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Pore Structure Characterization in Concrete Prepared with Carbonated Fly Ash

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Abstract. Carbon dioxide capture and storage (CCS) is a technique to address the global concern of continuously rising CO$_2$ level in the atmosphere. Fly ash is considered as a suitable medium for CCS due to presence of metal oxides. The fly ash which has already sequestered carbon dioxide is referred to as carbonated fly ash. Recent research reveals better durability of concretes using carbonated fly ash as part replacement of cement. In the present research pore structure characterization of the carbonated fly ash concrete has been carried out. Mercury Intrusion porosimetry test has been conducted on control concrete and concrete specimens using fly ash and carbonated fly ash at replacement levels of 25% and 40%. The specimens have been water cured for 28 days and 90 days. It is observed that porosity reduction rate is more pronounced in carbonated fly ash concrete compared to control concrete at higher water curing age. Correlation analysis is also carried out which indicates moderately linear relationship between porosity % and pore distribution with particle size and water curing.

1. Introduction

Recently the CO$_2$ concentration in atmosphere already crossed the value of 403.38 PPM [1] and is projected to touch the value of 800 PPM by 21$^{st}$ century. The predicted consequences of rising CO$_2$ level in the atmosphere include dramatic change in climate, leading to predictions of devastating consequences for both human and biota [2]. This motivated the research world to think about a safe and suitable strategy to mitigate the challenge. Strategies to reduce the CO$_2$ content of atmosphere include limiting the CO$_2$ production, adopting fuels having less carbon, enhancing the use of alternate energy sources [3, 4], utilising the produced CO$_2$ in different fields and capturing and storing the CO$_2$ safely through various technology. CCS (carbon capture and carbon storage) is one of the most promising approaches to reduce the carbon dioxide (CO$_2$) content in the atmosphere and thus the greenhouse effect [5-7]. Mineral carbonation comes under the chemical storage of CO$_2$, where both carbon capture and carbon storage is being done by solid carbonation. It is one of the most promising options for the permanent CO$_2$ fixation by forming stable carbonate mineral such as calcite, magnesite, siderite and dolomite etc. Fly ash (FA), the residue of coal power plant, has abundant availability and toxic nature. Being a hazardous pollutant, it is a great threat to the society. This needs safe disposal or productive reutilisation. FA after sequestering carbon dioxide is referred to as carbonated FA. Recently researches undertaken by the author to utilize carbonated FA as part replacement of cement in concrete have established the relevance of the cementitious nature exhibited by the material. Research indicates better alkali, acid and sulphate resistance by concrete which uses FA [8] and carbonated FA as part replacement of cement [9]. Porosity is one of the major parameters of the concrete influencing its behaviour related to both strength and durability. Pore structure is one of primary deciding factors for permeability [10] of the concrete, which influences the aggressive...
ingress of deteriorating ions and thus may be used as a predictor of structural durability. Concrete has a complex internal pore system. The capillary pores arising from cement particle spacing in the dispersion, smaller gel pores in inter layers of the C-S-H or other hydrate products, air voids and porous zone at aggregate cement interface [11] constitute the pore system. The objective of the present research is to characterize the pore structure of carbonated FA concrete. The characterization will include determination of porosity % and pores distribution. The objective also includes finding the existence of correlation of these parameters with water curing age, proportion of the FA and carbonated FA used in the concrete.

2. Experimental Program

In this research work three cementitious materials such as commercially available ordinary Portland cement (43 grade as per IS: 8114-1978), low Calcium FA (ASTM Class F) from national thermal power corporation (NTPC), Kaniha, Odisha and carbonated fly ash (CFA), prepared through mineral carbonation of FA through atmospheric carbonation ([9], [12] ) are used. Crushed granite (20mm maximum size) and river sand conforming to zone III of nominal maximum size of 4.75mm were used as coarse aggregate and fine aggregate respectively in the concrete mixture. Commercially available poly-carboxylic based super plasticizer and normal tap water was used in the experiment. The specific gravities of cement, FA and CFA were found as 3.1, 2.33 and 2.31, respectively. Their particle-size was analysed using Mastercizer-2000 (Malvern Instruments, Malvern, U.K.). Their respective granulometric data are also reported in Table 1.

| Constituent        | D10 (µm) | D50 (µm) | D90 (µm) | Mean size (µm) |
|--------------------|----------|----------|----------|----------------|
| Cement             | 1.860    | 8.939    | 31.946   | 16.79805       |
| Fly Ash            | 0.719    | 5.914    | 24.714   | 13.09198       |
| Carbonated fly ash | 0.060    | 8.329    | 32.416   | 15.89338       |

