Influence of Different Types of Cement & Pozzolonic Materials on Chloride Penetrability to Concrete

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Abstract: This paper presents the influence of different types of cement CEM-I, CEM-II/A-M, CEM-II/B-M, CEM-III/A as per BSEN-197-1 & pozzolonic materials Fly ash & GGBS on chloride penetrability to Concrete. Chloride-induced corrosion is one of the main mechanisms of deterioration of reinforced concrete structure & affecting the long-term performance of structures. So in this research work a detail experimental study has been conducted on penetrability of chloride ions in concrete by using Rapid chloride penetrability test (RCPT) as per ASTM C-1202 & calorimetric test by using 1% AgNO3 solution. The outcome of this research work shows that concrete made with Blast furnace slag cement CEM-III/A, Portland composite cement CEM-II/B-M & also concrete made with pozzolonic materials 25% Fly ash & 70% GGBS shows minimum penetration of chloride ions .Thus resistance of chloride penetrability to concrete with different cement is of following decreasing order CEM-III/A > CEM-II/B-M > CEM-II/A-M > CEM-I. So in this research work it shows that concrete made with cement having higher amount of pozzolonic materials [3] & also concrete made with partial replacement of normal Portland cement CEM-I with higher % of GGBS & Fly ash shows minimum penetration of chloride ions.

***IndexTerms* - CEM-I, CEM-II/A-M, CEM-II/B-M, CEM-III/A, Chloride, Fly Ash, GGBS, RCPT.**

I. Introduction

Corrosion of steel reinforcement in reinforced concrete structure & deterioration of concrete is one of the most common durability problem for reinforced concrete structures. Chloride-induced corrosion is one of the main cause for deterioration of reinforced concrete structure in marine environment & affecting the long-term performance of structure. Typically, the pore solution of concrete has a pH-value above 12.6 due to the presence of $Ca(OH)_2$, and even higher values can be observed for concrete rich in NaOH and KOH. The highly alkaline environment of the pore solution favors the formation of a passive oxide film of Iron oxide on the surface of the steel reinforcement and a high pH-value is therefore an important inhibiting factor with regard to corrosion initiation of reinforced steel in Concrete. The free chloride ions entered in concrete may cause depassivation of the protective Iron oxide film layer of reinforcement steel leading to corrosion of steel in concrete & it results increasing of steel volume & thus spalling of cover concrete. The chloride resistance depends on the permeability of the concrete and the thickness of clear cover to the reinforcement steel. So durability of the reinforced concrete structure against chloride attack is mainly depend on the chlorides penetrability resistance of concrete. In this research work a detail experimental study has been conducted on penetrability of chloride ions in concrete by using Rapid Chloride Permeability test (RCPT) method as per AASHTO T277 & ASTMC1202 & through calorimetric test by using 1% AgNO3 solution. For this research work a reference concrete mix M1 of C-30/37 grade was used by using normal Portland cement CEM-I & other samples mixes were prepared by changing the normal Portland cement CEM-I with other types of cement CEM-II/A-M, (mix M2), CEM-II/B-M (mix M3), CEM-III/A (mix M4) as per BSEN-197-1 & also partial replacement of normal Portland cement CEM-I with pozzolonic materials Fly ash 15% (mix M5) , 20% (mix M6), 25%(mix M7) & GGBS 50% (mix M8) ,60%(mix M9) & 70% (mix M10) keeping same w/c ratio & same quantity of other ingredients of concrete as per design mix of concrete C-30/37. The outcome of this research work shows that concrete made with Blast furnace slag cement CEM-III/A, Portland composite cement CEM-II/B-M & also concrete made with pozzolonic materials 25% Fly ash & 70% GGBS shows minimum penetration of chloride ions .Thus resistance of chloride penetrability to concrete with different cement is of following decreasing order CEM-III/A > CEM-II/B-M > CEM-II/A-M > CEM-I. So in this research work it shows that concrete made with cement having higher amount of pozzolonic materials [3] & also concrete made with partial replacement of normal Portland cement CEM-I with higher % of GGBS & Fly ash shows minimum penetration of chloride ions.

