Durability of concretes containing supplementary cementing materials in marine environments

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ABSTRACT: Marine environments are the most severe conditions for concrete structures. Corrosion of reinforced concrete structures is a major problem in the marine environments of the Persian Gulf region. Supplementary cementing materials have shown desirable performance when used in reinforced concrete structures Accelerated tests in simulated environments show that supplementary cementing materials can enhance the durability of concrete. This study show the performance of concrete specimens containing different supplementary cementing materials, such as silica fume, slag, trass (a natural pozzolan) and mixtures of cement and two pozzolans in severe environments Compressive strength, permeability, chloride diffusion, corrosion of reinforcing bars and carbonation depth, of concrete mixtures were measured at various ages The variables were cement types, supplementary cementing materials, water cement ratio and cover thicknesses. Concrete specimens maintained in submerged, wetting and drying and coastal environments of the Persian Gulf region. With respect to the alternate cycles of wetting and drying known as most severe condition, the superior performance of silica fume was followed by the mixtures of two supplementary cementing materials. All concrete mixtures containing natural or artificial pozzolans showed better performance when compared with the plain cement control concrete mixtures. From the results of this investigation. the use of supplementary cementing materials was recommended in the national concrete code for durability enhancement.

1- INTRODUCTION

Sustainability has been an important issue for the last decade. Many phases of cement and concrete technology can affect sustainability. The use of supplementary cementing materials, design of concrete mixtures with optimum content of cement and enhancement of concrete durability are the main issue towards sustainability in concrete industry. Durability of concrete structures in the severe environments is a major problem all over the world. The hot and aggressive condition of the Persian Gulf region have caused severe corrosion in the concrete structures. Survey of newly built and old concrete structures in the Persian Gulf region show that many of these structures are not able to satisfy their minimum service life [1]. However, the use of special cements and pozzolans in corrosive regions, has shown desirable performance of reinforced concrete and enhanced the durability of concrete [2-5]. Results of accelerated tests in simulated environments show that supplementary cementing materials can enhance the durability of concrete [6]. Attempt have been made to investigate the long term performance of concretes containing supplementary cementing materials in severe environments. The objective of these investigations is to create models for the prediction of service life of concrete structures and establish e model code for design [7-8]. This paper reported the results obtained on the concrete specimens maintained for four years in the marine environment of the Persian Gulf.

2-EXPERIMENTAL PROGRAM

2-1-Materials

Cement- ASTM Type 2 portland cement and ASTM Type 5 portland cement was used in this investigation.

Slag- slag-modified portland cement (I (SM) in accordance with ASTM C595) was incorporated in the mixtures.

Pozzolan- Trass as a natural pozzolan was used in this program.

Silica fume- A locally produced silica fume (in accordance with ASTM C1240) was used. The chemical composition of the cements and pozzolans are given in Table 1.

Aggregates- Crushed gravels and sand were used as coarse and fine aggregates, respectively. The properties of aggregates are shown in Table 2.

Superplasticizer- The superplasticizer was a conventional melamine-based admixture with a solids content of 40% and a pH of 8.

Steel Reinforcing Bars- The steel reinforcing bars met the requirements of Grade 60 of ASTM A 615/A 615 M.

2-2- Concrete Mixtures

Mixture proportions of concrete are summarized in Table 3. Water-cementitious materials ratios(W/Cm) were 0.35 and 0.4. The slump of the fresh concretes was kept between 5 to 8 cm and air content between 3 to 5%. 10×10×10 cm cubes were used for compressive strength and permeability tests. For carbonation test, 15×15×60 cm plain concrete specimens were used. In order to measure the corrosion potential, electrical resistance, and current density, steel bars and stirrups were embeded at cover depths of 3.5, 5, and 7 cm .

After casting, all the specimens were covered with water-saturated burlap and plastic sheets. The specimens were moist cured for 7 days, followed by 14 days of air drying. Following this, the specimens were transported to the Persian Gulf region and exposed in different conditions, namely in the air, in coastal area, tidal region of the sea (cycling wetting and drying), and submerged in the sea. Control unreinforced specimens of each mixture were kept in standard laboratory curing conditions.

