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Influence of different types of Cement & Supplementary Cementitious materials Fly ash & GGBS in concrete Carbonation

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Abstract This paper presents a laboratory investigation on the carbonation of concrete made with different types of cement CEM-I, CEM-II/A-M, CEM-II/B-M, CEM-III/A as per BSEN-197-1 & partial replacement of normal Portland cement CEM-I with supplementary cementitious materials Fly ash & GGBS at various proportions. The experiment was conducted on concrete samples after 28-days cured samples in an indoor environmental chamber having 3% CO2 supply with RH 60-70% for a period of 3- month. The fresh & hardened concrete Properties like workability, strength & carbonation of concrete made with different types of cement & partial replacement of normal Portland cement CEM-I with supplementary cementitious materials Fly ash & GGBS at various proportion was studied here. The study shows that the workability of concrete get reduced with cement having higher % SCM & also partial replacement of normal Portland cement CEM-I with higher % of SCM. The experiment on carbonation of concrete made with Portland composite cement CEM-II/B-M, Blast furnace slag cement CEM-III/A having % of SCM [3] & concrete made with partial replacement of normal Portland cement CEM-I with higher percentage of SCM like 25% Fly & 70% GGBS shows maximum depth of carbonation than concrete made with normal Portland cement CEM-I. The research work also shows that early age strength development at 7-days is maximum for concrete made with normal Portland cement CEM-I & minimum for concrete made with cement CEM-III/A having higher percentage of SCM (36-65%) [3] & also concrete made with replacement of cement CEM-I with 70% GGBS. This experimental work also shows that the concrete made with cement having higher percentage of SCM in CEM-III/A (36-65%) [3] & concrete having partial replacement of CEM-I with higher % of GGBS shows maximum strength gaining after 7-days.

Keywords — Carbonation, CEM-I, CEM-II/A-M, CEM-II/B-M, CEM-III/A, SCM, Fly ash, GGBS, Pore structure.

I. INTRODUCTION

The carbonation affect in concrete is one of the important durability concern of concrete due to corrosion of reinforcement steel. The effect of carbonation in concrete results in drop of concrete pH from 12.5 to below 9. The reduction in pH leads to corrosion of steel reinforcement in concrete and thus detorioration of concrete. Hence effect of carbonation in concrete should be considered during design stage based on the exposure classification. The rate of carbonation in concrete depends on the permeability of the concrete and the quantity of the hydroxides (CH) present in hydrated cement. In addition to that carbonation rate also depend on the exposure condition like presence of CO_2 & Relative humidity in the environment. The permeability of concrete depends on many factors like w/c ratio, densification of pore structure & also amount of CH in pore structure. In this research experimental work concrete made with different types of cement CEM-I, CEM-II/A-M, CEM-II/B-M, CEM-III/A & also concrete made with partial replacement of cement CEM-I with SCM like fly ash & GGBS in concrete shows the effect of carbonation in all different samples of concrete was studied here. The experiment shows that concrete made with cement having higher % of SCM & also concrete made with partial replacement of normal Portland cement CEM-I with higher % of SCM like Fly ash & GGBS shows maximum effect of carbonation on those concrete.

II. MECHANISM OF CARBONATION

Carbonation is a process, in which carbon dioxide from air penetrates into the concrete pore structures and then reacts with the calcium hydroxide present in pore structure which leads to the formation of calcium carbonate. In another aspect CO_2 is not reactive by itself. But, in the presence of moisture, it changes into dilute carbonic acid and react with $Ca(OH)_2$ present in pore fluids, which results formation of Calcium Carbonate ($CaCO_3$).The consumption of $Ca(OH)_2$ in pore fluids reduces the concrete alkalinity

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due to reduction of pH in concrete .The pH of the pore water in the hardened cement paste is generally between 12.5 to 13.5. The formation of carbonate will reduce the pH of the pore water in the cement paste to 9 or even below, which in turn will destroy the passivizing layer around the steel reinforcement embedded in concrete and thus initiate the corrosion process in steel. The reaction involved in carbonation process of concrete.

