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Studies on mechanical and microstructural properties of hematite modified concrete

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Abstract : High density or heavy weight concrete is manufactured by using heavy weight aggregates such as hematite, magnetite, goethite, limonite etc. Concrete containing hematite is an excellent radiation shielding material which is widely used in nuclear industries, particle accelerators and reactors. Two different types of M35 grade concrete were prepared the fly ash modified concrete (FAC) and a combination of fly ash (FA) and hematite modified concrete (HC). The cement was partially replaced with 20% of FA for FAC whereas the cement and fine aggregates were partially replaced with 20% of FA and 10% of hematite respectively for HC. The mechanical properties such as compressive, split tensile and flexural strength were compared in both types of modified concrete after curing period of 7, 28 and 56 days. The results showed that concrete containing hematite and fly ash exhibits higher strength than the fly ash modified concrete. Further durability studies such as porosity measurement and Rapid Chloride Permeability Test (RCPT) were carried out. Microstructural properties such as X-ray diffraction (XRD) and Field Scanning Electron Microscopy (FESEM) studies were also studied and discussed in detail in paper. Further, epifluorescence microscopic studies quantified the presence of microbial attachment on FAC and HC.
Keywords : Heavy weight concrete; Hematite; Fly ash.

1. Introduction

The production of cement is involving in energy consumption and produces enormous amount of carbon-dioxide which has green house effect. To reduce the cost and carbon dioxide emission from cement industry, the usage of supplementary cementitious material and waste materials is an effective method (Duschesne and Berube, 1995). The additional materials of cement especially fly ash have recently gained popularity, because it includes enough silicon dioxide (SiO2) and calcium oxide (CaO) (Karim et al, 2011). Fly ash is one of the by-products obtained from coal fired power plants and the replacement level ranges from 0-30 percent by weight of the cement. The fly ash generally contains calcium-bearing minerals and less iron content. Now a day's the fly ash modified concrete is getting more popular because of cheaper rate and easy availability especially for nuclear power plants which is not suitable for radiation shielding. For this radiation shielding application, various heavy weight aggregates such as barites (barium sulphate mineral ore), magnetite and hematite (iron ore) are used in heavy weight concrete (Gencel et al 2010). Hematite is a natural red rock which contains iron oxide having specific gravity ranges between 4.9 to 5.5 gcm-3 and has a mohs hardness between 5.5 to 6.5 (Gencel et al 2011). In general, the shielding of radiation increases with increase in concrete density. Concrete containing hematite is an excellent radiation shielding material which is widely used in nuclear industry (Osman et al, 2010). Apart from the shielding properties, it is very important to study the mechanical, durability and microstructural properties of the concrete. So this study has been planned the comparative study of fly ash modified concrete (FAC) and hematite modified concrete (HC), where HC was prepared by replacing the cement with 20 % of fly ash and 10 % of hematite as fine aggregates and analyzed the, pH, mechanical (compressive strength, split tensile strength and flexural strength) durability (porosity measurement RCPT and carbonation test), microstructural properties (XRD and FESEM) and microbial attachment on FAC and HC specimens.

2. Materials and Methods

To find the effect of hematite as fine aggregate, M35 grade of concrete was prepared by using Ordinary Portland Cement (OPC) (Coromandal brand, 43 grades) confirming to IS 8112. The fly ash was collected from Ennore Thermal Power Station, Chennai conforming to IS 3812. Hematite was obtained from the Chhattisgarh mines which are world famous high grade iron ores. The fine aggregates were 4.75 and coarse aggregates of 12.5 and 20.0mm in size were utilized for the mixture. Sulphonated naphthalene formaldehyde (SNF) based superplasticizer was purchased from Fosroc chemicals Ltd., Bangalore, India.

