Proceedings of the 4th International Conference on Civil Engineering for Sustainable Development
(ICCESD 2018), 9~11 February 2018, KUET, Khulna, Bangladesh *(ISBN-978-984-34-3502-6)*

SULFATE AND CHLORIDE RESISTANCE PROPERTIES OF PORTLAND CEMENT BLENDS

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ABSTRACT

Bangladesh is an alluvial deposited country. More than 53% area is affected by sulfate, salinity and chloride in water and soil. Sulfate can attack cement paste by affecting calcium aluminates in cements and chloride can attack reinforcement by penetrating into the concrete that causes a hazardous damage of existing building. Sulfate and chloride can severely damage the existing building in coastal regions. In this paper durability of cement is evaluated on the basis of strength of mortar cube and concrete cylinder test and the sulfate attack properties of cement is evaluated on the basis of length change of mortar bar specimens during exposure to sulfate solution and the Chloride attack properties is studied by Rapid chloride ion penetration test using Ordinary Portland Cement (OPC), Portland Composite Cement (PCC), 20% FA, 30% FA and 40% FA. The compressive strength of cube specimens in sulfate solution is tested with reference to the water sample. The compressive strength of cube sample exposed to sulfate solution was about 40.6 MPa and 37.2 MPa after 13 weeks and the corresponding linear expansion was obtained about 0.28% and 0.133% for OPC and PCC cement. The compressive strength of the cylindrical specimens was about 16.96 MPa for OPC and 18.34 MPa for PCC at the age of 28 days. The permeability of chloride ion of OPC sample was 22.8% higher than the PCC at the age of 28 days.

Keywords: *Blended cement; Sulfate attack; Length change; RCPT*

1. INTRODUCTION

Deterioration of concrete by sulfates of an external source is a commonly observed durability problem in concrete structures exposed to seawater, soils or groundwater containing high concentrations of sulfate ions. This durability problem, also known as sulfate attack, occurs after a series of chemical reactions between sulfate ions, cement paste and moisture, (Bosunia & Choudhury, 2001). Sulfate attack is a quite complex process and despite the vast number of research since its identification by USBR in 1908, research on this durability problem is still in progress. Coastal areas in Bangladesh are formed by a delta plain at the confluence of the Ganges (Padma), Brahmaputra (Jamuna), and Meghna Rivers and their tributaries. About 53% of the coastal area is affected by salinity and sulfate in soil and water. Sulfates (for example calcium sulfate, sodium sulfate, and magnesium sulfate) can attack concrete by reacting with hydrated compounds in the hardened cement paste.

Supplementary cementing materials (SCMs) contribute to the properties of hardened concrete through hydraulic or pozzolanic activity to avoid sulfate attack. Typical examples are fly ashes, slag cement (ground, granulated blast-furnace slag), and silica fume. Supplementary cementing materials are often added to concrete to make concrete mixtures more economical, reduce permeability, increase strength, or influence other concrete properties.

Due to high alkalinity of concrete a protective oxide film is present on the surface of steel reinforcement. This protective layer also can be lost due to the presence of chloride in the presence of water and oxygen. In reality the action of chloride inducing corrosion of reinforcement is more serious than any other reasons. Sulfate attacks the concrete whereas the chloride attacks steel reinforcements. Presence of high amount of sulfate and chloride in soil or water may reduce the design life of structures. Sulfate attack, salt crystallization and Chloride attack are more severe at coastal areas in Bangladesh.

In this study, cement is mixed with different ratio of fly ash (20%, 30% and 40%) and these are tested. After this, a suitable mix ratio is determined to reduce the sulfate attack risk of marine structures and the objects of this experiment are to evaluate the performance of commercially available Portland Composite Cement against chloride attack.

2. METHODOLOGY

Concrete strength is a great variable factor in case of stability. Concrete strength is also dependent on various factors as well as on mortar strength. In this thesis, we all have worked with mortar. For comparison of Portland Composite Cement (PCC), Ordinary Portland Cement (OPC) and cement with different composition of fly ash (20%, 30% and 40%) samples were prepared.

2.1 Materials

Different commercial brand of Ordinary Portland Cement, Portland Composite Cement, cement with 20% fly ash, 30% fly ash and 40% fly ash and local (shyllet) sand from Bangladesh were used in this study. The chemical composition of the material used in this study are summarized below in Table 1.