A. Step-I:

The first reaction is in the pores where carbon dioxide (CO_2) and water (H_2O) react to form carbonic acid (H_2CO_3)

$$CO_2 + H_2O = H_2CO_3$$

B. Step-II:

The carbonic acid then reacts with the calcium phases

$$H_2CO_3 + Ca(OH)_2 = CaCO_3 + 2H_2O$$

Once the $Ca(OH)_2$ has converted and is getting reduced or consumed from the hydrated cement paste, hydrated CSH (Calcium Silicate Hydrate) will liberate CaO which will also then also then convert to carbonate

$$H_2CO_3 + CaO = CaCO_3 + H_2O$$

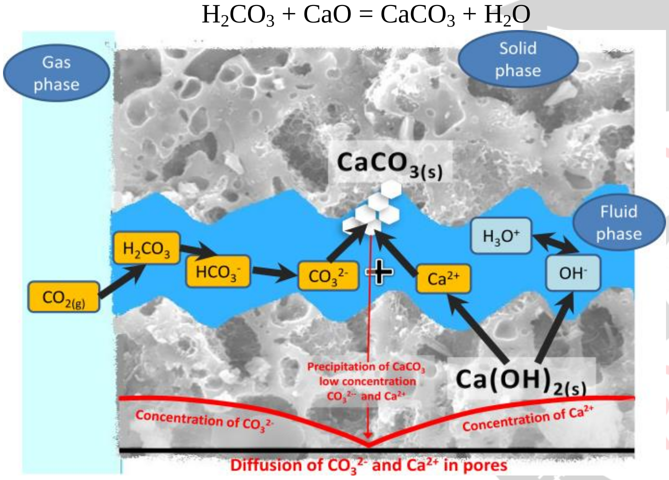

Fig-1: Carbonation mechanism in concrete.

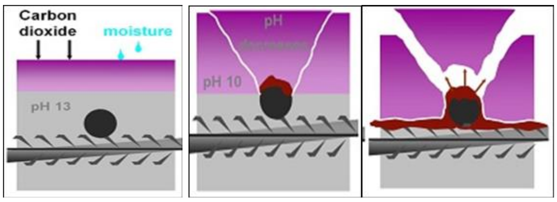

Fig-2: Corrosion of reinforcement steel due to carbonation.

III. MATERIALS

The different types of cement used for this research work was Portland cement CEM-I, Portland composite cement CEM-II/A-M, CEM-II/B-M & Blast-furnace slag CEM-III/A as per BSEN-197-1, & the SCM used for this research work was Pulverized Fly ash (F-type) & Ground granulated Blast furnace slag (GGBS).The coarse aggregate used for this experimental work was crushed Basalt rock & Fine aggregate of river sand having FM of 2.7 & the superplasticiser used in this research work was Poly carboxylate ether based of make BASF. The test results of all the materials are tabulated.

Table-1: Physical properties of cement.

Test Parameter	CEM-I	CEM-II /A-M	CEM-II /B-M	CEM-III /A
Sp. gr	3.15	2.7	2.8	2.92
fineness (Cm2 /gm.)	3630	3230	3670	4282
Soundness mm	0.7	2	1.5	1.4
Compressive strength at 7 Days	47.3	38.5	36.5	27.5
Compressive strength at 28-days 28 Days	55.2	48.4	48.4	42.6

Table-2: Chemical composition of different types of cement.

Component %	CEM-I	CEM-II/ A-M	CEM-II/ B-M	CEM-III /A
CaO	63.9	62.6	57.6	53.59
SiO2	21.7	20.3	23.3	24.45
Al2O3	5.19	4.23	6.31	8.97
Fe2O3	3.86	3.2	3.57	2.22
MgO	1.8	2.52	1.41	2.95
SO3	1.21	3.0	2.37	2.83
Na2O	0.172	0.338	0.098	0.282
K2O	0.439	1.02	1.08	0.661

Table-3: Physical properties of Fly Ash & GGBFS.

Test Parameter	Fly Ash	GGBFS
Sp Gravity	2.2	2.8
Blaine-Fineness (cm2/gm)	2240	2950

Table-4: Chemical composition of Fly Ash & GGBFS.

Component %	Fly Ash	GGBS
CaO	2.87	38.2
SiO2	56.3	35.5
Al2O3	23.6	18.7
Fe2O3	4.96	1.06
MgO	0.424	5.21
SO3	1.22	0.727
Na2O	0.33	0.245
K2O	2.09	0.004

Table-5: Physical properties of Coarse Aggregate.

Test Parameter	Test Results
Sp Gravity	2.87
Dry rodded Bulk Density in Kg/cum	1678
Water absorption in %	0.43
Aggregate Impact value in %	11.41
Loss Angel Abrasion in %	0.424

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Flakiness Index in %	21.22
Elongation Index in %	23.5
Grading Requirement (19-4.75 mm)	Satisfactory as per ASTMC33

Table –6: Physical properties of Fine Aggregate

Test Parameter	Test Results
Sp Gravity	2.54
75 micron passing in % by weight	1.75
Fineness Modulus	2.70
Water absorption in % by weight	1.54

Table-7: Properties of mixing water.

