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Strength behavior of mortar using slag with cement in sea water environment

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Abstract

This paper investigates the effect of sea water, mix proportion of cement slag, water binder ratio and curing period on the strength development of mortar in sea water environment at normal temperature and humidity. The strength development of mortar specimens made from various mix proportions of cement slag (100:0, 85:15, 70:30 and 55:45) is investigated. The test variables also include the various water binder ratios (0.42, 0.46 and 0.50) and normal as well as accelerated sea water environments were created for curing the test specimens. From the investigation, it has been revealed that cement slag mortar of mix ratio 70:30 has better resistance against strength deterioration for various water binder ratios at all curing conditions and curing ages. The water binder ratio of 0.46 provides higher compressive strength for all mix proportions of cement slag.

Keywords: OPC, slag, marine environment, chloride attack, compressive strength, mix proportion

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1. Introduction

Cement, mortar and concrete are the most widely used construction material all over the world. It is difficult to find out alternate material of construction which is suitable as that of such construction material form durability and economic point of view. The expanded uses of concrete have increased the interest of scientists/researchers for its use in aggressive environments such as marine environment. A well designed concrete structure can survive up to its design life without any major repair/maintenance work in adverse surrounding environment.

Sea water (SW) is a complex 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 upon geological location (Ref. Table 1). Compound of chloride form highest proportion i.e. about 89% of the total dissolved salts present in sea water, whereas sulfate compounds constitute second largest portion i.e. 10% of the total salt. Thus, in sea water, there are large amount of chloride and sulfates. Reinforced Concrete structures in sea water environments are often found to be deteriorated. So prior to the construction of any concrete structure in such location, proper steps should be taken to overcome the risk of deterioration of concrete due to chloride and sulfate attack.

Depending on the tidal range, nature, extent and mechanism of deterioration process, a reinforced concrete structure exposed to a marine environment can be divide into different zones like Atmospheric zone, Splash zone, Tidal zone and Submerged zone (Ref. Figure 1). The atmospheric zone is the upper most part extending upwards from the splash zone. In this zone, the air is heavily laden with moisture containing substantial quantities of salts and gases (Patil 1981). Due to temperature variation and wave action, freeze-thaw cycles may occur in some oceans. The splash zone extends upwards form the tidal zone and is the most critical area for offshore structures due to erosive effect of continuous salt water spray and wave action in presence of atmospheric O_2 and CO_2 (Ross 1988). The tidal zone experiences alternate wetting and drying action in seawater and is considered as the second most corrosive area (Gowda 1981). The submerged zone is defined as that lying between low water level and above the bed. The hydrostatic pressure increasing with depth can cause rapid penetration of harmful salt ions into the concrete and is regarded as the least corrosive zone due to non availability of O_2 and CO_2.

Table 1
Average Salt Concentration in Different Seas
(Biczok 1972)

Sea	Salt Concentration (%)
Mediterranean	3.8
Baltic	0.7
North sea and Atlantic	3.5
Black Sea	1.8
Dead Sea	5.3
Indian Sea	3.55

In a marine environment, chloride ion penetrating into the concrete from sea water reacts with $Ca(OH)_2$ liberated from cement hydration and form calcium chloroaluminate (Friedels Salt). On the otherhand, sulfate that penetrates inside concrete from sea water forms gypsum and a complex compound namely calcium sulphoaluminate (Ettringite). Both the products occupy a greater volume after crystallization in the pores of concrete than the compounds they replace. The formation of gypsum hydrate causes an increase in volume of 17.7% in concrete (Bougue 1971).

The action of principal sea salts namely, NaCl and $MgSO_4$ on hardened concrete as mentioned by several researchers is explained as follows (Mehta 1980; Mohammed et al. 2003)

