PHYSICAL AND MECHANICAL BEHAVIOR OF CONCRETE IN SEA WATER UNDER HIGH HYDROSTATIC PRESSURE

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ABSTRACT

As a part of a durability study of concrete exposed to sea water environment, the paper describes the effect of sea salts on the physical and mechanical properties of concrete under large hydrostatic pressure. Specially designed pressure vessels with temperature control system have been used to simulate the deep sea environmental effects. Accelerated test techniques such as increased salt concentration of curing water, small sized specimens, enhanced environmental temperature have been used. The deteriorative effects are measured by studying visual appearance, weight and volume change, compressive strength, permeability characteristics and X-ray diffraction patterns of concrete specimens exposed to artificial sea water environment over a period of one year. The test results reveal that ambient pressure has accelerated effects on the deterioration of concrete in deep sea water environment.

Keywords: Durability, Compressive Strength, Permeability, Marine Environment, Hydrostatic Pressure, Chloride Attack, Sulfate Attack.

INTRODUCTION

Cement concrete is finding extensive application in construction of marine structures either in precast or cast in situ forms as per requirements. The spurt of construction activities in relatively deeper oceans to produce hydrocarbons has given birth to many types of concrete structures like gravity platforms, oil reservoirs and others. The gravity type concrete platforms are becoming popular due to its excellent performance and least maintenance. Offshore structures stand subjected to different environmental conditions which can best be classified as foundation zones, submerged zones, tidal zones, splash zones etc. [1]

Failure or deterioration of concrete has been occasionally noted in tidal or splash zones but it has generally been assumed that concrete behaves reasonably well in submerged zones [2]. As marine resources exploration moves into deeper waters, the role of pressure becomes significant since pressure by itself, may ensure deeper penetration of harmful ocean- salts into the cement concrete. Since maintenance or repair of concrete structures in deep waters is practically impossible and costs associated with structural failures is enormous in magnitude, it becomes necessary to understand the behavior of marine cement concrete and its protective measures under high hydrostatic pressure.

Sea water (SW) is a complex delicately balanced solution of many salts containing living matter, suspended silt, dissolved gases and decaying organic material. The average salt concentration of sea water is about 3.5% although it varies from sea to sea depending on the geographical location (Ref. Table 1). The compounds of chloride form the highest proportion i.e. 88 to 89% of the total dissolved salts present in sea water whereas the sulfate compounds constitute the second largest proportion i.e. about 10% of the total salt. Apart from chemical action on hardened cement paste, the presence of chloride at the reinforcement bars (rebar) is mainly responsible for corrosion (3,4). In a marine environment, the chloride ion penetrate into the concrete either from water or sea winds carrying salts ions which destroy the passivity of steel and lead to initiation of corrosion. On the other hand, the principal reason for the deleterious attack of sulfate on concrete is the formation of gypsum and a complex compound known as calcium sulphaaluminate (ettringite). Both the products occupy a greater volume after crystallisation in the pores of concrete than the compounds they replace. Bogue [5] is of the opinion that the formation of gypsum hydrate causes an increase of 17.7% in volume. According to Mehta [6] the sulfate related expansion in concrete are associated with ettringite.

The action of principal sea salts namely, NaCl, MgCl₂, MgSO₄ and CaSO₄ on hardened concrete as mentioned by several researchers is explained as follows [1,7,8]

Both NaCl and MgCl₂ after reacting with Ca(OH)₂ of hydrated cement form calcium chloride, which being soluble, gets leached out leading to material loss and weakening.

\begin{align*}
\text{Ca(OH)₂} + 2\text{NaCl} & \rightarrow \text{CaCl₂} + 2\text{NaOH} \\
\text{CaCl₂} + (3\text{CaO}).\text{Al₂O₃} + 10\text{H₂O} & \rightarrow (3\text{CaO})\text{Al₂O₃}.\text{CaCl₂}. 10\text{H₂O} \\
\text{MgSO₄} & \rightarrow \text{Ca(OH)₂} + \text{MgCl₂} \\
2\{(3\text{CaO})_n\text{Al₂O₃}.12\text{H₂O}\} + 3\text{(MgSO₄}.7\text{H₂O}) & \rightarrow (3\text{CaO})\text{Al₂O₃}.(3\text{CaSO₄}).3\text{H₂O} + 2\text{Al(OH)₃} + 3\text{Mg(OH)₂} + 8\text{H₂O} \\
\end{align*}
MgSO₄ also reacts with Ca(OH)₂ and yields CaSO₄·2H₂O (gypsum), which in turn reacts with calcium aluminates hydrate to form additional calcium aluminates sulfate hydrate (ettringite)

