Enhancing the carbonation of MgO cement porous blocks through improved curing conditions

Unluer, C.; Al-Tabbaa, A.

2014

Unluer, C., & Al-Tabbaa, A. (2014). Enhancing the carbonation of MgO cement porous blocks through improved curing conditions. *Cement and concrete research*, 59, 55-65.

<https://hdl.handle.net/10356/106372>

<https://doi.org/10.1016/j.cemconres.2014.02.005>

© 2014 Elsevier. This is the author created version of a work that has been peer reviewed and accepted for publication by Cement and Concrete Research, Elsevier. It incorporates referee's comments but changes resulting from the publishing process, such as copyediting, structural formatting, may not be reflected in this document. The published version is available at: <http://dx.doi.org/10.1016/j.cemconres.2014.02.005>.

Downloaded on 26 Apr 2023 17:27:27 SGT

Enhancing the carbonation of MgO cement porous blocks through improved curing conditions

C. Unluer^{a,*}, A. Al-Tabbaa^b

^a School of Civil & Environmental Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798

^b Department of Engineering, University of Cambridge, Trumpington Street, Cambridge, CB2 1PZ, UK

* Corresponding author. Tel.: +65 91964970, E-mail address: ucise@ntu.edu.sg

Abstract:

The use of reactive magnesia (MgO) as the binder in porous blocks demonstrated significant advantages due to its low production temperatures and ability to carbonate, leading to significant strengths. This paper investigates the enhancement of the carbonation process through different curing conditions: water to cement ratio (0.6-0.9), CO₂ concentration (5-20%), curing duration (1-7 days), relative humidity (55-98%), and wet/dry cycling frequency (every 0-3 days), improving the carbonation potential through increased amounts of CO₂ absorbed and enhanced mechanical performance. UCS results were supported with SEM, XRD, and HCl acid digestion analyses. The results show that CO₂ concentrations as low as 5% can produce the required strengths after only 1 day. Drier mixes perform better in shorter curing durations, whereas larger w/c ratios are needed for continuous carbonation. Mixes subjected to 78% RH outperformed all the others, also highlighting the benefits of incorporating wet/dry cycling to induce carbonation.

Keywords: (A) Humidity; (B) Microstructure; (C) Carbonation; (C) Compressive Strength; (D) MgO

1. Introduction

Amongst all the greenhouse gases that cause anthropogenic climate change, carbon dioxide (CO_2), whose atmospheric concentrations have been rising over 30% when compared to the pre-industrial levels [1-4], makes the largest contribution from human activities. Out of the various methods proposed for cutting down the amount of CO_2 produced, mineral sequestration, where CO_2 is chemically stored in the form of solid carbonates by the carbonation of minerals, provides a permanent and safe solution since the formed carbonates are thermodynamically stable with a large sequestration capacity available worldwide. Two of the most common alkaline earth metals in nature, calcium and magnesium [5], are generally used for mineral CO_2 sequestration purposes due to their worldwide availability and relatively high purities. The solid material produced as a result of CO_2 sequestration can be utilized in a wide range of building materials [6, 7].

As the primary material in the construction industry, Portland cement (PC) presents a major potential in reducing the anthropogenic emissions of greenhouse gases due to its high global production of over 3 billion tonnes per year [8], causing the emission of almost the same amount of CO_2 , which represents 5-10% of global anthropogenic CO_2 emissions [9-11]. Alternative cement formulations with lower energy consumption and carbon footprints are currently being developed as a part of the sustainability initiatives aimed at reducing the environmental impacts of the construction industry. An example of these novel cement formulations is MgO cements, whose use in porous blocks facilitates safe and permanent storage of CO_2 .

Produced at $\sim 700\text{-}1000^\circ\text{C}$, reactive MgO hydrates at a similar rate to PC, thereby eliminating the expansion problems observed in the case of dead-burned MgO [12]. The sustainability advantages of MgO include its: (i) ability to carbonate and gain strength accordingly, (ii) considerable durability enhancement due to the higher resistance of the hydration and carbonation products in aggressive environments, (iii) lower sensitivity to impurities enabling the utilization of large quantities of waste

and industrial by-products [7, 13], and (iv) potential to be fully recycled where MgO is used alone as the binder as its carbonation process produces magnesium carbonates, which are the predominant source for the production of magnesia. Alternatively, certain limitations exist regarding the manufacture and implementation of MgO cements in the construction sector. These include the unfamiliarity, insufficient documentation and low record of reliability of MgO as opposed to the high validation and market confidence of PC; and the relatively low availability of the raw materials and proximity to existing production facilities, a majority of which is located in China, leading to increased environmental impacts. Table 1 provides a comparison of energy, raw material and CO₂ emissions of MgO and PC production, indicating the high carbonation potential of MgO (i.e. ratio of the mass of carbonated MgO to the mass of initially included MgO within a certain mix), which has been realized up to 100% in previous work [14].

Table 1

Sustainability factors of MgO and PC [15]

Sustainability Factors	Magnesia [16]	PC [17]
Total energy requirement (MJ/t)	2415	1760
Raw material required (t/t)	2.08	1.5
Carbon dioxide emissions (t/t)	1.4	0.85
Desirable carbonation rate	100%	none
Final emissions after carbonation (t/t)	0.22	0.37

The fundamental properties of reactive MgO and its use in cement formulations has been investigated in previous research, where the hydration behaviour [12, 18-20], microstructure [19], and carbonation performance [15, 21-24] were studied. The use of MgO alone was observed to have special advantages in terms of mechanical and durability performance and carbonation potential over the PC-MgO blends, depending on the application [15, 22, 25, 26], leading to successful commercial scale-up trials [23, 24]. This work showed that porous blocks containing 10% MgO for their cement component

achieved compressive strengths more than twice of the corresponding PC blocks under elevated CO₂ curing, where the strength development was directly related to the degree of carbonation.

In the case of unreinforced porous block applications where reactive MgO is used as the cement component, MgO hydrates to form brucite (Mg(OH)₂, magnesium hydroxide), which reacts with CO₂ and additional water to form a range of strength providing hydrated magnesium carbonates (HMCs) when subjected to the right curing conditions, as shown by Equations 1-4. The rate and degree of carbonation, the formation of HMCs, and the associated strength development depend on several contributing factors including composition and characteristics of MgO, block mix design, use of additives and admixtures, particle size distribution of the aggregates, particle packing, and porosity of the hardened concrete as well as curing conditions (namely relative humidity (RH), temperature, transport and partial pressure of CO₂) [13, 27-30]. Only a small number of these variables have been considered in previous work [12-22], which introduced the direct influence of the w/c ratio, RH and CO₂ concentration on the carbonation process of MgO cement porous blocks.

