EFFECT OF MAGNETITE BASED HEAVY WEIGHT CONCRETE IN DETERIORATION AND CORROSION RESISTANCE

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This paper discusses heavy density (HDC) concrete performance by partially replacing the fine and coarse aggregate in concrete with magnetite in its fine and coarser form. Three series of mixes, namely HDC-I, HDC-II and HDC-III, were developed for the research. HDC-I series contained 10% magnetite powder (MP) and 10% quartz powder (QP) as fine aggregates, whereas the HDC-II series had 15% magnetite power MP and 5% QP. The replacement level of magnetite aggregate as coarse aggregate was maintained constant by 30%, 40% and 50% for both the series. HDC-III series mix was made by replacing coarse aggregate with a significant content of 50%, 60% and 70% of magnetite aggregate by weight. Only 20% of magnetite powder was used for replacing the fine aggregate in HDC-III. Silica fume and nano-silica were also used in a constant replacement proportion in cement by 10% and 1%. Various tests related to the mechanical and durability characteristics of the concrete were performed. Compared with conventional concrete mix, the results revealed that increasing the proportion of magnetite aggregate leads to a considerable increase in unit weight and other mechanical properties. Also, it was observed that quartz powder and magnetite did not fetch any significant benefit in the mechanical properties.

Keywords: *Heavy density concrete; magnetite powder; magnetite aggregate; quartz powder; nano-silica; aggressive environment; impact test*

1. Introduction

Heavy density concrete is the most widely preferred material for unique construction works such as radiation shielding in nuclear power plants, hospital buildings involving radiation therapy and storage tanks for dumping hazardous radio wastes [1]. Concrete possessing a density higher than 2600 kg/m^3 is termed heavyweight concrete nowadays. Such concretes are used much for shielding purposes in nuclear reactors and radiotherapy rooms in hospitals [2]; factors that are responsible for improving the concrete shielding properties have been discussed by earlier researchers. Few of them are discussed in this section. Waly and Bourham [3] mentioned that concrete's shielding properties could be altered by modifying the composition of concrete and using additives with different specific density. Mohammed *et al.* [4] presented a detailed review of heavyweight concrete, discussing the requirements, materials, and heavyweight concrete applications. Jinjun Wang *et al.* [5] reported that water proportion plays a significant role in modifying heavy density concrete's shielding properties. But many researchers have developed HDC by choosing different aggregates as it is generally felt that aggregates play a significant role in influencing concrete properties. Akkurt *et al.* (2012) [6] had developed heavyweight concrete using different heavyweight aggregates siderite, barite and limonite for radiation shielding and mentioned that the aggregate present in the concrete play a vital role in improving shielding properties. The primary ore used predominantly in the making of heavy density concrete is barite [4]. ASTM 637 (1998) [7] has classified the aggregates to be used in HDC as natural minerals such as Hematite, Magnetite, Limonite and Barite and artificial aggregates using iron and steel. Few works were also done with Serpentine and Goethite, and as reported by Ahmed S O[8], the strength obtained using them was significantly less, and hence they are not preferred much in the making of heavyweight concrete. Though several works were done using such natural aggregates [9 - 12], the drawback is that they are costly, and researchers have tried different combination of aggregates and minerals to develop HWC economically. Osman Gencel *et al.* [13] have reported experimental investigations on HWC developed using fly ash and ferrochromium waste. Basyigit *et al.* [14] made HWC using aggregates of different mineral origin, namely Limonite and Siderite and reported that the obtained heavyweight concrete performed well as radiation absorbent.

Florence and Konstantin [15] have listed the use of nanotechnology in civil engineering, mentioning the benefits of using nano-sized mineral admixtures in concrete. Nano silica, nano TiO_2 are a few of the nano-sized cementitious materials used by the researchers to improve the mechanical, water absorption, and stiffness of standard concrete [16,17]. In the heavyweight concrete area, Tobbala [18], in his work, had pointed out the use of using nano ferrite as a partial replacement of cement and reported that the mechanical properties and gamma radiation shielding radiation of the heavyweight concrete got improved for a 2% replacement level of

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nano-ferrite. Heavyweight concrete involves aggregates possessing higher density, and it will affect the binding properties of cement and the interlocking characteristics of aggregates. So, the use of nanomaterials in cement can improve the binding action.

