Journal of Civil Engineering (IEB), 46 (1) (2018) 53-68

Journal of Civil Engineering IEB

Durability characteristics of fly ash blended concrete in marine environment

Md. Moinul Islam, A. K. M. Arifuzzaman, Md. Tarequl Alam and Md. Saiful Islam

Department of Civil Engineering
Chittagong University of Engineering & Technology, Chittagong 4349, Bangladesh

Received 05 December 2017

Abstract

This paper investigates the performance of fly ash concrete exposed to artificially made seawater. Concrete specimens of 100 mm cubical size were cast and cured for 28 days in plain water before exposure to different seawater environments. Physical as well as chemical aspects regarding the deterioration of OPC Concrete and fly ash concrete of cement fly ash ratios 90:10, 80:20 and 70:30 have been studied in plain water and artificially made seawater of normal and enhanced salt concentration over the periods of 30, 90 and 180 days. The specimens were taken out periodically and subjected to various tests including visual examination, weight change, volume change, compressive strength, ultrasonic pulse velocity, carbonation, chloride content and pH value at various depth levels. After 180 days curing, the loss in compressive strength as compared to plain water cured specimens of similar age are reported to lie in the range of 6.7% to 28.7% for OPC and 5.8% to 25.8% for 80:20 fly ash concrete. Also fly ash concrete of mix 80:20 exhibits 3% to 15% lower chloride penetration at 15 to 25 mm depth levels as compared to OPC concrete due to restricted penetration of sea slats in fly ash concrete. The study reveals that fly ash concrete of mix 80:20 may effectively improve the strength and durability characteristics of concrete.

Keywords: Fly Ash, Marine Environment, Chloride attack, Ultrasonic Pulse Velocity, Durability, Compressive strength.

1. Introduction

Concrete is the most widely used construction material for onshore/offshore structure all over the world. It is due to its inherent durable characteristics that provide excellent resistance to deterioration. Concrete consumption in the year of 2000 was estimated at 12 billion tons and due to rapid development of infrastructures of developing countries, it is expected that in year 2050, annual consumption of concrete would reach 18 billion tons per year (Mehta 2002). The expanded uses of concrete have increased the interest of scientists/researchers for its use in aggressive environment such as marine environment. Good quality concrete provides excellent protection to the embedded steel reinforcement against corrosion. A well design concrete can survive up to its design life without any major repair/maintenance work in adverse surrounding environment. The construction/repair cost as well as time and energy spent for marine structure are higher as compared to similar structures in other environment as the rate of deterioration in such location is reported to be higher than that for other structure. Thus, it is required to ensure satisfactory performance of structural concrete used for marine structure.

2. Marine environmental characteristics

Marine environment indicates the environment surrounded by seawater. Seawater is a complex solution of many salts and also containing living matter, suspended silt, dissolved gases and decaying organic materials. The term marine environment is generally well understood but the complexities inherent in it are not usually clear. The existence of this environment is not just over the sea, but it could be deemed to be extending over the coast and neighborhood of tidal creeks, backwaters and estuaries. 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.

Thus, the structures located around the adjacent areas of the sea have the equal possibilities to be affected by this environment. The average salt concentration of seawater is 3.5% although it varies from sea to sea depending upon geological condition (Ref. Table 1). Actually, seawater contains appreciable percentage of chloride ion and is reported as the most harmful to the hydrated product of cement as well as the embedded rebar. 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} (Tumidajski 1995).

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. Hence prior the construction of any concrete structure in such location, proper steps should be taken to overcome the risk of deterioration of concrete due to chloride, sulfate and other sea salt ion attack.

Table 1
Average salt concentration in different seas (Kaushik 1995)

Sea	Salt Concentration (%)
Mediterranean	3.8
Baltic	0.7
North sea and Atlantic	3.5
Black Sea	1.8
Dead Sea	5.3
Indian Sea	3.55

2.1 Chloride attack

The compounds of chloride form the highest proportion i.e. around 89% of the total dissolved salts present in SW. Regarding ionic composition, it provides about 55% of the total salt ion concentration. 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.

2.2 Sulfate attack

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.

2.3 Other attacks

The hydrated product of cement has a tendency to combine with atmospheric CO_2 and forms carbonates that partly neutralizes the alkaline pore solution of concrete. This is known as carbonation and as a result, the pH changes from about 13 to neutrality. When carbonation depth exceeds the depth of cover to reinforcement, the passivity of the steel is lost and the salt ions find a suitable environment leading to greater corrosion. Concrete is most vulnerable to carbonation when relative humidity is between 50% to & 80%. Below 50%, moisture film does not form on the surface of pores of concrete while above 75% the pores being possibly blocked with water don't provide the access of CO_2.

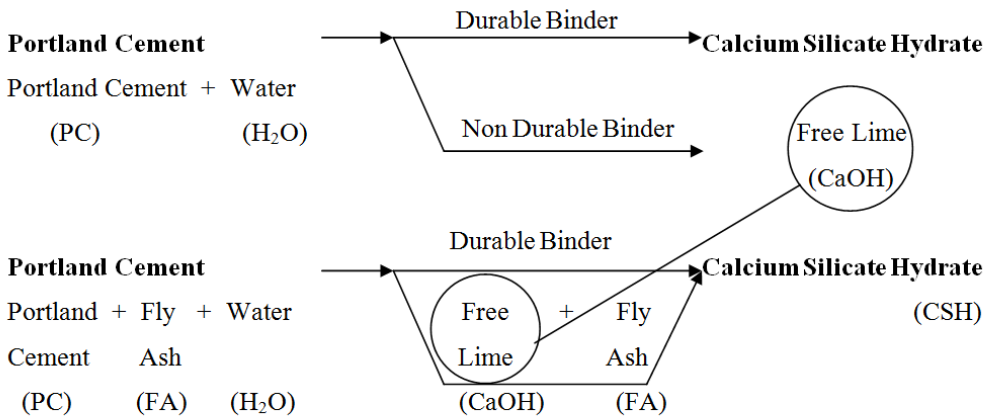

Fig. 1. Hydration mechanism of fly ash concrete.

3. Characteristics of fly ash as cementitious material

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 (Ozkan 2009). These mineral admixtures may impart proper resistance to chloride and sulfate induced deterioration by modifying the chemistry of pore characteristics of the hardened concrete (Zichao 2003).

