Effect of supplementary cementitious materials on carbonation rate and CO_2 uptake

Marie Joshua Tapas[1], Paul Thomas[2], Vute Sirivivatnanon[3]
[1]Research Associate, University of Technology Sydney
[2]Senior Lecturer, University of Technology Sydney
[3]Professor, University of Technology Sydney

Abstract
Carbonation, which pertains to the reaction of carbon dioxide (CO_2) with the calcium-bearing phases of the binder, is a natural process that leads to the modification of the pore solution, microstructure as well as various properties of the concrete. This process, although traditionally perceived as undesirable due to its role in increasing the susceptibility of the concrete steel reinforcement to corrosion, is gaining global interest as a possible means to reduce the carbon footprint of the construction industry. CO_2 sequestration in concrete is perceived to play a key role in improving the sustainability of concrete production. The carbonation process however remains not fully understood, particularly in binder systems with supplementary cementitious materials. This paper discusses the chemistry of carbonation, the change in phases due to carbonation and the influence of binder type on the carbonation rate and CO_2 uptake.

1. Introduction

The drive to reduce carbon dioxide emissions to net zero by 2050 has resulted in a significant interest in carbonation. CO_2 is the most dominant greenhouse gas emitted into the atmosphere and concrete production, owing to the calcination of limestone to produce cement, accounts for up to 8% of the global CO_2 emissions [1]. The calcination of limestone, $CaCO_3$ (Equation 1) accounts for about 55% of the CO_2 emitted during cement production [2].

$$CaCO_3\,(100g/mol) \rightarrow CaO\,(56g/mol) + CO_2\,(44g/mol) \quad (1)$$

The reverse process or the reabsorption of the CO_2 back into the concrete during its life cycle helps offset the emitted CO_2. Carbonation however has long been known to be a durability issue in steel-reinforced concrete structures [3, 4]. The ingress of CO_2 into the binder system results in the formation of carbonic acid (H_2CO_3), resulting in the decrease in the pH of the pore solution and the precipitation of $CaCO_3$. Low concrete pH (~9 or less) is detrimental to steel-reinforced concrete as steel begins to lose its passivation layer making it susceptible to corrosion. The carbonation process can be described by Equations 2 to 4:

$$CO_2 + H_2O \rightleftharpoons HCO^{3-}\,(\text{bicarbonate ion}) + H^+ \quad (2)$$

$$HCO_3^- \rightleftharpoons CO_3^{2-}(\text{carbonate ion}) + H^+ \quad (3)$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \quad (4)$$

During carbonation (as shown in Equation 4), CO_2 reacts with the calcium-bearing phases of the binder forming calcium carbonate ($CaCO_3$). Portlandite being the most soluble calcium source in the binder therefore is the primary reactant (Equation 5).

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad (5)$$

Carbonation is particularly a concern in binder systems with higher contents of supplementary cementitious materials (SCMs). It is known that the higher the SCM content, the higher the carbonation rate (i.e. the faster the progress of carbonation into the concrete) [3, 5, 6]. Corrosion study, on mixes based on OPC and mixes with higher SCM contents (i.e. contains fly ash, slag or silica fume), revealed that steel corrodes with greater rate when embedded in carbonated mortars with SCMs [7].The use of

SCMs in structural applications is however common as reducing cement or lowering the clinker factor is a primary strategy to lowering the embodied carbon of the concrete and to improve most durability properties including alkali-silica reaction, chloride ingress and sulfate attack.

As outlined above, carbonation is both a problem and a solution. This paper discusses the effect of carbonation on phase development of the binder and the influence of binder type on the carbonation rate and CO_2 uptake.

2. Effect of SCM content on carbonation depth

Phenolphthalein, which changes colour depending on the pH of the solution, is the most common indicator of carbonation used in the industry. Figure 1 shows the carbonation depths of mortars with no SCM, mortar with 50% slag and mortar with 70% slag after 1 week (7 days), 4 weeks (28 days) and 9 weeks (63 days) of exposure to 2%CO_2 50%RH 23 °C. The change in the colour of the phenolphthalein from pink to colourless indicates a drop in the pore solution pH to ≤9.5, which indicates that the area is carbonated. Consistent with existing literature, the plain OPC mortar exhibits the best resistance to carbonation (highest amount of pink region) while mortars with slag exhibit poorer resistance to carbonation.

