



Effect of By-product Phosphogypsum in Fly-ash Incorporated Concrete

¹Arunprathap K U, ²P Gokuldeepan, ³Dr.Sunilaa George,

¹ ME Student, Civil Engineering Department, Easa College of Engineering and Technology, Coimbatore

, ² Assistant Professor, Civil Engineering Department, Easa College of Engineering and Technology, Coimbatore

, ³ Professor & Head, Civil Engineering Department, Easa College of Engineering and Technology, Coimbatore

Abstract: Industrialization and urbanization has led to depletion of high quality construction materials. The cost of construction materials is increasing significantly, so are their availability. So alternate construction materials are to be found and exploited. The material Phosphogypsum and fly ash has been found to have certain properties which can be useful in the construction. Phosphogypsum is the primary byproduct of the wet-acid process for producing phosphoric acid from phosphate rock and fly ash is the by-product of coal. The aim of the project is to develop a sustainable concrete with improved strength, durability and having less maintenance by utilizing Phosphogypsum and fly ash. Mechanical strength for compressive strength, split tensile strength and flexural strength were conducted to find the optimum usage of alternative materials with proportions of 5%, 10% and 15% of total weight of concrete and durability tests of sulphate, chloride resistance and corrosion test were performed. From the studies, it is concluded that long term strength and durability has increased when fly ash concrete is modified by partially replacing cement with 10% of phosphogypsum. The phosphogypsum increases the workability of the concrete due to the combined lubricating effect of fly ash and phosphogypsum. The strength properties are similar to the addition of fly ash in concrete. From durability studies of rapid chloride permeability, with the inclusion of fly ash, chloride ingress capacity of concrete is decreased. Pore refinement and grain refinement due to reaction between fly ash and liberated lime improves impermeability. The reduction in permeability of concrete is mainly due to filling of the pores and voids with calcium carbonate precipitation.