2.1. Preparation of specimens

Two different concrete mix were prepared such as fly ash (FAC) modified concrete and hematite modified concrete (HC) in the Centre for Nanoscience and Nanotechnology, Sathyabama University, Chennai. Four different sizes of concrete molds such as 150×150×150mm cube, 100×100×100mm cube, 100×300mm cylindrical, 100×200mm cylindrical and 100×100×500mm rectangular prism specimens were casted. The 35×10mm of mortar specimens were casted for the microbial attachment studies. The mix design details of both FAC and HC specimens are shown in Table 1.

Table 1. Mix design (per cubic metre)

Concrete Type	Cement (Kg)	Fly ash (Kg)	Water (Kg)	Hematite (kg)	Fine aggregate (kg)	Coarse aggregate (kg)	Admixture (1.2% by wt of Cementitious materials)
FAC	300	75	157	-	783	1128	4.5
HC	300	75	157	78	705	1128	4.5

Design stipulations for specimens casting:
Concrete grade : M35
Type of cement : OPC 43grade confirming to IS 8112
Type of aggregate: Crushed angular gravel
Maximum size of the aggregate: 20.0mm
Type of mineral admixture: Siliceous type fly ash confirming to IS 3812 (part I)
Chemical admixture: Conplast SP-430 (Fosroc chemicals Ltd., Bangalore, India)
Workability: 100mm slump

2.2. Exposure studies

All the specimens were demoulded after 24 hours of casting and the specimens were kept for curing in fresh water. The cured specimens were withdrawn after 7, 28 and 56 days for further studies such as pH, mechanical, durability, microstructural properties and microbial attachment and the results were compared for FAC and HC specimens

2.2.1. pH studies

To hold the different components in the concrete structures, pH is an important factor. pH reduction in concrete effects the porosity and decrease the hydration products which will ultimately reduce the strength of the concrete. In this work both surface pH and crushed pH are determined for 7, 28 and 56 days fresh water cured FAC and HC specimens. The flat surface electrode (WTW SenTix- 3110) pH meter was used to analyze the surface pH of the specimens. 1gm of crushed concrete powder was taken in 100ml of beaker, added 10ml of Millipore water and pH was measured by pH meter (Hanna, HI-2211),

2.2.2. Compressive strength

Compressive strength is the capacity of the concrete structures to withstand loads and tends to break up on compression. The cube specimens of 150×150×150mm were tested for the compressive strength (AIMIL Ltd., Instrumentation and Technologies, Chennai) having a capacity of 2000 KN based on IS: 516-1959. Before testing the specimens were wiped and cleaned to remove the loosely bound materials. The test was performed for 7, 28 and 56 days fresh water cured FAC and HC specimens.

2.2.3. Split tensile strength

Tensile strength of the concrete is very important to determine the load at which the concrete splits due to tension failure. The standard size of 100×300mm concrete cylindrical specimen was placed horizontally between the loading surfaces of the machine. The compression load is applied diametrically and uniformly along the length of the cylindrical specimen until the failure occurs along the vertical diameter. For split tensile strength measurement, Aimil digital compression testing machine of 2000 KN were used for 7, 28 and 56 days fresh water cured FAC and HC specimens.

2.2.4. Flexural strength

Concrete rectangular prisms of standard size 100×100×500mm were used for the flexural strength (AIMIL Ltd., Instrumentation and Technologies, Chennai, 2000 KN). The load applied on the specimen was 180 kg/min and test was done for 7, 28 and 56 days fresh water cured FAC and HC specimens.

2.2.5. Porosity measurement

Vacuum saturation method was adopted for the porosity measurement for 28 days fresh water cured FAC and HC specimens. The dimensions of 50×100mm cylindrical concrete specimens were cored from the cylindrical specimen. Then, the specimens were weighed (W4) after oven drying at 105ºC. The specimens were kept in the vacuum desiccator at 1 bar pressure for 24 hr and it was filled with de-ionized water for water saturation. The vacuum in the desiccator was maintained for another 3hr and then allowed to saturate for another 1hr without vacuum pressure. The specimens were taken out and wiped with dry cloth to remove excess moisture and weighed in both air (W3) and buoyant mass (W2) was taken for the saturated specimen (Papzan et al, 2012 and Safiuddin and Nataliya, 2005).

