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Effect of sea water on the performance of fly ash concrete under freezing-thawing cyclic action

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Abstract

Deterioration of structural concrete exposed to freeze-thaw cycles is one of the most important durability problems under subzero temperature conditions. It becomes more devastating when subjected to marine environment. The discovery of vast oil and gas reservoirs in arctic/sub arctic regions has enhanced the interest of the scientists and technologists in evaluating the performance of structural concrete in such locations. As large no's of concrete structure has been constructed in deeper seas and aggressive environment, demand for durable concrete has also been increased simultaneously. Supplementary cementitious material such as fly ash may be used as partial replacement of cement for making more stable, dense, less absorptive and less permeable concrete having improved freeze-thaw durability. This paper presents a part of an experimental investigation on freeze–thaw effect of concrete specimens exposed to plain water as well as artificial seawater simulating marine environment over 180 cycles. Three different grades of concrete M38, M33 and M28, each with four different fly ash replacement level, 20, 30, 40 and 60% were used for the experimental program. Ordinary Portland cement (OPC) concrete was also used as reference concrete. The deteriorative effects on all concretes were measured by studying weight and volume change, compressive strength, permeability characteristics and rapid chloride penetration resistance of the deteriorated test specimens. Among all the concretes studied, the optimum amount of cement replacement is reported to be within 30 to 40%. The study reveals that fly ash concrete has better resistance against freeze-thaw deterioration due to pozzolanic activity of fly ashes that creates more durable calcium silicate hydrate (CSH) gel and fills capillaries and bleed water channels occupied by water soluble lime, which inhibits the penetration of aggressive species including chloride, which can effectively reduce the corrosion of the embedded steel reinforcement.

Keywords: Durability, Fly ash, Freeze-thaw, RCPT, Seawater, Water permeability

1. Introduction

Concrete deterioration for freeze-thaw cyclic action has been a major problem in cooler areas of different countries. Freeze-thaw deterioration begins when water enters into the voids of concrete. Leaching of calcium hydroxide, which is produced during the hydration of portland cement, provides greater voids for water to occupy, thereby aggravating the rate of deterioration. Freezing of water or salt solution in the concrete pores may cause severe deterioration and considerable reduction of service life. It is commonly known that plain water freezes at 0°C under normal atmospheric pressure. When water freezes, the volume increases by 9% as water turns to ice, generating high pressure in the adjacent concrete. However, water that is trapped within the capillary pores of concrete does not necessarily freeze at 0°C. The temperature at which water freezes in capillary pores is a function of the size of the pores and pore chemistry. As pore size decreases, the temperature required to freeze the water also decreases (Hale et al. 2009).

The marine environment is characterized by typical aggressive loading of various soluble salts in sea water. Typically, sea water contains about 3.5% soluble salts by weight (Shetty, 2002). The relative ionic concentrations are 18 gpl Cl^-, 12 gpl Na^+, 2.6 gpl $(SO_4)^{2-}$, 1.4 gpl Mg^{2+} and 0.5 gpl Ca^{2+}. Normally, pH of sea water is about 8. In a marine environment, in addition to its presence in original mix, the chloride ion penetrates into the concrete either from sea water or sea winds carrying sea salts and reacts with the hydrated cement products which produces complex compounds including Friedels salt which are leachable and expansive in nature. The chloride attacks also destroy the passivity of steel and lead to the initiation of rebar corrosion. On the other hand, the penetration of sulphate ions attack the hydrated cement matrix with the formation of gypsum and a complex compound known as calcium sulphoaluminate (ettringite). In this region with cold climate, the freeze-thaw damage is the most important issue among the durability problems in concrete structures, such as dams, hydraulic and offshore structures, and bridges and highway pavements, during their service.

Concrete has also been extensively used as the basic construction material for various types of offshore/onshore structure over the several decades. Concrete structures in such locations are always required to withstand physical, chemical and mechanical action of sea water under varying environmental condition throughout their life span. Thus structural concrete in cold coastal regions are exposed to coupling effects of freeze-thaw cycles and seawater corrosion. For reinforced concrete structures, other than the degradation of concrete materials, the existence of cracks under service loads is believed to be one of the main causes of deterioration of reinforced concrete structures serviced in cold marine environment or snow melting conditions (Diao et al. 2011). Chloride or other chemical ions would penetrate into concrete through cracks and induce corrosion of reinforcing steel bars. The amount of permeation is determined by the thickness of the concrete cover and the width of the cracks (Djerbi et al. 2008). To simulate the working conditions of reinforced concrete structures in cold coastal regions, the presence of structural loads in addition to the harsh environmental factors were considered in a number of recent studies (Diao et al. 2011).

The resistance of concrete to frost action depends on the strength of the paste, water/cement ratio, type of aggregate used, age of concrete, duration and extent to which the concrete is subject to freezing action. When a concrete structure is exposed to freezing environments, the pore solution in capillary pores changes into ice and expands by volume. Because of its volume expansion, unfrozen water tends to move into any available place nearby and the movement of the pore solution eventually builds up hydraulic pressure. When the expansive force exceeds the tensile strength of concrete, micro cracks start to generate and radiate to the surrounding cement paste (Pigeon and Pleau 1992).

One of the advances in concrete technology is the development of fly ash concrete and its use in it. Fly ash is a by-product from combustion of pulverized coal. As the coal is heated to high temperatures, it liquefies. It is thereafter cooled rapidly, which forms spherical particles. The fly ash consists mainly of silica (SiO_2), aluminium oxide (Al_2O_3), iron oxide (Fe_2O_3) and calcium oxide (CaO). Use of fly ash improves the workability of concrete slurry, reduce the heat of hydration of cement and increase the strength of concrete with age; therefore, it can improve the mechanical properties and durability of concrete (Berry and Malhotra 1980). Fly ash combines with calcium hydroxide to produce additional cementitious materials, thereby reducing the amount of calcium hydroxide that may be leached out of the concrete. Leaching of the calcium hydroxide increases concrete voids which can accelerate freeze-thaw damage. As a result, permeability and porosity are reduced. Fly ash also fills the minute voids creating a denser and less absorptive concrete. It reduces the amount of water required in the mix by approximately 2% to 10%, because the spherical shape of the fly ash particles reduces bleed channels and void spaces. Reduction of bleed channels limits the entrance of water; fewer void spaces mean less space for water to accumulate. High quality fly ash also produces more cohesive concrete which holds entrained air inside the concrete. Fly ash helps to produce higher compressive strengths in the long term that provide a strong concrete which resists the forces generated during the freezing of water in the voids. As a whole fly ash concrete is more stable, uniform, dense, less absorptive and less permeable—all factors which improve freeze-thaw durability. The performance of concrete with additions of fly ash is in many situations improved compared to that of concrete mixed with Portland cement only.

The fly ash can either be blended in the cement or added separately in the concrete at mixing. Fly ash is not cementitious by itself, but will together with cement, produce cementitious compounds. The primary contributor to the pozzolanic reaction in fly ash is the silica, which combines with calcium hydroxide and water to form the binder in concrete, calcium silicate hydrate (C–S–H). During hydration, the cement reacts with water and form durable binder. Most properties of the hardened cement paste are developed when tricalcium silicates (C_3S) and dicalcium silicates (C_2S) reacts with water, forming C–S–H ($C_3S_2H_3$) and calcium hydroxide (CH) (Illston, 2001). The silica in the fly ash in a finely divided form and in the presence of moisture, at ordinary temperatures, react chemically with calcium hydroxide liberated from the hydration of cement, forming cementitious compounds. The reaction is secondary, but it is not possible to differentiate the C–S–H produced from pozzolanic reactions, from that produced by cement hydration (Illston, 2001). Since this pozzolanic reaction is secondary, it will occur somewhat later than the hydration of the cement, for some ashes even up to one week after the hydration of the cement has started. The rate of strength development for concrete with fly ash is lower at the beginning than for concrete with plain Portland cement. However, concrete with fly ash does continue to gain strength, which means that after some weeks or months, the strength of this concrete will be higher than for the concrete containing ordinary Portland cement. The pozzolanic activity does improve the strength of the transition zone, i.e. the interface between the paste and aggregate, in the concrete by secondary effects. Furthermore, better packing of particles in the fresh state when fly ash is included will reduce the porosity, hence also leading to higher strength (Illston, 2001).