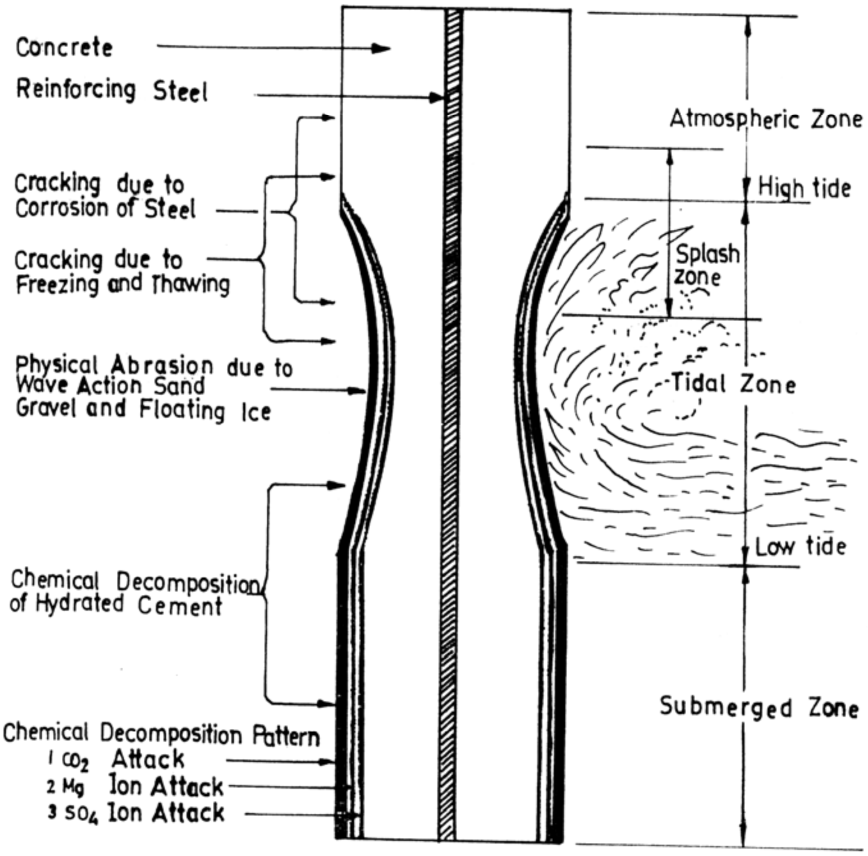

Fig. 1. Deterioration of Concrete Structure in Marine Environment (Mehta 1980)

NaCl present in seawater reacts with $Ca(OH)_2$ of hydrated cement and form calcium chloride. This calcium chloride reacts with the other cement products form to calcium chloroaluminate (Friedels salt)

$$Ca(OH)_2 + 2NaCl \longrightarrow CaCl_2 + 2NaOH \qquad (i)$$

$$CaCl_2 + (3CaO)Al_2O_3 + 10H_2O \longrightarrow (3CaO)Al_2O_3.\ CaCl_2.10H_2O \qquad (ii)$$

Calcium Chloroaluminate (Friedels salt)

$MgSO_4$ react with $Ca(OH)_2$ and yields $CaSO_4.2H_2O$ (Gypsum) which in turn reacts with calcium aluminates hydrate to form additional calcium aluminates sulfate hydrate (Ettringite).

$$Ca(OH)_2 + MgSO_4.7H_2O \longrightarrow CaSO_4.2H_2O + Mg(OH)_2 + 5H_2O \qquad (iii)$$

(Gypsum)

$$(3CaO)Al_2O_3.12H_2O + 3(CaSO_4.2H_2O) + 13\ H_2O \longrightarrow$$

$$(3CaO)Al_2O_3.(3CaSO_4).31H_2O \qquad (iv)$$

Calcium Aluminate Sulfate hydrate (Ettringite)

Friedels salts, calcium chloride and ettringite have detrimental effects on the durability of concrete. Friedels salts have a property of low to medium expansion. Calcium chloride may leach out from concrete which may increase the permeability of concrete leading to material loss and weakening. Formation of Ettringite is associated with expansion and cracking. Thus, these effects associated with the chemical reactions are responsible for some physical changes such as change in volume, weight, permeability and other properties of concrete.

Slag has been widely used as successful replacement material for ordinary Portland Cement (OPC) in making durable concrete for improving some properties of concrete in marine environment and for achieving environmental and economical benefits since the beginning of 20^{th} centuries (Eascalante et al. 2001). Slag is a by product of steel production. Its major chemical compounds are CaO, SiO_2, Al_2O_3, MgO, TiO_2 and MnO and hence similar to OPC, slag has the cementitious property. Due to its very high fineness, it can effectively fill the pores of the concrete which are very much helpful for reducing the permeability of concrete. Impermeable concrete restricts the penetration of sea water inside the concrete and therefore increases the durability of concrete in sea water environments.