Water to cement (w/c) ratio plays an important role in the permeability of mixes and the diffusion of CO₂ through porous blocks. Gaseous CO₂ readily dissolves into the pore water of concrete, turning into a carbonic acid solution, which neutralizes alkalis in the pore water, mainly consuming magnesium hydroxide. Carbonic ions dissociate from the carbonic acid solution, releasing protons,

which then react with magnesium ions to form a range of HMCs. During this process, water not only blocks pores and therefore hinders CO₂ diffusion, it also provides a medium for carbonation to take place, explaining the increase in carbonation depth as the RH or the amount of water in the pore structure increases [31]. The reduced permeability coefficient and lower diffusion rate in the case of lower water contents was studied by Powers et al. [32]. Alternatively, Cook and Hover [33] showed that an increase in the water content results in an increase in porosity which decreases as hydration proceeds, since the initial water is progressively used to form the hydration products.

The effect of the w/c ratio on the carbonation of MgO cements was also studied through varying saturation degrees between 2-98%, where modifications in the initial saturation levels (i.e. volume of water/volume of voids) of MgO-based masonry units led to different strengths [22]. Results indicate the increased rate of strength gained by the lower initial saturation levels, with a decline in strengths in the long term due to the absence of sufficient water for continuous carbonation. Samples initially subjected to 98% saturation and then let to dry to some extent resulted in higher strengths than those that had the same initial saturation level but were under a constant supply of water the entire time and hence maintained the imposed RH, showing that excessively high and low saturation levels inhibit the carbonation reactions. Also influenced by the variations in the surrounding atmosphere that result in the loss or gain of water within the mixes, low RHs delay the carbonation reactions, whereas an increase in RH results in a decrease of air-filled pores available for diffusion. This also affects the carbonation process since diffusion of CO₂ is much slower in water than it is in air, with a diffusion coefficient of $1390 \times 10^{-8} \text{ m}^2/\text{s}$ in air, whereas this value is 10^4 - 10^5 less in water [34, 35]. Since carbonation is retarded when the material is saturated with water, it is important to optimize the w/c ratio corresponding to maximum adsorption on the surface of the pores before capillary condensation, in order to achieve a maximum level of carbonation. The optimum range of RH for the highest rate of carbonation is reported to range between 40-80% [34, 36], depending on the mixture composition. Another study has shown that a significant increase in carbonation depth was observed when the RH was increased from 84% to 92% [37].

Another factor influencing the progress of carbonation is CO_2 concentration. An increase in the concentration of CO_2 increases the rate of carbonation, especially at high w/c ratios [34]. Vandeperre and Al-Tabbaa (2007) [38] reported an increase in stiffness with increasing CO_2 concentration from 5% to 20%, whereas both set of samples ultimately reached similar toughness values. Mixes subjected to lower RHs showed a lower rate of increase in stiffness in time and gradually stopped increasing, whereas an increase in RH led to continuous development of stiffness.

Part of an extensive investigation into the effect of the variables mentioned above, the work presented in this paper concentrates on the impact of different curing conditions on the carbonation process and investigates the carbonation potential of MgO in porous blocks. Around 60 million m^2 of blocks are produced per year in the UK [39], whereas in North America, the yearly production of blocks reached 8 billion units by 2007 [40]. Some of the applications where blocks are widely used include construction of road side paveways, garage and parking floorings, driveways, walls, and floor coverings of commercial buildings. The basic requirements for cement-aggregate blocks, specified in BS EN 771-3:2003, are categorized as shape and dimensions (390-440mm (l) x 75-225mm (w) x 190-215mm (h)), strength and density, and durability. The strength requirement for common commercially distributed masonry blocks is 7MPa [41, 42].

The carbonation reactions involved during mineral sequestration take place naturally, albeit very slowly under atmospheric conditions due to the low partial pressure of CO_2 in the atmosphere [43]. Therefore this research aims to facilitate the absorption of CO_2 emitted from the production of MgO by increasing the amount of CO_2 stored within porous blocks, where MgO is the main binding material, through improved curing conditions. CO_2 captured and recovered from flue gases emitted from power plants and engine exhausts can also be used during this process, eliminating any further damage to the environment. Since the concentration of CO_2 obtained from these sources ranges between 3% (e.g. natural gas-fired turbines) and 13% (e.g. coal-fired boilers) [44, 45], this work aims to minimize the CO_2 concentration needed to fit within this range, while satisfying the strength requirement for blocks, 7 MPa. The obtained results are presented in two main sections, studying the effects of: (i)

water/cement ratio, CO₂ concentration, and curing duration, and (ii) relative humidity and wet/dry cycling, on the carbonation of MgO cement porous blocks. Hence the objectives were to investigate:

- (i) The curing conditions that give rise to the maximum carbonation level and rate
- (ii) The ability of MgO-based blocks to carbonate in low CO₂ concentration levels
- (iii) The effect of different w/c ratios in enhancing the degree of carbonation and strength
- (iv) The use of different methods in the quantification of degree of hydration and carbonation of blocks with different compositions

2. Materials and methods

The MgO-cement formulations used for this study included reactive MgO from Richard Baker Harrison, UK; natural aggregates (sharp sand and gravel) from Ridgeons, Cambridge, UK; and pulverized fuel ash (pfa) from Ratcliffe-on-Soar power station in Nottingham, UK as part of the aggregates. The main chemical compositions of the MgO and pfa as well as some physical properties are presented in Table 2. In terms of cement content, MgO was kept constant at 10% by mass of the dry mix. Within this study, pfa was used as a filler in the blocks and made up 0% (i.e. n-mixes) or 5% (i.e. p-mixes) of the dry material. Addition of pfa as a partial replacement for cement not only enables the use of smaller amounts of cement, but also provides a solution for recycling this industrial by-product, therefore lowering the overall environmental impacts of the prepared mixes. Natural aggregates consisting of sharp sand (0-4mm, median particle diameter (D_{50})=0.7mm, coefficient of uniformity (C_U)=3.6) at 50%, and gravel (2-10mm, D_{50} =6.5mm, C_U =1.75) at 35% contents were used together with the 5% pfa to form the 90% content aggregate mix, as in related previous work [46, 47].