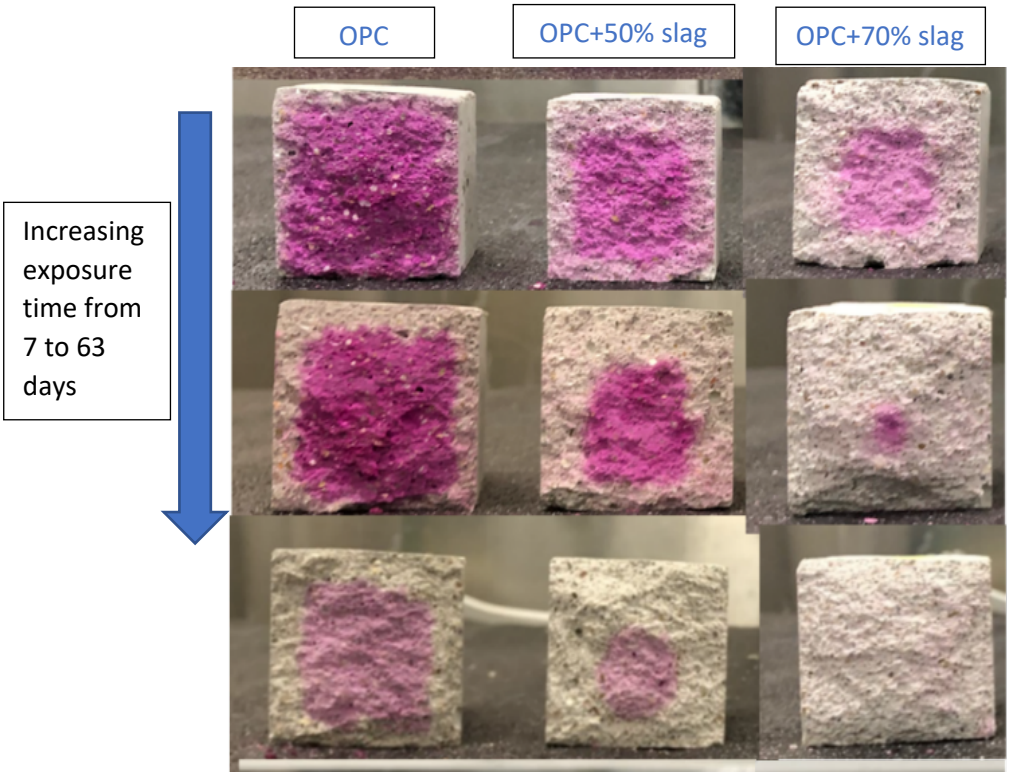

Figure 1 Photographs of the mortars after 7, 28, and 63 days exposure to 2% CO_2, 50%RH 23 °C showing the carbonation depth (data from authors' experimental work, unpublished)

Further, as can be observed from Figure 1, the higher the slag replacement, the poorer the carbonation performance. During carbonation, portlandite ($Ca(OH)_2$), which is the most soluble source of calcium in the binder, serves as a buffer and maintains the pH of the pore solution at a pH value of 12.5 by releasing OH^- and Ca^{2+} ions. The OH^- neutralizes the H^+ while Ca^{2+} binds CO_2 precipitating $CaCO_3$ [6]. Due to lower amount of portlandite, the carbonation of high-SCM binders occurs much faster than that of pure cement. Binders with higher slag content are also inherently less basic than pure cement binders due to dilution effect and the ability of SCMs to bind alkalis [8]. The lower alkalinity of high-SCM binders also means it takes less CO_2 to drop the pH.

3. Influence of carbonation on phase development

Figure 2 illustrates the effect of carbonation on phase development of an OPC binder [3]. The chart clearly shows that carbonation, on top of decreasing the pore solution pH, also modifies the composition of the phases in the binder. Whereas, portlandite reacts first, the rest of the calcium-bearing phases of the binder also react with CO_2 resulting in the decomposition of ettringite and decalcification of the calcium silicate hydrate (CSH) as shown by the drop in the CSH Ca/Si ratio with the progress of carbonation (Figure 2b) and the formation of more $CaCO_3$. Assuming full carbonation (i.e. all CaO present in the clinker will react), the total CO_2 bound is around 40 to 50g CO_2/100 g Portland cement [3] which is roughly equivalent to the CO_2 emitted during the limestone calcination process to produce cement clinker (i.e. 100grams $CaCO_3$ will produce 56grams CaO and 44grams CO_2, see Equation 1). OPC binders with SCMs will undergo similar phase changes except that the proportions of the reaction products will be different.