Table 1. Chemical compositions of cements and cement replacement materials

	Type 2	Type 5	Slag	Trass	Silica fume
SiO_2	20.96	21.47	23.08	24.24	95.1
Al_2O_3	4.2	3.95	5.5	4.25	0.6
Fe_2O_3	4.6	4.4	3.4	3.8	1.1
MgO	3.4	2.3	3.4	3.8	0.6
CaO	61.88	63.84	60.2	58.8	1.02
SO_3	1.79	2.17	2.64	3.82	1.2
$Na_2O+0.658\ K_2O$	1.47	1.01	1.08	1.26	-
C_3S	52.74	57.72	-	-	-
C_2S	20.31	18.01	-	-	-
C_3A	7.35	3.02	-	-	-

Table 2. Aggregate properties

	Specific Gravity	Absorption (%)	Fineness Modulus
Sand	2.53	2.6	2.7
Gravel	2.56	1.46	6.5

Table 3. Mixture proportions

Mixture	Cement type	CRM type	W/Cm	Water (kg)	Cement (kg)	CRM (kg)	Sand (kg)	Gravel (kg)
A1	Type 2	-	0.40	160	400	-	760	1050
A2	Type 2	-	0.35	140	400	-	760	1050
B1	Type 5	-	0.40	160	400	-	760	1050
B2	Type 5	-	0.35	140	400	-	760	1050
C1	Type 2	Silica fume	0.40	160	372	28	760	1050
C2	Type 2	Silica fume	0.35	140	372	28	760	1050
D1	Trass	-	0.40	160	400	-	760	1050
D2	Trass	-	0.35	140	400	-	760	1050
E1	Slag	Silica fume	0.40	160	380	20	760	1050

E2	Slag	Silica fume	0.35	140	380	20	760	1050

3- TEST METHODS

Half-cell potential (Ag/AgCl), polarization resistance, and cover concrete resistance were measured by a portable corrosion measurement device. Polarization resistance and concrete resistance were measured by DC impedence technique (Galvanostatic Pulse Technique). The applied currents were normally in the range of 10 to 100 μA and the typical pulse durations were between 5 to 30 seconds .

Micro-cell corrosion current was estimated based on the measured polarization resistance using the following expression:

$$I_{corr} = \frac{B}{R_P}$$

Where, Icorr= the micro-cell corrosion current density in μA/cm2. B = an emprical constant assumed to be 25 mV for actively corroding steel and 50 mV for passive steel. RP = the polarization resistance.

Carbonation depth of the specimens was measured by spraying a 1% phenolphthalein solution on freshly cut surfaces .

Acid soluble chloride-ion concentrations were determined at depths 0~10, 10~20, 20~30, 30~40, and 40~50 mm in accordance with ASTM C1152/C 1152M-97 test method .

The compressive strength and permeability of concrete mixtures under water pressure were measured for control concrete specimens.

4- RESULTS AND DISCUSSIONS

4-1- Corrosion Potential, Electrical Resistance, and Micro-cell Corrosion

The corrosion potential, concrete electrical resistance, and micro-cell current density were measured at 1 and 4 years. Test results are illustrated in Tables 4-8 and Figs 1-8.

Table 4. Current density and concrete resistance at 1 year, in the tidal region

Mixture	W/Cm	Current (μA/cm^2)			Resistance (kohm)		
		3.5cm	5cm	7cm	3.5cm	5cm	7cm
A1	0.40	0.99	0.91	0.64	1.8	1.7	1.6
A2	0.35	0.93	0.81	0.61	2.1	2.6	2.2
B1	0.40	2.97	1.84	0.87	1.0	1.9	1.9
B2	0.35	1.56	1.48	0.66	0.5	2.5	2.6
C1	0.40	0.97	0.88	0.67	1.8	2.0	2.1
C2	0.35	0.95	0.76	0.52	1.6	1.8	1.8
D1	0.40	1.75	1.22	1.12	0.8	1.9	2.1
D2	0.35	0.86	0.90	0.78	1.8	2.3	2.2
E1	0.40	1.97	1.86	1.54	1.4	1.3	1.7
E2	0.35	0.93	0.73	0.68	1.2	2.0	2.0

