

CARBONATION PERFORMANCE OF OPC-SLAG-FLY ASH BINDER SYSTEM

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Abstract

Corrosion of steel reinforcement in concrete is the leading cause of deterioration of concrete structures. Carbonation induced corrosion is prevalent in cements containing Supplementary Cementitious Materials (SCMs). In this study, the carbonation performance of cement containing fly ash and combination of slag and fly ash is investigated. Concrete specimens cast at two different water to cement ratios were subjected to accelerated and natural carbonation conditions. Effect of carbonation on pore structure properties of concrete like porosity and sorptivity was also investigated. The carbonation resistance of slag-fly ash blend was lower as compared to fly ash for the selected composition. Increase in porosity and rate of water absorption was observed on carbonation in blended cement systems.

Keywords: Carbonation, Empirical modeling, Porosity, Supplementary cementitious materials.

1. INTRODUCTION

Widespread availability, ease of use and long-term structural integrity make concrete the most used construction material in the world. Global demand for cement is increasing continuously and it is estimated to rise from approximately 3 billion tonnes in 2014 to 5 billion tonnes by 2030 [1]. This increased production will lead to an obvious increase in the carbon dioxide emission from the cement industry. Supplementary cementitious materials like fly ash, slag, metakaolin, rice husk ash, silica fume etc. available naturally or byproducts from other industries are being used as clinker replacement to reduce the environmental impact of cement industry [2,3].

Addition of SCMs as clinker replacement also has certain limitations related with it. For instance, fly ash based cement is associated with lower early strength and longer curing regime whereas the use of silica fume results in increased cost of concrete because of a higher dosage of admixture. In addition, transportation of SCMs from one part of the country to another has also cost associated with it. Thus, the percentage replacement of clinker by a particular SCM depends on many factors i.e. the material properties, availability and application

[4,5]. To overcome these limitations, a significant increase in the use of cement containing OPC and combination of SCMs has recently emerged. Using a combination of SCMs can help to compensate for the inadequacies of individual SCMs [6–8]. Besides, improving the properties of concrete, combinations of SCMs also help in bringing down the clinker factor and therefore creating a conducive environment to further reduce the emissions from cement industry. Use of blended cement containing a combination of SCMs like fly ash-silica fume, slag-fly ash, fly ash-metakaolin, slag-limestone, and calcined clay-limestone has been reported [9–12]. A growing interest is being observed recently in studying the properties of blended cement produced by replacing clinker with a combination of slag-fly ash [13–15]. The mechanical properties, fresh concrete properties and durability characteristics of this system are reported to be at par with Ordinary Portland Cement (OPC) even at lower clinker factor. Moreover, the Bureau of Indian Standards (BIS) published a standard IS 16415 in 2015, allowing replacement up to 65% of clinker by a combination of slag and fly ash. A large quantity of unused fly ash in India along with the availability of quality slag makes it a lucrative alternative.

However, low clinker factor cements are known to be susceptible to carbonation due to the dilution and pozzolanic effect. Due to a lower/negligible amount of calcium hydroxide in the hydrated system, other calcium bearing phases like calcium silicate hydrate (C-S-H), ettringite, etc. carbonate extensively, thereby, jeopardizing the integrity of the concrete [16–19]. Also, due to the difference in the molar solid volume of the cement hydrates and carbonation products, the microstructure of the concrete is altered. Increase in porosity and coarsening of pores are observed on carbonation, specifically in low clinker factor cements [20,21].

This emphasizes the need for research on performance of low clinker blended cements due to carbonation. In this study, a comparison is made between, OPC, OPC-fly ash (PPC) and OPC-Slag-fly ash (CC) binder systems. The performance of blended cement under accelerated and natural carbonation condition is investigated. In addition, changes occurring in pore structure properties on carbonation were also measured.