The present research investigates the possibilities of utilizing the shielding properties of HDC in the aggressive environment to resist the concrete from deterioration and the reinforcement from corrosion by modifying the proportions of aggregates used. In this regard, magnetite aggregate is chosen for the current research and was used both in its fine and coarser form. When heavyweight aggregates are used, it is evident that the total quantity of the conventional materials will come down as the addition of a few pieces of heavyweight aggregate and powder will make the desired quantity. But it will also develop pores in concrete. So, considering that, finer sized and nano-sized mineral admixtures were also used in the present research.

2. Materials and methods

2.1 Materials

The mineral admixtures were chosen such that they possess both filling and pozzolanic effect. Ordinary Portland cement was used for the research work and to ensure it basic tests such as specific gravity and initial setting time only were done and they were found to be 3.12 and 35 minutes.

Silica fume with size 0.638-micron meter was used as a replacing admixture for the cement to induce pozzolanic action. Nano silica of size 17 nano meter was used to function as a filling, and a pozzolanic material. The chemical components standard for the cementitious materials used is listed in Table 1. Heavyweight magnetite aggregate was used together with average coarse aggregate. Quartz powder possessing a size 655.6 nano meter and heavyweight magnetite powder of size 954.6 nano meter were used along with river sand as fine aggregate. The sizes of the nano silica was received from the suppliers and for the other mineral admixtures used in the research, the sizes were found using particle size analyzer. The essential physical characteristics of the mineral admixtures and the aggregates are tabulated in Table 2. From the chemical composition, it is seen that Magnetite powder possesses low SiO_2 content, which indicates that it cannot be used as a proper substitute for fine aggregate. Still, since the Fe_2O_3 content is very much higher, it can be used as a potential heavyweight fine aggregate when supported with suitable materials like quartz powder and other cementitious materials rich in silica.

2.2 Mix Proportion

The mix proportion was designed as specified by ACI 304.3R (1996) [19]. Including control, ten combinations were made with replacements done on cement, fine and coarse aggregates. Fine sand was replaced with heavyweight magnetite powder (MP) at an incremental rate of 5% starting from 10% and up to 20%; quartz powder (QP) was also used as a filler agent in river sand 0%, 5% and 10% by weight. Coarse aggregate was used initially in larger replacement levels of 70%, 60% and 50% by weight. With the fine heavyweight aggregate increase, the replacement levels in coarse aggregate were reduced by 50%, 40% and 30%. Table 3 shows the mix proportion details. Mixing of HDC was done in the usual manner specified in ASTM C192 (1998) [20].

2.4 Curing Environment

To study the behaviour of HDC in an aggressive environment, accelerated corrosion and deterioration techniques were adopted. Among the aggressive environment, as the effect due to

Table 1

Chemical composition of cementitious materials

Compounds	Cement (%)	Silica fume (%)	Nano silica (%)	Quartz powder (%)	Magnetite powder (%)
SiO_2	19.15	99.02	99.81	98.66	7.39
MgO	0.77	0.03	-	0.11	3.74
Al_2O_3	3.83	0.31	-	0.27	1.02
SO_3	3.62	0.05	0.05	100 ppm	0.01
Fe_2O_3	5.86	0.05	73 ppm	0.08	82.26
CaO	65.13	0.24	0.03	0.19	2.66
Na_2O	0.19	0.05	0.06	0.11	0.09
Cl	0.08	0.02	-	0.04	0.04
PbO	0.05	0.17	0.03	0.25	-
K_2O	0.8	0.29	-	0.02	0.13

Table 2

Physical properties of magnetite fine and coarse aggregate

Property	Magnetite		Normal aggregate	
	Fine	Coarse	Fine	Coarse
Sp. gravity (g/cm^3)	5.1	4.27	2.6	2.81
Fineness Modulus	-	7.1	3.2	6.83
Bulk density, kg/m^3	-	2830	-	1445
Loose density, kg/m^3	-	2711	-	1320
Impact resistance (%)	-	18.4	-	52
Abrasion resistance (%)	-	33	-	35.7
Water absorption (%)	-	.34	-	0.15