Mineral 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 (Erdogan 2014). 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 (Filho 2013). 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 (Serdar 2007). Due to continued pozzolanic reactivity, concrete develops strength at later age, which may exceed the strength of the concrete without fly ash as shown in Figure 1.

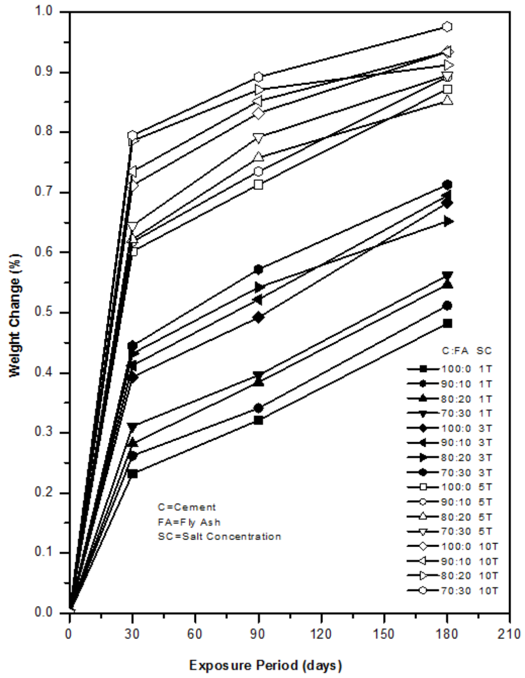

Fig. 2. Weight change-exposure time relation for fly ash concretes exposed to different marine environments.

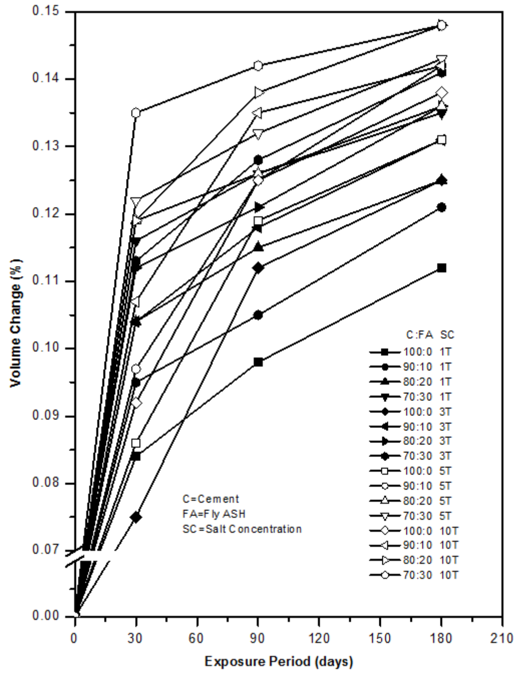

Fig. 3. Volume change-exposure time relation for fly ash concretes exposed to different marine environments.

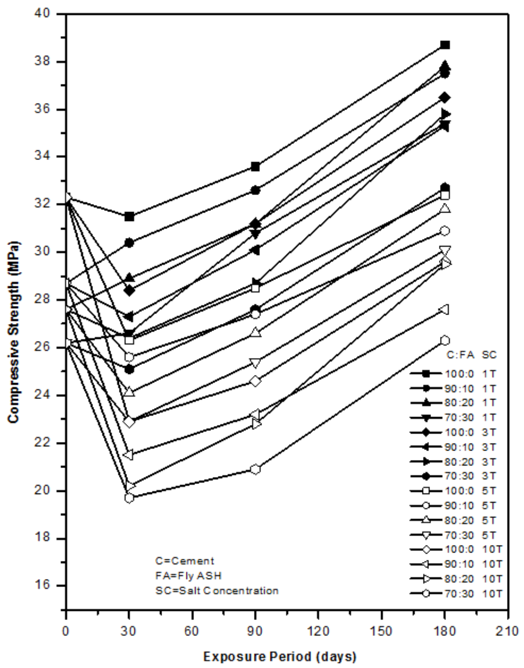

Fig. 4. Compressive strength-exposure time relation for fly ash concretes exposed to different marine environments.

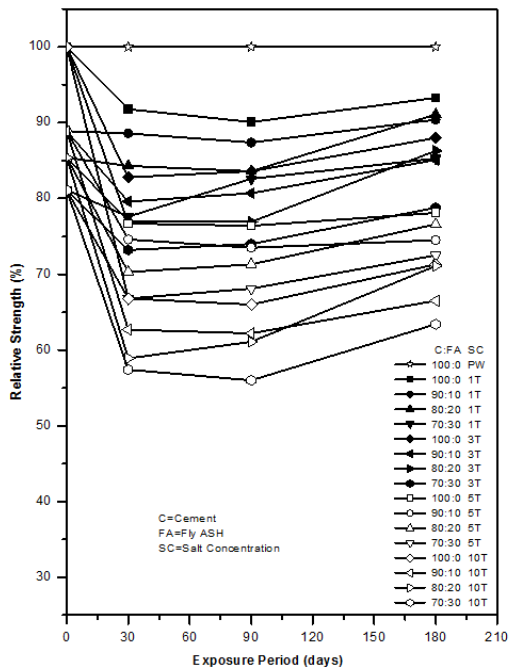

Fig. 5. Relative strength-exposure time relation for fly ash concretes exposed to different marine environments.

The pozzolanic reaction also contributes in 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 (Marthong 2012). 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 (Durán-Herrera 2011).

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 (Plank 2015). The beneficial use of coal burning power plant fly ash in concrete has increased the interest of researcher for the evaluation of the performance of such concrete exposed to various aggressive environments. The relevant studies indicate that the percentage of cement replaced with fly ash and their relative proportion for making concrete in such environment is very important (Juenger 2015).

