

Utilisation of Carbon Dioxide from Flue Gases to Improve Physical and Microstructural Properties of Cement and Concrete Systems

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ABSTRACT: The accelerated carbonation of cementitious systems is a developing technology, which may have the potential for the improved encapsulation of wastes and contaminated materials in cementitious systems and for the sequestration of carbon dioxide (CO₂). Most calcium silicate minerals are known to react readily with CO₂. The reaction products can cause rapid hardening and result in the production of monolithic materials. This investigation is aimed at developing a method of utilising CO₂ in cementitious systems and also improving their physical and micro-structural properties. Two different methods of utilising CO₂ in the manufacture of cement pastes were explored in this investigation. In the first method, specimens were cured in a controlled environment, enriched with CO₂, at different levels of temperature and a constant relative humidity. Method 2 involved manufacturing specimens with CO₂ saturated mixing water. Results of compressive strength, x-ray diffraction, thermal analysis, setting times and consistency were obtained, which are reported in this paper. The results indicated that the use of an enriched CO₂ environment had a beneficial effect on test specimens by increasing compressive strength compared to those manufactured with CO₂ saturated mixing water, which showed no effect, either beneficial or detrimental, to compressive strength at all ages. However, it is apparent that specimens manufactured using saturated CO₂ mixing water were most affected at early stages of hydration as represented by initial and final setting times, where both the initial and the final setting times were significantly reduced due to the presence of CO₂. It has also been found that the use of an enriched CO₂ environment increased the amount of calcium carbonate in the pore structure leading to a denser matrix, which may lead to an enhancement in durability of the mix.

1. INTRODUCTION

Portland cement is the largest utilised material in the world for construction purposes. The production of each tonne of Portland cement releases approximately an equal amount of carbon dioxide (CO₂) into the atmosphere, which globally accounts for up to 8% of the total CO₂ emissions in the world [Technical Advice Note, Historic Scotland 2003]. As a result of increased emphasis on the reduction of CO₂ emissions and the sustainability of the construction industry, the development of methods to reduce and utilise such waste materials is vital.

Natural carbonation, i.e., primarily the reaction of the gaseous carbon dioxide (CO₂) with calcium hydroxide (Ca(OH)₂) to form calcium carbonate (CaCO₃) and water (H₂O), of hydrated cement paste (hcp) has a significant influence on the properties of concrete. Natural carbonation of concrete has been

recognised as one of the most important ageing processes and involves the absorption of CO₂ by an initially alkaline hcp, which causes the pH of the concrete to decrease and CaCO₃ to form. However, when accelerated carbonation is applied to the hcp that is in 'green' state, then the reaction path differs from that of normal atmosphere carbonation [Ortiz de Urbina & Goumans 2003, Meima & van der Weijden 2002 2002]. This is because there is insufficient time for the normal hydration products to form. The reactions occurring here differ from those of the natural carbonation of cement hydrates in that calcium from the anhydrous phases enters the pore solution and initially precipitates with carbonate ions instead of only hydroxyl ions [Young & Berger 1974, Maries 1992]. As a result, an alkaline environment may still be achieved after the early hydration stage. In this alkaline environment the passive film of iron oxides that acts as a barrier

to the anodic dissolution of reinforcing bar will be stable and the steel is protected from corrosion [Anstice & Page 2005]. CO₂ from flue gases may be used to treat fresh concrete. Klemm [1972a, 1972b] showed that calcium based cement systems react readily when exposed to carbon dioxide either immediately after moulding or after a short period of normal curing. The reaction products can cause rapid hardening of the cement paste and result in the production of monolithic cement phases. Today accelerated carbonation is a developing technology, which may have the potential for the treatment of waste gases and the sequestration of CO₂, an important greenhouse gas [Ngala & Page 1997]. It has been estimated that flue gases have approximately 10 - 15% carbon dioxide content. Accelerated carbonation research work carried out by Ceukelaire [1993] used an atmosphere containing 10% CO₂. This may suggest that flue gases can be used for a similar treatment instead of using conventional bottled CO₂, thus reducing CO₂ being released into the atmosphere.

The utilisation of a new method, 'super critical carbonation', has recently been reported from USA to produce cement based composites and the manufacture of lightweight products [Rubin & Carey 1997]. In this process, CO₂ is used at temperatures and pressures within the supercritical region of the CO₂ phase diagram. However, research carried out at Queen's University Belfast indicated that carbonating cement based materials at elevated temperatures without the application of pressure could also lead to improvements in physical and micro-structural properties of concrete [Russell 2001].