KEYWORDS: Phosphogypsum and fly ash, Mechanical strength tests, Durability tests

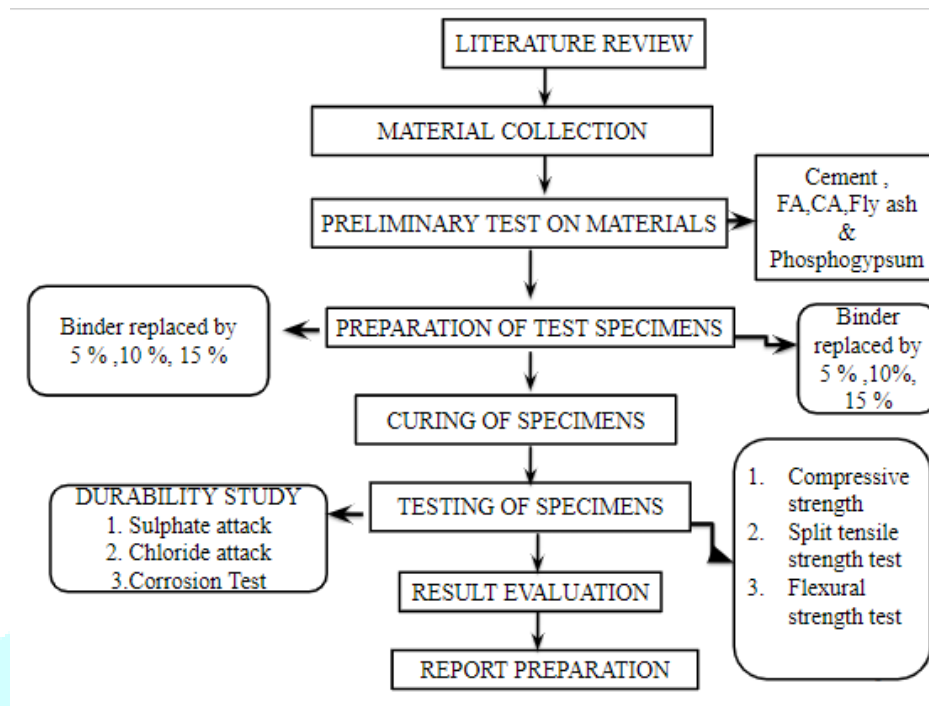
1. INTRODUCTION

In India, about 6 million tons of waste gypsum such as Phosphogypsum, flourogypsum etc. are being generated annually. Some attempts have been made to utilize Phosphogypsum as base and fill materials (in the form of cement-stabilized Phosphogypsum mix) in the construction of highways, runways, etc. More stringent environmental concerns over the last decade have resulted in legislation requiring Environmental Management Project Reports (EMPR) for any borrow pit or quarry established for the provision of road construction materials. This, together with the rapidly escalating value of property and hence expropriation costs for borrow pits, has resulted in an increase in the cost of providing natural materials for road construction. As materials probably make up about 70 percent of the cost of a typical rural road, significant benefits can be achieved by using materials that are already processed and stockpiled. By-product Phosphogypsum, despite having properties significantly different from conventional natural materials, has been shown in overseas studies to be a potentially useful road construction material, particularly when stabilized with cement.

Industrialization and urbanization has led to depletion of high quality construction materials. The cost of construction materials is increasing significantly, so are their availability. So alternate construction materials are to be found and exploited. The material Phosphogypsum has been found to have certain properties which can be useful in the construction of roads.

Phosphogypsum is a by-product which is generally dumped or kept unused, if these materials are not properly dumped they could cause environmental problems. Usage of these materials for road construction is proved safe and could be utilized in an efficient manner. Phosphogypsum is a cheap material, having a cost of around Rs.1.5/kg, therefore using this material would be cost effective. Phosphogypsum being a cost effective material can be utilized in various ways. If this material proves to be effective through the tests, then it could help in reducing the construction cost along with increase in quality.

II. METHODOLOGY



III. LITERATURE REVIEW

Mukherjee et al. (2017) carried out an experimental study to compare the self-healing of partially cracked conventional mortar (prepared with ordinary Portland cement) and cement - fly ash mortar. For cement - fly ash mortar, 20 % OPC has been replaced by class F fly ash. 21 All mortar specimens were casted with 1:3 binder to sand ratio (by weight) and with fixed 0.5 water/binder ratio. To generate micro cracks in mortar cubes, 28 day water cured specimens were subjected to direct compression (50% of corresponding 28 days compressive strength) in it. Healing environment consists of (a) curing in normal tap water for 120 days and (b) curing in normal air for 120 days separately. The compressive strength, ultrasonic pulse velocity, water absorption and rapid chloride ion permeability test on mortar specimens (with/without fly ash) confirm self-healing of cementitious composites in terms of recovery of its properties and the self-healing property is more prominent for fly ash mortar as compared to cement mortar.. FESEM with EDAX and XRD of the white deposition in the crack opening was found to be calcite precipitates. Kamalakkannan and Prakash (2014) developed a self-healing concrete with the high volume fly ash being replaced for the cement and putting it into practical application in the field of Construction Civil Engineering. Compressive strength of bacterial concrete is increased by 10 to 14 % than the conventional HVFA concrete. The split -tensile test and flexural test of conventional HVFA to Bacteria HVFA concrete is increased by 10.6%. Total ultimate load carrying capacity of the healed specimen is devastatingly higher. Since the load carried is about 85kN whereas the ordinary is about only 72kN. Hung and Su (2016) conducted extensive studies have shown that young Engineering Cementitious Composites (ECCs) have the potential to achieve effective self-healing. The present study focused on the medium-term self-healing performance of cracks in ECCs that are relevant in the medium and long-term stages of the material service life. For this purpose, the prepared ECC specimens were pre-cracked at an age of 180 days. The main experimental variables were the weight fraction of fly ash in ECCs (a fly ash to cement ratio of 1.2, 1.6, or 2.0) and the healing duration (7, 28, or 90 days). The medium-term self-healing performance is evaluated using a resonant frequency test followed by a uniaxial tensile test. In addition, 22 scanning electron microscopy and energy dispersive X-ray analyses were employed to study the micro-structure of the healed crack and identify the medium-term healing product, respectively. The results reveal that as long as water is present in the environment, ECCs has moderate medium-term self-healing ability, and can partially recover their tensile mechanical properties. As a conclusion, effective medium-term self-healing performance can be achieved within 90 days of conditioning for ECCs with a pre-strain of less than 1%.