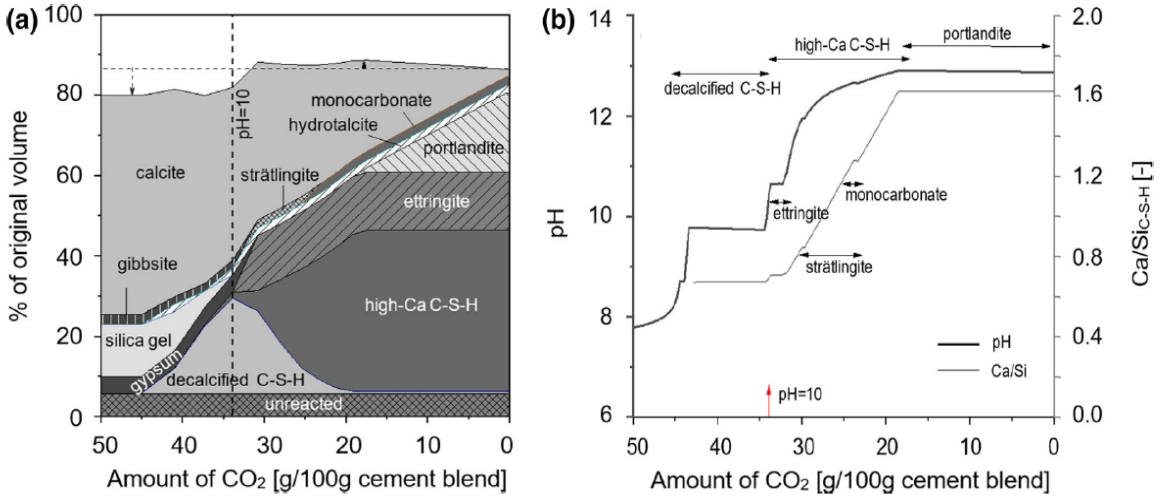

Figure 2 Effect of carbonation on phase development: a) changes in the phase assemblage and b) change in the pH and the Ca/Si ratio of the CSH [3]

The amount of CaO in the binder determines the total amount of CO_2 that can be bound assuming concrete reaches full carbonation. Therefore, considering blended cements contain less amount of calcium, their CO_2 binding capacity is also lower than OPC. The degree of carbonation can be identified by thermogravimetric analysis (TG) following mass loss as a function of temperature. The mortar samples in Figure 1 were analysed and the DTG curves obtained and reported in Figure 3 illustrate this clearly. As can be seen, the mortar with 50% slag forms less $CaCO_3$ than OPC translating to lower CO_2 binding capacity. Amount of $CaCO_3$ is depicted by mass loss between 300 to 800 °C. This means that whereas high slag binders carbonate faster, the capacity to bind CO_2 per g of binder is lower. It is precisely for this reason (i.e. less CaO to carbonate per layer/area) that the carbonation progresses faster in high slag binders. The disappearance of portlandite peak $Ca(OH)_2$ is also notable which indicates that the change in pH detected by the phenolphthalein solution is largely driven by the consumption of the portlandite, $Ca(OH)_2$.