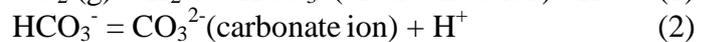
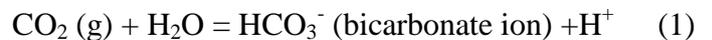
In this investigation two methods of accelerated carbonation were utilised to promote the rate and extent of carbonation at early ages of hydration. An initial investigation (Method 1) deals with the use of CO₂ in its natural state and utilises a carbonation chamber, with controlled temperature and relative humidity environments. In this chamber, samples were subjected to this treatment for certain periods of time. The source of CO₂ used in this investigation was ordinary bottled CO₂. Treated samples were then analysed to assess the effects an enriched carbon dioxide environment has on the compressive strength and micro-structural properties. After some consideration a second method of accelerated carbonation (Method 2) was introduced. In this method dry ice was used to saturate the mixing water with CO₂. It was assumed that through this method

CO₂ had the possibility to influence the total microstructure rather than just the surfaces of the specimens which is a limitation of Method 1. Again treated samples were then analysed to assess the effects enriched carbon dioxide mixing water has on the compressive strength and micro-structural properties.

1.1 Definition of the Carbonation Reaction

In the presence of carbonate ions the calcium ions in the pore solution in hydrated cement pastes precipitate and form calcium carbonate. This process is called carbonation. Calcium carbonate has a very low solubility. In concrete carbonation could result in all calcium compounds of the hydrated cement paste dissolving and forming calcium carbonate [Lagerbald 2004].

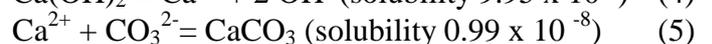
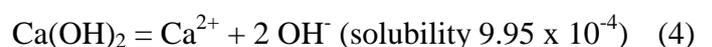
The concentration of CO₂ in the atmosphere is approximately between 0.03 and 0.05% [Jerga 2004]. Gaseous CO₂ cannot, however, react directly with the hydrates of the cement paste. Thus the CO₂ gas must first dissolve in water and form carbonate ions, which in turn could react with the calcium ions of the pore water. The type of carbonate ions depends on the pH of the hydrated cement paste. When CO₂ comes in contact with water at neutrality it forms bicarbonate. Inside concrete the pH is high and the bicarbonate dissociates and forms carbonate ions. Thus in the carbonated layer bicarbonate forms (due to low pH) but closer to the uncarbonated cement paste this carbonate ion forms and precipitates calcium carbonate crystals (CaCO₃). Calcium carbonate exists in three crystallographic forms, viz. aragonite, vaterite and calcite. Calcite and vaterite are commonly found in carbonated concrete. Presumably the metastable vaterite will transform to stable calcite with time. These reactions can be expressed by equations (1) and (2).



The carbonate ion will react with calcium ions in the pore solution to form calcium carbonate (Eq. 3).



This will lead to lower concentration of Ca²⁺, which in turn will lead to dissolution of calcium hydroxide (CH). The solubility of calcium carbonate (CC) is much lower than that of CH.



Thus CH dissolves and CaCO_3 precipitates and the process continues until all of the CH is consumed. Apart from CH the cement paste contains calcium silicate hydrate (C-S-H) and ettringite/monosulphate (AFt/AFm). All these phases are stabilised by high pH and Ca ions. Thus when the CH is consumed the C-S-H dissolves congruently. Parrott [1987] has highlighted that after approximately 5% CO_2 concentration very little extra weight gain occurred in a concrete sample (Fig. 1). This suggests that the most effective CO_2 percentage range was between normal atmospheric content (0.03%) and 5%. The experimental domain was set up with this parameter in mind.

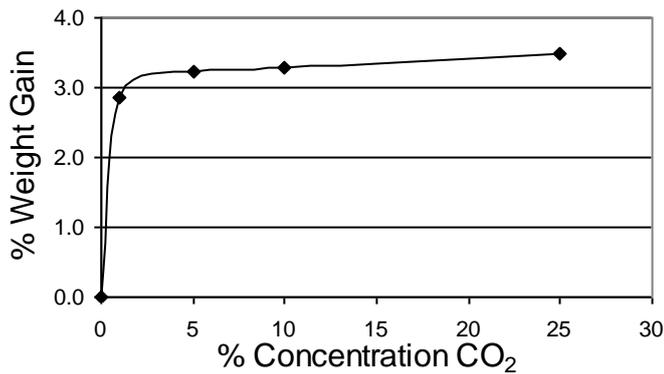


Figure 1. Weight gain due to carbonation at different carbon dioxide concentrations [Parrott 1987]