Test Parameter	Test Results
pH	7.5
Chloride Content in mg/l	250
Sulphate content ($S04^{-2}$) in mg/l	1.8
Total solids in mg/l	750
Total Alkalinity as $CaCO_3$ in mg/l	285

In this research work a reference concrete of C-30/37 was used with normal Portland cement CEM-I, as per BSEN-197-1 of 438 kg/cum with w/c ratio of 0.4. The coarse aggregate used as a graded aggregate by using combination of 19 mm (60%): 12.5 mm (40%).The design mix of reference concrete C-30/37 is tabulated here.

Table-8: Mix Design of reference mix C-30/37

Name of the Ingredient	Quantity in Kg/Cum
Cement content	438
Water content	175
Water Cement Ratio (W/C)	0.4
Total amount of Coarse aggregate	1142
Coarse Aggregate 19 mm [60%]	685.2
Coarse Aggregate 12.5 mm[40%]	456.8
Fine Aggregate	685
Superplasticiser @ 0.8 % by weight of cement	3.5

Table-9: Mix proportion of different mix in kg/cum.

Mix Details	Cement	SCM	CA	FA	SP
M1 CEM-I, 52.5N	438	NA	1142	685	3.5
M2 CEM-II/A-M (100%)	438	NA	1142	685	3.5
M3 CEM-II/B-M (100%)	438	NA	1142	685	3.5
M4 CEM-III/A (100%)	438	NA	1142	685	3.5
M5 CEM-I (85%) + FA (15%)	372.3	65.7	1142	685	3.5
M6 CEM-I (80%) + FA (20%)	350.4	87.6	1142	685	3.5
M7 CEM-I (75%) + FA (25%)	328.5	109.5	1142	685	3.5
M8 CEM-I (50%) + GGBS (50%)	219	219	1142	685	3.5
M9 CEM-I (40%) + GGBS (60%)	175.2	262.8	1142	685	3.5
M10 CEM-I (30%) + GGBS (70%)	131.4	306.6	1142	685	3.5

IV. EXPERIMENTAL SETUP

A. *COMPRESSIVE STRENGTH OF CONCRETE*

For compressive strength of concrete made with different types of cement & partial replacement of normal Portland cement CEM-I in reference mix M_1 with SCM like Fly ash & GGBS at various proportions. The cube samples were prepared of size 150 mm x150 mm x150 mm. The cube compressive strength of all different mix of concrete were evaluated after 7-days & 28-days of curing. The cubes were cured in fresh water at 25 degree centigrade for 28-days.

B. *CARBONATION TEST*

For carbonation test of concrete was conducted on all different mix cube sample of size of 100 mm x 100 mm x 100 mm. The casted cube samples were cured for 28-days at 25 degree centigrade. After 28-days of curing period in fresh water at 27 degree centigrade the samples were dried at 105°C to a constant mass and then stored in carbonation chamber for a period of 90 days at 25°C with relative humidity 65% and 3% CO_2 supply. The concrete cube samples after 90-days of exposure at CO_2 chamber were removed from carbonation chamber & split the cube specimen vertically in two part & then by spraying 1% phenolphthalein solution on the split part of the cube samples the effect of carbonation on concrete were worked out through visual inspection. The carbonated part of the concrete shows colorless & noncarbonated concrete become pink color. The depth of carbonated part were calculated through scale measurement.

Fig-3: Concrete samples at Carbonation chamber.

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V. RESULTS & DISCUSSION

A. Fresh Concrete Properties.

The experimental work shows lesser workability of concrete mixes with same w/c ratio of concrete made with Portland composite cement of type CEM-II/B-M & Blast furnace slag cement CEM-III/A having high composition of SCM 21-35% in CEM-II/B-M [3] & 35-64 % slag in CEM-III/A [3] than concrete with normal Portland cement CEM-I. The experiment also revealed that workability of concrete made with Fly ash up to 15% shows slightly higher than concrete made with normal Portland cement CEM-I with same w/c ratio due to ball bearing effect of spherical shape of Fly ash particles [1]. However concrete made with Fly ash on higher % like 25% Fly ash shows slightly drop in workability due to excessive cohesiveness of the mix with same w/c ratio. On the other hand concrete made with partial replacement of Portland cement CEM-I with GGBS the workability of concrete get dropped as the % of GGBS in concrete get increased due to angular shape of the GGBS particles [1]. The shape of the particles for both Fly Ash & GGBFS has been studied through SEM with high resolutions.

