Jordan Journal of Civil Engineering, Volume **17**, No. **3**, **2023**
DOI: https://doi.org/10.14525/JJCE.v17i3.08

CO_2 Curing of Reactive Powder Concretes Modified by Waste Limestone Powder

Hamid Rahmani 1)* ***and Nooshin Mohammadzade*** 2)

1) Associate Professor, Civil Engineering Department, University of Zanjan, Zanjan, Iran.
* Corresponding Author. E-Mail: hrahmani@znu.ac.ir
2) MSc Student, Civil Engineering Department, University of Zanjan, Zanjan, Iran.
E-Mail: Nooshin.mohamadzadeh@gmail.com.

ABSTRACT

Incorporating waste stone powders into the production of reactive powder concretes (RPCs) can be eco-friendly. Since high cementitious material content is used in producing RPCs, CO_2, as a harmful greenhouse gas, was used for carbonation curing in this study. For this purpose, waste limestone powder was substituted by 0%, 18%, 36% and 54% of silica sand and the specimens were cured in water for up to 90 days in a CO_2 chamber for up to 48 hours. The physical and mechanical properties of the concrete and the specimens' CO_2 uptake were measured at different ages. Results showed that the 28-day compressive strength of the moist cured RPCs was higher than 100 MPa and the properties of the RPCs were improved by increasing limestone substitution. CO_2 curing of the RPCs significantly increased the samples' compressive strength and limestone-powder substitution as silica sand significantly decreased the carbonation and autogenous shrinkages of the RPCs. Moreover, carbonation curing can make eco-friendly limestone-modified RPCs, where their properties are improved.

KEYWORDS: CO_2 curing, Reactive powder concrete, Waste limestone powder, Shrinkage.

INTRODUCTION

Sustainable development meets the present needs without compromising the ability of future generations to meet their own needs (Aïtcin and Mindess, 2011). Protecting the environment and natural resources must be ingrained in strategy-making and development. Production of decorative rocks worldwide reveals that the relevant industry is being flourished. Around 6000 stone production plants in Iran annually produce 9 million tons of debris, about 60% of which is dedicated to limestone. Nearly 50% of the stones are reduced to dry waste in the extraction, cutting and polishing processes in producing decorative rocks (Savadkoohi and Reisi, 2020). Fig. 1, taken in the Kasra stone production plant (Zanjan, Iran), shows that additional 5 mm is the cut-off to produce a 20-mm thick natural limestone, comprising 50% of the entire dry waste, predominately in slurry or powder form. The wastes are exorbitantly transferred by trucks to the countryside and hilled up, impairing the environment.

These wastes can be used in conventional and novel concretes to preserve the environment and develop sustainability. Hence, limestone and granite waste powders have been extensively used in concretes or mortars as fillers or fine aggregates (Ramezanianpour et al., 2009; Liu and Yan 2010; Singh et al., 2016; Tu et al., 2018; Wang et al., 2018; Chakherlou and Shervani Tabar, 2019; Savadkoohi and Reisi, 2020; Zhang et al., 2020; Lin Chan and Zhang 2023). For instance, Singh et al. (2016) reported that the workability of concretes decreases with the substitution of granite waste as fine aggregates (Singh et al., 2016). Furthermore, researchers introduced optimal values of stone powders to promote concrete properties (Chakherlou and Shervani Tabar, 2019; Savadkoohi and Reisi, 2020).

Reactive powder concrete (RPC), among different

Received on 11/12/2022.
Accepted for Publication on 29/4/2023.

types of concretes, has a remarkable ability to incorporate stone powders in the constituents due to its fine ingredients. As a new cement-based material, RPC was introduced in 1990 by Richard and Cheyrezy (Richard and Cheyrezy, 1995). Coarse aggregates are removed in RPC and fine aggregates, such as silica sand and quartz powder with a maximum grain size of 0.6 mm, are used to provide homogeneous concrete. Large amounts of cementitious materials, such as cement, silica fume, pozzolanas, meager water-to-binder ratio (W/B), fibers and a considerable volume of superplasticizer are needed to produce RPC as a type of ultra-high-performance concrete (UHPC). The W/B ratio is determined based on the fluidity of the fresh concrete and the maximum density of the demolded reactive powder concrete (Richard and Cheyrezy, 1995), typically less than 0.2. Therefore, some parts of cement particles would not be fully hydrated even by suitable curing. Although the dense structure of RPC leads to obtaining suitable properties, pozzolanic materials, mainly silica fume, play an essential role in obtaining extreme performance by filling micro-pores, consuming up the portlandite (calcium hydroxide) produced by cement hydration and forming secondary-hydrated calcium-silicate (C-S-H) chains (Eq. 1).

$$(Portlandite)Ca(OH)_2 + SiO_2 \rightarrow C - S - H$$
$$(Secondary\ C - S - H). \qquad (1)$$

Moreover, it is necessary to use an optimum content of pozzolanic materials. For instance, Ge et al. (2023) have reported that excessive cement replacement with slag powder or fly ash reduces the strength of RPCs in the early stage and increases water absorption (Ge et al., 2023). Fibers prevent cracks from opening and improve the mechanical properties, such as rupture modulus and mainly ductility of RPCs (Richard and Cheyrezy, 1995; Dugat et al., 1996; Bayard and Plé, 2003). Also, using steam or autoclave curing and pressure applied on the fresh concrete significantly improve the microstructure of RPC (Yazici et al., 2013; Canbaz 2014). Another advantage of RPC is its feasibility in constructing precast concrete (Tadros et al., 2020).

When the stone powder was used as a cement-replacement material, results usually showed decreased concrete properties. In contrast, an increase in the properties was reported in the case of fine-aggregate substitution. However, more substitution of stone powders as fine aggregate diminishes the concrete properties (Ramezanianpour et al., 2009; Liu et al., 2011; Rajasekar et al., 2018; Chakherlou and Shervani Tabar, 2019; Savadkoohi and Reisi, 2020). For instance, Savadkoohi and Reisi (2020) investigated using stone-cutting waste in producing RPCs. Results showed that the mechanical properties of RPC were improved by incorporating granite waste up to 30% replacement of silica sand (Savadkoohi and Reisi, 2020).

Similarly, Venkatesan et al. (2022) reported that substituting granite powder with cement at the optimum level of 15% enhances the performance of RPC (Venkatesan et al., 2022). Also, the effects of ground limestone powder on the fluidity and strength of RPC were studied by Liu et al. (2011), showing a significant increase in flexural strength of RPC by increasing limestone-powder substitution up to 30% and a considerably decreased viscosity with the addition of ground limestone powder (Liu et al., 2011). The same results were reported by Chakherlou and Shervani Tabar (Chakherlou and Shervani Tabar, 2019). Moreover, Rajasekar et al. (2018) substituted granite waste as quartz powder with up to 40% replacement ratios and the results showed that replacing granite waste up to 30% enhances compressive strength (Rajasekar et al., 2018).

However, the concrete industry uses large volumes of raw materials and their production requires a large amount of energy, where about 1 ton of CO_2 is liberated per ton of cement production. This amount is about 7% of the world's CO_2 emissions and is estimated to be increased in the following decades, causing worldwide climate change. Therefore, considerable efforts are needed to reduce the CO_2 emissions associated with the concrete industry (Shao et al., 2006; Aïtcin and Mindess, 2011).

CO_2 gas capturing or storing is a method for reducing greenhouse-gas emissions. The captured CO_2 can be permanently stored in underground geological formations or injected at great depths into the ocean to dissolve (Mourits, 2012). Conversely, a more intriguing option introduced by Berger is to use CO_2 gas to cure concrete elements (Berger et al., 1972). Calcium and calcium-silicate minerals can chemically react with CO_2, converting them into calcium carbonates. Portland cement can be efficiently used to mineralize CO_2, where such direct sequestration of CO_2 is called carbonation curing or CO_2 curing of cement-based materials. Since RPCs contain a considerable amount of cementitious materials, it is estimated that the mineralization of CO_2 will be significant, where 1 kg cement can absorb 0.5 kg CO_2 to form 1.5 kg silica gel and calcium carbonates according to the following reaction (Berger et al., 1972; Shao et al., 2006):

$$C_nS + (n-x)CO_2 + yH_2O \rightarrow C_xSH_y + (n-x)CaCO_3. \quad (2)$$

Although Eq. 2 is the primary reaction in obtaining the strength of concretes, CO_2 gas can react with the hydration product of cement particles, such as calcium hydroxide (CH) and C-S-H and turn them into silica gel and calcium carbonates (Eqs. 3 and 4) (Meng et al., 2019). When CH is consumed, the media's pH will drop and other phases will break down (Tu et al., 2018).