Termkhajornkit et al. (2015) commented that autogenous and drying shrinkage causes cracks in concrete. Nevertheless, most of these types of cracks occur before 28 days. The slow hydration of fly ash after 28 days results in the crack sealing by these hydrated products and prolong the service life. This research investigates the self-healing ability of fly ash-cement paste. The study focused on the compressive strength, porosity, chloride diffusion coefficients, hydration reactions and hydrated products. The research focuses on behaviour after 28 days. From the experimental study, the fly ash-cement system has the self-healing ability for cracks that occur from shrinkage. The self-healing ability increased with fly ash content.

IV. EXPERIMENTAL STUDY

Fly ash

Fly ash, coal combustion residue, is a pozzolanic material that reacts with $\text{Ca}(\text{OH})_2$ from cement hydration and produces C-S-H gel. But this reaction requires less free water than the hydration reaction of cement. IS 3812:2003 gives specification for fly ash for use as pozzolana. Table 3.1 shows the chemical composition of fly ash. Fly ash is effective for improving various properties of concrete such as long term compressive strength, permeability and resistance to chloride diffusion. The C-S-H gel produced by the pozzolanic reaction of fly ash may seal micro cracks, and accordingly it is expected that the concrete made with cement and fly ash may show self-healing ability. In this study, fly ash was collected from Hindustan Newsprint Limited, Velloor, Kottayam.



Chemical composition of fly ash

Compound	Content (% wt)
SiO_2	54.60
Al_2O_3	27.53
Fe_2O_3	5.43

Phosphogypsum

Phosphogypsum was collected from FACT, Ambalamukal. Phosphogypsum is generated from filtration process in phosphoric acid plants where insoluble gypsum (and other material) are separated from the product. Phosphogypsum is a grey coloured, damp, fine grained powder, silt or silty-sand material with a maximum size ranges between 0.5mm and 1mm and the majority of the particles are finer than 0.075mm. The specific gravity of Phosphogypsum ranges from 2.3 to 2.6. The maximum dry bulk density is likely to range from 1470 to 1670 kg/m^3 .

Phosphogypsum consists primarily of calcium sulphate dehydrate with small amounts of silica, usually as quartz and unreacted phosphate rock, radioactive material (like Radium, Uranium), heavy metals namely arsenic, cadmium, chromium, mercury and fluoride. The concentration of the metals depends on the composition of the phosphate rock.

The following are the main concerns with respect to management of Phosphogypsum:

- High fluoride concentration (in the range of 0.5 -1.5 %) may leach fluoride and contaminate the groundwater, if not stored and handled properly.
- Presence of radio-nuclide Radium - 226 which upon decay may emit harmful alpha particles.
- May contain heavy metals (Cd, Cr, Pb etc) that may enter into the food chain through potable water and agriculture products.

Chemical Constituents Percentage

Compound	Content (% wt)
CaO	31.2
SiO_2	3.92
SO_3	42.3
R_2O_3	3.6
MgO	0.49
Phosphate , Fluoride	18.49

Tests on materials

Tests on Aggregate

The tests done on M-sand are sieve analysis and specific gravity test.

Sieve analysis

Sieve analysis is used to assess the particle size distribution (also called gradation) of a granular material. The gradation test is performed with a set of sieves on a sample of fine aggregate in the laboratory according to IS: 2386 part 1 and the gradation curve obtained is illustrated in next chapter.

Specific gravity test

Specific gravity is the ratio of the weight in air of a given volume of dry sample to the weight of an equal volume of distilled water at 4 °C. Using pycnometer the specific gravity of fine aggregate was determined according to IS 2386:1963 part 3 (reaffirmed 2011).