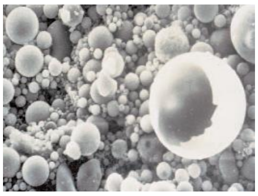

Fig- 4: SEM image of Fly Ash

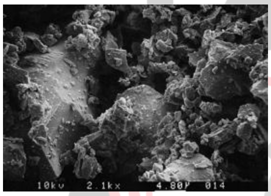

Fig-5: SEM image of GGBFS

Table-10: Workability of different mix.

Mix Details	Slump in mm	Consistency of Mixes
M1	170	Moderately Cohesive
M2	160	Cohesive
M3	150	Cohesive
M4	145	Cohesive
M5	180	Cohesive
M6	160	Highly Cohesive
M7	150	Highly Cohesive
M8	160	Moderately cohesive
M9	150	Highly cohesive
M10	140	Highly Cohesive

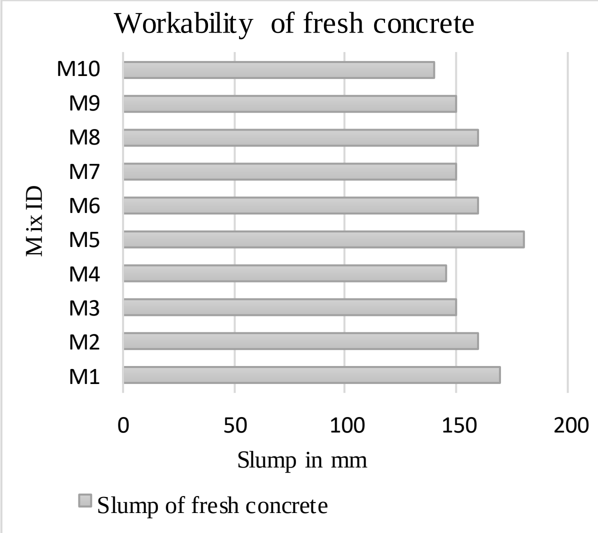

Fig-6: Workability of fresh concrete.

B. Compressive Strength of Concrete.

The average compressive strength at 7-days for mix M1 with normal Portland cement CEM-I & mix M2 with Portland composite Cement of type CEM-II/A-M shows significantly higher strength at early age of 7-days as compared to mix with other two types of cement like mix M3 with Portland Composite cement of type CEM-II /B-M & mix M4 with Blast furnace slag cement CEM-III /A .It is also observed that on partial replacement of normal Portland cement with pozzolonic materials Fly ash 15% , 20% & 25% in mix M5, M6 M7 & GGBS 50%, 60% & 70% mix M5, M6 M7 shows apparently lower strength at early age of 7-days . The experimental works also revealed that at 28-days mix with normal Portland cement CEM-I (M1) shows maximum strength , however mix with Portland composite cement of type CEM-II/A-M also shows significantly higher strength than mix with other two types of cement like Portland composite cement of type CEM-II/B-M & mix with Blast-furnace slag cement CEM-III/A .The strength gaining at both 7-days & 28-days are in lower side with cement CEM-II/B-M & CEM-III/A due to reduced level of clinker part & increased part of pozzolonic materials for both CEM-II/B-M(Clinker-65-79% & Pozzolonic materials part-21-35%)[3] & CEM-III/A(Clinker-35-64% & Blast furnace slag part-36-65%)[3]. Hence, for cement with higher the part of Pozzolonic materials & reduced level of clinker shows lower strength at 7-days & 28-days but at the same time strength gaining after 7-days is prominently more in cement CEM-II/B-M & CEM-III/A. It is observed that on partial replacement of normal Portland cement CEM-I with pozzolonic material Fly ash 15%, 20% & 25% in mix M5, M6 M7 & also mix with GGBS 50%, 60% & 70% in mix M8, M9 & M10 shows lower strength development at early age of 7-days as compared to mix (M1) with normal Portland cement CEM-I with same w/c ratio. The initial age strength development in the Mix M1, M2 are maximum due to higher % of clinker [3] part in cement CEM-I & CEM-II/A-M. However it is also observed that mix with 25% Fly ash (M7) shows maximum strength at 28-days as compared to15% & 20% Fly ash in the mix (M5 &M6). So with increase in Fly ash content up to 25% will increase 28-days strength but at same time early age strength is in lower side