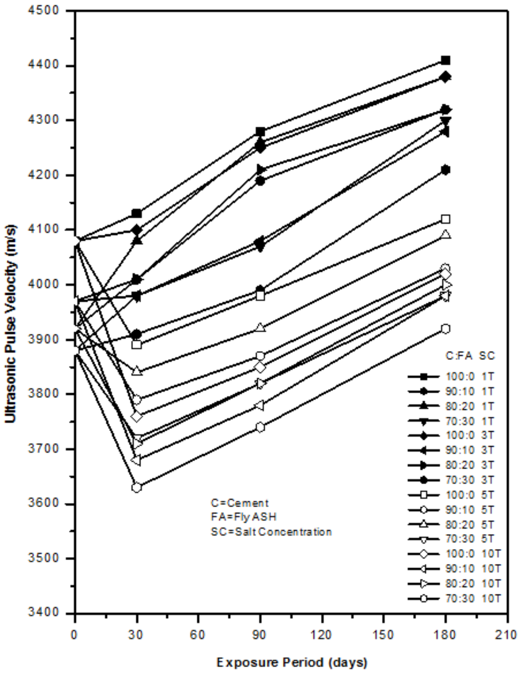

Fig. 6. UPV-exposure time relation for fly ash concretes exposed to different marine Environments.

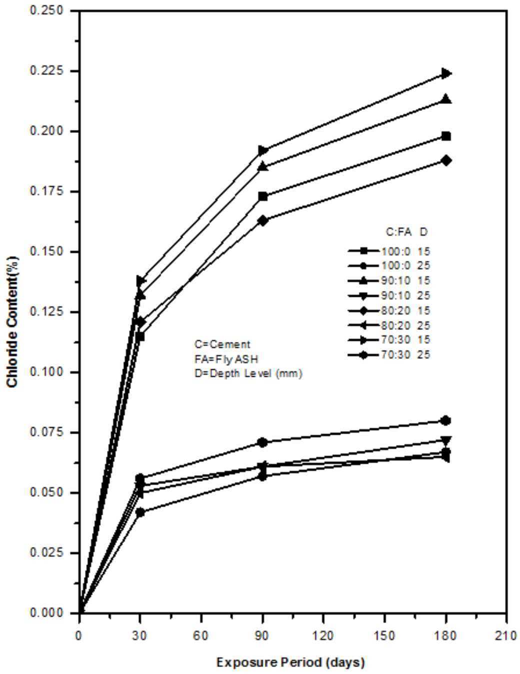

Fig. 7. Chloride content-exposure time relation for fly ash concretes exposed to sea water of 5T concentration.

The progress of cement hydration reaction and the rate of penetration of different salt ions in tropical condition are reported to be much faster than those of cold countries like Europe and North America. A judicious use of fly ash in concrete making can decrease the incidence of chloride induced corrosion of the reinforcement in concrete structures (Haque 1992). Concrete mixes made by replacing cement with fly ash are reported to show better results for compressive strength, tensile strength, flexural strength, freezing and thawing resistance, shrinkage, permeability and abrasion resistance than conventional concrete mixes (Tarun 1996). Fly ash has dual effects in concrete i.e. as a micro-aggregate and as a pozzolana.

Fly ash improves the interfacial bond between the paste and the aggregates in concrete (Poon 2001). According to Malhotra (2000), the concrete incorporating moderate and high volumes of fly ash showed superior resistance against strength deterioration, rebar corrosion and the penetration of chloride ions compared to the control concrete specimen.

4. Research significance

The net cement production in the world is expected to increase form about 1.4 billion tons in 1995 to around 5 billion tons in the year of 2040 (IEA 2006). Portland cement is the most important constituent of concrete. Unfortunately, cement manufacturing consumes large amount energy about $7.36*10^6$ kJ per ton of cement (Tarun 2003). Also, approximately 1 ton of CO_2 is released into the atmosphere during the production of 1 ton of cement (Min-Hong 2001). This would lead to the emission of about 2 billion tons to CO_2 in the atmosphere every year (Alain 2000).

Table 2
Physical properties and chemical analysis of Ordinary Portland Cement and Fly Ash

Physical properties	ASTM Type-I cement	Fly ash
	Fineness	
Passing #200 Sieve, %	95%	99%
Blains, m^2/kg	340	400
	Chemical analysis, %	
Calcium oxide, CaO	65.18	8.6
Silicon dioxide, SiO_2	20.80	59.3
Aluminum oxide, Al_2O_3	5.22	23.4
Ferric oxide, Fe_2O_3	3.15	4.8
Magnesium oxide, MgO	1.16	0.6
Sulfer trioxide, SO_3	2.19	0.1
Sodium Oxide, Na_2O	Not measured	3.2
Loss on ignition	1.70	Not measured
Insoluble residue	0.6	Not measured

In order to reduce the harmful greenhouse effect, use of cement must be replaced with other environmentally friendly and efficient cementitious material such as fly ash (Mark 2006). It also ensures the proper utilization of fly ash, by-product of coal combustion in power plants, in an effective way which otherwise been dumped making environmental hazard. Relevant literature reveals that addition of fly ash in making structural concrete reduces the permeability of concrete, which in turns resist the penetration of harmful salt ions within the concrete structure. Performance of fly ash concrete as a partial replacement of cement in aggressive environments and their relative proportion is very important. Optimum use of fly ash must be ensured to achieve the desired strength as well as durability requirement of the structural concrete. This paper investigates the durability aspects including strength behavior of fly ash concrete in seawater environment. Concrete test specimens made from various fly ash cement ratios were exposed to seawater of different concentration over a period of 180 days to get an idea for optimum mix ratio of fly ash concrete in such location.

5. Experimental program

The experimental program was carried out to study the different aspects of deterioration of fly ash concrete specimens such as compressive strength, ultrasonic pulse velocity, variation of concrete alkalinity, chloride content at different depth levels in plain water and in laboratory made seawater of different concentrations over a period of 6 months. The variable parameters studied and the materials involved were as follows:

(a) Cement: Ordinary Portland cement of ASTM Type-I was used as binding material. Its physical properties and chemical composition are given in Table 2.

(b) Fly ash: ASTM Class F Fly ash was used in this investigation which is normally produced by burning anthracite or bituminous coal. It was collected from Barapukuria Thermal Power Station, Bangladesh. Chemical compositions of the used fly ash are given in Table 2.

(c) Aggregates: Locally available natural sand passing through 4.75 mm sieve and retained on 0.075 mm sieve was used as fine aggregate with fineness modulus of 2.59 and specific gravity 2.68. The coarse aggregate was crushed stone with a maximum nominal size of 12.5 mm with fineness modulus 6.50 and specific gravity 2.69. Both the aggregates were washed carefully before use in the concrete mix. The grading of the aggregates is shown in Table 3.

