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Effect of Sea Water on the Quaternary Cement Concrete

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ABSTRACT

Most of the buildings are made of concrete; hence, the consumption of cement, freshwater, river sand, and coarse aggregate has increased, leading to environmental pollution and natural source depletion. The percentage of the ocean on the Earth's surface is 71%. Hence seawater is available in abundance. If the freshwater is replaced by seawater, there would be sustainable development in the construction industry. In this study influence of the composition of Portland cement - fuel ash - metakaolin – silica fume binders partially mixed with seawater on the strength and durability of the concrete have been investigated. The percentage of replacement of freshwater by seawater was 5%, 10%, 15%, 20%, 25%, and 100%. The effects of concrete mixing with seawater on compressive strength and its durability were studied.

Keywords:

Concrete, Fly ash, Metakaolin, Silica fumes, Sea water.

1. Introduction

Due to the rise in population, there has been an increase in infrastructure demand. Most of the buildings are made of concrete and hence the consumption of cement, freshwater, river sand, and coarse aggregate has increased leading to environmental pollution and natural source depletion. Among these resources, freshwater is facing the extreme scarcity with increased demands due to changing lifestyle in major parts of the world. India has experienced increase in per capita demand in recent past. The world is witnessing a sustained growth in infrastructural development and huge investments are being made for the extensive construction projects. Concrete is one of the major construction materials throughout the world owing to its design versatility, availability, and cost efficiency but is a high-energy and pollution-intensive building material. Ordinary Portland cement (OPC) is widely used in concrete production and its manufacturing puts a heavy environmental burden by emitting large amount of CO_2 in the atmosphere. It has been reported that 1 ton of cement production releases nearly 0.87 tons of CO_2 [1] and thus supplementary cementitious materials (SCM) are added to reduce the carbon footprints of the cement. Binary [2], ternary [3] and quaternary [4] cement blends have been researched in past using fly ash, slag, metakaolin, rice husk ash, etc. that also provides a method to manage these industrial wastes in a sustainable way.

