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EFFECT OF FLY ASH ON HYDRATION CHARACTERISTICS OF CONCRETE IN SEA ENVIRONMENT

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Abstract- The gradual penetration of sea salts from sea environment and the subsequent formation of expansive/leachable compounds lead to cracking, spalling and even structural distresses of exposed concrete. The study covers the durability characteristics of fly ash concrete in sea environment over a period of 180 days. The variables studied were four different replacement levels of cement with fly ash, various salt concentration of the curing solution (1T, 3T, 5T and 10T) and different exposure periods (30, 90 180 days) to simulate the tidal marine condition and to have accelerated effect. After specific exposure periods, the performance of fly ash concrete was assessed by measuring its compressive strength, carbonation depth, chloride content at various depth levels. Fly ash concrete of mix 80:20 is found to exhibit upto 15% lower chloride content than Ordinary Portland Cement concrete at 15 to 25 mm depth level although the strength reduction is reported to only 1.5%.

Keywords: Chloride attack, Compressive strength, Durability, Fly ash, Sea Environment.

1. INTRODUCTION

The term marine environment is generally well understood but the complexities inherent in it are not usually clear. Marine environment is not just over the sea, but it could be deemed to be extending over the coast and neighbourhood of tidal creeks, backwaters and estuaries [1]. Broadly, it covers the area where concrete becomes wet with seawater and wherever the wind will carry salt-water spray, which may be as far as few kms inland [2]. In the marine environment, concrete structures deteriorate mainly due to the corrosion of steel bars in concrete caused by the chloride and sulfate ingress form seawater. Transport properties affect the durability of concrete because they control the supply of aggressive species such as chloride and sulfates mainly responsible for deterioration. The ionic radii of chloride and sulfate ions are 1.81 Å and 2.30 Å respectively whereas the diffusion coefficient for sulfate is $2*10^{-8}$ cm^2 S^{-1} and for chloride is $3*10^{-7}$ cm^2 S^{-1} [3]. Due to larger diffusion coefficient, chloride ions penetrate at a faster rate than that of sulfate. On the other hand, as sulfate (having two negative ions) holds more negative ion than that of chloride (one negative ion), its action on deterioration process is more dangerous.

Chloride ions may cause adverse effect including the formation of cracks on hardened concrete in variety of ways. It is generally attributed to the formation of expansive product namely Friedls salt ($3CaO.Al_2O_3.CaCl_2.10H_2O$) (Calcium chloroaluminate) which has a property of low to medium expansion. Also the formation of excess calcium chloride, which may leach out, results in increased permeability of concrete [4]. Sulfate constitutes the second largest component of the anionic components available in SW. Sulfate attack is generally attributed to formation of expansive ettringite ($3CaO.Al_2O_3.3CaSO_4.\ 31H_2O$) (Calcium aluminate sulfate) and gypsum. Both ettringite and gypsum occupy a greater volume as large as 20% after crystallization in the pores of concrete than the compounds they replace. Thus the crystalline product inducing stresses inside the concrete may result in the surface cracking known as softening type of attack. The formation of gypsum hydrate causes an increase in volume of 17.7% in concrete [5].

Concrete mixes prepared by supplementary mineral admixtures such as Slag, Fly ash, Silica fume as partial replacement of ordinarily Portland cement gives a new idea to reduce the permeability of concrete [6]. In marine environment, fly ash has been widely used as successful replacement material for ordinary Portland cement in making durable concrete for improving some properties of concrete and also for achieving environmental and economical benefits since the beginning of 20th centuries. Fly ash is finely divided residue resulting from the combustion of powdered coal and transported by the flue gases and collected by electrostatic precipitation. Its major chemical compounds are similar to OPC but in different proportion and has some cementitious property. Fly ash particles are spherical, have a very high fineness and also have a diameter between less than 1µm and 100µm. The specific surface area of fly ash is usually between 250 and $600m^2/kg$ [7]. These mineral admixtures may impart proper resistance to chloride and sulfate induced deterioration by modifying the chemistry of pore characteristics of the hardened concrete [8]. Such admixtures having high fineness react with the product liberated at early ages during hydration and form secondary C-S-H gel (also referred as tobermorite gel). This gel is less densed and has more volume than primary C-S-H gel. Therefore, it fills all the pores inside concrete and makes the concrete more impermeable thereby reducing the risk of chloride and sulfate induced deterioration.