Table 1: Chemical composition of cementitious materials

Com-pounds	PCC Concentration Unit, %	OPC Concentration Unit, %
SiO_2	26.735	21.27
Al_2O_3	13.635	5.34
Fe_2O_3	3.500	2.28
CaO	53.489	63.92
MgO	2.552	3.91
SO_3	1.744	2.32
Na_2O	0.123	0.47
K_2O	0.907	-
TiO_2	0.915	-
P_2O_5	0.058	-
MnO	0.221	-

2.2. Mix Design Ratio

The mixture of mortar for casting the cube and bar specimens were completed with a water-cement ratio of 0.485 for blends of Portland cement with pozzolan or slag. 1 part of cement was added to 2.75 parts of sand by mass.

The concrete mix for every cylindrical specimen was based on the weight of materials. The ratio of the concrete mixture was 1 (cement): 2.2 (fine aggregate): 3.5 (coarse aggregate), with a water to cement ratio of 0.6. For casting 20% FA, 30% FA, 40% FA sample the OPC cement were replaced by fly ash. The mix proportion in Kg shows below in Table 2.

Table 2: Mixing composition of samples

Batch No.	Sample type	Cement	Fine aggregate	Coarse aggregate	Fly Ash (FA)
		kg	kg	kg	kg
1	OPC	5.70	12.6	20	-
2	PCC	5.70	12.6	20	-
3	20% FA	4.56	12.6	20	1.14
4	30% FA	4.00	12.6	20	1.71
5	40% FA	3.42	12.6	20	2.28

2.3. Preparation and Test of Cement Mortar Specimens

2.3.1. Strength

Two groups of cube specimens are prepared for testing compressive strength according to ASTM C 109 standards. Each group consists of 21 nos. of cube (2"x2"x2") total 126 nos. of sample. After achieving 20 MPa strength of the samples, one group was immersed in sulfate (5% Na_2SO_4) solution by covering the curing tank with a plate or tape. Each liter of solution contains 50 g Na_2SO_4 dissolved in 900 mL water and diluted with additional distill water to obtain 1 L of solution. The mixing temperature of the solution is 23°C±2°C. The solution must contain pH range of 6.0 to 8.0. The immersed solution need to be cover up so that no air can enter into the container. For immersing the specimens in sulfate solution that is prepared the day before immersion. Compressive strength test was performed at the age of 1, 2, 3, 4, 8 and 13 weeks starting from the day of sulfate immersion.

2.3.2. Length Change

Length change was measured for the bar specimens (250±2.5 mm) with two different set of sample one in water and another one in sulfate solution at 1,2,3,4,8,13 day time interval according to ASTM C 1012 (ASTM, 2004) and ASTM C 157 (ASTM, 2006). Each set of mortar bar consists of 6 nos. of bar. The measurement was performed by a length comparator. The distances between the bolts with the formwork were 250±2.5 mm, the length inside the specimen is 7.5±0.5 mm and outside the specimen is 5 mm. Sample was placed vertically between the two stud at top and bottom. The data of each sample length was then recorded for the two group of specimen. Before the recording of length of a specified sample the base of the comparator in which gage stud on the lower end of the bar fits was cleaned. The length of the mortar specimens was measured in ±0.001 error range with the length comparator device. At the measurements, great cares were taken to calibrate dial indicator and to clean the grooves in which the specimens were put.

2.4. Preparation and Test of Concrete Cylindrical specimens

2.4.1. Strength

Five group of concrete such as OPC, PCC, 20%, 30%, 40% cylinders of diameter 100 mm (4 in) x height 200 mm (8 in) were casted by five batch. From design data 20%, 30%, 40% of Ordinary Portland cement were replaced by Fly Ash separately during casting of 18 cylindrical specimen for compressive strength test. According to mix design without any replacement of cement by Fly Ash, 12 OPC and PCC cylindrical specimen were casted for compressive strength test. These samples were curing both normal water and Na_2SO_4 water. So, total 60 Nos. of 100 mm (4 in) diameter & 200 mm (8 in) height cylindrical samples were needed for compressive test.