Table 3

Material proportions

Mix Ratio		**1 (360kg/m^3)**			**1.7 (621 kg/m^3)**			**3.6 (1284 kg/m^3)**			
Mix ID		**Cementitious material (%)**			**Fine Aggregate (%)**			**Coarse aggregate (%)**		**w/c**	**Super plasticizer**
		Cement	**SF**	**NS**	**Sand**	**MP**	**QP**	**CA**	**MA**		
C		100	0	0	100	-	-	100	-	0.40	0
HDC-I	HDC1	89.5	10	10	80	10	10	70	30	0.41	1-1.5 / per 100 kg of cement
	HDC2	89.5						60	40		
	HDC3	89.5						50	50		
HDC-II	HDC4	89.5				15	5	70	30		
	HDC5	89.5						60	40		
	HDC6	89.5						50	50		
HDC-III	HDC7	89.5				20	-	50	50		
	HDC8	89.5						40	60		
	HDC9	89.5						30	70		

sulphate attack is considered severe [21] (Gunyisei 2010), the specimens were exposed to 0.1N sulphuric acid for 60 days completion of the initial 28 days water curing period. Karthikeyan and Dhinakaran 2017 [22] have performed studies on deterioration and corrosion of concrete using ceramic waste powder, and the same procedure was adopted here also.

3. Results and discussion

3.1 Density of concrete

Waley and Bourham [3] developed heavyweight concrete using combinations such as magnetite and lead oxide, barite and ferrophosphorus. They reported that the density of concrete increased with increased usage of special aggregates and decreased specific coarse aggregate content. This was found to be confirmed with the current project also in which magnetite aggregate has been used in both fine and coarser form. Table 4 summarizes the fresh and hardened density of concrete specimens. ASTM C138-17 [23] was used for performing the test. The results indicate that all the samples made with magnetite heavyweight aggregates possessed a dry unit weight more than the required criteria of 2600 kg/m^3. Also, it is well known that the density of concrete is directly proportional to aggregates' specific gravity. From Table 4, it is clear that the specific gravity of magnetite aggregate, which is 4.27 g/cm3 is 65.8% higher than the normal aggregate enabling the concrete to reach a higher density when used as aggregate. The density values were increasing gradually from 2733 kg/m^3 to a maximum of 4774 kg/m^3 and later started decreasing. The presence of magnetite, both fine and coarse, has to lead to an increase in density values; also the values were affected by QP. HDC1, HDC2, HDC3 having 10% QP showed a lower density, and the values increased gradually when the magnetite powder content increased by 15%

and reached higher density for were for the series HDC7, HDC8, HDC9 with no QP and having only MP used in 20% as fine aggregate. The results convey that in addition to coarse aggregate replacement in heavy density concrete, replacement materials in fine aggregate also play a vital role.

Table 4

Density of fresh and hardened concrete

Mix Id	Density, (kg/m^3)	
	Fresh concrete	Hardened concrete
C	2923	2579
HDC1	3143	2733
HDC2	3372	2776
HDC3	3425	2795
HDC4	3492	2818
HDC5	4316	3394
HDC6	4491	3489
HDC7	5841	4774
HDC8	5319	4302
HDC9	4922	3946

3.2 Workability

Fig.1 depicts the slump values of all mixes, and all have achieved the target slump. The values obtained ranged between 75 mm and 100 mm for the adopted w/c ratio of 0.4. Combinations made with QP showed higher slump values than those without QP. HDC1 and HDC2 have shown higher slump values. Replacing coarse magnetite aggregate in smaller proportions such as 30% and 40% lead to higher slump values. The use of heavyweight aggregates in small proportions required a smaller quantity of magnetite aggregate pieces for making the concrete. They lacked proper bonding and interlocking, leading to larger slump values. This problem got rectified when magnetite aggregate was used in moderate proportions of 50% along with a suitable ratio of 20% heavyweight