The use of fly ash as concrete admixture not only extends technical advantages to the properties of concrete but also contributes to the environmental pollution control. The thermal power plant produces a large amount of fly ash as by product with the production of electricity. The disposal of these materials becomes a serious environmental problem. The use of fly ash as a partial replacement of cement in concrete making is, therefore, attracting scientists and technologists towards its effective utilization with a view to economic as well as other consideration. Cement is the backbone for global infrastructural development. It is estimated that global production of cement was about 1.3 billion tons in 1996. Production of every tone of cement emits carbon dioxide to the tune of about 0.87 ton [9]. 7% of the world's carbon dioxide emission is attributable to Portland cement industry. Because of significant contribution to the environmental pollution and to the high consumption of natural resources like limestone etc., it would not be wise to produce more and more cement without thinking the proper substitute for it. The main objectives of using fly ash concrete are to reduce heat generation and the porosity/permeability which lead to improve the durability characteristics of concrete.

Fly ash, when used in concrete, contributes to the strength of concrete due to its pozzolanic reactivity. However, since the pozzolanic reaction proceeds slowly, the initial strength of fly ash concrete tends to be lower than that of concrete without fly ash. Due to continued pozzolanic reactivity, concrete develops strength at later age, which may exceed that of the concrete without fly ash. The pozzolanic reaction also contributes to making the texture of concrete dense, resulting in decrease of water permeability. It should be noted that since pozzolanic reaction can only proceed in the presence of water, fly ash concrete should be cured for long period. Thus, fly ash concrete used in under water structures such as dams will derive full benefits of attaining improved long term strength and water tightness. Sufficiently cured concrete containing good quality fly ash shows dense structure which offers high resistance to the infiltration of deleterious substances. The pozzolanic reactivity reduces the calcium hydroxide content, which results in reduction of passivity to the steel reinforcement but at the same time, the additional secondary cementitious material formed make the paste structure dense and thereby gives more resistance to the corrosion of reinforcement. Although fly ash is an industrial waste, its use in concrete significantly improve the long term strength and durability and also reduce the heat of hydration.

This paper investigates the effect of fly ash on the hydration system of OPC with regards to its resistance to chloride and sulfate induced deterioration. The test data may provide useful information regarding the utilization of fly ash as an active admixture in the field of cement and concrete. Various fly ash cement ratios (100:0, 85:15, 70:30 and 55:45) as well as sea water of different concentration (1T, 3T, 5T and 10T) have been used to get the idea for optimum mix of fly ash cement in making durable concrete. This will also alleviate economic, social and environmental problems caused by fly ash.

2. EXPERIMENTAL PROGRAM

A comprehensive experimental program was carried out to investigate the effect of fly ash on hydration characteristics of concrete expose to sea environment. The materials and variables studied are explained below:

2.1 Materials Used

Cement: ASTM Type-I Ordinary Portland cement was used.

Fly ash: ASTM Class F fly ash was used for this study. Chemical compositions of OPC and fly ash are given in **Table-1**.

Aggregates: The coarse aggregate used was crushed stone with a maximum nominal size of 12.5 mm, having specific gravity 2.69, fineness modulus 6.5 and unit weight 1625 kg/m^3; whereas the fine aggregate was river sand, having specific gravity 2.68, fineness modulus 2.59 and unit weight 1495 kg/m^3.

Table-1 Chemical compositions of OPC and fly ash

Composition	Content (%)	
	OPC	Fly ash
CaO	64.18	8.6
SiO_2	20.80	59.3
Al_2O_3	5.88	23.4
Fe_2O_3	3.32	4.8
MgO	1.16	0.6
SO_3	2.37	0.1
Loss on ignition	1.7	--
Insoluble residue	0.6	--

2.2 Variable Details

In the present investigation, fly ash has been used as blended admixture. A particular mix ratio of 1:1.5:3 and water/cement ratio of 0.43 were used for making test specimen. Different variables used are listed bellow:

(a) Plain water and artificial seawater of four different concentration 1T, 3T, 5T and 10T was used as curing water. 1T concentration seawater is simulated in laboratory by mixing tap water with exact amount and proportion of different chemical compounds as specified in **Table-2**. Similarly 3T, 5T and 10T solution is made by

using the salts contents 3, 5 and 10 times of 1T solution.
(b) Four different grades of concrete with cement fly ash ratios 100:0, 90:10, 80:20 and 70:30 were used for this investigation.
(c) Three different exposure periods of 30, 90 and 180 days were used for this investigation. The specimens were periodically tested for chloride content at various depth levels, carbonation depth and compressive strength to assess the effect of fly ash on hydration characteristics of concrete.