Chloride ions from sea water and de-icing salts can penetrate into concrete by transport of chlorides in water, diffusion of the ions in water and by absorption. If the chloride ions reach the reinforcement, corrosion may occur. Not all of the chlorides in the concrete do affect the corrosion of steel; some ions are chemically bound to the hydration products from the cement, whereas others are physically bound being adsorbed on the surface of the gel pores. It is only the free chloride ions that can damage the reinforcement. The penetration of chloride ions is also dependent on the permeability of the concrete; a more permeable concrete will lead to less resistance against penetration. (Neville, 2003). Concrete with fly ash has shown better resistance against chloride penetration than concrete with ordinary Portland cement. This is partly due to that fly ash creates a denser structure, which reduces the permeation and also concrete with fly ash binds the chloride ions better, thus leaving fewer ions free (Dhir, 1999). The active alumina (Al_2O_3), which exists in larger amounts in fly ash than in Portland cement, is able to bind the chloride ions. According to Dhir (1999), the binding capacity was found to be at maximum at a replacement of fly ash of 50% of the cement, but optimum at about 30%. Concrete with fly ash replacing 33% of the cement, the binding capacity was four times larger than for ordinary Portland cement. Furthermore, the binding capacity increased with the concentrations of chloride ions. Replacement of the cement by 30% fly ash was found to improve the resistance against chloride ions with two to four times. A more mature concrete will be less permeable, thus more resistance regarding chloride ingress.

Permeability is the most important aspect of concrete durability. It is inversely linked to durability in that the lower the permeability, the higher the durability of concrete (Joshi and Lohtia 1997). To be durable, concrete must be relatively impervious (Berry and Malhotra, 1986). The single parameter that has the largest influence on permeability/durability is w/c ratio. As the w/c ratio is decreased, the porosity of the paste is decreased and the concrete become more impermeable. Clearly, the permeability of concrete plays an important role in durability because it controls the rate of entry of moisture that may contain aggressive chemicals and the movement of water during heating or freezing. This leads to enhanced durability because aggressive agents without entering inside the concrete cannot attack the concrete nor the reinforcing steel embedded in it (Bremner and Thomas, 2004).

The key to prevention of sulfate attack is to tie up the free lime and calcium aluminates to eliminate the possibility of ongoing reactions. Increased sulfate resistance of concrete containing fly ash may be explained by the reaction of silica, alumina and ferric oxide found in fly ash with calcium hydroxide liberated during the hydration of Portland cement to form relatively stable cementitious compounds. Greater impermeability of such type of concrete reduces penetration of sulfate solutions and results in improved resistance to sulfate attack. Fly ash not only reduces the permeability of the concrete, but because of reaction of these materials with available alkalis, it removes that essential component required for Alkali Aggregate reaction (AAR) and thus it is an effective means of reduction the risk of AAR occurring.

Naik et al. (1992) investigated freezing and thawing resistance of high-volume Class C and Class F fly ash paving concretes. The concrete mixtures were proportioned with of 20 and 50% Class C fly ash, and 40% Class F fly ash. The 40% Class F fly ash concrete mixture exhibited the highest durability factor amongst all the three mixtures tested. The average durability factor for the 50 percent Class C fly ash mixture was 90.

Drahushak-Crow and von Fay (1991) studied freezing and thawing durability of concretes made with three different fly ashes. Fly ash concrete mixtures were proportioned for five different cement replacement levels (10, 30, 50, 75, 100 %) with fly ash. The number of cycles to failure depended greatly upon type of fly ash, amount of cementitious content, and type of curing.

Bortz (2010) studied the influence of source of fly ash on the durability regarding scaling under freeze/thaw. The source of the fly ash, which affects the properties of the fly ash, had high impact on the resistance of freeze/thaw scaling. The amount of fly ash was 67% of cement content and it replaced the cement on a one-to-one basis.

Achintya and Prasad (2003) studied the behavior of concrete in the freeze-thaw environment of seawater. In this study, concrete samples were completely submerged in plain water and simulated seawater, and also in a non submerged state. This study showed that specimens subjected to seawater underwent change in size and shape along with substantial abrasion, erosion, and crumbling on the surface, whereas exposed surfaces of samples become uneven when subjected to plain water and the atmospheric condition.

2. Research significance

Among the several durability problems that arise in concrete exposed to a marine environment, those have been studied extensively are the chemical attack of sea water on cement paste, concrete and the corrosion of embedded steel. Very limited research works have been documented on the freeze-thaw action of sea water on concrete. The relevant information presented in literature varies to a great extent or debatable. It is important to have detail information regarding the concrete durability on freezing and thawing in sea water in view of the increasing use of concrete in the sub-arctic/arctic region. The freeze-thaw action on structural concrete in the splash/tidal zone has its own characteristics and is dependent on ambient air and sea water temperature. In addition, the chemical attack of the sea water on the cement constituents is found to lead to a more pronounced deterioration in the concrete structure. The major aim of this work is to evaluate the freezing and thawing durability of concrete made with Class F fly ash. The properties evaluated were the weight change, volume change, compressive strength, water permeability, RCPT and freezing and thawing resistance of concrete with or without fly ash. The results of this investigation would provide data for establishing appropriate mix proportions for concretes subjected to freezing and thawing resistance against sea water and deicer salts.

3. Experimental program

The experimental program was planned to study the suitability of fly ash as partial replacement of cement in making structural concrete taking into consideration of the compressive strength, water permeability and rapid chloride penetration test (RCPT) value of hardened concrete exposed to Freezing-Thawing environment plain as well as sea water.

3.1 Materials used

(a) Cement: ASTM Type-I Ordinary Portland Cement (OPC) was used as binding material. Chemical compositions of OPC are given in Table 1.

(b) Fly ash: A low calcium fly ash obtained from Boropukuria (Bangladesh) compiling with ASTM Class F Fly ash was used as supplementary cementitious material. Chemical analysis of the fly ash conducted using X-ray fluorescence (XRF) study is shown in Table 1.

(c) Aggregate: Locally available natural sand passing through 4.75 mm sieve and retained on 0.075 mm sieve was used as fine aggregate. The coarse aggregate was crushed stone with a maximum nominal size of 12.5 mm. Grading and physical properties of the aggregates are given in Table 2.

Table 1
Chemical composition (%) of Ordinary Portland Cement and fly ash

Constituents	Composition	OPC	FA
Calcium oxide	CaO	65.18	0.65
Silicon di-oxide	SiO_2	20.80	51.49
Aluminum oxide	Al_2O_3	5.22	31.60
Ferric oxide	Fe_2O_3	3.15	2.80
Magnesium oxide	MgO	1.16	0.28
Sulfur tri-oxide	SO_3	2.19	0.19
Sodium oxide	Na_2O	--	0.18
Loss on ignition	--	1.70	4.2
Insoluble residue	--	0.6	--

-- = not measured items.