2.4.2. RCPT Sample

Chloride ion penetration test was carried out according to ASTM C 1202 (ASTM, 2006). In this study the penetration was measured in terms of the total passing charge through a slice of cylinder in 6 hrs. For this test a set of cylindrical specimens (Ø4 in. x 6 in.) was prepared with a ratio of 1:2.4:3.35 by weight for each brand of cement. Six different types of samples were prepared for RCPT.OPC, PCC, 20%,30%,40% OPC replaced by Fly Ash samples were prepared. After demolding the sample was cut into Ø 4 in. x 2 in. in size after curing with Na_2SO_4 water for the experimental setup. The setup was completed by arranging #100 sieve, voltage supply, multi-meter, cable, M-seal. Then the amount of charge passing and voltage were recorded by multimeter and the temperature was recorded with a thermo-meter.

3. RESULTS

3.1. Development of compressive strength of concrete

The following Table 3 shows the development of compressive strength of the cement mortar cube against the exposure time in sulfate solution up to the age of 91 days.

The initial strength of OPC, PCC, 20% FA, 30% FA, 40% FA in water was 22.45, 19.47, 21.57, 21.20, 8.43 MPa, respectively and sulfate strength of those was 21.25, 17.93, 19.73, 21.90, 7.93 MPa, respectively. At early age up to 28 days, strength in water solution was higher than the strength in sulfate solution. At the age of 4 weeks (28 days) the maximum strength in sulfate solution was 30% FA about 34.2 MPa and 40% FA showed the lowest strength was about 13.70 MPa. The strength of sulfate solution started to cross the strength of water solution after 28 days. According to ASTM standards 28 days minimum strength need to be 25 MPa. From the table below the compressive strength of both water and sulfate solution were greater than the standards strengths.

Table 3: Development of Compressive strength of mortar cube

Mixture designation		**Compressive strength (MPa) in Sulfate**				
	7 days	14 days	21 days	28 days	56 days	91 days
OPC	22.45	27.80	31.90	34.20	35.00	35.55
PCC	19.47	25.80	27.07	28.27	30.87	32.43
20% FA	21.57	25.07	25.53	25.83	29.47	34.17
30% FA	21.20	23.10	25.67	25.90	28.53	37.80
40% FA	8.43	9.47	11.53	11.83	12.47	15.63

After 4 weeks the sample strength in sulfate solution became higher than water solution. At the later age (13 weeks) the value of compressive strength of PCC and 30% FA in sulfate solution was almost 40.65 and 39.03 MPa. So, the relationship represents that the strength is higher in contact of sulfate for OPC.

3.2. Development of Compressive strength of Concrete

The following plot represents the relationship between the compressive strength of concrete cylinder and the immersion time in sulfate solution. The time scale was plot in days. The results showed that the compressive strength of the concrete increased when Fly Ash used in concrete by replacement of OPC. But at a time the compressive strength became decreased by using high percentage of Fly Ash.

Also for the curing type the compressive strength changed. When the cylinder was curing in normal water the compressive strength was high but the compressive strength was decreased by 5%-15% for curing by $\mathrm{Na_2SO_4}$ water. For OPC cylinder specimen it has observed that the compressive strength decreased when using $\mathrm{Na_2SO_4}$ water for curing. For PPC cylinder specimen it has observed that the compressive strength decreased when using $\mathrm{Na_2SO_4}$ water for curing. For 20% FA (Fly ash) cylinder specimen it has observed that the compressive strength decreased when using $\mathrm{Na_2SO_4}$ water for curing. For 30% FA (Fly ash) cylinder specimen it has observed that the compressive strength decreased when using $\mathrm{Na_2SO_4}$ water for curing. For 40% FA (Fly ash) cylinder specimen it has observed that the compressive strength decreased when using $\mathrm{Na_2SO_4}$ water for curing.