Slag cement has been used in different concrete projects of the United States of America for the last several decades. Besides, earlier usage of slag cement in Europe and elsewhere demonstrate the long term performance of slag concrete in many ways. Use of slag is also noticeably increasing for the last several years due to its characteristic properties like improved workability, restrained heat of hydration, easier finishability, higher compressive strength, lower permeability and superior resistance to alkali silica reaction due to penetration of chloride ions and sulfate ions (Islam et al. 2007). It has been observed that slag can be effectively used to reduce the pore sizes and cumulative pore volume considerably leading to more durable and impermeable concrete (Pal et al. 2002). Industrial slag, in general, has the potential to replace cement in high percentage because of its in built cementitious property (Hwang et al. 1986). Although the strength development is remarkably reduced at early ages of curing due to having low initial rate of hydration of slag, the structural benefit of low heat of hydration of slag in decreasing the thermal cracking of mass concrete is significant. The risk of thermal cracking in slag concrete is seen to be lower than ordinary Portland cement (Takashi et al. 2000). In Europe, the production of 1 ton OPC generates about 1.2 ton CO_2 while the production of 1 ton slag generates only 0.45 ton of CO_2 (SCA America). In addition, concrete made with slag has a lower content of chromium, which is responsible for skin irritation of workers handling concrete materials without any skin protection (Kulkarni 1994).

Although extensive research has been conducted on the use of slag as partial replacement of cement in concrete, a few works are documented regarding the durability of slag concrete in sea water environment. The relevant information presented in literature varies to a greater extent or debatable. This paper investigates the strength behavior of slag cement mortar in sea water environment. The use of slag as partial replacement of cement in slag cement mortar exposed to artificial sea water environment has been studied particularly form the development of the compressive strength point of view. Various slag cement ratios (100:0, 85:15, 70:30 and 55:45) as well as different water binder ratios (0.42, 0.46 and 0.50) have been used to get the idea for optimum mix ratio. The test data may provide useful information regarding the use of slag concrete in sea water environment which may help to make proper management of slag thereby resulting environmental benefit in a society.

2. Experimental program

Experimental studies were carried out using both normal and accelerated curing environment over a period of 180 days. The variable parameters studied and the materials involved were as follows:

(a) Cement: Ordinary Portland Cement (OPC) conforming to ASTM C150 was used as binding material. The physical properties and chemical compositions of OPC are given in Table 3.

(b) Slag: Electric arc furnace slag was used in this investigation. Chemical compositions of the used slag are given in Table 4.

(c) Sand: Locally available natural sand passing through 4.75 mm sieve and retained on 0.015 mm sieve was used. Properties of this sand conform to ASTM C150 requirement.

2.1 Variables studied

(a) Curing water: Plain water (PW) as well as artificially made sea water (SW) of concentration 1N and 3N were used for curing the test specimens. 1N sea water means normal sea water made by mixing tap water with exact amount and proportion of principal salts found in natural sea water which is given in Table 2. Thus 3N will have salt concentration enhanced to 3 times as for normal sea water. The enhanced concentration was used to obtain accelerated effects.

(b) Mortar quality: Four different mortar mixes were made by using three water cementitious material ratio of 0.42, 0.46 and 0.5 with a cementitious material sand ratio of 1:3. Four different mix proportions of cement and slag as cementitious material were 100:0, 85:15, 70:30 and 55:45. Cement slag ratio 100:0 i.e. plain mortar was also cast for comparing its properties with that of slag cement mortar.

(c) Exposure period: Test specimens were tested periodically after the specified curing periods of 30, 90 and 180 days in plain water, 1N and 3N sea water environments.

(d) Size of specimens: 50 mm x 50 mm x 50 mm cube specimens were prepared as per ASTM standard.

(e) Curing Environment: A total of 350 mortar specimens were cast in the laboratory. After casting, the specimens were kept at 27^0C temperature and 90% relative humidity for 24 hours. After demoulding, all the specimens were cured in plain water for 30 days at room temperature. After 30 days plain water curing, the specimens were submerged in tanks containing PW, 1N and 3N sea water for different exposure periods.