II. MECHANISM OF CHLORIDE INDUCED CORROSION

The corrosion of embedded reinforcement Steel in concrete is an electrochemical process .The embedded steel reinforcement is inherently protected against corrosion by passivation of the steel surface due to the high alkalinity (pH > 12.5) of the concrete. The major two cause of corrosion of steel is either due to reduction of concrete pH due to carbonation or by damaging of thin passivizing layer of Iron oxide on embedded steel reinforcement due to ingress of chloride ions in concrete. The schematic representation of corrosion mechanism of embedded reinforcing steel is hereby explained.

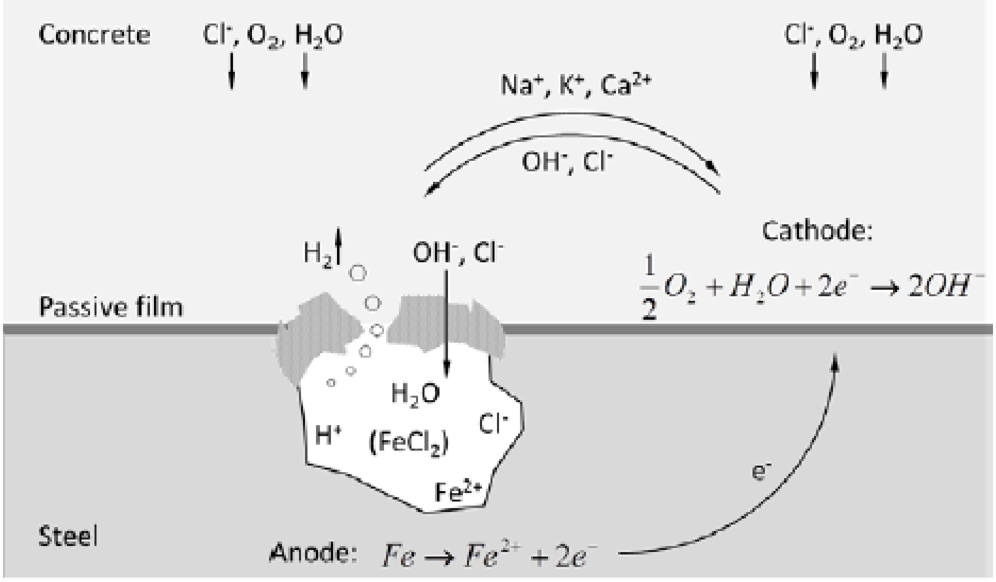

Figure 1: Mechanism of chloride induced corrosion of steel reinforcement

III. EXPERIMENTAL SETUP

Standardized testing procedures adopted as Rapid chloride permeability test (RCPT) of concrete as per AASHTO T277 & ASTM C 1202. According to ASTM C1202 test, a water-saturated, 50 mm thick, 100 mm thick diameter concrete specimen is subjected to a 60 v applied DC voltage for 6 hours using the apparatus and the cell arrangement as shown in Figure-2. In one reservoir is a 3.0 % NaCl solution and in the other reservoir 0.3 M NaOH solution is used. The total charge passed is determined and this is used to rate the concrete as per Table-I & resistivity of chloride ions penetrability in concrete. After the sample is removed from the cell at the end of the 6 hours the sample is again using for chloride penetrability test by calorimetric method using 0.1M AgNO3 solution. In addition to the RCPT of concrete as per ASTMC1202 the compressive strength of concrete with different types of cement & partial replacement of Portland cement with pozzolonic materials Fly ash & GGBS at various proportion has been studied here. The size of sample used for evaluation of concrete compressive strength at different age is 150mm x 150mm x 150mm cube samples. The sample used for RCPT was cured for 28-days & the test was conducted after 28-days of curing only.

