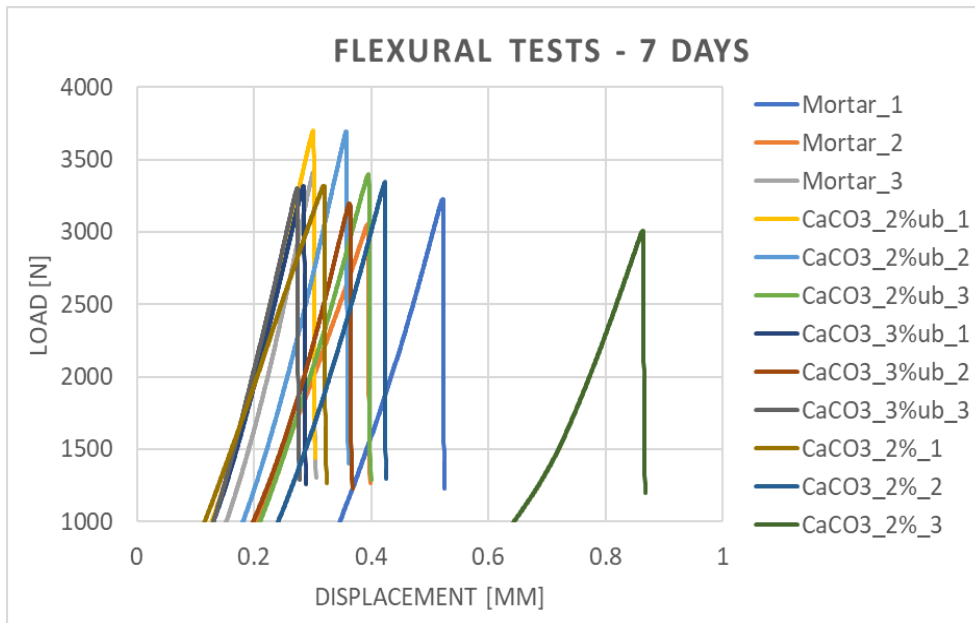


Figure 3. Flexural tests: Load-Displacement curves, 7 days.