Deterioration of Concrete in Ambient Marine Environment

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Abstract

Structural concrete exposed to marine environment deserves special attention as the diffused sea salts chemically react with harden cement matrix and forms various expansive/leachable compounds leading to loss of material, strength, cracking, spalling etc. This study cover the effect of sea water on the specimens cast from two grades of concrete exposed to simulated marine environment over a year. Enhanced salt concentration i.e. 1N, 3N, 6N, 12N of the curing solution was used to get the accelerated effect. Several destructive and non destructive tests including XRD study were performed to assess the state of deterioration. From test results, it is observed that concrete exposed to sea water of different concentration suffers a loss of compression strength of around 19% and 33%, respectively as compared to 28 days and 365 days of plain water cured concrete.

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1. INTRODUCTION

Concrete, a stone like material, having the capability to take the shape and dimension of the desired structure has been used as the basic construction material over the several decades. As a durable, economic and more or less maintenance free construction materials, the use of concrete has been extended for the construction of marine onshore/offshore structure from the very early period. In addition, the availability of natural resources like petroleum crude, gas etc. has further increased the demand of such construction activities in marine location [1]. Thus, a large number of concrete structures of the earth are exposed to sea water either directly or indirectly. For several reasons, the effect of sea water on concrete deserves special attention. The coastal, onshore and offshore structures are exposed to simultaneous action of a number of physical, chemical and mechanical deterioration processes [2].

The sea environment, commonly known as marine environment is generally divided into three zones depending upon their nature and effect on the exposed structure. Concrete in each environment zone is subjected to different types/nature of attacks as shown in Table 1. Besides physical and chemical reactions, the structural concrete in the tidal zone also faces mechanical forces and therefore deterioration is generally observed to be more severe. Moreover, the structure in the tidal zone faces alternate wetting and drying cycles which accelerates chemical action of salts and water on reinforcing steel and concrete around it [3].

The structures located in tidal and atmospheric zone are more vulnerable to aggressive action of sea water than those which are continuously and fully submerged in water due to the reasons given below:

(i) The presence of $O_2$ is in adequate quantity and hence the corrosion of steel in concrete is much faster as rate of corrosion depends on the availability of oxygen.

(ii) In the portion of concrete structure above sea level, the water rises upwards by capillary action, which when evaporates leaves behind crystals salts. With the progressive wetting and drying cycles, this crystalline growth gradually increases causing tensile stresses and on exceeding the tensile strength, disintegration of concrete surface takes place.

(iii) Due to fluctuation of sea water level, the leached salts and corroded concrete fragments gets washed away and erosion of concrete takes places which results in the loss of concrete mass.

(iv) The mechanical impact of sea waves in active tidal zone continuously increases the wear and tear of concrete.

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TABLE 1. Different attack zone of marine environment

<table>
<thead>
<tr>
<th>Zone descriptions</th>
<th>Type of attack</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmospheric zone - where the parts of structure are above the highest high tide level or splash zone.</td>
<td>Chemical and physical.</td>
</tr>
<tr>
<td>Tidal zone - the parts of the structure located between the highest high tide and lowest low tide zones.</td>
<td>Chemical, physical, and mechanical.</td>
</tr>
<tr>
<td>Submerged zone - where the parts of structure always remain submerged in sea water.</td>
<td>Chemical and physical.</td>
</tr>
</tbody>
</table>

Experience has shown that most severe attack of sea water on concrete occurs just above the level of high water i.e. the splash zone. The portion between low and high water marks is less affected and the parts below the water level which are continuously remaining immersed are least affected [4]. The splash zone is characterized by the continuous contact with highly aerated sea water, erosive effect of salt water spray, temperature gradient and wave action in presence of atmospheric O₂ and CO₂ gas [5].

