

# EFFECT OF FREEZE-THAW ACTION ON PHYSICAL AND MECHANICAL BEHAVIOR OF MARINE CONCRETE

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## ABSTRACT

*The deterioration of structural concrete in marine environment and its progress with time is a problem of great importance. Particularly, in splash/ tidal zone, salt water spray and alternate wetting–drying cycles often lead to a build up of salt ions within the concrete pores. Moreover, concrete under alternate freeze-thaw actions suffers worstly on account of accumulated ice pressure and also due to gradual penetration of salt ions in it and the formation of expansive/ leachable compound including the rebar corrosion may lead to cracking, spalling and even the structural distress. This paper presents a part of an experimental study on the freeze–thaw effect of concrete specimens exposed to artificial seawater simulating the arctic marine environment over a period of 15 months. The test specimens made from two different grades of concrete were subjected to artificial freeze-thaw environment under different condition. The test variables include the concrete grade, seawater concentration, exposure condition, and the deteriorative effects were measured by studying the visual appearance, weight and volume change, compressive strength, permeability characteristics and XRD patterns of the deteriorated test specimens. The test results show that after 360 cycles of freezing and thawing, concrete in sea water losses about 75% of its compressive strength as compared to the strength of plain water cured concrete of similar age.*

**Keywords:** Chloride Attack, Compressive Strength, Durability, Freeze-thaw Action, Marine Environment, Permeability, Sulfate Attack

## 1.0 INTRODUCTION

Concrete has been used as a basic structural material for various types of offshore/onshore structure over the several decades. Concrete structures in such locations are always required to withstand physical, chemical and mechanical action of sea water under various environmental condition throughout their life span. Moreover, the recent discovery of oil and natural gases in arctic and sub-arctic region has drawn the attention of scientists and researchers to study the performance of concrete structures in such locations. Tidal action causing alternate wetting and drying cycles, abrasion and salt water spray due to wave thrust, high ambient pressure due to large hydrostatic head, freeze-thaw (F-T) cycles due to climatic change, wide variation of ambient temperature and humidity are the major physical and mechanical loadings of marine environment. While, the chemical loadings include the gradual penetration of detrimental sea salt ions into the cement mortar matrix which, after chemical reaction, initiate the decomposition of mortar matrix and also the corrosion of the embedded rebars.

The term marine environment is generally well understood but the complexities inherent in such an environment is not clear. It is not just over the sea, but it could be deemed to be extending over the coast and the neighbourhood of tidal wave, backwater and estuaries [1]. Broadly, it covers the area where concrete becomes wet with sea water and wherever the wind will carry

salt water spray which may be up to a few miles inland [1,2].

Depending on the tidal range, sea water (SW) actions, nature, extent and mechanism of deterioration process, a structure exposed to a marine environment can be divided into four different zones (Refer Figure 1). Structural concrete at the upper part of the splash zone and at atmospheric zones are reported to experience the effect of alternative freezing and thawing. In this location, the air is heavily laden with moisture and contains substantial quantities of salt and gas [3]. Winds are more frequent with a maximum velocity as much as 250 km/hour and the ambient temperature may range from 50°C in the Persian/Arabian Gulf to -45°C in the arctic region [4].

Typically, sea water contains about 3.5% soluble salts by weight [5]. The relative ionic concentrations are 18 gpl Cl<sup>-</sup>, 12 gpl Na<sup>+</sup>, 2.6 gpl (SO<sub>4</sub>)<sup>2-</sup>, 1.4 gpl Mg<sup>2+</sup> and 0.5 gpl Ca<sup>2+</sup>. Normally, pH of sea water is about 8. However due to the presence of decaying organic matter, highly carbonated sea water show a pH value of 7 or less.

In splash zone, the building up of salt ions takes place due to wave thrust and continuous salt water spray. In cold climatic region, during freezing process, the pore water inside the concrete freezes and expand in volume creating huge pressure on the adjacent concrete. Also the penetrated sea salts in pore water reacts with the hydrated cement products and form the expansive compounds like Ettringine, Friedels salt and some

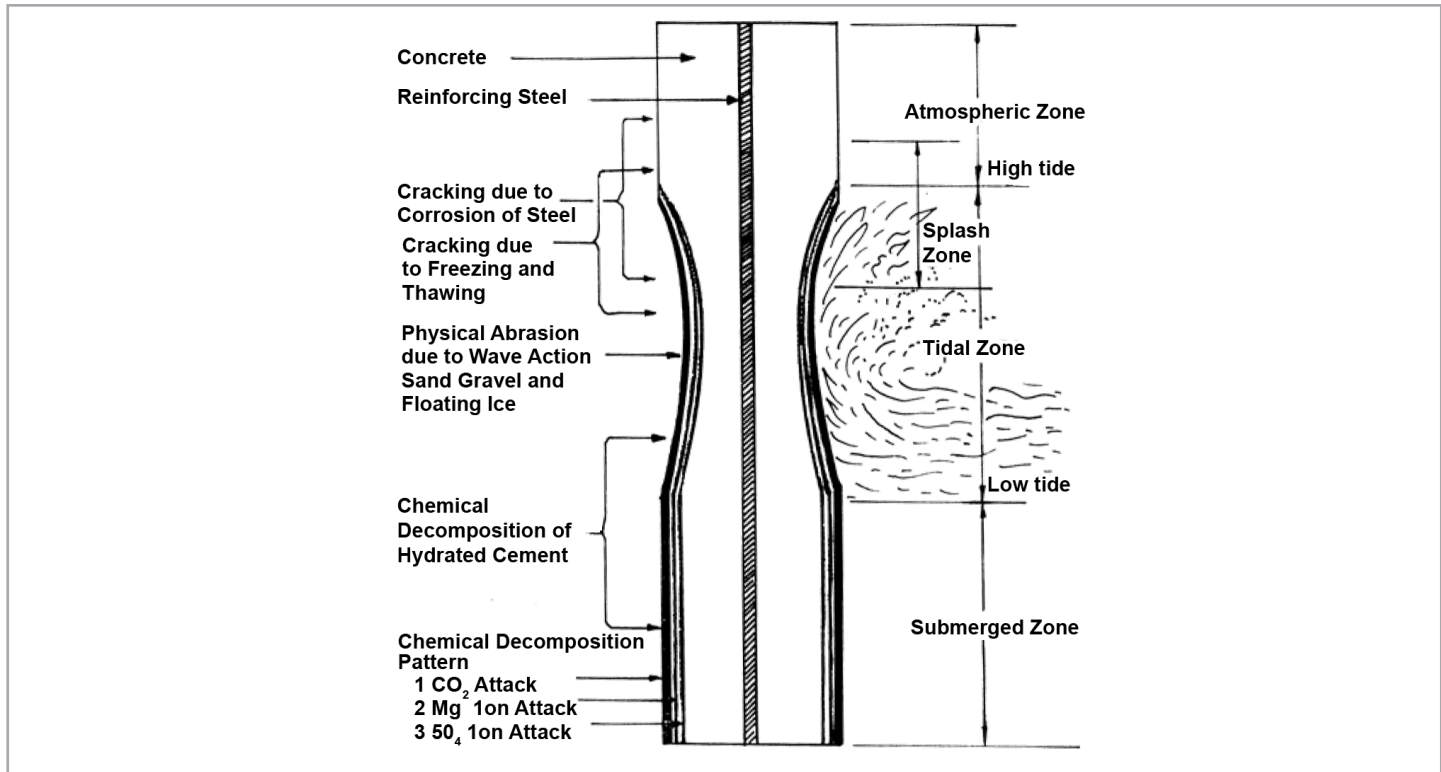


Figure 1: Diagrammatic representation of deterioration of structural concrete exposed to sea water [8]

leachable compounds. Thus in alternate freezing and thawing process, the damage in marine concrete is caused by two fold expanding activities followed by leaching of the soluble leachable compounds during thawing periods which makes the concrete more permeable thereby allowing more harmful salts ions to penetrate inside.