Table-2 : Specified salt contents of artificial seawater used in experimental program*

Salt	Chemical formula	Amount (gm)	Remarks
Sodium chloride	$NaCl$	27.2	These amounts of salts were dissolved in plain water to prepare 1000 gm of seawater of 1T concentration
Magnesium chloride	$MgCl_2$	3.8	
Magnesium sulfate	$MgSO_4$	1.7	
Calcium sulfate	$CaSO_4$	1.2	
Potassium sulfate	K_2SO_4	0.9	
Calcium carbonate	$CaCO_3$	0.1	
Magnesium bromide	$MgBr_2$	0.1	
Total		**35.00**	

*** Handbook of Ocean and Under Water Engineering, Myers, Holm and Mc. Allister.**

2.3 Specimen Preparation and Curing

Around 200 cubical specimens of 100 mm size were prepared for the whole investigation program. All the specimens were precured for 28 days in plain water at 27°C. After that, the specimens were placed in seawater of different concentration (1T, 3T, 5T and 10T) as well as plain water for different exposure periods (30, 90, 180 days). Some of the specimen were split into two halves and subjected of a carbonation test with the help of phenolphthalein indicator solution. Concrete powder was drilled out form surface, 15 mm and 25 mm depths with the help of masonry drill. The drilled powder was then ground further to pass through #200 sieve and kept in sealed plastic bags to avoid carbonation.

3. RESULTS AND DISCUSSION

The specimens made from OPC and fly ash concrete are exposed to plain water and seawater of different concentration for various exposure periods. Plain water cured concrete specimens are considered as control specimen and used to compare the detrimental effect of marine environment on concrete specimens.

3.1 Carbonation

As per requirement of experimental program, carbonation depth identification was performed on the test specimens taken out from the environment after specific exposure periods. The specimens were split into two haves and the phenolphthalein indicator solution was sprayed on the freshly broken surface. In most of the cases, it is observed that the depth of carbonation is too little to measure. Regardless of type of concrete, most of the test specimens cured in both plain and seawater, show no sign of carbonation. Only in a few specimens exposed for longer curing period, carbonation depths of 0.5 to 1.0 mm are observed. Relatively higher depths of carbonation are observed for OPC concrete as compared to fly ash concrete. In case of fly ash concrete, all the pores are filled up by hydration product. Thus the atmospheric CO_2 get a limited chance to penetrate inside the fly ash concrete specimens. In this study, it is observed that the resistance for CO_2 penetration is higher for fly ash concrete than that of OPC concrete exposed to identical environmental condition.

3.2 Chloride Content

The amount of chloride ions (expressed as % of concrete mass) diffused into OPC and fly ash concretes exposed to seawater of different concentration are shown in **Fig.1 to Fig.4**. From the test results, it is observed that with the increase in exposure period and concentration of seawater, the amount of chloride diffusion is increased. After 90 days exposure period, for fly ash concrete of cement fly ash mix 80:20 exposed to seawater of 3T concentration the chloride content at 15 mm death level is found as 0.125% whereas the corresponding value in seawater of 5T and 10T concentration is 0.163% and 0.520% respectively. Also for the same concrete, the chloride content at the same depth level is reported as 0.140%, 0.188% and 0.621% after exposure in 3T, 5T and 10T seawater for the period of 180 days. Close observation of the data/curves shows that, at initial ages, chloride penetration is higher for fly ash concrete than that of OPC concrete. But in later ages, the rate of chloride ion penetration into fly ash concrete is reduced. At early ages i.e. after 30 days, OPC concrete exposed to seawater of 5T and 10T concentration shows the chloride content value of 0.115% and 0.312% respectively at 15mm depth level, whereas for identical condition 80:20 fly ash concrete show the same value as 0.121% and 0.382% respectively. On the other hand, for the same condition and after 180 days exposure period, chloride content is found as 0.198% and 0.642% for OPC concrete whereas the corresponding values are 0.188% and 0.621% for 80:20 fly ash concrete and these values are lower than the previous value. This may be due to reduction of the production of $Ca(OH)_2$ by pozzolanic reaction of fly ash. The rate of ingress of aggressive ions into the concrete is reduced due to reduction of concentration of hydroxide ions and hence the pore structures of concrete are refined after hydration. Similar observation regarding chloride and sulfate induced deterioration due to the effect of fly ash in concrete are reported by Ziacho [7]. Among all the concretes, fly ash concrete cast with cement fly ash ratio of 80:20 shows higher resistance against chloride penetration than OPC and other fly ash concretes for all curing condition and longer exposure periods. The higher resistance of fly ash contents in concrete indicates its suitability for use as structural concrete in marine environment.