$$\text{Porosity}\,(\%) = W3 - W4 / W2 - W3 * 100 \qquad (1)$$

2.2.6. RCPT

The deterioration of concrete in the aggressive environment due to the chloride ion ingression is one of the severe problems. As per ASTM C 1202, standard size of 50×100mm cylindrical concrete specimens were used to measure the electrical conductance from one end of the specimen to the other end. One end of the specimen was immersed in 3% sodium chloride and the other end with 0.3N sodium hydroxide and throughout the measurement 60V DC was maintained across the ends of the specimens. The total charge passed during this period was calculated in terms of coulombs using the trapezoidal rule (ASTM C 1202-97). This test was done for 7, 28 and 56 days fresh water cured FAC and HC specimens.

2.2.7. Carbonation test

The Carbonation test is very much significant for concrete specimens as it deteriorates its structures when exposed in different environments. The carbonation and chloride attack is the main source of concrete deterioration which leads to corrosion of reinforcement (Basheer et al 1996). The cubes of 100x100x100mm dimensions of FAC and HC were used for this test and exposed in open atmosphere and carbonation chamber (UT/HTC-220) for accelerated carbonation test with temperature (20oC), relative humidity (65%) containing atmospheric CO2. The carbonation depth was measured after 28 and 56 days by using bench saw concrete cutting machine (Darien Electrical, Chennai). The cube specimens were cut into 10-15 mm from the edge by spraying the 1% of phenolphthalein in the solution of 70% ethyl alcohol on a freshly broken surface (RILEM Committee, 1988). The non-carbonated and carbonated area was found as purple and colorless repectively. The colorless area was measured as carbonation depth.

2.2.8. XRD studies

XRD technique is used to identify crystalline phases in the concrete. The 28 days fresh water cured FAC and HC specimens were powdered and analyzed by Brag Brentano geometry method. The XRD analysis was made for this study by Rigaku 9kW, SmartLab, with Cu Kα radiation (λ = 1.5406 Å). The scan step was 0.02º per second and two theta ranges was 10 to 90º. The x-ray tube voltage was 30KV and current 100mA was used throughout the analysis. The XRD pattern was analyzed with by Joint Committee on Powder Diffraction Standards (JCPDS).

2.2.9. FESEM studies

The FESEM analysis was carried out for fly ash powder and hematite to identify the structures of these two materials. The changes in morphology were observed for 28 days fresh water cured FAC and HC specimens. This was examined under Carl Zeiss, SUPRA® 55 with GEMINI® Technology. All specimens selected for this study were sputter coated with gold for conductivity of the surface.

2.2.10. Epifluorescence microscopy studies

The mortar specimens of 35x10mm were used for the microbial attachment studies under epifluorescence microscope. The FAC and HC specimens were cured in fresh water for 28 days to visualize and compare the attachment of microbes on the concrete surface. The specimens were rinsed with sterile water and dried in sterile chamber and the surface was flooded using 0.1% acridine orange (AO). After 2 min, excess stain was drained off and the specimens were washed in sterile water, dried out and analyzed using epifluorescence microscope (Nikon Eclipse E600, excitation filter BP 490; barrier filter O515). AO binds with DNA and emits green fluorescence upon excitation at 480–490 nm and when it binds with RNA orange-red fluorescence will be attained, where, the active living cells and biofilm will fluorescence orange (Vinita et al, 2014).

3. Results and Discussions

3.1 pH studies

The surface pH value was constantly equal as 12-13 after 7, 28 and 56 days for both the specimens of FAC and HC exposed in fresh water. The crushed pH showed reduction in pH in FAC (12.50) compared to HC (12.55) in 56 days. Generally, the decrease of pH in concrete structures lowers the strength of the concrete as it becomes more porous and as a result, it decreases the formation of hydration products. The pH value was found more in HC specimens compared to FAC.