The mix design calculations for M30 grade concrete were performed as per IS: 10262 (BIS 2009). Total five types of concrete were prepared in the laboratory for investigation in accordance with IS: 516-1959. Control concrete (CC) was made using 100% cement as binding material and two set (Low and High) of fly ash concrete (LFC and HFC) as well as carbonated fly ash concrete (LCFC and HCFC) were cast using FA and CFA at cement replacement level of 25% and 40%, respectively. A constant water/binder ratio of 0.38 with slump value of around 100 mm was used in the experiment. The total 24 numbers of concrete cubes (150 mm) from each type were cast to perform the compressive strength, durability and pore structure characterisation test. After 24 h, they were removed from the mould and kept in the water curing chamber for curing period of 28 and 90 days. To conduct the compressive strength test of the concrete six numbers of cubes from each type were taken out of the curing chamber and dried in shade at the end of 28 and 90 days of water curing. The test was carried out in a compressive testing machine of 2000KN capacity (CTM Digital) in the concrete laboratory of SCE, KIIT University at the loading rate of 0.2-0.4 N/mm²/s. To determine the durability characteristics of the concrete against chemical attack, each type of concrete cubes were allowed to immerse in three chemicals such as 5% Sodium chloride, 5% Sodium sulphate, and 1% Sulphuric acid at the end of 28 and 90 days of water curing. After 120 days of chemical curing the compressive strength of the concrete were measured following the similar procedure. The compressive strength value was considered as the average of strength value of three samples. For the pore structure characterisation, slices of 8 mm φ and 2mm thickness concrete specimens have been obtained from the core of the 28 and 90 days water cured concrete cube. The specimens were immersed in ethyl alcohol for eight days and dried in oven at 60°C for mercury intrusion porosimeter (MIP) test by Quantachrome Poremaster.

3. Experimental Results

3.1 Particle size distribution:

From the granulometric data along with their size fractions as presented in Table 1 it is observed that the D₉₀ and D₅₀ values of all the samples are ranging between 24.741µm - 32.416µm and 5.914µm -
8.939µm, respectively, hence all the samples have the capacity of adequate hydration as all have the mean particle size less than 45µm [13, 14]. Both the FA and carbonated FA have finer particles than the cement [15] and the smaller particles add to fineness and strength on hydration as the pozzolanic reaction can be highly activated when the particle size is small.

3.2 Compressive strength of concrete under normal water and chemicals:
As presented in the Table 2, the compressive strength value for CFC though less for 28 days water curing, but with increasing water curing period it behaved in a better manner showing significant higher strength value. Further, it displayed best resistance to chemicals for both the water curing ages. Though CC performed better in initial ages, but both the FA and CFC have shown much higher resistance to chemicals compared to that of CC. This is due to the filling of smaller size pores, voids and air spaces of cement particles by the FA and carbonated FA. This results in packing of the concrete material tightly, restricting the permeation of harmful ions.

3.3 Mercury intrusion porosimetry (MIP) test:
From MIP test information on several parameters related to porosity are obtained. These parameters include total intrusion volume, total pore area, median pore radius, average pore radius, bulk density, apparent skeletal density and porosity %. The porosity % and pore size distribution are two critically studied factors which influence utility aspects of concrete specimens in structural usages. Information retrieved relating to these important parameters are tabulated in Table 2. Figure 1 and Figure 2 represent the histogram of total intrusion volume and porosity percentage in concrete specimens for 28 and 90 days of water curing period, respectively. The intrusion volume vs pore diameter plots from the machine generated data for concrete specimen water cured for 28 and 90 days have been furnished in Figure 3 and Figure 4, respectively. The pore percentage distribution in three major influencing zones for concrete specimen water cured for 28 and 90 days have been tabulated in Table 3. Figure 6 illustrates the pore percentage distribution of concrete specimens over volume, water cured for period of 28 and 90 days.