Table 2
Grading and physical properties of coarse and fine aggregate

Properties	Coarse Aggregate	Fine Aggregate
Grading of Aggregates		
Sieve Size (mm)	Cumulative % Passing	
25.0	100	--
12.5	100	--
9.5	45	--
4.75	0	100.0
2.36	--	94.0
1.18	--	78.5
0.6	--	55.5
0.3	--	13.0
0.15	--	2.5
Physical Properties of Aggregates		
Specific Gravity	2.67	2.59
Unit Weight	1635 kg/m^3	1540 kg/m^3
Fineness Modulus	6.45	2.57
Absorption Capacity	0.8 %	1.2 %

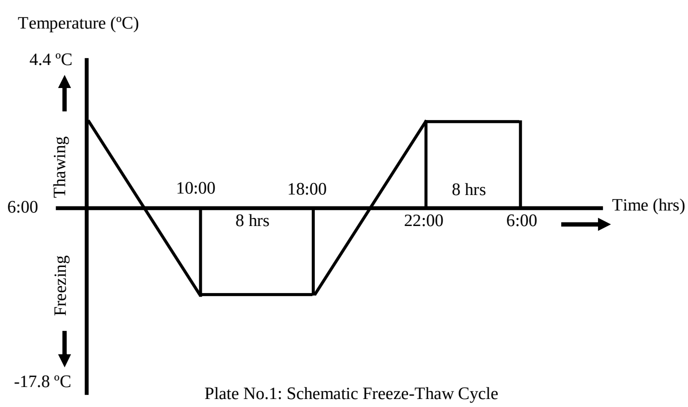

Plate No.1: Schematic Freeze-Thaw Cycle

3.2 Variables Studied

(a) Curing Water: Plain water (PW) as well as artificially made sea water (SW) was used for curing the specimens. SW was made by mixing tap water with exact amount and proportion

of principal salts found in natural sea water. The composition of artificial sea water is given in Table 3.

(b) Exposure Condition: Freezing-Thawing arrangement was created in a freeze-thaw chamber. In each freeze-thaw cycle, the temperature was varied from (-17.8^{0}C) to (+4.4^{0}C) over a total period of 24 hours (8+4 hours for freezing and thawing; 7+5 hours kept at two terminal temperatures) (Refer to Plate No.1).

(c) Exposure Periods: 30, 90 and 180 freeze-thaw cycles after 28 days of procuring in plain water.

Table 3
Specified salt contents of artificial SW used in experimental program (Mayers, 1996)

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 SW
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	

Table 4
Mix proportions and properties of fresh concrete

Mixture constituent & properties	Grade of Concrete		
	M38	M33	M28
Cement (kg/m^3)	500	480	435
Water (kg/m^3)	218	224	218
Sand (kg/m^3)	520	530	545
Stone Chips (kg/m^3)	1120	1130	1150
water/cement Ratio	0.44	0.47	0.50
Slump (mm)	60	63	68
Air content %	1.1	1.2	1.3

3.3 Mix design and sample preparation

Three different grades of concrete namely M38, M33 and M28 were used in the program. Four different mix proportions of cement fly ash (80:20, 70:30, 60:40 and 40:60) were used as cementitious material. Cement fly ash mix ratio of 100:0 i.e. plain concrete specimens were also cast as reference concrete for comparing the properties of fly ash concrete. Fly ash concrete means the concrete made by using cement and fly ash as cementitious material with sand, stone chips and water. Relevant information of different concrete mixes is given in Table 4.

3.4 Size of specimens

A total of 240 no's of cylindrical specimen of size 150 mm diameter and 175 mm high and 360 no's cubical specimens of 100 mm size from five different types of fly ash concretes were cast as per requirement for conducting water permeability and strength test. Another 360 nos of cylindrical specimen of size 100 mm diameter and 50 mm height were also prepared for Rapid chloride permeability test. The whole experimental program including the various parameters/variables studied, test conducted are summarized in Table 5. The small size of specimen i.e. 100 mm cube was selected in order to accommodate large number of specimens in the limited sized curing tanks. The specimens were demoulded after 24 hours of casting and cured in plain water at 27±2°C. Concrete specimens were designated as per grade of concrete and amount of fly ash as a percentage of total cementitious material. Thus M38FA40 concrete means grade of concrete is M38 and cement fly ash mix ratio is 60:40.

4. Experimental procedures

4.1 Strength

The concrete specimens were tested for compressive strength at 30, 90, 180 and 360 freeze-thaw cycles in accordance with the BS EN 12390-3:2009. The reported strength in each case is taken as the average of three tests results.

4.2 Freezing-thawing test

In ASTM C 666, two procedures of freezing-thawing test are defined: Procedure A, rapid freezing and thawing in water, and Procedure B, rapid freezing in air and thawing in water. In this study, the Procedure A was used and according to this procedure, the temperature of the curing water condition concrete specimens was lowered from 4 to -17.8 °C and raised it from -17.8 to 4 °C in 4 hours.

4.3 Water permeability test

Water permeability test was carried out at 30, 90, 180 and 360 freeze-thaw cycles. The cylindrical specimens were dried in the oven at 105°C and then coated with epoxy coating in the circular side to prevent water leakage from the side during the test. After placing the specimen in the apparatus, a water pressure of (500 ±50) kPa was applied for (72 ± 2) hours. After the saturation of the specimen, the flow rate reading was taken from connected burette by measuring the changing of volume of water with time. Coefficient of permeability is calculated by using the following equation,

$$k = (QL/AH) \quad (1)$$

where, k = permeability coefficients (m/s), Q = flow rate (m^3/s), A = area (m^2), L = depth of specimen (m), H = head of water (m). Depth of water penetrated in the test specimen was calculated in accordance with the BS EN 12390-8:2009. The reported strength is taken as the average of two tests results at each test point.

4.4 Rapid chloride penetration tests

Cylindrical sample of 100 mm diameter and 200 mm height were prepared in accordance with ASTM C39. Two slices, each with a thickness of 50 mm, were cut from the cylinders. The cut cylinders were left to dry in laboratory condition for 24 hrs before application of epoxy coatings around the cylindrical surface. After this conditioning, the specimens were placed in the testing cells. The testing consisted of monitoring the amount of electrical current passing through the specimen, when a potential difference of 60 V DC is maintained across the specimen for a period of 6 hours. In this test, chloride ions are forced to migrate out of NaCl solution subjected to a negative charge, through the concrete, into a NaOH solution maintained at a positive potential. The total charge passed, in coulomb, is used as an indicator of the resistance of the concrete to the penetration of chloride ions. At the end of 30, 90, 180 and 360 cycles of freeze-thaw, the cylinder specimens were tested for RCPT as per ASTM C1202. The average result of three test specimens was taken as the representative data. ASTM guidelines concerning the chloride ion penetrability are given in Table 6.

Table 5
Experimental program for the investigation

Mix Type	Freeze-Thaw Cycles*	Exposure condition	Total No.** of specimen for Strength	Total No.*** of specimen for Permeability	Total No.** of specimen for RCPT
	(a)	(b)	(c=a*b*3)	(d=a*b*2)	(e=a*b*3)
M38FA0	0	Plain water & Sea water	24	16	24
M38FA20	30		24	16	24
M38FA30	90		24	16	24
M38FA40	180		24	16	24
M38FA60			24	16	24
M33FA0	0	Plain water & Sea water	24	16	24
M33A20	30		24	16	24
M33FA30	90		24	16	24
M33FA40	180		24	16	24
M33FA60			24	16	24
M28FA0	0	Plain water & Sea water	24	16	24
M28FA20	30		24	16	24
M28FA30	90		24	16	24
M28FA40	180		24	16	24
M28FA60			24	16	24
	Total		360	240	360

* 28 days procuring, ** 3 samples for compressive strength & RCPT test, *** 2 samples for permeability test

Table 6
Guidelines for chloride-ion penetrability based on charge passed (ASTM C 1202)

Charge passed, Coulombs	Chloride ion penetrability
>4000	High
2000-4000	Moderate
1000-2000	Low
100-1000	Very Low
<100	Negligible

5. Results and discussion

The specimens made from OPC and fly ash concrete are exposed to plain water and sea water for different freeze-thaw cycles. The test results obtained after specific periods were critically analyzed, discussed and presented in graphical form to arrive at some conclusions there from.