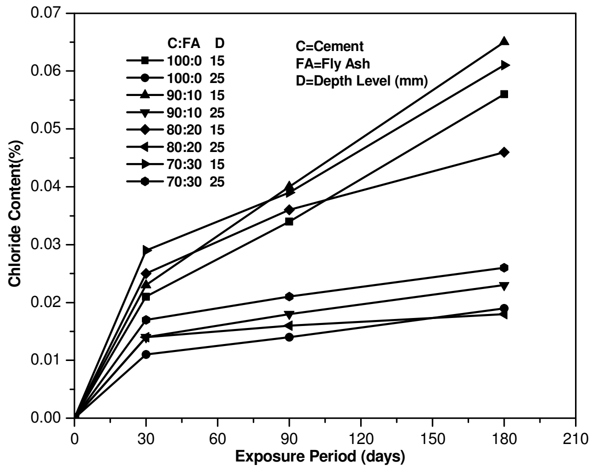

Fig.1: Chloride content-Exposure time relation for fly ash concrete exposed to seawater of 1T concentration

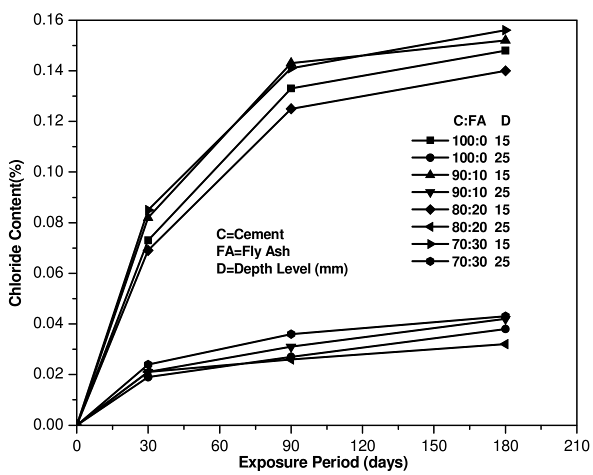

Fig.2: Chloride content-Exposure time relation for fly ash concrete exposed to seawater of 3T concentration

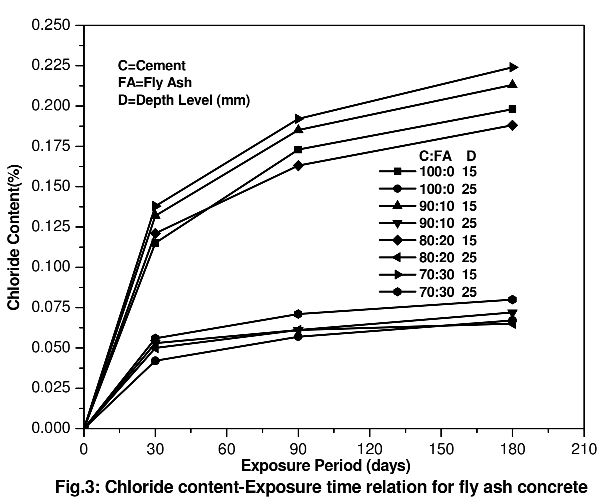

Fig.3: Chloride content-Exposure time relation for fly ash concrete exposed to seawater of 5T concentration