In arctic and sub-arctic region, the nature of deterioration of concrete structures in the sea is dependent on the condition of exposure. The part of the structure that remains fully submerged will be subjected to chemical attack mainly, whereas the section of the structure that is above the high tide level will be affected by frost action in air and by the corrosion of the reinforcement. The concrete in the tidal zone will not only be vulnerable to wetting and drying, frost action and corrosion of reinforcement but also to chemical decomposition of the cement paste [6].

## 2.0 FREEZE-THAW EFFECT OF MARINE CONCRETE

Freezing is a gradual process and depends on the rate of heat transfer, progressive increase in the concentration of dissolved salts in pore water and the pore size distribution. Fresh concrete contain a considerable quantity of free water and on freezing, discrete ice lenses are formed which expands about 9% in volume. The increased volume of the ice lenses disrupts the fresh concrete causing nearly permanent damage to concrete. The fully hardened concrete is also vulnerable to frost damage, particularly to the effect of alternate cycle of freezing and thawing. The severest condition for frost action arise when concrete has more than one face exposed to weather and in such a position it remains wet for a long period.

One of the theories attributes the damage directly to the empty space available being insufficient to accommodate the

additional solid produced when the free water held in concrete freezes. Second theory attributes the failure to the production of pressure due to the growth of ice lenses parallel to the surface of the concrete owing to the migration of water from capillaries like the phenomena of frost heaving in soils. Another theory explains the failure to the generation of water pressure within the capillary cavities as the ice crystals grow. In all these theories, the permeability, rate of absorption and degree of saturation of the concrete are all important factors. Freezing starts at the surface in the largest cavities and gradually extends to smaller cavities. Water contained in the gel pores are too small to get frozen till the temperature goes below  $-78^{\circ}\text{C}$  [5]. In practice, no ice is formed in the gel pores. The resistance of concrete to frost action depends on the strength of the paste, water/cement ratio, type of aggregate used, age of concrete, duration and extent to which the concrete is subject to freezing action.

It has been estimated that the freezing of water in the hardened concrete may exert a pressure of about 14 MPa which is large enough to exceed its tensile strength and consequently the damage occur [5]. The extent of damage varies from surface scaling to complete disintegration as ice is formed, starting at the exposed surface to the concrete and progressing through its depth.

In a marine environment, in addition to its presence in original mix, the chloride ion penetrates into the concrete either from sea water or sea winds carrying sea salts and reacts with the hydrated cement products which produces complex compounds including Friedels salt which are leachable and expansive in nature. The chloride attacks also destroy the passivity of steel and lead to the initiation of rebar corrosion. On the other hand, the penetration of sulphate ions attack the hydrated cement matrix with the formation of gypsum and a complex compound known as calcium sulphotoaluminate (ettringite). Bogue [7] is of the

opinion that the formation of gypsum hydrate causes an increase of 17.7% in volume. The action of principal sea salts namely NaCl, MgCl<sub>2</sub>, MgSO<sub>4</sub> and CaSO<sub>4</sub> on hardened concrete results in the formation of the expansive/leachable compounds like Calcium chloroaluminate (Friedels Salts), Calcium aluminate sulfate hydrate (Ettringite), CaCl<sub>2</sub> *etc.* [8,9,10].

The reaction products such as Friedels salt has a property of low to medium expansion. The formation of excess calcium chloride, being leachable, results in increased permeability of structural concrete leading to materials 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 [11] considers leaching, expansion, formation of weak compounds as the various causes of concrete deterioration when subjected to chloride or sulfate attack.

From the above discussion, it is clear that the structural concrete exposed to a marine environment with alternate freezing and thawing cycles faces twofold problems regarding deterioration. Concrete in such locations are required to withstand the stress resulting from the increased volume of frozen pore water and also from the expansive hydrated products caused by the action of sea salts. The leachable nature of some hydrated compounds lead to the formation of porous concrete which allows more objectionable salts ions to come in contact with the interior unaffected concrete and thereby enhancing the deterioration mechanism. Detwiler *et al.* [12] assessed the durability of concrete in Freezing and Thawing by examining the microstructure of the deteriorated concrete specimens with the help of scanning electron microscope and suggested to include microscopic examination of laboratory test specimens to predict the behaviour of concrete under freeze-thaw condition. Whiting *et al.* [13] studied the frost resistance of concrete subjected to a deicing agent namely NaCl at different concentration (1.5, 3 and 10%) and under various ambient condition (30%, 47%, 72% and 88% RH). Concrete specimens fully saturated in 3% NaCl solution exhibited greater expansion for successive F-T cycle. Wright *et al.* [14] carried out an investigation into methods of carrying out accelerated freezing and thawing test on concrete and showed that damage occurred more rapidly when specimens were frozen immersed in water than frozen in air although the rate of freezing was lower.

Zamam *et al.* [15] studied the deterioration of concrete due to freezing and thawing and to deicing chemical use and showed that the visual estimation could be extremely misleading in terms of strength characteristics and maximum loss in strength was recorded for saturated solution. Chandra and Xu [16] studied the influence of presaturation and F-T test condition on length changes of Portland Cement Mortar. It was seen that swelling depended upon the salt concentration gradient and was greater in dilute salt than in saturated salt solution. Maximum deterioration was observed at 3% NaCl solution. Mosongo *et al.* [6] in their Freeze-Thaw test on concrete in sea water found that surface effects probably could play an important role in the deterioration mechanism of concrete under arctic condition.

Among the several durability problems that arise in concrete exposed to a marine environment, those that have

been studied extensively are the chemical attack of sea water on cement paste, concrete and the corrosion of embedded steel. Very limited research works have been documented on the freezing and thawing in sea water. The relevant information presented in literature varies to a great extent or debatable. It is important to have a detail information regarding the concrete durability during freezing and thawing in sea water in view of the increasing use of concrete in the sub-arctic/arctic region. The freeze-thaw action on concrete structures in the splash/tidal zone has its own characteristics and is dependent on ambient air and sea water temperature. Concrete in this location can thaw at temperature as low as -1°C by the action of waves and tides and can freeze to temperature as low as -50°C when exposed to air [6]. These severe conditions, in combination with the chemical attack of the sea water on the cement constituents, are found to lead to a more pronounced deterioration in the concrete structure.

In this investigation, the freeze-thaw durability of two different grades of concrete has been studied in a laboratory simulated artificial marine environment representing the structural concrete exposed to arctic/sub-arctic region. The similar study was also conducted in fresh water environment for comparison. Physical, mechanical as well as chemical aspects of concrete deterioration in such location has been examined with view to compare the data reported by other researchers in the similar field.