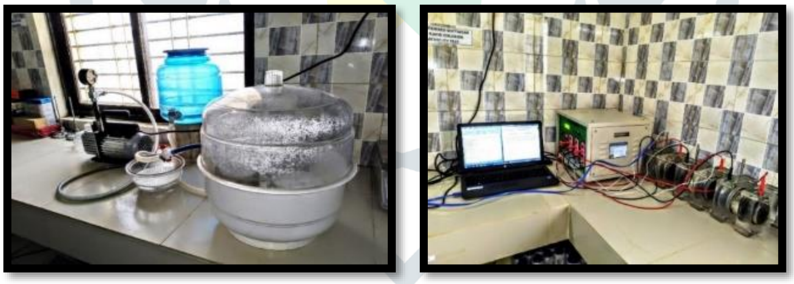

Figure-2: RCPT test of concrete as per ASTMC1202

Table-1: RCPT rating as per ASTMC1202

Charge Passed (Coulombs)	Chloride Ion Penetrability
>4000	High
2000-4000	Moderate
1000-2000	Low
100-1000	Very Low
<100	Negligible

IV. MATERIALS

The 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 cement CEM-III/A as per BSEN-197-1. The pozzolonic materials 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 is of crushed Basalt rock & Fine aggregate of river sand having FM of 2.7. The super plasticizer used in this research work was of Polycarboxylate ether based of make BASF. The test results of all the materials tabulated here.

Table-2: 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-3: 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
SiO_2	21.7	20.3	23.3	24.45
Al_2O_3	5.19	4.23	6.31	8.97
Fe_2O_3	3.86	3.2	3.57	2.22
MgO	1.8	2.52	1.41	2.95
SO_3	1.21	3.0	2.37	2.83
Na_2O	0.172	0.338	0.098	0.282
K_2O	0.439	1.02	1.08	0.661

Table-4: Physical properties of Fly Ash & GGBFS.

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

Table-5: Chemical composition of Fly Ash & GGBFS.

Component %	Fly Ash	GGBS
CaO	2.87	38.2
SiO_2	56.3	35.5
Al_2O_3	23.6	18.7
Fe_2O_3	4.96	1.06
MgO	0.424	5.21
SO_3	1.22	0.727
Na_2O	0.33	0.245
K_2O	2.09	0.004
MnO	0.0416	0.595
TiO_2	0.476	0.400
P_2O_5	0.453	0.0172

Table-6: 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
Flakiness Index in %	21.22
Elongation Index in %	23.5
Magnesium Sulphate Soundness in %	14
Grading Requirement (19-4.75 mm)	Satisfactory as per ASTMC33

Table –7: 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-8: 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

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

Table-9: 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
Super plasticiser @ 0.8 % by weight of cement	3.5

Table-10: Mix proportion of different mix in kg/cum.

Mix Details	w/c Ratio	Cement	SCM	CA	FA	Superplasticiser
M1 CEM-I, 52.5N	0.4	438	NA	1142	685	3.5
M2 CEM-II/A-M (100%)	0.4	438	NA	1142	685	3.5
M3 CEM-II/B-M (100%)	0.4	438	NA	1142	685	3.5
M4 CEM-III/A (100%)	0.4	438	NA	1142	685	3.5
M5 CEM-I (85%) + FA (15%)	0.4	372.3	65.7	1142	685	3.5
M6 CEM-I (80%) + FA (20%)	0.4	350.4	87.6	1142	685	3.5
M7 CEM-I (75%) + FA (25%)	0.4	328.5	109.5	1142	685	3.5
M8 CEM-I (50%) + GGBS (50%)	0.4	219	219	1142	685	3.5
M9 CEM-I (40%) + GGBS (60%)	0.4	175.2	262.8	1142	685	3.5