In tidal/splash zone, where concrete is repeatedly wetted by sea water with alternate periods of drying during which pure water evaporates, some of the dissolved salts are left behind in the form of crystals mainly sulphates. These crystals re-hydrate and grow upon subsequent wetting and thereby exert an expansive force on the surrounding hardened concrete. Such progressive surface weathering known as salt weathering occurs in particular when the temperature is high. Salt water can also rise by sorption, that is, by capillary action where evaporation of pure water from the surface leaves behind salt crystals which when re-wetted can cause disruption.

1. 1. Chloride Attack  Chloride attack is one of the most important aspects considering the durability of concrete and is particularly important because it primarily causes the corrosion of reinforcement in concrete. It is statistically reported that over 40 percent of structural failure occur due to the corrosion of reinforcement. Chloride enters the concrete from cement, water, aggregate, admixtures and by diffusion from the ambient environment. 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.

The chloride salts presence in sea water reacts with the hydrated products of cement and form calcium chloroaluminate and calcium chloride [6]. The calcium chloroaluminate also known as Friedels salts has a property of low to medium expansion. Calcium chloride being soluble gets leached out leading to material loss, weakening as well as strength reduction of concrete.

According to Metha [7], MgCl₂ after reacting with Ca(OH)₂ of hydrated cement forms calcium chloride, which being soluble, gets leached out leading to material loss and weakening. Possible reactions are given below:

\[
\text{Ca(OH)}_2 + \text{MgCl}_2 \rightarrow \text{CaCl}_2 + \text{Mg(OH)}_2
\]

1. 2. Sulfate Attack  Sulfate constitute the second largest component of the anionic components available in SW. Total contents of sulfate amounts, 3.5 to 3.75 i.e. around 10 to 11 percent of the total salts in SW are present as sulfate of calcium, sodium and magnesium. According to Nevile [8], concrete attacked by sulfates presents a characteristics whitish appearance. The damage is found initially at the edges and corners of the structures and then followed by progressive cracking and spalling of concrete.

The sea salt magnesium sulfate after reacting with hydrated C₃A and Ca(OH)₂, a hydrated products of cement, yields calcium aluminate sulfate hydrate (ettringite) and calcium sulfate (gypsum). Both these products i.e. gypsum and ettringite occupy a greater volume after crystallization in the pores of concrete than the compounds they replace. Bogue [9] is of the opinion that the formation of gypsum causes an increase of 17.7% in volume. Where magnesium ions are present, the development of Mg(OH)₂ results in a volume increase of about 20 percent.

Exertion of pressure by growing ettringite crystals results in surface cracking known as softening type of crack. Gypsum formation as a result of cation exchange reactions is also capable of causing expansion [10]. It is reported that deterioration of hardened Portland cement paste by gypsum formation goes through a process leading to the reduction of stiffness and strength followed by expansion, cracking and eventual transformation of the materials into a mushy or non-cohesive mass. Thus, the sulfate attack in sea water is associated with a progressive loss of strength and loss of mass of structural concrete.

The ionic radii of chloride and sulfate ions are 1.81 Å and 2.30 Å, respectively [11]. Also, the diffusion coefficient for sulfate is 2*10⁻² cm² S⁻¹ and for chloride is 3*10⁻³ cm² S⁻¹ [12]. Due to larger diffusion coefficient, chloride ions penetrate at a faster rate than that of sulfate. On the other hand, as sulfate holds two negative ions higher than that of chloride (one negative ion), its action on deterioration is more dangerous. Thus, both chloride and sulfate penetration may have detrimental effects on concrete exposed to marine environment.

For concrete structures permanently immersed in sea water, where a steady state of saturation and salt concentration is reached, the deterioration of concrete is
not characterized by expansion caused due to large amount of ettringite formed as a result of sulfate attack. Instead, it mostly takes the form of erosion or loss of solid constituents from the mass [13]. Ettringite as well as gypsum are soluble in the presence of chloride and can be leached out by the sea water.

Heller and Ben-Yair [14] stressed that all chlorides present in sea water combine with Portland cement to form calcium chloroaluminate. Gjorv and Vennesland [15] studied the rate of chloride diffusion from sea water to concrete made with different types of cement and observed that the chloride penetration in Portland cement was as much as two to five times higher than that in blended cement concrete.