The other natural resource used in bulk amounts for concreting is freshwater which is excessively overused and is getting depleted. There are numerous sources of wastewater that have been tried previously for use in concrete mixtures, like domestic and industrial effluent, sea and alkali, waters, mine and mineral waters, and oily and brackish waters from oil wells [5]. If the freshwater is replaced by seawater, then there would be sustainable development in the construction industry and also a reduction in the transportation cost of the coastal structures. Reinforced cement concrete has poor resistance to corrosion and if seawater is used in Ordinary Portland cement it will further increase the rate of corrosion of concrete leading to the reduced life of the concrete structures. Many literature have reported that interaction of seawater with cement paste leads to carbonation, sulphate attack and chloride ion attack. It is reported that addition of mineral admixtures assures low permeability to aggressive anions and offer excellent durability for concrete structures in seawater. Different binders such as pulverized fuel ash (PFA) and metakaolin (MK) along with Portland cement and synthetic seawater have been tested. The percent replacement of cement was 10%, 20%, 30%, 40%. The results show that both PC-PFA and PC-PFA-MK blends improve the compressive strength during seawater exposure and also reduced the Chloride concentration and penetration depth [6]. Thus, using it in quaternary cement blends can minimize these problems due to the presence of supplementary cementitious materials.In this study influence of the composition of quaternary cement binder prepared from fly ash, metakaolin and silica fumes partially mixed with seawater on the strength and durability of the concrete were investigated. The percentage of replacement of freshwater by seawater was 5%, 10%, 15%, 20%, 25%, and 100%. The effects of mixing concrete with seawater mixing on the compressive strength and its durability were studied. Rapid Chloride Permeability Test and Scanning Electron Microscopy tests were also carried out to study the properties of concrete. Experimental studies have been conducted [7] on slag cement concrete and seawater to understand the durability of slag concrete against seawater corrosion. The specimens were immersed in artificial seawater and tested under wet-dry cycles after moist curing for 28 days. The results showed that the control group compressive strength was always higher than the slag concrete specimens. The strength of the slag concrete continued to increase up to 1 year but in the case of concrete only with cement, after 180 days the strength tends to decrease. The value of electrical resistance of slag concrete was highest when the slag substitution ratio was 20% - 30%. In order to minimize chloride ion diffusion, the slag replacement with 20% was suggested as the optimum value. Concrete incorporating ground blast furnace slag (GBFS) and ground basaltic pumice (GBP) was experimented to determine the seawater resistance. The samples were immersed in seawater. The results show that the addition of GBFS and GBP improved the compressive strength of concrete in seawater and was very effective in corrosion resistance [8]. Experiments were conducted to determine the relationship between porosity, compressive strength, age and also a model of the relationship between porosity and compressive strength of self-compacting concrete using seawater. Portland composite cement (PCC), seawater, crushed stone, sand, and super plasticizer were used in this experiment. The results showed that the compressive strength increased and the porosity decreased with the increasing age due to the addition of seawater. This was due to the increasing quantity of formation of CSH (tobermorite). The relationship between compressive strength and porosity at self-compacting concrete with seawater was approximated σss=σ0 (1-p)k with σ0=119.6 dan k = 7.502.[9]. Studies has been conducted adding 0-6% by weight of metakaolin in concrete and artificially created sea water. (Qiu Li et.al (2015). Two types of curing conditions were selected in the study namely standard curing condition and the Chloride curing condition. The results showed that when metakaolin was added there was an increase in compressive strength of concrete for both, freshwater and seawater. Also, when metakaolin was added there was an increase in compressive strength for curing of concrete both in normal and NaCl solution [10]. Experiments were conducted on potassium magnesium phosphate cement (MKPC) along lime-stone powder, water, silica fume and seawater to understand microstructure, phase composition, physical and mechanical properties of MKPC paste. The results showed that seawater mixing increases the initial setting time and also improved the fluidity of fresh MKPC pastes. The compressive strength of the MKPC pastes decreased due to the seawater mixing but when 5% silica fumes and 5% limestone is added then there is an improvement in compressive strength. The structure of hardened MKPC paste was compact when seawater along with limestone and silica fume was used. SEM analysis showed that the mixed sample containing seawater also cured in seawater for 180 days had more columnar crystal and some amorphous phase, while that mix sample containing seawater but cured in freshwater had a lot of porous amorphous phases but few crystalline phases. Mixed sample containing seawater silica fume and limestone, cured in seawater for 180 days had columnar crystals, needle-like crystals, and a little gel phase while the mixed sample containing seawater, silica fume, and limestone, cured in the water had many columnar crystals and some gel phases. Thus, the hardened structure of MKPC paste made by seawater can be made more compact by using a suitable quantity of limestone powder and silica fume [11]. The effect of saline water on concrete with cement partially replaced with silica fume and fine aggregate replaced with stone dust was studied. The percentage replacement with silica fume was 5%, 10%, 15% and 20%. From the results, it was concluded that 33% of the maximum strength attained in 28 days was attained in 7 days with 15% of silica fumes. Also, the compressive strength by replacing cement with silica fume by 13% was highest [12]. Studies was performed on high-performance concrete (HPC) pastes with various mineral admixtures in simulated seawater. The materials used in the experiment were limestone powder, cement, silica fume, ground granulated blast-furnace slag (GGBS), fly ash, water reducing agent such as polycarboxylate. The results show that in concrete with fresh water, the compressive strength was highest in fly ash paste and lowest in silica fume after 360 days of curing. This increase in compressive strength of fly ash may be due to the reaction between fly ash and Ca(OH)2, which results in a large amount of C-S-H gel formation, and hence the strength of paste is enhanced. In concrete with simulated/artificial seawater, the compressive strength was highest in fly ash paste and lowest in limestone powder paste at 360 days. Between 180 days to 360 day's strength of fly ash paste became the highest. In the comparison of pure cement paste the addition of fly ash, silica fume, and GGBS improved the durability of paste in simulated seawater. The results show that in concrete with fresh water, the expansion rate was highest in pure cement paste and lowest in silica fume at 360 days while in simulated seawater the highest was in limestone powder paste and lowest in silica fume paste. The reason for the higher expansion rate in limestone powder paste may be due to formation of the more expansion products. The denser structure was observed in the paste with admixtures [13]. Utilization of waste material is a major concern in today's world so as to ensure that nothing goes waste and society can witness sustainable development. Hence, to support an environmentally sustainable world, the construction industry provides an opportunity to use a high volume of these industrial wastes as a partial replacement of cement not only to save the depletion of construction raw materials but to protect the environment from degradation and to reduce the CO_2 release.

2. Material and methods

The following materials have been used in the present work. Cement: Ordinary Portland cement of grade 43 (OPC 43, Figure 1) was used as per conforming to IS 8112 [14]. The physical properties of cement are shown in Table 1.

Figure 1. Cement.

Aggregates, River sand pertaining to the zone-II of IS 383:1970 [15] was been used as fine aggregate (Figure 2 and Table 2). Crushed stone of 20 mm is used as a coarse aggregate (Figure 3 and Table 3).

Table 1. Properties of cement.

Characteristics	Unit	Result	Requirement
Consistency	%	28.20	-
Initial setting time	min	150	30 Min.
Final setting time	min	245	600 Max.
Fineness	m^2/kg	278	225 Min.
Specific gravity	g/cm^3	3.14	-
Soundness			
a) Le-Chatlier		1.5	10 Max.
b) Auto Clave		0.06	0.8 Max.
Compressive Strength			
a) 72 ± 1 hours	MPa	30.50	23 Min.
b) 168 ± 2 hours	MPa	40	33 Min.
c) 672 ± 4 hours	MPa	50.50	43-58

Figure 2. Fine Aggregate.

Table 2. Physical properties of fine aggregates.