M10 CEM-I (30%) + GGBS (70%)	0.4	131.4	306.6	1142	685	3.5

V. RESULTS & DISCUSSION

a) FRESH CONCRETE PROPERTIES

From the fresh concrete test results it has been observed for same w/c ratio the workability of concrete mixes with Portland composite cement of type CEM-II/B-M & Blast furnace slag cement CEM-III/A is lower side due to high composition of pozzolonic materials in cement, like 21-35% in CEM-II/B-M [3] & 35-64 % slag in CEM-III/A [3]. However on partial replacement of Portland cement with 15% Fly Ash shows higher slump due to spherical shape of the Fly Ash particles & its ball bearing effect during plastic stage of concrete [1] & at the same time it was also noticed that when the percentage of Fly Ash was increased up to 25% the workability of mix is got reduced due to its excessive cohesiveness or adhesiveness of the mix. On the other hand on replacement of Portland cement CEM-I with GGBS the workability of concrete get reduced due to its long, flaky & elongated crystalline shape. The shape of the particles for both Fly Ash & GGBFS has been studied through SEM with high resolutions.

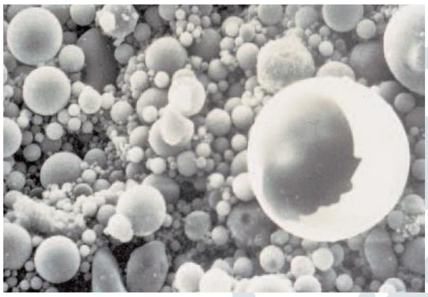

Figure 3: SEM image of Fly Ash

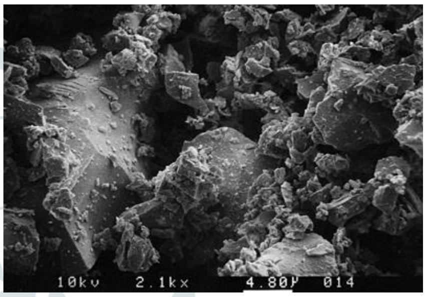

Figure 4: SEM image of GGBFS

Table-11: 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

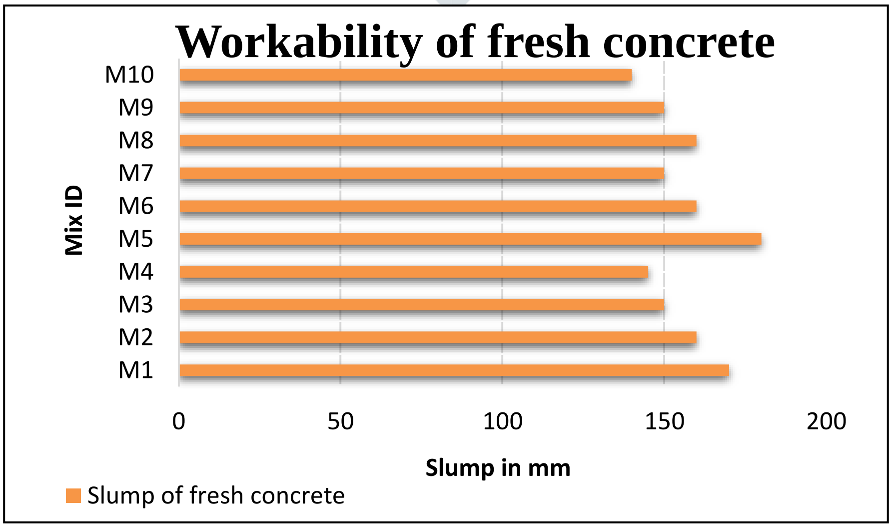

Figure-5: Workability of different concrete mix

b) HARDENED CONCRETE COMPRESSIVE STRENGTH OF DIFFERENT MIX

The average compressive strength of three specimen concrete cubes at 7-Days & 28-Days for different concrete mix are tabulated below in Table-12.