Table 2
Composition of Artificial Sea Water *

Salt	Chemical formula	Amount (gm/liter)	% of total salt	Remarks
Sodium chloride	NaCl	27.21	77.74	These amounts of salts were dissolved in plain water to prepare 1000 gm of Sea water of 1N Concentration
Magnesium chloride	$MgCl_2$	3.81	10.89	
Magnesium sulfate	$MgSO_4$	1.66	4.74	
Calcium sulfate	$CaSO_4$	1.26	3.60	
Potassium sulfate	K_2SO_4	0.86	2.46	
Calcium carbonate	$CaCO_3$	0.12	0.34	
Magnesium bromide	$MgBr_2$	0.08	0.23	
Total		35.00	100.00	

* Handbook of Ocean and Under Water Engineering, Myers, Holm and Mc. Allister.

Table 3
Physical properties and Chemical composition of OPC

Characteristics	Value
Blaine's Specific surface (cm^2/gm)	2460
Normal Consistency (%)	26
Soundness by Le Chatelier's Test (mm)	3.5
Specific gravity	3.15
Setting Time	
(a) Initial (min.)	75
(b) Final (min)	185
Loss on ignition	1.95
Insoluble matter	1.56
SiO_2 (silica)	15.58
Al_2O_3	16.67
Fe_2O_3	3.53
CaO	63.50
MgO	1.32
SO_3	2.58

Table 4
Chemical composition of slag

Constituent	Percentage
CaO	36
SiO_2	29
Al_2O_3	15
Fe_2O_3	1.5
MgO	4
SO_3	1
Free lime	1.5

Table 5
Compressive Strength (MPa) for Slag Cement Mortar Exposed to Sea Water of Different Concentration

W/B Ratio	Mix. Prop. C:S	Curing Period O* day	Curing Period 30 days			Curing Period 90 days			Curing Period 180 days		
			Curing Condition			Curing Condition			Curing Condition		
		PW	PW	1N	3N	PW	1N	3N	PW	1N	3N
0.42	100:0	21.3	24.5	24.3	22.5	28.5	27.9	25.6	31.0	29.7	27.5
	85:15	19.5	22.9	21.8	20.0	26.0	24.2	22.5	28.6	25.6	24.1
	70:30	20.2	23.8	22.0	21.3	27.4	26.7	24.5	30.1	28.8	26.8
	55:45	19.6	22.9	21.3	20.2	26.3	24.3	22.7	28.5	26.5	23.8
0.46	100:0	27.1	31.0	27.8	27.2	35.4	33.7	32.1	38.5	36.4	34.1
	85:15	23.8	27.5	24.7	22.7	30.8	29.4	26.5	34.5	31.7	28.6
	70:30	26.2	30.0	27.2	25.2	33.9	31.7	30.1	37.4	35.1	33.5
	55:45	23.8	27.4	25.6	22.4	31.0	29.2	26.5	34.0	32.9	28.4
0.50	100:0	25.4	29.2	26.0	24.2	32.8	30.6	27.2	35.1	32.3	30.0
	85:15	23.1	26.6	22.2	21.3	29.7	25.4	23.4	32.3	28.9	26.6
	70:30	24.0	27.9	24.2	23.4	31.2	29.2	27.8	34.0	31.8	29.7
	55:45	23.5	27.2	23.1	21.8	30.5	27.2	24.9	32.8	29.7	27.3

* Means 30 days procuring in PW

3. Results and discussion

The results of the test specimens have been critically analyzed and presented both in graphical and tabular forms. Figures 2 to 4 presents the experimental results of compressive strength of mortars for different mix proportions of cement and slag, different water binder ratios, curing environments and curing periods. These figures clearly demonstrate that the mortar specimens with cement slag proportion of 70:30 gives lower strength deterioration for all water binder ratios. Compressive strength increases with age for any curing condition and water / binder ratio. The test data of Table-5 shows that the difference between 30 days and 90 days compressive strength for 100:0, 85:15, 70:30 and 55:45 slag mortar are 4.0, 3.1, 3.6 and 3.4 MPa for water binder ratio 0.42; 4.4, 3.3, 3.9 and 3.6 MPa for water binder ratio 0.46 and 3.6, 3.1, 3.3 and 3.3 MPa for water binder ratio 0.50 respectively. On the other hand, for the same mix ratios, the differences between 90 days and 180 days compressive strengths are 2.5, 2.6, 2.7, and 2.2 MPa for water binder ratio 0.42; 3.1, 3.7, 3.5 and 3.0 MPa for water binder ratio 0.46 and 2.3, 2.6, 2.8 and 2.3 MPa for water binder ratio 0.50 respectively. It indicates that like plain cement mortar, the strength gaining of slag concrete is not higher at early age of curing and the gain in strength occurs at relatively higher rate in later ages of curing. Such observation reflects the actual material property of slow hydration rate of slag at the early age of curing.