3.2. Compressive strength

The compressive strength of the FAC and HC of 7, 28 and 56 days cured specimens were plotted in the figure 1a. It shows after 7 days of curing the strength for FAC was 28.9N/mm2 and HC was having 28.1N/mm2. But after 28 days, FAC strength was 39.5 N/mm2 and HC was 49.7778 N/mm2. Same trend of strength was found in 56 days exposed specimens where FAC strength was 47.9 N/mm2 and 53.926 N/mm2. The increase in strength of the HC is due to the specific density of the hematite particles which may decrease the porosity of the concrete and therefore, there will be attenuation of the γ-rays increases (Al-Humaiqani, 2013). It has been reported that incorporation of hematite in concrete significantly increases the compressive strength and stress- strain behavior of the concrete (Oluokun and Malak 1999).

3.3. Split Tensile strength

The split Tensile strength was recorded for 7, 28 and 56 days cured specimens of FAC and HC which is shown in figure 1b. From the test data, it is evident that the tensile strength of the FAC on 7, 28 and 56 days was 1.77, 2.8 and 4.10 N/mm2 whereas HC specimens had 2.32, 3.607 and 3.607 N/mm2 respectively. The split tensile strength is 7% higher than in HC than FAC at 56 days, because there will a chance of decreasing the pores and stronger bonding between the cement paste and aggregates (Osman, 2012).

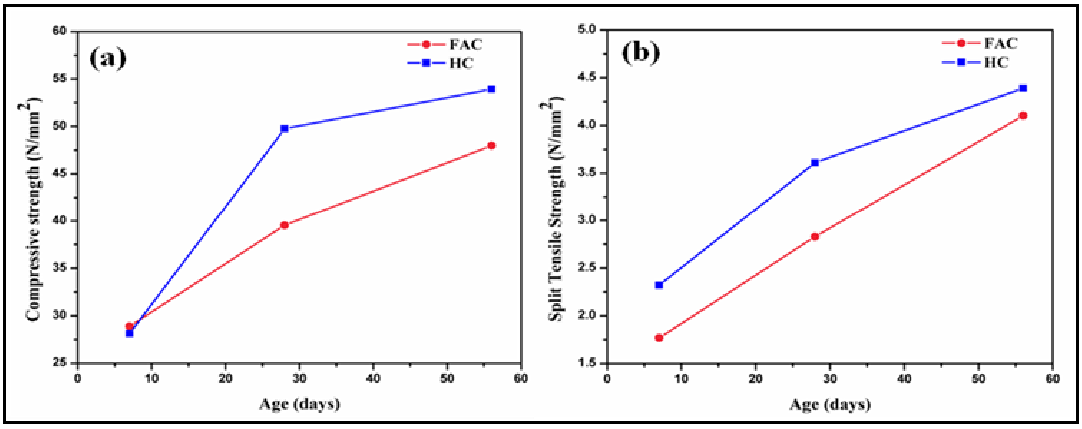

Figure 1. (a) Compressive strength and (b) Split tensile strength of FAC and HC

3.4. Flexural strength test

The flexural strength of FAC and HC were determined for 7, 28 and 56 days (figure.2). It also shows that at 7 days of exposure both FAC and HC are having the value of 7.5 N/mm2. After 28 days of exposure, FAC showed 9.0 N/mm2 and HC showed 12.0 N/mm2 of strength. At 56 days the strength was 16.5 N/mm2 and 21.0 N/mm2 for FAC and HC respectively. The increase in flexural strength in HC may be due to the good bonding between the hematite, aggregate and paste (Osman, 2011).