\[
\begin{align*}
\text{Ca(OH)}_2 + \text{MgSO}_4 \cdot 7\text{H}_2\text{O} & \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{Mg(OH)}_2 + 5\text{H}_2\text{O} \\
\text{(Gypsum)} & \\
(3\text{CaO})_\text{Al}_2\text{O}_3 \cdot 12\text{H}_2\text{O} + 3(\text{CaSO}_4 \cdot 2\text{H}_2\text{O}) + 13\text{H}_2\text{O} & \rightarrow (3\text{CaO})_\text{Al}_2\text{O}_3 \cdot (3\text{CaSO}_4) \cdot 3\text{H}_2\text{O} \\
\text{Calcium aluminates sulfate hydrate (Ettringite)} & (vi)
\end{align*}
\]

The reaction products such as Friedels salt has a property of low to medium expansion. The formation of excess calcium chloride, which may leach out results in increased permeability of concrete leading to material loss and weakening. Formation of ettringite is associated with expansion and cracking. Thus the detrimental effects associated with the chemical reactions manifest themselves as physical effects, such as change in volume, weight, permeability and other properties of concrete.

Bryant Mather [9] considers leaching, expansion, formation of weak compounds as the various causes of concrete deterioration when subjected to chloride or sulfate attack. The sulfate induced deterioration of concrete is time dependent in nature; the reported diffusion rates of sulfate ions through concrete are smaller by one to two orders of magnitude compared to those for chlorides [10]. The relatively larger ionic radius of sulfate ion (2.30 Å) compared to the chloride ion (1.71 Å) appears to be one possible reason for the relatively lower diffusion rate of sulfate through structural concrete [11]. Some researchers [12] have recommended the use of precast concrete instead of cast-in-situ concrete in places where sulfate attack is expected.

The overall performance of concrete is dependant upon its permeability. It is not a simple function of its porosity, but depends on the size, distribution and continuity of the pores and the relationship is highly non-linear. Permeability of cement paste mainly depends on the water-cement ratio (w/c) and degree of hydration. Low and medium grade of concretes are generally associated with high w/c ratio and for such concrete permeability becomes another significant factor in its deterioration.

The harmful salt ions enter the body of concrete at various depths under pressure [2] and start reacting with the hydrated cement products and the embedded steel. This results in disintegration of concrete which, in turn, increases its permeability and provide greater access to the detrimental ions for penetration inside. Burry and Domone [13] have shown that penetration of SW into concrete is a function of both the depth of water and time. Possible penetration would be about 75 mm at the end of 20 years at a depth of 26 meter and about 500 mm at a depth of 140 meters.

Haynes et al [14] studied the SW absorption, compressive strength and permeability of high strength concrete at 0 m, 150 m and 6092 m depth of water. It was observed that concrete absorbed SW to greater extent at higher depths. The compressive strength of concrete increased and its permeability decreased with time.

Brown et al [15] conducted tests on a number of concrete prisms containing mild steel bars immersed in SW in pressure cylinder under a pressure equivalent to 100 m head for one year. The test results indicated that although complete saturation by SW had occurred the rebar was still bright i.e. there was no trace of corrosion.

Krishnomoorthy and Kawadkar [2] have shown through their experimental investigation that pressure plays a significant role in the deterioration of cement concrete exposed to SW wherein chemical and morphological changes occur at a rapid rate.

Although extensive research has been conducted on the durability of concrete in splash/tidal zone conditions, very few works were documented regarding the study of behavior of concrete under large hydrostatic pressure. The relevant information presented in literature varies to a greater extent or debatable. The paper reports a comprehensive experimental investigation regarding the physical and morphological changes of concrete exposed to deep sea environment particularly under high hydrostatic pressure. Different physical and chemical aspect of concrete exposed to simulated deep sea underwater environment has been studied to provide useful information relevant to the construction, repair and maintenance of reinforced concrete (RC) structure in such locations.

**Experimental Program**

Experimental studies were carried out using both normal and accelerated test techniques over a period of 12 months. The different test parameters studied and the materials involved were as follows:

**Materials Used**

Ordinary Portland Cement (OPC) conforming to IS 269-1976 was used as binding material. The physical properties and chemical compositions of the same is given in Table-2 . Crushed stone (20mm down grade, FM-6.95) and sand (FM-2.63) conforming to IS 383-1970 were used as course and fine aggregate respectively. Commercial grade salts were used for making artificial sea water which was procured in a single lot to avoid variation in effective ion concentration (16).