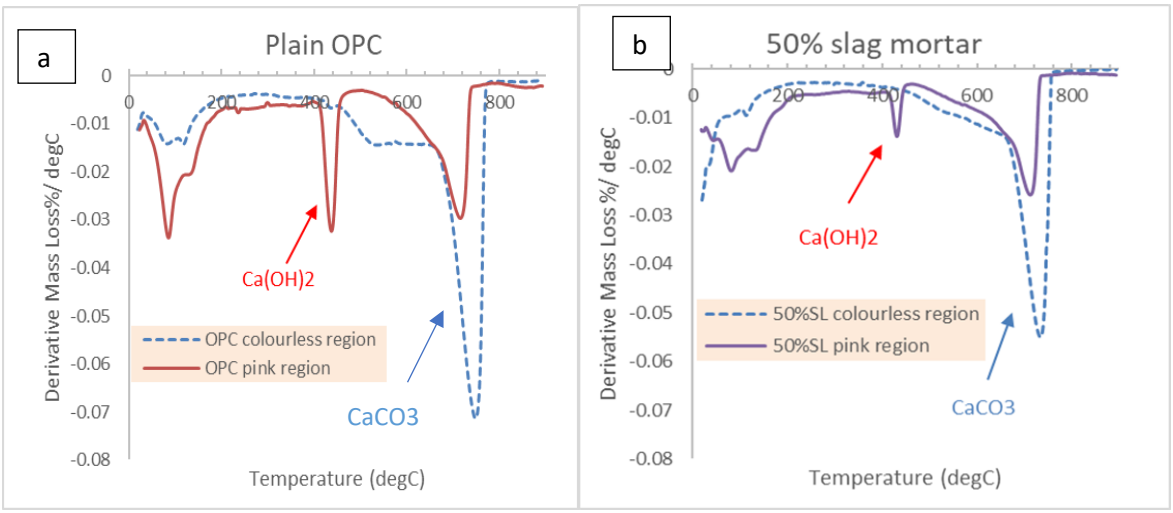

Figure 3 DTG curves of a) OPC mortar and b) mortar+50%slag. The samples for TG analysis were obtained from the mortars in Figure 1 that were subjected to accelerated carbonation, 2%CO_2, 50%RH and 23 °C (data from authors' experimental work)

4. Carbonation rate and quantification of CO_2 uptake

Carbonation depth as a function of time can be described by Equation 6, where, D is the depth of carbonation, k is the carbonation rate constant, and t is time. Using this relationship, the carbonation depth at any time t can be determined. This relationship is however likely to overestimate the degree of carbonation at later ages as it assumes steady state diffusion. At later ages of the concrete, an increase in time may translate to much lower increase in carbonation depths due to continued hydration and pore refinement (i.e. t exponent can be less than 0.5) [9].

$$D = k \times t^{0.5} \quad (6)$$

The rate of carbonation primarily depends on the rate of diffusion of CO_2. Therefore, the carbonation rate is affected by the type of binder, the strength of the concrete (which is affected by the porosity) and the exposure conditions including temperature, humidity and amount of available CO_2. Optimum carbonation rate occurs at humidity between 40-80% [9]. Concrete that is in a dry environment will also carbonate but at a lower rate due to the lack of water to dissolve CO_2 and facilitate the interaction of ions in the binder. Similarly, concrete buried in soil will also carbonate but very slowly due to the slowness of exchange reactions (i.e. CO_2 moves slower in very wet environments) [10]. Higher temperature also gives a higher rate of carbonation.

Lagerblad [10] suggested that the carbonation rate constant of most common concrete could be chosen from Table 1 by categorizing the concrete based on strength and exposure conditions. The higher the grade of the concrete, the lower the carbonation rate constants. Moreover, buried and wet concretes have lower carbonation rate constants that exposed, sheltered and indoor concretes. It is also worth noting that for this particular case (Nordic countries), the indoor concrete is exposed to higher temperatures than outdoor concrete countries and therefore has higher carbonation rate constants. The values for the concretes are also for exposed "naked" concrete. The k value should be adjusted for concretes that are covered by paints, wallpapers, carpets, etc as these covers are known to result in the decrease in the carbonation rate.

Table 1 Carbonation rate constants (CEM I) for various concrete cylinder strengths and concrete exposure conditions as used in the Nordic investigation of CO_2 uptake [9, 10]

Exposure condition	Compressive strength			
	<15 MPa (mm/(year)$^{0.5}$)	15–20 MPa (mm/(year)$^{0.5}$)	23–35 MPa (mm/(year)$^{0.5}$)	>35 MPa (mm/(year)$^{0.5}$)
Exposed	5	2.5	1.5	1
Sheltered	10	6	4	2.5
Indoors	15	9	6	3.5
Wet	2	1.0	0.75	0.5
Buried	3	1.5	1.0	0.75

The carbonation rate is also affected by the presence of supplementary cementitious materials and hence, Lagerblad [10] recommended some correction factors based on empirical data for concrete with fly ash, slag, silica fume and limestone, increasing with higher levels of SCM substitution. The effect of SCM on the carbonation coefficient is shown in Figure 4 [3]. The amount and type of SCM affect the carbonation coefficient. The higher the SCM content, the higher the carbonation coefficient. At the same replacement level, carbonation coefficient is higher for fly ash (FA) and silica fume (SF) blended concretes and mortars, than for Limestone (LS) or Blast Furnace Slag (BFS) blended concretes and mortars. Pozzolanic materials are higher in SiO_2 and consume portlandite in the binder, thereby increasing the susceptibility of the concrete to carbonation.