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as compared to mix M1 with normal Portland cement. But at the same time by adding GGBS 50%, 60% & 70% of total cemetitious materials the strength development at both 7-days & 28-days were getting reduced as compared to the mix M1 with normal Portland cement (CEM-I) due to replacement of cement CEM-I with pozzolonic material GGBS . It is also observed that higher the GGBFS content in the mix its strength development at both 7-days & at 28-days are comparatively in lower side as compared to other mixes .The strength of mix with 50% GGBFS (M8) is slightly higher than 70% GGBFS(M10) & also the strength development of GGBFS based mix is in lower side as compared to mix with Fly ash based mix due to higher % of siliceous part in Fly ash than GGBS which helps to produce more Calcium Silicate Hydrate (C-S-H) gel on pozzolonic reaction with hydrated cement part Calcium hydroxide Ca(OH)2. The strength of concrete is governed due to formation of C-S-H gel in concrete. The following pozzolonic reaction involve in the mechanism of strength development due to pozzolonic material.

$$Ca(OH)_2 + SiO_2 = C\text{-}S\text{-}H + H_2O$$

Table-11: Compressive strength of concrete at 7-Days & 28-Days

Mix	7-Days Strength in N/mm2	28-Days Strength in N/mm2
M1	54.8	66.4
M2	51.7	65.3
M3	43.4	61.5
M4	36.01	48.5
M5	46.4	53.5
M6	45.0	54.2
M7	43.8	58.9
M8	44.4	54.9
M9	40.4	51.1
M10	33.2	48.8

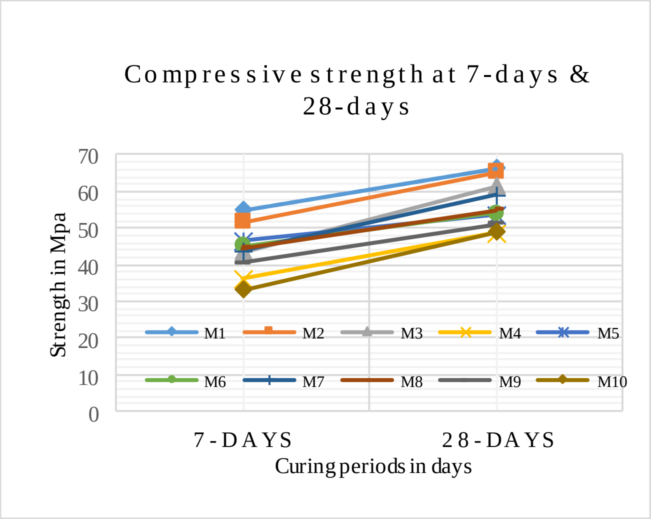

Fig-7: Compressive strength at 7-days & 28-days.

C. Carbonation test of samples.

The carbonation test of concrete was performed by using 1% phenolphthalein solution. The carbonation depth of concrete made with different types of cement & partial replacement of normal Portland cement CEM-I with SCM Fly ash & GGBS shows that concrete made with cement CEM-II/B-M (mix M3) & CEM-III/A (mix M4) having higher percentage of SCM part in cement [3] shows more influence of carbonation in concrete than concrete made with normal Portland cement CEM-I (mix M1) .The experiment also shows that concrete made with partial replacement of normal Portland cement CEM-I with higher % of Fly ash (25%) in mix M7 & GGBS (70%) in mix M10 shows maximum carbonation effect . The Fly ash & GGBS combine with Calcium hydroxide present in pore fluid & turn in to formation of secondary phase of Calcium silicate hydrate (C-S-H), which will improve the densification of pore volume & at the same time pH of the pore water get reduced. However in case of GGBS which is having high percentage of Calcium oxide (CaO) which is again react with hydrated Calcium hydroxide (CH) & thus produce Calcium carbonate ($CaCO_3$) [6] which will further reduce the concrete pH & thus results more carbonation effect in concrete made with higher % GGBS in concrete as compared to concrete made with normal Portland cement & Fly ash based concrete [4] [5]. The changes in pore structure densification due to formation of secondary phase of C-S-H on reaction of hydrated calcium hydroxide (CH) and GGBS is not very much significant in GGBS concrete & thus reduction in CH content in pore fluid and hence the carbonation rate increased. The reason for the same is that GGBS had prominent amount of free lime (CaO) content in its composition and thus greater amount of hydrated products C-S-H formed on pozzolonic reaction with a large specific surface area & hence samples were easily carbonated [6]. However, if the concrete pore structure densification does not govern even after reduction in CH on pozzolonic reaction, the carbonation may proceed even faster due to presence of fewer carbonizing materials available per unit area of CO_2 to react with for initiation of Carbonation [7] .This is why carbonation tends to proceed faster in concrete containing pozzolonic materials Fly ash & GGBS.