### 3.0 EXPERIMENTAL PROGRAM

An experimental investigation together with the creation of artificial marine environment was carried out over a period of 15 months. The material used and the variables studied were as follows:

#### Materials Used:

Ordinary Portland Cement (OPC) conforming to IS 269-1976 from a single lot was used as binding material. The physical properties and chemical composition of the cement is given in Table-1. Coarse Aggregates were 20 mm down well graded crushed stone having fineness modulus (FM) of 6.95 while Fine Aggregates used were well graded coarse sand of FM 2.63 and both the aggregates conformed to IS 383-1970 requirements. Commercial grade salts were used for making artificial sea water which was procured in a single lot to avoid the variation in effective ion concentration.

#### Variables Studied:

##### (a) Curing Water:

Plain water (PW) as well as artificially made sea water (SW) were used for curing the specimens. SW was made by mixing tap water with exact amount and proportion of principal salts found in natural sea water. The composition of artificial sea water is given in Table-2.

##### (b) Exposure Condition:

The alternate Freezing-Thawing arrangement was created in a F-T chamber. In each F-T cycle, the temperature was varied from (-27°C) to (+27°C) over a total period of 30 hours (12+12

hours for freezing and thawing; 3+3 hours kept at two terminal temperatures). The test specimens were kept in three separate states namely (i) Submerged (SUB) in SW, (ii) Submerged in PW and (iii) Atmospheric (ATM)

**(c) Concrete Grade:**

Two different grades of concrete namely concrete A and B. The relevant information of the concrete mixes is given in Table-3.

**(d) Exposure Periods:**

30, 90, 180 and 360 F-T cycles.

**(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, stress-strain characteristics and X-ray diffractometry (XRD).

A total number of 84 specimens were cast from two different concrete mixes as per test requirements. Plain water (PW) was used to cast all the specimens. The specimens after 28 days PW curing at 27°C were exposed to different conditions in the F-T chamber. Separate Galvanized Iron (GI) tanks were used for PW, SW and ATM state of exposure. After a specific period of exposure, the specimens were taken out for various tests as stated above. The coefficient of permeability of the test specimens were determined according to IS: 3085-1965 based on Darcy's law whereas the compressive strength were determined as per IS: 516-1959. Various nondestructive tests including visual examination, weight and volume change, permeability tests were carried out before conducting destructive tests. Concrete chips were collected from different points of the deteriorated specimens for XRD studies. The experimental program including the various tests conducted are summarised in Table-3. The results of the investigations are presented and discussed below.

**Table 1: Physical properties and Chemical Composition of Cement (OPC)**

(Source: Associated Cement Company, India)

Sl. No.	Characteristics	Value obtained (experimental)	As Per IS: 269-1976
1.	Fineness (90 $\mu$ Sieve) %	9.5	<10
2.	Blaine's Sp. surface (cm <sup>2</sup> /g)	2560	>2250
3.	Normal Consistency	24	---
4.	Soundness by Le Chatelier's Test (mm)	0.35	<5
5.	Specific gravity	3.15	3.15
6.	Setting Time		
	Initial (min.)	31	>30
	Final (min)	63	<600
7.	Compressive Strength (MPa)		
	(i) 3 days	23.70	>16.0
	(ii) 7 days	33.5	>22.0
8.	Loss on ignition	1.99	<4
9.	Insoluble matter	1.43	---
10.	SiO <sub>2</sub> (silica)	17.40	---
11.	Al <sub>2</sub> O <sub>3</sub>	11.56	---
12.	Fe <sub>2</sub> O <sub>3</sub>	2.51	---
13.	CaO	60.05	---
14.	MgO	1.30	<5
15.	SO <sub>3</sub>	2.68	---

Table 2: Composition of artificial sea water

Salt Type	Chemical Formula	Amount (gm)	Remarks
Sodium Chloride	NaCl	27.20	These amounts of salts were dissolved in plain water to prepare 1000 gm of Sea water of 1N concentration
Magnesium Chloride	MgCl <sub>2</sub>	3.80	
Magnesium Sulfate	MgSO <sub>4</sub>	1.70	
Calcium Sulfate	CaSO <sub>4</sub>	1.20	
Potassium Sulfate	K <sub>2</sub> SO <sub>4</sub>	0.90	
Calcium Carbonate	CaCO <sub>3</sub>	0.10	
Magnesium Bromide	MgBr <sub>2</sub>	0.10	
		<b>Total: 35.0</b>	

Table 3: Experimentation programme in freeze-thaw environment

Concrete	Compressive Strength (MPa)	Specimen Size (mm)	Specimen No.	Environmental Conditions				Test	
				Exposure States	Curing Solution	Temp. Condition			
						F-T cycle (± 27°C)	Const. Temp (+ 27°C)		
A B	46.0 53.0	D=150 H=150	24	SUB	SUB (1N)	30	-----	a) Visual Examination b) Weight change c) Volume change d) Permeability e) Compressive strength f) Stress-strain characteristics g) X-ray diffractometry	
						90	-----		
						180	-----		
						360	-----		
A B	46.0 53.0	D=150 H=150	24	SUB	PW	30	-----		
						90	-----		
						180	-----		
						360	-----		
A B	46.0 53.0	D=150 H=150	24	ATM	---	30	-----		
						90	-----		
						180	-----		
						360	-----		
A B	46.0 53.0	D=150 H=150	12	SUB	PW	30	38 days		
						90	112 days		
						180	225 days		
						360	450 days		
Total : 84 Nos									
Concrete A: Mix 1:1.15:2.20, w/c=0.39, 28 days cube strength=46.0 MPa Concrete B: Mix 1:1:2.10, 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; D=Diameter; H=Hight; F-T: Freezing and Thawing.									



#### 4.0 RESULTS AND DISCUSSION

Concrete specimens after specific period of alternate F-T exposure in the submerged states of sea water, plain water and in atmospheric states are taken out for conducting various tests. After visual inspection, it is seen that concrete in sea water have lost their dimensional stability with substantial erosion and splitting/crumbling on the surface (Refer to Plate No.1) whereas in PW and in ATM states, concrete surface tend to become uneven. Some changes in colour from the original dark gray to lime gray in the specimens in sea water have also been observed which indicates either the salts deposition on the concrete surfaces or leaching out of portlandite,  $\text{Ca}(\text{OH})_2$ . Also interior surfaces have indicated a higher level of saturation with increasing number of F-T cycles both in sea and plain water environments.

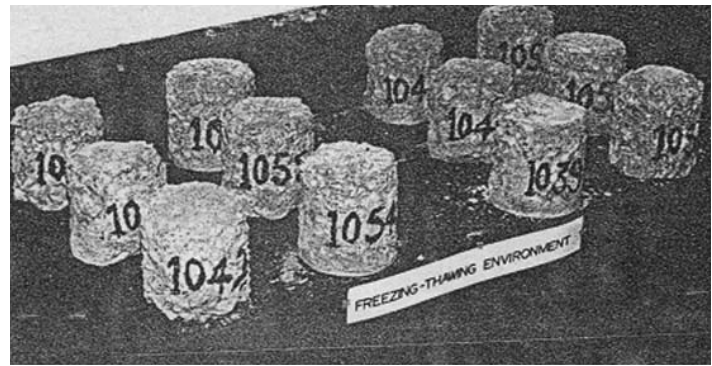


Plate no. 1: Concrete specimens after 360 cycles of freezing and thawing in seawater