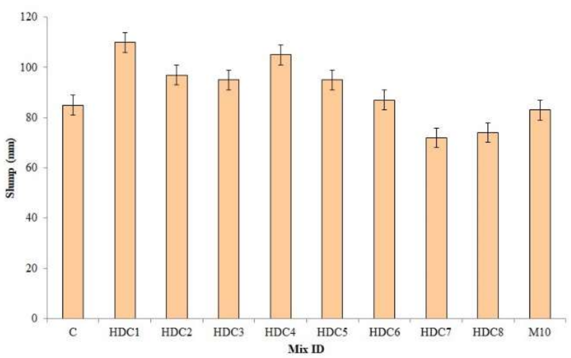

Fig. 1 - Slump values

magnetite powder, as seen in HDC7 and HDC8. The use of heavyweight magnetite coarse aggregate in larger proportions may also cause the resulting stiff mix, which is a danger as it may sometimes turn out to be brittle. So, from HDC7 to HDC9, where no QP was added, and only magnetite aggregates were added in a relative proportion along with normal aggregate, the slump values were within the expected range. It indicates that with a proper ratio of heavyweight magnetite aggregate and normal coarse aggregate, the expected slump could be achieved due to appropriate interlocking.

3.3 Compressive strength and splitting tensile strength

Strength tests were performed on cubes and cylinders as per BS 1881-108 [24]. Strength was found to increase with an increase in magnetite percentage in powder form as fine aggregate and coarser condition in coarse aggregate. Pawel Sikora *et al.* [25], in their experimental investigations, reported that incorporation of magnetite powder in cement improved the strength of the specimens in a heated and unheated state. In present research, it was observed that MP added to the mix in both fine and coarse aggregates has shown significant contribution to strength when added in larger quantities (HDC7, HDC8, and HDC9). With its high fineness and high silica content, Silica fume acted both as a filler agent and pozzolanic material. In the present work since it is used along with nS, the filling effect led to better strength of the mixes. HDC1, HDC2 and HDC3 possessed less strength compared to HDC7 and HDC8. When added in smaller quantities, heavy density aggregate affected the strength, which is already evident from the slump results. The same effect continued in the present research, too, but controlled with the increased quantity of MP in sand replacement. The addition of MP in less amount (10%) affected the strength, and a gradual increase in strength was observed with increased quantities (15% and 20%) of MP. Yu-Cheng *et al.* (2004) [26] reported in their studies that the compressive strength and elastic modulus of heavyweight concrete increased with an increase in the iron ore content. It was found to be true for the current research also like the use of MP in less quantity (10%) affected the strength, and a gradual increase was observed with increased quantities (15% and 20%) of MP. So, in addition to the presence of silica fume and nano-silica in the present mix, MP also helped in attaining higher strength. Figure 2 illustrates this clearly.

The splitting tensile strength results also reflected the compressive strength properties. All the specimens possessed a higher tensile strength than the control specimen. Here also the strength of the mixes increased with an increase in the