2. EXPERIMENTAL PROGRAMME

2.1 Method 1: Enriched CO_2 Curing Environment

Cement paste samples (21 numbers) were manufactured using Class 42.5N Portland cement at a water-cement ratio of 0.4. Cube moulds of size 50x50x50mm were used to manufacture the test specimens. The samples along with their mould were placed in an accelerated carbonation chamber immediately after casting and treated under different treatment conditions (Table 1). The variables in this investigation included carbon dioxide concentration (atmospheric concentration - i.e. 0.03%, 1% and 5%), temperature (20, 30 and 40 $^{\circ}\text{C}$) and duration of exposure (1, 3 and 7days), with relative humidity kept constant at 65%.

Table 1. Experimental variables in Method 1

Variable	Levels		
CO_2 %	0.03	1	5
Temperature $^{\circ}\text{C}$	20	30	40
Duration of Exposure (Days)	1	3	7

At the end of 24 hours, one set of samples was demoulded and tested. All other specimens were returned to the carbonation chamber immediately after demoulding for continuing with the treatment, as summarised in Table 1. Once the treatment was completed, samples were labelled and placed in an environmental chamber at a constant temperature of 20 (± 1) $^{\circ}\text{C}$ and a relative humidity of 65 (± 1)%, where they remained until required for testing. The testing schedule is shown in Table 2, with a list of tests to be carried out at each curing age.

Table 2. Schedule of hardened paste testing (enriched CO_2 environment) – Method 1

Age	Test Method
1	Compressive Strength (CS) X-ray Diffraction (XRD) Thermal Analysis (TA)
3	CS, XRD, TA Optical Microscopy (Thin Section).
7	CS, XRD, TA
14	CS, XRD, TA
28	CS, XRD, TA
91	CS, XRD, TA

2.2 Method 2: Enriched CO_2 Mixing Water

Cement paste samples were manufactured using CO_2 saturated mixing water. Mixing water was produced by adding dry ice until water was completely saturated with carbon dioxide. This was achieved by monitoring pH levels of the mixing water and when pH levels stabilised it was assumed that the mixing water had reached its saturation point. Temperature levels of mixing water were also monitored and maintained at 20 $^{\circ}\text{C}$ prior to mixing. Mixing initiated immediately after preparation of mixing water to eliminate, as much as possible, loss of CO_2 from the mixing water. Procedures for mixing and casting from Method 1 were also used in this method.

After casting, samples were placed in a constant temperature room at 20 (± 1) $^{\circ}\text{C}$ and a relative humidity of 65 (± 1)% and were then covered with plastic sheeting to eliminate evaporation of water from the top surface of the samples. After 24 hours all samples were demoulded, with one set being tested and analysed and the remaining samples being wrapped in damp hessian cloth and then sealed in plastic sample bags before being returned to the constant temperature room, where the samples were stored until required for testing. Table 3 highlights

the schedule of testing, illustrating test ages and testing to be carried out on each testing age.

Table 3. Schedule of fresh and hardened paste testing (enriched CO₂ mixing water)

Age	Test Method
0-6 hrs	Consistency and Setting Times
1 day	Compressive Strength (CS) Thermal Analysis (TA)
7 days	CS, TA
28 days	CS, TA
91 days	CS, TA

2.3 Test methods

2.3.1 Compressive strength

Triplicate samples were tested in compression at all testing ages. Testing was performed using a compression machine at a constant load rate of 50kN per minute [BS 1881 Part 201]. The load at failure was noted and an average value was obtained from tests carried out on the three replicate samples. The average values were then presented in graphic form for further analysis and interpretation.

2.3.2 X-Ray diffraction

Powder samples from specimens treated with Method 1 were obtained by drilling 5mm into the top of the cube using a masonry drill bit of 10mm diameter. Powder samples were taken from the top (trowel finished surface) of the cube as this face was exposed to the treatments for a longer period than other faces due to the fact that other faces were shielded by the cube moulds for 24 hours. Samples from specimens treated with Method 2 were obtained from the centres of the cubes used to obtain the compressive strength. Samples for X-ray diffraction (XRD) were ground and the analysis performed using Cu K α radiation between 6 and 60^o at 1^o/min and at an angular resolution of 0.1^o 2 θ . The X-ray diffraction data was collected using a PC. Identification of the phases was made by comparison with a library of known patterns available in X'PERT High Score software in Queen's University Lab and ICCD PDF database. A quantitative assessment of concentrations was obtained from the relative peak heights representing each crystal.