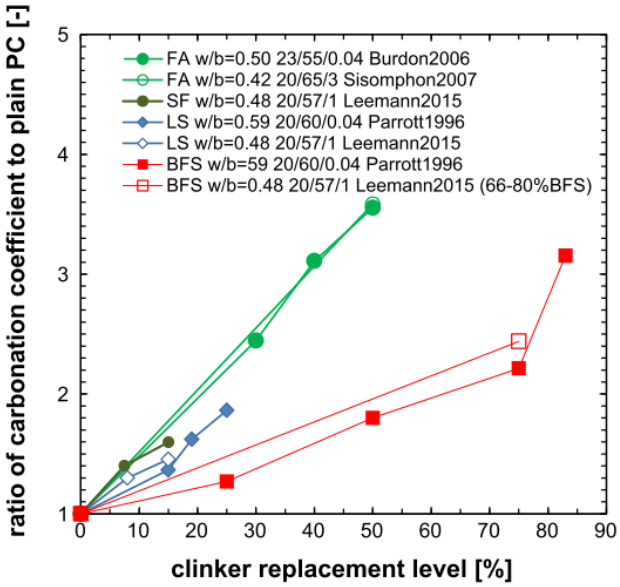

Figure 4 Effect of clinker replacement on the carbonation coefficient. All samples have been cured for 28 days and FA= fly ash, SF=silica fume, LS=limestone and BFS=blast furnace slag [3]

There are several approaches to determine the CO_2 uptake of concrete (kg CO_2/m^3 concrete). The maximum theoretical CO_2 uptake assumes that all CaO from the cement will eventually carbonate and convert to CO_2 and hence defined by Equation 7, where C= mass of Portland cement clinker per m^3 concrete, CaO=mass fraction of CaO in the cement clinker, M_{CaO}= molar mass of CaO and M_{CO2}= molar mass of CO_2. However, since it has been widely reported that the CaO from SCMs also carbonates and not only from cement, Equation 8, where B= mass of binder per m^3 concrete has also been proposed [11].

$$CO_2 \text{ uptake} = C \times CaO_{cement} \times M_{CO2}/M_{CaO} \quad (7)$$

CO_2 uptake= B x CaO_{binder} x M_{CO2}/M_{CaO} (8)

Pade and Guimaraes proposed a more conservative assumption that the amount of CO_2 absorbed per volume of carbonated concrete can be calculated from Equation 9 [9], where 0.75 is the fraction of CaO available for reaction (this assumes that a maximum of 75% of the available CaO in the cement can be converted to calcium carbonate). Extended to the binder system, that equation becomes Equation 10 where B= mass of binder per m^3 concrete.

CO_2 uptake= 0.75 x C x CaO_{cement} x M_{CO2}/M_{CaO} (9)

CO_2 uptake= 0.75 x B x CaO_{binder} x M_{CO2}/M_{CaO} (10)

In order to determine the accuracy of the proposed estimation methods of CO_2 uptake, paste specimens made up of pure OPC, OPC+50% slag and OPC+70% slag have been prepared and subjected to accelerated carbonation conditions, 2%CO_2, 23 °C and 50% RH (same binder as the mortar samples presented in Figure 1). After 63 days, the carbonated regions (colourless when sprayed with phenolphthalein) were subjected to thermogravimetric analysis to determine bound CO_2 content. Between temperatures 300-800 °C, the $CaCO_3$ in the binder decomposes, producing CaO and releasing CO_2 (Equation 1). The mass loss within the region therefore corresponds to bound CO_2. Once bound CO_2 content is known, the ratio M_{CO2}/M_{CaO}=0.79 can be used to convert bound CO_2 to reacted CaO. The cement used in this study has 63% CaO while slag contains 42% CaO from XRF oxide analysis.