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O. \quad (3)$$

$$(CaO)_x(SiO_2)(H_2O)_z + xCO_2 \rightarrow xCaCO_3 + SiO_2(H_2O)_t + (z-t)H_2O. \quad (4)$$

Mentioned reactions lead to accelerated hydration, early strength gains, elimination of $Ca(OH)_2$ in the cement paste, efflorescence and permeability reduction, as the advantages of curing concrete in a CO_2-rich atmosphere. Applying this type of curing on the industrial scale is currently under active consideration. Concrete moist surfaces in direct contact with carbon dioxide will be rapidly carbonated, but a layer of already carbonated concrete will slow down the carbonation of the fresh concrete interior layers (Escobar et al., 2013). This process, in turn, is controlled by the water saturation of the capillary pores. The carbonation speed is not only governed by concentration gradients, interconnection of pores and thickness of the already carbonated concrete, but also by the size and geometry, degree of water saturation, type of binder, temperature, exposure time, paste volume and the partial pressure of CO_2. (Shao and Shi, 2006; Shi and Wu, 2008; Zhan et al., 2016b; Long et al., 2023). For instance, Long et al. (2023) indicated that the increment of pore water saturation produced by the carbonation process would reduce the CO_2 diffusivity and consequently decrease the carbonation speed (Long et al., 2023). Furthermore, research revealed that an optimum content exists for some parameters, maximizing the carbonation speed. For instance, porous concretes seem to have an optimum water saturation at a higher degree than denser concretes (Lagerblad, 2005).

Most concrete structures, however, contain reinforcements that may rust when the concrete is carbonated. Therefore, non-reinforced concretes, particularly precast elements, have a great potential to eco-friendly absorb the most harmful gas (CO_2) as much as possible in case of carbonation curing by adjusting the critical parameters, such as the relative humidity (RH) of the chamber, curing temperature, pressure, CO_2 concentration, the concrete's porosity and water-to-cement ratio (Shao and Shi, 2006; Shi and Wu, 2008; Zhan et al., 2016b), where the amount of carbonated materials is needed to be monitored in a time frame (Lagerblad, 2005). Researchers have systematically studied carbonation curing of calcium-silicate minerals and improvements in compressive strength, surface hardness and durability of non-reinforced cement-based products have been reported (Young et al., 1974; Goodbrake et al., 1979; Qin et al., 2019). In addition, CO_2 curing of plain and some novel concrete-containing different cement replacement materials has been investigated (Monkman and Shao, 2006; Shi and Wu, 2008; Kou et al., 2014; Zhan et al., 2016b; Zhan et al., 2016a; Ahmad et al., 2022; Qin et al., 2019; Rahmani and Gheib, 2019). For instance, Monkman and Shao (Monkman and Shao, 2006), Kou et al. (2014) and Zhan et al. (2016) have investigated slag-cement concretes and recycled-aggregate concrete performances under carbonation curing, respectively (Kou et al., 2014; Zhan et al., 2016b; Zhan et al., 2016a). Also, Ahmad et al., Shi and Wu and Rahmani and Montazegheib systematically studied CO_2 curing of self-compacting, lightweight and pervious concretes, respectively (Shi and Wu, 2008; Ahmad et al., 2022; Rahmani and Gheib, 2019).

Several researchers have investigated the carbonation curing of concretes containing limestone powder. For instance, Tu et al. (2018) investigated CO_2 curing of plain concretes, in which limestone powder was substituted as cement up to 50%. Results showed that 10% limestone substitution improves concrete's properties (Tu et al., 2018). However, there are a few research studies on the CO_2 curing of RPCs (Cao et al., 2022), where they considered the combination of 10% CO_2 and 90% air as the carbonation curing media. Therefore, CO_2 curing of RPCs is investigated in this study, where waste limestone powder was substituted as silica sand. Since the size distribution of waste limestone powder is finer than that of the silica sand, it is predicted that waste limestone powder can improve the packing density of silica sand. Therefore, more substitution of limestone powder can be considered. Consequently, the present study's main objects are consuming waste limestone powder in RPCs as much as possible and simultaneously improving the mechanical and physical properties of RPCs utilizing carbonation curing.

MATERIALS AND METHODS

Materials

Binders: Locally sourced ordinary Portland cement type II and silica fume, respectively, produced by Kordestan and Iran ferroalloy companies, were used in this study as binders. Table 1 shows their chemical compositions and physical properties.

Table 1. Chemical composition and physical properties of the binders

	CaO %	**SiO_2 %**	**Fe_2O_3 %**	**Al_2O_3 %**	**MgO %**	**SO_3 %**	**Na_2O %**	**K_2O %**	**L.O.I %**	**Specific gravity**	**Specific surface (cm^2/g)**
Cement	64	21.5	4.32	4.69	1.45	2.34	0.17	0.56	4.1	3.2	3250
Silica fume	0.49	96.4	0.87	1.32	0.97	0.1	0.31	1.01	-	2.5	20000

Silica sand (S): A locally sourced silica sand with 0.7% water absorption, a specific gravity of 2.6 and a fineness modulus of 2.68 was used as the aggregate to produce RPC mixtures. Fig. 2 shows silica sand's particle-size distribution, indicating that its nominal maximum size is 1.1 mm and it lacks particles finer than 300 microns.

Limestone powder (LP): The waste limestone powder was retrieved from filter presses in the Kasra stone production plant in Zanjan, Iran. Its water absorption capacity and specific gravity were 1% and 2.7, respectively. Fig 2 shows the grading curve of the limestone powder, pointing out that its nominal maximum size is 2 mm and a half of it is finer than 75 microns. The combination grading curve of the silica sand plus limestone powder is shown in Fig. 2, indicating that the substitution of waste limestone powder significantly improves the grading curve.

Fibers: Chopped basalt fiber, 20 mm long, with 15-µm diameter and elastic modulus of 82 GPa was used in the RPC mixes.

Superplasticizer: The polycarboxylate-based ABAPLAST WR-4610 superplasticizer with a specific gravity of 1.12 was used to keep the workability of the RPCs constant.

Silica gel: Renewable silica gel with a grain size of 3-6 mm was used to absorb the evaporated water in the CO_2 chamber during the carbonation curing of the RPCs. The silica gel's water-absorption capacity was measured at 40%.