Measured according to BS EN 196-3:1995 [48], the standard consistence (SC) of the MgO and pfa pastes were 0.60 and 0.39, respectively. The SC of MgO alone was much higher than that of PC at 0.26 [25]. The dry components were initially mixed in a bench-scale food mixer, after which the previously determined amount water was added and the mixtures were placed in equal quantities in

cylindrical moulds with 50mm diameter. Mixes inside the moulds were then pressed with a uniaxial press by applying a force of 5 kN. This produced samples 65-75mm high, which were then immediately de-moulded and placed in the relevant curing environments under a constant temperature of 20°C. The effects of water/cement ratio (0.6-0.9), CO₂ concentration (5-20%), curing period (1-7 days), RH (55-98%), and wet/dry cycling frequency (every 1-3 days) on the progress of carbonation were studied individually by investigating density, strength, microstructure and carbonation quantification results. Table 3 summarizes the different mix compositions used. Two different compositions were utilized for the entire set of experiments, where the main difference was the pfa content: (i) p-mixes: 10% MgO, 5% pfa, 85% aggregates, and (ii) n-mixes: 10% MgO, 90% aggregates (sand:gravel at a ratio of 10:7). All samples were cured in the same outside environment and incubator whose CO₂ concentration and RH were adjusted accordingly to obtain the required curing conditions.

Samples cured under each RH were subjected to four different wet/dry cycling frequencies: 0-day cycling (i.e. control mix, kept constant in the incubator under dry conditions at all times), 1-day cycling (i.e. samples subjected to dry conditions first for 24 hours and then moved into wet conditions for further 24 hours), 2-day cycling (i.e. moved every 48 hours) and 3-day cycling (i.e. moved every 72 hours) until testing day. For dry curing, different salts listed in Table 4 were used to prepare supersaturated solutions, which were then placed in steel trays in the incubator two days before the start of the experiment to bring the RH down to the required level from the initial level ranging between 70-90%. The RH was continuously monitored and maintained at these required dry levels by renewing the salt solutions at certain frequencies. The wet environment was provided by placing the samples in a plastic container with a water level of ~2 cm. The plastic container was semi-closed to maintain high moisture levels with regular spraying.

The performance of blocks was assessed through density measured before carbonation and at each stage of testing by determining the change in mass and dimensions of the sample to obtain the volume; and unconfined compressive strength (UCS) measured on a Control Advantest 9 apparatus

by uni-axial loading in triplicates. The microstructures of representative samples from outer surfaces were observed by imaging fracture surfaces in a scanning electron microscope (SEM), JEOL JSM-5800 LV, facilitating elemental composition analysis. Quantification of CO₂ absorbed was achieved by the XRD-RIR technique and dissolving samples in HCl acid. The acid digestion method involved neutralization of solutions containing CO₂ and chemical decomposition of the carbonates through their reaction with HCl acid, explained by the following reactions:

X-ray diffraction (XRD), conducted on a Siemens D500 Diffractometer, provided qualitative and quantitative analyses of the crystalline phases present within the mixes. The samples were broken down to small pieces (e.g. <5mm) and then quartered before being ground down to 125µm to be analyzed under XRD. The relative diffraction peaks of various carbonates, Mg(OH)₂ and MgCO₃ in each mix were identified by using XRD analysis under the operating conditions of Cu Kα radiation (40 kV, 40 mA); scan rate: 2°/step; 2θ: 5-50°. The Reference Intensity Ratio (RIR) technique [49-53], which involves scaling the obtained diffraction data to the diffraction of a standard reference, was applied for the quantitative analysis of the phases present by making use of fluorite (CaF₂) at 20 wt% as the internal standard phase [54]. The integrated intensity of fluorite was compared to that of the phases of interest. Calibration curves for MgO and Mg(OH)₂, which were the components used for the purposes of quantitative analysis, were straight lines through the origin i.e. y=kx, where x is the RIR of the phase analyzed and y is the weight fraction of the component investigated. The value of k was 0.2886 and 0.3651 for MgO and Mg(OH)₂, respectively [15]. The RIR was acquired through dividing the integrated intensity of the strongest line of the phase with that of the standard.

Table 2

Chemical composition and physical properties of the MgO and pfa used, based on supplier datasheets (NM = not measured)

	CaO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	MgO	Specific gravity	Mean diameter (μm)	Specific Surface area (m ² /g)	Loss on ignition (%)
MgO	2.0	1.0	NM	NM	>94.0	3.00	45.0	16.3	2.0
Pfa	6.8	49.3	9.7	24.1	1.1	2.26	12.0	2.6	3.9

Table 3

Composition of the mixes produced for studying the effects of water/cement ratio, CO₂ concentration, and curing duration

Mix	MgO (%)	Pfa (%)	Sand (%)	Gravel (%)	w/c
p-0.6					0.6
p-0.7	10	5	50	35	0.7
p-0.8					0.8
p-0.9					0.9
n-0.6					0.6
n-0.7	10	0	53	37	0.7
n-0.8					0.8

Table 4

Dry conditions in the incubator for studying the effects of RH and wet/dry cycling

Mix	RH (%)	Salt used to provide the required RH
p-98 & n-98	98	-
p-84	84	Potassium Chloride
p-78 & n-78	78	Sodium Chloride

p-67	67	Cupric Chloride
n-55	55	Sodium Bromide

3. Results and discussion

3.1 Effect of water/cement ratio, CO₂ concentration, and curing duration

3.1.1 Density and strength development

Fig. 1 shows the density and strength development of p-mixes and n-mixes subjected to 7 days of accelerated carbonation at 10% CO₂ concentration and 98% RH. An average of 3% increase in density was observed after 7 days of carbonation of both mixes, corresponding to the formation of HMCs. Most mixes indicated significant strength developments, with values reaching 10.6 MPa and 4.0 MPa after only 1 day of carbonation of p-mixes and n-mixes, respectively. Carbonation of p-mixes led to 110% higher strengths than n-mixes, confirming that the lower densities of the former provided relatively more porous structures available for strength development through the formation of HMCs.

Strength results showed variations in accordance with the w/c ratios. Mixes with a w/c of 0.6 revealed poor compaction and crumbling during testing since their dry nature did not facilitate continuous carbonation. As water is necessary for both hydration and carbonation to take place, the low w/c ratios of these mixes delayed hydration and the subsequent carbonation processes, leading to small proportions of HMCs, also confirmed by the quantification results presented in Section 3.1.3.

Alternatively, relatively wet mixes with a w/c of 0.9 included pores saturated with water, thereby hindering the transport of CO₂ through the samples and delaying the formation of HMCs, which eventually led to low UCS results within the presented time frames. This effect was also confirmed by the detailed study of the crystalline phases, where the presence of brucite was observed at all stages

of carbonation. As shown in Fig. 3, the fact that brucite was present quite extensively even after 1 day shows that hydration has taken place, whereas the rate of carbonation was not as high as it is in other mixes.