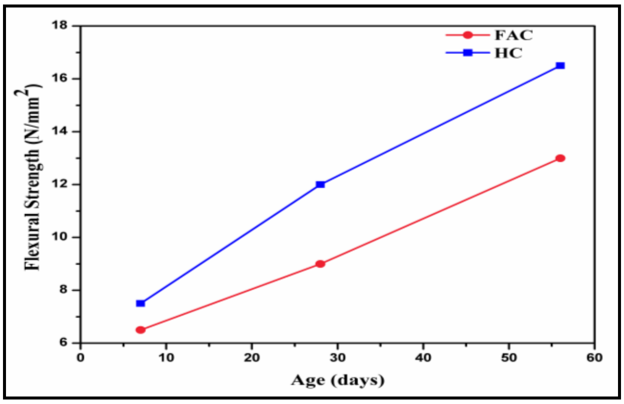

Figure 2. Flexural strength of FAC and HC

3.5. Porosity measurement

Water absorption is one of the parameter which is directly related to concrete porosity. Figure. 3(a) revealed the water absorption greater in FAC (4.225%) than HC (2.19%) for 28 days fresh water cured specimens. The porosity was observed more in FAC (7.91%) than HC (5.02%), so it showing 36.5% less of porosity in HC compared to FAC. This may be due to the hydration product fills the pores that will decrease the water absorption capability (Papzan and Taksiah 2012).

3.6. RCPT results

A comparative study of chloride permeability test for 7, 28 and 56 days fresh water cured of FAC and HC were plotted in figure 3(b). The charge passed in the FAC was 2219, 544 and 517 coulombs for 7, 28 and 56 days whereas in HC it shows 1375, 322 and 277 coulombs respectively. It has been reported that the use of fly ash reduced the permeability from 3000 Coulomb to 1000 Coulomb (Patel et al, 2004 and Nehdi, 2004). This less permeability HC compared to FAC may due to the packed particles of hematite and less porous nature of the concrete.

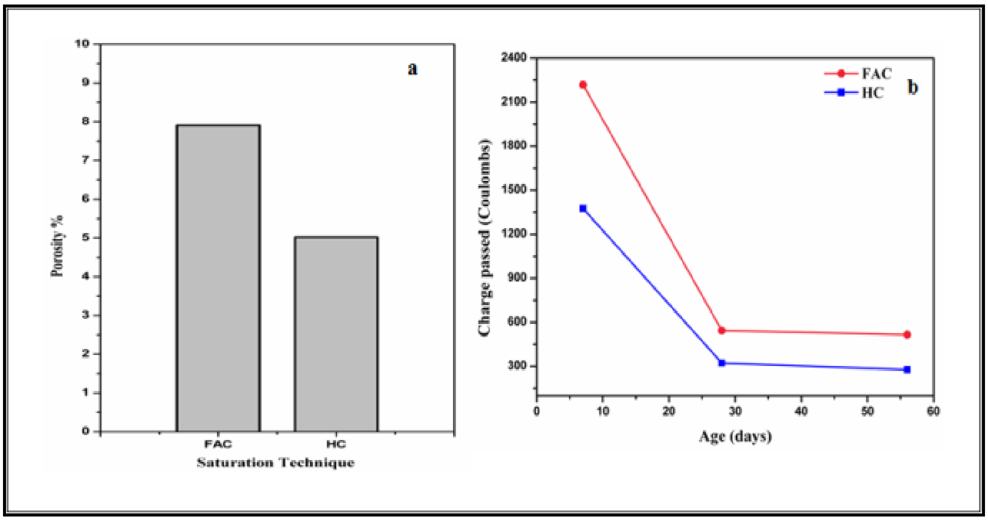

Figure 3. (a) Porosity (b) RCPT of FAC and HC

3.7. Carbonation Test

Carbonation test results were analyzed after 28 days in open atmosphere exposure of FAC and HC specimens which were having nil carbonation effect. During the accelerated carbonation test, the 28 days FAC specimens was showing 1mm whereas HC showed nil carbonation depth. The same trend was found in the 56 days open atmosphere and accelerated carbonation conditions. The less carbonation result in HC specimens can be compared with the durability and chloride permeability of the concrete (Bertos, 2004).