Figure (1): Cutting off a limestone block rock in Kasra stone production plant, Znjan, Iran

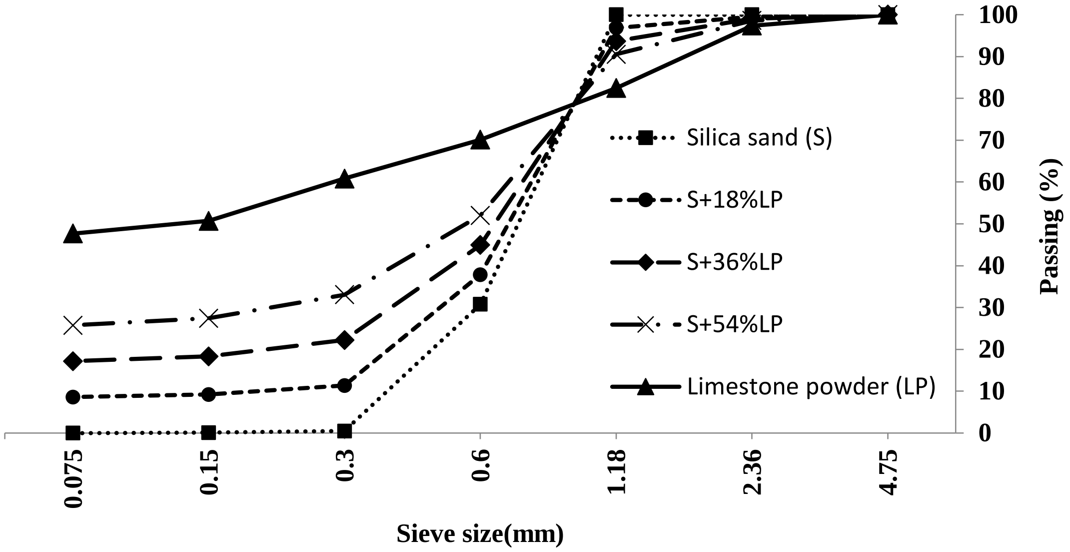

Figure (2): Grading curve of the silica sand (S) and limestone powder (LP) in different combinations

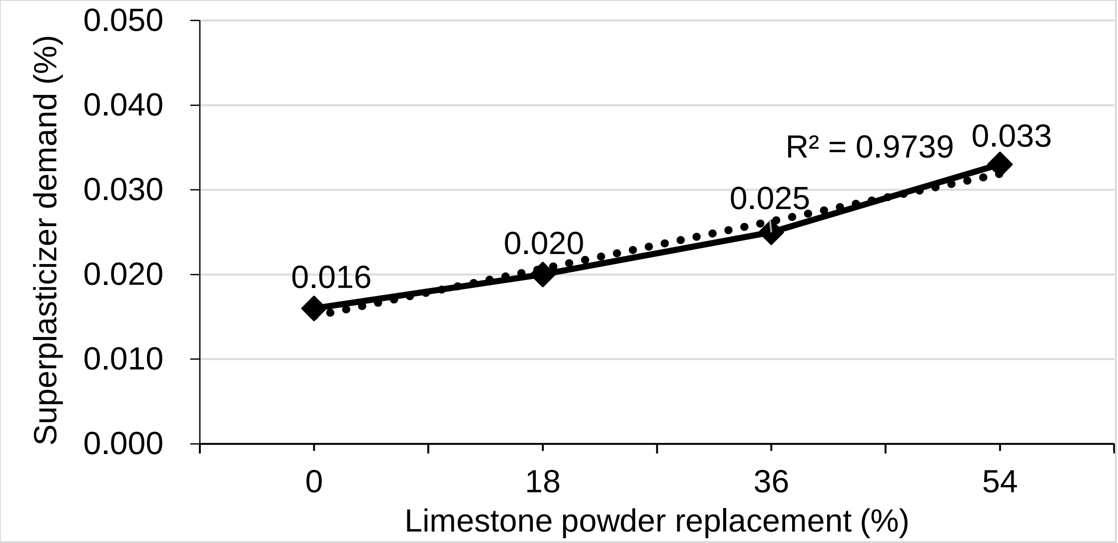

Figure (3): Superplasticizer demand over limestone powder substitution to obtain constant workability

Mix Designs and Sample Preparation

The present study aims to investigate further substituting waste limestone powder as silica sand in the RPCs. Since previous studies have revealed that limestone powders improve the concretes' properties by substituting up to 30% of silica sand and the initial assessment showed that 54% replacement of limestone powder led to the densest packing of the dry materials of the RPC, mixtures with 0%, as a control mixture, 18%, 36% and 54% of limestone powder replacement were considered in this research. Proportions of the considered mix designs are shown in Table 2, where a water-to-binder ratio of 0.27, a silica fume-to-binder ratio of 0.25, a fiber content of 9 kg/m^3 and a binder content of 1200 kg/m^3 were kept constant in the mixtures. Moreover, the workability of the mixtures, measured using the flow-table test, was kept constant (18-20 cm) by incorporating the superplasticizer.

Table 2. Details of the considered mix designs

	Cement (kg/m^3)	Silica fume (kg/m^3)	Silica sand (kg/m^3)	Limestone powder (kg/m^3)	Basalt fiber (kg/m^3)	W/B
LP0	900	300	1100	0	9	0.27
LP18	900	300	902	198	9	0.27
LP36	900	300	704	396	9	0.27
LP54	900	300	506	594	9	0.27

Fig. 3 shows the superplasticizer demand to achieve the desired workability, where the ratio of superplasticizer by mass of binder was linearly increased by increasing waste limestone powder. Reduction of workability in the case of limestone substitution has been widely reported in the literature (Ramezanianpour et al., 2009; Liu et al., 2011; Chakherlou and Shervani Tabar, 2019).

Conventional mixing methods are inadequate for producing RPCs due to their finer ingredients and low water-to-binder ratio. For instance, Hiremath and Yaragal (2017) reported that RPC mixes made with a low-speed mixer have a porous structure and using a high-speed mixer improves the quality of RPCs (Hiremath and Yaragal, 2017). The following process is therefore used to produce a homogenous mixture in the present study based on the recommendations. First, all dry ingredients of RPC, including cement, silica fume, silica sand, limestone powder and basalt fiber, were mixed at the slow speed of a standard mortar mixer for 5 min. Subsequently, water and superplasticizer were added to the mixture and mixing was continued for further 5 min. Then, the mixer was stopped for 30 s and RPCs on the sides of the bowl collected and scraped down into the batch. Finally, the batch was mixed at a high speed for 5 min to get a homogenous mixture. Thanks to the mixture being highly cohesive and uniform, it was poured into metallic molds at two layers with dimensions of 50×50×50 mm (for compressive strength), 40×40×160 mm (for flexural strength) and 25×25×285 mm (for shrinkage measurements), immediately after mixing, ready to be compacted. The specimens were kept in the molds for 24 h at room temperature with relative humidity (RH) of 95%. Then, the specimens were demolded and subsequently cured in a water bath (moist curing for up to 90 days) or the CO_2 chamber (CO_2 curing for up to 48 h). Moreover, the specimens were dried for 24 hours at 50 ºC in an oven before the carbonation process to reduce their moisture content near the optimal content. This process is called *preconditioning* in carbonation curing (Shi et al., 2012; Zhang and Shao, 2016).

Experiments

This study investigated compressive and flexural strengths, drying, carbonation and autogenous shrinkages, as well as the CO_2 uptake of the RPCs. The mechanical experiments were conducted after 7, 28 and 90 days of moist curing and 6, 12, 24 and 48 hours of CO_2 curing.

Compressive-and flexural-strength tests were performed according to ASTM C109 and ASTM C348, respectively, where the setup for concrete specimens was used for the compressive tests.

Drying shrinkage of concrete is the reduction in volume caused by water withdrawal from the hardened concrete in unsaturated air. Carbonation shrinkage is the reduction in volume caused by the chemical reaction between CO_2 and cementitious materials. Drying and carbonation shrinkages can result in the formation of cracks. However, autogenous shrinkage refers to the volume reduction of cementitious materials by hydration. Since the absolute volume of hydration products is about 10% smaller than the sum of the absolute volume of the reacted cement and water, autogenous shrinkage develops as soon as the hydration reaction starts and it can be very significant in low-w/b ration concretes, such as RPCs.

Since drying, autogenous and carbonation shrinkages most likely occur in the cement paste and the content of the cement paste together with the water-to-binder ratio was considered constant in the mixtures (see Table 2), no significant difference is expected with the specimens containing different amount of waste limestone powder. Accordingly, only the control and mixture containing 54% waste limestone powder (LP54) were considered to measure the mentioned shrinkages. Drying, carbonation and autogenous shrinkages of the prismatic specimens were determined by length-change measurements in the unsaturated moist state, CO_2 media and sealed state, respectively, at the considered ages, according to ASTM C490. The sealed media were created using self-adhesive waterproof tape on all sides of the specimens and silicone adhesive beyond the pins to prevent moisture loss. Autogenous shrinkage was measured after demolding the prismatic specimens for 24 h. Two specimens were considered for each test and their average was reported.