2. METHODOLOGY AND EXPERIMENTS

2.1 Materials

Clinker and gypsum were procured from a cement plant based in Gujarat, India. Processed slag was procured from Goa, India whereas fly ash was procured from National Thermal Power Corporation (NTPC) in Uttar Pradesh, India. The fly ash used was classified as *Siliceous Pulverized Fly Ash* according to IS 3812 (Part 1):2003 [22]. The chemical composition of raw materials measured using X-ray fluorescence (XRF) is given in Table 1. OPC was produced by grinding clinker (97%) and gypsum (3%) in a laboratory-scale ball mill. The particle size distribution of raw materials measured using laser granulometry is shown in Figure 1. The D50 was measured to be 20.5, 17.5 and 12.9 μm for OPC, fly ash and slag respectively. The PPC was prepared by interblending OPC (70%) and fly ash (30%) homogenously in a ball mill without charge. CC was prepared similarly by mixing OPC (55%), slag (30%) and fly ash (15%) in the given proportion. Crushed stones were used as coarse aggregate whereas river sand was used as fine aggregate in the preparation of the concrete.

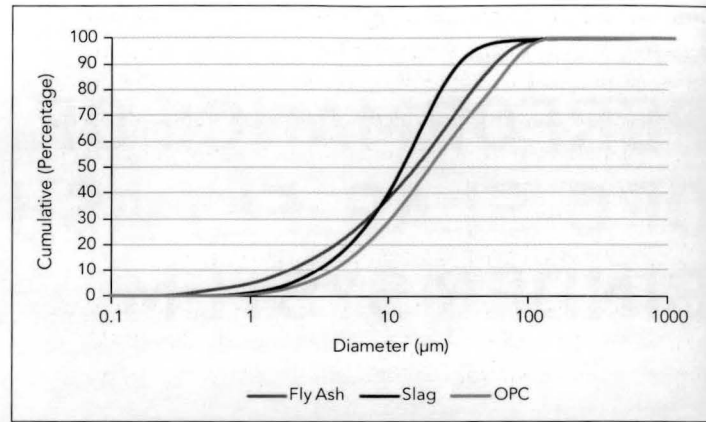


Figure 1: Particle size analysis of raw materials measured using laser granulometry.

Table 1: Chemical and physical properties of raw materials

	CLINKER	GYPSUM	FLY-ASH	SLAG
SiO ₂	21.07	2.77	58.82	32.26
Fe ₂ O ₃	4.32	0.36	6.19	1.93
Al ₂ O ₃	4.65	0.62	30.62	23.16
CaO	65.16	32.62	1.01	33.88
MgO	2.13	1.20	0.41	7.01
SO ₃	0.77	38.75	0.12	–
Na ₂ O	0.38	0.06	0.19	0.010
K ₂ O	0.20	0.037	1.30	0.37
LOI	0.96	23.02	1.11	1.08

2.2 Sample Preparation and Exposure Conditions

Concrete was cast at a water to cement ratio of 0.35 and 0.45 with a total water content of 162 kg/m³. Water reducing admixture was used to improve the workability of the concrete. Concrete cubes (15x15x15 cm) and cylinders (Diameter:10 cm, Height: 20 cm) were cast to measure the compressive strength of the concrete and change in pore structure characteristics of concrete respectively. Concrete prisms (50x10x10 cm) were cast to measure the carbonation depth. The details of the mix design of concrete are given in Table 2. The concrete specimens were left in the casting area and were demolded after 24 hours of casting. Thereafter, the specimens were cured in water for 120 days. After the end of the curing regime, the compressive strength (Table 2) of the concrete was measured on cube specimens. Disc samples were cut from cylindrical specimens each having a height of 5 ± 0.2 cm, which were used to measure porosity and sorptivity before and after carbonation. Epoxy was applied on the circumferential side of the cylinders and on the top and bottom part of the prisms in order to have unidirectional carbon dioxide ingress in the concrete. Thereafter, all the specimens were conditioned at 27°C temperature and 60% relative humidity for 15 days.

Table 2: Mix design (for 1 m³ of Concrete)

BLENDS	CEMENT (kg)	COARSE AGGREGATE (kg)		FINE AGGREGATE (kg)	ADMIXTURE (kg)	WATER (kg)	COMPRESSIVE STRENGTH (MPa)
		20 mm	10 mm				
OPC (0.35)	463	708	472	638	2.31	162	53.56 ± 1.90
PPC (0.35)	463	688	459	620	1.85	162	56.36 ± 5.99
CC (0.35)	463	691	461	623	2.31	162	46.49 ± 2.72
OPC (0.45)	360	720	480	707	1.44	162	43.25 ± 2.84
PPC (0.45)	360	705	470	692	1.44	162	38.23 ± 0.39
CC (0.45)	360	707	471	695	1.44	162	30.28 ± 1.72

After the end of the conditioning period, disc samples and one set of prism specimens were placed in an accelerated carbonation chamber set at 3% carbon dioxide concentration, 27°C temperature and 60% relative humidity whereas the other set of prism specimens were placed in a sheltered condition in the natural environment.