Plate no. 2: Concrete specimens after 30 cycles of freezing and thawing in PW

Plate no. 3: Concrete specimens after 30 cycles of freezing and thawing in SW

Plate no. 4: Concrete specimens after 90 cycles of freezing and thawing in PW

Plate no. 5: Concrete specimens after 90 cycles of freezing and thawing in SW

Visual examination

Concrete specimens exposed in the sea water and plain water is taken out after specific cycles of freeze-thaw, for conducting various tests. After visual inspection, it is seen that concrete specimens in sea water have lost their dimensional stability with substantial erosion and splitting/crumbling on the surface whereas in plain water, concrete surface tend to become uneven *(Refer to Plate No.2 to 7).* Some changes in color from the original dark gray to lime gray of the specimens in sea water have also been observed which indicates either the salts deposition on the concrete surfaces or leaching out of portlandite, $Ca(OH)_2$. Also interior surfaces have indicted a higher level of saturation with increasing number of freeze-thaw cycles both in sea and plain water environments.

Weight change

The change in weight of the specimens of concrete grade M38, M33 and M28 in different exposure conditions and for various freeze-thaw cycles have been illustrated in Fig.1, Fig.2 and Fig.3 respectively. A close examination reveals that at the end of 30 cycles of freeze-thaw, the specimens in sea water exhibit a higher percentage (nearly 1.1 to 2.6%) of weight gain as compared to the plain water cured specimens (nearly 0.9 to 2.2%). This increase in weight may be primarily due to the ingress of sea water or plain water into the concrete. After 90 cycles, a significant difference in the trend of weight change for the concrete specimens exposed to sea water has been found to occur as compared to that for the specimens placed in plain water. In this condition plain water cured specimen exhibit higher percentage of weight gain as compared to sea water cured concrete. After 180 cycles of freeze-thaw, a considerable change (loss) in the weight lying between -0.4 and 0.6% is observed for the concretes exposed to the plain water environment whereas for the similar specimens placed in sea water, this change is found to lie in the range of -2 to -6.6%. The higher loss in weight of the specimens exposed to sea water is primarily due to crumbling of outer surfaces of the specimens caused by crystallization of sea salts in the voids of concrete and their subsequent expansion during freeze-thaw cycles. Also after 180 cycles of freeze-thaw, the change in weight of the concretes M38, M33 and M28 concrete exposed to plain and sea water environment was found to lie in the range of -3.6 to 0.6%, -4.8 to 0.4% and -6.6 to 0.5% respectively. So, it is clear that higher grade concrete has better resistance against weight change compared to lower grade concrete in freeze-thaw action. Also it is seen that, fly ash concrete shows better resistance against weight change as compared to plain concrete particularly after long Freeze-Thaw loading. It may be due to the development of its resistance to water/salt ions penetration inside concrete as the rate of hydration of fly ash concrete in relatively slow.