Table-12: Concrete compressive strength of different mixes at 7-Days & 28-Days respectively

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

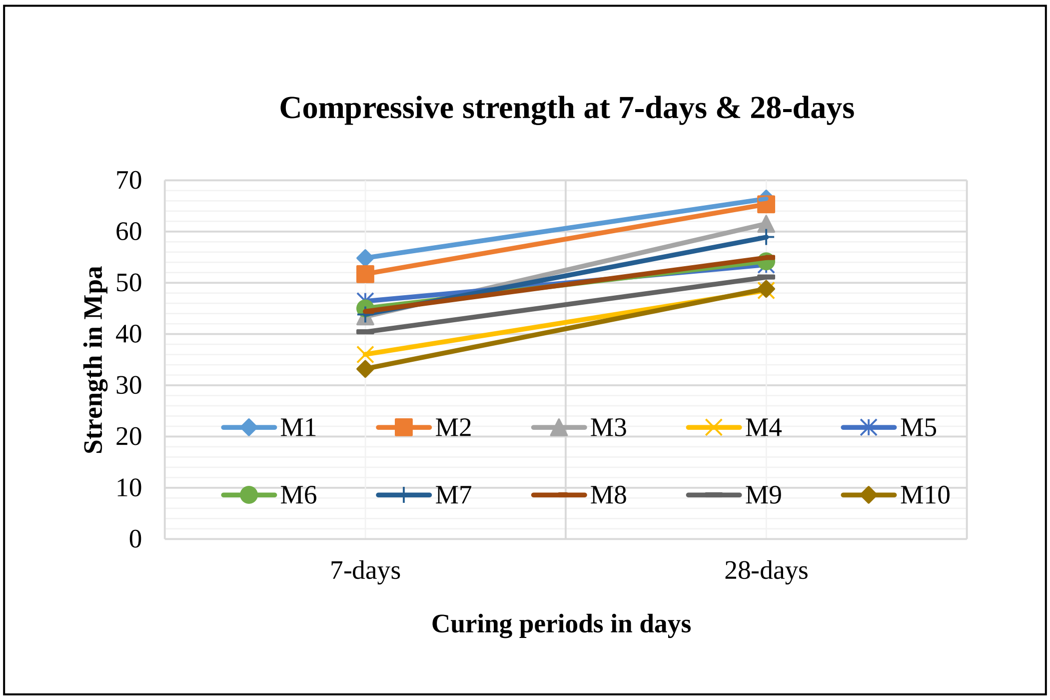

Figure-6: Compressive strength of different concrete mix at 7-days & 28-days.

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 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.

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

c) CHLORIDE PERMEABILITY OF DIFFERENT CONCRETE MIX AS PER ASTM C1202

The chloride permeability to concrete with different types of cement CEM-I, CEM-II/A-M, CEM-II/B-M, CEM-III/A & partial replacement of Portland cement with Fly ash & GGBS at various proportion is hereby tabulated below in Table-13.

Table-13: Average RCPT value in Coulombs

Mix ID	Av RCPT (Coulombs)
M1	1232
M2	1185
M3	1115
M4	1087
M5	1048
M6	958
M7	741
M8	725
M9	617
M10	582