2.3 Carbonation Depth Measurement

Carbonation depth was measured on the prism specimens kept in accelerated condition after 1, 3, 7, 14, 28, 60, 90 and 120 days of exposure whereas for the samples placed in the natural

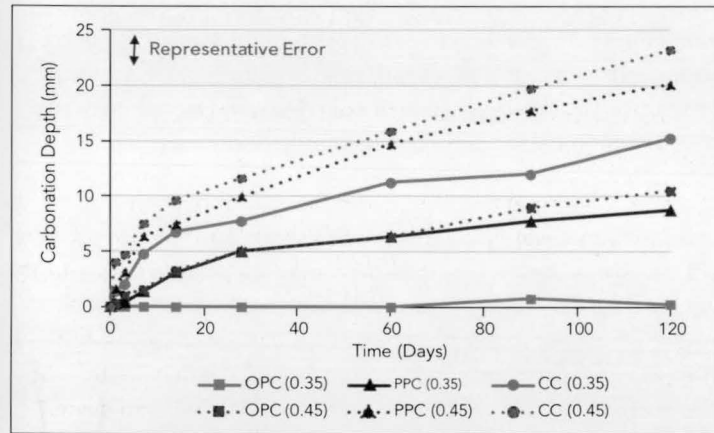


Figure 2: Carbonation depth of samples placed in accelerated carbonation condition.

condition the carbonation depth was measured at the end of 6, 12, 18 and 24 months using 1% phenolphthalein indicator solution [23,24]. The indicator maintains pink colour in the non-carbonated region whilst it turns colorless in the carbonated region. A length of approximately 5 cm was cut from the prism using a shear cutter for the measurement. The remaining part of the prism was kept back in the chamber after applying epoxy on the freshly broken surface for testing at later ages. The carbonation depth value is reported as an average of maximum carbonation depth measured on all four sides of the broken prism sample.

2.4 Porosity and Sorptivity

The effect of carbonation on the pore structure of concrete cast at a water to cement ratio of 0.35 was studied by measuring the change in porosity and sorptivity on concrete samples placed in accelerated condition. The porosity was measured in accordance with ASTM C642 [25], whereas sorptivity was measured according to the guidelines mentioned in ASTM C1585 [26]. The measurements were made after 30, 60 and 90 days of exposure.

3. RESULTS

3.1 Carbonation Depth

Figure 2 shows the carbonation depth of the samples placed in the accelerated condition. The carbonation depth measured in cement containing SCMs was higher than OPC. The CC blend, in general, showed lower carbonation resistance as compared to PPC. Although, the difference in carbonation depth seems to be reduced at higher water to cement ratio. Similar results were obtained for the samples placed in natural exposure condition (Figure 3).

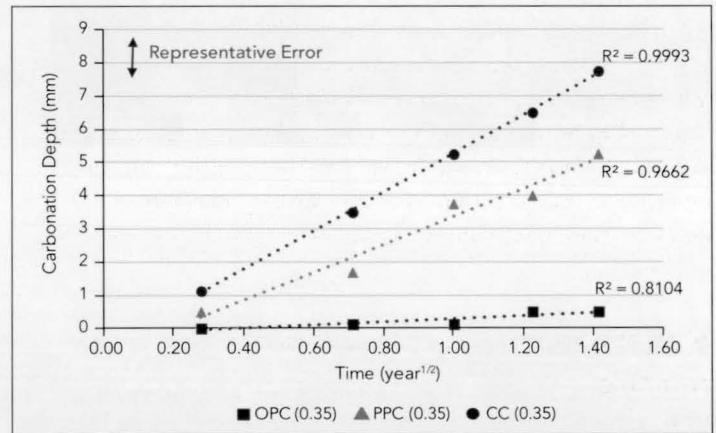


Figure 3: Carbonation depth of samples placed in natural sheltered condition.