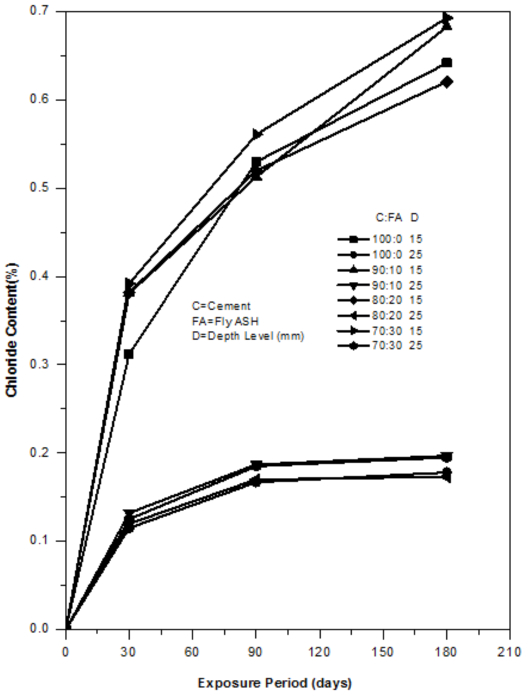

Fig. 8. Chloride content-exposure time relation for fly ash concretes exposed to sea water of 10T concentration.

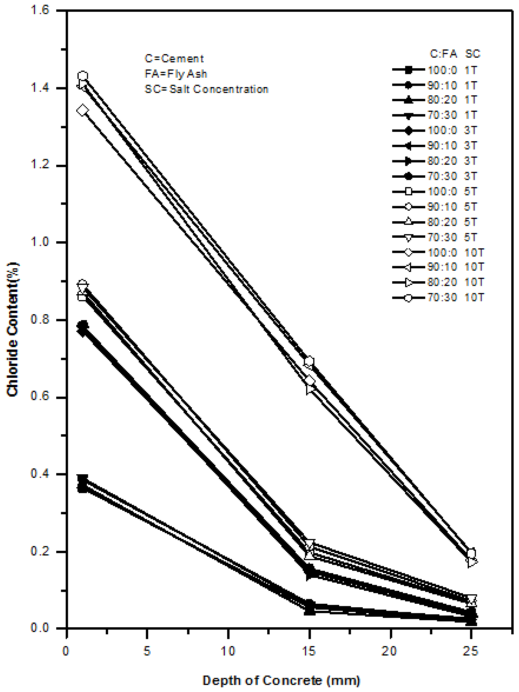

Fig. 9. Chloride concentration profile for fly ash concretes exposed to different marine environments (Age 6 months).

5.1 Variables studied

In the present investigation, fly ash has been used as blended admixture. Fly ash was added to the concrete mix as partial replacement of OPC. Three different replacement levels were used. For comparison, a concrete mix made from 100% OPC was also included in this program. Table 4 describes the mixture proportion of concrete used for the present study. Different variables studied are listed below:

(a) Curing Solution: Plain water (PW) as well as seawater (SW) of four different concentrations (1T, 3T, 5T and 10T) was used for curing test specimens. The 1T seawater means normal seawater made in the laboratory by mixing tap water with exact amount and proportion of different salts generally found in natural seawater (Ref. Table 5). Thus 3T, 5T and 10T seawater have salt ion concentrations enhanced to 3, 5 and 10 times chemical compounds respectively as that of 1T solution. The enhanced concentration was used to obtain accelerated effects.

(b) Concrete Quality: Four different grades of concrete with cement fly ash ratios 100:0, 90:10, 80:20, 70:30 designated as C100FA0, C90FA10, C80FA20, C70FA30 respectively were used for this investigation.

(c) Exposure Periods: Test specimens were tested periodically after the specific curing periods of 30, 90 and 180 days.

5.2 Specimen preparation and curing

Around 375 cubical specimens of 100 mm size from three different grades of fly ash concretes (with 10%, 20% and 30% cement replacement) and OPC concrete were prepared as described in Table 6. The specimens were taken out from mould after 24 hours of casting and cured in plain water at 27±2º C. After 28 days plain water curing, they were placed in seawater of different concentration (1T, 3T, 5T, 10T) as well as plain water for different exposure periods (30, 90, 180 days).

5.3 Test conducted

After specific exposure period, several destructive and non-destructive tests were performed. The non-destructive tests comprise of visual appearance, change in weight and volume, ultrasonic pulse velocity (ASTM C597) etc. Destructive tests include determination of compressive strength (BS EN 12390-3:2009), carbonation depth, pH value, and chloride contents at various depths levels. Some of the specimen were split into two halves and subjected to carbonation test with the help of phenolphthalein indicator solution. Concrete powder was drilled out form surface (0-3 mm), 15 mm and 25 mm depths levels 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. Out of the total chloride content, the water soluble chloride is reported to be responsible for rebar corrosion in concrete and hence, only water soluble chloride content was determined by silver nitrate titration according to Volhard method and was expressed as a percentage of the concrete mass. Using same powder sample, the pH values of concrete at different depth levels were determined.

6. Results and discussions

The concrete specimens made from OPC and fly ash concrete are exposed to plain water as well as seawater of different concentration for various exposure periods. Plain water cured concrete is considered as datum and used to compare the detrimental effect of marine environment on concrete specimens. The test results obtained after specific periods were critically analyzed, discussed and presented in graphical form to arrive at some conclusions there from.

6.1 Visual examination

Outer surface of the specimens indicates no sign of cracks or damages. Specimens cured in plain water showed almost no color change whereas the specimens cured in seawater showed some color change from off white to grey. This change in color occurs due to salt deposition.

6.2 Weight change

The weight changes for fly ash concretes exposed to different environments are shown in Figure 2. Increases in weight are seen to vary in between 0.06% to 0.98%. After 180 days plain water curing, the weight change value is 0.28% for OPC concrete, whereas these values are 0.30%, 0.31% and 0.32% for C90FA10, C80FA20 and C70FA30 concrete respectively. Thus, a clear trend of increasing weight change with the increasing percent of cement replacement is noticed. In case of seawater curing, after 180 days curing, C70FA30 concrete shows a weight change of 0.90% and 0.98% for seawater concentration of 5T and 10T. Thus, with increasing salt concentration in curing solution, higher percentage increase in weight is observed without showing any definite pattern. This may be due to penetration of higher amount of salt inside concrete. Weight change values after 180 days curing in seawater of 5T concentration are 0.872%, 0.892%, 0.852% and 0.895% for OPC, C90FA10, C80FA20 and C70FA30 concrete respectively. Overall observation indicates that C80FA20 concrete shows relatively lower percentage increase in weight change indicating its greater resistance against weight change compared to other specimens.