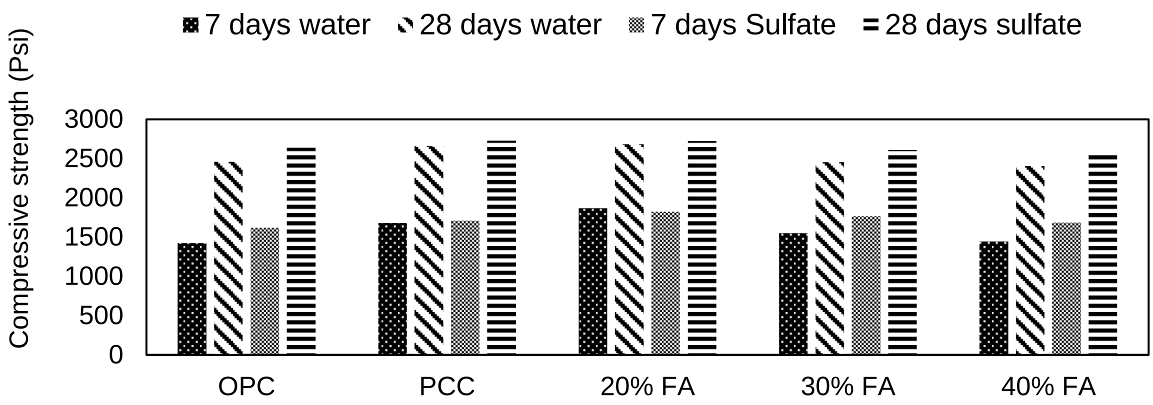

Figure 1: Comparison of compressive strength of concrete cylinder

Due to the externally and internally sulfate attack the loss of bond between the cement paste and aggregate were occurred. So every time the compressive strength of Na_2SO_4 water curing sample was 5%-15% less than normal water curing sample for sulfate attack. And for using higher percentage of fly ash the compressive strength gradually decreased because of the property of using extensive amount of fly ash the cement paste and aggregate bond become loss.

3.3. Resistance of Sulfate attack

From the graph of Expansion vs Time, it is seen that the highest length change of the mortar bars specimens of OPC is 0.078% and the lowest length change was PCC an 40% FA was about 0.013 % at 28 days.

The expansion rate at later age will become stable. The expansion after 8 weeks in sulfate solution of OPC, PCC and 30% FA sample was 0.280%, 0.032% and 0.166% in sulfate solution. The lowest length change of the mortar bars specimens is 0.001% at 28 days.In water, length change of mortar bar is lower than the length change of mortar bar in sulfate solution.

After 8 weeks the expansion of mortar bar became stable for PCC, 20% FA and 30% FA. Because in sulfate solution, ettringite is produced and as a result, cube specimens are expanded and its length change is increased with respect to time. After 8 weeks the expansion of mortar bar became stable for PCC, 20% FA and 30% FA. Because in sulfate solution, ettringite is produced and as a result, cube specimens are expanded and its length change is increased with respect to time.

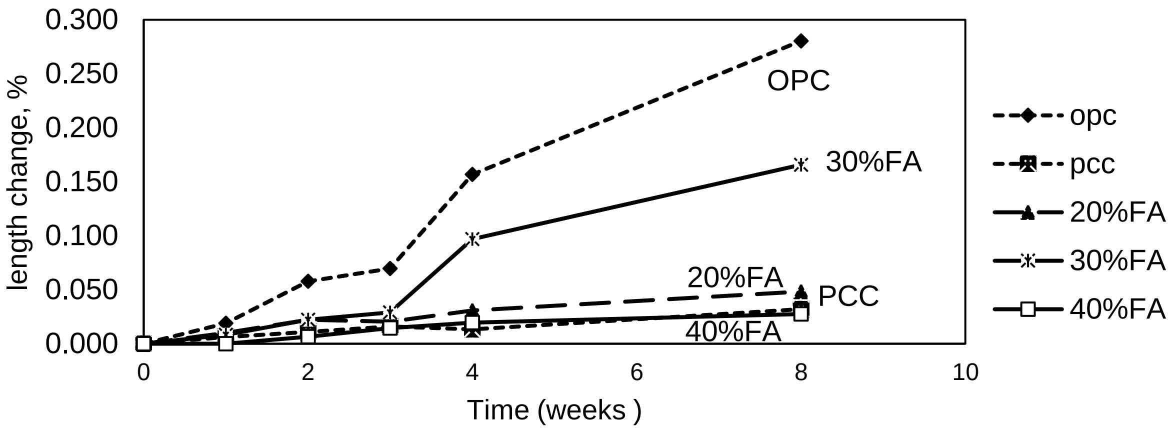

Figure 2: Comparison of length change with sulfate immersed time

The expansion rate in both water and sulfate was rapid at early age because the water absorption rate at early age increases while dry concrete was immersed for curing. When the sample immersed in sulfate solution, the sulfate is replaced by water molecule. The size of sulfate particle is larger than the water molecule, the expansion rate was initially high. After time passes the pore structure of the samples developed, the amount of water and sulfate in the pore space decreases with time.