Figure 5 to 7 presents the result of compressive strength of mortars made from various mix proportions of slag concrete for various water binder ratios. These figures clearly shows that for all curing condition and exposure periods, water binder ratio of 0.46 provides higher strength than those obtained for water binder ratio of 0.42 and 0.50. This may be due to the fact that in case of water binder ratio of 0.42, water might be insufficient for the complete hydration of binding materials. On the other hand, for water binder ratio of 0.50, water might be more than that of required amount.

Also form Table-5, it is clear that compressive strength of mortar decreases as the salt concentration of sea water increases although the rate of decrease is not proportional. However, this is due to the presence of salt in seawater. These salts enter into the mortar and form some expansive compounds inside mortar that causes micro cracks and consequently the strength is reduced.

Figure 8 to 10 represent the relative compressive strength of mortar with respect to plain cement mortar at various curing ages, curing conditions and different mix proportions of cement slag. After the exposure period of 180 days, it is seen that, the strength deterioration for cement slag mortar of mix proportion 100:0, 85:15, 70:30 and 55:45 are 11.3%, 14.6%, 10.6% and 15.1% for water binder ratio of 0.42; 11.4%, 15.3%, 10.1% and 14.5% for water binder ratio of 0.46 and 14.5%, 16.2%, 12.3% and 15.6% for water binder ratio of 0.50. Thus the rate of strength deterioration for cement slag mortar of mix ratio 70:30 is seen to be relatively lower than other mortar mixes used in the study.

4. Conclusion

Based on the limited number of tests conducted and variables studied as stated above, the following conclusions can be drawn:

- The development of compressive strength for cement slag mortar is not significant at the early age of curing. The gain in strength occur at relatively rapid rate at later ages of curing.

- Mix proportion of slag with cement has a significant effect on strength development of slag mortar. Out of mix proportions 85:15, 70:30 and 55:45, the 70:30 mortar mix shows higher compressive strength for all water binder ratio.

- The rate of compressive strength deterioration of cement slag mortar mix 70:30 is observed to be lower than any other cement slag mortar for all water binder ratios.

- As usual, effect of water binder ratio plays an important role on the compressive strength development of mortar. For all slag mortar, water binder ratio of 0.46 provides a higher compressive strength than the water binder ratio of 0.42 and 0.5. Hence, it is necessary to pay careful attention to the mixing water in making slag concrete in marine environment.

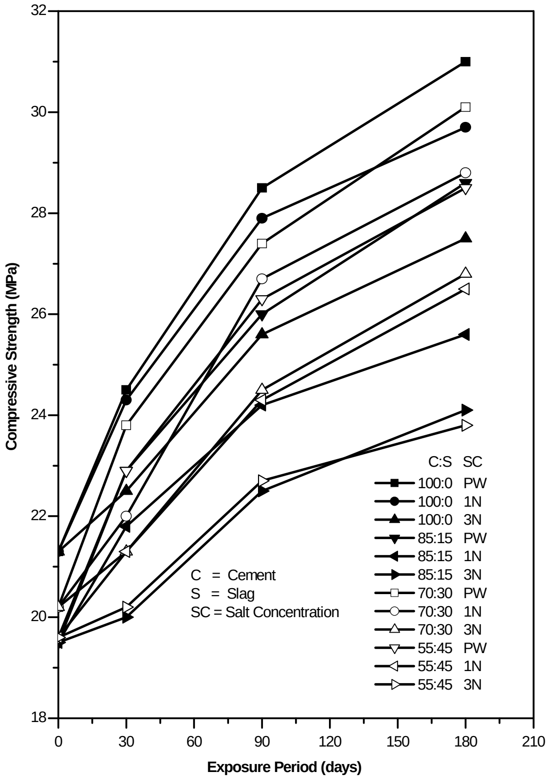

FIG.2 Compressive Strength-Exposure Time Relation for Slag Cement Mortar Exposed to Sea Water of Different Concentration (W/B=0.42)