3.2 Alteration in Pore Structure Characteristics

The porosity of concrete measured using boiling water test is shown in Figure 4. The porosity of the non-carbonated sample (NC) was measured at the end of the conditioning regime. The porosity of PPC and CC system was lower than OPC prior to carbonation. CC system had the lowest porosity even with only 50% clinker factor. The lower porosity in blended cements can be attributed to refined pores due to the pozzolanic reaction of

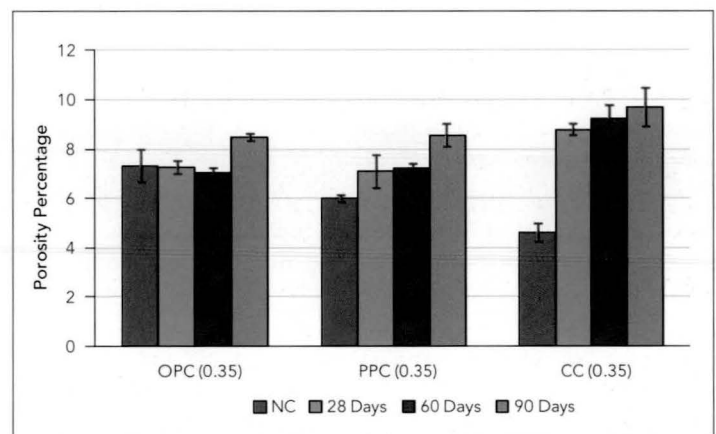


Figure 4: Porosity of carbonated samples at different ages of exposure in accelerated condition.

SCMs. Similarly, the rate of water absorption measured using capillary sorption test was the lowest in CC (Figure 5). However, the opposite trend was observed in carbonated samples. The porosity and sorptivity of carbonated PPC and CC concrete increase with exposure age. The increase was highest in case of CC blend.

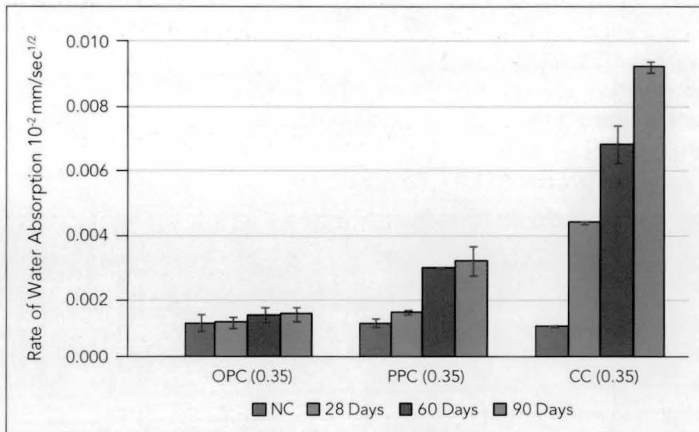


Figure 5: Sorptivity of carbonated samples at different ages of exposure in accelerated condition.

4. DISCUSSION

The carbonation resistance of blended cements, in general, is known to be lower than the OPC system [16,21,27,28]. The carbonation resistance of concrete is influenced by physical and chemical parameters of concrete along with environmental parameters. Concrete with higher compressive strength tends to have higher carbonation resistance [28,29]. The compressive strength of PPC was similar to OPC; however, the carbonation resistance of PPC was significantly lower. On a similar line, the rate of carbonation is higher in concrete with higher porosity due to the availability of more porous space for the diffusion of carbon dioxide. However, in spite of lower initial porosity, the carbonation resistance of PPC and CC was inferior to OPC.

Calcium hydroxide produced from clinker hydration helps primarily in maintaining high alkaline content in concrete. The amount of calcium hydroxide available in OPC is more, hence, has higher buffering capacity against pH change induced by carbonation. Moreover, calcium carbonate formed on carbonation of calcium hydroxide has 11-14% higher solid volume depending on the polymorph of calcium carbonate precipitated, which results in the reduction in porosity of concrete, thereby assisting in the reduction of the rate of carbonation [16,30]. However, in absence of or lower quantity of CH in blended cements, other hydration products carbonate, which does not necessarily result in a reduction

in porosity of concrete [20]. The measured values of porosity and sorptivity on carbonated samples further substantiate the notion. The increased porosity and sorptivity on carbonation could be because of the increase in the volume of capillary pores. Coarsening of pore structure on carbonation has been reported in literature [17,31,32]. The pores of concrete strongly influence the performance of concrete. With an increase in the capillary pore volume, the susceptibility of concrete from other deterioration forms could become prominent.