3.8. XRD results

XRD studies of 28 days fresh water cured FAC and HC specimens were shown in figure. 4 of the presences of calcium silicate hydrate, calcium hydroxide and silicon dioxide. The Iron oxide peak at 27.8 and 63.9 (JCPDS: 06-0502) was observed only in HC, which is evident the presence of hematite. The peaks observed at 20.9. 26.6, 45.7, 59.9, 68.1, 77.5 and 79.9 corresponds to silicon dioxide (JCPDS: 46-1045) and calcium hydroxide peaks were showed at 18.0 and 34.1 (JCPDS: 44-1481). Further, calcium aluminum silicate hydrate peaks showed at 22.1, 23.7, 27.7, 29.1 and 36.5 (JCPDS: 39-1381) and calcium silicate hydrate peak observed at 50.1 (JCPDS: 33-0305). The intensities of all these hydration peaks were decreased in HC specimens which are due to the progress in formation of additional CSH by the consumption of calcium hydroxide that increases the interfacial strength between cement paste and fine aggregates, subsequently increases the mechanical properties (Abo-El-Enein, 2014).

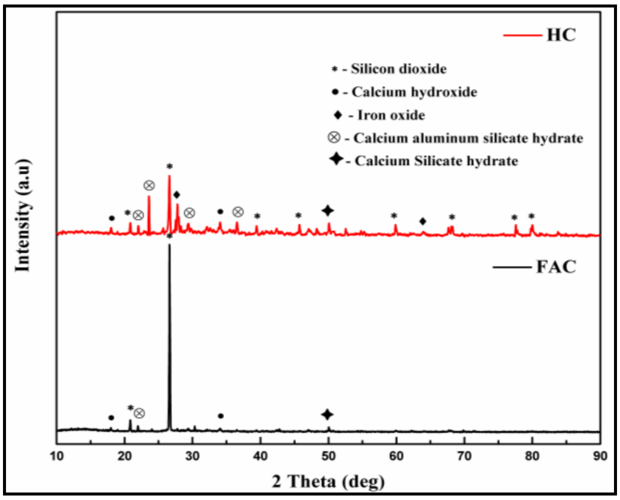

Figure 4. XRD patterns of FAC and HC

3.9. FESEM

The general microstructural image of fly ash (ball bearing) and hematite as fine aggregate particles (lamellar structure) was shown in figure 5a and b respectively. The presence of Fe (63%), Si (0.81%) and O2 (35.46%) were confirmed by the EDAX spectrum of weight percentage analysis of the hematite. This finely divided artificially added silica takes part in the additional calcium silicate hydrate (CSH) and Si and Fe ions tend to form highly polymerized layered structures in the hematite concrete (Wild, 1986) showed in figure 5d. Due to the rough surface texture of the hematite aggregate the bond strength increases which in turn consequently increases the mechanical properties (Gencel, 2011). Addition of fly ash on the concrete produces smooth surface due to the ball bearing nature of the fly ash which is evident from the figure 5c.

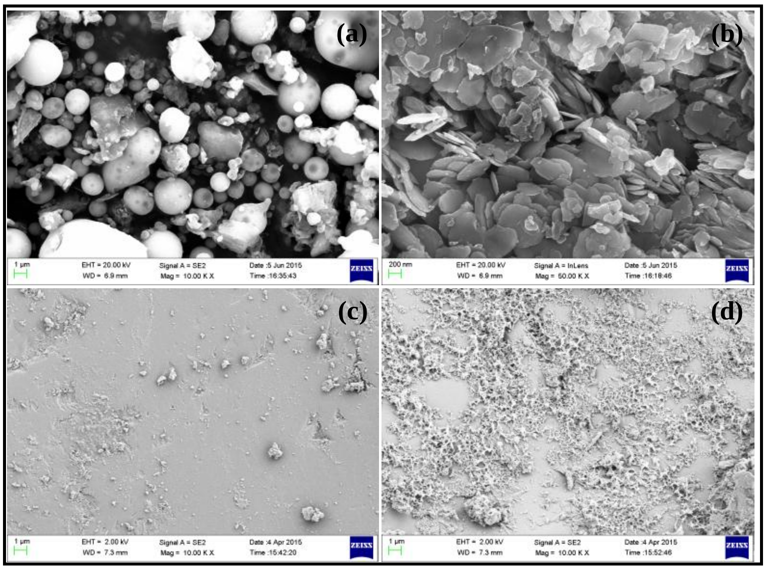

Figure 5. Scanning electron micrograph of (a) FA (b) hematite as fine aggregate (c) FAC and (d) HC