Table 3
Grading of aggregates

Coarse aggregate		Fine aggregate	
Sieve size, mm (in)	Cumulative percentage retained	Sieve size, mm (in)	Cumulative percentage retained
19	0	4.75	0
12.5	0	2.36	4.5
9.5	54	1.18	20.5
4.75	100	0.6	47.5
–	–	0.3	87.9
–	–	0.15	98.8
–	–	Pan	100

Table 4
Mixture proportion and properties of concrete used

Mixture constituent & properties	Mix Type*			
	C100FA0**	C90FA10	C80SA20	C70FA30
Cement (kg/m^3)	375	338	300	263
Fly Ash (kg/m^3)	--	47	90	135
Water (kg/m^3)	169	166	164	161
Sand (SSD) (kg/m^3)	728	728	728	728
Stone chips (SSD) (kg/m^3)	1148	1148	1148	1148
Slump, mm	62	66	67	69
Air content, %	1.4	1.3	1.2	1.4
Unit weight (kg/m^3)	2332	2339	2342	2347

** C – Cement; FA – Fly Ash; C90FA10 means Cement: Fly Ash = 90:10*
*** C100FA0 means OPC Concrete*

6.3 Volume change

The changes in volume of fly ash concretes exposed to plain water and seawater of various concentrations has been shown in Figure 3. Increase in volume change is seen to vary in between 0.082% to 0.131%. After 180 days curing in plain water, OPC concrete shows a volume change of 0.104% whereas for C90FA10, C80FA20 and C70FA30 concrete, the corresponding values are 0.125%, 0.113% and 0.131% respectively for similar curing condition. Thus in PW curing, OPC concrete shows better resistance against volume change than fly ash concrete. It is also observed that in most of the cases, percentage of volume changes increase with the increase in seawater concentration. After 180 days exposure period, C80FA20 concrete shows the volume change of 0.12%, 0.131%, 0.136% and 0.142% in 1T, 3T, 5T and 10T seawater. Volume change is caused by the formation of expansive compound after chemical reaction of seawater with hydrated cementitious products. The volume change values after 180 days curing in seawater of concentration 5T are 0.142%, 0.136% and 0.143% for C90FA10, C80FA20 and C70FA30 concrete whereas the corresponding value is 0.138% for OPC concrete. Fly ash concrete shows relatively better resistance against volume change during later age of curing. The resistance against volume change particularly at later ages may be due to the slower rate of hydration of fly ash and its ability to resist the production of expansive compound in concrete. Also after 180 days curing in seawater of 10T concentration, volume change values are 0.131%, 0.148%, 0.142% and 0.148% for OPC, C90FA10, C80FA20 and C70FA30 concrete respectively. However the overall volume change data indicate that the percentage volume change is relatively lower for C80FA20 concrete among all the fly ash concrete studied.

Table 5
Specified salt contents of artificial seawater used in experimental program (Myers, 1969)

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 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	

Table 6
Experimental program for the investigation

Mix Type	Curing / Exposure period	No. of test specimen*	Environmental condition: Exposure state	Environmental condition: Curing solution (PW/SW)	Total no of specimen	Types of test
	(a)	(b)	(c)	(d)	(e=a*b*c*d)	
C100FA0	28 days (precuring)	3	SUB	PW	3	1. Weight change. 2. Volume change 3. Compressive strength 4. UPV 5. Carbonation 6. Chloride content 7. pH value
C90FA10		3			3	
C80FA20		3			3	
C70FA30		3			3	
C100FA0	30 days, 90 days, 180 days (after precuring)	6**	SUB	PW, 1T, 3T, 5T, 10T	90	
C90FA10		6			90	
C80FA20		6			90	
C70FA30		6			90	
Total specimen required for the whole program					372	

SUB: Submerged, Specimen size: 100 mm (4 in) Cube
* *The number of replication for each test = 3*
** *3 samples for compressive test + 3 samples for chemical test*

6.4 Compressive strength

The compressive strength of OPC and fly ash concretes exposed to different marine condition has been graphically presented in Figure 4. Also for the ease of comparison, the relative compressive strengths are plotted in Figure 5. The strength values corresponding to “0” day curing period mean the strength of the specimens after 28 days plain water curing. In the case of plain water curing, for OPC concrete, compressive strength for 30 days exposure period is 34.3 MPa whereas this value for C70FA30 concrete is 28.5 MPa. But after 180 days curing, compressive strength values are 41.5 MPa and 39.1 MPa for OPC concrete and C70FA30 concrete respectively. It may be due to slow hydration rate of fly ash as mentioned by Ogwa (1980). The gain in strength at early age, although comparatively lower, fly ash concrete attains almost the same strength as that of OPC concrete at the later age of curing.

Table 7
Chloride Content (%) for Fly Ash Concretes Exposed to Different Marine Environments for Various Depth Level

Mix proportion (C:FA)	Exposure period (Days)	1T			3T		
		Cover Depth(mm)					
		1-3	15	25	1-3	15	25
C100FA0	30	0.141	0.021	0.011	0.404	0.073	0.019
	90	0.259	0.034	0.014	0.602	0.133	0.027
	180	0.365	0.056	0.019	0.771	0.148	0.038
C90FA10	30	0.157	0.023	0.014	0.415	0.082	0.021
	90	0.265	0.040	0.018	0.631	0.143	0.031
	180	0.386	0.065	0.023	0.785	0.152	0.042
C80FA20	30	0.144	0.025	0.014	0.405	0.069	0.021
	90	0.261	0.036	0.016	0.612	0.125	0.026
	180	0.372	0.046	0.018	0.781	0.140	0.032
C70FA30	30	0.162	0.029	0.017	0.421	0.085	0.024
	90	0.271	0.039	0.021	0.625	0.141	0.036
	180	0.390	0.061	0.026	0.785	0.156	0.043
		5T			10T		
C100FA0	30	0.574	0.115	0.042	0.732	0.312	0.115
	90	0.721	0.173	0.057	1.073	0.530	0.167
	180	0.862	0.198	0.067	1.342	0.642	0.178
C90FA10	30	0.584	0.132	0.053	0.819	0.381	0.132
	90	0.763	0.185	0.061	1.183	0.513	0.187
	180	0.892	0.213	0.072	1.405	0.683	0.197
C80FA20	30	0.531	0.121	0.050	0.752	0.382	0.120
	90	0.731	0.163	0.061	1.093	0.520	0.170
	180	0.872	0.188	0.065	1.412	0.621	0.173
C70FA30	30	0.589	0.138	0.056	0.825	0.392	0.125
	90	0.753	0.192	0.071	1.212	0.561	0.185
	180	0.884	0.224	0.080	1.432	0.693	0.195