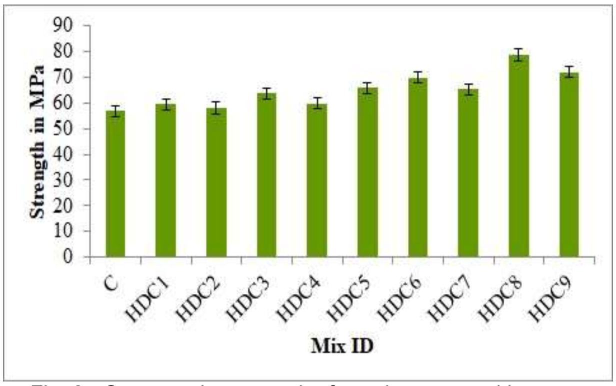

Fig. 2 - Compressive strength of specimens cured in water

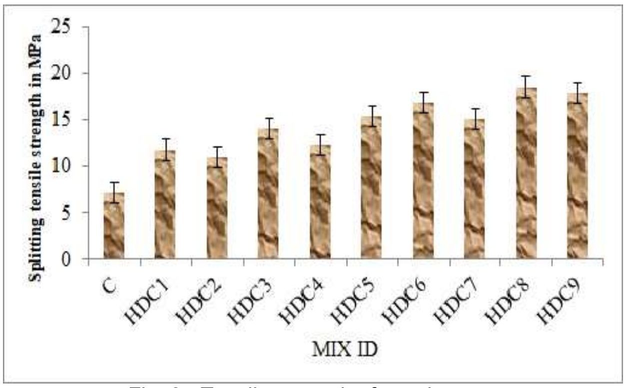

Fig. 3 - Tensile strength of specimens

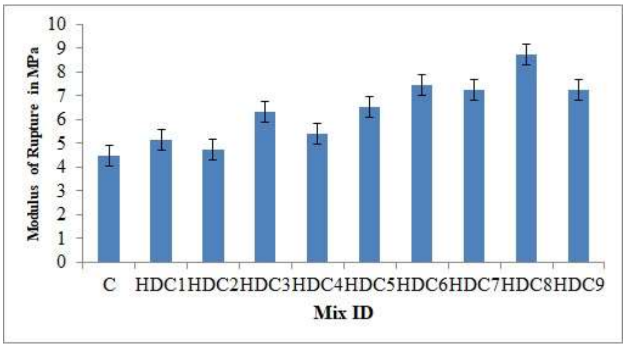

Fig. 4 - Flexural strength of specimens

proportion of magnetite aggregate. Thus, the mix with a higher proportion of magnetite aggregate (HDC8) showed higher tensile strength than other mixes and the specimens' overall performance in the HDC-III series (HDC7, HDC8, HDC9) were better than the other combinations. These details are illustrated in Fig. 3.

3.4 Modulus of rupture

Fig. 4 depicts the modulus of rupture values for the specimens. The test was performed as per ASTM C78 [27] guidelines. Though fibres were not added, this test was performed to check the specimens' brittleness due to the addition of heavyweight aggregates. The results proved that heavy weight aggregates sustained the loads better than normal aggregates and delayed the rupture time. The mix series HDC6, HDC7, HDC8, and HDC9 with coarse magnetite aggregate added in larger proportion registered higher strength values. of 66.3%, 61.8%, 94.64% and 61.4%, respectively, than the control. There is a drop in the values after HDC8, indicating that increasing the MP coarse aggregates up to 70% did not improve flexural strength.

3.5 Impact test

Earlier in Table 2, the aggregate impact values of magnetite aggregates and normal aggregates were mentioned as 18.4% and 52%, respectively. It indicates that the broken pieces were found to be less when magnetite was subject to impact testing. So, it is evident that magnetite coarse aggregates are better at resisting impact loads. It is correct when comparing the impact values of concrete cylinder specimens cast using magnetite and normal aggregates. The impact strength results are presented in Table 5. The test was conducted as per ACI 544 [28]. Since fibres were not used, the control specimens got crushed earlier, and samples with magnetite bear the impact resistance by withstanding more blows. Also, it was found that there is no drastic increase in the number of blows and the resistance improved with increases in magnetite, either in coarse or fine form. HDC1 to HDC3 possessed less impact strength, and HDC4, HDC5 and HDC6 specimens showed moderate resistance against impact. The impact values of HDC7, HDC8 and HDC9 were higher.

3.6 Rate of deterioration

Fig.5 and Fig.6 show the specimens' strength and deterioration rate after exposed to H_2SO_4 acid. It is apparent from the figures that HDC1, HDC2 and HDC3 specimens are poorly affected. The deterioration rate gradually decreased from HDC1 to HDC8 HDC1, which had the least magnetite content of 30% in coarser form and 10% in fine form showed a higher deterioration of 59.97% among. Use of heavyweight aggregates in lower percentages of 30%, 40% failed to offer effective resistance against deterioration. Also, it is clear from Fig.11 that the deterioration rate decreased when the proportion of magnetite in coarse and fine aggregate increased. The II series of HDC, namely HDC4, HDC5, HDC6, possessed moderate deterioration rates. The increase of MP in fine aggregate had helped filling up the pores to some extent making the deterioration moderate. The last of the HDC series, namely HDC7, HDC8, HDC9, possessed less deterioration rate, intimating those heavyweight aggregates in a larger proportion in fine aggregate and coarse aggregate have filled the pores efficiently, making the deterioration gradually decrease by 19.82%, 20.14% and 22.43%.