Table 2. Test results for concrete specimen water cured for 28 and 90 days

| Water curing period in days | Type of concrete | Compressive strength (MPa) | Compressive strength under chemical attack for 120 days (MPa) | MIP Test Results |
|----------------------------|-----------------|----------------------------|-------------------------------------------------------------|-----------------|
|                            |                 |                            | Total intrusion volume (ml/g)                               | Total pore area (sqm/g) | Bulk density (gm/cc) | Porosity % |
|                            |                 |                            |                                                             |                              |                             |            |
| 28                         | CC              | 43.62                      | 32.35                                                       | 30.89                        | 25.99                        | 0.0673     | 7.627 | 1.981 | 13.332 |
|                            | LFC             | 39.9                       | 34.18                                                       | 34.01                        | 28.03                        | 0.052      | 6.568 | 1.892 | 9.838  |
|                            | HFC             | 38.76                      | 25.4                                                        | 24.85                        | 22.8                         | 0.05       | 4.509 | 1.796 | 8.98  |
|                            | LCFC            | 31.96                      | 23.98                                                       | 33.82                        | 30.51                        | 0.052      | 4.505 | 1.924 | 10.158 |
|                            | HCFC            | 25.45                      | 20.61                                                       | 26.77                        | 26.56                        | 0.068      | 7.162 | 1.822 | 12.480 |
| 90                         | CC              | 49.36                      | 35.94                                                       | 31.41                        | 35.64                        | 0.0646     | 6.427 | 1.972 | 12.739 |
|                            | LFC             | 51.62                      | 47.79                                                       | 40.4                         | 43.38                        | 0.0405     | 3.254 | 1.861 | 7.537  |
|                            | HFC             | 52.01                      | 50.07                                                       | 47.23                        | 47.39                        | 0.0430     | 3.868 | 1.794 | 7.714  |
|                            | LCFC            | 42.88                      | 39.04                                                       | 51.01                        | 44.12                        | 0.0420     | 4.642 | 1.931 | 8.110  |
|                            | HCFC            | 38.92                      | 35.88                                                       | 44.4                         | 43.02                        | 0.0431     | 3.230 | 1.826 | 7.870  |

4. Discussion on MIP test results
4.1 Variation of total intruded volume and porosity %:
It can be observed from Figure 2, that FC show the best performance followed by CFC at 28 days water curing. HCFC show the highest cumulative intruded pore volume percentage as almost approaching 70%. A decrease in total intrusion volume has been observed for all the concrete specimens with increasing water curing age, the decrease of intrusion volume in CC is much low, thus
indicating almost a slow release of hydrate products during 28 to 90 days water curing. However, in FC and CFC the difference in the intrusion volume is appreciably larger compared to CC. The CFC display the best performance with a higher degree release of hydrate products compared to all other concrete. This indicates accelerated chemical transition, formation and deposition of the extra hydrated product within this curing period those are responsible for densification of the CFC and FC specimens in a faster rate.

From Figure 3, it can be inferred that for specimens water cured for 28 days, CC displayed the highest porosity % followed by the HCFC, LCFC and LFC, the HFC being the lowest. Low porosity associated with FC may be explained in light of denser pore structure arising from low particle size and secondary hydration of FA. With the FA addition to the cement, physically it serves as the nucleation sites for the cement hydration products. Thus, it helps the cement grain to achieve a higher degree of hydration. In addition, chemically FA particles also undergo the hydration process (pozzolanic reaction) in presence of water and Ca(OH)₂ thus giving the extra C-S-H gel. Due to these dual effects of FA, the extra gel formed helps in increasing the solid volume of the cement paste and adds extra solids to the concrete material. These extra solid deposited in the pore space filling the capillary pores and thus the making the microstructure packed and dense [16]. An improvement in porosity through decrease in porosity % is also noticed with increase in curing period. It is seen that the CFC performs in a better way to reduce its porosity % with water curing age in comparison to that of FA concrete and the CC. This is due to the continuous and gradual increase of hydration rate with time thus developing the microstructure more and more with the global refinement of continuous pores filling. In case of CFC along with the extra hydration products, the calcite (CaCO₃) present in carbonated FA, additionally fill the micro pores of the material helping dense packing of the microstructures in a higher degree.
Figure 5. Pore % distribution for concrete specimen water cured for period of 28 days

4.2 Pore size distribution:
As observed from Figure 3 to Figure 5 the 28 days water cured samples, with respect to the pores in the size range from 0 to 106 nm, HCFC has the highest proportion followed by LFC, CC, LCFC and HFC. Regarding the pores in the size range of 107 to 1051 nm, HFC leads followed by LCFC, LFC, CC and HCFC. For the pore diameter > 1051 nm, HCFC has the highest proportion and LCFC, the lowest. With increase in water curing period, it is observed that pore % in larger size is also higher in CC and CFC, when compared to the FC specimens. For CC and LFC, the percentage of macro pores (107 to 1051 nm) only, increased whereas for all other concrete it decreased whereas for the mega pores of pore diameter > 1051nm, in FC only it has decreased. It is also noted that the micro pores % increases with water curing days with a faster rate in case of HFC and LCFC, and its rate is lowest for the CC. The percent of mega pores for CC also increases but for FC it is greatly reduced with curing period. It indicates the fine pores filling in case of CC is the slowest and for HFC it is the highest. It can be inferred that inclusion of FA lead to the densification of pore structure of the concrete.