Table 5. Current density and concrete resistance at 4 years, in the tidal region

Mixture	W/Cm	Current (μA/cm^2)			Resistance (kohm)		
		3.5cm	5cm	7cm	3.5cm	5cm	7cm
A1	0.40	2.84	2.38	2.79	0.8	1.2	1.2
A2	0.35	2.03	1.56	1.22	0.8	1.5	1.7
B1	0.40	3.86	3.11	2.21	0.4	0.5	0.7
B2	0.35	3.25	2.33	2.06	0.5	1.3	1.4
C1	0.40	1.95	2.03	1.96	1.2	1.3	1.3
C2	0.35	1.76	1.66	1.52	1.8	2.1	2.8
D1	0.40	1.90	2.37	1.68	1.1	1.3	1.5
D2	0.35	1.99	1.74	1.55	1.3	1.4	1.8
E1	0.40	2.76	2.12	1.82	0.9	1.4	1.8
E2	0.35	2.72	1.91	1.31	1.0	1.7	2.4

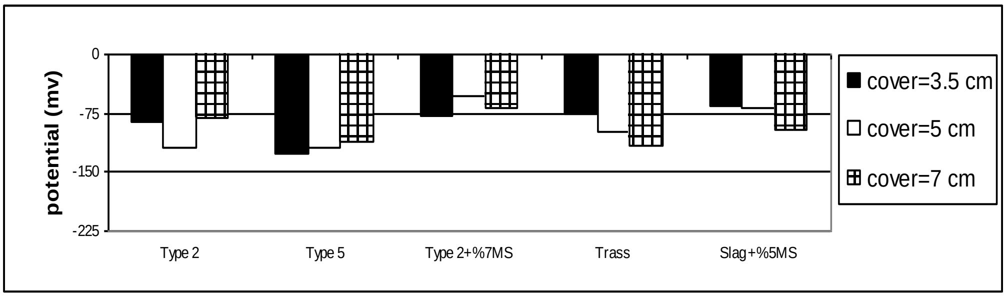

Figure 1. Half-cell potential at 1 year, (W/Cm)=0.4, in the tidal region

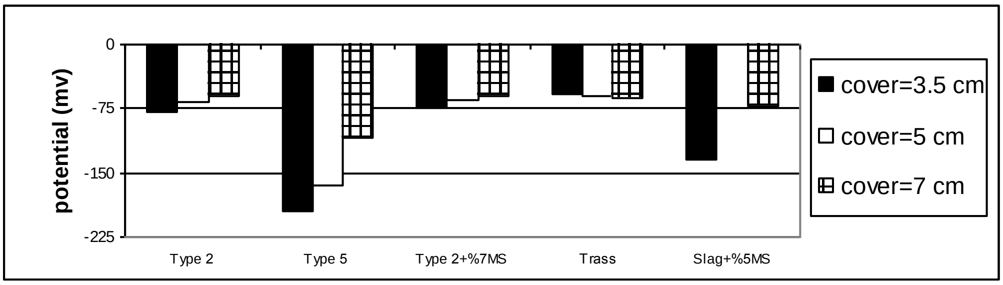

Figure 2. Half-cell potential at 4 years, (W/Cm)=0.4, in the tidal region

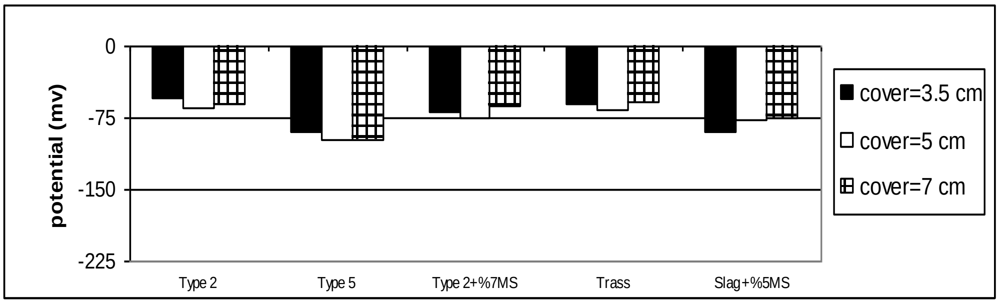

Figure 3. Half-cell potential at 1 year, (W/Cm)=0.35, in the tidal region

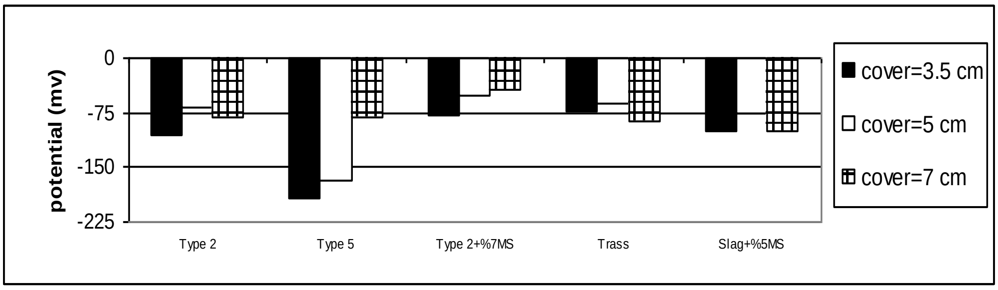

Figure 4. Half-cell potential at 4 years, (W/Cm)=0.35, in the tidal region