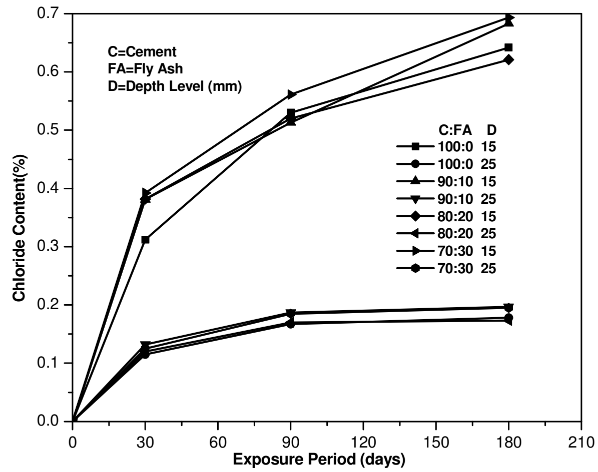

Fig.4: Chloride content-Exposure time relation for fly ash concrete exposed to seawater of 10T concentration

3.3 Compressive Strength

The compressive strengths of OPC and slag concretes exposed to plain water have been presented in **Fig.5**. Compressive strengths corresponding to "0" days curing age represent the 28 days plain water cured strength. In case of plain water curing, OPC concrete shows higher strength at initial ages than that for fly ash concrete. But for relatively longer curing periods, the differences between the results are seen to be decreased. In case of plain water curing, for OPC concrete, compressive strength for 30 days exposure period is 34.3 MPa whereas this value for fly ash concrete of cement fly ash mix 90:10, 80:20, 70:30 are 32.6, 32.0, 31.5 MPa respectively. But after 180 days curing, compressive strength values are 41.5, 40.1, 40.9 and 41.3 MPa for OPC concrete and fly ash concrete of cement fly ash mix 90:10, 80:20, 70:30 respectively. This is due to slow hydration rate of fly ash and for this; gain in strength at early age is comparatively lower although after longer curing period, fly ash concrete attains almost the similar strength as that of OPC concrete.

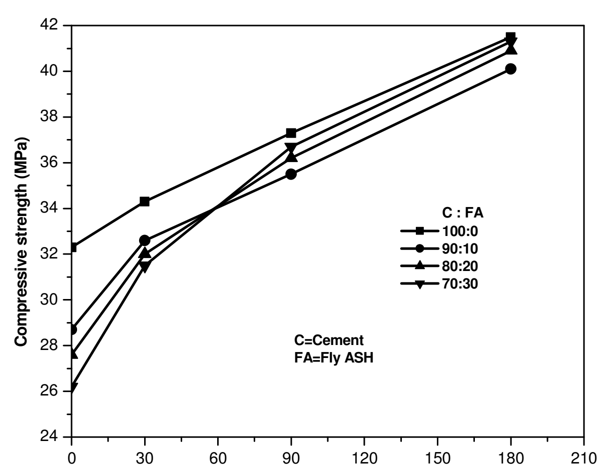

Fig.5: Compressive strength-Exposure time relation for fly ash concrete exposed to plain water

4. CONCLUSIONS

Based on the limited number of test variables, exposure condition/periods and the results of the investigation conducted on different fly ash concrete exposed to seawater of various concentrations for varying periods up to 180 days, some logical conclusions are drawn and summarized below:

(1) The amount of water soluble chlorides diffused into the concrete are observed to range from 0.011% to 1.432% by weight of concrete mass depending on the depth of penetration, amount of cement replacement and salt concentration of curing environment.

(2) After 180 days curing in sea environments, fly ash concrete of cement fly ash mix 80:20 shows around 3% to 15% lower chloride content than OPC concrete at 15 and 25 mm depth level. Among various replacement level cement fly ash mix 80:20 shows much better resistance against chloride penetration.

(3) Concretes exposed to seawater show little or no measurable depth of carbonation. After 180 days curing period, carbonation depths ranging from 0.5 to 1.0 mm are observed at some spots in a few specimens. Higher depths of carbonation are observed for OPC concrete as compared to fly ash concrete.

(4) OPC concrete exhibited around 1% to 3% higher compressive strength as compared to fly ash concrete after 180 days curing period in plain water.

In general, fly ash concrete made of blending fly ash with cement in different proportion plays an important role on hydration characteristics of concrete. It provides higher resistance against chloride and sulphate ion penetration, which indicates its suitability in resisting corrosion of rebar in concrete. Among the fly ash concretes studied, concrete of cement fly ash mix 80:20 is found to be most effective in resisting the adverse effect of marine environment.

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