Smolczyk [16] obtained X-ray diffractograms of the mortar specimen after immersion in MgCl\(_2\) solution and detected the formation of chloroaluminate (\(C_2A.CaCl_2.10H_2O\)) known as Friedel’s salt. Kalousek and Benton [17], Mohammed T.U. and Hamida [18] and Suzukawa [19] have the same opinion about the formation of chloroaluminate compounds.

According to Suzukawa [19], the deterioration of hardened cement mortar in MgCl\(_2\) and CaCl\(_2\) solution is due to an increase in the porosity of mortar caused by the dissolution of calcium hydroxide. David Darwin et al. [20] found the effect of MgCl\(_2\) more detrimental than NaCl with regards to loss of material, reduction in stiffness and strength of the exposed concrete.

According to Neville [8], concrete attacked by sulfates has a characteristics whitish appearance and the damage is found initially at the edges and corners of the structure which is followed by progressive cracking and spalling of concrete. The principal reason for the deleterious attack of sulphate is the formation of gypsum and a complex compound known as calcium sulphoaluminate (ettringite) [8, 17].

These products occupy a greater volume after crystallization in concrete pores than the compounds which replace and induce pressure to the surrounding mass thereby resulting in its cracking and spalling.

Although extensive investigation including laboratory as well as field exposure studies on durability of concrete exposed to marine conditions have been carried out for the last several decades, there are still many features of the mechanism of sea water attack on concrete which remains obscure. The relevant information presented in literature varies to a great extent or debatable. It is important to identify the various causes of concrete deterioration in marine environment which are physical, mechanical and chemical in nature. The primary objective of this investigation is to carry out a comprehensive experimental study covering the physical, mechanical and morphological changes of concrete exposed to marine condition over a period of one year.

2. RESEARCH SIGNIFICANCE

The deteriorative effect of sea salts in ambient condition of marine environment on structural concrete is an important issue for the scientists/researchers over the several decades. It is very much essential to know the mechanism of sea water attack and its consequences on the service life of inshore/offshore structures as early failure/damage of such structures are reported in the case histories of maritime RC structures. Most of the durability problems including structural damage/distress are observed in the tidal/splash zone due to the variety of reasons stated before. Such problems becomes very severe for RC structures exposed to tropical marine environment where sea salts diffused within the concrete get the favorable environment i.e. high ambient temperature and humidity to react chemically with hydrated cement matrix and the embedded rebar [21]. The study cover the investigation carried out on two grades of concrete that are exposed to simulated marine conditions. Several destructive as well as non destructive tests have been carried out periodically on the exposed specimens to assess the change in properties and morphology of concrete. The test results have been critically analyzed / examined with a view to get useful information relevant to the construction, repair and maintenance of RC structures in those locations.

3. EXPERIMENTAL STUDY

The experimental program was planned considering the various parameters including different exposure states, creation of simulated tidal/splash zone environments, conducting various test of concrete specimen after specific-exposure period etc. Normal as well as accelerated test techniques were used so as to get long term effects within short period. The material used and the variables studied were as follows.

3.1. Materials Used

Ordinary Portland Cement (OPC) conforming to IS 269-1976 was used and procured from a single lot in order to avoid its strength variation. The physical properties and chemical composition of the cement is given in Table 2. 20 mm down well graded crushed stone of fineness modulus (FM) 6.95 and well graded coarse sand of FM 2.63 were used as coarse and fine aggregate respectively. Both materials conformed to IS 383-1970 requirements. Commercial grade salts were used for making artificial sea water of different concentration and was procured in a single lot to avoid the variation in effective ion concentration.
3.2 Variable Studied

(a) Curing Water/Solution Plain water (PW) as well as artificially made sea water (SW) of different concentration (1N, 3N, 6N, and 12N) were used for curing the test specimens under different state of exposure condition. 1N means normal sea water made by mixing tap water with exact amount and proportion of principal salts found in natural sea water. Thus, 3N, 6N and 12N will have salt concentration enhanced to 3, 6 and 12 times, respectively as that for normal sea water. The enhanced concentrations were used to obtain accelerated effects on the hydration mechanism and also on the deterioration of concrete specimens. The composition of artificial sea water is given in Table 3.

