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Effect of Different Supplementary Cementitious Material on the Microstructure and its Resistance Against Chloride Penetration of Concrete

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EFFECT OF DIFFERENT SUPPLEMENTARY CEMENTITIOUS MATERIAL ON THE MICROSTRUCTURE AND ITS RESISTANCE AGAINST CHLORIDE PENENTRATION OF CONCRETE

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Synopsis: Various research programes on long term durability of concrete are going on through -out the world. An attempt is made to study the microstructure of the concrete with the addition of different SCM like fly ash, GGBS, metakaolin, silica fume, and rice husk ash. In this paper, data is presented in a simplified manner for the sake of convenience. Hydration is a continuous process and so microstructure of HPC and interfacial zone (ITZ) can change with age and effect of environment by the influencing agents present in it.

Rapid chloride permeability test (RCPT) is carried out on the various samples prepared with fly ash, GGBS, metakaolin, silica fume, and rice husk, are presented in this paper.

Key words: Durability, microsture, flyash, GGBS, silica fume, rice husk ash, metakaolin, RCPT

INTRODUCTION

The humid and harsh environment of the coastal zone of India leads to more attention towards the durability as many structures built fairly recently are getting dilapidated prematurely. Concrete structures in the coastal zone show significant deterioration due to corrosion of steel reinforcement caused by chloride ingress. Concrete containing different supplementary cementitious materials have received considerable attention as a good means of improving the durability of reinforced concrete structures.

As a reaction to the problem of the premature failure of structure, codes and standards have in recent modifications emphasized the need for durability, measures i.e. a move to limited w/cm, higher strength design approach for severe exposure. Indian standards have given various limiting values for different exposure conditions (1).

In the present study, severe exposure condition is considered for which Indian standard specifies minimum cementitious content 320 kg/m^3, w/cm ratio 0.45 and strength of 25 MPa. The objective of study is to assess cementing material systems and their microstructure, which are capable of limiting chloride ingress in concrete.

The Macro properties are governed by the microstructure of the material. On a micro scale, concrete is a multi-phase material consisting of hydrated cement paste (hcp), additions, sand, gravel or other aggregates (2).

Out of various tests to determine permeability, one of the standard tests is given by ASTM-C 1202.This test method, which is adopted for critical evaluation of chloride permeability in our country at present stage and we have used the same method to study the chloride permeability of the concrete with fly ash, ggbs, metakaolin, silica fume, and rice husk.

Fly Ash

Fly Ash is used as the blending agent to achieve durable concrete; the addition rate of the fly ash is normally 25% to 40% by mass of cement. The effect of the fly ash concrete depends on combinations of paste enhancement, water reduction and pozzolanic reactivity, resulting in pore refinement in the paste fraction of the concrete. The main beneficial effect of fly ash is related to the refinement of pore structure by pozzolanic reaction reducing diffusion rate and electric conductivity of concrete.

Ground Granulated Blast Furnace Slag

Ground granulated blast furnace (ggbs) has an ability to replace large amounts of portland cement when early strength is not of serious concern. Pore enhancement is probably more pronounced with ggbs than with pozzolana, this is reflected in excellent performance in seawater. To achieve acceptable sulphate resistance with slag concrete a slag content of at least 60% must be present in the binder (3). Early strength development is slow and careful curing is critical for achieving full potential of concrete**.**

Silicafume

Silica fume (SF) contains 85% to 98% silica (SiO_2) with spherical particle of mean size in the range 0.10 to 0.20 microns, which are amorphous (glassy). The optimum range of silica fume when used as an individual blending agent normally in conjunction with HRWR is 5 to 15% by mass of cement. The unique feature of silica fume is its extreme fineness and consequent rapid pozzolanic reaction with cement to produce early strength.

Because SF is about two order magnitudes finer than that the other binder components it has a special role in overall filler effect that is significant in improving bond between the cement paste and aggregate particles (3). It is observed that cohesiveness is increased and naturally eliminates the bleeding tendency in concrete. SF reduce the total volume of porosity in concrete and the pore structure is refined, making the concrete less susceptible to damage by chemical attack.

Metakaolin

Metakaolin (MK) is pure kaolinite clay, which has been heated in to nearly 800°C and processed further. It is usually fine and increases water demand (not as much as SF) and is effective in improving characteristics of the interfacial zone between aggregate and paste fractions in concrete.