The results of the calculations are tabulated in Tables 2 and 3. Table 2 shows the %mass loss due to release of CO_2 which was then used to calculate the %CaO reacted in the binder. The limestone content of the cement is about 7.5% and has been accounted for in the results. The results from the pastes are consistent with the results of mortar samples in Figure 3. The higher the cement content, the higher the CO_2 uptake of the binder. The use of pastes for the calculation of bound CO_2 is to eliminate the effect of the fine aggregates in the results.

Table 2 %Mass loss due to release of CO_2 obtained from DTG curves used to calculate the amount of CaO (%) that has reacted and the amount of $CaCO_3$ (%) in the binder (data from authors' unpublished work)

Binder at 63 days accelerated carbonation	**%mass loss due to release of CO_2 ($CaCO_3$→ CaO + CO_2)**	**% CaO reacted**	**% $CaCO_3$ in the binder***
OPC	21.97	27.97	49.94
OPC+50%slag	18.52	23.57	42.08
OPC+70%slag	15.25	19.40	34.65

*the limestone from the cement has been accounted for

Table 3 shows the expected amount of bound CO_2 following the assumptions in Equations 7-10 in comparison with the bound CO_2 determined from TG. Results show that the equations used in literature to estimate CO_2 uptake assuming that 100% of the cement (Equation 7) or that the CaO from all components of the binder including SCMs (Equations 8 and 10) are converted to $CaCO_3$ overestimate the CO_2 uptake.

From Tables 2 and 3, it is also clear that at the point where phenolphthalein changes colour from pink to colourless, not all CaO has been converted to $CaCO_3$. The experimentally determined CaO reacted in the case of pure cement is in fact only about 28% (Table 2), far less than the 63% CaO available. Therefore, although it is very notable from the TG curves (Figure 3) that portlandite has been fully consumed and C-S-H region has been depleted (both mortar and paste TG results), C-S-H is definitely still present but has just decalcified (i.e. has lower Ca/Si ratio).

Table 3 Calculation of CO_2 uptake based on Equations 7 to 10 compared to the experimentally determined CO_2 content of the cement.

100% OPC	**Available CaO**	**g CO_2 /g of cement max***	**Expt (TG) gCO_2/g measured**
Equation 7 (cement)	0.63	0.50	0.22
Equation 9 (0.75*cement)	0.47	0.37	0.22
OPC+50% slag			
Equation 8 (binder)	0.53	0.41	0.19
Equation 10 (0.75*binder)	0.39	0.31	0.19
OPC+70% slag			
Equation 8 (binder)	0.48	0.38	0.15
Equation 10 (0.75*binder)	0.36	0.29	0.15

*available CaO was converted to bound CO_2 using M_{CO2}/M_{CaO}=0.79

Considering that cement has the capacity to bind more CO_2 but carbonation depth is always lower than binders with SCMs at any given time 't' due to higher amount of CaO to carbonate, carbonation should therefore be assessed within a time frame to determine which binder system is able to absorb more CO_2 during the lifecycle of the concrete. The CO_2 uptake in a carbonated region can be calculated if the carbonation depth is known. Multiplying the carbonated volume (m^3) with the experimentally determined g CO_2 /g of binder in Table 2 and the amount of binder kg /m^3, the total amount of CO_2 bound in the carbonated region can be calculated.

Although the determination of CO_2 uptake seems fairly simple, in reality this is complex. Pade and Guimares [9] have investigated the atmospheric carbonation process considering 100 years life cycle of concrete structures present in Denmark, Iceland, Norway and Sweden. In this study, the grade of the concrete, type of binder, part of structure where concrete was used, exposure conditions, life cycle (service life + demolished) have all been considered. For demolished structures, more surface area is available and therefore the carbonation process occurs at a much faster rate. The time frame for carbonation is also very important. As can be observed, high SCM concretes although bind less CO_2 per g of binder, carbonate at a significantly higher rate than plain OPC binder.