(b) Exposure State and Condition Five brick masonry tanks with concrete base slab were made for creating different environments like sea water environment of various environments (1N, 3N, 6N and 12N), plain water and of no liquid i.e. atmospheric state. Six steel bar racks were kept over the masonry tanks to stack the specimens for exposing their maximum surfaces to the environment during drying period of alternate wetting-drying cycles. The different state of exposure were submerged state (SUB), alternate wetting and drying state (AWD) and the non submerged state i.e. atmospheric state (ATM). In each alternate wetting-drying cycle, the specimens were kept in submerged state for 12 hours in different environment and followed by 12 hours drying in a cyclic fashion. The specimens of SUB state were in constant submerged condition while specimens of ATM state were at constant dry condition.

(c) Concrete Grade Two different high grades of concrete named concrete A and B. The relevant information of the concrete mixes is given in Table 4.

(d) Exposure Periods To assess the deterioration effects of sea water with time, four exposure periods i.e. 1, 3, 6 and 12 months were selected.

(e) Type and Size of the Test Specimens 150mm dia X 150mm high cylindrical specimens. The use of relatively small size specimen was used to accommodate large numbers of specimens in the specified tanks.

(f) Relevant Tests Visual inspection/examination, weight and volume change measurement, compressive strength, permeability, stress-strain characteristics and X-ray diffractometry (XRD) study.

3.3 Casting and Testing Techniques A total 264 number of specimens were cast from two different concrete mixes as per test program and requirements. Plain water (PW) was used as mixing water to cast all the test specimens. A series of specimens of 150mm cubical size and 150mm diameter with 150mm height cylindrical size were cast from same concrete mixes to compare the compressive strength of two different sizes of specimens and no difference of strength was observed.

### TABLE 2. Physical properties and chemical composition of cement (Ordinary Portland cement); Source: Associated Cement company, India.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Characteristics</th>
<th>Value obtained (Exp.)</th>
<th>As Per IS: 269-1976</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Fineness (90 µm Sieve) %</td>
<td>9.5</td>
<td>&lt;10</td>
</tr>
<tr>
<td>2.</td>
<td>Blaine’s Specific surface (cm²/g)</td>
<td>2560</td>
<td>&gt;2250</td>
</tr>
<tr>
<td>3.</td>
<td>Normal Consistency Soundness by Le Chatelier’s Test (mm)</td>
<td>24</td>
<td>---</td>
</tr>
<tr>
<td>4.</td>
<td>Setting Time Initial (min.)</td>
<td>31</td>
<td>&gt;30</td>
</tr>
<tr>
<td>5.</td>
<td>Specific gravity</td>
<td>3.15</td>
<td>3.15</td>
</tr>
<tr>
<td>6.</td>
<td>Final (min)</td>
<td>63</td>
<td>&lt;600</td>
</tr>
<tr>
<td>7.</td>
<td>Compressive Strength (MPa)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(i) 3 days</td>
<td>23.70</td>
<td>&gt;16.0</td>
</tr>
<tr>
<td></td>
<td>(ii) 7 days</td>
<td>33.50</td>
<td>&gt;22.0</td>
</tr>
<tr>
<td>8.</td>
<td>Loss on ignition</td>
<td>1.99</td>
<td>&lt;4</td>
</tr>
<tr>
<td>9.</td>
<td>Insoluble matter</td>
<td>1.43</td>
<td>---</td>
</tr>
<tr>
<td>10.</td>
<td>SiO₂ (silica)</td>
<td>17.40</td>
<td>---</td>
</tr>
<tr>
<td>11.</td>
<td>Al₂O₃</td>
<td>11.56</td>
<td>---</td>
</tr>
<tr>
<td>12.</td>
<td>Fe₂O₃</td>
<td>2.51</td>
<td>---</td>
</tr>
<tr>
<td>13.</td>
<td>CaO</td>
<td>60.05</td>
<td>---</td>
</tr>
<tr>
<td>14.</td>
<td>MgO</td>
<td>1.30</td>
<td>&lt;5</td>
</tr>
<tr>
<td>15.</td>
<td>SO₃</td>
<td>2.68</td>
<td>---</td>
</tr>
</tbody>
</table>