Effect of seawater on the compressive strength of fly ash concrete has also been explained in terms of relative strength. In case of 30 days curing period, reduction of strengths as compared to plain water curing are 8.2%,17.2%, 23.3% and 33.2% for OPC concrete cured in seawater of 1T.3T, 5T and 10T concentration, whereas the corresponding values are 5.5%, 9.9%, 16.3% and 25.7% for C70FA30 concrete and also for C80FA20 and C90FA10 concrete, the corresponding values are 4.6%, 11.9%, 18.6%, 30.0% and 6.4%, 15.4%, 20.4%, 32.3% respectively. This may due to entrance of seawater into concrete, which reacts with hydrated product of cement and fly ash that form ettringite or frields salt. Due to formation of these expansive compounds, micro cracks are developed inside the concrete and their subsequent propagation with the progress of hydration weakens the bond between hydrated product and aggregate particles. Ultimate result is the deterioration of concrete and the loss in compressive strength (Wee, 2000). After 180 days curing, the strength reduction values are 6.7%, 12.0%, 21.9% and 28.7% for OPC concrete, 8.9%, 15.4%, 21.7% and 30.8% for C70FA30 concrete; 5.8%, 10.6%, 20.3% and 25.8% for C80FA20 concrete and 7.9%, 13.2%, 23.8% and 31.8% for C90FA10 concrete cured seawater of 1T, 3T, 5T and 10T concentration respectively. From the above discussion, it is clear that fly ash concrete shows comparatively higher compressive strength when cured in seawater of different concentration for various curing periods. Among all the fly ash concretes, C80FA20 concrete shows the highest strength at larger curing periods and in any curing condition. The higher strength development at later periods may be due to the higher degree of fineness of fly ash which after hydration blocks the pores inside the concrete thereby reducing its permeability. As a result, entrance of seawater i.e. penetration of salt ions in concrete is restricted and thus the rate of deterioration decreases that ultimately leads to impart higher concrete compressive strength.

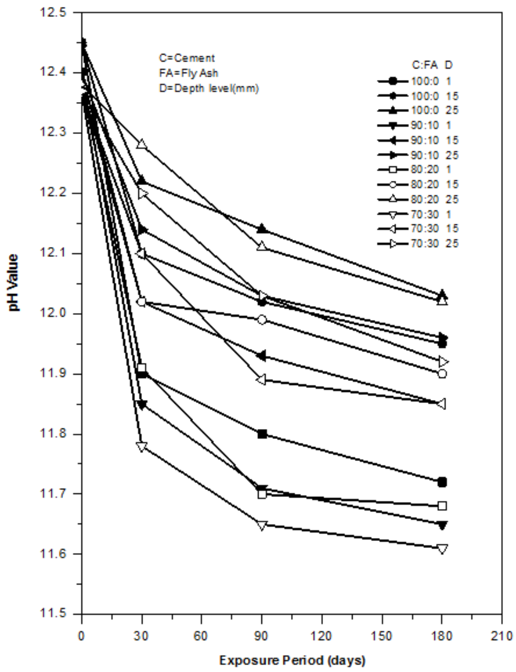

Fig. 10. pH value – exposure time relation for fly ash concretes exposed to sea water of 5T concentration.

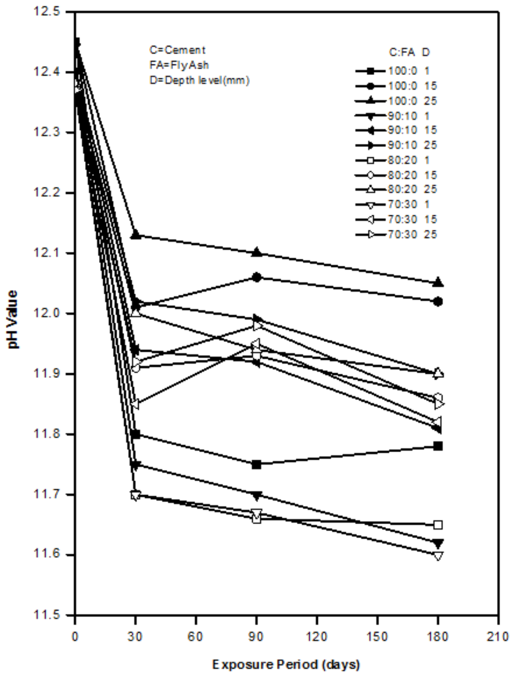

Fig. 11. pH value – exposure time relation for fly ash concretes exposed to sea water of 10T concentration.

6.5 Ultrasonic pulse velocity

Figure 6 shows the relationship between ultrasonic pulse velocity of OPC and fly ash concretes and exposure periods for different curing solutions. In plain water curing, OPC concrete shows higher UPV value than fly ash concrete. For 30 days curing in plain water, UPV values are 4290, 4240, 4180 and 4070 m/s for OPC, C90FA10, C80FA20 and C70FA30 concrete respectively. This is due to slow hydration rate of fly ash. Also for seawater curing, UPV values for OPC concrete is higher than that for fly ash concrete at initial age of curing. But for longer exposure period the differences between the results are seen to be decreased. After 30 days exposure to seawater of concentration 10T, the UPV values are 3760, 3680, 3710 and 3630 m/s for OPC, C90FA10, C80FA20 and C70FA30 concrete respectively. But after 180 days curing in 10T seawater, UPV value for OPC concrete is 4020 m/s whereas the corresponding value for C90FA10, C80FA20 and C70FA30 concretes are 3980, 4000 and 3920 m/s respectively. Since UPV is a measure for the stiffness of the hardening concrete mass, the stiffness seems to develop at slower rate with increasing fly ash content. This statement is attributed to the fact that the hydration of the fly ash is not initiated until the lime liberated during the hydration of OPC provides the correct alkalinity (Robeyst 2008). As a result, the rate of deterioration becomes slower and the corresponding UPV value increases at later ages. At relatively longer curing periods, complete hydration of fly ash takes place that produce an impermeable concrete, which prevents the easy penetration of seawater into the concrete. Also the differences of UPV values after 180 days curing for exposure in PW and 10T seawater solution are 510, 500, 410 and 470 m/s for OPC, C90FA10, C80FA20 and C70FA30 concrete respectively. However, the UPV results of the specimens are observed to have similar trends to those of compressive strength results. Also, from the UPV study, it is clear that for longer exposure period, C80FA20 concrete provides better resistance against deterioration.

