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Full Length Research paper

Examinatıon of durablity of high performance concrete (hpc) that has been subjected to $MgSO_4$ and NaCl corrosıon against freezing and thawing

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In this study, freezing and thawing effect over four different high performance concrete (HPC) (0P15Z "0% Pumice + 15% Zeolite", 5P10Z, 10P5Z and 15P0Z) which has been waited in three different cure medium (H_2O, $MgSO_4$ and NaCl) for two years was examined. For this reason, four type of High Performance Concrete (HPC) was produced to substitute for, instead of cement. The produced concretes was cured in lime saturated water of 23 ± 2°C, 7500 Mg/L $MgSO_4$ and 5% NaCl solutions for two years. Before starting the freezing and thawing cycle over the concretes, ultrasonic pulse velocity values were obtained by 28 days of compressive strength. The freezing and thawing experiment over the samples taken out of the cure mediums at the end of two years was made regarding fast freezing - thawing in air from ASTM C 666 standard. At the end of 30 freezing and thawing cycle, concrete compressive strength, weight loss, ultrasonic pulse velocity and durability factor over the samples were determined. The results of the experiment proved that there are important differences in, between values due to mineral admixture type and cure medium.

Key words: High performance concrete (HPC), pumice, zeolite, freeze and thaw.

INTRODUCTION

Nowadays, it is required that buildings constructed with high performance and traditional concrete should be able to carry securely the loads to which they will be subjected to, through out their entire service lives and should be durable against various effects. Lots of researches made over durability of concrete have shown that one of the most important factors causing corrosive effect over concrete is frost effect.

Construction search having properties such as resistance, ductility, saturation and durability has increased the interest to materials which are fibrous and high performance concrete. The usage area of such materials has been widening in present and important steps have been taken to develop the properties of composites (Yıldırım and Ekinci, 2006; Do et al., 1993; Hordijk et al., 1995; Demir, 2007).

While water freezes at 0°C at normal free conditions, water inside concrete freezes at lower degrees since it is solution of different salts. When water freezes, there is an approximate 9% volume increase. Beyond this fact, as much the sizes of the spaces in which water fills as small, the freezing degree of water is so low. It is observed that since gel spaces are very small, most of the freezing action occurs in capillary spaces (Arslan, 1995; Johnston, 1997).

The effect of temperature degree is caused by increase in compressive strength of ice as the warmth increases. As the temperature degree of the medium is above -6°C, no noteworthy harmful effects occur over the concretes. The repetition number of freezing - thawing events increases the damage caused by the freezing event over the concrete. For this reason, the durability of concrete against freezing depends mostly on the climatic conditions of the region. The most inconvenient condition is when freezing event occurs at night, the temperature will be over zero degrees centigrade in the mornings. In such a case, freezing - thawing events within one year will repeat many times and as a result of this repetition, the

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concrete will break into pieces in a couple of years (Neville, 2003). The amplitude occurs as a result of freezing of water inside the concrete which causes some tensile stresses. Cracks occur or current crack get bigger at the places where these stresses reaches its tensile strength. Whenever the ambient temperature is over zero, the ice in the spaces becomes water again. However, if these freezing and thawing events are repeated many times, the cracks get wider and merge with each other and a cracking network occurs. The continuation of the event causes first, the separation of tiny pieces from the concrete and later the concrete completely crashes. From these explanations, it is understood that there are two more factors other than the properties of material in the observed damage of concrete from freezing. These are; the ambient temperature to be below zero and the repetition number of the freezing and thawing events (Johnston, 1997).

In studies related with durability, it has been observed that there are effects of fibers over freezing - thawing durability. The studies performed over concrete in 5% sodium sulphate solution and steel fibrous concrete show that the dynamic module of the samples after 300 cycles decrease in a serious manner. It has been observed that the elasticity modules of the samples which are both kept in solution and water and which the water/cement ratio is 0.44 have shown serious rate of decreases until 300 cycles and it has not been possible to exceed these cycle number. The elasticity module decrease of the samples having 0.26 and 7 water/cement ratio especially of the ones which are kept in solution is much higher than those kept in water. The cycle number of the samples having 0.32 water/cement ratio is in between the cycle numbers of samples having 0.44 and 0.26 water/cement ratios. Steel fibrous concretes are broken in higher cycle numbers when compared with the fibreless concretes. Even the fibrous samples with the same water/cement ratio which are kept in solution show a higher performance when compared with the fibreless samples kept in water (Singh and Kaushik, 2003).