### TABLE 3. Composition of Artificial Sea Water

<table>
<thead>
<tr>
<th>Salt Type</th>
<th>Chemical Formula</th>
<th>Amount (gm)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Chloride</td>
<td>NaCl</td>
<td>27.20</td>
<td>These amounts of salts were dissolved in plain water to prepare 1000 gm of Sea water of 1N concentration</td>
</tr>
<tr>
<td>Magnesium Chloride</td>
<td>MgCl₂</td>
<td>3.80</td>
<td></td>
</tr>
<tr>
<td>Magnesium Sulfate</td>
<td>MgSO₄</td>
<td>1.70</td>
<td></td>
</tr>
<tr>
<td>Calcium Sulfate</td>
<td>CaSO₄</td>
<td>1.20</td>
<td></td>
</tr>
<tr>
<td>Potassium Sulfate</td>
<td>K₂SO₄</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td>Calcium Carbonate</td>
<td>CaCO₃</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>Magnesium Bromide</td>
<td>MgBr₂</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>35.0</td>
<td></td>
</tr>
</tbody>
</table>
TABLE 4. Experimental program in a simulated marine environment

<table>
<thead>
<tr>
<th>Concrete Mix</th>
<th>Compressive Strength (MPa)</th>
<th>Specimen Size (mmXmm)</th>
<th>Specimen No.</th>
<th>Environmental Conditions</th>
<th>Exposure Periods (Days)</th>
<th>Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>46.0</td>
<td>D=150mm</td>
<td>24</td>
<td>ATM</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>53.0</td>
<td>H=150mm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>46.0</td>
<td>D=150mm</td>
<td>24</td>
<td>SUB PW</td>
<td>90</td>
<td>a)Visual Examination</td>
</tr>
<tr>
<td>B</td>
<td>53.0</td>
<td>H=150mm</td>
<td></td>
<td></td>
<td>180</td>
<td>b) Weight change</td>
</tr>
<tr>
<td>A</td>
<td>46.0</td>
<td>D=150mm</td>
<td>24</td>
<td>AWD PW</td>
<td>365</td>
<td>c) Volume change</td>
</tr>
<tr>
<td>B</td>
<td>53.0</td>
<td>H=150mm</td>
<td></td>
<td></td>
<td></td>
<td>d) Permeability</td>
</tr>
<tr>
<td>A</td>
<td>46.0</td>
<td>D=150mm</td>
<td>24</td>
<td>SUB 1 N</td>
<td>90</td>
<td>e) Compressive strength</td>
</tr>
<tr>
<td>B</td>
<td>53.0</td>
<td>H=150mm</td>
<td></td>
<td></td>
<td>180</td>
<td>f) Stress-strain characteristics</td>
</tr>
<tr>
<td>A</td>
<td>46.0</td>
<td>D=150mm</td>
<td>24</td>
<td>SUB 3 N</td>
<td>365</td>
<td>g) X-ray diffractometry</td>
</tr>
<tr>
<td>B</td>
<td>53.0</td>
<td>H=150mm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>46.0</td>
<td>D=150mm</td>
<td>24</td>
<td>SUB 6 N</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>53.0</td>
<td>H=150mm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>46.0</td>
<td>D=150mm</td>
<td>24</td>
<td>SUB 12 N</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>53.0</td>
<td>H=150mm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Total: 264 nos.