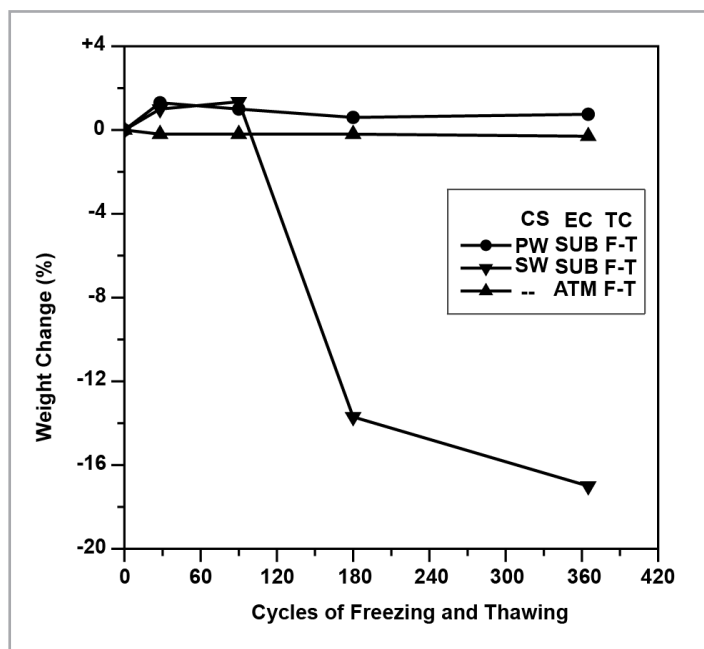


Figure 1(a): Weight change - Freeze-thaw relation for concrete-A CS-Curing Soln.; EC-Exp. Cond.; TC-Temp. Cond.

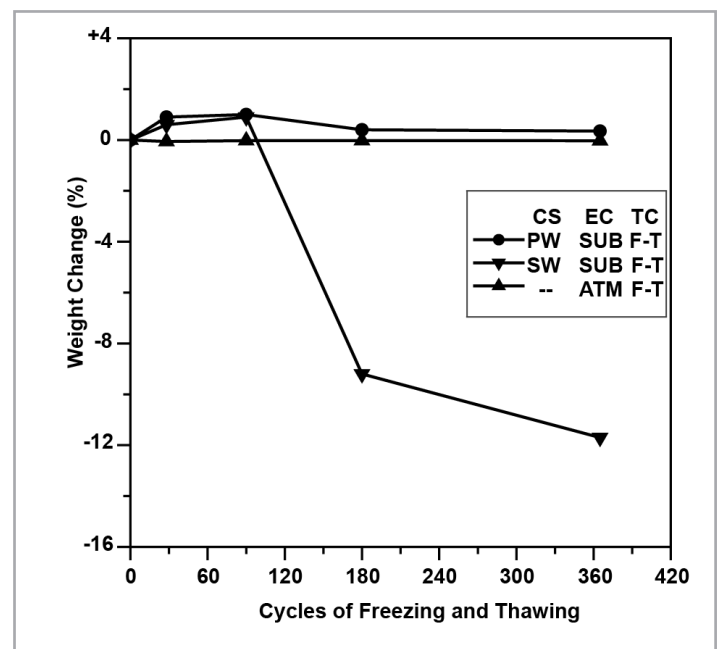


Figure 1(b): Weight change - Freeze-thaw relation for concrete-B CS-Curing Soln.; EC-Exp. Cond.; TC-Temp. Cond.

The change in the weight of the specimens of concrete A and B in different exposure conditions have been illustrated in Figures 1(a) and 1(b) respectively. A close examination reveals that initially in the first about 90 cycles, the submerged specimens exhibit a higher percentage (nearly 0.7 to 1.4 percent) of weight gain as compared to the atmospheric state specimens (nearly 0.2 to 0.3 percent). This increase in the weigh may be primarily due to the ingress of salt water or plain water into the concrete. After 90 cycles, a significant difference in the trend of the weight change of the concrete specimens exposed to sea water has been found to occur as compared to that for the specimens placed in plain water or in the atmospheric state. After 360 cycles of freeze-and-thaw, a considerable change in the weight lying between -16.5 percent and -11.5 percent is observed for the concretes A and B exposed to the sea water environment whereas for the specimens placed in plain water or in the atmospheric state, the changes in the weight are found to lie in the range of +0.3 to +1.0 percent and -0.2 to -0.1 percent respectively for both the concretes. The considerable loss of weight of the specimens exposed to

sea water is primarily due to crumbling of outer surfaces of the specimens caused by crystallisation of sea salts in the voids of concrete and their subsequent expansion during freeze-thaw cycles.

The volume changes in the specimens of concretes A and B for the above mentioned environment states are illustrated in Figures 2(a) and 2(b) respectively. It is clear from these figures that the specimens in the submerged state either in sea or plain water have exhibited a volumetric expansion of nearly 0.03 to 0.07 percent till the first 30 cycles of freezing-and-thawing, whereas a volume reduction of 0.03 to 0.07 percent has been found in the specimens placed in the atmospheric state. The increase in volume may be attributed to the ingress of sea or plain water inside the concrete mass. After 30 cycles of alternate freezing-and-thawing, the volume of the concrete specimens placed in sea water has been found to decrease due to surface erosion and splitting and after 360 cycles, this reduction is observed to lie between 1.2 and 1.7 percent for the two concretes A and B. For the specimens placed in plain water or in the atmospheric

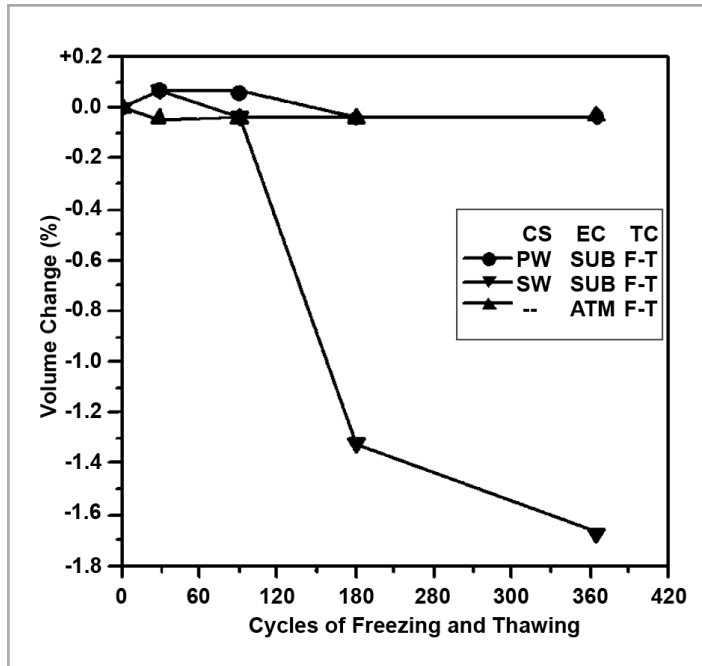


Figure 2(a): Volume change - Freeze-thaw relation for concrete-A CS-Curing Soln.; EC- Exp. Cond.; TC-Temp. Cond.