**Variables Studied**

(a) **Curing water**

Plain water (PW) as well as sea water (SW) of different concentration (1N, 3N) were used for curing in which the specimens were subjected to hydrostatic pressure simulating the artificially created deep sea environments. 1N means normal seawater made by mixing tap water with exact amount and proportion of principal salts found in natural seawater. Thus 3N will have salt concentration enhanced to 3 times as for normal seawater. The enhanced concentration was used to obtain accelerated effects. The composition of artificial sea water is given in Table 3.

(b) **Exposure condition**

Specially fabricated cylindrical vessels were used to achieve high hydrostatic pressure and varying temperature environmental loading for accelerated experimentation. The pressure vessels have been fitted with appropriate hydraulic
values so that the desired pressure may be applied and maintained over the required duration of the tests. The Pressure levels are 0, 1.5 and 3.0 MPa. The temperature variations are: 27°C, 50°C and 65°C.

(c) Concrete quality:
Two different grades of concrete namely concrete A and B. The relevant information including mix proportion is given in Table 4.

(d) Exposure periods:
1, 3, 6 and 12 months.

(e) Type and size of test specimens:
150 mm dia X 150 mm high cylindrical specimens.

(f) Relevant tests:
Visual examination, Weight change, Volume change, Compressive strength, Permeability and X-ray diffractometry (XRD).

A total number of 200 specimens were cast from two different concrete mixes as per test requirements. The specimens after 28 days plain curing at 27°C, were submerged in specially designed pressure vessels containing 1N and 3N sea water at different pressure and temperature levels for different exposure periods. Enhanced temperature was used for accelerated test effects.

In this study, the coefficients of permeability of the test specimens were determined according to IS: 3085-1965 based on Darcy’s law. The compressive strengths were determined as per IS:516-1959 specification and the change in volume of the concrete specimens were measured using water displacement technique. After a specific period of exposure, the specimens were taken out from time to time and were subjected to various tests. Nondestructive tests including visual examination, weight and volume changes, if any, permeability tests were carried out before conducting compressive strength test. Concrete chips were collected from different levels of the deteriorated specimens for XRD studies.

Results and Discussion
Visual examination of the specimens of concrete A and B after 12 months exposure in controlled pressure and temperature environment shows that the external surfaces tend to become uneven. Changes in color from dark grey to light grey is observed whereas interior concrete shows no such colour change. It may be due to the salt deposition on the exposed surfaces. A high level of wetness has been found particularly in specimens kept in high pressure and temperature environment. A whitish compound namely brucite is also seen around the coarse aggregate of the tested concrete specimens.

The change in weight of the specimens under the various pressure temperature environments has been shown in Figures 1.1 and 1.2. It is seen that weight change stabilises at around + 1.3% although no definite pattern of weight change with increasing pressure and temperature has been observed.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Characteristics</th>
<th>Value Obtained (experimental)</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</td>
<td>24</td>
<td>–</td>
</tr>
<tr>
<td>4.</td>
<td>Soundness by Le Chatelier’s Test (mm)</td>
<td>0.35</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>5.</td>
<td>Specific Gravity</td>
<td>3.15</td>
<td>3.15</td>
</tr>
<tr>
<td>6.</td>
<td>Setting Time</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Initial (min.)</td>
<td>31</td>
<td>&gt; 30</td>
</tr>
<tr>
<td></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>33.5</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>FeO₂</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>
The specimens in PW and 3N sea water under atmospheric pressure shows a maximum weight change of 0.70% and 0.84% respectively. Figures 1.3 and 1.4 show the change in volume of concrete A and B respectively in different SW environments. The volume of concrete is seen to increase with the increase of duration of exposure period. The volume change stabilises at around +0.08% for both the concrete. The corresponding changes in concrete in PW and 3N sea water under atmospheric pressure is around 0.065% and 0.80%. No noticeable difference is observed between the change in volume of test specimen in PW and SW. It may be due to the influence of high environmental pressure.

The increase in weight and volume of concrete in SW is due to the attack of sulfate ion resulting in the formation of expansive compounds like ettringite (E) and salt crystallisation in the pores causing water to be displaced from the voids.