3.4. Resistance to chloride ion penetration

The chloride ion penetration test was measured by the total charge (expressed in coulomb) passed through a slice of concrete cylinder in 6 h at age of 7, 14, 21 & 28 days. The relationship between the amount of passing charge through the concrete cylinder and time is represented in the following Figure-3. The passing charge through OPC, PCC, 20% FA, 30% FA & 40% FA was measured. The passing charge was generally very high for low percentage Fly ash sample at the age of 7 days. High charge passed 5070 coulomb in OPC sample at 7 days.

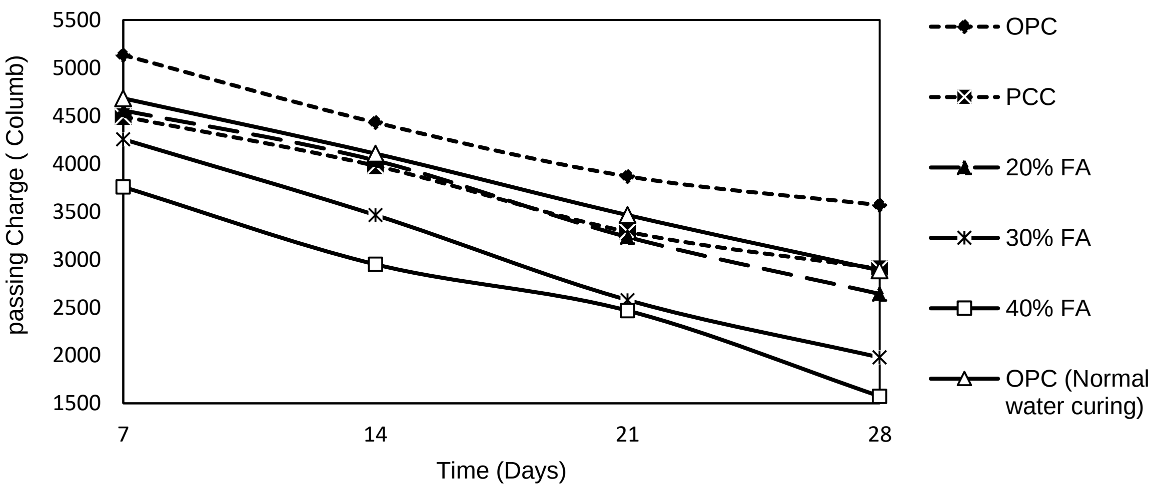

Figure 3: Comparison of chloride ion penetration with sulfate immersed

After 14 days the highest passing charge for OPC was still in high range. At the age of 21 & 28 days passed charge through OPC sample was still higher than other samples. The OPC sample in normal water curing the amount of charged was lower than OPC sample curing by

Na_2SO_4 water. The amount of charge in coulomb at 7, 14, 21 & 28 days of OPC sample (curing in Na_2SO_4 water) is 5133 C, 4430 C, 3868 C & 3567 C respectively. And the amount of charge in coulomb at 7, 14, 21 & 28 days of OPC(N) sample (curing in normal water) was 4682 C, 4105 C, 3512 C, & 2887 C respectively. So the Na_2SO_4 solution reduce the resistance of chloride ion penetration in concrete. Because the fly ash with blended cement reduces the pore of the concrete that resists more chloride ion passing through the concrete.

4. CONCLUSION

This study was carried out in three parts. First, measurement of the compressive strength of 2x2x2 in samples. Second, measurement of the length change of 250 $\pm$2.5 mm cement mortar. Third, analysis the compressive strength by Φ4 in x 8 in cylindrical specimens. And finally chloride ion penetration test of the cylindrical specimens. All the sample casing was carried by same amount of mix proportion with different type of cement. The fly ash was replaced by the same amount of cement by weight. From this study, we all have concluded that the 30% FA sample showed the greater strength after 13 weeks and the length change of 30% FA was the largest compared to other composition of FA. Looking at the strength at 28 days the sample shows a higher expansion rate is reasonable. After long time the strength is developing and length change is dropping. Studying the concrete cylindrical specimen the PCC, OPC and 30% FA gives almost same amount of strength with a great variety of length change. The Chloride ion permeability of 30% FA is low in the scale ASTM standard category.

So Instead of OPC and PCC we can use 30% FA cement by replacing 30% cement by Fly ash for reducing environmental effect by using wastage.

ACKNOWLEDGEMENTS

We would like to express my deepest appreciation to Almighty Allah that this project has been finalizing within the limited time frame. We would also like to thanks all those who provided us the possibility to complete this report for their co-operation to complete this study.

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