Table 6. Current density and concrete resistance at 1 year, in the dry condition

Mixture	W/Cm	Current (μA/cm^2)			Resistance (kohm)		
		3.5cm	5cm	7cm	3.5cm	5cm	7cm
A1	0.40	1.12	0.77	0.80	2.2	2.7	3.9
A2	0.35	0.53	0.41	0.22	3.9	4.5	4.3
B1	0.40	1.20	0.80	0.60	2.7	3.1	2.8
B2	0.35	0.60	0.54	0.41	4.5	5.5	5.0
C1	0.40	1.10	0.70	0.42	3.5	3.5	4.5
C2	0.35	1.50	0.80	0.36	3.5	4.0	4.0
D1	0.40	1.30	0.55	0.55	3.5	4.1	5.5
D2	0.35	0.72	0.53	0.45	4.0	5.5	5.8

E1	0.40	1.02	0.60	0.45	3.0	5.0	4.6
E2	0.35	0.70	0.70	0.45	5.0	5.0	5.2

Table 7. Current density and concrete resistance at 4 years, in the dry condition

Mixture	W/Cm	Current (µA/cm2)			Resistance (kohm)		
		3.5cm	5cm	7cm	3.5cm	5cm	7cm
A1	0.40	0.25	0.27	0.30	6.0	6.5	6.0
A2	0.35	0.26	0.19	0.22	6.0	6.1	6.1
B1	0.40	0.49	0.35	0.27	4.9	4.8	5.6
B2	0.35	0.38	0.25	0.24	5.2	5.7	5.8
C1	0.40	0.38	0.29	0.24	5.8	5.9	6.1
C2	0.35	0.32	0.28	0.21	6.3	6.5	6.7
D1	0.40	0.31	0.29	0.27	5.8	5.9	6.1
D2	0.35	0.32	0.33	0.25	6.1	6.0	5.9
E1	0.40	0.33	0.32	0.25	5.1	5.4	5.8
E2	0.35	0.22	0.26	0.24	6.0	6.0	6.1