Concrete A: Mix: 1:1.15:2.20; w/c=0.39, 28-days cube strength = 46.0 MPa
Concrete B: Mix: 1:1.2:2.10; w/c=0.36, 28-days cube strength = 53.0 MPa
SW: Sea Water; PW: Plain Water; 1N: Normal sea water concentration;
ATM: Atmospheric State; SUB: Submerged state; AWD: Alternate wetting & drying; D: Diameter; H: Height.
The specimens after 28 days PW curing were exposed to different environments as per requirement of exposure states and environmental conditions. Separate masonry tanks and mild steel racks were used for PW, SW and ATM state of exposure in order to get the individual environmental effect on the specimens. After a specific period of exposure, the specimens were taken from different environments for various tests stated above. Nondestructive test including visual examination, weight and volume change measurement, permeability test etc. were carried out before conducting the destructive tests. In this study, the coefficients of permeability of the test specimens were determined according to IS: 2085-1965 based on Darcy’s law where as the compressive strength were determined as per IS: 516-1956. Concrete chips were collected from different points of the deteriorated specimens for XRD studies. Average of the three observations at each test point has been considered in making the test results.

The variation of the ambient temperature over the exposure periods of 28 days, 90 days, 180 days and 365 days are respectively as $27^\circ C$ to $32^\circ C$, $27^\circ C$ to $35^\circ C$, $27^\circ C$ to $40^\circ C$, $27^\circ C$ to $40^\circ C$ to $30^\circ C$ (see Figure 1). The whole experimental program including the various parameters/variables studied, test conducted are summarized in Table 4.

### 4. RESULTS AND DISCUSSION

The test results obtained at different phases of exposure were critically analyzed and followed by relevant discussion as mentioned below:

#### 4.1. Visual Examination

The concrete specimens after different exposure periods were taken out for conducting various tests. The test specimens were inspected very carefully for surface deformation, color change, if any, and then tested for systematic nondestructive as well as destructive tests. A visual examination of the concrete specimens of both grades exposed to different concentrations of sea water for 365 days duration indicates that the external surfaces tend to become uneven. The change in color from dark grey to lime grey has been observed in outer surfaces of the specimens exposed to sea water, but the interior surfaces of the tested specimens have shown no change in color. This may be due to salt deposition on the exposed surfaces. A greater degree of saturation has also been observed with increasing exposure periods which indicates that the concentration of sea water into the interior of the concrete specimens continues for a long period. The fractured surfaces, as obtained after compression strength tests, showed a uniform distribution of coarse aggregates in the mortar. A whitish compound namely brucite has also been observed around the aggregate which is confirmed by XRD study.

![Figure 1. Atmospheric temperature variation for ambient temperature](image)

#### 4.2. Weight Change

The changes in the weight of the concrete specimens have been shown Figures 2(a) and 2(b) for different environment states / condition. It is seen that the weight changes are very marginal. The graphs show that the submerged specimens undergo higher percentages of weight change as compared to those subjected to the AWD environment. This may be due to higher amount of sea water penetration inside the concrete mass. Non-submerged specimens, on the other hand, show a decrease in weight which may be attributed to the loss of moisture. At 365-day, the weight change of the concrete specimens exposed to sea water environment gets stabilized at about +1.2 per cent, whereas for the non-submerged state, the corresponding change is about -1.5 per cent. However, no definite pattern of the weight increase with increasing salt concentrations was observed. In figures, some specimens are seen to show an increase in weight followed by a decrease under longer exposures.

#### 4.3. Volume Change

Changes in the over-all volume of the concrete specimens exposed to the various environmental states/conditions have been presented in Figures 3(a) and 3(b). It is seen that the volume changes are again very small and to the extent of ±0.12 per cent. The specimens in submerged state show a slightly higher volume increase compared to those subjected to the AWD state, whereas in the case
of the non-submerged specimens, there is a decrease in the volume. It appears that the voids of concrete in the submerged state remain saturated with sea water which prevents any drying shrinkage.