4.1 Prediction of Carbonation Depth

The rate of carbonation in natural condition is sluggish in nature due to the low concentration of carbon dioxide in the atmosphere. To evaluate the long-term performance of concrete under carbon dioxide practically is not viable. Hence, to predict the carbonation performance of concrete used in the study use of semi-empirical model proposed by the authors in [27].

$$x = \sqrt{\frac{7.2 \times D \times [CO_2] \times \left(\frac{[CO_2 \text{ Natural}]}{[CO_2]}\right)^{0.25} \times \left(e^{\frac{Q}{R} \left(\frac{1}{T_{ref}} - \frac{1}{T}\right)}\right) \times t}{[RA] \times CF}}$$

$$D = \frac{1.44 \times 10^{-4} \times (1 - RH)^{1.2}}{\left(s \times \frac{w}{c}\right)^2 \times \left(\frac{c}{w} - 1\right)^{0.25}}$$

where x: carbonation depth (m), t: time (sec), [CO₂] and [CO₂ Natural] is the concentration of carbon dioxide in accelerated test and concentration of carbon dioxide in atmosphere (mol/m³), [RA]: concentration of reserve alkalinity (mol/m³), CF: clinker factor, Q is the activation energy for carbon dioxide diffusion in concrete (39000 J/mol K), T_{ref}: reference temperature (298 K), R: universal gas constant (8.314 J/mol K), T: actual test temperature, D: diffusion coefficient (m²/s), S: compressive strength of concrete at 120 days, w/c: water to cement ratio and RH: external relative humidity. The value of reserve alkalinity was to calculate the carbonation depth using above formula was also obtained from [27].

Figures 6 and 7 show the experimental carbonation depth and predicted carbonation depth using the semi-empirical model for accelerated carbonation condition. A reasonable agreement is observed between experimental and modeled depth for PPC and CC blends at different water to cement ratio. The model also gave reliable estimates for natural exposure condition as shown in Figure 8. The average relative humidity (50%), temperature (26.2°C) and carbon dioxide concentration (0.035%) around the year in Delhi was used for the computation.

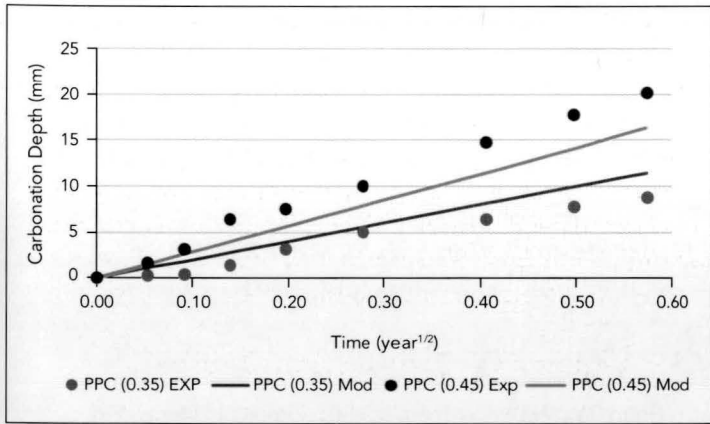


Figure 6: Experimental and modeled carbonation depth for PPC concrete placed in accelerated condition.

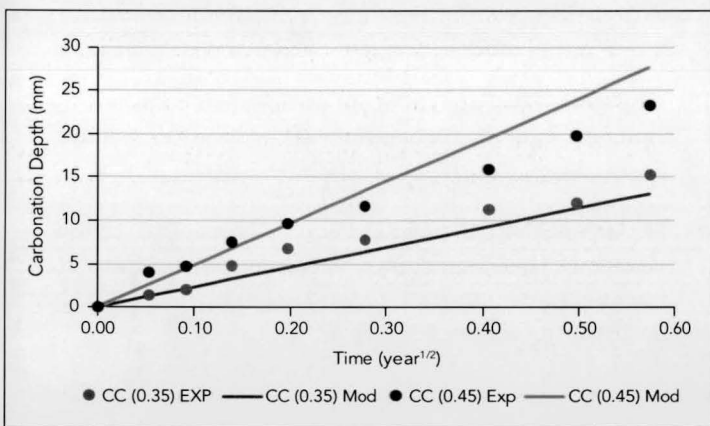


Figure 7: Experimental and modeled carbonation depth for CC concrete placed in accelerated condition.