A w/c of 0.7 resulted in the highest strength results in general for both sets of mixes. An increase in the w/c ratio from 0.7 to 0.8 had a positive impact on the strength development of p-mixes for longer durations of curing. Mixes with lower w/c ratios performed better in shorter curing durations due to the fast diffusion of CO₂ through the unsaturated pore network, whereas larger amounts of water were needed for carbonation to proceed for longer periods, as the initially available water was consumed during the formation of HMCs. These findings were in agreement with those stated in the literature [32, 55], underlining the segmentation of capillary pores for lower w/c ratios, accompanied with lower permeability coefficients.

The strength development of mixes with a w/c ratio of 0.7 over 7 days of accelerated carbonation at varying CO₂ concentrations is shown in Fig. 2. The density of both set of mixes subjected to 5%, 10%, and 20% CO₂ concentrations increased by ~1%, 4%, and 8% at the end of 7 days, respectively. While a higher increase in density was obtained as the CO₂ concentration increased, this trend was not necessarily reflected in the strength results. N-mixes performed very similarly under different CO₂ concentrations, especially during the first 3 days, indicating that CO₂ concentration is not the limiting factor in this case and carbonation can be improved through mix design. The difference in performance with varying CO₂ concentrations is more obvious for longer durations of curing (i.e. 7 days). On the other hand, although p-mixes show clear distinctions at early stages of carbonation, the strength results converge for longer durations. Both 10% and 20% CO₂ concentrations led to the same strength result of p-mixes, 24 MPa after 7 days of carbonation, highlighting the redundancy of the higher CO₂ concentration for longer periods.

Strengths as high as 7.0 MPa and 17.4 MPa were obtained by p-mixes after 1 and 7 days of carbonation under 5% CO₂ concentration, showing that the strength requirement for blocks, 7 MPa, can be achieved only after 1 day of carbonation under CO₂ concentrations as low as 5%. Going from 1 to 7 days, average increases in strength of ~160%, 120%, and 70% were attained by p-mixes subjected to 5%, 10% and 20% CO₂ concentrations, respectively. The rapid strength development under lower CO₂ concentrations signifies the diminishing differences between strength results for longer durations of carbonation. This is a good indication that after a certain point (e.g. 3 days), CO₂ concentration is not the limiting factor for the complete carbonation of MgO.

(a)

(b)

Fig. 1. Mixes with different w/c ratios at 10% CO₂ and 98% RH analyzed for (a) density and (b) strength

(a)

(b)

Fig. 2. Mixes with a w/c of 0.7 and 98% RH under different CO₂ concentrations analyzed for (a) density and (b) strength

3.1.2 Solid phases assemblage

Since they performed better than n-mixes in terms of strength, p-mixes were further evaluated for their crystalline composition, and quantification of their hydration and carbonation degrees. XRD diffractograms of p-mixes are shown in Fig. 3. Peaks of nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$), hydromagnesite ($4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) and dypingite ($4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$) were evident in all mixes even after only 1 day of carbonation, along with unhydrated MgO, indicating that not all the MgO initially included within the formulations was consumed in the formation of brucite and then HMCs. No brucite was observed in mixes p-0.6 and p-0.7, corresponding with the lower w/c ratios, which led to limited hydration and subsequent carbonation. Although overlapping with hydromagnesite, some peaks of brucite were evident in mixes p-0.8 and p-0.9, evident from both the peak at $18.7^\circ 2\theta$ and the bimodal peak at $38.0^\circ 2\theta$, as opposed to the corresponding single peaks of p-0.6 and p-0.7 at $38.0^\circ 2\theta$. This was linked with the higher w/c ratios of the former group. Also confirmed by the increasing strength results and reflected in the quantification results, the intensity of the brucite peak within mixes p-0.8 and p-0.9 reduced as the curing duration increased from 1 to 7 days (i.e. as carbonation progressed), since the formation of HMCs involves the use of water, thus progressively reducing the available water for the hydration process.

One of the most interesting findings of this study was the small presence of artinite, $\text{Mg}_2(\text{CO}_3)(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ peaks in most mixes, along with lansfordite, $\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$, after 1 day of carbonation of p-0.8. Having a lower stability field of CO_2 concentration than nesquehonite [56], lansfordite decomposes into nesquehonite [57, 58]. A strong peak of giorgiosite, $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5-6\text{H}_2\text{O}$, which belongs to the same group (group III) with hydromagnesite and dypingite due to the five Mg ions it contains, was observed within mix p-0.7 at 3 days. With its very similar chemical formula to that of dypingite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$), giorgiosite could be present as a transformation phase during the formation of further dypingite. On the other hand, the presence of artinite within mixes that

were subjected to accelerated levels of CO₂ differs from the findings of Marini [29], who suggested that formation of artinite requires less CO₂ than the amount present at ambient levels.

XRD diffractograms of p-0.7 subjected to different CO₂ concentrations are also presented in Fig. 3. In addition to dypingite, hydromagnesite, and artinite, all samples indicated the formation of nesquehonite, whose peak intensity increased with the CO₂ concentration. This particular HMC, with an elongated needle-like structure, raises the solid volume upon its conversion from brucite, therefore reducing the overall porosity and increasing stiffness. This change corresponds well with the increase in density observed after carbonation, also leading to high strength results. This finding is in agreement with several studies [27, 28, 30], showing that nesquehonite forms at ambient temperatures and elevated CO₂ levels. Although the thermal decomposition of nesquehonite into hydromagnesite is said to take place at temperatures higher than 50°C [57, 59-61], this transition was observed at ambient temperatures within the scope of this study since both hydromagnesite/dypingite and nesquehonite co-existed in all mixes.

Fig. 3. XRD diffractograms of all p-mixes with varying w/c ratios and CO₂ concentrations

3.1.3 Quantification of hydration and carbonation

A comparison between p- and n-mixes subjected to varying CO₂ concentrations in terms of their degree of hydration, carbonation, and MgO conversion measured by XRD analysis after 7 days of carbonation is provided in Table 5. Degree of hydration was calculated from the amount of MgO left unhydrated, whereas the amount of brucite that did not combine with the present water and CO₂ to form HMCs was used to calculate the degree of carbonation. Degree of MgO conversion was computed by multiplying the degree of hydration with degree of carbonation, therefore taking both processes into account. The absence of a brucite peak within p-mixes led to 100% carbonation, while n-mixes demonstrated incomplete carbonation. The degree of MgO conversion increased with CO₂ concentration, linked with the continuous formation of HMCs. The small difference between the results obtained by p-0.7 subjected to 10% and 20% CO₂ was consistent with the UCS results, indicating that after a certain point, CO₂ concentration was not the limiting factor for continuous carbonation. Incorporating the hydration and carbonation degrees, the degree of MgO conversion increased with curing time and was greater for p-mixes than n-mixes. The highest degrees of MgO conversions, 82% and 80%, were achieved by p-0.7 under 20% and 10% CO₂ concentrations, respectively, leading to the highest strength results amongst all mixes.