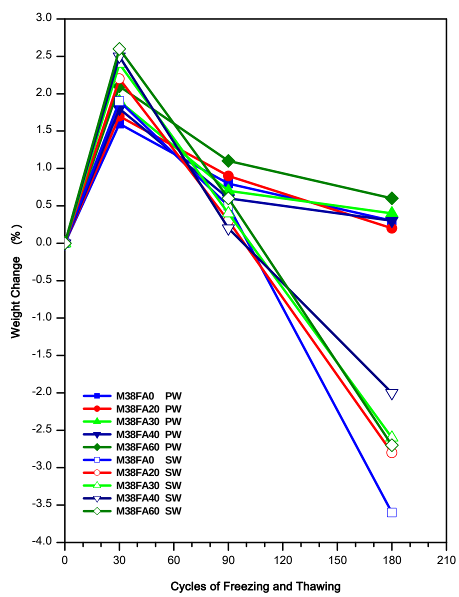

Fig.1: Weight Change - Freeze Thaw Relation for M38 Grade Concrete

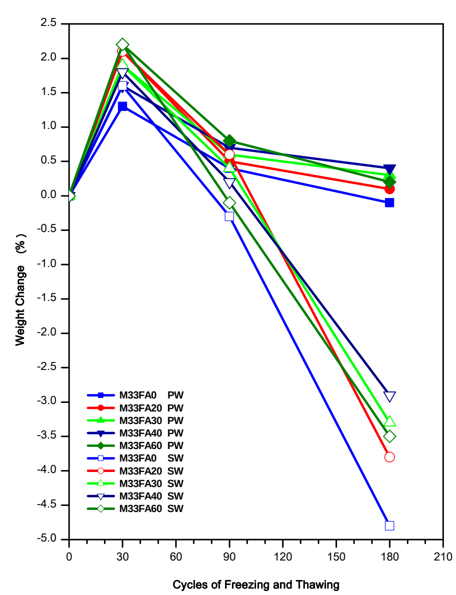

Fig.2: Weight Change - Freeze Thaw Relation for M33 Grade Concrete

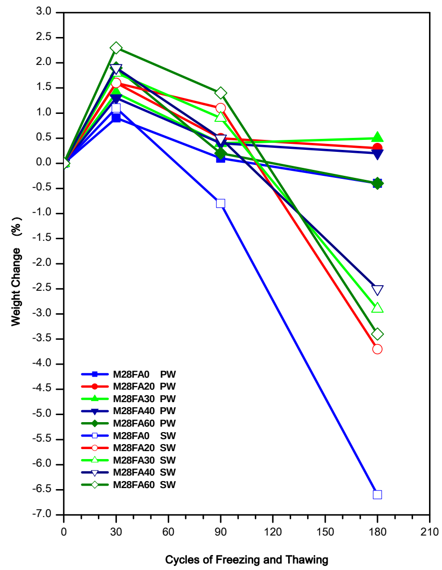

Fig.3: Weight Change - Freeze Thaw Relation for M28 Grade Concrete

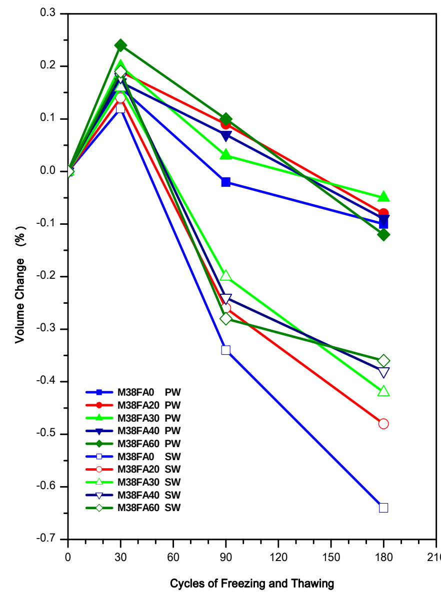

Fig.4: Volume Change - Freeze Thaw Relation for M38 Grade Concrete

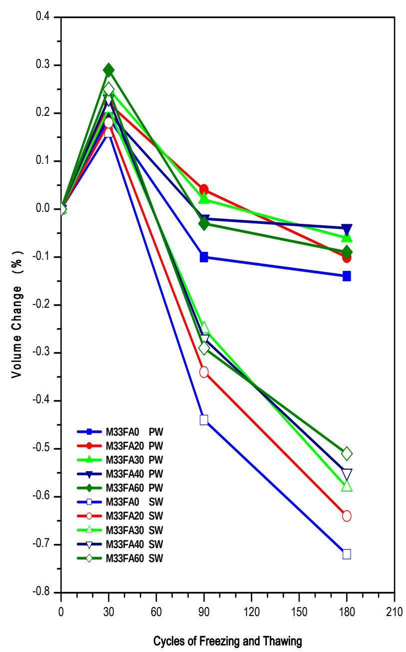

Fig.5: Volume Change - Freeze Thaw Relation for M33 Grade Concrete

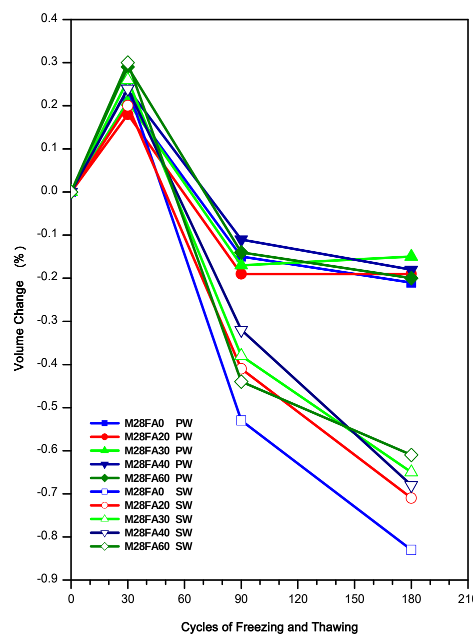

Fig.6: Volume Change - Freeze Thaw Relation for M28 Grade Concrete

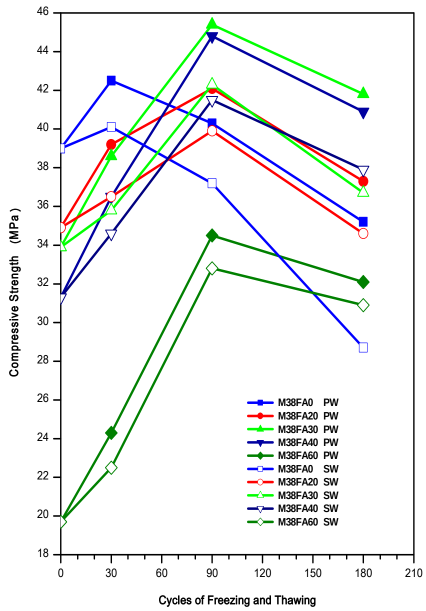

Fig.7: Compressive Strength - Freeze Thaw Relation for M38 Grade Concrete

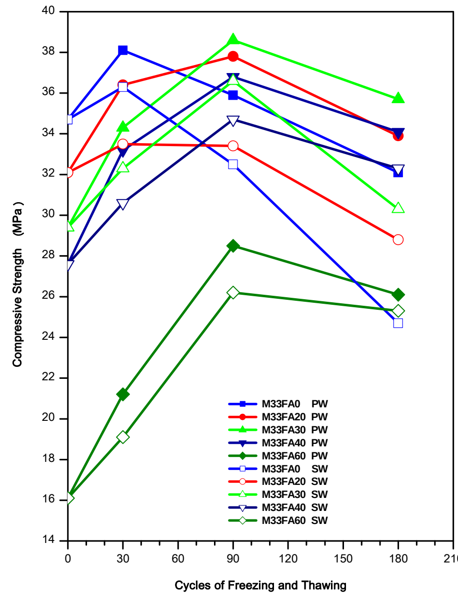

Fig.8: Compressive Strength - Freeze Thaw Relation for M33 Grade Concrete

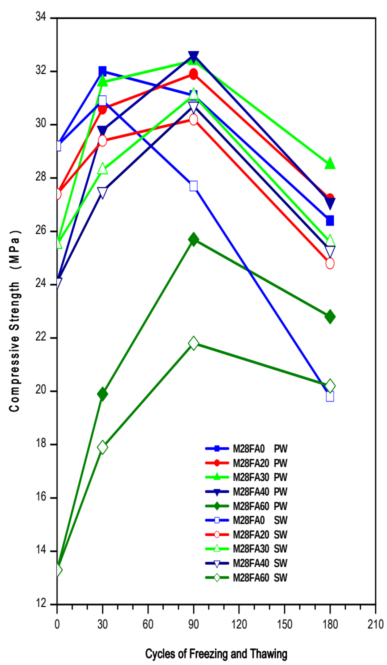

Fig.9: Compressive Strength - Freeze Thaw Relation for M28 Grade Concrete

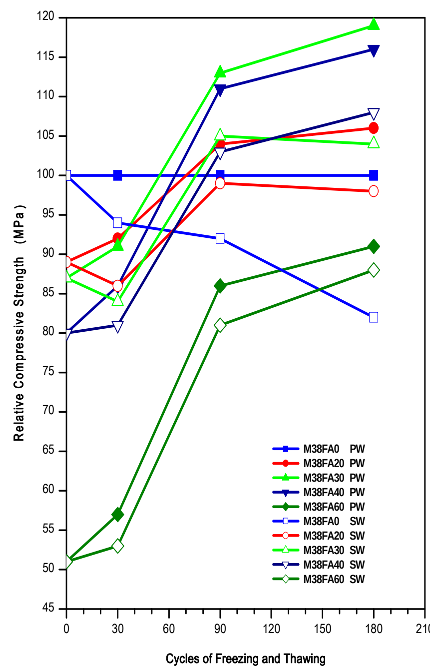

Fig.10: Relative Compressive Strength - Freeze Thaw Relation for M38 Grade Concrete

Volume change

The volume change in fly ash concrete of grade M38, M33 and M28 exposed to sea water and plain water for different period of freeze-thaw cycle are illustrated in Fig.4, Fig.5 and Fig.6 respectively. The change in volume are observed to, more or less, follow the same trend as for changes in weight. It is clear from the figures that the effect of sea water on the volume change of concrete specimens is relatively higher than that of plain water under Freeze-Thaw action. At the initial stage, i.e. after 30 cycles of freeze-thaw, volume of all the specimens are observed to be increased. It may be attributed due to hydration reaction of cement in presence of ingress of sea or plain water inside the concrete mass. At the end of 90 cycles, sea water cured concrete specimens have exhibited volumetric change of nearly -0.2 to -0.53%, whereas a volume change of -0.19 to 0.1% has been found in the specimens placed in the plain water. The volume change of the concrete specimens placed in sea water and plain water has been found to decrease due to surface erosion and splitting. After 180 cycles of Freeze-thaw, this reduction is observed to lie between -0.04 to -0.21% for plain water and -0.36 to -0.83% for sea water cured concrete. The decrease in volume resulting from erosion/crumbling of outer surfaces of concrete may be attributed due to the deposition of chemical compounds into the voids of concrete, the crystallization as well as their expansion due to freezing of the entrapped water inside the voids. Also higher grade concrete has better resistance against volume change compared to lower grade concrete in freeze-thaw action. After 180 cycles of freeze-thaw, the change in volume of M38, M33 and M28 grade concrete exposed to plain and sea water environment was found to lie in the range of -0.05 to -0.64%, -0.04 to 0.72% and -0.15 to -0.83% respectively. It is also clear from the figures that fly ash concrete shows much more resistance against volume change as compared to OPC concrete for relatively higher cycles of freeze-thaw.

Compressive strength

Compressive strength of OPC and fly ash concrete of three different grades M38, M33 and M28 has been graphically presented in Fig.7, Fig.8 and Fig.9. Also for the ease of comparison, the relative compressive strengths at different freeze-thaw cycles and in different curing water are plotted in Fig.10, Fig.11 and Fig.12. A close examination of these curves indicates that the strength increases during the first 90 cycles of freeze-thaw in sea water as well as in plain water for all grades of concrete and after that it starts to decrease. This decrease in the compressive strength has been found to be significant at 180 cycles of freeze-thaw. It is noted that in comparison to the 28 day compressive strength of plain water cured concrete at constant temperature of 27^0C, the compressive strength of the concrete specimens subjected to 180 cycles of freezing and thawing have been found to lie in the ranges of 78 to 82% for sea water and 89 to 95% for plain water.

