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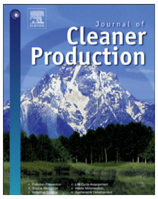

Development of low-carbon cementitious materials via carbonating Portland cement–fly ash–magnesia blends under various curing scenarios: a comparative study

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ABSTRACT

This study investigates a potential approach to produce low-carbon cementitious materials via using fly ash and reactive MgO as cement replacements, exposed to a pressurized CO_2 curing regime. Pressurized CO_2 with a concentration of 99.9% and pressures ranging from 0.1 MPa to 1.0 MPa were employed to accelerate the carbonation of MgO–fly ash–PC (Portland cement) blends in which up to 60% of PC was replaced with reactive MgO and fly ash. The carbon footprint of each cementitious material produced under various curing scenarios is evaluated based on life cycle assessment. Results indicate that after exposure to pressurized CO_2, the cement pastes exhibited fast CO_2 uptake, rapid compressive strength gain and microstructure densification due to the formation of carbonate products in terms of $CaCO_3$ and/or (Ca, Mg)CO_3 due to the incorporation of Mg^{2+} at the presence of MgO. The addition of fly ash facilitated carbonation, as it produced a more permeable microstructure for the ingress of CO_2. A more rapid CO_2 uptake and compressive strength development of the cement pastes was obtained as higher-pressure CO_2 was used. In comparison to moist curing, pressurized CO_2 curing yielded less carbon emissions. The CO_2 emissions of the cement pastes decreased with increasing fly ash content as cement replacement but increased with the increase of MgO content from 20 to 40% by mass.

1. Introduction

The occurrence of carbonation processes throughout the life of reinforced concrete products can result in the deterioration of concrete, but this natural chemical process can also offset greenhouse gas emissions. Given the high CO_2 emissions of cement during the manufacturing stage, researchers have investigated how to use the natural carbonation process of concrete that occurs throughout its service life to act as a mechanism for CO_2 absorption (Pade and Guimaraes, 2007; Galan et al., 2010). CO_2 is chemically combined in carbonates in the form of aragonite, vaterite and calcite, which partially offsets the CO_2 originally emitted during the manufacturing process of cement clinker (Pade and Guimaraes, 2007; Galan et al., 2010). Pade and Guimaraes (2007) have estimated CO_2 uptake by (i) determining the carbonation depth, (ii) calculating the volume of carbonated concrete, and (iii) the amount of CO_2 absorbed per volume of carbonated concrete. They reported that between 33% and 57% of CO_2 produced during calcination was reabsorbed through carbonation. It should be recognized that a wide range of percentages of CO_2 being produced during calcination and then reabsorbed due to carbonation processes is possibly due to the wide range (21–75%) of CaO assumed to be available for carbonation. Additionally, some studies account for the effect of concrete demolition and recycling, which will influence the CO_2 uptake calculation (Pade and Guimaraes, 2007; Jonsson and Wallevik, 2005; Engelsen et al., 2005). Based on the reported results, the percentage of CO_2 absorbed is potentially significant.

In some cases for unreinforced concrete, carbonation was proved to have some beneficial effects on the properties of cement materials, including microstructure densification, mechanical strength improvement and hazardous waste treatment (García-González et al., 2006; Chi et al., 2002; Monkman and Shao, 2010;

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Bertos et al., 2004). For carbonated cementing materials, these beneficial effects were closely associated with the formation of $CaCO_3$ (Shi and Wu, 2009; Shao and Lin, 2011), magnesium carbonates (Liska and Al-Tabbaa, 2009; Liska et al., 2008; Vandeperre and Al-Tabbaa, 2007) or magnesian calcite (de Silva et al., 2009; Mo and Panesar, 2012, 2013; Panesar and Mo, 2013). However, due to the low concentration of CO_2 in the atmosphere (approximately 0.04%), the natural carbonation process is very slow. In order to benefit from carbonation processes and to increase the rate of reaction, reports in the literature have examined several approaches. The first approach varies the CO_2 (concentration or high pressure) in curing regimes (Shi and Wu, 2009; Shao and Lin, 2011; Rostami et al., 2012). Increasing the pressure and concentration of CO_2 could enhance the ingress and diffusion of CO_2, and increase the solubility of CO_2 in liquid and thus reduce the pH value, which in turn facilitates the formation of Mg^{2+} through the dissolution of $Mg(OH)_2$ (Harrison et al., 2013). The second approach is to incorporate alternative cement formulations of reactive magnesia (MgO) cement blends, which are used to develop low-carbon cementing materials (Liska and Al-Tabbaa, 2009; Liska et al., 2008; Vandeperre and Al-Tabbaa, 2007). In the presence of Mg^{2+}, magnesium calcite ($(Ca, Mg)CO_3$) was formed as a result of incorporating Mg^{2+} into $CaCO_3$ (de Silva et al., 2009), which can be described as $Ca^{2+} + Mg^{2+} + CO_3^{2-} \rightarrow (Ca, Mg)\,CO_3$. The accelerated carbonation of MgO-containing cement blends shows a potential way to prepare low-carbon construction materials, as it integrates the two processes of producing binder and sequestering CO_2. A third approach uses materials that create a relatively porous microstructure to encourage diffusion reactions. The diffusion of CO_2 was considered to be one of the key factors governing the carbonation rate of the cement materials, which is influenced by moisture content (Bary and Sellier, 2004; Morshed and Shao, 2013), relative humidity (Galan et al., 2013), as well as the pore structure (Sulapha et al., 2003). A permeable structure of cement materials is favorable to the diffusion of CO_2 in the cement materials, which in turn facilitates the carbonation. Based on the published literature, strategies such as preparing porous blocks or mixing specimens with a coarser particle size distribution along with gap-grading were used to enhance carbonation, as they increase CO_2 accessibility and transportation (Liska and Al-Tabbaa, 2009; Liska et al., 2008; Sulapha et al., 2003). The incorporation of mineral admixtures particularly with less pozzolanic reactivity (e.g., fly ash) was also reported to decrease the carbonation resistance of blended cement as it made the cement materials more permeable (Sisomphon and Franke, 2007; Khunthongkeaw et al., 2006).