The sulphate ions in water, over ground and in sea water can cause corrosion in concrete buildings. The harmful effect of sulphate attack is caused by formation of ettringite and plaster of Paris of which the volume increases to much after chemical reaction of sulphate ions with aluminous (C_3A) and calcic ($Ca(OH)_2$) components available in hard concrete. Reaction products cause the aggregate - cement mud adherence to be affected in negative manner by creating amplitude in harden concrete and causes crack formation and increase in permeability. In advance level exposures, concrete is completely broken down into pieces (Skalny et al., 2002).

In this study, four types of concretes have been produced to replace cement in concrete since they include high amount of silica and they have high pozzolanic activity. The produced concretes have been kept in specified corrosive mediums for two years. At the end of freezing - thawing tests performed over these four types of concrete that were kept in corrosive mediums; pres-sure durability over concrete, weight loss, sonic velocity decrease and durability factors were graphically determined, the effects of different concrete types over these properties were compared. At the end of the experiments, it has been aimed to determine differences and to make comparisons in between values obtained in the used mineral admixture type both in concrete and in cure medium.

MATERIALS AND METHODS

Material

In this study, PÇ 42.5 (CEM I 42,5 R) cement was used. As aggregate, 0/2 and 2/4 sand, 4/8 and 8/16 aggregate was used, and the used aggregate is basalt type aggregate and the specific weights was found to be 2.13, 2.30, 2.55 and 2.63 g/cm^3 respectively. The pumice used in the study is from Nevşehir / Türkiye region and zeolite is from Balıkesir - Bigadiç/Türkiye. Water obtained from Ancara Provincial Municipality Water Supply Network was used as mixing water in the study. Besides, Glenium 51 type new generation super plasticizer of Degussa Construction Chemicals Industry Company concrete admixture was used. The properties of the used cement, pumice and zeolite are given in Table 1.

Method

For the HPC mixture design, method specified in TS 802 and ACI 211, 1 standards and material amounts which was used in the mixture was determined by using Microsoft Excel base program regarding the literature (TS 802, 1985; ACI 211.1, 1994). According to the type and ratio of the mineral admixture to be used as a supplement in concrete (0P15Z "0% Pumice + 15% Zeolite", 5P10Z, 10P5Z and 15P0Z), four types of concrete were produced.

3 cylinder samples of 10 x 20 cm sizes from each concrete group used was subjected to freezing – thawing experiment after being cured in H_2O, $MgSO_4$ and NaCl solutions. The material amount used in the mixture of the used samples and fresh concrete properties are given in Table 2.

The produced concrete was placed into (10 x 20) cm sized hard cylinder plastic cases without allowing the concrete to be decomposed. Concrete which was waited in mould for 24 h and which have been formed was cured for 28 days in 23 ± 2°C lime saturated water. Later, the concrete samples was taken out of the water and were placed in 7500 Mg/L $MgSO_4$, 5% NaCl solutions and 23 ± 2°C lime saturated water which has been cured for two years. In order to keep the solution concentrations stable, pH controls was made in specific periods by pH meter. At the end of two years, the freezing - thawing phases was started over the samples taken out of the solutions. Freezing - thawing experiment over concrete were performed according to ASTM C 666 procedure B: freezing - thawing conditions in fast weather over 10 x 20 mm size cylinder samples (ASTM C 666-92, 1999).

It is required to know the time interval the temperature in the closet to bring the inner temperature of the sample up to -18°C in order to perform the freezing - thawing cycle in accordance with ASTM C-666. In this scope, in order to determine the sample inner temperature, a thermocouple was placed during casting inside one witness sample. From the experiment, it was determined that the time interval for the inner temperature of the sample having inner temperature of 20°C deep freeze in the first cycle to bring to -18°C as 3 h 45 min. The sample reached 4.5°C at 45 min in a water bath having thawing temperature of 6°C. In th next step, the samples were kept inside the deep freezer again and 3 h 15 min was

Table 1. The chemical, physical and mechanical properties of cement.