At early ages of curing, OPC concretes i.e. no fly ash concrete achieves relatively higher compressive strength as compared to fly ash concrete. Test result shows that after 30 cycles of freeze-thaw, compressive strength for OPC concrete is around 8%, 9%, 14% and 43% higher than M38FA20, M38FA30, M38FA40 and M38FA60 concrete respectively. At initial age of curing, compressive strength is seen to decrease with the increase of fly ash content when compared with OPC concrete. For relatively larger freeze thaw cycles, compressive strength of the fly ash concrete specimens up to 40% cement replacement level are higher than that of OPC concrete. Compressive strength after 180 cycles of freeze-thaw for M38FA20, M38FA30 and M38FA40 concrete is higher by around by 6%, 19% and 16% respectively than OPC concrete. Cement normally gains its maximum strength within 28 days. During that period, lime produced form cement hydration remains within the hydration product. Generally, this lime reacts with fly ash and imparts more strength and for this reason, concrete made with fly ash will have lower strength than cement concrete at early ages of curing and higher strength at the later ages of curing. Conversely in cement concrete, this lime would remain intact and with time it would be susceptible to the effects of weathering, loss of strength and durability. M28 grade concrete also shows almost similar trend. Test result shows that compressive strength after 30 cycles of freeze-thaw for OPC concrete is around 4%, 1%, 7% and 38% higher than M28FA20, M28FA30, M28FA40 and M28FA60 concrete respectively. On the other side at the end of 180 cycles of freeze-thaw, compressive strength for M28FA20, M28FA30 and M28FA40 concrete are respectively 3%, 8% and 4% higher than no fly ash concrete. The same strength for M33FA20, M33FA30 and M33FA40 concretes are respectively 5%, 11% and 6% higher and for M38FA20, M38FA30 and M38FA40 concrete are respectively 6%, 19% and 16% higher as compared to OPC concrete of similar grade.

Test results also show that compressive strength of both OPC and fly ash concrete is reduced when it is exposed to seawater as compared to plain water curing. At the end of 90 cycles of freeze-thaw, compressive strength for M38FA20, M38FA30 and M38FA40 concrete is around 8%, 16% and 15% higher than 28 days compressive strength of OPC concrete when cured in plain water; whereas the same value is around 2%, 8%, and 6% higher for M38FA20, M38FA30 and M38FA40 concrete respectively as compared to OPC concrete when cured in sea water. The increase in strength upto the first 90 cycles may due to the fact that the specimens do not get saturated fully by sea water during this period. After 90 cycles, the specimens get saturated considerably by sea water and after crystallization of the salts together with their reaction with cementitious products within the body of concrete results in a significant decrease in the compressive strength.

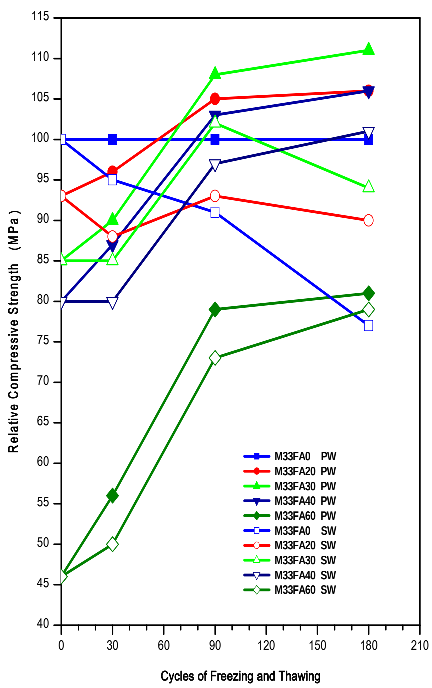

Fig.11: Relative Compressive Strength - Freeze Thaw Relation for M33 Grade Concrete

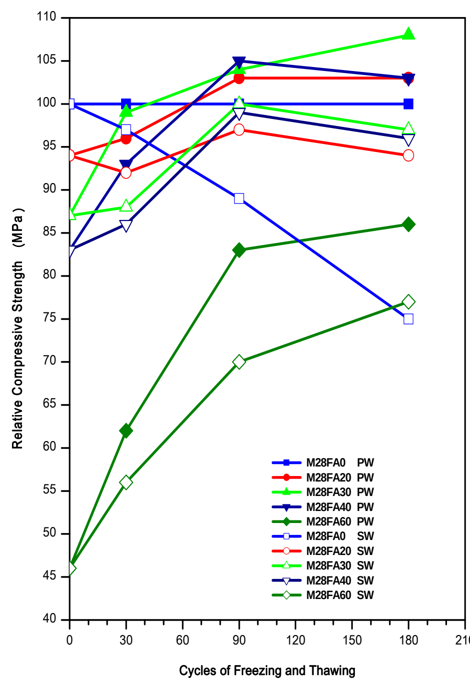

Fig.12: Relative Compressive Strength - Freeze Thaw Relation for M28 Grade Concrete

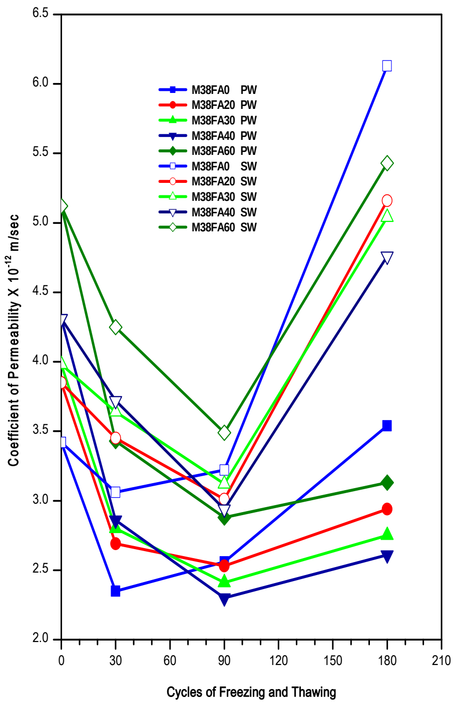

Fig.13: Permeability - Freeze Thaw Relation for M38 Grade Concrete

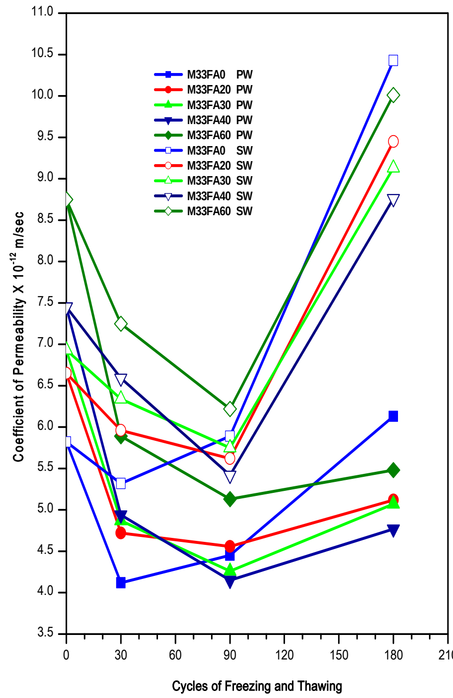

Fig.14: Permeability - Freeze Thaw Relation for M33 Grade Concrete

Rate of strength deterioration for different types of concrete is observed to vary with the grade of concrete and is lower for the higher grade concrete. Among all the concrete studied, after 180 cycles of freeze-thaw in seawater deterioration of compressive strength deterioration is about 26%, 11%, 6%, 3% and 21% for M38FA0, M38FA20, M38FA30, M38FA40 and M38FA60 concrete respectively as compared to 28 day strength of OPC concrete; whereas the same strength is seen to decreased by around 29%, 17%, 13%, 7% and 27% for M33FA0, M33FA20, M28FA30, M33FA40 and M33FA60 concrete respectively compared to the 28 days strength of no fly ash concrete. Also at the end of 180 cycles of freeze-thaw, the overall strength gaining for M38 grade concrete is around 9% & 12% higher as compared to M33 grade and M28 grade concrete respectively in plain water; whereas this value is 7% & 10% higher as compared to M33 grade and M28 grade concrete in sea water, which indicates that compressive strength gaining is relatively faster for higher grade concrete as compared to lower grade concrete.