The higher hydration degrees achieved by n-mixes when compared to p-mixes suggest that the presence of pfa may have hindered the hydration process to some extent within the latter. This was possibly due to the common ion theory, which suggests that in the presence of two sparingly soluble salts with a common ion, the solubility of the initially less soluble salt will further decrease during their physical interaction [62]. In this case, the CaO present within pfa can hydrate, forming portlandite, whose solubility (2.4×10^{-2} mol/L) is higher than that of brucite (1.5×10^{-4} mol/L). The coexistence of portlandite and brucite, both containing an OH⁻ ion, results in a reduction in the solubility of the latter, leading to a slower hydration of MgO, as observed in the results obtained here. On the other hand,

although brucite formed extensively in the absence of pfa, its conversion into HMCs was lower, possibly due to the slower diffusion of CO_2 through the relatively denser n-mixes when compared to p-mixes. Although n-mixes demonstrated higher degrees of hydration (i.e. conversion of MgO into brucite) at all durations, it was the 100% carbonation (i.e. conversion of brucite into HMCs) achieved by p-mixes that explains their higher strength results, since brucite does not provide any microstructural strength.

Quantification values of p-mixes subjected to 10% CO_2 at varying w/c and curing durations are listed in Table 6. The increase in the degree of MgO conversion with curing time was obvious for all mixes. Mixes p-0.7 and p-0.8 achieved very similar conversions from 3 days onwards, also reflected by their mechanical performances. Mixes p-0.6, p-0.7, and p-0.8 achieved 100% carbonation in general, corresponding to the absence of the brucite peak during XRD analysis. The lower degrees of carbonation achieved by p-0.9 were linked with the slow diffusion of CO_2 under high w/c ratios.

Carbonation degrees of p-mixes measured by dissolving the samples in HCl acid are shown in Fig. 4, where the consistent trend between the results obtained by the two methods used for quantification purposes, XRD and HCl acid ingress, is evident. The results obtained by HCl acid analysis varied between 19-35%, 29-46%, and 34-50% after 1, 3, and 7 days of carbonation, respectively. The significant difference between the degrees of carbonation after 1 and 3 days of carbonation, after which a more gradual increase was observed for most mixes, indicate that carbonation took place much faster during the first 3 days of curing, whereas smaller increments of the CO_2 absorbed were recorded between 3 and 7 days.

Although there was a good agreement between the results in general, values obtained by XRD analysis (i.e. degree of MgO conversion) were mostly higher than those of HCl acid ingress (i.e. degree of carbonation), possibly linked with the discrepancies during HCl acid testing. The presence of amorphous phases invisible to XRD but soluble in acid, the high volatility of the acid, and the heat

emitted as a result of the rigorous reaction between the carbonated samples and HCl acid all influence the total weight loss. While dissolving the samples within HCl acid gives direct measurements of the CO₂ content within each mix, XRD analysis involves the calculation of hydration and carbonation through the presence of relevant peaks, which is not as straightforward as the former process. Another possibility is that the small sample broken down into powder form for XRD analysis may not be entirely representative of the parent block, which contained a high proportion (i.e. 35% by mass) of coarse aggregates that were hard to break into powder form. Therefore, differences in results obtained by these two methods are expected, especially since one is presented in terms of the “degree of carbonation” whereas the other one uses “degree of MgO conversion”, which incorporates both the degree of hydration and carbonation obtained by XRD. Another way to compare these methods is by observing the relationship between UCS and carbonation degree values obtained by each method, as shown in Fig. 5. R-squared values, realized by incorporating a linear trendline on the UCS vs. degree of MgO conversion/carbonation data, were obtained as 0.80 and 0.64 for XRD and HCl acid analyses, respectively. This is a good indication of the direct correlation between the degree of carbonation and strength values. Results obtained by XRD analysis were favored in this case due to the higher correlation coefficient, whereas the residual plots indicating the errors from the trendline suggest that there was no heteroskedasticity.

Table 5

Quantification of hydration and carbonation degrees of mixes with a w/c of 0.7 at 1-7 days subjected to varying CO₂ concentrations by XRD analysis

Mixes	MgO (w/w)	Brucite (w/w)	Degree of Hydration (%)	Degree of Carbonation (%)	Degree of MgO Conversion (%)	UCS (MPa)
n-5%CO ₂ -7d	0.0072	0.0756	93	44	41	12.8
n-10%CO ₂ -1d	0.0289	0.0504	71	51	36	4
n-10%CO ₂ -3d	0.0231	0.0455	77	59	46	8.1
n-10%CO ₂ -7d	0.0121	0.0609	88	52	46	13.8
n-20%CO ₂ -7d	0.0036	0.0527	96	62	60	15
p-5%CO ₂ -7d	0.0360	0	64	100	64	17.41
p-10%CO ₂ -1d	0.0580	0	42	100	42	10.6

p-10%CO ₂ -3d	0.0420	0	58	100	58	16.9
p-10%CO ₂ -7d	0.0200	0	80	100	80	23.53
p-20%CO ₂ -7d	0.0180	0	82	100	82	24.00

Table 6

Quantification of hydration and carbonation degrees of p-mixes subjected to 10% CO₂ concentration at varying w/c and curing durations by XRD analysis

Mixes	MgO (w/w)	Brucite (w/w)	Degree of Hydration (%)	Degree of Carbonation (%)	Degree of MgO Conversion (%)	UCS (MPa)
p-0.6-1d	0.065	0	35	100	35	9.3
p-0.6-3d	0.057	0	43	100	43	19.1
p-0.6-7d	0.034	0	66	100	66	21.1
p-0.7-1d	0.058	0	42	100	42	10.6
p-0.7-3d	0.042	0	58	100	58	16.9
p-0.7-7d	0.020	0	80	100	80	23.5
p-0.8-1d	0.061	0.0100	39	82	32	4.7
p-0.8-3d	0.038	0	62	100	62	17.4
p-0.8-7d	0.016	0	84	100	84	25.0
p-0.9-1d	0.073	0.0210	27	46	13	2.2
p-0.9-3d	0.066	0.0180	34	63	22	6.2
p-0.9-7d	0.059	0.0095	41	84	34	17.6