Since the cementitious content of the mixtures was kept constant, it is predicted that there is no significant difference in the CO_2-uptake content of the RPCs. Even so, the carbonation depth was assessed using a solution of phenolphthalein indicator that appears colorless at the carbonated area. Moreover, CO_2-uptake content was determined by measuring the mass loss of the RPC powders between 500ºC and 850ºC and using Eq. 5, where M_{850} and M_{500} are the powder mass at the relevant temperatures (Zhan et al., 2016b; He et al., 2018). No additional specimens were considered for these experiments. First, CO_2-cured flexural specimens were tested for the considered purpose and then, the phenolphthalein indicator was sprayed on the fractured surface of the specimens and the carbonation depth was determined. Additionally, some powder was prepared using a drill at the exact location for each specimen to measure the CO_2 uptake, where the drill dug a thorough hole in the middle of the broken prismatic specimens.

$$CO_2\text{uptake (\%)}=\frac{M_{500}-M_{850}}{M_{500}}\times 100. \tag{5}$$

Moreover, a scanning electron microscope (SEM), a powerful tool, was used to explain unknown items.

Carbonation Curing of the Specimens

The setup assembled in previous research (Rahmani and Gheib, 2019) was also used for CO_2 curing of RPCs. The *preconditioning* process was applied to the specimens before carbonation curing started. Then, the specimens were placed in the chamber, where some silica gels were needed to absorb the evaporated water and then, a vacuum was applied to the chamber. Afterwards, 97% pure CO_2 gas was injected into the chamber with the pressure inside adjusted to 1 bar using a regulator to supply CO_2 gas continuously. Since the structure of RPCs will be highly dense, it is supposed that the concretes will need more time for proper carbonation. Therefore, the period of carbonation curing was considered equal to 6, 12, 24 and 48 h and then, the specimens were ready to be tested.

RESULTS AND DISCUSSION

Compressive Strength

The results of the compressive-strength tests are shown in Figs. 4 and 5. Fig. 4 shows the compressive strength of waste limestone-modified RPCs in the case of moist (Fig. 4-a) and carbonation curing (Fig. 4-b). Fig. 5 shows compressive- (Fig. 5-a) and relative compressive-strength development of waste limestone-modified RPCs over curing time in case of carbonation curing to the relevant 28 days' compressive strength of moist cured ones (Fig. 5-b). Fig. 4-a shows that the RPCs obtained the desired compressive strength even after seven days of moist curing, in which they covered about 80% of 28 days' compressive strength after seven days of moist curing. All RPCs obtained more than 100 MPa compressive strength after 28 days of moist curing, where increasing waste limestone powder substitution increased compressive strength. Liu et al. reported similar results, indicating that a certain amount of ground limestone powder leads to higher strength of RPCs due to the physical-filling effect and reduction of the nucleation barrier (Liu et al., 2010). Savadkoohi and Reisi (2020) reported that a 30% replacement of granite waste silica sand in the RPC increases compressive strength by 78% (Savadkoohi and Reisi, 2020). Since in this study the waste limestone powder substitution of up to 54% improves the grain-size distribution of the aggregates (see Fig. 2), compressive strength was significantly increased despite increasing the specific surface of the aggregate. Also, compressive-strength development is significant at later ages, increasing to 26% at 90 days, implying further curing of RPCs.

Figures 4-b and 5 show that increasing CO_2 curing time increases compressive strength. However, the increasing rate depends on the waste limestone replacement fraction. All RPCs obtained more than 100 MPa compressive strength after 24 h of CO_2 curing, indicating that at least 24 h of carbonation curing is needed to obtain the desired compressive strength.

Moreover, a decrease and an increase in compressive strength were observed by increasing the replacement ratio of limestone powder at the earlier (6-12 h) and later (24-48 h) ages of CO_2 curing, respectively (see Fig. 4-b). Since limestone powder makes RPCs denser and consequently reduces time-dependent carbonation reactions, limestone powder prevents more carbonation in the depth of the concretes at the earlier age of 6-12 h of CO_2 curing. Consequently, increasing limestone powder substitution decreased compressive strength. However, by increasing the carbonation time, the dense structure of the RPCs leads to an increase in compressive strength.

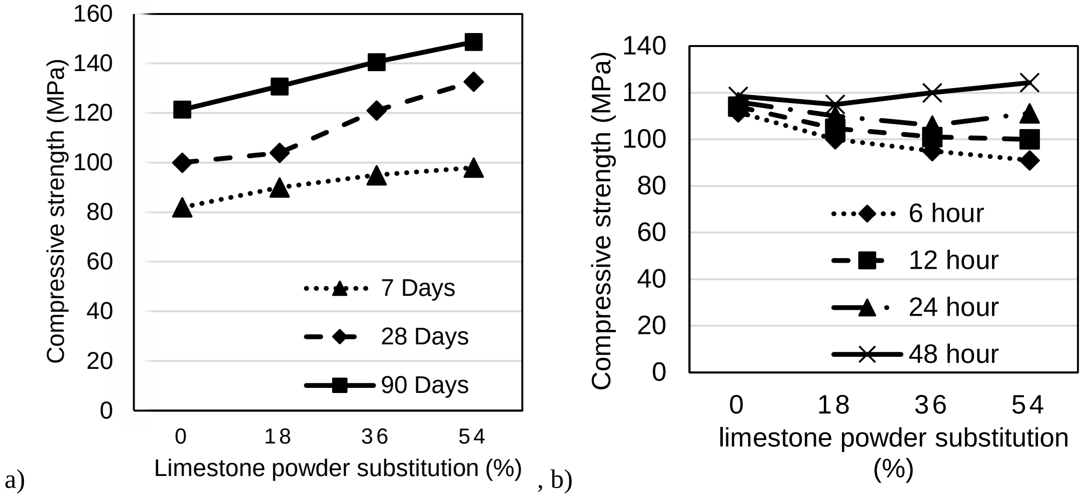

Figure (4): **Compressive strength of RPCs, a) moist-cured and b) CO_2-cured**

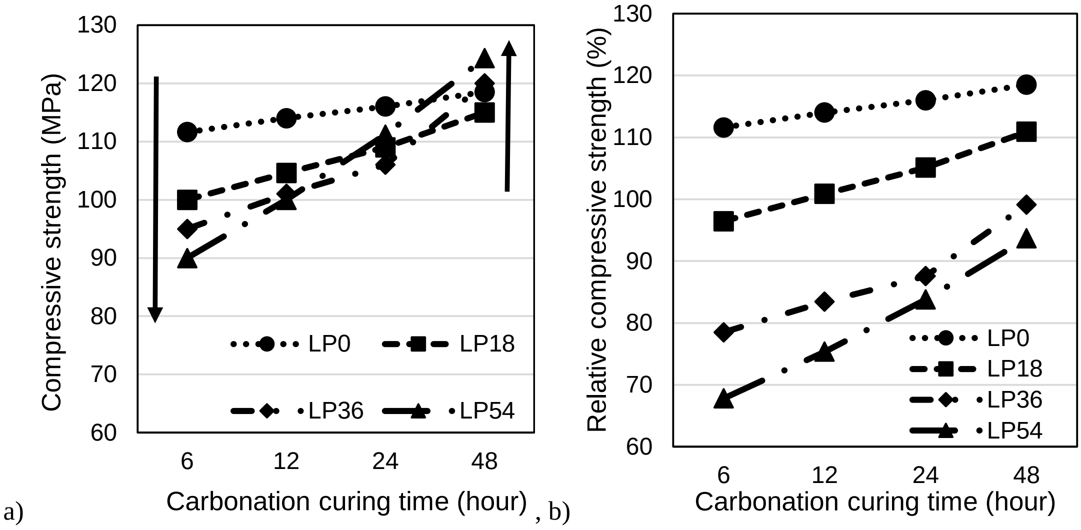

Figure (5): Compressive-strength development of RPCs over carbonation curing time a) real and b) relative to the relevant 28-day-moist-cured

Fig. 5-a shows that the compressive strength rate increases by increasing the waste limestone substitution, where the RPC with 54% limestone substitution showed the minimum compressive strength after six h of CO_2 curing. However, it obtained the maximum strength after 48 h of CO_2 curing. Also, the relative compressive strength of the concretes to the relevant 28 days moist-cured compressive strength is shown in Fig. 5-b, indicating that more than 67, 75, 83 and 93% of 28-day moist-cured compressive strength were obtained after 6, 12, 24 and 48 h of CO_2 curing. Therefore, it is suggested that the curing time of the RPCs in the carbonation media would be more than 24 h. Also, the increase rate in the compressive strength is linearly dependent on the curing time for any substitution of waste limestone powder, increased by increasing the substitution fraction. For instance, the rate of strength increase in the CO_2 chamber is calculated at 0.16 MPa/h for LP0, while

this rate is obtained at 0.61 MPa/h for LP54.