![Figure 2(a). Weight change- exposure period relation concrete-A, CS-curing soln; EC- envirn. Condn.](image1)

![Figure 2(b). Weight change- exposure period relation concrete-B, CS-curing soln; EC- envirn. Condn.](image2)

On the other hand, small scale swelling of some specimens has also been detected. In case of the specimens placed in atmospheric state, the loss of moisture from the concrete mass results in decrease in the volume. After exposure of 365 days to sea water, the changes in volume stabilize around +0.10 to +0.12 per cent, whereas in the non-submersed state, the corresponding volume change lies in the change of -0.10

![Figure 3(a). Volume change- exposure period relation concrete-A, CS-curing soln; EC- envirn. Condn.](image3)

![Figure 3(b). Volume change- exposure period relation concrete-B, CS-curing soln; EC- envirn. Condn.](image4)
to -0.12 per cent. Again, no definite pattern of volume change with increasing salt concentration has been observed.

4. 4. Permeability Characteristics Permeability characteristics of concrete A & B exposed the corrosive as well as the non-corrosive environments as described in Table 4 have been graphically presented in Figures 4(a) and 4(b), respectively.

For comparison, the permeability of the concretes exposed to plain water decreases as in case of plain water cured concrete and the subsequent behavior is just the opposite. At 365-day exposure to sea water, the permeability of concrete is found to lie in the range of 6 to $11 \times 10^{-14}$ m/sec, whereas the corresponding value for concrete exposed to plain water is found to lie in the range of 0.5 to $1.25 \times 10^{-14}$ m/sec. The decrease in permeability due to reduction in the pore sizes coupled with the loss of pore connectivity may be explained on the basis of hydration of cement resulting in crystallization of the compounds in the voids of concrete mass [22]. The increase in permeability after prolonged period of exposure may be due to sulfate attack products that get dissolved into non aired water with passage of time.

4. 5. Compressive Strength For the different environment states/conditions of exposure, the compressive strength of the specimens of concrete A and B have been presented in Figures 5(a) and 5(b), respectively. It is seen that in most of the environments, the strength increases during the first 90 days and afterwards decreases. The 90-day compressive strengths have been found to lie in the range of 92 to 119 per cent for both the concretes, whereas the corresponding values at 365 days are observed to lie in the range of 85 to 105 per cent when compared with 28 days strength of plain water cured concrete. To obtain better ideas about the strength deterioration of concrete, the observed compressive strength data for concrete A and B has been expressed as relative strength of the same concrete exposed to plain water for the similar exposure period. They have been presented in Figures 6(a) and 6(b).
The overall strength losses for the two concretes over the 365-days period are observed to lie in the range of 5 to 15% and 18 to 32%, respectively as compared to 28 days and 365 days strength of the concretes cured in plain water. Also, the concrete specimens in AWD state of SW shows around 22% higher strength deterioration than SUB state under identical condition of exposure. The loss of concrete strength may be attributed to the sea salt ion attack resulting in the formation of expansive weak compounds like ettringite (E), thaumasite (TH), and calcium aluminate hydrate together with leaching action of some of the hydrated product inside of the pores [3].

4. 6. Stress-strain Characteristics Stress-strain relationship for the specimens of the two concretes A and B after exposure to the various environment states/conditions mentioned in Table 4 have been presented in Figures 7(a) to 7(d). The curves show the stress strain values obtained from uniaxial compression of the test specimens exposed for 28 days and 365 days.
The stress-strain curves indicate that the ultimate strength varies with respect to the deterioration of the concrete while the strain values corresponding to ultimate strength lies very close to 0.2 per cent in all cases. In addition, the shape of these curves for the deteriorated concretes is very much similar to that of the un-deteriorated concrete. It is also observed that the AWD action of 12N, 6N, 3N and 1N sea water have caused higher loss of strength as compared to the action of SUB state on the specimens kept in the similar sea water solutions. Although, the ultimate compressive strength is found to decrease from about 55 MPa to 42 MPa, the strain values lie in a narrow range of 0.16 per cent to 0.24 per cent.