Fig. 4. Comparison of the 2 different quantification methods for carbonation degree

Fig. 5. Relationship between UCS and carbonation degree measured by XRD and HCL acid analyses

3.2 Effect of RH and wet/dry cycling

3.2.1 Density and strength development

UCS results of mixes p-0.7 and n-0.7 subjected to 10% CO₂ under different RHs and wet/dry cycling frequencies for 18 days are shown in Figs. 6(a) and (b). The initial densities of p- and n-mixes ranged between 2.06-2.18 g/cm³ and 2.15-2.22 g/cm³, respectively. The extra humidity provided by higher RHs increased the density of both set of mixes; while those subjected to 67% and 55% RH demonstrated the lowest densities due to the relatively dry environment under which they were cured. Samples subjected to 78% RH outperformed all other RHs in the case of both p- and n-mixes, achieving strengths as high as 34 MPa and 24 MPa after 18 days curing, respectively. Amongst p-mixes subjected to 4 different RHs ranging between 67-98%, the highest strength results, 34 MPa, were achieved under 78% RH, followed by 28.7 MPa at 98% RH. Containing 5% pfa within their formulations, p-98 and p-78 resulted in ~130% and 680% higher strengths on average than the corresponding n-mixes without pfa, n-98 and n-78, respectively. This difference in strength was more pronounced for those that were not subjected to any cycling. As the RH decreased, the gap between the performances of the two mix groups increased, corresponding to an overall difference of ~400%, demonstrating that including small amounts of pfa helped to endure the dry environments and resulted in strength results four times higher than those mixes where it was completely eliminated.

P-mixes that were not subjected to any wet/dry cycling, denoted as RH-0d, indicated a consistent strength development over 18 days of carbonation due to the continuous supply of CO₂, overriding any potential benefits of cycling on carbonation and hence strength development. The absence of cycling enabled these samples to have uninterrupted access to accelerated levels of CO₂ during the entire 18 days of carbonation, which was certainly beneficial when compared to ambient CO₂ levels available in the wet environment. However, wet/dry cycling also promoted carbonation by presenting alternative transport and reaction media. This was achieved through the provision of water that was

needed for the formation of HMCs by the wet environment, whereas optimal gas transport took place in the dry environment.

In general, strength development of p-mixes under varying RHs did not show a significant change with cycling frequencies, whose effect on strength development was more visible after 12 days of carbonation. All p-78 mixes subjected to different cycling frequencies achieved the same strength, 34 MPa, after 18 days of carbonation, which was slightly higher than that of no cycling, 32 MPa. It is possible that incorporating cycling into the carbonation process of p-mixes resulted in a delay in the formation of strength providing HMCs. The benefit of cycling was more evident for n-mixes where samples subjected to 1-day cycling achieved the highest strengths at all times, followed by 2-days, 3-days, and no cycling. Alternatively, p-mixes that were not subjected to any cycling outperformed all the others at up to 12 days of carbonation, showing that applying cycling with certain frequencies can benefit the strength development of mixes at longer durations of carbonation by establishing the right conditions for the further development of HMCs.

(a)

(b)

Fig. 6. Development of UCS with curing time under different RHs and wet/dry cycling for (a) p-mixes, and (b) n-mixes

3.2.2 Solid phases assemblage

The microstructure of p-98, p-84, p-78 and p-67 at 18 days of carbonation are shown in Figs. 7(a)-(d). Hydromagnesite/dypingite and nesquehonite were identified as the main HMCs forming after carbonation. SEM micrographs for mix p-98 demonstrated the dense formation of nesquehonite whereas hydromagnesite/dypingite was the main HMC forming in the case of mixes subjected to drier conditions. A much denser formation of hydromagnesite/dypingite was seen in p-78 than in p-67, which was in agreement with the UCS results.

Stoichiometry can also be used to explain the reasoning behind the formation of hydromagnesite/dypingite in dry conditions (i.e. provided by the set RH in the incubator), and nesquehonite under high RHs (i.e. enhanced by continuous spraying). The molar ratio of $\text{MgO}:\text{H}_2\text{O}$ within dypingite is 5:6. Corresponding to 10% of the overall compositions, each sample within this study contained 30g of MgO , which would need to combine with 16.2g of water to form into dypingite. With a w/c ratio of 0.7, all mixes contained 21g of water, which was sufficient even under low RHs for the formation of dypingite. On the other hand, the molar ratio of $\text{MgO}:\text{H}_2\text{O}$ within nesquehonite is 1:3, necessitating 40.5g of water for the formation of nesquehonite. In this case, since the already included 21g of water is not sufficient for nesquehonite formation, an additional 19.5g of water, which can be provided through high RHs enhanced by wet/dry cycling or extra water spraying, is necessary.

Containing 39.1% water within its chemical composition as opposed to the 19.3% in hydromagnesite and 22.3% in dypingite, nesquehonite is also transformed with the loss of water. One reason for the high strength results obtained by samples which were subjected to wet/dry cycling could be due to the enhancement of nesquehonite production, whose formation as opposed to other HMCs has been seen to result in higher strength results in related previous work [14, 46, 47]. Higher frequencies of cycling may have also led to larger amounts of nesquehonite formation since samples subjected to frequent cycling were not exposed to the dry environments long enough for the decomposition of nesquehonite into other HMCs that contain less water within their structures, hence providing a more favorable condition for the formation of nesquehonite.

Fig. 7. SEM images of mixes (a) p-98, (b) p-84, (c) p-78, and (d) p-67

4. Conclusions

The effects of curing conditions including water/cement ratio, CO₂ concentration, curing duration, RH, and wet/dry cycling frequency on the carbonation of MgO cement porous blocks have been studied in

detail to provide the highest potential for the amount of CO₂ absorbed that would also lead to significant strength results. The different factors investigated collectively indicate that none of the curing conditions are independently the only determinant for the continuous progress of carbonation. Mixes with different compositions were compared, showing that small additions of pfa to porous block mixes led to increased rate and amount of carbonation. This was also reflected as improved mechanical performances when compared to mixes where pfa was completely eliminated.