Water permeability

Permeability characteristics of M38, M33 and M28 grade concrete exposed to different environment for various freeze-thaw cycles are graphically presented in Fig.13, Fig.14 and Fig.15. Fly ash concrete shows relatively higher value of permeability coefficient compared to OPC concrete for early age of curing. But at later age of curing reverse trend was observed. Coefficient of permeability value for M28FA20, M28FA30, M28FA40 and M28FA60 concretes are 9%, 2%, 6% and 31% higher as compared to M28FA0 concrete, 14%, 19%, 22% and 46% higher for M38FA20, M38FA30, M38FA40 and M38FA60 concrete compared to M38FA0 concrete for 30 cycles of freeze-thaw in plain water. But this value for 20%, 30%, 40% and 60% cement replaced fly ash concrete for 180 cycles of freeze-thaw are observed respectively 12%, 19%, 21% and 9% lower for M28 grade concrete and 17%, 22%, 26% and 12% lower for M38 grade concrete. Fly ash has high fineness and can react with the products liberated during hydration. It forms secondary C-S-H gel that fills all the pores inside concrete specimen that makes the concrete dense and compact, as a result coefficient of permeability decreases with the increase of fly ash content upto certain level. Similar trend was also observed for freeze-thaw action in sea water. After 30 cycles of freeze-thaw in sea water, coefficient of permeability value for M33FA20, M33FA30, M33FA40 and M33FA60 concretes are 16%, 25%, 31% and 47% higher as compared to M33FA0 concrete of similar freeze-thaw condition; whereas the permeability value for M33 grade concrete is decreased by 15%, 18%, 20% and 43% for 20%, 30%, 40% and 60% cement replaced fly ash concrete compared to OPC concrete of similar condition in plain water.

It is seen that as the concrete exposed to sea water loses its mass due to surface erosion and splitting, the coefficient of permeability increases significantly; whereas concrete exposed to plain water show relatively lower changes in their permeability. After 180 cycles, the permeability of concrete specimens exposed to sea water has been found to lie in the range of 4.76 to 14.52 x 10^{-12} m/sec, whereas the corresponding value for the concretes placed in plain water lies in the range of 2.61 to 8.35 x 10^{-12} m/sec. Thus, it is seen that the permeability of concrete at the end of 180 cycles of freeze-thaw exposed to sea water in the freezing-thawing environment is about two times the permeability value of the concrete placed in plain water environments. Thus, it is seen that at the end of 180 cycles of freeze-thaw, the permeability of concrete exposed to sea water in the freezing-thawing environment is at about two times the permeability value of the concrete placed in plain water environments. The larger increase in the permeability of the concrete specimens in the freezing-thawing environment of sea water may be due to the formation of relatively greater amounts of total expansive/leachable compounds as compared to plain water environments.

Relatively lower values of coefficient of permeability are found to associate with relatively higher grade of concrete. Among all the concrete studied, for 180 cycles of freeze-thaw, coefficient of permeability value as compared to OPC concrete was observed as 12%, 19%, 21% and 9% lower for M28FA20, M28FA30 M28FA40 and M28FA60 concrete respectively, 16%, 17%, 22%, and 11% lower for M33FA20, M33FA30, M33FA40 and M33FA60 concrete respectively, 17%, 22%, 26% and 12% lower for M38FA20, M38FA30, M38FA40 and M38FA60 concrete respectively for plain water condition; whereas the same value for 20%, 30%, 40%, 60% cement replaced fly ash concrete in sea water was observed as 65%, 54%, 46% and 66% higher for M28 grade concrete, 54%, 49%, 43% and 63% higher for M33 grade concrete and 46%, 42%, 34% and 53% higher for M38 grade concrete as compared to OPC concrete of similar grade in plain water. Overall observation revels that fly ash concrete has better resistance against water permeability. Permeability decreases very rapidly at the initial ages of curing and the rate depends on grade of concrete. The progressive decrease in permeability may be connected to the micro voids dispersed in the mortar matrix of the concrete. As the hydration of cement progresses, crystallization of compounds take place as a result of which the concrete micro voids keep on getting subdivided into capillary micro pores of increasingly smaller sizes. Many of the micro pores lose their connectivity with the passage of time. The reduction in pore sizes coupled with the loss of pore connectivity result in a substantial progressive decrease in the permeability. Among all the fly ash concretes studied upto 180 cycles of freeze-thaw in plain water and sea water, 30% and 40% cement replaced fly ash concrete shows better result from water permeability test point of view.

Rapid chloride penetration

Rapid chloride penetration test (RCPT) value for OPC and fly ash concrete for 30, 90 and 180 of freeze-thaw in plain water and sea water are graphically presented in Fig.16, Fig.17 and Fig.18. In case of OPC concrete, amount of passing charge is observed as 3896, 5213 and 6198 coulombs for M38, M33 and M28 grade concrete; whereas the similar value for fly ash concretes of cement replacement level of 20%, 30%, 40% and 60% are 3224, 3025, 3216 and 3949 coulombs for M38 grade concrete, 5134, 4784, 4435 and 5467 coulombs for M33 grade concrete and 6783, 6891, 7105 and 7518 coulombs for M28 grade concrete at 30 cycles of freeze-thaw in plain water. For longer cycles of freeze-thaw, fly ash concrete show better resistance against chloride ion penetration. After 90 cycles of freeze-thaw, rapid chloride penetration values are respectively 5%, 11%, 8% lower in plain water and 20%, 13%, 17% higher in sea water for M38FA20, M38FA30, M38FA40 concretes; 4%, 10%, 6% lower in plain water and 13%, 8%, 11% higher in sea water for M33FA20, M33FA30, M33FA40 concretes and 2%, 6%, 8% lower in plain water and 16%, 12%, 9% higher in sea water for M28FA20, M28FA30, M28FA40 concretes respectively as compared to the RCPT value of OPC concrete of similar grade and under same span of freeze-thaw cycle in plain water. The incorporation of pozzolanic materials improved the resistance to chloride penetration of concrete as confirmed by other researchers (Janotka, 2000). A close observation of the data shows that fly ash concrete has relatively better resistance against chloride ion penetration and hence the use of fly ash in structural concrete may inhibits the risk rebar corrosion. Effects of sea water on RCPT values for freeze-thaw cycles are more noticeable as compared to plain water. After 180 cycles of freeze-thaw, rapid chloride penetration values are 2%, 8%, 4% lower for M38FA20, M38FA30, M38FA40 concretes; 7%, 11%, 14% lower for M33FA20, M33FA30, M33FA40 concretes and 6%, 9%, 12% lower for M28FA20, M28FA30, M28FA40 concretes in plain water; whereas the same value is 5%, 10%, 11% higher for M38FA20, M38FA30, M38FA40 concretes; 7%, 3%, 2% higher for M33FA20, M33FA30, M33FA40 concretes and 12%, 5%, 3% higher for M28FA20, M28FA30, M28FA40 concretes respectively in sea water as compared to the RCPT values of OPC concrete of similar grade in plain water.