3.10 Epifluorescence microscopy

Figure 6 is showing the attachment of microorganism in FAC and HC specimens exposed in fresh water. The FAC specimen is showing red fluorescence which is indicated the presence of biofilm (Figure 6a) whereas no attachment of biofilm with green fluorescence was seen in HC specimens (Figure 6b). The active fluorescing cells are found more in FAC (Vinita et al, 2012) than HC.

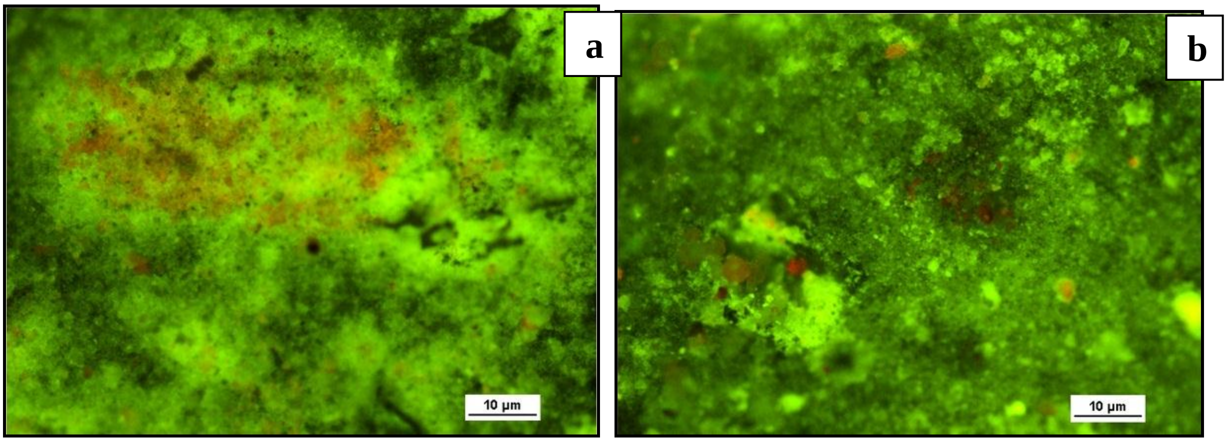

Figure 6. Specimens cured in fresh water (a) FAC (b) HC specimens

4. Conclusions

1. Least pH reduction was observed in HC than FAC specimens after 56 days in fresh water curing conditions.
2. The compressive strength, split tensile strength and flexural strength test after a curing period of 7, 28 and 56 days HC exhibits higher strength than the FAC due to the finer and denser hematite aggregate.
3. Porosity measurement and RCPT were conducted for both FAC and HC concrete specimens cured for 7, 28 and 56 days. It was found that HC showed less porosity and permeability than FAC. The carbonation test results confirmed that there was no carbonation in the open atmospheric condition up 56 days in both FAC and HC specimens. However, during accelerated carbonation, the 1 mm carbonation depth was found after 28 and 56 days only in FAC specimens.
4. XRD analysis revealed the formation of less intense hydration peaks shows the progress of formation of CSH in the HC.
5. FESEM of HC showed rough surface texture and polymerized layer structure due to the addition of hematite fine aggregates whereas in FAC the surface was smooth.
6. Epifluorescence microscopy studies indicated less microbial attachment on the HC compared to FAC specimens.
7. Apart from nuclear power plants shielding applications, the HC can be used to avoid the exposure of radioactive waste. HC modified concrete can be also used as counter weights, abrasion resistant concrete and off-shore pipelines. The performance of hematite modified concrete in different environments will be important in future to know its other shielding applications.

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