6.6 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 halves and the phenolphthalein indicator solution was sprayed on the freshly broken surface. Almost all the specimens either OPC or fly ash concrete did not show any measurable depth of carbonation. However, after 180 days curing periods, in few OPC concrete specimens, sign of carbonation was noticed (although not measurable) at some spots of the surface level.

6.7 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 Figure 7 to Figure 8 and in Table 7. On the other hand in Figure 9, the chloride concentration profile for fly ash concretes have been drawn at an exposure period 180 days.

For this study, only water soluble chloride in concrete has been determined. 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. Close observation of the 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 the fly ash concrete is reduced. At the early ages i.e. after one month, OPC concrete exposed to seawater of 10T concentration shows the chloride content value of 0.312% at 15mm depth level, whereas for identical condition C90FA10, C80FA20 and C70FA30 concrete shows the corresponding value as 0.381%, 0.382% and 0.392% respectively. On the other hand, for the same condition and after 180 days exposure period, chloride content is found as 0.642% for OPC concrete and the corresponding values are 0.683%, 0.621% and 0.693% for C90FA10, C80FA20 and C70FA30 concrete respectively. The chloride content value for C80FA20 concrete is seen to be lower than the other mix. It might be due to the fact that amount of $Ca(OH)_2$ produced during hydration of cement is reduced by pozzolanic reaction. As a result, the rate of ingress of chloride and sulfate ions into the concrete is reduced due to reduction of the concentration of hydroxide ions available for counter diffusion and the pore structures of concrete after hydration are refined. Similar observation regarding chloride and sulfate induced deterioration due to the effect of fly ash in concrete are reported by Ziacho (2003).

Study of the curves shows that, at initial ages, chloride penetration is higher for fly ash concrete than that of OPC concrete. After longer exposure period, due to proper hydration, fly ash concrete becomes more impermeable and resists the penetration of chloride ions. Fly ash has high fineness and can react with the products liberated during hydration and form C-S-H gel. The gel fills all the pores inside concrete and makes it more impermeable (Oner 2003). Thus the higher resistances of fly ash contents indicate its suitability for use as structural concrete in marine environment.

6.8 pH Value

The variation of alkalinity for fly ash concrete exposed to seawater of various concentration and different exposure periods are shown in Figure 10 and Figure 11. pH value of concrete powder extracted from different depth levels of the exposed specimens have been used to study the change of alkalinity in concrete. pH value of 28 days plain water cured concrete are found as 12.45, 12.40, 12.38 and 12.37 for fly ash concrete made by replacing cement by 10%, 20%, and 30% respectively. pH value for all types of concrete are observed to be gradually decreased in seawater environment with time. For example, in case of fly ash concrete of mix C80FA20, cured in seawater of 3T concentration, pH value of concrete at 15mm depth level for exposure periods of 30, 90 and 180 days are 12.28, 12.02 and 11.85. The reduction of pH value in the subsequent exposure periods may be due to gradual action of dissolved CO_2 and salt ions with $Ca(OH)_2$ that produces poor alkaline compounds together with the leaching of some calcium compound in seawater. Close observation of the figure reveals that regardless of type of concrete, salt concentration of curing water and exposure period, the variation of pH with depth level of concrete is very small. The values are seen to vary in the range of 11.60 to 12.42.

Also pH value for concrete at different depth levels decreases as the concentration of seawater increases for any exposure periods although the differences are very marginal. Lower pH value of concrete under seawater might be due to reaction of sea salts with the hydrated cement products forming some new compounds with relatively lower alkalinity in nature.

However; the variation of pH in both fly ash and plain concrete at different exposure periods and seawater solution are not significant. Thus, it is observed that both fly ash and OPC concrete behave in a similar manner in respect to their reserve alkalinity of the pore solution.

7. Conclusion

Based on the limited number of test variables, exposure periods and result of the investigation conducted on different fly ash concrete specimens exposed to seawater of various concentrations for varying periods up to 180 days, the following conclusions can be drawn. This investigation may provide some necessary information related to the use of fly ash concretes for the construction of marine onshore/offshore reinforced concrete structure.

Both OPC and fly ash concretes exposed to seawater environment show changes in color form off-white to grey. Fly ash concrete shows better resistance against weight and volume change than OPC concrete. The gain in compressive strength of fly ash concrete is seen to be lower at early ages of curing. After 180 days exposure in seawater, the losses in compressive strength as compared to plain water cured concrete of similar age lie in the range of 6.7% to 28.7% for OPC concrete, 7.9% to 31.8% for C90FA10, 5.8% to 25.8% for C80FA20 and 8.9% to 30.8% for C70FA30 concrete respectively. Thus, fly ash concrete C80FA20 showed least strength deterioration. The ultrasonic pulse velocity values of both OPC and fly ash concrete specimens are observed to lie in the range of 3010 m/s to 4360 m/s in different seawater environment. For longer curing periods, fly ash concretes show relatively higher UPV values as compared to OPC concrete for any curing solution which indicate the slower rate of hydration of fly ash in concrete. C80FA20 concrete shows higher UPV values than the other concrete mix. Concretes exposed to seawater did not show any measurable depth of carbonation. However; after long curing period, carbonation was observed at some spots in a few OPC concrete samples. The amount of water soluble chlorides diffused into the concrete, at various depth levels of 15 and 25 mm are observed to lie in the range from 0.011% to 1.432 % by weight of concrete mass. C80FA20 concrete shows much better resistance against chloride penetration for longer curing period. Concrete specimens exposed to different seawater environment indicate marginal changes in alkalinity of concrete. pH values for all types of concretes corresponding to any depth level and curing condition are found to lie in the range of 11.6 to 12.35 which is well above the limiting value of 11.5 for the initiation of rebar corrosion by carbonation process. In general, it is observed that fly ash blended cement concrete in different proportion can improve the strength and durability characteristics of concrete in marine environment. Fly ash, due to high fineness, during hydration with cement greatly reduces the permeability of concrete thereby limiting the penetration of sea salt ions into it. Among all the concretes studied fly ash concrete (C80FA20) is found to be most effective in resisting the adverse effect of marine environment.