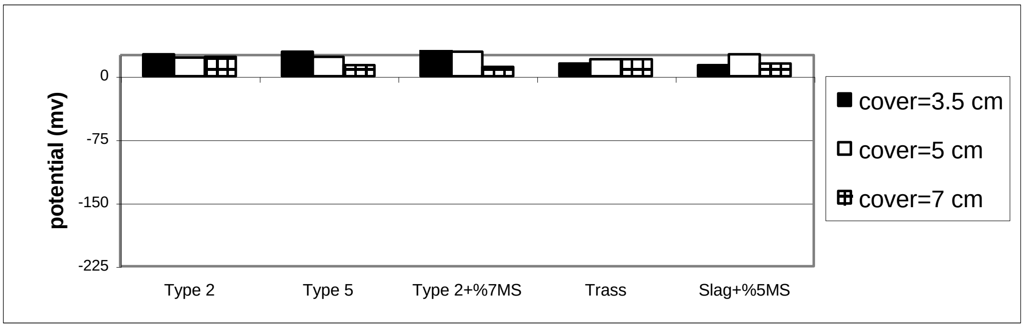

Figure 5. Half-cell potential at 4 years, (W/Cm)=0.4, in the dry condition

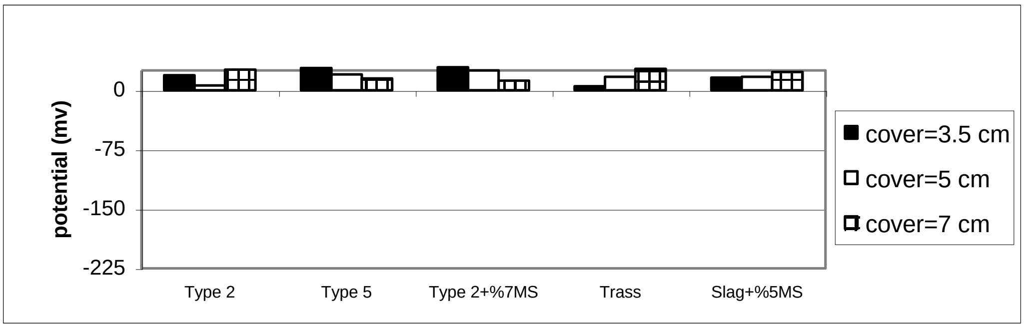

Figure 6. Half-cell potential at 4 years, (W/Cm)=0.35, in the dry condition

Table 8. Current density and concrete resistance, in the submerged condition

		1 years		4 years	
Mixture	W/Cm	Current (µA/cm2)	Resistance (kohm)	Current (µA/cm2)	Resistance (kohm)
		7cm		7cm	
A1	0.40	1.52	1.2	1.37	2.1
A2	0.35	1.15	2.0	0.85	1.7
B1	0.40	1.87	1.1	1.39	0.8
B2	0.35	1.95	1.2	0.85	1.0
C1	0.40	0.75	1.5	0.82	1.3
C2	0.35	0.40	2.2	0.76	1.7
D1	0.40	0.90	1.3	1.45	1.1

D2	0.35	1.00	1.6	1.31	1.4
E1	0.40	1.25	1.9	1.13	1.6
E2	0.35	1.10	2.2	0.82	2.0

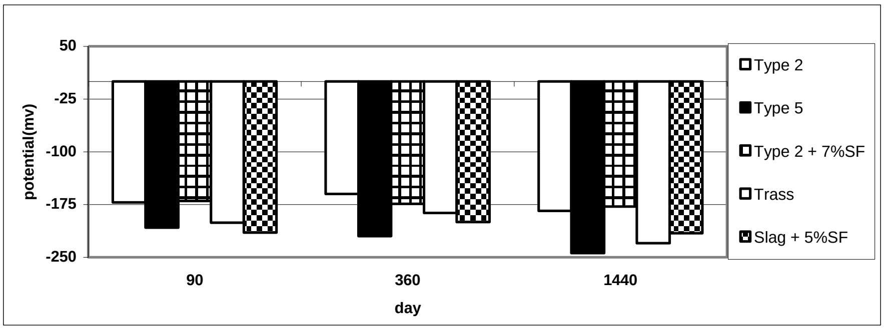

Figure 7. Half-cell potential versus age ; (W/Cm)=0.35,cover=7cm, submerged condition

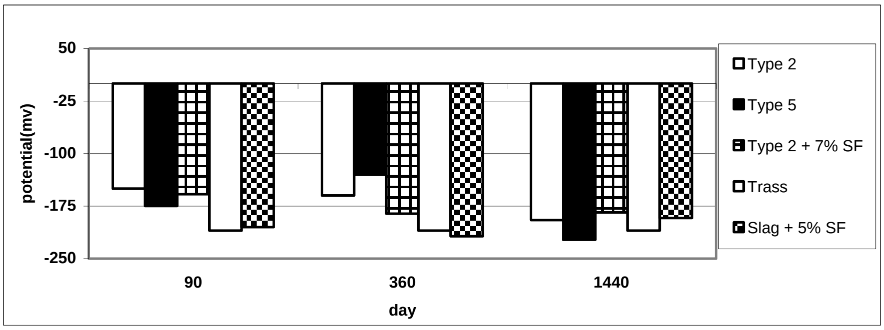

Figure 8. Half-cell potential versus age ; (W/Cm)=0.4,cover=7cm, submerged condition

For the tidal region, concretes made with ASTM Type 5 cement, and slag cement with 5% silica fume showed more negative potentials. For concretes with ASTM Type 2 cement, Type 2 with 7% silica fume, and trass cement, less negative potentials were observed. Higher current density and lower electrical resistance were observed for the specimens made with ASTM Type 5 cement and cover thicknesses of 3.5 and 5 cm, when compared with other specimens. For these concrete mixtures, current density increased and electrical resistance decreased with time. Concretes containing trass cement and ASTM Type 2 cement with 7% silica fume and (W/Cm)=0.35 showed lower current density and higher electrical resistance. For greater cover depth, a tendency of lower negative potential, lower current density, and higher electrical resistance was observed.