Property		PÇ 42,5	Pumice	Zeolite
Physical and mechanical properties				
Blaine fineness m^2/kg		314	474.9	290.5
Specific gravity kg/m^3		3.08	2.39	2.23
Setting (min)	Start	135	---	---
	Finish	200	---	---
Compressive strength (kg/cm^2)	7 days	244	---	---
	28 days	424	---	---
Chemical properties				
Components		**(%)**	**(%)**	**(%)**
SiO_2		19.80	71.93	77.54
Al_2O_3		5.61	13.14	13.25
Fe_2O_3		3.42	1.07	0.936
CaO		62.97	0.76	2.156
MgO		1.76	0.73	0.945
SO_3		2.95	0.02	0.06
Na_2O		0.47	4.10	0.05
K_2O		0.87	4.42	3.39
Loss of Ignition		2.17	4.11	-
Bogue composition				
C_3S		54.88	-	-
C_2S		15.88	-	-
C_3A		9.08	-	-
C_4AF		10.41	-	-

Table 2. Material amount in the mixture for each concrete group.

Material	Type	Specific Weight (g/cm^3)	15P0Z weight (kg)	10P5Z weight (kg)	5P10Z weight (kg)	0P15Z weight (kg)	General total (kg)
Sand	0 - 2	2.13	85.57	87.5	89.44	91.38	353.89
Sand	2 - 4	2.30	34.65	35.43	36.21	37	143.29
Aggregate.	4 - 8	2.55	51.22	52.37	53.54	54.7	211.83
Aggregate	8 - 16	2.63	66.03	67.52	69.02	70.52	273.09
Cement	PÇ 42.5	3.08	110.04	106.83	103.63	100.42	420.92
M. Admixtur	Pumice	2.39	19.42	12.57	6.1	0	38.09
M. Admixtur	Zeolite	2.23	0	6.28	12.19	17.72	36.19
SPA	Glm. 51	1.112	1.68	1.63	1.58	2	6
Water	System Water	1	38.84	37.7	36.57	35.44	148.55
Properties of fresh concrete				**15P0Z**	**10P5Z**	**5P10Z**	**0P15Z**
Water / Cement Ratio				0.3	0.3	0.3	0.3
Slump (cm)				7.2	7.7	8.1	8.7
Theoretic results of unit weight (kg/m^3)				2163	2165	2167	2169
Experimental results of unit weight (kg/m^3)				2295	2357	2356	2293

required for the central temperature to be reached at -18℃ and cycles were adjusted as 3 h 15 min at -20℃ and 30 cycles were performed. At the start and end of the cycles performed over the samples, weight measurement and ultrasonic transition speed measurements were made.

Dynamic elasticity module percentage value "P" and durability factor "DF" of the samples after the freezing - thawing cycles was calculated by using the following formulae. In the formulae; transi-

Table 3. Some properties of samples which have not been subjected against corrosion.

Concrete Type	Admixture Replacement Ratio (%)		Unit Weight (kg/m^3)	Capillary Water Absorption Coefficient (cm^2/sn) x 10^{-6}	Visible Space Ratio (%)	28 days Compressive strength (MPa)
	Pumice	Zeolite				
0P15Z	0	15	2330.62	1.130	2.51	83
5P10Z	5	10	2333.52	1.712	2.73	79
10P5Z	10	5	2348.80	0.672	2.81	66
15P0Z	15	0	2356.20	2.875	2.49	61

tion frequency after the freezing - thawing cycles was denoted as "n_1", transition frequency before starting the cycles as "n", the foreseen cycle number until a specified value (30) was reached at as "N", the cycle value at which the experiment is ended was given as "M". In the experiments performed under the scope of this study, N and M values were regarded as 0 each (Yıldırım, 2002).

$$P = (\frac{n_1^2}{n^2}).100 \quad (1)$$

$$DF = \frac{P.N}{M} \quad (2)$$

FINDINGS AND DISCUSSION

In Table 3, data about unit weight, water absorption and pressure durability determinations over the four different types of concretes which have not been subjected to freezing - thawing cycle and 7500 Mg/L $MgSO_4$, 5% NaCl solutions are given and in Table 4, data about unit weight, water absorption and pressure durability determinations over the four different types of concretes which was subjected to freezing - thawing cycle and 7500 Mg/L $MgSO_4$, 5% NaCl solutions are given.