2.3.3 Thermogravimetric analysis (TGA)

TG is an important analytical technique that is applied to concretes and cements. In TG, the

properties of a material are investigated by continuous heating at a constant rate [Ramachandran 2001]. In this study the weight changes were determined as the sample was heated at a uniform rate of 10^oC per minute up to 1000^oC. TG was used to quantify hydration products formed with particular attention being applied to calcium hydroxide and calcium hydroxide levels, as these levels were to be used to confirm whether carbonation in the mixes would have occurred or not. The first derivative of change of mass can also be used for identification purposes as it involves weight losses [St. John & Poole 1998].

2.3.4 Consistency test

Consistency tests were carried out on all paste samples in Method 2 according to BS EN 196-3:1994. This was done to assess the effect on consistency that CO₂ may have at the initial stages of hydration. It is widely assumed that CO₂ may react with Ca(OH)₂ to form CaCO₃ and H₂O. This test was carried out to gauge whether this extra water has any effect on consistency, thus also possibly highlighting the point at which CO₂ begins to react with the cement hydrates.

2.3.5 Setting time

Setting time tests were also carried out on all paste mixes in Method 2 to assess the effect the saturated CO₂ mixing water had on the initial and final setting times. The test was carried out to BS EN 196-3:1995.

3. RESULTS AND DISCUSSION

As stated previously, two different methods of utilising CO₂ were considered during the course of this study, one creating an increased CO₂ environment and the other creating CO₂ saturated mixing water. Results are also presented in this order.

3.1 Method 1

3.1.1 Compressive Strength

In enriched CO₂ environment method, three cubes from each mix were crushed at the age of 1, 3, 7, 14, 28 and 91days. From the three results, an average compressive strength was calculated at each of these ages. The results in Figs. 2 to 4 represent the compressive strengths of mixes exposed to different CO₂ concentrations at three different temperatures.

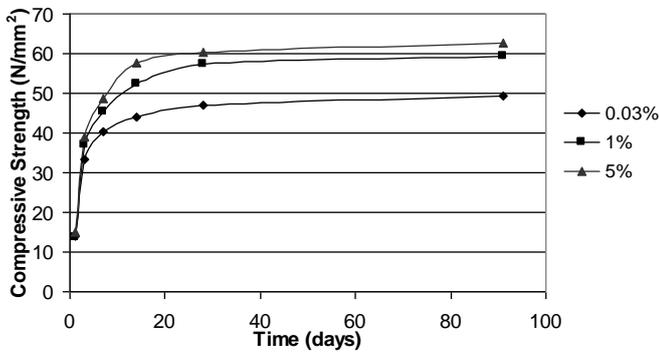


Figure 2: Compressive strengths of samples treated at 20°C and 0.03, 1 and 5% CO₂ concentration

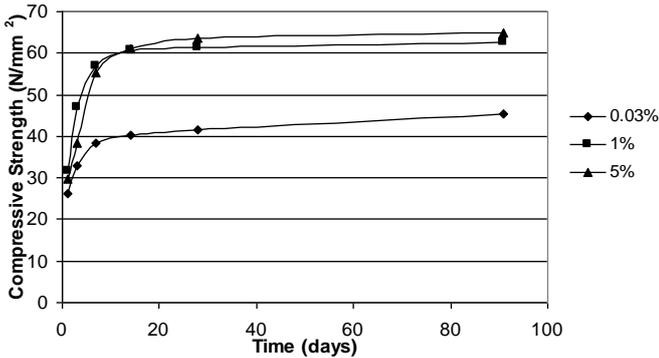


Figure 3: Compressive strengths of samples treated at 30°C and 0.03, 1 and 5% CO₂ concentration

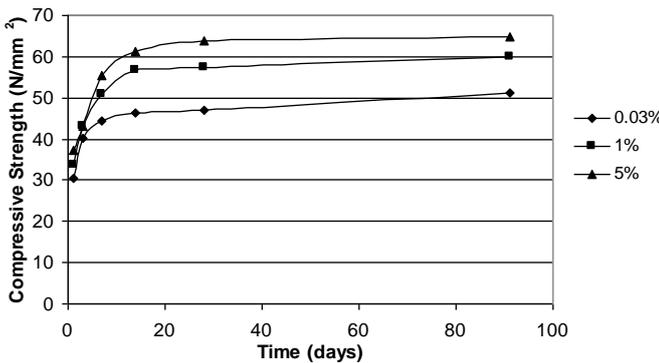


Figure 4: Compressive strengths of samples treated at 40°C and 0.03, 1 and 5% CO₂ concentration