Tests on Coarse Aggregate

The sieve analysis, specific gravity and water absorption tests are done on coarse aggregate.

Sieve Analysis

According to IS 2386:1963 part 1(reaffirmed 2011) sieve analysis was performed and the gradation curve is given in next chapter.

Water Absorption and Specific gravity Test

The specific gravity and water absorption of crushed angular aggregate was determined as per IS2386:1963 part 3 (reaffirmed 2011).

Tests on fresh concrete

Workability of concrete is defined as the ease with which the concrete can be mixed, transported, placed and compacted. To determine the workability of concrete, a slump test was carried out. It was conducted as per IS 1199:1959 (reaffirmed 1999). The apparatus used for doing slump test are slump cone and tamping rod. Figure 3.2 shows the slump test to determine the workability of fresh concrete.



Slump test

Tests on hardened concrete

The mechanical strength tests (compression and tension) were conducted on hardened concrete. Also durability tests (sulphate and chloride resistance, corrosion test) were done.

Compressive Strength Test

The compressive strength is defined as the resistance to failure under the action of compressive forces. It is an important parameter to determine the performance of concrete during service conditions. The cubes were cast on the basis of different mix combinations. The compressive strength test was conducted after water curing of 7 days and 28days. Load should be applied gradually till the specimen fails. Load at the failure divided by area of the specimen gives the compressive strength. The compressive strength test was conducted as per IS 516-1959 (reaffirmed 1999). Compressive strength testing of concrete cube using 2000KN capacity compression testing machine is depicted in figure 3.3.



Compressive strength test on cubes

Split Tensile Strength Test

The concrete is brittle and hence it is very weak in tension and is not expected to resist direct tension. The split tensile strength test is indirect tension strength in which test is carried out by placing a cylindrical specimen horizontally between the loading surface of the compression testing machine and the load is applied until the cylinder failure along the vertical diameter. The cylindrical specimen having dimensions 300mm diameter and 150mm length is used. The split tensile strength test was conducted as per IS 5816-1999 (reaffirmed 2004). Split tensile strength test was conducted for specimens with varying proportion of fly ash as binder in concrete. Figure 3.4 illustrates the cracked cylindrical specimen subjected to split tensile strength test.



Fig. 3.4 Split Tensile strength test on cylinders

Flexural Strength Test

Concrete is relatively strong in compression and weak in tension. The flexural strength was determined by means of a beam test. Beam specimens having size 100 x 100 x 500 mm were used. A concrete beam on bending will break on tension face. Expensive Universal Testing Machine was used for flexural strength test. The flexural strength test was conducted as per IS 516:1959 (reaffirmed in 2013). The loading was done without shock and increased continuously at a rate of loading of 180 kg/min as two point load.



Fig. 3.5 Flexural Strength Test on Concrete Beam

Sulphate Resistance Test

The effect of sulphate attack on concrete is assessed by immersing 28 days water cured cubes in 5% Sodium sulphate solution. The cubes were weighed prior to immersion in sodium sulphate solution for assessment of weight loss. The cubes were tested for compression after 28, 56 and 90 days of exposure to sodium sulphate solution. The effect of sulphate attack on strength loss was assessed by testing the compressive strength of concrete cubes at respective test ages and comparing them with water cured concrete specimen of same age. The percentage of strength loss was then calculated. Similarly percentage of weight loss was also assessed comparing the weight of specimen prior to exposure and after exposure at different test ages.

Chloride Resistance Test

The effect of chloride attack on concrete is assessed by immersing 28 days water cured cubes in 1% hydrochloric acid solution and tests were conducted in the same manner as described in case of sulphate resistance test.