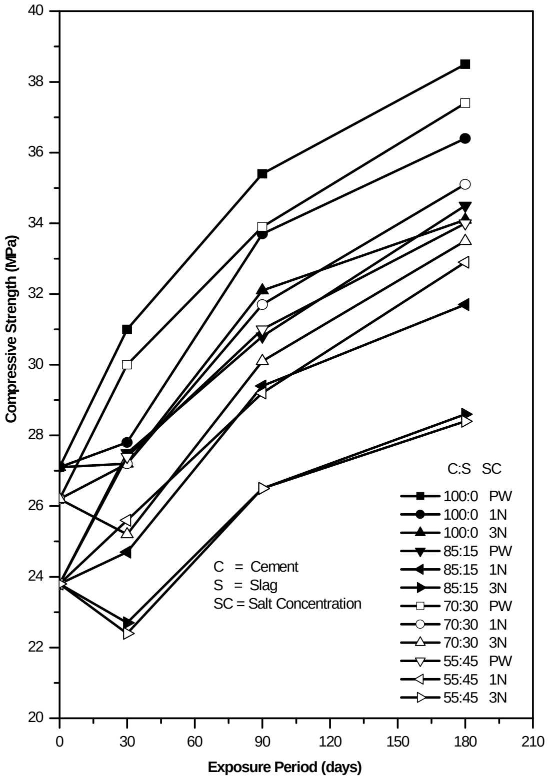

FIG.3 Compressive Strength-Exposure Time Relation for Slag Cement Mortar Exposed to Sea Water of Different Concentration (W/B=0.46)

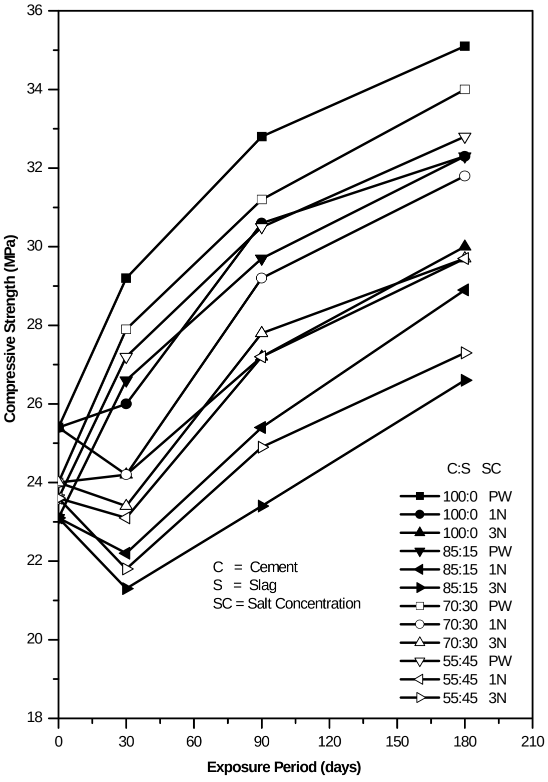

FIG.4 Compressive Strength-Exposure Time Relation for Slag Cement Mortar Exposed to Sea Water of Different Concentration (W/B=0.50)

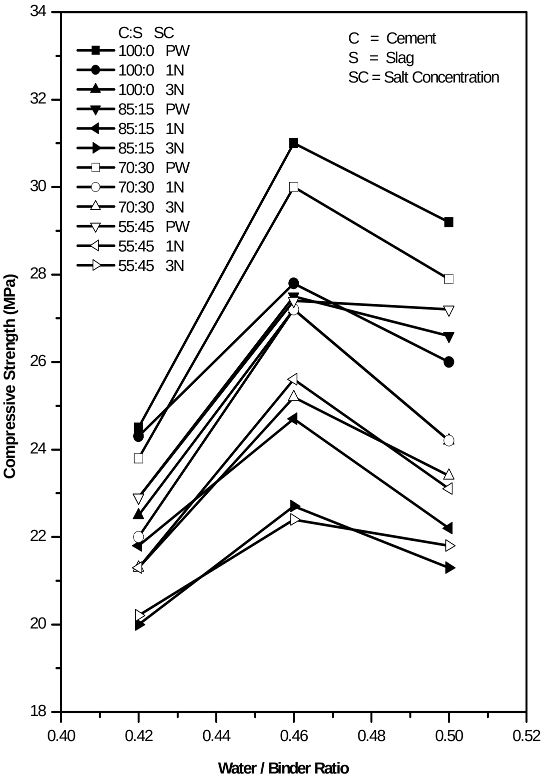

FIG.5 Compressive Strength-Water Binder Ratio Relation for Slag Cement Mortar Exposed to Sea Water of Different Concentration (Curing Period 30 Days)