3.7. Corrosion measurement

Half-cell potential test was performed as per ASTM C876-15 [29] on cylinders of size 60 mm x 120 mm with 12 mm rod inserted, and Fig.13 depicts the values of the HCP test conducted on HDC specimens. The corrosion values are

Table 5

Impact strength

Mix Id	No. of blows for first crack	Energy (kN-m)	No. of blows for failure	Energy (kN-m)
C	5	243.5	8	389.6
HDC1	7	340.9	15	730.5
HDC2	9	438.3	18	876.6
HDC3	10	487	19	925.3
HDC4	12	584.4	19	925.3
HDC5	13	633.1	22	1071.4
HDC6	15	730.5	24	1168.8
HDC7	17	876.6	25	1217.5
HDC8	18	730.5	30	1461
HDC9	17	827.9	23	1120.1

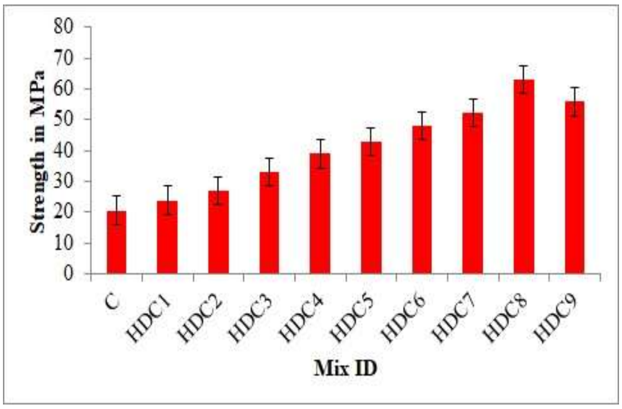

Fig. 5 - Strength after exposing to H_2SO_4

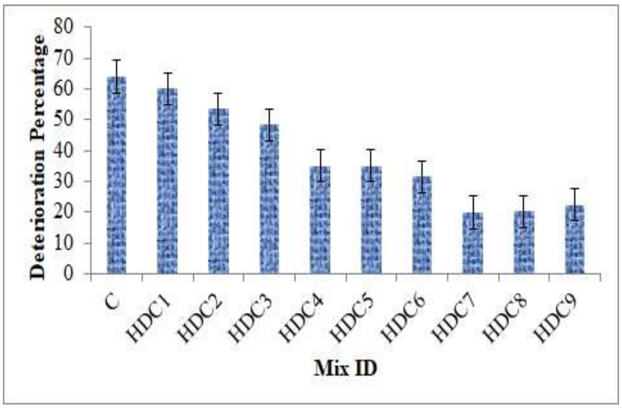

Fig. 6 - Rate of deterioration

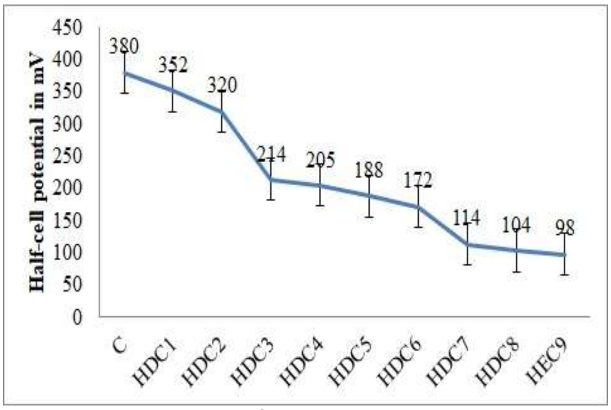

Fig. 7 **-** Half-cell potential values

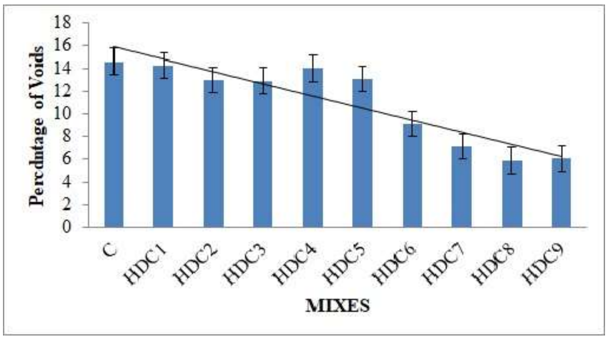

Fig. 8 - Porosity values

expressed in terms of mV. A larger potential value indicates that the specimen has corroded more. From Figure 7, it is understood that control specimens have corroded more as they possessed a higher value of -380 mV. The negative sign indicates that the corrosion has occurred. Comparing the potential values of specimens in the HDC-I series, the HDC1 has corroded next to control, and all the values in that series were in the high-risk zone as they possessed higher potential values. HDC-II series, though, had the same replacement levels of coarse magnetite aggregate as HDC-I, kept intermediate corrosion risk due to the increased amount of MP in fine aggregate by 15%. Among them, HDC6 which had a higher replacement level of 15% MP in fine aggregate and 50% magnetite as coarse aggregate, has shown better resistance against corrosion. HDC-III series possessed corrosion resistance values of 114 mV, 104 mV and 98 mV, respectively, for HDC7, HDC8 and HDC9. The specimens have better resistance against corrosion, which is understood from the low potential values. It is once again proved that increasing the magnetite content in any form, either as coarse or fine aggregate results in better shielding action.

3.8. Sorptivity