Rapid Chloride Permeability Test

Corrosion is mainly caused by the ingress of chloride ions into concrete which reduces the original resistance of concrete. Rapid chloride permeability test (RCPT) is a quick test able to measure the rate of transport of chloride ions in concrete. This test was conducted as per ASTM 1202-2005 method. Details of experimental set up are shown in Figure 3.6 and figure 3.7. Concrete cylinder specimen of size 95 mm diameter and 50mm thickness were cast using elastomeric rubber moulds and allowed to cure for 28 days. The saturated specimens are mounted in the plexiglass chambers and the sealant applied. One side of the chamber is filled with 3% sodium chloride solution (that side of the cell will be connected to the cathode terminal of the power supply) and other side sodium hydroxide solution of 0.3 N was poured and connected to anode terminal. The terminals are then connected to the 60V DC power supply and the current read in mA on the digital readouts every ½ hour for 6hours. The interpretation of the result is that the larger the current magnitude transferred during the test, the greater the permeability of the sample. The concrete which is more permeable will show higher charge transfer vice versa. The method has shown good correlation with chloride tests. The following formula can be used to calculate the average current flowing through one cell.

$$Q = 900(I_0 + 2I_{30} + 2I_{60} + 2I_{90} + 2I_{120} + \dots + 2I_{300} + 2I_{330} + I_{360}) \quad (3.6)$$

Where Q is the current flowing through one cell (coulombs), I_0 is the current reading in amperes immediately after voltage is applied, and I_t is the current reading in amperes at t minutes after voltage is applied. The value is adjusted for specimen diameters other than 95mm. ASTM 1202-2005 contains a table which shows the rating of chloride permeability based on coulomb values.



Fig. 3.6 Moisture trap



Fig. 3.7 Rapid chloride permeability apparatus

The moisture trap is a water trap used to ensure that the air being sucked by the vacuum pump from the desiccator is completely dry and doesn't count in the pump oil. This will ensure a trouble free operation of the vacuum pump for longer years of use.

TEST RESULTS

WORKABILITY TEST RESULTS

Slump value of fly ash mixes

Sl. No	Specimen	Notation	Slump Values(mm)
1	Conventional mix	CM	75
2	Fly ash-5%	F5PG0	79
3	Fly ash-10%	F10PG0	80
4	Fly ash-15%	F15PG0	80

Compressive strength

Compressive strength test was conducted according to IS 516:1959 (Reaffirmed in 2013). The improvement of compressive strength from a period of 7 and 28 days for mixes with varying percentages of fly ash is presented in table

Compressive strength results fly ash mixes

Specimen	Compressive strength(N/mm ²)	
	7 th day	28 th day
CM	14.26	21.8
F5PG0	14.25	22.22
F10PG0	17.86	22.5
F15PG0	17.83	21.89

From the results it is observed that on addition of fly ash, 28 day strength decreases with addition of fly ash after 10%. The decrease in strength may be due to the slow hydration process since fly ash is a slow reactive pozzolans which delays the hydration process. Therefore the fly ash percentage is optimized to 10%, for making concrete.

Split tensile strength results of various mixes

Specimen	Split tensile strength(N/mm ²)	
	7 th day	28 th day
CM	2.41	2.44
F5PG0	3.65	3.97
F10PG0	3.6	3.89
F15PG0	3.62	3.87

Flexural strength results of various mixes

Specimen	Flexural strength(N/mm ²) at 28 th day
CM	10.12
F5PG0	9.76
F10PG0	9.52
F15PG0	9.35

Slump value of phosphogypsum modified fly ash mixes

Sl. No	Specimen	Notation	Slump Values(mm)
1	Conventional mix	CM	80
2	Fly Ash-10%, phosphogypsum 5%	F10PG5	80
3	Fly Ash-10%, phosphogypsum 10%	F10PG15	82
4	Fly Ash-10%, phosphogypsum 15%	F10PG25	83

Compressive strength results phosphogypsum modified fly ash mixes

Specimen	Compressive strength(N/mm ²)	
	7 th day	28 th day
F10PG5	16.26	23.8
F10PG10	16.25	24.22
F10PG15	19.86	23.5

Split tensile strength results of phosphogypsum modified fly ash mixes

Specimen	Split tensile strength(N/mm ²)	
	7 th day	28 th day
F10PG5	4.41	4.44
F10PG10	5.65	5.97
F10PG15	5.6	5.89