As evident from the results in Figs. 2 to 4 it is clear that the compressive strength increased for all mixes with increase in curing age. Increased curing temperature also had an influence on early age compressive strengths, especially at 1 day. It is also evident that an increased CO₂ concentration had a positive effect on the compressive strength of all mixes, especially after 3 days of treatment. There may be some reasons as to why 1 and 3 day compressive strengths are quite similar for the mixes treated at different CO₂ concentrations. Firstly, the cubes remained in the moulds for the first 24 hours of treatment, which might have limited the effect of

the CO₂ to only the top trowel-finished surface. Secondly, a water-cement ratio of 0.4 was used in all mixes. This was quite a high value to use in a paste mix, which resulted in a quite wet mix. Water is necessary to promote the reaction of CO₂, but too much water limits the reaction due to blockage of pores in the solid. The water takes part in the salvation and hydration of the carbon dioxide. It dissolves the Ca²⁺ ions from the solid that will react to form the CaCO₃. Therefore, it influences the amount of product generated, which is also related to the strength development [Bertos 2004].

After approximately 3 days, compressive strengths for samples treated with 1 and 5% CO₂ increased considerably in comparison to untreated mixes (0.03% CO₂) up to 91 days curing. It is considered that the calcium carbonate formed in the pores due to the reaction of carbon dioxide with calcium is responsible for this increase in compressive strength. Compressive strengths for mixes treated at 1 and 5% CO₂ vary very little at all ages. From Figs. 2 to 4 it is evident that samples treated at 5% CO₂ have a slight increase in compressive strength at all ages compared to samples treated at 1% CO₂. Reasons for this small change have already been highlighted in the introduction [Parrott 1987].

3.1.2 Thermal analysis

Powder samples were obtained by drilling to a depth of 5mm in the specimens, as mentioned earlier. Samples were then further ground down to the required fineness. Figures 5 and 6 illustrate calcium carbonate and calcium hydroxide contents from the paste samples treated with 0.03 and 5% CO₂ respectively.

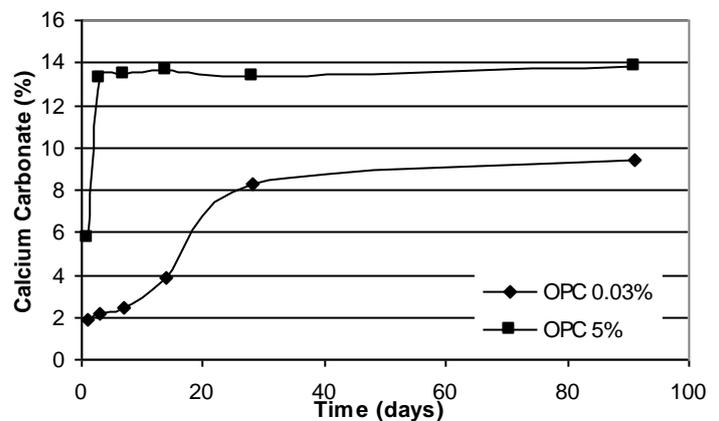


Figure 5: Calcium carbonate content of samples treated in CO₂ enriched environment

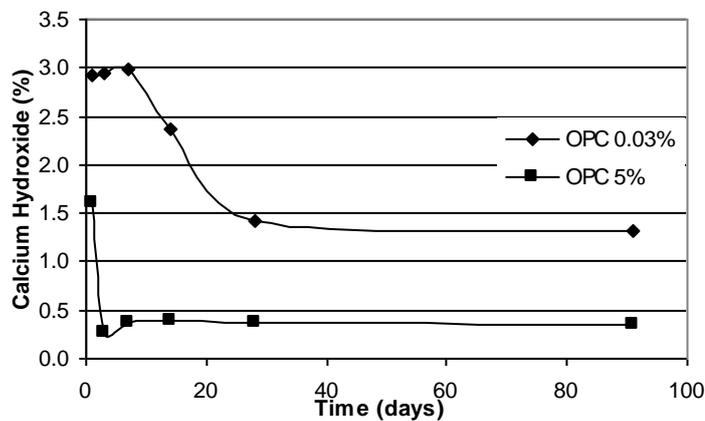


Figure 6. Calcium hydroxide content of samples treated in CO₂ enriched environment