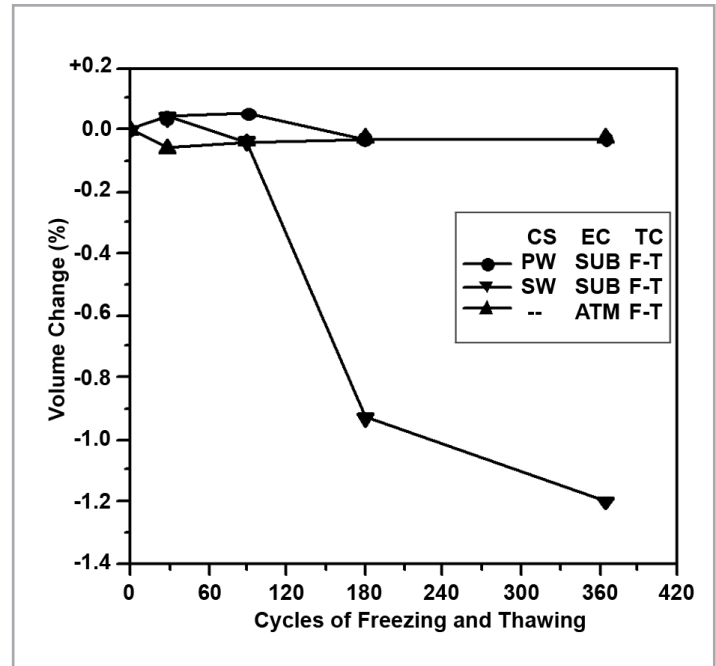


Figure 2(b): Volume change - Freeze-thaw relation for concrete-B CS-Curing Soln.; EC-Exp. Cond.; TC-Temp. Cond.

states, the corresponding reduction in the volumes is about 0.04 percent. The decrease in volume resulting from erosion/crumbling of outer surfaces of concrete may be attributed to the deposition of chemical compounds into the voids of concrete, the crystallisation as well as their expansion due to freezing of the entrapped water inside the voids.

Permeability characteristics of the concrete specimens exposed to different environmental conditions have been graphically illustrated in Figure 3(a) for concrete A and in Figure 3(b) for concrete B. For comparison, the coefficient of permeability of the specimens placed in plain water at a constant temperature of  $27^{\circ}\text{C}$  has been plotted in the same Figures. It

is seen that as the concrete exposed to sea water, it loses its mass through surface erosion and splitting, the coefficient of permeability increases significantly, whereas concrete exposed to plain water or placed in the atmospheric states show only marginal changes in their permeability. After 360 cycles, the permeability of concrete specimens exposed to sea water has been found to lie between  $43$  and  $67 \times 10^{-14}$  m/sec, whereas the corresponding value for both the concretes placed in plain water or in the atmospheric states lies in the range of  $8$  to  $10 \times 10^{-14}$  m/sec. Thus, it is seen that the permeability of concrete exposed to 1N concentration of sea water in the freezing-and-thawing environment is at about 5 to 7 times the value of the permeability coefficient

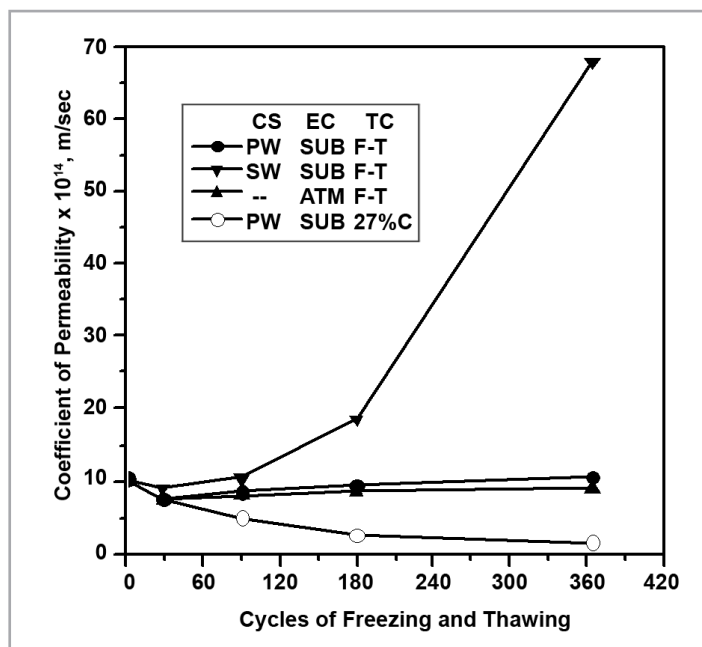


Figure 3(a): Permeability - Freeze-thaw relation for concrete-A CS-Curing Soln.; EC-Exp. Cond.; TC-Temp. Cond.

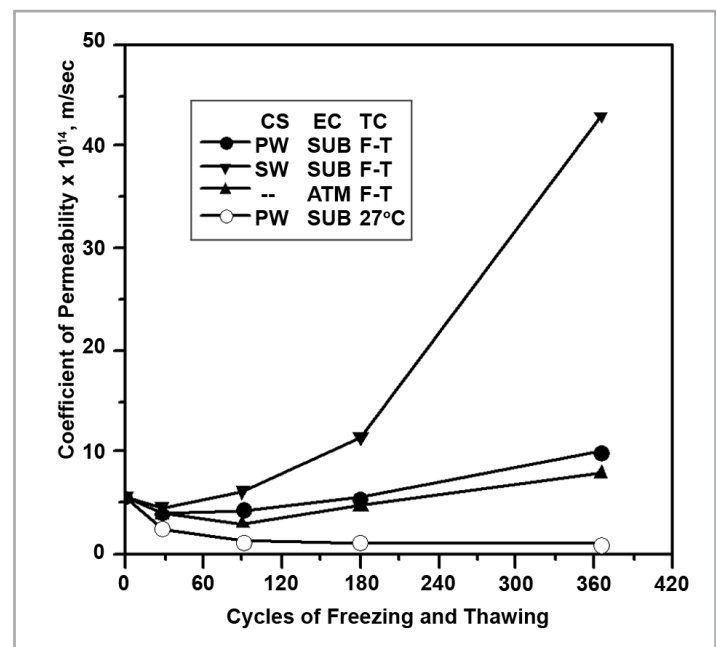


Figure 3(b): Permeability - Freeze-thaw relation for concrete-B CS-Curing Soln.; EC-Exp. Cond.; TC-Temp. Cond.

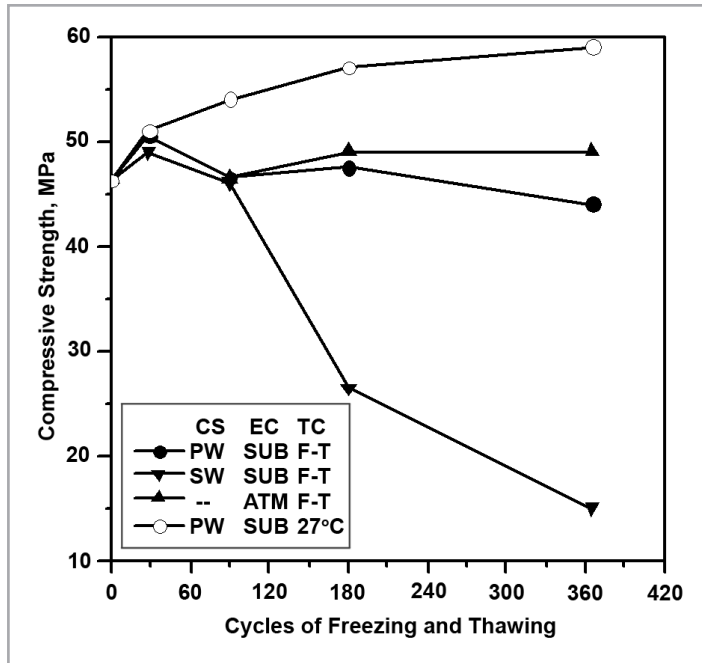


Figure 4(a): Compressive strength - Freeze-thaw relation for concrete-A CS-Curing Soln.; EC-Exp. Cond.; TC-Temp. Cond.