Flexural strength results of various mixes

Specimen	Flexural strength(N/mm ²) at 28 th day
F10PG5	12.12
F10PG10	11.76
F10PG15	11.52

Percentage decrease of Compressive Strength (Sulphate Resistance)

Type of concrete	28 day strength (N/mm ²)			56 day strength (N/mm ²)			90 day strength (N/mm ²)		
	water cured	Na ₂ SO ₄ cured	% decrease	water cured	Na ₂ SO ₄ cured	% decrease	water cured	Na ₂ SO ₄ cured	% decrease
F10PG5	46.6	44.61	8.66	51.33	47.64	11.8	52.33	47.14	14.74
F10PG10	42.32	40.98	7.5	52.6	50.22	8.9	53.2	49.81	10.9
F10PG15	57.95	56.28	7.09	59.79	57.22	8.6	61.95	58.3	10.3

Percentage decrease of Weight (Sulphate Resistance)

Type of concrete	28 day strength (N/mm ²)			56 day strength (N/mm ²)			90 day strength (N/mm ²)		
	water cured	Na ₂ SO ₄ cured	% decrease	water cured	Na ₂ SO ₄ cured	% decrease	water cured	Na ₂ SO ₄ cured	% decrease
F10PG5	12.404	12.385	4.23	12.384	12.35	4.6	12.405	12.338	4.8
F10PG10	12.41	12.396	4.17	12.386	12.368	4.25	12.402	12.37	4.38
F10PG15	12.89	12.876	4.16	12.91	12.89	4.23	12.895	12.866	4.33

Variation in weight of cubes due to chloride attack

Specimen	Percentage Weight Difference in %	
	28 Days	56 Days
F10PG5	5.86	5.8
F10PG10	4.91	4
F10PG15	5.83	4.91

Variation in compressive strength of cubes due to chloride attack

Specimen	Percentage Difference in Compressive Strength of Cube in N/mm ²	
	28 Days	56 Days
F10PG5	12.39	11.69
F10PG10	9.56	8.31
F10PG15	8.35	8.13

RCPT ratings of concrete (Source: ASTM C 1202:2005)

Charge passed (C)	Chloride ion penetrability
>4000	High
2000-4000	Moderate
1000-2000	Low
100-1000	Very low
<100	Negligible

Chloride permeability of various concrete mixes

Type of concrete	Charge passed (C)	Chloride ion penetrability
F10PG5	2587.8	Moderate
F10PG10	2397.3	Moderate
F10PG15	1516.6	Low

Conclusion

Strength properties like compressive strength, split tensile strength and flexural strength properties were evaluated. The fly ash inclusion increases the workability of the concrete due to the lubricating effect of fly ash. From the results it is observed that on addition of fly ash, 28 day strength decreases with addition of fly ash after 10%. The decrease in strength may be due to the slow hydration process since fly ash is a slow reactive pozzolans which delays the hydration process. So the optimum percentage of fly ash was fixed as 10% for the present study.

The phosphogypsum increases the workability of the concrete due to the combined lubricating effect of fly ash and phosphogypsum. The strength properties are similar to the addition of fly ash in concrete. 10% replacement of phosphogypsum is fixed as the optimum percentage. The durability of phosphogypsum modified fly ash concrete is mainly due to filling of the pores and voids with calcium carbonate precipitation. Thus the dense and compact structure will reduce the permeability and thus increase durability of concrete structures. The fly ash and calcium hydroxide combine in cementitious compounds trapping the calcium hydroxide so that it is no longer available for reaction with sulphates. This prevents the formation of gypsum.

From durability studies of rapid chloride permeability, with the inclusion of fly ash, chloride ingress capacity of concrete is decreased. Pore refinement and grain refinement due to reaction between fly ash and liberated lime improves impermeability. The reduction in permeability of concrete is mainly due to filling of the pores and voids with calcium carbonate precipitation.

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