References

Alain, Bilodeau. and V., Mohan., Malhotra. (2000). “High-Volume fly ash system: Concrete solution for sustainable development”, ACI Materials Journal, 97(1), 41-47.

ASTM C150, “Standard specification for Portland cement,” Annual book of American Society for Testing Materials Standards, Vol. 04.01, (2011), 156-164.

ASTM C597-09, “Standard test method for pulse velocity through concrete”, Annual book of American Society for Testing Materials Standards, Vol. 04.02, (2011), 326-329.

ASTM C618-08a, “Standard specification for coal fly ash and raw or calcined natural pozzolan for use as a mineral admixture in concrete,” Annual book of American Society for Testing Materials Standards, Vol. 04.02, (2011), 336-339.

BS EN 12390-3:2009, “Testing of hardened concrete, Part 3: Compressive strength of test specimen,” (2009), 1-19.

Durán-Herrera, A., Juárez, C. A., Valdez, P. and Bentz, D. P. (2011). “Evaluation of sustainable high-volume fly ash concretes”, Journal of Cement and Concrete Composites, 33(1), 39-45.

Erdogan, ST., Over, D. and Tokyay, M. (2014). “Effect of pozzolan content and fineness on early hydration of interground blended cements”, Journal of Advanced Concrete Technology, 12, 101–110.

Filho, J. H., Medeiros, M. H. F., Pereir, E., Helene, P. and Isaia, G. C. (2013). “High volume fly ash concrete with and without hydrated lime: Chloride diffusion coefficient from accelerated test”, Journal of Materials in Civil Engineering, 25, 411-418.

Haque, M., N. KayyaliI, O., A. and Gopalan, M., K. (1992), “Fly ash reduces harmful chloride ions in concrete”, ACI Materials Journal, 89(3), 238-241.

IEA (International Energy Agency), (2006). Energy Technology Perspectives: Scenarios & Strategies to 2050”, Paris, 2006.

Juenger, M. C. G. and Siddique, R. (2015). “Recent advances in understanding the role of supplementary cementitious materials in concrete”, Cement Concrete Research, 78, 71-80.

Kaushik, S. K. and Islam, S. (1995). “Suitability of sea water for mixing structural concrete exposed to a marine environment”, Cement and Concrete Composite Journal, 17, 177-185.

Malhotra, V., M., Zhang., M., H. and Leaman., G., H. (2000). “Long-Term performance of steel reinforcing bars in portland cement concrete and concrete incorporating moderate and high volumes of ASTM Class F Fly Ash”, ACI Materials Journal, 97(4), 409-419.

Mark, Reiner. and Kevn., Rens. (2006), “High-Volume fly ash concrete: Analysis and application”, Practice Periodical on Structural Design and Construction, 11(1), 58-64.

Marthong, C. and Agrawal, T. P. (2012). “Effect of fly ash additive on concrete properties”, Journal of Engineering Research and Applications, 2(4), 1986–1991.

Mehta, P. K. (2002). “Greening of the concrete industry for sustainable development”, ACI Concrete International, 24(7), 23-28.

Min-Hong, Zhang, Marcia, C., Blanchette. and V., M., Malhotra. (2001). “Leachability of trace metal elements from fly ash concrete: Results from column-leaching and batch leaching tests”, ACI Materials Journal, 98(2), 126-136.

Myers, Holm. and Mc., Allister, Handbook of Ocean and Under Water Engineering, McGraw-Hill Education, 1969.

Ogawa, K., Uchikawa, H., Takenoto, K. and Yasui, I. (1980), “The mechanism of the hydration in the system CS Pozzolana”, Cement and Concrete Research, 10(5), 683-696.

Oner, M., Erdogdu, K. and Gunlu, A. (2003). “Effect of components fineness on strength of blast furnace slag cement”, Cement and Concrete Research Journal, 33(4), 463-469.

Ozkan, Sengul. and Mehmet, Ali. Tasdemir. (2009). “Compressive strength and rapid chloride permeability of concretes with ground fly ash and slag”, Journal of Materials in Civil Engineering, 21(9), 494-501.

Plank, J., Sakaib, E., Miao, C. W., Yu, C. and Hong, J. X. (2015).“Chemical admixtures - Chemistry, applications and their impact on concrete microstructure and durability”, Cement Concrete Research, 78, 81-89.

Poon, C., S., Lam., L. and Wong., Y., L. (2001). “A study on high strength concrete prepared with large volumes of low calcium fly ash”, Cement and Concrete Research, 30(3), 447-455.

Robeyst, N., Gruyaert, E., Grosse, C. U. and Belie., N. D. (2008). “Monitoring the setting of concrete containing blast-furnace slag by measuring the ultrasonic P-Wave velocity”, Cement and Concrete Research, 38, 1169-1176.

Serdar, Aydin. and Bulent, Baradan. (2007). “Effect of pumice and fly ash incorporation on high temperature resistance of cement based mortars”, Cement and Concrete Research, 37, 988-995.

Tarun, R. Naik., Shiw, S. Singh. and Mohammad, M., Hossain., (1996), “Permeability of high strength concrete containing low cement factor”, Journal of Energy Engineering, 122(1), 21-39.

Tarun, R., Naik. Ramme., B., W., Kraus., R., N. and Rafat Siddique (2003). “Long-Term performance of high-volume fly ash concrete pavements”, ACI Materials Journal, 100(2), 150-156.

Tumidajski, P. J., Chan, G. W. and Philipose, K. E. (1995). “An effective diffusivity for sulfate transport into concrete”, Cement and Concrete Research, 25(6), 1159-1163.

Wee, T., H., Surayavanshi, A., K., Wong., S., F. and Rahman, A. (2000). “Sulfate resistance of concrete containing mineral admixtures”, ACI Materials Journal, 97(5), 536-549.

Zichao, Wu. and Tarun, R. Naik. (2003). “Chemically activated blended cements”, ACI Materials Journal, 100(5), 434-439.