Thus, the value of 0.2 per cent strain may be considered as the failure strain for high strength concrete even when exposed to aggressive environments.

4. 7. X-ray Diffraction studies

X-ray diffractograms of the concrete specimens exposed to various sea water environments at 28 days and 365 days exposure are presented in Figures 8(a) to 8(d).

The maximum intensities and the approximate percentage of the chemical compounds detected form the figures have been calculated and critically studied. It is observed that the percentages of most of the compounds (expansive or non-expansive) in the concrete specimens exposed to sea water over 28 days remain constant or increase as compared to the corresponding percentages of the compounds in plain water cured concrete specimens of same age. At 365-day exposure time and in the submerged as well as alternate wetting-and-drying states, the percentage of the expansive compounds (Ettringite, Thaumasite etc) increase, whereas the non-expansive compounds (Brucite, Portlandite etc) decrease in the concrete specimens exposed to sea water as compared to identical plain water cured specimens. For the specimens placed in atmospheric state, the formation of expansive compounds like thaumasite (TH) is greatly inhibited as compared to the specimens in the submerged or AWD state. Gypsum could not be detected in any concrete specimens cured either in sea or plain water for any duration upto 365-days.
Figure 8(a). X-Ray Diffractograms of Specimens after Exposure to PW

Figure 8(b). X-Ray Diffractograms of Specimens after Exposure to 1N SW

Figure 8(c). X-Ray Diffractograms of Specimens after Exposure to 6N SW

Figure 8(d). X-Ray Diffractograms of Specimens after Exposure to 12N SW

KEY
5. SUMMARY AND CONCLUSIONS

After analyzing & interpreting the test results for the two grades of concrete exposed to various sea water environments 1N, 3N, 6N, 12N and under different conditions of exposure SUB, AWD & ATM states at a temperature range of 27°C to 40°C to 30°C over the period of one year, the following conclusions are drawn:

(a) Concrete exposed to sea water is found to acquire a lime grey color from the original dark grey color. The fractured surfaces of the tested specimens show a uniform distribution of the coarse aggregates and a vesicular mortar structure. A whitish compounds, brucite, has also been found deposited around the coarse aggregates to some extent.

(b) Concrete gains somewhat higher weight in SUB state than AWD state in sea water and is found to stabilize at about 1.2% whereas a loss in weight of around 1.6% occurs in ATM state of exposure.

(c) The volumetric expansion of the concrete in AWD state is less than that for SUB state in all sea water environments and a reduction in volume is observed in ATM state. However, for both the concrete, the overall increase in volume stabilizes at about +0.12 per cent whereas the decrease in volume in ATM state is about -0.12 per cent. Thus, concrete in sea water also faces the problem relating to dimensional stability.

(d) The permeability of concrete exposed to sea water of different salt concentration is found to decrease initially for a period of around 90 days followed by a gradual increase with exposure period. The 365-day permeability of concrete in different sea water environment is found as 8 to 12 times the permeability of normally cured concrete.

(e) The compressive strength of concretes in SW is found to increase initially up to 90 days and then decreases for both the concretes. The loss in the compressive strength after 365-day exposure is observed to vary from 5 to 15% and 18 to 32%, respectively as compared to 28 days and 365 days strength of plain water cured concrete. Furthermore, concrete in AWD state shows around 22% higher strength deterioration than SUB state under identical conditions.

(f) The stress-strain characteristics of the concrete exposed to SW are very similar to those of concrete cured in PW. The failure strain is observed to be constant at around 0.2% although the ultimate strength varies from 45 MPa to 55 MPa which indicates that stress-strain relationship is not affected by sea water attack.

(g) Structural concrete exposed to tidal/splash zone is observed to be more vulnerable to deterioration than atmospheric/submerged zone.

(h) X-ray diffraction studies confirm the formation of relatively higher percentage of expansive and leachable products in concrete exposed to SW which are mainly responsible for strength deterioration and increased permeability.

6. REFERENCES


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