Rice Husk Ash

Rice husk ash (RHA) is an active pozzolana produced by controlled burning of rice husk, which is an agricultural waste. RHA increases water demand of concrete, a problem that can be counteracted by incorporating superplasticizer. It is suggested that the use of RHA & fly ash in combination may offer complementary and synergistic effect on properties of concrete. In a ternary blend concrete fly ash compensates the reduction in workability due to high demand of RHA, while its progressive reaction with $Ca(OH)_2$ contributes to the later age strength. RHA improves the cohesiveness fresh Concrete mixture.

RAPID CHLORIDE PERMEABILITY TEST (RCP Test)

Corrosion is mainly caused by the ingress of chloride ions into concrete annulling the original passivity present. The RCPT has been developed as a quick test able to measure the rate of transport of chloride ions in concrete.

RCPT is based on the principle that negatively charged chloride ions are attracted to a positive electrode and consists of measuring the total charge passed through a sample over the six hours test duration when a direct current (D.C.) potential difference of 60 V is applied across the end of the samples. The quality of material is quantitatively assessed based on the total charge passed during the test, which is considered to be a measure of the chloride permeability of concrete.

RCPT involves two steps: Sample preparation including conditioning, saturation and setting up the test and monitoring the amount of electrical current passing through the sample during six hours test duration as described in ASTM C 1202 – 94. Fig. 1 represents the RCPT setup. The conditioning of the sample should be properly done as per the guideline given in standard (4).

RCPT test is carried on the Concrete core taken from the concrete cubes, which were cured for 28 days the results are given in table 6.

INITIAL SURFACE ABSORPTION (ISAT)

The ISAT test specified in BS 1881 part 5 is used for measuring initial surface absorption of Concrete. The test is carried on 28 days cured concrete samples. Samples were properly cleaned and dried which is the critical condition for the test since results are greatly influenced by the existing moisture conditions as well as surface cleanliness. The test consists of the measurement of water flow into the test specimen through a known surface area. Measurement of the volume flow is obtained by measurement of the length of flow along a capillary of known dimension. Fig 2 represents the ISAT setup.

Initial surface absorption to determine by rate of flow of water into concrete per unit area at a stated interval from the start of the test and at constant applied head. The results are given in table 5.

MICROSTRUCTURE.

Concrete is often considered as a two-phase material with hcp as a binder and aggregate as filler, which are bonded together at the interfaces.

Reinhardt (2) reported that the structure of calcium silicate hydrate (C-S-H) is not constant in space and time. The average C/S. ratio is about 1.75 with a local variation of 1.20 to 2.30 at ages up to a few years. In (C-S-H) the silicate ions are chains of a few tetrahedra. With increasing age, the local variation of C/S ratio decreases and chain length increases to form a more stable material (5)]

If mineral additions like pozzolana, silica fume, or ground granulated blast furnace slag (ggbs) are added to portland cement the C-S-H produced is similar to the one with portland cement; however C/S ratio falls between 1.40 to 1.60 with pozzolana, and 1.0 to 1.20 with silica fume or slag. It has been observed that mean chain lengths are greater (5), especially in the case of addition of silica fume i.e. the material become highly polymerized.

Reinhardt (2) reported that the outer product has lower c/s ratio than the inner product at early age whereas the C/S ratio levels out in mature paste. The reason for that is that larger particles react slower (smaller surface / volume ratio) than smaller ones and that the outer product catches the small particles during hydration. This causes that inner and outer product can only be distinguished clearly for a single grain.

Van Breuqel (6,2) has shown the growth of outer product of cement and reactive pozzolanic materials with simultaneous embedment of smaller particles in a hydration model and computer simulation, which shows embedding of particles in outer shell of hydrating particles and shows the situation of a larger cement grain at a certain stage of hydration. Inner and outer product have formed the latter of which contains embedded particles with diameter small than the width of the outer product particles which protrude from the outer product are bridging the inner particle distance between larger grains and determine the strength of hcp for a great deal. Finely ground reactive materials like silicafume, metakaolin increase the volume of embedded material in the outer product which leads to a densification and consequently to an increase of strength.