All concrete mixtures showed no corrosion activity and very low current densities after 48 months of exposure in the air. These concretes showed very significant and high electrical resistances. For the dry exposure condition after 4 years, there were no significant differences in the concrete electrical resistance, corrosion current density and corrosion potential for concrete mixtures made with different cements, for the different cover depths, and various water-cementitious materials ratios.

For all of the concrete mixtures in a submerged condition and after 12 months, a very high negative potential was observed. However, the current densities were low. The results show that although chloride-ions have penetrated into the concrete and have reached the surface of reinforcement, due to the lack of oxygen, there is little micro-cell corrosion. For the wet and submerged condition, no significant difference in performance of concretes with different cements and W/Cm was observed.

4-2- Carbonation Depth and Chloride-ion Diffusion

In the tidal region and dry condition, carbonation depth of specimens were negligible irrespective of the types of cement. In the tidal region, for all concrete mixtures, higher chloride-ion concentration was observed at the surface after 1 year. However it was reduced to a negligible value at deeper depths. Mixtures of Type 5 portland cement show the highest chloride content. Mixtures made with containing pozzolanic cement and Type 2 portland cement with 7% silica fume exhibit the lowest chloride content .

Comparision of Chloride content of specimens in the tidal zone showed that Type 5 portland cement mixtures with water-cement ratio of 0.4 showed the worst performance .

This data complies with the results obtained in intensity and potential of concrete mixtures. It also reveals that corrosion of reinforcement should have been occurred in such mixtures. In order to clarify the corrosion condition, concrete specimens made with Type 5 portland cement were tested after four years. Figure 9 shows the chloride profile of the concrete mixture. It is clearly seen that the amount of chlorides at the reinforcement level is well above the threshold level. Heavily corroded bars were observed when broken specimens were visualy inspected.

The $\sqrt{c_x - c_b}$ diagram by x is plotted and its linear curve fitting (y=ax+b) is computed :

$y= -0.0378x + 2.102$ (Type 5)

$y= -0.0361x + 1.403$ (slag+5%silica fume)

C_s and D is then computed by the following equations:

$C_s= b^2 + C_b$

$D=(b/a)^2\times(1/(4\pi t)$

The results are inserted in the table 9.

Table 9. The computed Cs and D

Type of cement	C_s (% by mass of concrete)	D (mm^2/yr)
Type 5	4.417	61.5
Slag + %5 sf	1.97	30.05

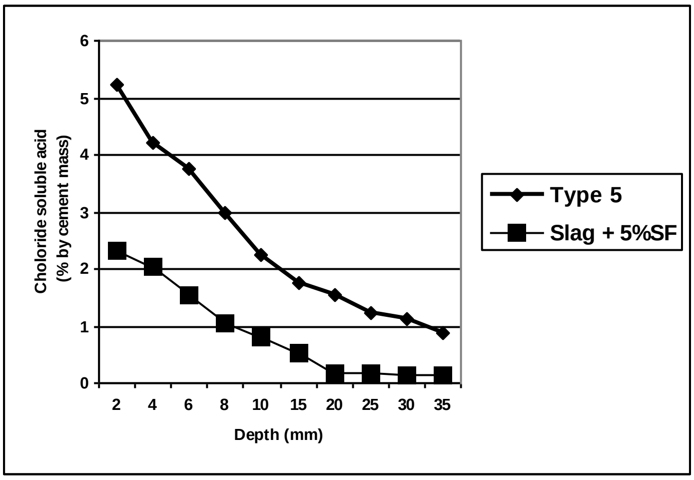

Figure 9. Profile of acid soluble chloride ion concentrations, (W/Cm)=0.40, in the tidal region at 4 years

4-3-Compressive Strength and Permeability

Compressive strength test results for concrete mixtures under standard curing conditions are shown in Figs 10,11. It can be seen that the compressive strength of all concrete mixtures is above 60 Mpa at 4 years, regardless of W/Cm ratio.