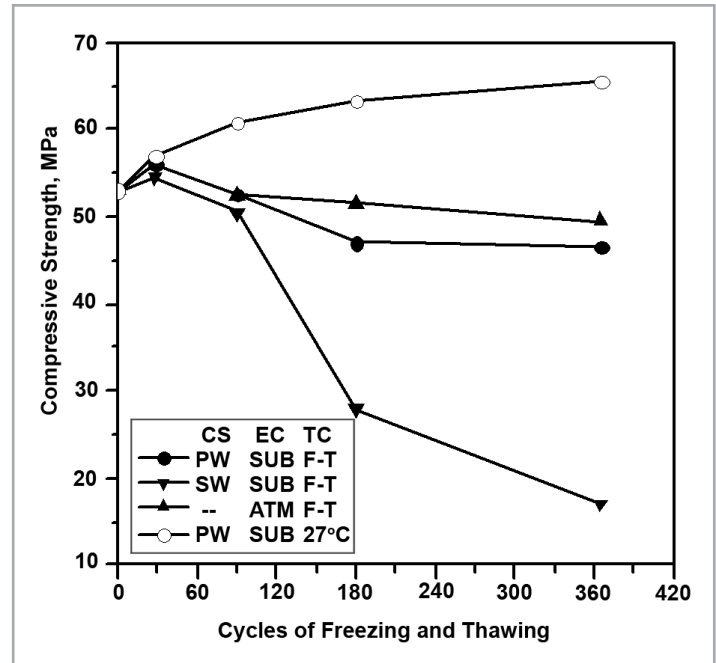


Figure 4(b): Compressive strength - Freeze-thaw relation for concrete-B CS-Curing Soln.; EC-Exp. Cond.; TC-Temp. Cond.

(8 to 10 x 10<sup>-14</sup> m/sec) of the concrete placed in the other environments mentioned above. Also after 360 cycles, the permeability of the concrete specimens submerged in plain water or placed in dry (ATM) state in the freezing-and-thawing environment are around 8 times the permeability of concrete placed in plain water at a constant temperature of 27°C. The larger increase in the permeability of the concrete specimens in the freezing-and-thawing environment of sea water may be due to the formation of relatively greater amounts of total expansive/leachable compounds as compared to other environments.

Compressive strength of the test specimens of concrete A and B exposed to the different environment states are shown in Figures 4(a) and 4(b) respectively. A close examination of these curves indicates that the strength increases during the first 30 cycles of freeze-and thaw in sea water environment, whereas it decreases thereafter. This decrease in the compressive strength has been found to be significant after 180 cycles and most significant after 360 cycles. On the other hand, when submerged in plain water and kept in dry (ATM) state in similar environment, the decrease in the compressive strength is found to be only marginal. It may be noted that in comparison

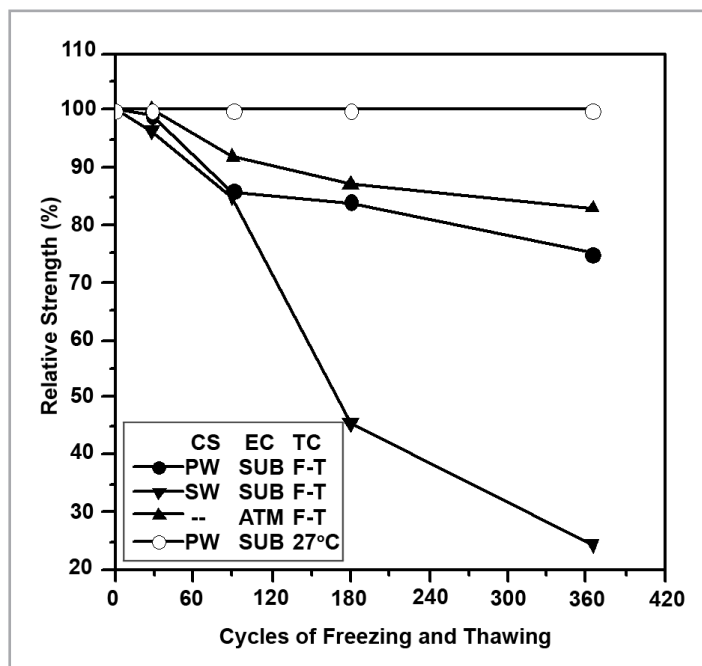


Figure 5(a): Relative strength - Freeze-thaw relation for concrete-A CS-Curing Soln.; EC-Exp. Cond.; TC-Temp. Cond.

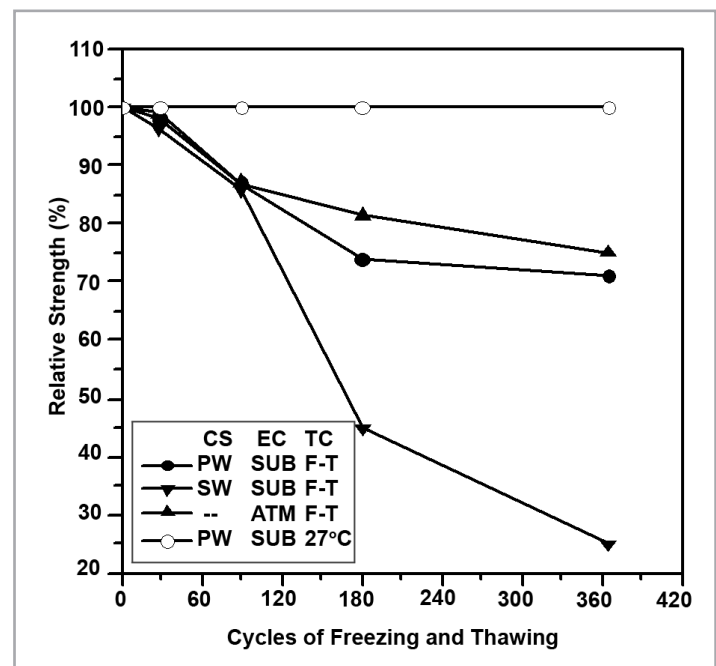


Figure 5(b): Relative strength - Freeze-thaw relation for concrete-B CS-Curing Soln.; EC-Exp. Cond.; TC-Temp. Cond.



to the 28 day compressive strength of plain water cured concrete at constant temperature of 27°C, the compressive strength of the specimens subjected to 360 cycles of freezing-and thawing in sea water, plain water and in ATM state have been found to lie respectively in the ranges of 30 to 32 percent, 89 to 95 percent and 92 to 106 percent for the two concretes. The comparison of the strengths at the same ages of the normally cured concrete specimens and the specimens subjected to freezing-and-thawing actions in different environment states are graphically presented in Figures 5(a) and 5(b) for concretes A and B respectively. It is seen that the compressive strength of the concrete specimens subjected to 360 cycles of freezing-and-thawing in sea water,

plain water and in ATM state lie in the range of 20 to 25 percent, 70 to 75 percent and 75 to 83 percent respectively for the two concretes. Thus, the losses of the compressive strength of concrete specimens after 360 cycles of freezing-and-thawing in sea water, plain water and in atmospheric state (ATM) are around 70, 8, and 5 percent respectively as compared to 28 days strength of normally cured concrete. The corresponding values are 75, 28, and 20 percent respectively as compared to 450 days (360 cycles) strength of normally cured concretes. The increase in strength after the first 30 cycles may due to the fact that the specimens do not get saturated fully by sea water during this period under normal atmospheric pressure. After 360 cycles,