Table 3. % distribution of pores in concrete specimen water cured for 28 and 90 days

| Range of Pore sizes | 28 days Water Curing | 90 days water curing |
|---------------------|-----------------------|----------------------|
| 0-106 nm            | CC 67.16 LFC 67.31 HFC 62 LCFC 64.02 HCFC 67.88 | CC 65.94 LFC 67.44 HFC 69.05 LCFC 69.84 |
| 107-1051 nm         | CC 25.37 LFC 26.92 HFC 34 LCFC 32.2 HCFC 23.36 | CC 26.32 LFC 29.88 HFC 30.23 LCFC 23.81 |
| >1051 nm            | CC 7.47 LFC 5.77 HFC 4 LCFC 3.78 HCFC 8.76 | CC 7.74 LFC 2.22 HFC 7.44 LCFC 2.33 |

5. Correlation Analysis
To determine the existence and significance of a linear relation between dependent and independent variable, the correlation analysis is performed and a relationship between volume fraction, water curing age and porosity parameters related to the various concrete is obtained. The volume fraction denotes the ratio of volume of cementitious materials to the volume of cement in concrete specimens without any replacement. The concrete specimens prepared constitute of cement, FA and carbonated FA as cementitious materials. Assuming spherical shape of the particle, the volume of the particles can be computed using the Eqs. 1-3. $V_i$ is the volume of any cementitious particle, whose radius is $r_i$, $x_i$ is the proportion of the cementitious particle in terms of percentage and $r_c$ is the mean particle size of the OPC 43. $VF = \sum x_i V_i / V_c$; where, $V_i = 4/3 \pi r_i^3$ and $V_c = 100 \times 4/3 \pi r_c^3$ (1)

The Pearson product moment correlation coefficient (PCC) between two parameters is calculated as ratio of the covariance to the product of standard deviations of the two variables. The PCC of porosity % with respect to the water curing age and volume fraction is provided in Table. 4.

Table 4. Pearson Correlation coefficient for porosity % with Volume fraction and Water Curing Age

|                      | Volume fraction | Water curing age | Porosity % |
|----------------------|-----------------|-----------------|------------|
| Volume fraction      | 1               |                 |            |
| Water curing age     | -9.59215E-18    | 1               |            |
| Porosity %           | 0.616162478     | -0.509437784    | 1          |
The above table indicates a moderately positive correlation between volume fraction and porosity % and thus, an increase in volume fraction will result in higher porosity %. This clearly establishes that, the replacement of cement with smaller particles of FA or carbonated FA will reduce the porosity % in concrete specimen thus will reduce the permeability. Reduction in permeability results in improved resistance against the chemical attack. The experimental results of reduced strength loss in FC and CFC against acid, sulphate and chloride attack are set of the evidences. Table 5 offers the PCC relating the volume fraction and water curing age with the distribution of pore sizes. The data offer a moderate positive correlation between volume fraction and the pore % at higher size. The distribution is more towards higher size pores at higher volume fraction i.e. in CC. Similarly, water curing age has a moderate positive correlation with the pore size distribution favouring to smaller pores.

Table 5. Pearson correlation coefficients for pores distribution to water curing age and volume fraction

| Volume fraction | Water curing age |
|-----------------|------------------|
| Water curing age | -9.59215E-18     |
| Pore distribution 0-106 nm | 0.290566975 | 0.533294782 |
| Pore distribution 107-1051 nm | -0.586587493 | -0.270035599 |
| Pore distribution >1051 nm | 0.681325048 | -0.043190589 |

6. Conclusion

The conclusions drawn from the porosity test performed on the concrete specimens are outlined in the following lines. The porosity percentage at 28 days of water curing is the least for the high FC and the highest for the control concrete. However, at 90 days of water curing the porosity % remained high for control concrete whereas both the FC and CFC show almost nearly equal value with very low porosity %. With water curing age, the porosity of control concrete slightly decreased whereas the rate of decrease in case of FC was found medium and for CFC was the fastest. This may be predicted due to the high rate of hydration in case of FC and CFC in the later water curing age. Further, with water curing age the total intrusion pore volume decreases at high rate in case of CFC than that of FC and CC. The Pore distribution in CFC and FC tends to be more in the finer zone (<10⁶nm) compared to those in control concrete. From the correlation analysis, it was concluded that a moderately positive linearity exists between volume fraction and porosity % and a moderately negative linearity exists between water curing period and porosity %.

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