Permeability characteristics of concrete specimen exposed to corrosive and non-corrosive environment have been graphically presented in Figures 1.5 and 1.6. It is observed that the permeability values decrease initially for a period of about 3 months and then increase at the later period whereas the concrete in PW shows a continuous reduction with time. After 12 months of exposure, the permeability of concrete is found to lie in the range of 101 to 125 percent as compared to 28 days compressive strength of normally cured concrete. After 12 months, the compressive strengths were observed to be about 91 to 112 percent. The compressive strength of specimens in SW under different exposure condition and ages are compared with PW cured specimens for similar ages to get the relative strength (%) as shown in Figures 1.9 and 1.10. The loss of strengths over 12 months lie in the range of 15 to 26 percent, the maximum being under the pressure of 3 MPa. Thus the high ambient pressure is seen to be a decisive factor for strength deterioration of marine concrete exposed to large hydrostatic pressure.

The strength deterioration of concrete specimens is attributed to the formation of expansive weak compound like ettringite (E), thaumasite (TH), calcium aluminate hydrate (CAH) due to sulfate attack. Some crystalline products formed in the voids of concrete have also leached out in SW. X-ray diffractograms of the concrete specimens are shown in Figure 1.11. For comparison, the XRD pattern of concrete specimens cured in PW under atmospheric pressure and in 3N SW under 3.0 MPa pressure associated with 3 different temperatures for the periods of 1 and 12 months are shown in the same figure. A careful comparative study among the peaks shows that in sea water the percentages of all expansive compounds and the quartz increase and those of the other compounds decrease as compared to the PW cured concrete for similar duration. This clearly indicates that after 12 month exposure, the formation of the expansive compounds like ettringite (E), thaumasite (TH), and calcium aluminate hydrate (CAH) is higher due to the sulfate action as compared to the strength imparting compound like calcium silicate hydrate. The expansion compounds being lighter in density having low compressive strength causes the strength deterioration as revealed in Figures 1.9 and 1.10.

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### 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><strong>Total</strong></td>
<td></td>
<td><strong>35.0</strong></td>
<td></td>
</tr>
</tbody>
</table>

### Table 4: Concrete mix proportion and Relevant Proportion

<table>
<thead>
<tr>
<th>Concrete</th>
<th>Mix Proportion</th>
<th>W/C Ratio</th>
<th>Chloride Level</th>
<th>28 Days Compressive Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1:1.15:2.20</td>
<td>0.39</td>
<td>0.010</td>
<td>48.0</td>
</tr>
<tr>
<td>B</td>
<td>1:1.2:1.10</td>
<td>0.36</td>
<td>0.008</td>
<td>53.5</td>
</tr>
</tbody>
</table>
Conclusion
Based on the limited number of tests and variable studied as stated above over a period of 12 months, the following conclusions can be drawn:

(a) Concrete undergoes some change in colour from original dark grey to light grey.
(b) Concrete gains weight and shows volumetric expansion at all pressure and temperature. The change in weight and volume is seen to be stabilised at around +1.3% and 0.08% respectively.
(c) The compressive strength of concrete increases by 25% in the initial 3 months and then decreases by around 26% over a period of 12 months as compared to 28 days normally cured concrete.

Figure 1.1: Weight Change - Exposure time relation for concrete A in PW / 3N, P-Pressure (MPa), T-Temp. (˚c)

Figure 1.2: Weight Change - Exposure time relation for concrete B in PW / 3N SW, P-Pressure (MPa), T-Temp. (˚c)

Figure 1.3: Volume Change - Exposure time relation for concrete A in PW / 3N, P-Pressure (MPa), T-Temp. (˚c)

Figure 1.4: Volume Change - Exposure time relation for concrete B in PW / 3N SW, P-Pressure (MPa), T-Temp. (˚c)

Figure 1.5: Permeability - Exposure time relation for concrete A in PW / 3N, P-Pressure (MPa), T-Temp. (˚c)

Figure 1.6: Permeability - Exposure time relation for concrete B in PW / 3N SW, P-Pressure (MPa), T-Temp. (˚c)

Figure 1.7: Compressive Strength - Exposure time relation for concrete A in PW / 3N, P-Pressure (MPa), T-Temp. (˚c)
Concrete exposed to seawater under high pressure exhibited an initial decrease in permeability followed by a gradual increase in permeability with time. After 12 months exposure, the permeability values of salt affected specimens were about 7 to 14 times the permeability values of PW cured concrete.

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

Ambient hydrostatic pressures is seen to be a decisive factor for concrete deterioration in deep sea marine environment.

REFERENCES


Figure 1.11: X-Ray diffractograms of concrete specimens after exposure to PW & 3N SW under different temperature and hydrostatic pressure