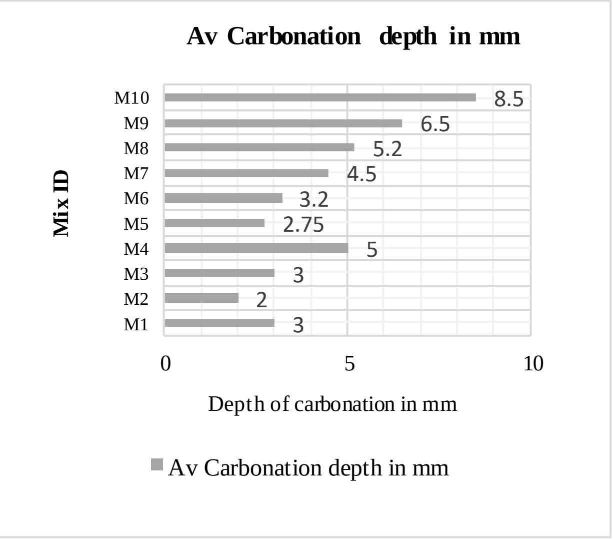

Fig-8: Carbonation depth of concrete samples.

It has been observed that addition of GGBS led to a greater

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carbonation rate, which is consistent with the trend observed by Osborne [4] and Papadaki [5]. The changes in pore structure were not very much adequate in GGBS concrete to counteract with CH & thus reduction in CH content in pore fluid and hence the carbonation rate increased. The reason for the same is that GGBS had prominent amount of free lime (CaO) content in its composition and thus greater amount of hydrated products C-S-H formed on pozzolonic reaction with a large specific surface area & hence samples were easily carbonated [6]. However, if the concrete pore structure densification does not govern even after reduction in CH on pozzolonic reaction, the carbonation may proceed even faster due to presence of fewer carbonizing materials available per unit area of CO_2 to react with for initiation of Carbonation [7] .This is why carbonation tends to proceed faster in concrete containing pozzolonic materials Fly ash & GGBS.

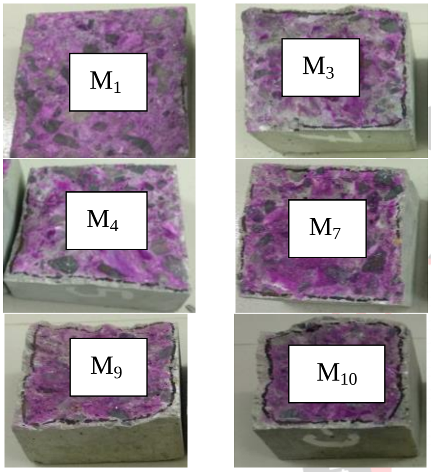

Fig-9: Carbonation test by using 1% phenolphthalein solution.

VI. CONCLUSION

The following are the outcome of the research experiment work.

[1] The workability of concrete made with cement having higher % of SCM in Portland composite cement CEM-II/B-M & Blast furnace slag cement CEM-III/A shows reduced level of workability than concrete made with normal Portland cement CEM-I. Also concrete made with partial replacement of normal Portland cement CEM-I with higher % of Fly ash & GGBS shows significant reduction in workability than concrete made with normal Portland cement CEM-I with same w/c ratio.

[2] The early age strength development of concrete made with cement having higher % of SCM in Portland composite cement CEM-II/B-M, Blast furnace slag cement CEM-III/A & also concrete made with replacement of normal Portland cement with higher % of SCM Fly ash & GGBS shows significantly lower strength than concrete made with normal Portland cement CEM-I with same w/c ratio.

[3] The strength gaining of concrete made with cement Blast furnace slag cement CEM-III/A & also concrete made with higher % SCM Fly ash & GGBS shows significantly higher strength gaining after 7-days than concrete made with normal Portland cement CEM-I .

[4] The concrete made with cement having higher % of SCM in CEM-III/A , CEM-II/B-M & also concrete made with partial replacement of normal Portland cement CEM-I with 70% GGBS & 25% Fly ash shows significantly maximum carbonation in concrete than concrete made with normal Portland cement CEM-I .

[5] The experiment also shows that concrete made with higher percentage of GGBS shows maximum depth of carbonation than Fly ash based concrete.

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