Interfaces

Mineral additions, which react with cement paste, i.e. ggbs, fly ash, microsilica, metakaolin are bonded with hydrated cement paste and have only clear interfaces when they are not dissolved. At early ages microsilica and metakaolin is completely integrated due to its small particle sizes. They are embedded in the outer product of cement grain. Other additions form weak interfaces but these are densified during ongoing hydration.(2)

Ultra fine supplementary cementitious material has the ability to pack more closely to the aggregate surface. When using inert admixtures only filling in the interfacial zone with such particles may be inadequate to improve micro structural homogeneity. This is where the pozzolonic reactivity of the mineral admixture becomes important. Because pozzolanic admixtures with CH produces secondary (C-S-H) having a greater volume than the original solid reactants, the effect of the presence of the mineral admixture in the interfacial zone results in the production of a more homogeneous microstructure and a better bond between paste and aggregate. Pozzolanic admixtures are found to improve the integrity of the interfacial zone of the concrete.

EXPERIMENTAL DETAILS

a) Material characteristics

i) Cement

Ordinary Portland cement confirming to IS 12269 was used. The physical and chemical properties are given in table 1a & 1c.

ii) Supplementary cementitious materials

The physical and chemical properties of supplementary cementitious materials fly ash, ggbs, micro silica, metakaolin and rice husk ash is given in table 1b & 1c.

iii) Aggregates

The coarse aggregate used was of basaltic nature. The properties of aggregates are given in table 2. Locally available river sand confirming to zone II of IS 383:1970 used for the trials.

iv) Admixture

Polycarboxylate ether based admixture was used.

v) Mix Proportions

The mix proportion for the experiments is given in table 3

Group I :-proportions have 40 % fly ash by weight of cementitious material and MS, MK, RHA of 4.5% by weight of total cementitious material.

Group II:- proportions have 30 % fly ash by weight of cementitious material and MS, MK, of 5.25% by weight of total cementitious material.

Group III:- proportions have 60 % ggbs by weight of cementitious material and MS, MK, RHA of 3.0% by weight of cementitious material.

Group IV:- proportions contain cement 92.5 % and MS, MK, RHA of 7.5%.

Group V:- proportions have 37 % & 27.75 % fly ash by weight of cementitious material and MS, MK of 7.5% by weight of total cementitious material.

For all groups cementitious content is 320 Kg/m^3 and water cementitious ratio 0.45 by weight and admixture of 0.7% by weight of cementitious material.

vi) Workability

All mixes were designed for high workability having slump value 130mm to 150mm required for actual projects.

RESULTS

Cubes (15 cm edge) were prepared from the proportions indicated in the various groups and were tested for the following parameters.

Fresh State: Density and workability in terms of slump, given in table 4

Hardened state:

i. Initial surface absorption test (ISAT) at the age of 28 days and results are shown in table 5 and fig 3.
ii. Rapid chloride permeability test (RCPT) at the age of 28 days results are shown in table 6.

CONCLUSIONS:

- Initial surface absorption of a mix having 40 % fly ash is 69 percent and a mix having 30 percent fly ash is 56 % compared to the concrete without fly ash after 60 minutes. By further addition of MS, MK in a 30 and 40 % fly ash mix, absorption is further reduced.
- Initial surface absorption of a mix having 60 % ggbs is 81 % compared to the concrete without slag.
- The addition of MS and MK in drastically reduces surface absorption levels.
- At the same dosage of MS and MK the absorption at 20 min. of MS is lower at 3.0 %, 4.5%, and 5.25% than MK. Where as at 7.5% dosage both MS and MK show similar trends.
- Ternary blend mixes shows lower absorption value.
- RCPT value of mix having 40% fly ash is higher than 30 % fly ash.
- Concrete mix with slag shows lower chloride permeability as compared to fly ash mixes.

- RCPT value of a ternary blend concrete are lower than binary blend concrete.
- Photomicrograph (fig.4) of concrete shows voids in the gel and photomicrograph (fig.5) of concrete with MS shows very dense gel without any voids. Which also confirmed by both ISAT and RCP test value.
- All above experimental results confirms, there is reduction in permeability which will helpful in increasing the service life of the structure made with various mixes shown in group I to group V.
- Mixes were designed in such a way that is can be adopted for project use without any difficulty.

LIMITATIONS

The above observations and conclusion is based on the limited data and further investigation is still progress for long-term period of 3 months.