Additionally, when CO_2 curing time was increased from 6 to 12 h, the compressive strength of LP0 and LP54 was increased by 2% and 11%, respectively. The dense structure of RPCs prevents CO_2 gas penetration; therefore, improvements are insignificant at the early stages of CO_2 curing. Consequently, these improvements are linearly increased for later ages.

The mixture containing 54% of waste limestone powder showed higher compressive strength in both curing cases when carbonation curing was considered more than 24 h. However, the mixture with no substitution of limestone powder showed minimum and maximum compressive strength in the case of moist and carbonation curing, respectively, when the carbonation-curing time was less than 12 h.

Flexural Strength

The results of flexural-strength tests with the replacement ratio of waste limestone powder as silica sand are shown in Fig. 6, where the flexural strength of moist-cured RPCs was significantly increased by increasing the curing time. However, flexural strength or rupture modulus diminished considerably in the case of CO_2 curing, while the carbonation time had no considerable effect. Since basalt fibers were decomposed under the CO_2 curing of RPCs, flexural strength was dramatically decreased in the case of carbonation curing. Fig. 7 shows the SEM image of the fractured surface for the RPCs containing 36% replacement of limestone powder in case of moist and carbonation curing. Basalt fibers soundly subsisted in the moist-cured specimens (Fig. 7-a), while they were decomposed when the specimens were cured in the CO_2 chamber (Fig. 7-b). Apparently, basalt minerals can react with CO_2 gas (Schaef et al., 2009).

Meanwhile, the flexural strength of the RPCs is about 0.15-0.2 of its compressive strength at the age of 7 days of moist curing, which is decreased up to 0.12 by increasing the curing time up to 90 days. However, these values are decreased to 0.055-0.075 for carbonation curing of the RPCs, similar to the high-strength concretes ratio. This means that the basalt fibers' performance disappeared in the case of CO_2 curing. Moreover, it is evident in Fig. 6 that the substitution of limestone powder decreases flexural strength in the case of moist curing. However, flexural strength was increased by increasing the replacement ratio of limestone powder. Therefore, it can be understood that the replacement of limestone powder has diverse outcomes of compressive and flexural strengths. The dense structure of the limestone-modified RPCs cannot promote the flexural strength of the RPCs, since micro-cracks substantially govern the flexural strength in the interfacial transition zones, which depends on the thickness of the paste around the aggregates. Since the limestone powder was finer than the silica sand, its replacement increased the specific surface of the aggregates, consequently reducing the paste's thickness around the aggregate and, thus, the rupture modulus. The obtained results were contrary to those of Liu et al. (Liu et al., 2010) and Savadkoohi and Reisi in the case of moist curing, in which a 60% increase in flexural strength was observed by substituting 30% granite waste as silica sand in the RPC (Savadkoohi and Reisi, 2020).

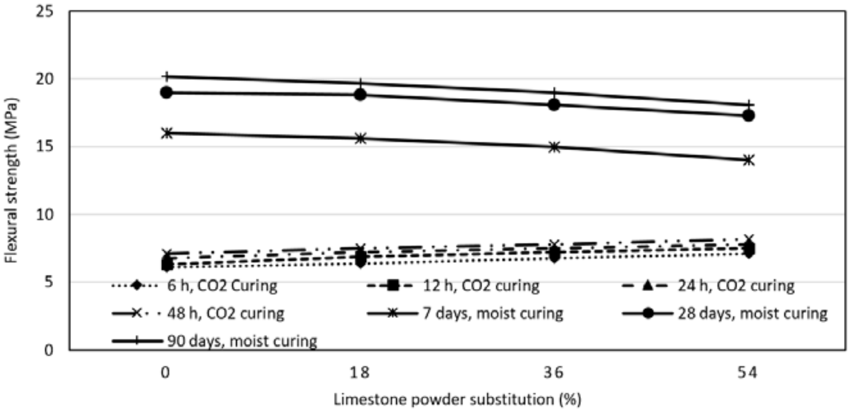

Figure (6): Flexural strength of the limestone-modified RPCs in case of moist and carbonation curing

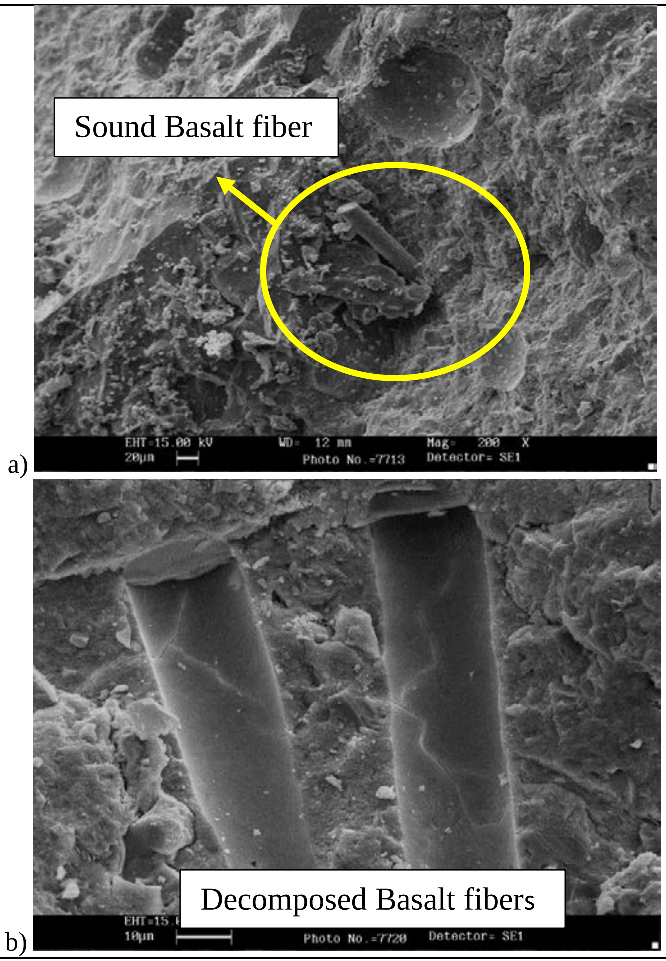

Figure (7): The fractured surface of 36% limestone-modified RPCs, a) moist-cured, b) CO$_2$-cured

Shrinkages

Drying Shrinkage

The drying shrinkage of the specimens was measured according to the length change in moist and dry conditions. First, the lengths of 28 days of moist-cured specimens were measured in SSD condition. Then, the specimens were retained in the dry air of the laboratory and their length changes were measured after 2, 3, 7, 14, 21, 28 and 42 days of the laboratory exposure. It is clear that the specimens were dried and the drying shrinkage was developed. Fig. 8 shows that the drying shrinkage was increased by increasing the drying exposure time, but 54% limestone substitution as silica sand decreased the shrinkage in the first three days. However, an increase in shrinkage was observed at later ages, up to 42 days. The dense structure of limestone-modified RPC prevents water withdrawal at earlier ages. However, since the limestone powder's water absorption is more than the silica sand and consequently, the content of dryable water in the 54% limestone-modified RPC is more than the control one, the drying shrinkage was increased at the later ages. Notably, the results of the drying shrinkages are consistent with those of similar studies (Tam et al., 2012; Ahmad et al., 2014). For instance, Tam et al. reported that the drying shrinkage of RPCs with W/B=0.2 varied between 400 and 1100×10^{-6} depending on the superplasticizer's content (Tam et al., 2012).