Mixes with lower w/c ratios performed better in shorter curing durations, whereas larger w/c ratios were needed for carbonation to proceed for longer periods. Mixes subjected to 10% CO₂ concentration performed as well as those cured under 20% CO₂, confirming that after a certain point CO₂ concentration is not the limiting factor for the complete carbonation of MgO. CO₂ concentrations as low as 5% were sufficient in providing the necessary strength requirement for blocks (i.e. 7 MPa) only after 1 day of carbonation, thereby reducing the overall cost if implemented commercially on a larger scale. CO₂ captured and recovered from flue gases emitted from power plants or other industrial processes can be used during this process, eliminating any further damage to the environment, while satisfying strength requirements.

Although high RHs are known to benefit the progress of carbonation since dry curing environments do not favor hydration and carbonation processes, strength development does not necessarily follow a linear trend with RH, given that optimal gas transport takes place in a dry environment. Since the provision of water is needed for the formation of HMCs as opposed to the dry environment requirement for the most favorable gas transport, an optimum RH corresponding to the maximum amount of carbonation exists for each mix composition. Subjected to different RHs ranging between 55-98%, mixes cured under 78% RH outperformed all the others studied within the scope of this work, highlighting the benefits of incorporating wet/dry cycling, depending on the frequency of cycling and duration of curing.

References

- [1] K.S. Lackner, D.P. Butt, C.H. Wendt, H.J. Ziock, in: Advanced coal-based power and environmental systems, Morgantown, West Virginia, 1998, pp. 8.
- [2] K.S. Lackner, H.J. Ziock, P. Grimes, Carbon dioxide extraction from air: Is it an option?, in: 24th International Conference on Coal Utilization & Fuel Systems, Clearwater, Florida, 1999, pp. 885.
- [3] J.T. Houghton, Climate change 2001: the scientific basis, Cambridge University Press Cambridge, 2001.
- [4] C.D. Keeling, T.P. Whorf, Atmospheric CO₂ records from sites in the SIO air sampling network, Trends: A compendium of data on global change, 2009 (2005).
- [5] F. Goff, K.S. Lackner, Carbon dioxide sequestering using ultramafic rocks, Environmental Geoscience, 5 (1998) 89-101.
- [6] F. Pearce, Green Foundations, New Scientist, 175 (2002) 39-41.
- [7] J.W. Harrison, Reactive Magnesium Oxide Cements, in: PCT/AU/00077, 2001.
- [8] USGS, Minerals Information Yearbook: Cement Statistics and Information, in, US Geological Survey, 2012.
- [9] V.M. Malhotra, Role of supplementary cementing materials in reducing greenhouse gas emissions, in: O.E. Gjorv, K. Sakai (Eds.) Concrete technology for a sustainable development in the 21st century, E&FN Spon, London, 2000.
- [10] IPCC, Mineral carbonation and industrial uses of carbon dioxide in IPCC Special Report on Carbon Dioxide Capture and Storage, in, Intergovernmental Panel on Climate Change 2004, pp. 321-337.
- [11] USGS, Mineral Commodity Summaries, in, US Geological Survey, 2011, pp. 198.
- [12] L.J. Vandeperre, M. Liska, A. Al-Tabbaa, Hydration and mechanical properties of magnesia, pulverized fuel ash, and portland cement blends, Journal of Materials in Civil Engineering, 20 (2008) 375-383.
- [13] J.W. Harrison, TecEco Eco-Cement masonry product update – Carbonation=Sequestration, in, 2005.

- [14] C. Unluer, A. Al-Tabbaa, Impact of hydrated magnesium carbonates additives on the carbonation of reactive MgO cements, *Cement and Concrete Research*, 54 (2013) 87-97.
- [15] M. Liska, A. Al-Tabbaa, Ultra-green construction: reactive magnesia masonry products, *Proceedings of the ICE-Waste and Resource Management*, 162 (2009) 185-196.
- [16] M.A. Shand, *The Chemistry and Technology of Magnesia*, Wiley, New York, 2006.
- [17] H.F.W. Taylor, *Cement Chemistry*, Academic Press, New York, 1990.
- [18] L.J. Vandeperre, M. Liska, A. Al-Tabbaa, Mixtures of pulverized fuel ash, Portland cement and Magnesium oxide : strength evolution and hydration products, in: *6th International Conference on the Science and Engineering of Recycling for Environmental Protection*, Yugoslav Engineering Academy, Belgrade, 2006, pp. 539-550.
- [19] L.J. Vandeperre, M. Liska, A. Al-Tabbaa, Microstructures of reactive magnesia cement blends, *Cement and Concrete Composites*, 30 (2008) 706-714.
- [20] M. Liska, L.J. Vandeperre, A. Al-Tabbaa, Mixtures of pulverised fuel ash, Portland cement and magnesium oxide: characterisation of pastes and setting behaviour, in: *WASCON*, Belgrade, 2006, pp. 563-573.
- [21] L.J. Vandeperre, M. Liska, A. Al-Tabbaa, Reactive magnesium oxide cements: Properties and applications, in: *International Conference on Sustainable Construction Materials and Technologies*, 2007, pp. 397-410.
- [22] M. Liska, L.J. Vandeperre, A. Al-Tabbaa, Influence of carbonation on the properties of reactive magnesia cement-based pressed masonry units, *ICE Journal of Advances in Cement Research*, 20 (2008) 53-64.
- [23] M. Liska, A. Al-Tabbaa, K. Carter, J. Fifield, Scaled-up commercial production of reactive magnesia cement pressed masonry units. Part I: Production, *Proceedings of the ICE - Construction Materials*, 165 (2013) 211-223.
- [24] M. Liska, A. Al-Tabbaa, K. Carter, J. Fifield, Scaled-up commercial production of reactive magnesia cement pressed masonry units. Part II: Performance, *Proceedings of the ICE - Construction Materials*, 165 (2013) 225-243.
- [25] M. Liska, Properties and applications of reactive magnesia cements in porous blocks, in: *PhD Thesis*, Department of Engineering, University of Cambridge, Cambridge, UK, 2009.