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Table 1a:Physical properties of cement

Characteristics	*Cement*
Specific gravity	3.12
Specific Surface area,m^2/Kg	328.0
Setting Time, Min. a) Initial b) Final	 120 205
Comp. Strength, MPa a) 3 days b) 7 days c) 28 days	 46.9 55.4 66.9

Table 1 b: Physical properties of different SCM

Characteristics	*Fly ash*	*ggbs*	*SF*	*MK*	*RHA*
Specific gravity	2.28	2.78	2.23	2.53	2.06
Specific Surface area, m^2/Kg	456.4	480	1800(BET)	--	--

Table 1b Chemical properties of cement and different SCM

Characteristics	*Cement*	*Fly ash*	*ggbs*	*SF*	*MK*	*RHA*
SiO_2	21.20	61.90	36.5	90.5	52.24	87.0
Al_2O_3	4.50	28.90	11.67	0.7	43.18	0.80
Fe_2O_3	3.80	3.50	1.01	0.8	0.60	0.70
CaO	63.50	1.60	38.95	<0.1	1.03	1.40
K_2O	------	0.81	0.42	1.45	------	2.50
Na_2O	------	0.05	0.34	0.33	------	0.10
LOI	1.15	0.58	1.28	4.45	------	8.50

Table 2: Properties of aggregates

Sr. No	*Properties*	*Crushed Basalt*	*Natural river sand*
1	Fineness modulus	7.0	3.60
2	Specific gravity	2.81	2.72
3	Shape	Angular	Rounded
4	Maximum size aggregate	25 mm	< 4.75 mm

Table 3:Mix proportion details

Group	*Identifiction*	*Cement*	*Fla,*	*ggbs*	*MS*	*MK*	*RHA*	*Total agg.*	*Water*
		Quantities Kg per m^3							
	Con 1	320	0	0	0	0	0	2060	144
I	Con 2	192	128	0	0	0	0	2026	144
	Con 7	177.6	128	0	14.4	0	0	2020	144
	Con 8	177.6	128	0	0	14.4	0	2020	144
	Con 9	177.6	128	0	0	0	14.4	2020	144
II	Con 14	224	96	0	0	0	0	2036	144
	Con 15	207.2	96	0	16.8	0	0	2036	144
	Con 16	207.2	96	0	0	16.8	0	2036	144
III	Con 3	128	0	192	0	0	0	2036	144
	Con 10	118.4	0	192	9.6	0	0	2036	144
	Con 11	118.4	0	192	0	9.6	0	2036	144
	Con 12	118.4	0	192	0	0	9.6	2036	144
IV	Con 4	296	0	0	24	0	0	2056	144
	Con 5	296	0	0	0	24	0	2056	144
	Con 6	296	0	0	0	0	24	2056	144
V	Con17	177.6	118.4	0	24	0	0	2036	144
	Con 18	177.6	118.4	0	0	24	0	2036	144
	Con 21	207.2	88.8	0	24	0	0	2036	144
	Con 22	207.2	88.8	0	0	24	0	2036	144

Table 4: Properties of fresh concrete

Group	Identification	*Slump, mm*		*Density, Kg/m^3*
		0 min	*30 min*	
	con 1	150	100	2540
I	con 2	150	100	2490
	con 7	160	100	2570
	con 8	160	100	2510
	con 9	130	80	2470
II	con 14	150	90	2570
	con15	140	95	2550
	con 16	145	100	2520
III	con 3	150	90	2500
	con 10	120	80	2590
	con 11	130	90	2490
	con 12	125	80	2480
IV	con 4	150	80	2500
	con 5	150	90	2520
	con 6	140	85	2490
V	con 17	140	90	2540
	con 18	140	90	2570
	con 21	150	100	2550
	con 22	150	95	2490

Table 5 : Initial surface absorption results

Group	Identification	*ISAT value, ml/m^2/sec*			
		10 min	*20min*	*30 min*	*60 min*
I	con 1	0.022	0.021	0.017	0.016
	con 2	0.013	0.011	0.013	0.011
	con 7	0.003	0.005	0.008	0.007
	con 8	0.005	0.008	0.013	0.010
	con 9	0.006	0.011	0.012	0.011
II	con 1	0.022	0.021	0.017	0.016
	con 14	0.013	0.008	0.012	0.009
	con15	0.003	0.006	0.007	0.005
	con 16	0.015	0.010	0.008	0.008
III	con 1	0.022	0.021	0.017	0.016
	con 3	0.007	0.013	0.021	0.013
	con 10	0.005	0.008	0.007	0.007
	con 11	0.005	0.009	0.008	0.006
	con 12	0.006	0.01	0.011	0.009
IV	con 1	0.022	0.021	0.017	0.016
	con 4	0.000	0.002	0.001	0.001
	con 5	0.000	0.002	0.001	0.001
	con 6	0.001	0.003	0.003	0.004
V	con 1	0.022	0.021	0.017	0.016
	con 17	0.002	0.006	0.006	0.004
	con 18	0.005	0.006	0.006	0.005
	con 21	0.002	0.003	0.004	0.004
	con 22	0.003	0.004	0.004	0.005