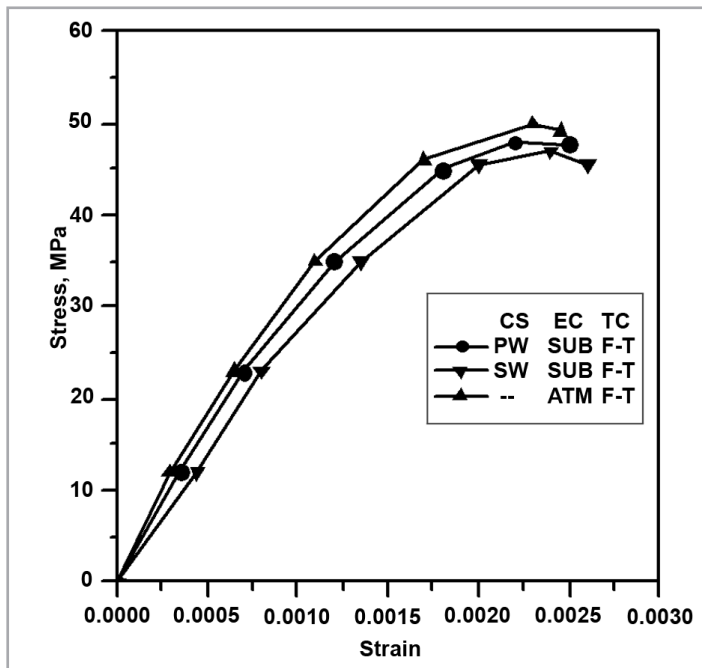


Figure 6(a): Stress-strain curves in compression for concrete-A, after 30 cycles of freezing and thawing

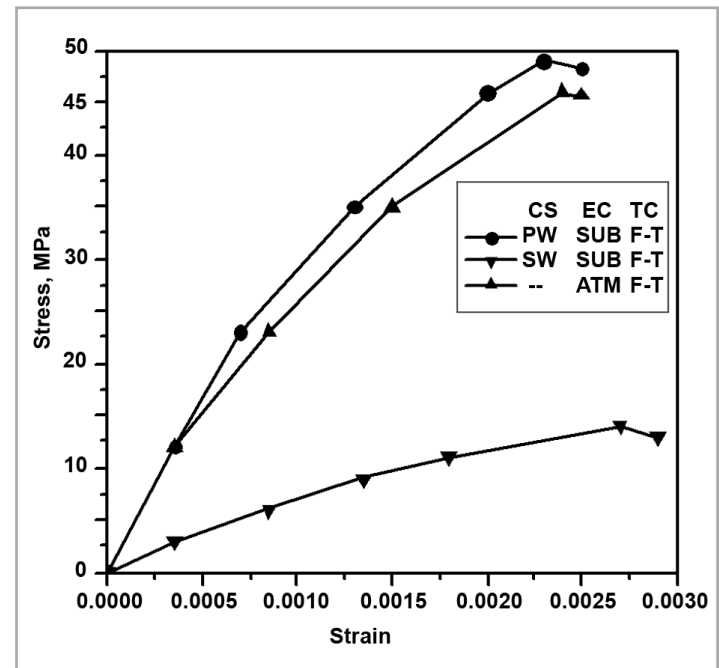


Figure 6(b): Stress-strain curves in compression for concrete-A, after 360 cycles of freezing and thawing

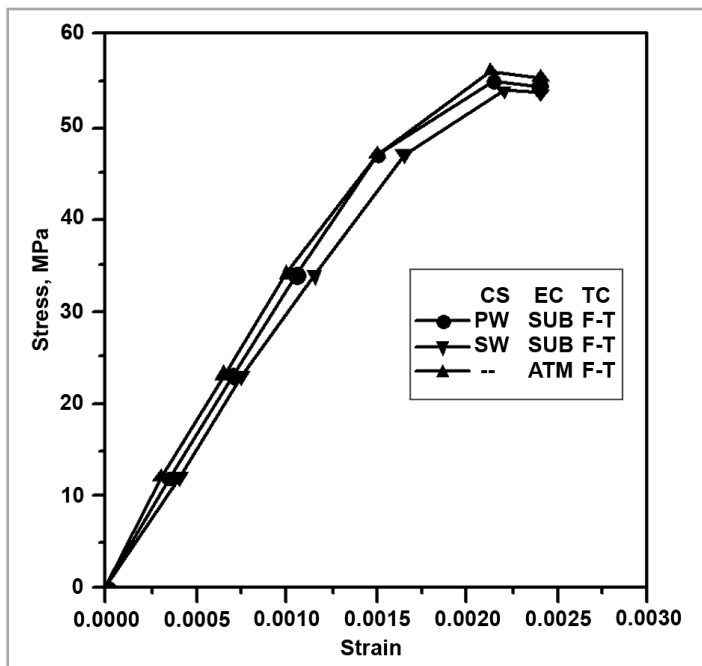


Figure 7(a): Stress-strain curves in compression for concrete-B, after 30 cycles of freezing and thawing

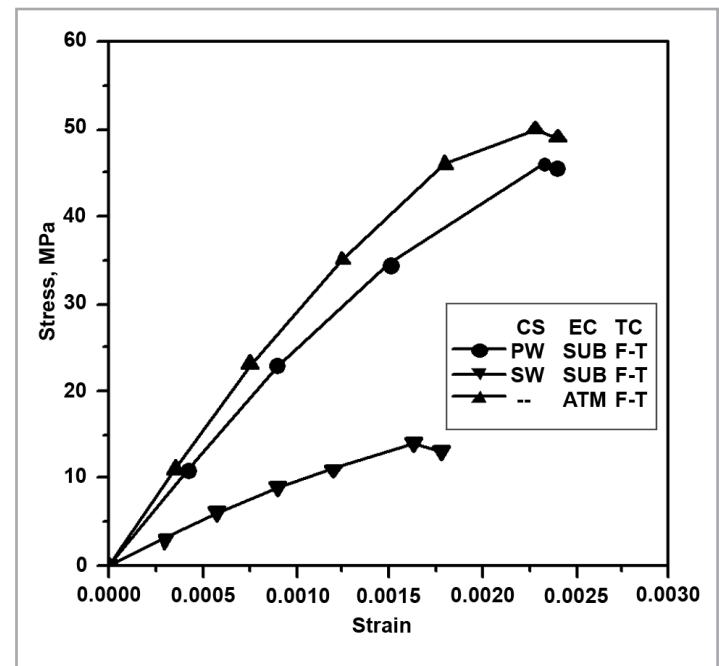


Figure 7(b): Stress-strain curves in compression for concrete-B, after 360 cycles of freezing and thawing