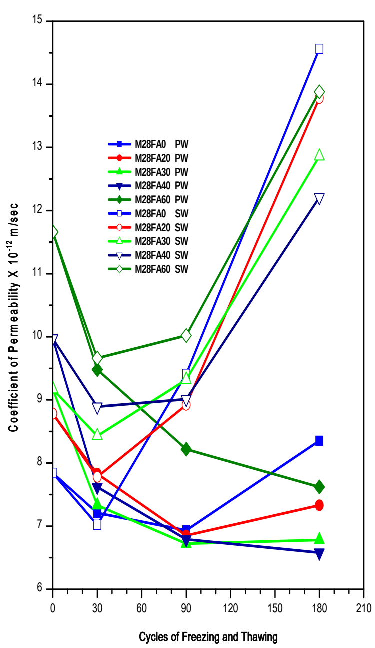

Fig.15: Permeability - Freeze Thaw Relation for M28 Grade Concrete

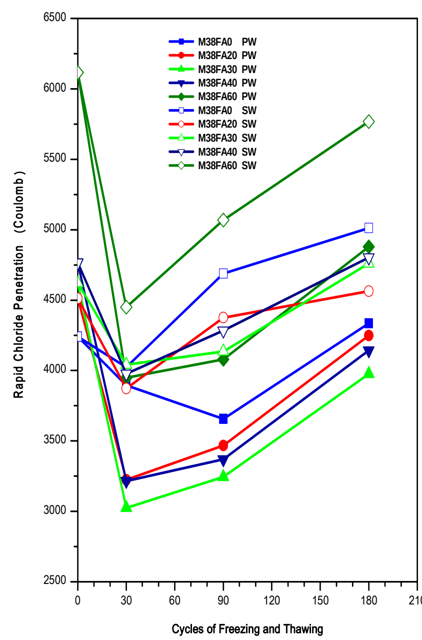

Fig.16: Rapid Chloride Penetration - Freeze Thaw Relation for M38 Grade Concrete

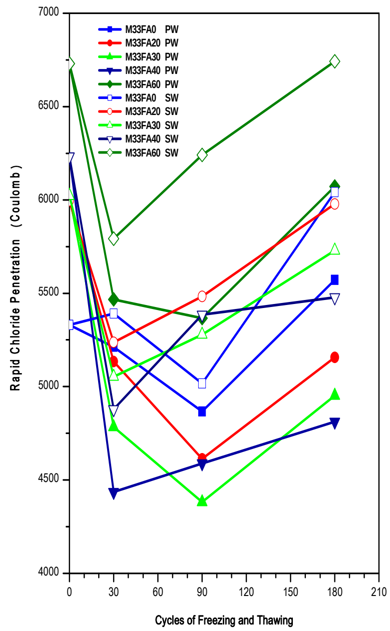

Fig.17: Rapid Chloride Penetration - Freeze Thaw Relation for M33 Grade Concrete

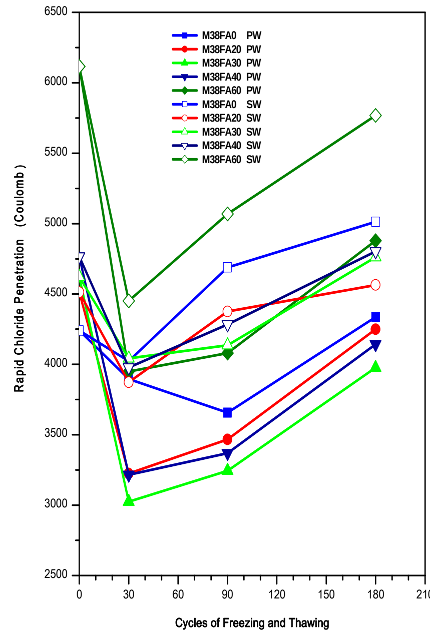

Fig.16: Rapid Chloride Penetration - Freeze Thaw Relation for M38 Grade Concrete

Relative RCPT values of fly ash concrete compared to OPC concrete is observed to vary with the grade of concrete and replacement level of fly ash with cement. After 30 cycles of freeze-thaw, rapid chloride penetration values are 77%, 71%, 76%, 93% for plain water and 91%, 95%, 94%, 105% for sea water for M38FA20, M38FA30, M38FA40, M38FA60 concretes respectively; 96%, 90%, 83, 103% for plain water and 98%, 95%, 92%, 109% for sea water for M33FA20, M33FA30, M33FA40, M33FA60 concretes respectively and 108%, 109%, 113%, 119% for plain water and 111%, 112%, 114%, 125% for sea water for M28FA20, M28FA30, M28FA40, M28FA60 concretes respectively as compared to RCPT value of 28 days plain water cured of OPC concrete. Also after 180 cycles of freeze-thaw, RCPT values for 20%, 30%, 40%, 60% replacement level concrete are 101%, 94%, 98%, 115% for plain water and 108%, 112%, 113%, 136% for sea water for M38 grade concrete; 97%, 93%, 90%, 114% for plain water and 112%, 107%, 103%, 126% for sea water for M33 grade concrete; 101, 99%, 96%, 122% for plain water and 120%, 112%, 110%, 115% for sea water for M28 grade concrete respectively as compared to 28 days plain water cured OPC concrete of similar grade. This is due to high fineness of fly ash. It can react with the products liberated during hydration, forming secondary C-S-H gel that fills all the pores inside concrete. As a result the pore spaces inside the concrete specimen are reduced, that makes the concrete dense and compact and makes it more impermeable (Sarkar et al, 1995). As a result flow of charge through the concrete sample is decreased. It was also observed that at the end of 180 cycles of freeze-thaw, the overall RCPT values for M38 grade concrete is around 2% and 4% lower for plain water and around 5% and 9% lower for sea water as compared to M33 and M28 grade concrete respectively.

6. Conclusions

The main objective of the study was to evaluate the performance of fly ash concrete using Boropukuria coal ash under the action alternate Freezing-Thawing in sea water environment.

Specimens from three grades of concrete with different cement replacement level were used in plain water as well as sea water environment over 180 Ferrze-Thaw cycles to observe the deteriorative effect. The results of the Freeze-Thaw investigation were critically analyzed and interpreted. Based on the limited number of tests and variables studied over the specific freeze-thaw cycles, the following conclusions are drawn:

(1) Concrete under the cyclic Freeze-Thaw action in sea water shows more deterioration in terms of surface erosion, crumbling etc than in plain water. Hence concrete under Freeze-Thaw action in sea water can be considered much more vulnerable to deterioration than in plain water.

(2) Chloride penetration resistance for fly ash concrete is observed to be relatively higher as compared to OPC concrete. After 180 cycles of freeze-thaw, 30% and 40% fly ash mix concrete showed better resistance of around 9% in plain water and 6% in sea water against chloride penetration.

(3) A significant change in permeability (k value) characteristics of concrete in freeze-thaw environment is observed particularly when exposed to sea water. Also fly ash concrete shows better resistance against water permeability. After 180 cycles of freeze-thaw, fly ash concrete with 30% and 40% cement replacement level showed lower coefficient of permeability of around 21% in plain water and 28% in sea water as compared to OPC concrete.

(4) Sea water causes the most detrimental effect on the compressive strength of concrete, the loss being of the order of 7% in plain water and 17% in sea water after 180 cycles of freeze-thaw action. The study reveals that 30% and 40% blending of fly ash in concrete exhibited the best results with respect to resistance against compressive strength deterioration. Such concrete shows higher compressive strength of around 12% in plain water and 22% in sea water as compared to OPC concrete after 180 cycles of freeze-thaw action.

(5) The loss in weight of concrete specimen is found to the extent upto 6.7% in sea water and around 2.2% in plain water due to surface erosion and crumbling in the freeze-thaw environment. Fly ash concrete shows better resistance against weight change as compared to OPC concrete.

(6) Concrete also shows a significant decrease in volume as much as 0.83% in sea water and around 0.21% in plain water under freeze-thaw action. Also it is observed that fly ash concrete has better resistance regarding dimensional instability as compared to OPC concrete.

(7) The use of fly ash in cement production reduces the problem of its disposal, saving the valuable fertile lands and the use of clinker, the production of which consumes a lot of energy and natural resources.

(8) Higher grade concrete showed better resistance against strength deterioration, lower coefficient of permeability value and lower rapid chloride penetration as compared to lower grades of concrete.

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