Using the data in Table 4, Figures 1- 4 were drawn and over these graphics, the durability of the concrete which has been subjected to corrosive cure mediums for two years affected by the freezing and thawing cycles can be examined.

In Figure 1, the following observations was made;

1. Concrete pressure durability at reference cure medium (H_2O) is maximum at 5P10Z, minimum at 15P0Z concrete types.
2. Concrete pressure durability at NaCl and $MgSO_4$ corrosive medium is maximum at 0P15Z, minimum at 15P0Z concrete types.
3. According to reference cure medium, maximum durability loss in NaCl corrosive medium is at 5P10Z concrete type and minimum durability loss is at 10P5Z concrete type.
4. According to reference cure medium, maximum durability loss in $MgSO_4$ corrosive medium is at 5P10Z concrete type and minimum durability loss is at 0P15Z concrete type,
5. Small increments in respectively 0P15Z and 15P0Z concrete types in both NaCl and $MgSO_4$ corrosive mediums regarding concrete pressure durability.

Even the durability losses are expected as a result of corrosive mediums and freezing – thawing cycles, minimizing these losses have been our main goal as has been the main goal of most of the other researchers. In this context, since the zeolite mineral admixture consists more of silica when compared with pumice mineral admixture, it has increased the pozzolanic property. The zeolites have the property to dehydrate the water they keep in their bodies when they are heated and to rehydrate these water in their bodies whenever they are cooled. Whenever these properties are regarded, concrete types having more zeolite content are superior when compared with other concrete types in corrosive mediums and against freezing and thawing effects.

In Figure 2 the following observations were made regarding durability factor;

1. Durability factor is maximum at (5P10Z), minimum at (0P15Z) concrete types at reference cure medium (H_2O),
2. According to reference cure medium NaCl corrosive medium, maximum durability factor loss is at 10P5Z concrete type and minimum durability factor loss is at 15P0Z concrete type, besides, while there is a durability loss occurring in all concrete types, there is a durability gain in 0P15Z concrete type,
3. According to reference cure medium $MgSO_4$ corrosive medium, while there is a maximum durability gain in 10P5Z concrete type, there are increases in durability factors at all concrete types.

Since durability factors shown in Table 4 have been calculated according to velocity of sound and since there is an inverse proportion with decrease in velocity of sound; lower levels are seen as high in here. This means that whenever there is a decrease in velocity of sound, durability increases. In this context, whenever the literature is examined about the sulphate effect at the concrete, in the spaces of the concrete there occurs material formation named candlot dust, ettringite or cement bacil ($CaO.Al_2O_3.3CaSO_4$ $31H_2O$) which occurs at the end of reaction of gypsum ($CaSO_42H_2O$) that has been formed during the cement hydratation with tricalcium aluminate

Table 4. Some properties of samples which have been subjected against corrosion.

Concrete type	Cure medium	Weighting Measurement (g)		Weight loss (%)	Ultrasonic pulse velocity (km/sn)		Decrease in ultrasonic pulse velocity (%)	Durability factor (%)	Compressive strength at the end of 2 years (MPa)
		Initial weighting	Final weighting		Initial measure	Final measure			
0P15Z	H_2O	3644	3637.5	0.18	4.95	4.03	18.5	66	75
	$MgSO_4$	3627.5	3618.5	0.25	4.79	4.02	16.0	70	65
	NaCl	3648	3641	0.19	4.83	4.01	16.9	68	76
5P10Z	H_2O	3644	3636	0.22	4.57	4.05	11.3	78	86
	$MgSO_4$	3681	3669	0.33	4.61	4.16	9.7	81	51
	NaCl	3632	3625	0.19	4.54	3.93	13.4	74	58
10P5Z	H_2O	3921	3912.5	0.22	4.84	4.12	14.8	72	67
	$MgSO_4$	3623	3607	0.44	4.84	4.44	8.2	84	52
	NaCl	3614	3605	0.25	4.88	3.98	18.4	66	66
15P0Z	H_2O	3614	3596	0.50	4.94	4.08	17.4	68	54
	$MgSO_4$	3622	3614.5	0.21	4.90	4.17	14.8	72	56
	NaCl	3708	3698	0.27	4.94	4.05	18.0	67	51