As evident from Fig. 6, both calcium carbonate and calcium hydroxide follow the trends which were explained in the introduction. In the presence of an enriched CO₂ environment CaCO₃ content rapidly increases in the initial 24 hours compared to the sample treated in atmospheric CO₂. This also agrees with calcium hydroxide contents which have been significantly depleted after 24 hours compared with the atmospheric treated samples. This validates Eqs. (4) and (5), which state that CO₂ depletes Ca(OH)₂ and forms CaCO₃. Both Ca(OH)₂ and CaCO₃ contents stabilise after 24 hours, which may suggest that accelerated carbonation is only influential up to 24 hours. It may be possible that CaCO₃, which is approximately 17% larger than Ca(OH)₂, causes the pores to be blocked and consequently did not allow the diffusion of CO₂ further into the specimen [Van Gerven 2004].

3.1.3 X-Ray diffraction

XRD was used to identify and quantify the crystalline content of samples treated in Method 1. In this investigation the Rietveld method, using PANalytical X'PERT Highscore Plus software was utilised to quantify the crystalline materials. With the calcium hydroxide values obtained from TG used as an internal standard the amorphous content was calculated. XRD patterns and data can be seen in Figure 7 and Table 4 respectively.

The XRD results show both qualitatively and quantitatively that CH levels were depleted and CaCO₃ levels rose with increased levels of CO₂ concentration in the treatments. The XRD pattern shows a huge increase of CaCO₃ between the sample treated at 0.03% CO₂ and the sample treated at 5% CO₂. It can also be seen from both the patterns and

quantities of minerals that CH levels almost completely depleted for the sample treated at 5% CO₂. It can be assumed that CH was decalcified by CO₂ to form CaCO₃ and H₂O (Eqs. 4 and 5). This would strengthen the argument that the increase of CaCO₃ in the pores may be responsible for the increased compressive strength results. However, the XRD results highlight an aspect that the compressive strength results failed to do. The compressive strength results show similar results for samples treated at 1 and 5% CO₂ concentration at all ages. The XRD has shown that CaCO₃ and CH levels in both samples are quite different. This may warrant further investigation and may lead to an increase in durability properties for the latter samples, even though compressive strengths are only marginally separated.

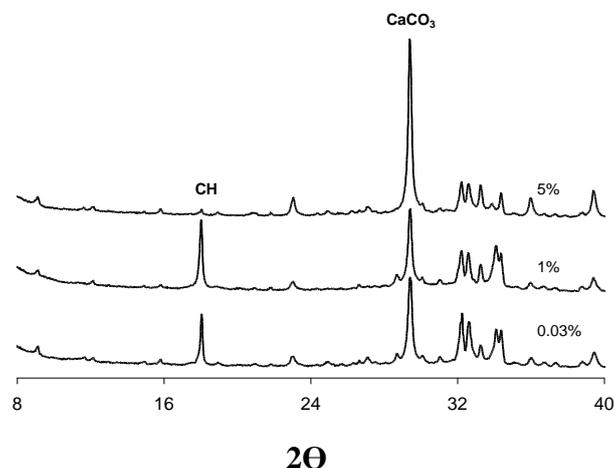


Figure 7. XRD pattern for samples cured for 28 days and treated at 30°C and at various CO₂ concentrations for 7 days

Table 4. Mineralogical composition of noncarbonated (0.03%) and carbonated (5%) samples after 28 days

Cement Minerals	Notation	Quantity of Minerals (%)	
		0.03% CO ₂	5% CO ₂
Portlandite	CH	9.6	0.8
Calcite	CaCO ₃	34.6	61.3
Ettringite	AFt	3.7	3.6
Alite	C ₃ S	29.8	17.7
Belite	C ₂ S	12.9	6.4
Brownmillerite	C ₄ AF	3.5	2.2
Aluminate	C ₃ A	5.9	7.9

3.2 Method 2

3.2.1 Compressive strength

In enriched CO₂ mixing water method, three cubes from each mixture were crushed at the age of 1, 7, 28 and 91 days. From the three results, an average compressive strength was calculated. Results are shown in Fig. 8. These results represent the compressive strengths of mixes manufactured with ordinary water and enriched CO₂ water.