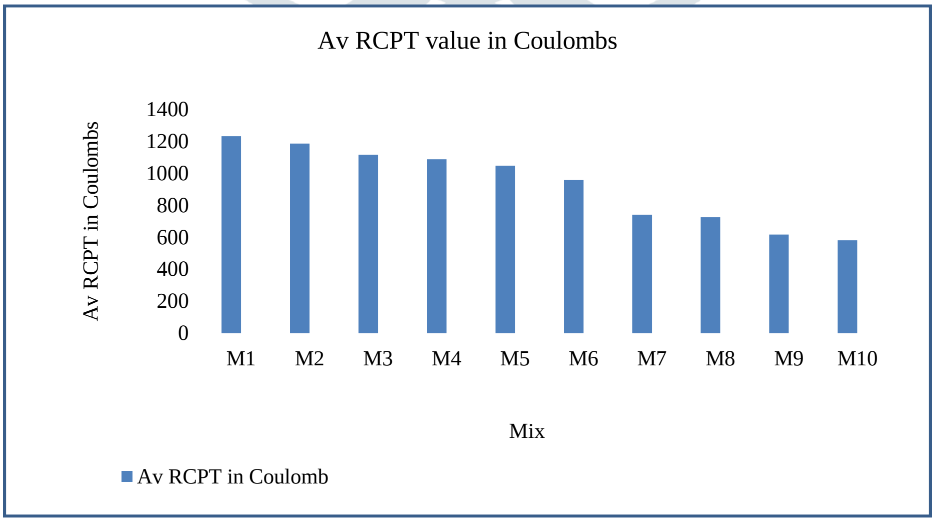

Figure-7: RCPT value in Coulombs

From the above results it has been observed that Chloride penetrability to concrete mix M1 with normal Portland cement CEM-I shows maximum Chloride penetrability than mix with other types of cement CEM-II/A-M & CEM-II/B-M & CEM-III/A. It is also observed that concrete made with Portland composite cement CEM-II/B-M (Clinker-65-79% & Pozzolonic mix part-21-35%) [3] & mix M4 with Blast furnace slag cement (Clinker-35-64% & Blast furnace slag part-36-65%) [3] Shows minimum chloride penetration as compared to concrete made with other types of cement CEM-I, CEM-II/A-M & CEM-II/B-M due to higher % of slag content in CEM-III/A (36-65%) [3]& ability of chloride binding capacity is more in cement CEM-III/A due to higher % of slag content. The test results also shows that concrete made with partial replacement of Portland cement CEM-I with Fly ash 25% in mix M7 & 70% GGBS in mix M10 shows minimum penetrability of chloride ion in concrete with same w/c ratio . The chloride penetrability of concrete made with higher % pozzolonic materials Fly ash (25%) & GGBS (70%) is minimum due to higher composition of Al_2O_3 in Fly ash & GGBS which helps to increased chloride binding capacity & thus reduce chloride penetrability in concrete with pozzolonic materials Fly ash & GGBS.

d) CHLORIDE PERMEABILITY TEST OF CONCRETE SAMPLE WITH 0.1M $AgNO_3$ SOLUTION:

The concrete samples which was being used for RCPT the same sample was used for chloride penetrability test through calorimetric method by using 0.1M $AgNO_3$ solution .From the test results it shows that among different types of cement, concrete mix M1 made with normal Portland cement CEM-I shows maximum penetration depth & minimum penetration depth in concrete mix M4 made with Blast-furnace slag cement .It is also observed that concrete mix M7 made with 25% Fly ash & concrete mix M10 made with 70% GGBS shows minimum penetration depth .The test results shows that concrete made with cement having rich % of pozzolonic material in cement & also concrete made with partial replacement of normal Portland cement with higher percentage of pozzolonic materials Fly ash & GGBS shows maximum resistance of chloride penetration in concrete due to increased chloride binding capacity of pozzolonic material.