Table 6 illustrates the sorption coefficient values obtained by plotting the water volume divided by the specimen area and the square root of time. The test was performed as per ASTM C1585-13 [30]. The sorption coefficients are inversely proportional to the strength. HDC8 specimen, which possessed a higher compressive strength value, showed a lower sorption coefficient of 0.003. The control specimen had the highest sorption coefficient. The lower sorption values are obtained for the mixes with a higher magnetite quantity in both coarser and finer form. From HDC6 to HDC9, no extreme variation was observed in the sorption values. It proves that the presence of magnetite helps to reduce the capillary action by filling up pores. Though SF and nS were also present in it and helped resist water penetration, they could not show their potential effects in other mixes from C, HDC1 to HDC5, where the sorption coefficients varied invariably.

Table 6

Sorption coefficient values

Mix Id	Sorption Coefficient
C	0.242
HDC1	0.192
HDC2	0.187
HDC3	0.179
HDC4	0.167
HDC5	0.15
HDC6	0.128
HDC7	0.045
HDC8	0.003
HDC9	0.012

3.9. Porosity

ASTM C642-13[31] guidelines were followed for testing the specimens for porosity. Fig.8 shows the mixes' porosity values, and they seemed to follow the same trend as compressive strength and sorption values. It is apparent from the HDC-I and HDC-II series results that the use of heavyweight aggregate in smaller quantities, as 30% and 40%, lead to pores in the mix. Also, less usage of MP affected the homogeneity of the mixture, thereby forming pores. The use of heavyweight aggregates in larger proportion filled the pores effectively. It is evident from the HDC-III series results where the volume of pores was less for HDC7, HDC8 and. HDC9, ranging between 5% and 7%, with HDC8 possessing the least volume of pores.

4. Conclusions

Based on the above discussion relevant to the experiments, the following conclusions have arrived

- The HDC-III series consisting of HDC7, HDC8, HDC9 performed well in normal water as they possessed decreased deterioration rate and potential corrosion values.
- However, increasing the magnetite content in coarse aggregate up to 70% did not yield improved strength, and there was a drop in the mechanical properties at 70% replacement levels.
- The performance rate from the experimental results can generally be expressed, as shown below.

  HDC-III > HDC-II > HDC-I
- Increasing the heavyweight aggregate improved the strength and durability characteristics compared to the control concrete, and using them in smaller proportions did not give satisfactory results.

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