Carbonation Shrinkage

First, the length of 24-h moist-cured specimens was measured in SSD condition as the initial length. After placing them in the CO$_2$ chamber after *preconditioning*, their length changes were measured after 6, 12, 24 and 48 h of carbonation curing. Clearly, the carbonation mechanism releases water and the silica gel around the specimens absorbs the evaporated water and then, the carbonation shrinkage is developed. Fig. 9 shows that the carbonation shrinkage was increased by increasing the carbonation time, but 54% limestone substitution as silica sand significantly decreased the shrinkage of the RPC. Since 54% limestone substitution as silica sand changed the structure of RPC to the dense state, this dense structure prevents more carbonation and consequently, the carbonation shrinkage of the 54% limestone-modified RPCs was significantly decreased. Also, it is clear that the carbonation shrinkage of the limestone-modified concretes is substantially less than the drying shrinkage. However, the carbonation shrinkage of the RPCs with no limestone substitution is more than the drying shrinkage. Therefore, it is strongly proposed to use limestone powder in the case of CO_2 curing.

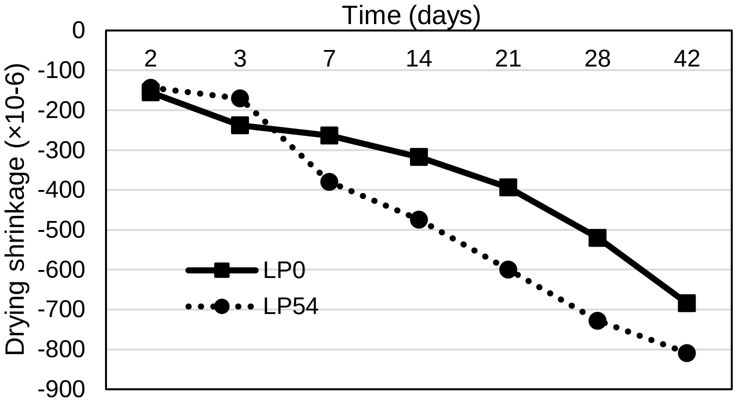

Figure (8): The drying shrinkage of RPCs

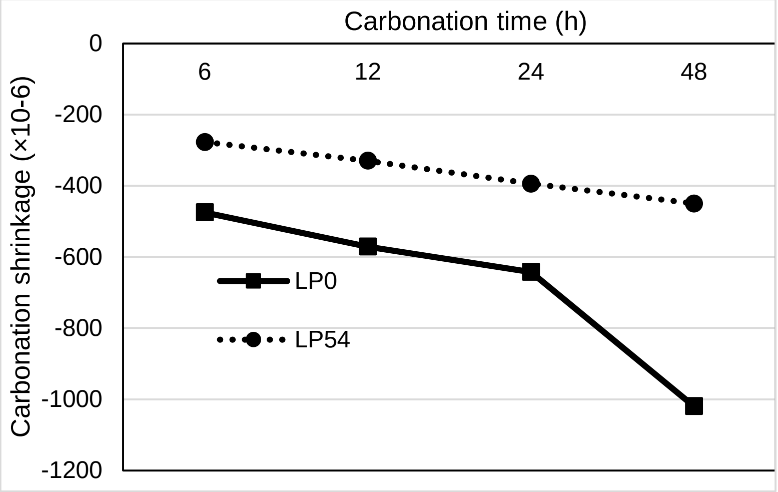

Figure (9): The carbonation shrinkage of RPCs

Autogenous Shrinkage

First, the length of 24-h moist-cured specimens was measured in SSD condition as the initial length and then, all sides of the specimens were sealed up and retained in the laboratory room for up to 70 days. The secondary length of the specimens was measured after 28, 56 and 70 days and consequently, the autogenous shrinkage of the specimens was calculated. Results of the autogenous shrinkage are shown in Fig. 10, indicating that the autogenous shrinkage of the RPCs increases with time. However, it is still considerably less than drying and carbonation shrinkages. Moreover, limestone powder substitution as silica sand significantly decreased the autogenous shrinkage, since limestone powder acts like porous aggregates and internal curing occurred in the specimens, reducing the autogenous shrinkage. The results are consistent with the outcomes reported by Mo et al., which indicated that internal curing utilizing superabsorbent polymer reduces autogenous shrinkage (Mo et al., 2017).

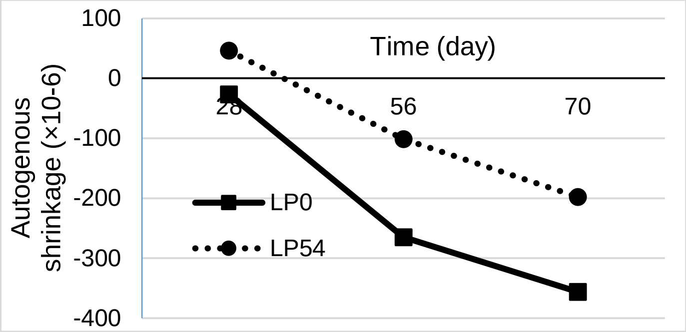

Figure (10): **The autogenous shrinkage of RPCs**

CO_2 Uptake

Carbonation depth was determined by phenolphthalein, which loses color when pH is less than ten, corresponding to the carbonated depth. Since the water-to-binder ratio of the RPCs was low, the dense structure of the RPCs prevented more penetration of CO_2 gas and therefore, the carbonation depth was insignificant. For instance, carbonation depth was measured at about 1.5-2 mm for LP54 after 48 h of carbonation curing. Since there are no apparent differences between the results, this test was ignored in the present study.

Correspondingly, the CO_2 uptake of the RPCs was measured and the results are shown in Fig. 11, indicating that increasing the carbonation time leads to more absorbed CO_2 by the RPCs while the carbonation process is not linearly proportional to the carbonation time despite the limestone powder's linear substitution. Additionally, since the carbonation depth is small and the powder was prepared across the total thickness of the specimens, the CO_2 uptake of the specimens was considerably low. Moreover, CO_2 uptake was increased by increasing the waste limestone powder substitution, where the rates depend on the carbonation curing time and the amount of limestone substitution. Relative CO_2 uptakes of the RCPs after 12 and 48 h of CO_2 curing to the relevant control concretes are shown in Fig. 12, indicating that the carbonation process was significantly intensified by increasing the limestone-replacement ratio despite producing a dense structure of the RPCs. For instance, a 9% increase in CO_2 uptake for LP18 from 12 to 48 h of CO_2 curing reached 29% for LP54. It is supposed that CO_2 gas separately reacts with limestone grains which may contain reactive compounds, such as quicklime.

Therefore, it is recommended to consider the CO_2 curing time of RPCs over 48 h regarding the CO_2 uptake results. In comparison, a 24-h CO_2 curing time is enough to obtain suitable mechanical properties.