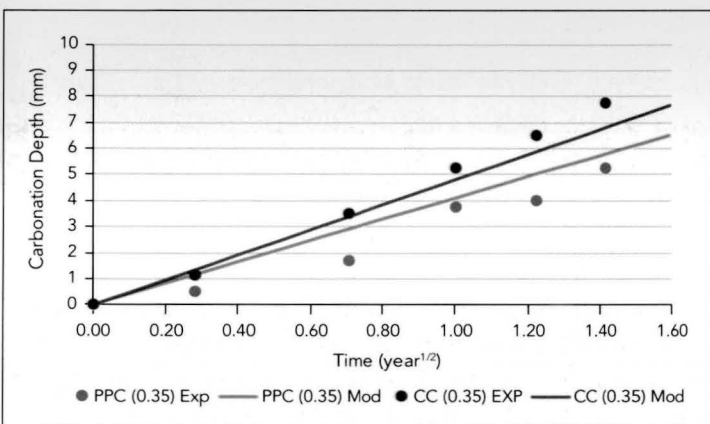


Figure 8: Experimental and modeled carbonation depth for CC and PPC concrete placed in natural condition.

The extent of carbonation in PPC and CC concrete after 25 and 50 years in natural sheltered exposure condition was predicted using the model (Table 3). The performance of CC is significantly lower than OPC and PPC system. The performance of CC (0.35) is similar to PPC (0.45) w/c, even though the compressive strength of CC (0.35) is approximately 20% higher.

The poor performance of CC is due to lower clinker factor and consumption of calcium hydroxide by the SCMs. This implies that carbonation resistance of cement is primarily dependent on the total alkalinity of the system [27,33]. At higher water to cement ratio, the carbonation resistance of blended cements worsen as compared to OPC. The effect of clogging of pores due to carbonation of calcium hydroxide is not considered in the empirical model; hence, the carbonation depth of OPC systems is slightly over predicted.

Table 3: Predicted carbonation depth in natural sheltered condition (mm)

	OPC (0.35)	OPC (0.45)	PPC (0.35)	PPC (0.45)	CC (0.35)	CC (0.45)
25 Years	15.17	17.31	20.45	30.67	33.67	52.59
50 Years	21.46	24.48	28.93	43.51	47.62	74.38

High CO₂ emissions during the production of OPC and continuous increase in cement demand makes it imperative to use cements with lower clinker factor. Composite cement does show some interesting results in terms of carbonation resistance even at a clinker factor of 50%. The carbonation performance at of composite cement can be improved by increasing the clinker factor or by changing the proportion of slag to fly ash. However, it is vital to investigate the influence of other deterioration processes on concrete due to change in pore structure characteristics on carbonation.

5. CONCLUSIONS

In this study, a preliminary investigation on carbonation resistance of OPC-fly ash and OPC-slag-fly ash were carried out using accelerated and natural conditions. The long-term performance of concrete under natural exposure condition was predicted using a semi-empirical model.

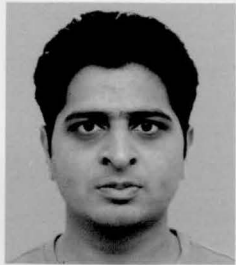
- The carbonation resistance of OPC-slag-fly ash composite cement was lower as compared to OPC and PPC. The carbonation performance reduced with an increase in the water to cement ratio.
- The porosity and sorptivity of the blended system increased on carbonation. Lower quantity or absence of calcium hydroxide and extensive carbonation of other hydration phases is the primary reason for the increase.

The results show that not only are low clinker cements more susceptible to carbonation, the increase in porosity due to carbonation would also lead to a further increase in the rate of carbonation. It can be seen from the results that it is important to increase the cover depth of concrete when low clinker cements, like composite cement, are used at locations where carbonation can lead to corrosion.

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