Higher compressive strengths are expected at later ages for concretes containing pozzolans. Relatively higher strength was observed in the case of ASTM Type 5 and Type 2 portland cement concrete mixtures when compared with Trass, Type 2 + Silica fume and Slag cement mixtures. However, concrete mixtures containing ASTM Type 5 portland cement showed undesirable performance in terms of corrosion. Permeability under water pressure for all concrete mixtures was low irrespective of the type of cement and water-cement ratios used in this investigation.

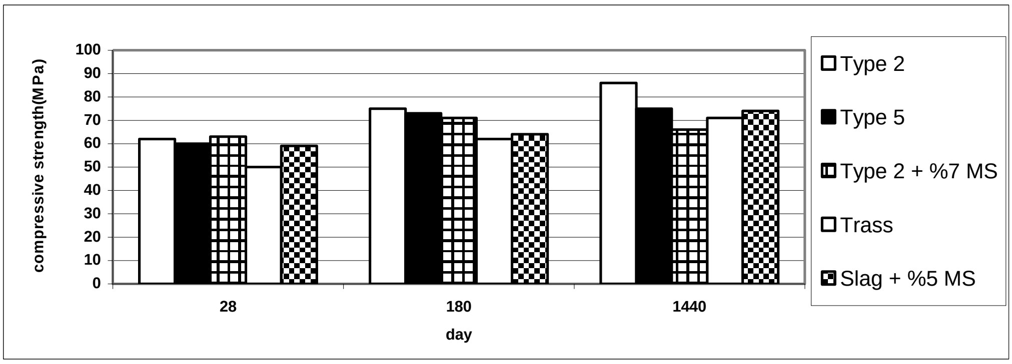

Figure 10. Compressive strength of concrete versus age ; (W/Cm=0.35)

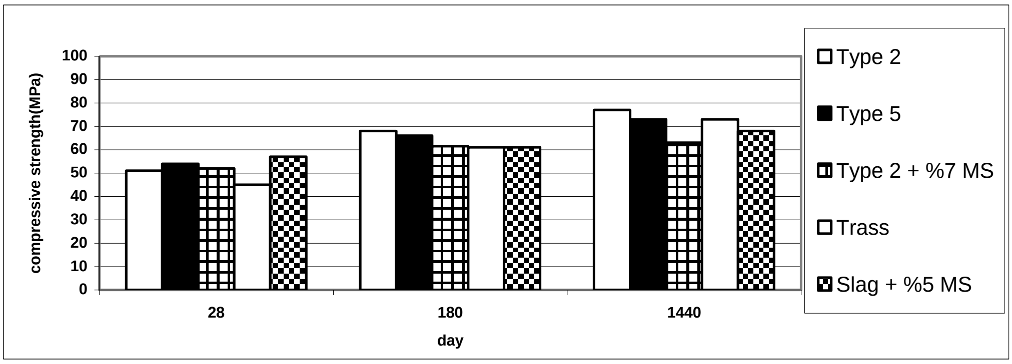

Figure 11. Compressive strength of concrete versus age ; (W/Cm=0.4)

5- CONCLUSIONS

From the results obtained in this investigation, the following conclusions can be drawn:

- For specimens exposed to the tidal region, concrete mixtures made with Type 5 portland cement having 3.5 and 5 cm cover thicknesses showed undesirable performance. Severe reinforcement corrosion was observed in the specimens after 4 years. The best performance was obtained for concrete mixtures containing Trass cement and ASTM Type 2 portland cement plus silica fume.
- In totally submerged specimens, although corrosion potential is high and concrete electrical resistance is low, current density is negligible after 4 years. No corrosion observed in all concrete mixtures.
- All concrete mixtures showed no activity and very low current densities after 4 years of exposure in air. These concretes showed high electrical resistances. For this exposure condition, there was no significant difference in the performance of concrete mixtures made with different cements and for various cover thicknesses.
- In general, exposure in the tidal region was the worst condition for concrete mixtures when compared with the submerged and dry conditions.

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