($4CaO.Al_2O_3.19H_2O$) which is one of the components of the cement. This formation gives damage by causing inner stresses. However, the increase in durability factor in Figure 2 have filled the spaces in the concrete body of these two materials and causes decreases in velocity of ultrasonic and so causes increase in durability factor.

Whenever the decreases in velocity of ultra sonic in Figure 3 are analyzed, since there is an inverse proportion in between durability factor and sound transition velocity in negative direction, the complete opposite explanations mentioned for the durability factor analysis can be made for sound transition velocity. This case can be clearly seen whenever Figures 2 and 3 are analyzed. Whenever concrete types showing different sound permeability in different cure mediums are examined, it has been observed that 10P5Z concrete type causes maximum decrease in ultra sonic velocity in NaCl corrosive medium and 15P0Z concrete type causes maximum decrease in ultra sonic velocity in $MgSO_4$ corrosive medium. This can be caused by pozzolanic activity and fineness of zeolite mineral being higher than pumice.

Increase in zeolite replacement ratio against decrease in pumice replacement ratio in Figure 4 reference cure medium has decreased weight loss against freezing and thawing cycles. Notwithstanding, it has been observed that 15P0Z and 10P5Z concrete types have displayed a good performance considering weight loss when the reference medium is compared with NaCl corrosive medium. Whenever $MgSO_4$ corrosive medium is compared with reference cure medium, on the contrary of other concrete types, 15P0Z concrete type displays maximum performance by showing decrease in weight loss.

RESULTS

At the end of the experiments, the observations after the data which were obtained from the four different concrete types were compared according to the durability in reference cure medium given in Table 5.

While especially weight loss is analyzed during the experiments, it has been decided that 30 freezing - thawing cycles are inadequate and the performed analysis will be more understandable if the cycle amount is 100 - 200 - 300. But this amount has been found sufficient to have an idea about durability and durability factor. In the surfaces of the concretes which were exposed to $MgSO_4$ corrosion at the end of 30 freezing and thawing cycle, light grey color change has been observed. Besides, blistering, spalling and micro cracks over the surface have been observed due

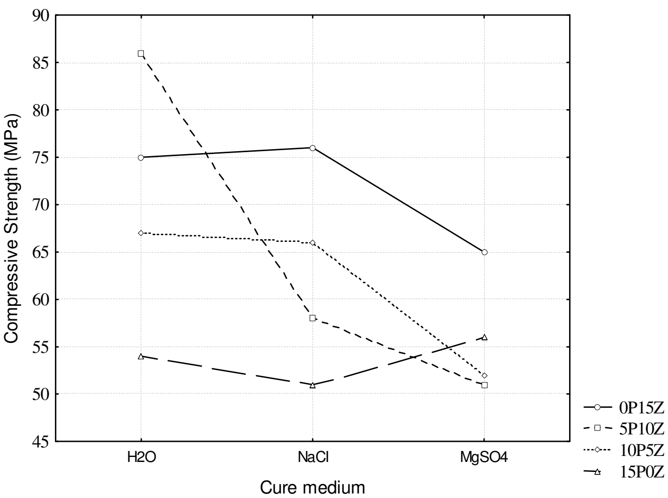

Figure 1. Pressure durability as a result of freezing - thawing cycle.