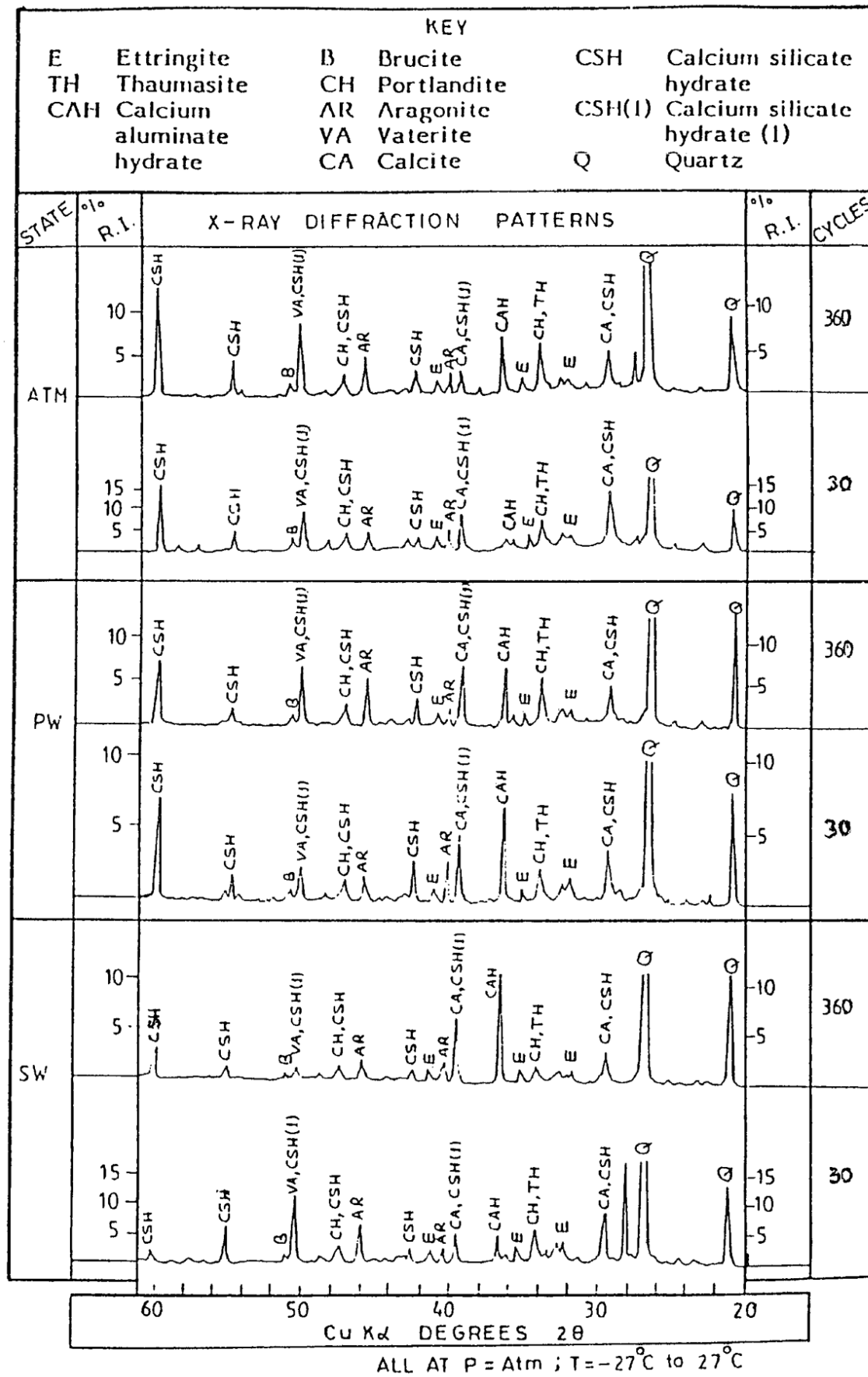


Figure 8: X-ray diffractograms of concrete specimens after exposure to SW, PW and ATM state in freeze-thaw environment

the specimens get saturated considerably by sea water and after crystallisation of the salts together with their reaction with cementitious products within the body of concrete results in a significant decrease in the compressive strength.

The characteristic stress-strain curves of concretes A and B after 30 and 360 cycles in different environment states have been drawn in Figures 6(a), 6(b), 7(a) and 7(b) respectively. It may be seen from these figures that the general shape of the stress-strain curves has not changed and except for the ultimate strength value  $\sigma_0$ , it is similar to that of normal plain water cured concretes in all cases. Although, there is a substantial decrease in the ultimate strength  $\sigma_0$  in the sea water environment, the strain  $\epsilon_0$  corresponding to the ultimate strength  $\sigma_0$  is of the order of 0.22 percent which is similar to normal concrete.

X-ray diffractograms of the concrete specimens exposed to different environmental states after 30 and 360 cycles of freezing-and-thawing have been shown in Figure 8. The maximum intensities and the approximate percentages of the chemical compounds detected from Figure 8 have been calculated and critically studied. It is seen from these diffractograms that in all environments viz. sea water, plain water or ATM state, same cementitious compounds of the non-expansive group such as brucite (B) as well as of the expansive group such as ettringite (E), thaumasite (TH) and calcium aluminate hydrate (CAH) are formed but their percent contents are different. As the number of cycles of freezing-and-thawing increases, the percentages of non expansive compounds are found to decrease, whereas the amounts of the expansive compounds like ettringites (E), thaumasite (TH), and calcium aluminate hydrate (CAH) increase. It results in decreasing the concrete strength after the formation of microcracks due to the presence of such expansive/light density compounds.

## 5.0 CONCLUSION

The results of the investigation carried out on two grades of high strength concrete A and B exposed to SW, PW and ATM states over 360 nos of alternate freezing and thawing have been critically analysed and interpreted. Based on the limited number of tests and variables studied over specific periods, the following conclusion can be drawn:

- (a) Concrete exposed to Freeze-Thaw cyclic loading in sea water is much more vulnerable to deterioration including erosion, splitting and crumbling than in plain water and in atmospheric state of exposure.
- (b) Due to substantial erosion and splitting of concrete specimens in the Freeze-Thaw environment, the loss in weight is found to the extent of 11.5 to 16.5% in sea water and the corresponding loss is around 2% for the specimens placed in plain water or in the ATM state.
- (c) Concrete also shows a significant decrease in volume as much as 1.7% in sea water under freeze-thaw environment. Concrete specimens exposed to plain water and in dry (ATM) state show a decrease in volume of around 0.04 percent.
- (d) A significant change in permeability (k value) characteristics of concrete in Freeze-Thaw environment is observed particularly when it is exposed to sea water. The k value of concrete in sea water is found to be 5 to 7 times the value obtained in plain water or in ATM state exposure and nearly 8 times the permeability of similar concrete cured in plain water at 27°C.
- (e) Sea water causes the most detrimental effect on the compressive strength of concrete, the loss being in the range of 70 to 75% after 360 cycles of freezing and thawing as compared to the strength of normal plain water cured concrete at similar age. The compressive strength loss of concrete under freeze-thaw action in plain water and in the ATM state is around 8% and 3% as compared to the 28 day compressive strength of normally cured concrete.
- (f) X-ray diffraction studies confirm the formation of relatively higher percentage of expansive products in concrete exposed to sea water which are also responsible for strength deterioration and increased permeability.
- (g) The stress-strain characteristics of concrete is seen to be unaffected by alternate Freeze-Thaw action of sea water. ■

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