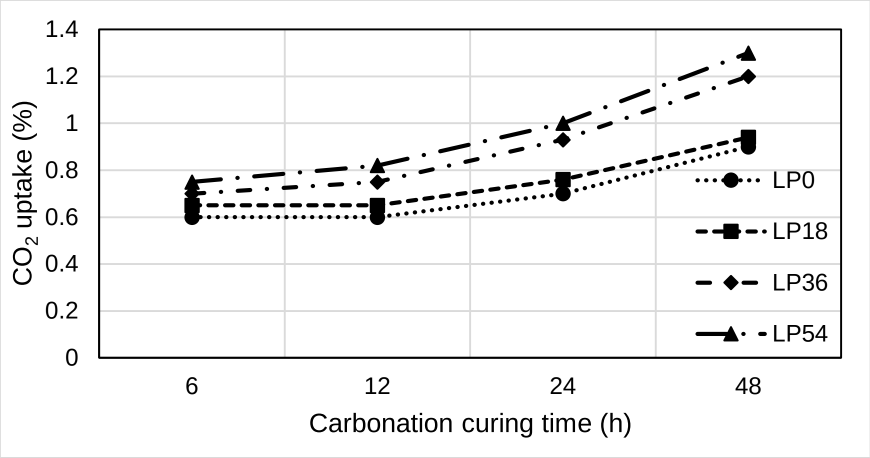

Figure (11): **CO_2 uptake of RPCs over carbonation curing time**

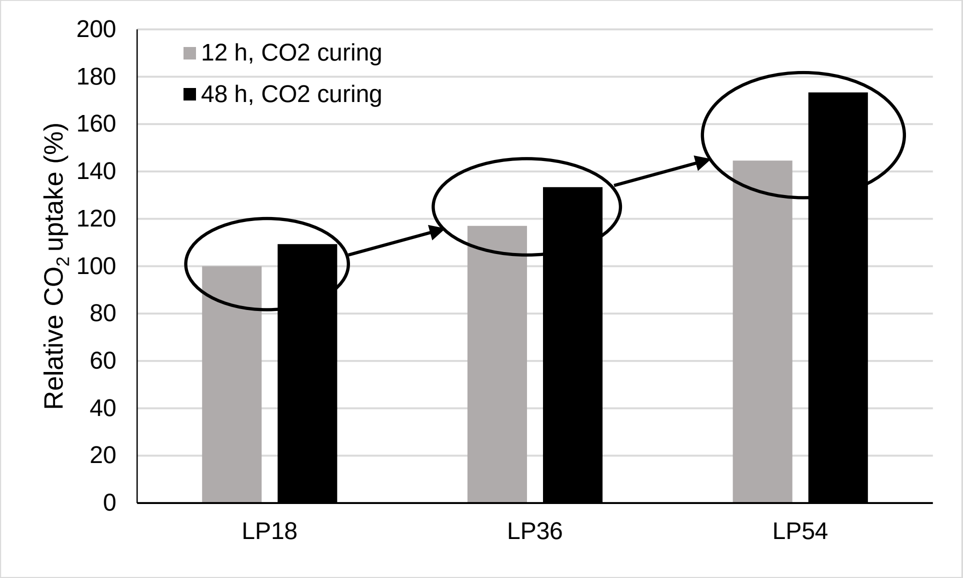

Figure (12): **Relative CO_2 uptake of RPCs over carbonation curing time to the relevant control concrete**

CONCLUSIONS

An experimental program was conducted to investigate the effects of CO_2 curing on the physical and mechanical properties of RPCs where waste limestone powder was substituted for silica sand for up to 54%. Moist and CO_2 curing were applied for up to 90 days and 48 h, respectively, where the CO_2 uptake of the mixtures was separately investigated. The conclusions emanating from the experimental results are as follows:

1- Waste limestone powder and CO_2 gas can be eco-friendly when used in producing RPCs, where their properties are even improved.

2- The carbonation reactions of the limestone-modified RPCs continuously proceeded up to 48 h of CO_2 curing and needed more time to complete the reactions.

3- CO_2-cured RPCs obtained up to 80% of the compressive strength of 28-day moist-cured RPCs.

4- Substituting waste limestone powder as silica sand increased compressive strength and CO_2 uptake by increasing the replacement ratio. For instance, 54% substitution of waste limestone increased compressive strength and CO_2 uptake up to 32% and 73%, respectively.

5- SEM images showed that basalt fibers are inadequate for CO_2 curing, particularly in RPCs. Since basalt fibers are decomposed during the carbonation curing, the flexural strength of CO_2-cured RPCs significantly diminished.

6- Waste limestone powders significantly decreased the carbonation and autogenous shrinkages of RPCs.

Acknowledgments

The authors gratefully acknowledge the University of Zanjan for supporting this study as an MSc thesis.

REFERENCES

Ahmad, S., Assaggaf, R.A., Adekunle, S.K., Al-Amoudi, O.S.B., Maslehuddin, M., and Ali, S.I. (2022). "Influence of accelerated carbonation curing on the properties of self-compacting concrete mixtures containing different mineral fillers". Eur. J. Environ. Civ. Eng., 26 (1), 76-93. https://doi.org/10.1080/19648189.2019.1649197

Ahmad, S., Zubair, A., and Maslehuddin, M. (2014). "Effect of the key mixture parameters on shrinkage of reactive powder concrete". Sci. World J., 2014 (1), 1-8, Article ID. 426921. https://doi.org/10.1155/2014/426921

Aïtcin, P.C., and Mindess, S. (2011). "Sustainability of concrete". CRC Press, London.

Bayard, O., and Plé, O. (2003). “Fracture mechanics of reactive powder concrete: Material modeling and experimental investigations”. Eng. Fract. Mech., 70 (7-8), 839-851. https://doi.org/10.1016/S0013-7944(02)00153-4

Berger, R.L., Young, J.F., and Leung, K. (1972). “Acceleration of hydration of calcium silicates by carbon dioxide treatment”. Nat. Phys. Sci., 240 (97), 16-18. https://doi.org/10.1038/physci240016a0

Canbaz, M. (2014). “The effect of high temperature on reactive powder concrete”. Constr. Build. Mater., 70 (1), 508-513. https://doi.org/10.1016/j.conbuildmat.2014.07.097

Cao, H., Liang, Z., Peng, X., Cai, X., Wang, K., Wang, H., and Lyu Z (2022). “Research into carbon dioxide curing's effects on the properties of reactive powder concrete with assembly unit of sulphoaluminate cement and ordinary Portland cement”. Coatings, 12 (2), 1-13. https://doi.org/10.3390/coatings12020209

Chakherlou, J., and Shervani Tabar, B. (2019). “Use of limestone powder instead of a part of silica sand in reactive powder concrete”. Modares Civ. Eng. J., 18 (6), 51-61.

Dugat, J., Roux, N., and Bernier, G. (1996). “Mechanical properties of reactive powder concretes”. Mater. Struct. Constr., 29 (4), 233-240. https://doi.org/10.1007/bf02485945

Escobar, M.M., Di Paolo, A., and Vazquez, A. (2013). “Carbon dioxide uptake by concrete modified with carbon nanotube”. Proc. Int. Conf. Offshore Mech. Arct. Eng., OMAE 6, Paper No. OMAE2013-11475, V006T11A024; 1-5. https://doi.org/10.1115/OMAE2013-11475

Ge, W., Wang, A., Zhang, Z., Ge, Y., Chen, Y., Li, W., Jiang, H., Shuai, H., Sun, C., Yao, S., and Qiu, L. (2023). “Study on the workability, mechanical property and water absorption of reactive powder concrete”. Case Stud. Constr. Mater., 18. e01777. https://doi.org/10.1016/j.cscm.2022.e01777

Goodbrake, C.J. Young, J.F., and Berger, R.L. (1979). “Reaction of beta-dicalcium silicate and tricalcium silicate with carbon dioxide and water vapor”. J. Am. Ceram. Soc., 62 (3-4), 168-171. https://doi.org/10.1111/ j.1151-2916.1979.tb19046.x

He, P., Shi, C., and Poon, C.S. (2018). “Methods for the assessment of carbon dioxide absorbed by cementitious materials”. Carbon Dioxide Sequestration Cem. Constr. Mater., Woodhead Publishing, 103-126. https://doi.org/10.1016/B978-0-08-102444-7.00006-X

Hiremath, P.N., and Yaragal, S.C. (2017). “Influence of mixing method, speed and duration on the fresh and hardened properties of reactive powder concrete”. Constr. Build. Mater., 141 (1), 271-288. https://doi.org/10.1016/j.conbuildmat.2017.03.009

Kou, S.C., Zhan, B.J., and Poon, C.S. (2014). “Use of a CO_2- curing step to improve the properties of concrete prepared with recycled aggregates”. Cem. Concr. Compos., 45 (1), 22-28. https://doi.org/10.1016/j.cemconcomp.2013.09.008

Lagerblad, B. (2005). “Carbon dioxide uptake during concrete life cycle: State-of- the-art”. Swedish Cement and Concrete Research Institute.