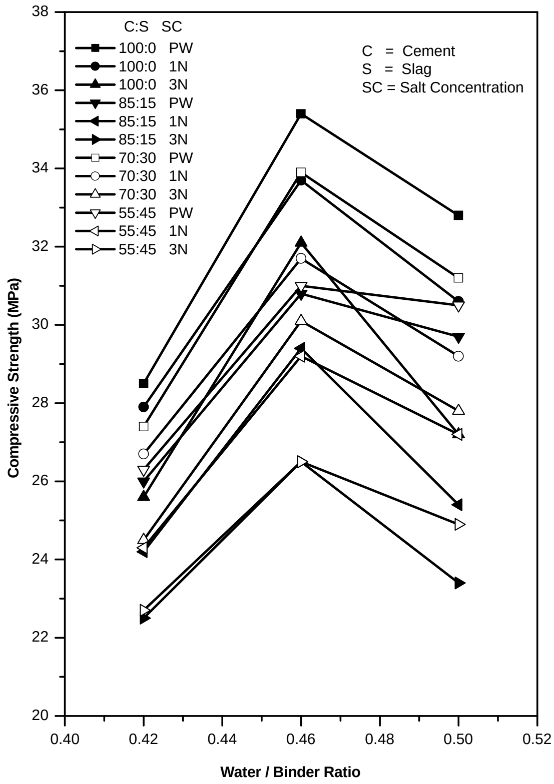

FIG.6 Compressive Strength-Water Binder Ratio Relation for Slag Cement Mortar Exposed to Sea Water of Different Concentration (Curing Period 90 Days)

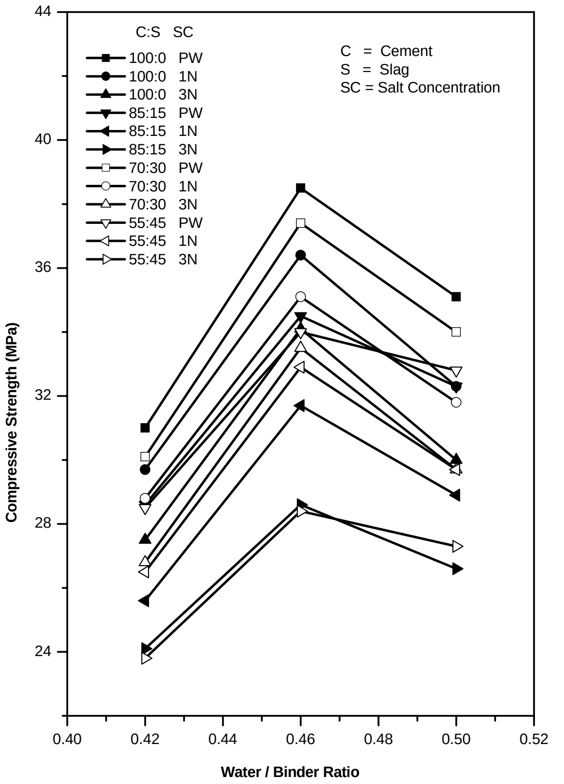

FIG.7 Compressive Strength-Water Binder Ratio Relation for Slag Cement Mortar Exposed to Sea Water of Different Concentration (Curing Period 180 Days)