- [26] M. Liska, A. Al-Tabbaa, Performance of magnesia cements in pressed masonry units with natural aggregates: production parameters optimisation, *Construction and Building Materials*, 22 (2008) 1789-1797.
- [27] P.J. Davies, B. Bubela, The transformation of nesquehonite into hydromagnesite, *Chemical Geology*, 12 (1973) 289-300.
- [28] E. Königsberger, L.-C. Königsberger, H. Gamsjäger, Low-temperature thermodynamic model for the system $\text{Na}_2\text{CO}_3\text{-MgCO}_3\text{-CaCO}_3\text{-H}_2\text{O}$, *Geochimica et Cosmochimica Acta*, 63 (1999) 3105-3119.
- [29] L. Marini, Geological Sequestration of Carbon Dioxide. Thermodynamics, kinetics and reaction path modelling, 1st ed., Elsevier, Oxford, 2007.
- [30] Y. Xiong, A.S. Lord, Experimental investigations of the reaction path in the $\text{MgO-CO}_2\text{-H}_2\text{O}$ system in solutions with various ionic strengths, and their applications to nuclear waste isolation, *Applied Geochemistry*, 23 (2008) 1634-1659.
- [31] V.G. Papadakis, C.G. Vayenas, M.N. Fardis, Experimental investigation and mathematical modeling of the concrete carbonation problem, *Chemical Engineering Science*, 46 (1991) 1333-1338.
- [32] T.C. Powers, L.E. Copeland, J.C. Hayes, H.M. Mann, Permeability of portland cement paste, *Journal of American Concrete Institute*, 51 (1954) 285-298.
- [33] R.A. Cook, K.C. Hover, Mercury porosimetry of hardened cement pastes, *Cement and Concrete Research*, 29 (1999) 933–943.
- [34] A.M. Neville, *Properties of Concrete*, 4th ed., Addison Wesley Longman Limited, Essex, 1997.
- [35] M. Richardson, Carbonation of reinforced concrete. Its causes and management, in, Dublin, 1988.
- [36] A.V. Saetta, B.A. Schrefler, R.V. Vitaliani, 2-D model for carbonation and moisture /heat flow in porous materials, *Cement and Concrete Research*, 25 (1995) 1703– 1712.
- [37] S.K. Roy, K.B. Poh, D.O. Northwood, Durability of concrete - accelerated carbonation and weathering studies, *Building and Environment*, 34 (1999) 597– 606.
- [38] L.J. Vandeperre, A. Al-Tabbaa, Accelerated carbonation of reactive MgO cements, *Advances in Cement Research*, 19 (2007) 69-79.
- [39] CBA, Market Trends, in, Cement Block Association, <http://www.cba-blocks.org.uk/files/stats.download.pdf>, 2011.
- [40] PCA, Concrete Masonry Units, in, Portland Cement Association, 2009.

- [41] Forticrete, Masonry design guide, in, 2010.
- [42] B.S.I., BS EN 771-3:2011 Specification for masonry units. Aggregate concrete masonry units (dense and lightweight aggregates), in, 2011.
- [43] M. Fernández Bertos, S.J.R. Simons, C.D. Hills, P.J. Carey, A review of accelerated carbonation technology in the treatment of cement-based materials and sequestration of CO₂, *Journal of Hazardous Materials*, 122 (2004) 193-205.
- [44] D.G. Chapel, C.L. Mariz, J. Ernest, Recovery of CO₂ from flue gases: commercial trends, in: Canadian Society of Chemical Engineers Annual Meeting, Saskatoon, Saskatchewan, Canada, 1999.
- [45] C.L. Mariz, Carbon dioxide recovery: large scale design trends, *Journal of Canadian Petroleum Technology*, 37 (1998) 42-47.
- [46] C. Unluer, A. Al-Tabbaa, Green construction with carbonating reactive magnesia porous blocks: Effect of cement and water contents, in: 2nd International Conference & Environmental Construction Exhibition, Dubai, 2011.
- [47] C. Unluer, A. Al-Tabbaa, Effect of aggregate size distribution on the carbonation of reactive magnesia based porous blocks, in: 18th Annual International Sustainable Development Research Conference, Hull, UK, 2012.
- [48] B.S.I., BS EN 196-3:1995 Methods of testing cement: Determination of setting time and soundness, in, British Standards, UK, 1995.
- [49] C.R. Hubbard, R.L. Snyder, RIR-measurement and use in quantitative XRD, *Powder Diffraction*, 74 (1988) 74.
- [50] C.R. Hubbard, E.H. Evans, D.K. Smith, The reference intensity ratio, I/I_c , for computer simulated powder patterns, *Journal of Applied Crystallography*, 9 (1976) 169-174.
- [51] R.L. Snyder, The use of reference intensity ratios in X-ray quantitative analysis, *Powder Diffraction*, 7 (1992) 186.
- [52] Q. Johnson, R.S. Zhou, Checking and estimating RIR values, *Advances in X-ray Analysis*, 42 (2000) 287-296.
- [53] S.S. Al-Jaroudi, A. Ul-Hamid, A.R.I. Mohammed, S. Saner, Use of X-ray powder diffraction for quantitative analysis of carbonate rock reservoir samples, *Powder Technology*, 175 (2007) 115–121.
- [54] B.D. Cullity, S. Stock, *Elements of X-ray Diffraction*, Prentice Hall, 1972.

- [55] D. Whiting, Permeability of selected concretes, in: ACI (Ed.) Permeability of Concrete, Detroit, Michigan, 1988, pp. 195-221.
- [56] D.W. Ming, W.T. Franklin, Synthesis of lansfordite and nesquehonite, Soil Science Society of America Journal, 49 (1985) 1303-1308.
- [57] D. Langmuir, Stability of carbonates in the system $\text{MgO-CO}_2\text{-H}_2\text{O}$, Journal of Geology, 73 (1965) 730-754.
- [58] R.M. Dell, S.W. Weller, The thermal decomposition of nesquehonite $\text{MgCO}_3\cdot\text{H}_2\text{O}$ and magnesium ammonium carbonate $\text{MgCO}_3\cdot(\text{NH}_4)_2\text{CO}_3\cdot 4\text{H}_2\text{O}$, Transactions of the Faraday Society, 55 (1959) 2203-2220.
- [59] J.H. Canterford, G. Tsambourakis, B. Lambert, Some observations on the properties of dypingite, $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2\cdot 5\text{H}_2\text{O}$, and related minerals, Mineralogical Magazine, 48 (1984) 437-442.
- [60] I.M. Power, S.A. Wilson, J.A. Thom, G.M. Dipple, G. Southam, Biologically induced mineralization of dypingite by cyanobacteria from an alkaline wetland near Atlin, British, Columbia, Canada, Geochemical Transactions, 8 (2007) 1-16.
- [61] S.A. Wilson, M. Raudsepp, G.M. Dipple, Verifying and quantifying carbon fixation in minerals from serpentine-rich mine tailings using the Rietveld method with X-ray powder diffraction data, American Mineralogist, 91 (2006) 1331-1341.
- [62] P. Atkins, The Elements of Physical Chemistry, 3rd ed., Oxford University Press, Oxford, 2001.