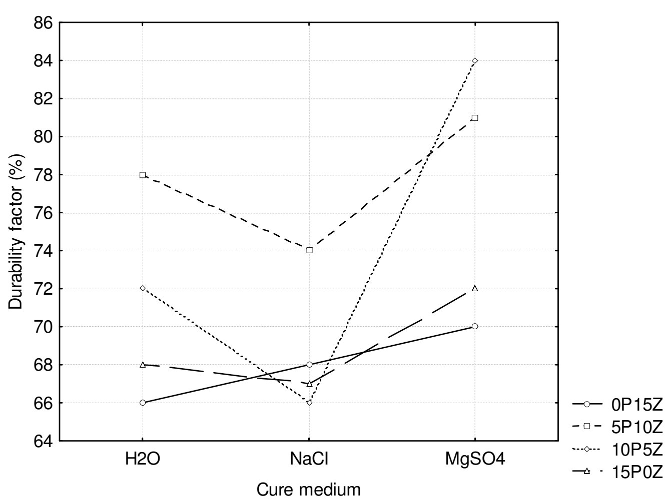

Figure 2. Durability actors as a result of freezing - thawing cycle.

to ettringite which occurs as a result of sulphate reaction and freezing and thawing effect. Over the samples which have been exposed to NaCl corrosion, whitish crystal flowering has been observed. Even chlorine ion diffusion has not been examined in NaCl corrosive medium, it can be said that chlorine diffusion is high in concrete at concrete types where pumice replacement ratio is high and the reason of this is the porous structure of pumice mineral. However, the weight loss as a result of freezing and thawing were not observed in the body of the concrete but in the corners. It is thought that the usage of 0P15Z and 5P10Z concrete types will be more advantageous than the other concrete types in areas such as Cold Storage Depots, in structures under cold weather conditions or in other mediums where the cold weather will be effective. Besides, 10P5Z and 15P0Z concrete types can also display a better performance by protecting the freezing and thawing effect.

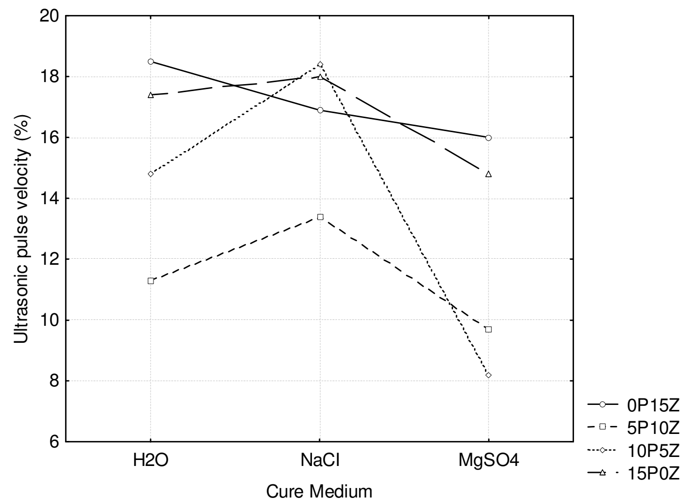

Figure 3. Decrease in ultrasonic pulse velocity as a result of freezing – thawing cycle.

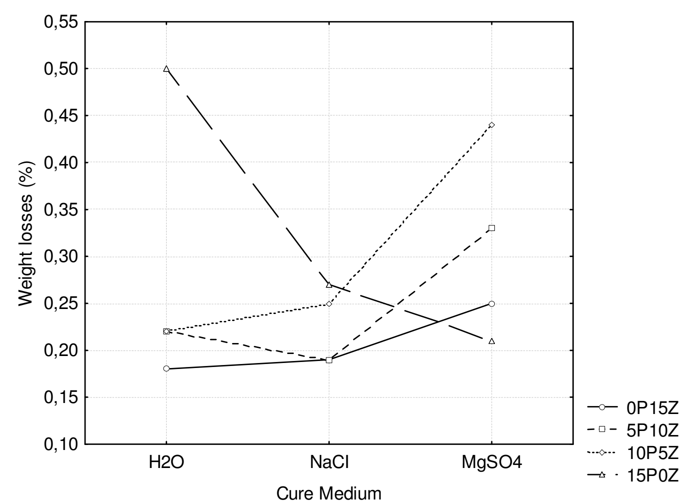

Figure 4. Weight losses as a result of freezing - thawing cycle.

Table 5. Comparison of blended concretes according to reference cure medium by durability.

Concrete type		0P15Z	5P10Z	10P5Z	15P0Z
Cure Medium	NaCl	***	*	**	**
	$MgSO_4$	**	*	*	***

Represents: (*), Worse; (**), Same; (***), Better levels.

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