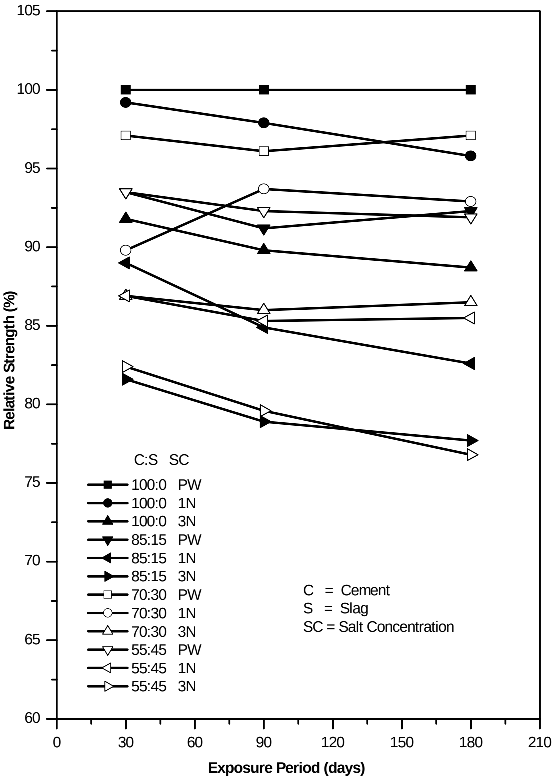

FIG.8 Relative Strength-Exposure Time Relation for Slag Cement Mortar Exposed to Sea Water of Different Concentration (W/B=0.42)

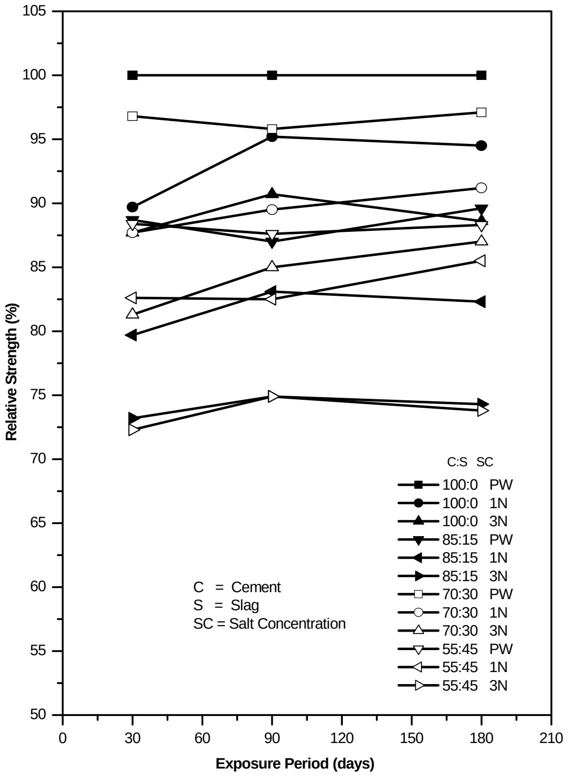

FIG.9 Relative Strength-Exposure Time Relation for Slag Cement Mortar Exposed to Sea Water of Different Concentration (W/B=0.46)

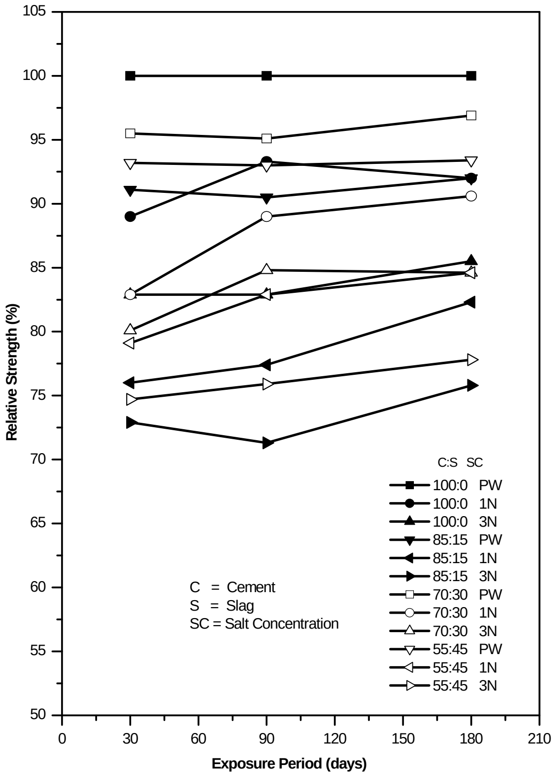

FIG.10 Relative Strength-Exposure Time Relation for Slag Cement Mortar Exposed to Sea Water of Different Concentration (W/B=0.50)

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