In recent years, CO_2 with a high concentration or high pressure has also been used to accelerate the carbonation of industrial solid wastes (e.g., iron powder (Das et al., 2014), fly ash (He et al., 2013; Wee, 2013), blast furnace slag (Siriwardena and Peethamparan, 2015)) for the purpose of sequestering CO_2. In addition, the carbonated alkali industrial wastes, e.g. steel-making slag, lime, etc. were used as cementitious materials (Ghouleh et al., 2015), supplementary cementitious materials (Jo et al., 2015), or aggregates for concrete (Bodor et al., 2016). Although the benefits resulting from the abovementioned carbonations of cement, magnesia cement, and alkali industrial wastes are being increasingly investigated, research on quantifying the carbon footprint of each carbonated materials is still needed.

Motivated by developing low-carbon cementitious materials, this study examines the interplay between two primary experimental variables (CO_2 pressure level and curing duration) to quantify the effect of using pressurized CO_2 carbonation on the early-age strength development of different mix designs, and the corresponding carbon footprint of each mix based on life cycle assessment. Four mix designs were considered, including varying proportions of Portland cement (PC), fly ash (FA), and reactive MgO. The justification for selecting MgO in the paste blends is attributed to its ability to enhance the microstructure of carbonates and improve the mechanical properties. The basis for selecting FA to be included in the blends is largely associated with its ability to result in a more permeable microstructure that is conducive and facilitates carbonation reactions. It is expected that subjected material to pressurized CO_2, and utilizing industrial byproducts, the net result would be a lower carbon footprint, defined by the combined effect of CO_2 emissions during manufacture and the CO_2 absorbed during the curing process. This study provides estimates of the net CO_2 footprint of the materials based on the estimated quantity of CO_2 uptake during the curing processes. The properties in terms of microstructure and compressive strength, and CO_2 footprint of the same cement mixes subjected to conventional moist curing and CO_2 curing, were comparatively investigated. This knowledge is essential to further evolve low CO_2 cement materials and novel CO_2 curing technology for precast cement products.

2. Materials and method

2.1. Raw materials

Type P.II 52.5 PC supplied by the Onada Cement Corp. in Nanjing, China was used. It consists of 52.1% C_3S, 23.1% C_2S, 7.6% C_3A, and 8.1% C_4AF. FA was provided by the Huaneng Power Plant in Nanjing. This FA had an ignition loss of 8.84% and a low CaO content of 3.34% as shown in Table 1, and was classified as type III according to the Chinese standard of FA used for cement and concrete (Standard, 2005), which had relatively low pozzolanic reactivity and was not widely used in conventional concrete. The reactive MgO was supplied by Liyang Special Materials Company in China. The MgO was produced by calcining magnesite at approximately 800 °C, and consisted mainly of periclase as well as a small amount of undecomposed magnesite. The chemical compositions of these raw materials are shown in Table 1. Three mix designs for the cement blends were used in this study, in which up to 60% of the PC was replaced with MgO and FA. The three blended cement mixes were designated as M20F20 (20% MgO and 20% FA), M20F40 (20% MgO and 40% FA), and M40F20 (40% MgO and 20% FA). For comparison, a mix design of M0F0 consisting of 100% PC was used.

2.2. Cement paste preparation and curing

For each mix design, the cement blends were mixed at the same water-to-binder ratio of 0.40 until homogenous mixtures were obtained. The mixtures were cast into cubic molds with a size of

Table 1
Chemical compositions of Portland cement, magnesia, and fly ash/weight%.

Materials	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	LOI
Portland cement	19.41	2.97	4.39	64.73	0.89	0.54	0.18	2.16	2.40
Magnesia	0.51	0.35	0.47	0.41	87.94	0.01	0.14	0.18	8.48
Fly ash	48.10	4.56	30.19	3.34	2.38	1.16	0.69	0.68	8.84

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