5. Conclusions

This study outlines the chemistry of carbonation and its effect on phase development of binders as well as investigates the effect of SCM, particularly slag, on CO_2 uptake and quantification of bound CO_2 in concrete. Important findings are summarized below:

1. Carbonation not only results in the drop of the pore solution pH, but also in the modification of the phases present in the binder. Changes occurring in the binder include full consumption of the portlandite, decomposition of ettringite and decalcification of the calcium silicate hydrate (C-S-H).
2. SCM increases the rate of carbonation. The higher the SCM replacement, the higher the carbonation rate. The higher rate of carbonation in binders with SCMs is primarily due to less amount of CaO to carbonate per layer/per gram of binder and the lower starting pH of binders with SCMs requiring less CO_2 to drop the pH.
3. The type of SCM affects the carbonation rate. At equivalent replacement level, concretes with pozzolanic SCMs such as fly ash or silica fume will carbonate faster than concrete with a latent hydraulic SCM such as slag. This is due to the limited availability of portlandite in binders with fly ash and silica fume (consumed by pozzolanic reactions) and overall lower CaO content in concretes with pozzolanic SCMs.
4. The change in the colour of the phenolphthalein indicator is triggered by the consumption of the portlandite in the binder.
5. CO_2 uptake is affected by the type of binder. Binders with higher CaO content like a pure OPC binder will have a higher CO_2 uptake per g of binder. The higher the SCM replacement, the lower the CO_2 uptake per g of binder.

6. Since carbonation is a natural process and is a reverse of the calcination process of limestone to produce cement, all concretes given sufficient time will eventually carbonate. Quantification of the CO_2 uptake therefore must be considered within a fixed time frame to assess the beneficial effect of SCMs.
7. Based from the calculations carried out, the equations assuming that the entire CaO of the cement or even 75% of the CaO from the binder reacts to form $CaCO_3$ overestimate the amount of bound CO_2. Correct identification of reacted CaO (or maximum available CaO for carbonation) is very critical in predicting CO_2 uptake in the lifetime of a structure. This value can be experimentally determined by thermogravimetric analysis of various types of binders.

Acknowledgement

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References

[1] K.L. Scrivener, V.M. John, E.M. Gartner, Eco-efficient cements: Potential economically viable solutions for a low-CO2 cement-based materials industry, Cement and Concrete Research 114 (2018) 2-26.
[2] VDZ, Decarbonisation Pathways for the Australian Cement and Concrete Sector, 2021.
[3] S. von Greve-Dierfeld, B. Lothenbach, A. Vollpracht, B. Wu, B. Huet, C. Andrade, C. Medina, C. Thiel, E. Gruyaert, H. Vanoutrive, I.F. Saéz del Bosque, I. Ignjatovic, J. Elsen, J.L. Provis, K. Scrivener, K.-C. Thienel, K. Sideris, M. Zajac, N. Alderete, Ö. Cizer, P. Van den Heede, R.D. Hooton, S. Kamali-Bernard, S.A. Bernal, Z. Zhao, Z. Shi, N. De Belie, Understanding the carbonation of concrete with supplementary cementitious materials: a critical review by RILEM TC 281-CCC, Materials and Structures 53(6) (2020) 136.
[4] P.H.R. Borges, J.O. Costa, N.B. Milestone, C.J. Lynsdale, R.E. Streatfield, Carbonation of CH and C–S–H in composite cement pastes containing high amounts of BFS, Cement and Concrete Research 40(2) (2010) 284-292.
[5] E. Gruyaert, P. Van den Heede, N. De Belie, Carbonation of slag concrete: Effect of the cement replacement level and curing on the carbonation coefficient – Effect of carbonation on the pore structure, Cement and Concrete Composites 35(1) (2013) 39-48.
[6] M. Saillio, V. Baroghel-Bouny, S. Pradelle, M. Bertin, J. Vincent, J.-B. d'Espinose de Lacaillerie, Effect of supplementary cementitious materials on carbonation of cement pastes, Cement and Concrete Research 142 (2021) 106358.
[7] M. Serdar, S. Poyet, V. L'Hostis, D. Bjegović, Carbonation of low-alkalinity mortars: Influence on corrosion of steel and on mortar microstructure, Cement and Concrete Research 101 (2017) 33-45.
[8] M. Thomas, The effect of supplementary cementing materials on alkali-silica reaction: A review, Cement and Concrete Research 41 (2011) 1224–1231.
[9] C. Pade, M. Guimaraes, The CO2 uptake of concrete in a 100 year perspective, Cement and Concrete Research 37(9) (2007) 1348-1356.
[10] B. Lagerblad, Carbon Dioxide Uptake during Concrete Life Cycle - State of the Art, 2005.
[11] A. Younsi, Long-term carbon dioxide sequestration by concretes with supplementary cementitious materials under indoor and outdoor exposure: Assessment as per a standardized model, Journal of Building Engineering 51 (2022) 104306.