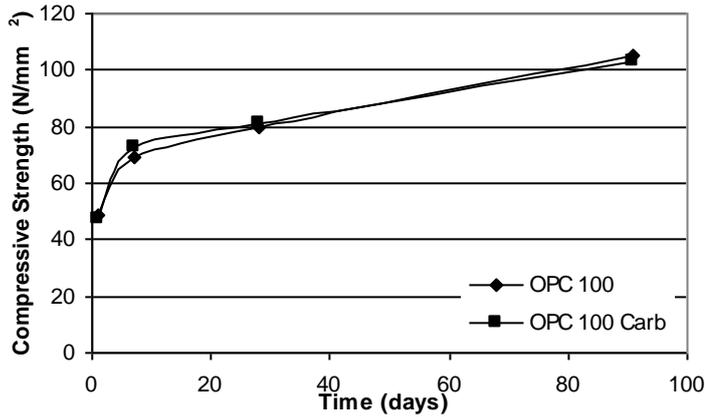


Figure 8. Compressive strengths of OPC paste samples utilising CO₂ enriched mixing water

Figure 8 demonstrates that by using enriched CO₂ mixing water the compressive strengths are neither detrimentally nor beneficially affected. It is found that compressive strengths are almost comparable at all ages when using the two mixing water types. These results do not follow the same trend as was achieved when using an enriched CO₂ curing environment, when improved strengths were achieved, especially at later ages. It may be considered that the enriched CO₂ curing environment had a more substantial effect on strengths because samples were exposed to the CO₂ for 7 days. It may also be assumed that the CO₂ absorbed in the mixing water is consumed quite early in the hydration stages and that any effects due to this may have only occurred at the early hydration stage. It was therefore deemed necessary to carry out some early hydration tests to assess the effects CO₂ may have on the fresh properties of the paste.

3.2.2 Consistency Test

Consistency tests were carried out to assess whether any extra water through the reaction of CO₂ and Ca(OH)₂ (Eqs. 4 and 5) may have been produced.

Table 5 highlights that CO₂ enriched mixing water has no effect on consistency, compared to ordinary mixing water and this would suggest that CO₂ does not contribute in any way in the initial stages of hydration.

Table 5. Comparison of consistency of OPC paste samples in Method 2

Mixture	Consistency (%)
OPC + water	0.30
OPC + carbonated water	0.30

3.2.3 Setting time

The setting time test was carried out to assess whether CO₂ becomes influential after the initial stages of hydration and possibly highlight a change in microstructure that occurred after consistency testing had been carried out. Table 6 illustrates that both the initial and final setting times have been reduced when CO₂ enriched mixing water has been used compared to ordinary mixing water. This suggests that CO₂ has become active somehow after the initial stages of hydration have occurred. A theory that may explain this may be that the carbonate ion (CO₃²⁻) may react with the calcium ion (Ca⁺) in the C-S-H that surrounds and protects the unreacted C₃S grains, thus accelerating the dissolution of the barrier, resulting in faster hydration of C₃S and thus faster setting times. This may also explain why no variations in results could be seen at initial hydration stage as C₃S would not have hydrated enough to release HSiO₄, which in turn reacts with Ca to form C-S-H.

Table 6. Initial and final setting times of OPC paste samples in Method 2

Mixture	Initial setting time (min)	Final setting time (min)
OPC + water	268	345
OPC + carbonated water	215	260

3.2.4 Thermal analysis

Powder samples were obtained from cubes crushed in the compression machine. The samples were taken from the centre of the cube and ground to the required fineness before analysing. Results displayed in Figs. 9 and 10 highlight that manufacturing paste samples using enriched CO₂ mixing water had no

significant effect on calcium carbonate or calcium hydroxide levels at the different test ages. This compares with compressive strengths which were also unaffected using this method of accelerated carbonation. It is also evident that $\text{Ca}(\text{OH})_2$ levels are slightly increased for samples prepared with non-carbonated water at the ages of 7, 28 and 91 days. This was unexpected and is contradictory to results obtained in Method 1. It may be possible that CO_2 is somehow being consumed or released from the matrix before it has sufficient time to react with cement hydrates. However, this contradicts setting time results which highlighted quicker setting times when this method of accelerated carbonation was used. It is unclear what is happening with the CO_2 after the initial hydration period. This part of the experimental programme may warrant further investigation to get a clearer understanding as to the processes occurring within the matrix.