Lin Chan, C., and Zhang, M. (2023). “Effect of limestone on engineering properties of alkali-activated concrete: A review”. Constr. Build. Mater., 362, 129709. https://doi.org/10.1016/j.conbuildmat.2022.129709

Liu, J., Song, S., Sun, Y., and Wang, L. (2011). “Influence of ultrafine limestone powder on the performance of high-volume mineral admixture reactive powder concrete”. Adv. Mater. Res., 152-153 (1), 1583-1586. https://doi.org/10.4028/www.scientific.net/AMR.152-153.1583

Liu, S., and Yan, P. (2010). “Effect of limestone powder on microstructure of concrete”. J. Wuhan Univ. Technol. Mater. Sci., 25 (2), 328-331. https://doi.org/10.1007/s11595-010-2328-5

Long, J., Peng, Z., Feng, H., and Yang, A. (2023). “Study of carbonation-depth prediction of unsaturated concrete considering carbonation-produced water”. Jordan J. Civ. Eng., 17 (1), 83-96. https://doi.org/10.14525/jjce.v17i1.08

Meng, Y., Ling, T.C., Mo, K.H., and Tian, W. (2019). “Enhancement of high-temperature performance of cement blocks *via* CO_2 curing”. Sci. Total Environ., 671 (1), 827-837. https://doi.org/10.1016/j.scitotenv.2019.03.411

Mo, J., Ou, Z., Zhao, X., Liu, J., and Wang, Y. (2017). "Influence of superabsorbent polymer on shrinkage properties of reactive powder concrete blended with granulated blast furnace slag". Constr. Build. Mater., 146 (1), 283-296. https://doi.org/10.1016/j.conbuildmat.2017.04.105

Monkman, S., and Shao, Y. (2006). "Assessing the carbonation behavior of cementitious materials". J. Mater. Civ. Eng., 18 (6), 768-776. https://doi.org/10.1061/(ASCE)0899-1561(2006)18:6(768)

Mourits, F. (2012). "Capture and sequestration of greenhouse gases in Canada". Natural Resources Canada, Ottawa.

Qin, L., Gao, X., and Chen, T. (2019). "Influence of mineral admixtures on carbonation curing of cement paste". Constr. Build. Mater., 212 (1), 653-662. https://doi.org/10.1016/j.conbuildmat.2019.04.033

Rahmani, H., and Gheib, M.M. (2019). "CO_2 curing of hydrated lime-modified pervious concretes". Mag. Civ. Eng., 92 (8), 106-114. https://doi.org/10.18720/MCE.92.9

Rajasekar, A., Arunachalam, K., and Kottaisamy, M. (2018). "Durability of ultra-high-strength concrete with waste granite sand as partial substitute for aggregate". J. Comput. Theor. Nanosci., 15 (2), 446-452. https://doi.org/10.1166/jctn.2018.7108

Ramezanianpour, A.A., Ghiasvand, E., Nickseresht, I., Mahdikhani, M., and Moodi, F. (2009). "Influence of various amounts of limestone powder on performance of Portland limestone-cement concretes". Cem. Concr. Compos., 31 (10), 715-720. https://doi.org/10.1016/j.cemconcomp.2009.08.003

Richard, P., and Cheyrezy, M. (1995). "Composition of reactive powder concretes". Cem. Concr. Res., 25 (7), 1501-1511. https://doi.org/10.1016/0008-8846(95)00144-2

Savadkoohi, M.S., and Reisi, M. (2020). "Environmental protection based sustainable development by utilization of granite waste in reactive powder concrete". J. Clean. Prod., 266, 121973. https://doi.org/10.1016/j. jclepro.2020.121973

Schaef, H.T., McGrail, B.P., and Owen, A.T. (2009). "Basalt- CO_2-H_2O interactions and variability in carbonate mineralization rates". Procedia-Energy, 1 (1), 4899-4906. https://doi.org/10.1016/j.egypro.2009.02.320

Shao, Y., Mirza, M.S., and Wu, X. (2006). "CO_2 sequestration using calcium-silicate concrete". Can. J. Civ. Eng., 33 (1), 776-784.

Shao, Y., and Shi, C. (2006). "Carbonation curing for making concrete products: An old concept and a renewed interest". In: 6th International Symposium on Cement and Concrete. 19- 22 September, China, 2, 823-830.

Shi, C., He, F., and Wu, Y. (2012). "Effect of pre-conditioning on CO_2 curing of light-weight concrete block mixtures". Constr. Build. Mater., 26 (1), 257-267. https://doi.org/10.1016/j.conbuildmat.2011.06.020

Shi, C., and Wu, Y. (2008). "Studies on some factors affecting CO_2 curing of light-weight concrete products". Resour. Conserv. Recycl., 52 (8-9), 1087-1092. https://doi.org/10.1016/j.resconrec.2008.05.002

Singh, S., Khan, S., Khandelwal, R., Chugh, A., and Nagar, R. (2016). "Performance of sustainable concrete containing granite cutting waste". J. Clean Prod., 119 (1), 86-98. https://doi.org/10.1016/j.jclepro.2016.02.008

Tadros, M.K., Gee, D., Asaad, M., and Lawler, J. (2020). "Ultra-high-performance concrete: A game changer in the precast concrete industry". PCI J., 65 (3), 33-36. https://doi.org/10.15554/pcij65.3-06

Tam, C.M., Tam, V.W.Y., and Ng, K.M. (2012). "Assessing drying shrinkage and water permeability of reactive powder concrete produced in Hong Kong". Constr. Build. Mater., 26 (1), 79-89. https://doi.org/10.1016/ j.conbuildmat.2011.05.006

Tu, Z., Shi, C., and Farzadnia, N. (2018). "Effect of limestone powder content on the early-age properties of CO_2-cured concrete". J. Mater. Civ. Eng., 30 (8), 1-12. https://doi.org/10.1061/(ASCE)MT.1943-5533.0002232

Venkatesan, B., Kannan, V., and Sophia, M. (2022). "Utilization of granite powder and glass powder in reactive powder concrete: assessment of strength and long-term durability properties". Can. J. Civ. Eng., 49 (6), 885-898. https://doi.org/10.1139/cjce-2021-0258

Wang, D., Shi, C., Farzadnia, N., Shi, Z., and Jia, H. (2018). "A review on effects of limestone powder on the properties of concrete". Constr. Build. Mater., 192 (1), 153-166. https://doi.org/10.1016/j.conbuildmat.2018.10.119

Yazici, H., Deniz, E., and Baradan, B. (2013). “The effect of autoclave pressure, temperature and duration time on mechanical properties of reactive powder concrete”. Constr. Build. Mater., 42 (1), 53-63. https://doi.org/10.1016/j.conbuildmat.2013.01.003

Young, J.F., Berger, R.L., and Breese, J. (1974). “Accelerated curing of compacted calcium silicate mortars on exposure to CO_2”. J. Am. Ceram. Soc., 57 (9), 394-397. https://doi.org/10.1111/j.1151-2916.1974.tb11420.x

Zhan, B.J., Poon, C.S., and Shi, C.J. (2016a). “Materials’ characteristics affecting CO_2 curing of concrete blocks containing recycled aggregates”. Cem. Concr. Compos., 67 (1), 50-59. https://doi.org/10.1016/j.cemconcomp.2015.12.003

Zhan, B.J., Xuan, D.X., Poon, C.S., and Shi, C.J. (2016b). “Effect of curing parameters on CO_2 curing of concrete blocks containing recycled aggregates”. Cem. Concr. Compos., 71 (1), 122-130. https://doi.org/10.1016/j.cemconcomp.2016.05.002

Zhang, D., and Shao, Y. (2016). “Early-age carbonation curing for precast reinforced concretes”. Constr. Build. Mater., 113 (1), 134-143. https://doi.org/10.1016/j.conbuildmat.2016.03.048

Zhang, K., Liu, F., Yue, Q., and Feng, J. (2020). “Effect of granite powder on properties of concrete”. Asia-Pacific J. Chem. Eng., 15 (S1), e2468. https://doi.org/10.1002/apj.2468.