Table 6: RCPT Results

Identification	Chloride ion permeability, coulombs
Con1	3201
Con7	2150
Con15	1460
Con10	726
Con17	885

Fig 1 :Initial surface absorption test set up

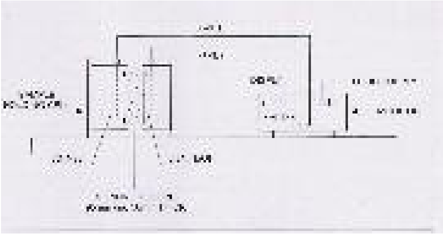
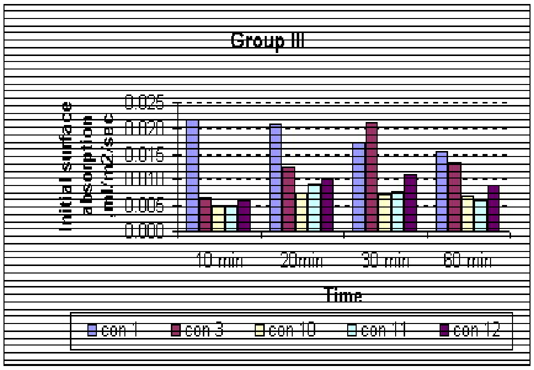
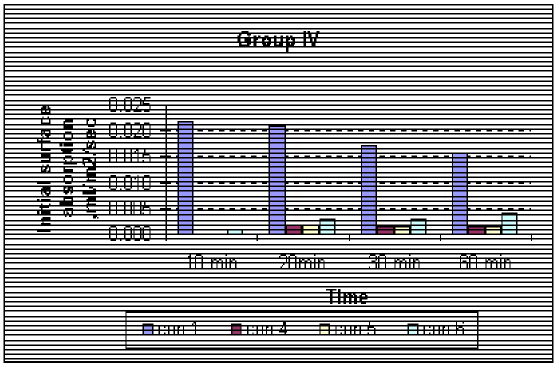
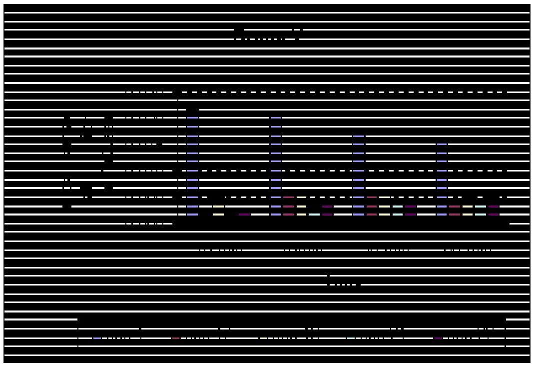


Fig 2:Schematic diagram of RCP test

Fig 3 : Initial surface absorption of different groups







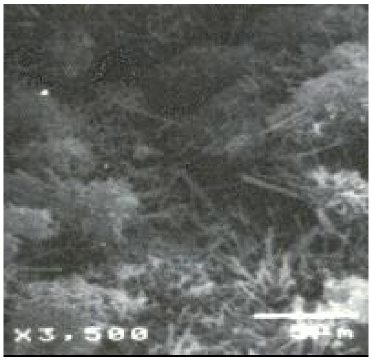


Fig 4 : Photomicrograph of a concrete –con1

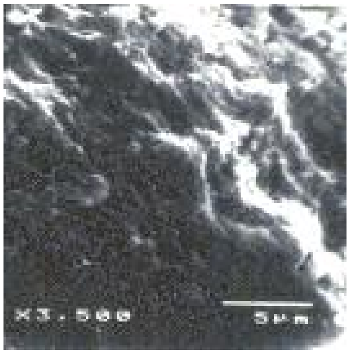


Fig. 5 Photomicrograph of concrete with microsilica-con4