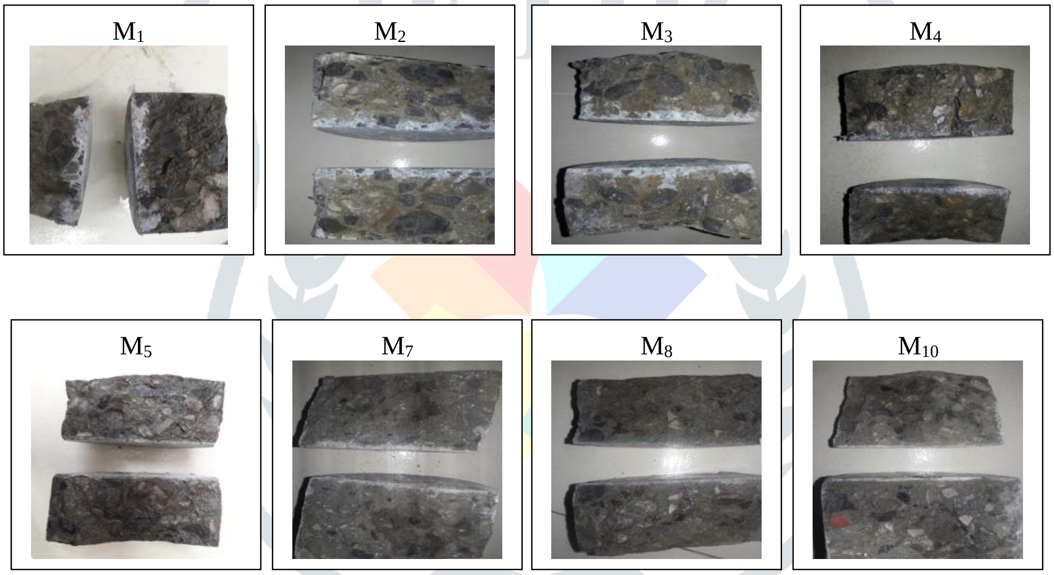

Figure-8: Penetration depth of chloride ions in concrete by using 0.1 M $AgNO_3$.

Table-14: Average penetration depth of chloride ions in concrete

Mix ID	Av penetration depth of Chloride ions in mm
M1	10
M2	9
M3	9
M4	8
M5	8
M6	6
M7	4
M8	4

M9	3
M10	2

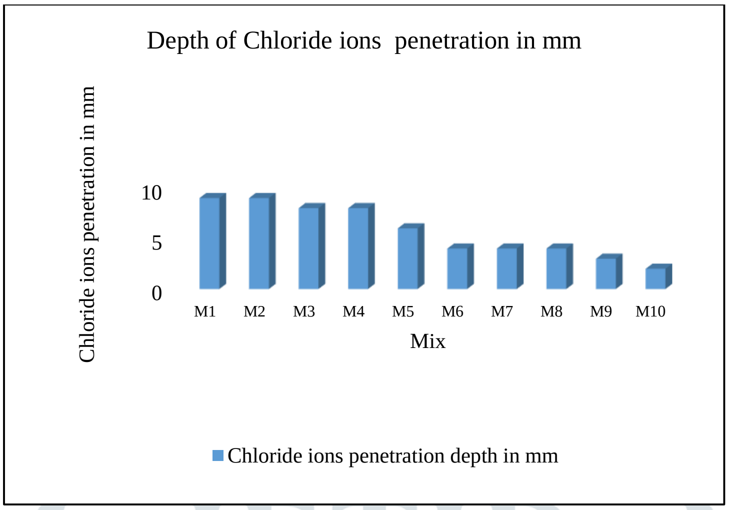

Figure-9: Average depth of chloride ions penetration to concrete.

VI. Conclusion

From the experimental research work on chloride permeability to concrete made with different types of cement & also concrete made with partial replacement of Portland cement with pozzolonic materials Fly ash & GGBS at various proportions. The followings are the outcome of the research work.

1) The workability of fresh concrete made with Portland composite cement of type CEM-II/B-M, Blast furnace slag cement CEM-III/A & addition GGBS shows fall in workability with same w/c ratio & at the same time by addition of Fly ash up to 15% shows increased workability.
2) The early age strength of concrete made with Portland composite cement of type CEM-II/B-M & Blast furnace slag cement CEM-III/A is significantly lower side than concrete mix made with normal Portland cement CEM-I.
3) The strength development of concrete mix made with Portland composite cement of type CEM-II/B-M, Blast furnace slag cement CEM-III/A & mix with addition of 25% Fly ash & 70% GGBS shows maximum strength gaining after 7-days.
4) The chloride permeability of concrete made with cement having rich content pozzolonic material & also concrete made with partial replacement of normal Portland cement CEM-I with higher % of pozzolonic materials Fly ash & GGBS shows minimum penetration of chloride ions due to increased chloride binding capacity of pozzolonic materials Fly ash & GGBS due to presence of high composition of Al_2O_3 in Fly ash & GGBS.

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