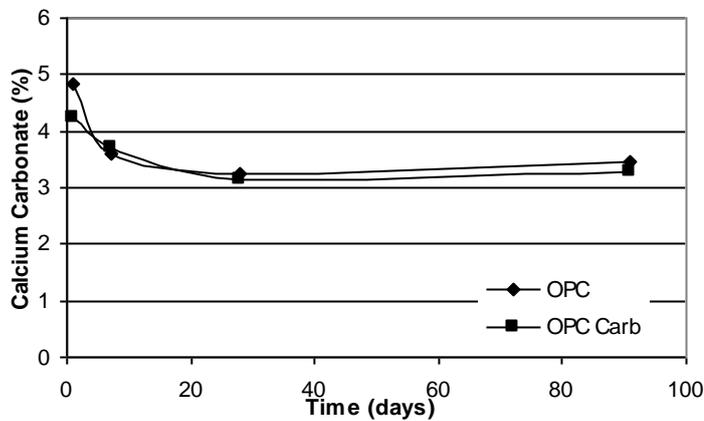


Figure 9: Calcium carbonate content of samples manufactured with CO_2 enriched mixing water

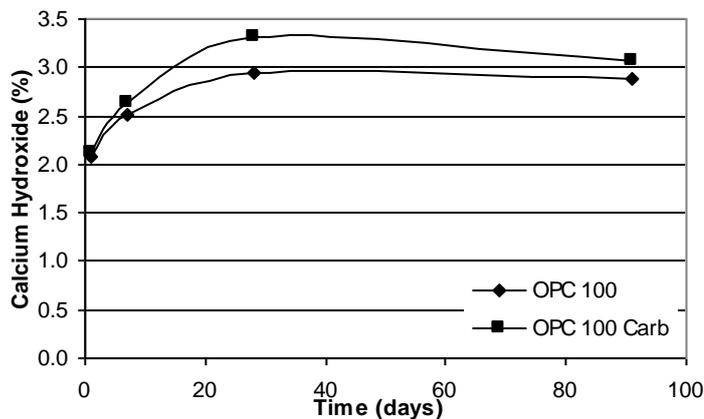


Figure 10: Calcium hydroxide content of samples manufactured with CO_2 enriched mixing water

4. CONCLUSIONS

On the basis of this investigation to study the effectiveness of two different methods to utilise CO_2 on the physical and micro-structural characteristics of portland cement pastes, the following conclusions have been drawn:

- (i) The method to utilise an enriched CO_2 curing environment proved to be extensively superior to the enriched CO_2 mixing water with regard to improved compressive strengths and micro-structural changes.
- (ii) The effects of the utilisation of an enriched CO_2 curing environment on various properties were as follows:

(a) Increased compressive strength of all samples at all ages. 1% CO_2 concentration was shown to have a notable impact on compressive strength, especially after 3 days of treatment for all mixes compared to samples treated at normal atmospheric CO_2 concentrations (0.03%). Whilst 5% CO_2 concentrations also showed improvements in compressive strength, these improvements were only slightly higher than those for 1% CO_2 concentration. These results support the statement by Parrott (1987) that minimal increase in sample weight occurs after approximately 1% CO_2 concentration.

(b) XRD results would suggest a modest difference in CaCO_3 levels between 1% and 5% CO_2 concentrations, which would conflict with Parrott's statement. On this evidence it would seem that even if increased CO_2 levels have minimal effects on compressive strength, compared to lower level concentrations, there may, however, be beneficial improvements in the durability properties of the sample. It is therefore proposed that higher levels of CO_2 concentrations should also be considered especially if improved durability properties are required. Results from the petrographic thin sections also confirmed that increased CO_2 concentrations have a beneficial effect on the depths of carbonations achieved, which would also have a positive effect on the durability properties of a sample.

- (iii) The utilisation of enriched CO_2 mixing water resulted in the following conclusions:

(a) No beneficial or detrimental effects to compressive strength were highlighted at any test age.

(b) Calcium carbonate and calcium hydroxide levels were largely unaffected, which is contrary to results from Method 1 and contrary to Eqs 1 to 5 stated in the introduction.

(c) Consistency tests have proven that CO₂ has no influence on the fresh paste properties at early hydration stages. However, setting times were affected, with specimens manufactured with enriched CO₂ mixing water showing reduced setting times of approximately 25% compared to control specimens.

(iv) The work carried out so far has shown the potential for CO₂ to be used as a treatment for fresh cement pastes to improve early age properties. Improvements in compressive strength and microstructural properties have been highlighted due to the action of CO₂. It may now be possible to use CO₂ from other sources such as flue gases and use it to further improve certain properties of fresh and hardened concretes.

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