Type		Natural Sand	-
Grading Zone		Zone-II	-
Specific gravity	g/cc	2.58	2.1 to 3.2
Silt Content	By Vol.	4.25	8.0 Max.
Water absorption	%	1.25	5.0 Max.
Bulk Density	g/cc	1.72	kg/ltr
Moisture Content	%	Nil	-
Sieve Analysis, % of passing	Passing		
4.75	%	100	100
2.36	%	98	90-100
1.18	%	76.4	75-100
0.6	%	52.8	55-90
0.3	%	32.8	35-59
0.15	%	13.6	8-30
0.075	%	4	0-10
By $MgSO_4$ (Loss in Wt.)	%	3.09	15.0 Max.
By Na_2SO_4 (Loss in Wt.)	%	2.86	10.0 Max.
Total Deleterious Material			
(i) Material finer than 75 Micron		1.87	3.0 Max.
(ii) Coal & Lignite		0.2	1.0 Max.
(iii) Clay Lumps		0.27	1.0 Max.
Total Deleterious Material	%	0.47	2.0 Max.

Figure 3. Coarse Aggregate.

Table 3. Physical properties of Coarse aggregate 20mm

Characteristics	**Unit**	**Result**	**Requirement**
Specific gravity,	g/cc	2.8	2.1 to 3.2
Water absorption	%	0.5	5.0 Max.
Bulk density, g/c kg/ltr	kg/ltr	1.64	-
Sieve Analysis	Passing		
40mm	%	100	100
20mm	%	85.5	85-100
12.5mm	%	25	0-20
10mm	%	13.5	0-5
4.75mm	%	7	
Pan	%	0	
Elongation Index	%	12.73	-
Flakiness Index	%	19.27	-
Combined Flakiness and Elongation Index	%	32	40 Max.
Deleterious Material			
Material finer than 75 Micron		Nil	1.0 Max.
Coal & Lignite		0.08	1.0 Max.
Clay Lumps		0.06	1.0 Max.
Total Deleterious Material		0.14	2.0 Max.
Aggregate Impact Value	%	19	30/45 Max. for wearing/ non waring surface
Aggregate Crushing Value	%	25	30 Max.
10% Fine Value		30.81	-

To prepare the quaternary cement blends, supplementary cementitious materials, like, fly ash, silica fumes and metakaolin have been used to replace cement. The physical and chemical properties of these SCMs have been shown in Table 4.

Table 4. Physical and chemical properties of SCM.

Description	FA	SF	MK
Physical characteristics			
Specific gravity,	1.64	2.2	1.76
Blaine's fineness, cm^2/g	3710	16020	8740
Chemical composition (%)			
SiO_2	57.9	88.31	51.48
Al_2O_3	31.78	0.89	47.83
Fe_2O_3	4.2	1.60	0.39
CaO	0.87	1.28	1.56
MgO	0.51	0.15	0.10
MnO	0.32	0	0
K_2O	0.28	1.98	0.19
Na_2O	0.15	0.40	0.07
LOI	2.76	2	0.56

Artificial sea water has been prepared to achieve the concentration as described in Table 5. Ingredients.

Table 5. Concentration of salts in sea water.

Name of the Salt	Concentration of Salt (mg/l)
NaCl	10.5
$MgSO_4$	2.665
$SrCl_2$	0.008
KCl	0.38
$CaCl_2$	0.4
KBr	0.065
$CaCO_3$	0.140

The mix design for M35 concrete has been prepared using IS 10262 [16]. 70% cement, 20% fly ash, 5% silica fumes (SF) and 5% metakaolin (MK) has been used to prepare the concrete mix. The water cement ratio has been kept as 0.45. 2% of plasticizer SP-430 have been used to attain the slump in the range of 100 to150. The binder: fine aggregates: coarse aggregate ratio from the design mix was worked out as 1:1.98:2.63. Different percentages of sea water (5, 10, 15, 20, 25, 100) has been used to replace fresh water in the mixing water have been used in the present study and the mixes prepared are detailed in table 6.

Table 6: Types of Mix and its Symbol

Sl. No.	**Percentage of Replacement**	**Mix**	**Symbol**
1.	100% Fresh Water	M0	FW100-SW0
2.	5% Fresh water replacement with Sea Water	M1	FW95-SW5
3.	10% Fresh water replacement with Sea Water	M2	FW90-SW10
4.	15% Fresh water replacement with Sea Water	M3	FW85-SW15
5.	20% Fresh water replacement with Sea Water	M4	FW80-SW20
6.	25% Fresh water replacement with Sea Water	M5	FW75-SW25
7.	100% Fresh water replacement with Sea Water	M6	FW0-SW100

Five specimens for each mix proportion have been prepared for the repeatability and reproducibility purposes. Standard concrete cubes of dimension 150x150x150 mm were prepared for different curing ages (7, 28, 56, 90 days). Compressive strength test was carried out after each curing stage. Durability test has been performed using the rapid chloride penetration test (RCPT). The morphological characteristics have been studied using scanning electron microscopy (SEM).

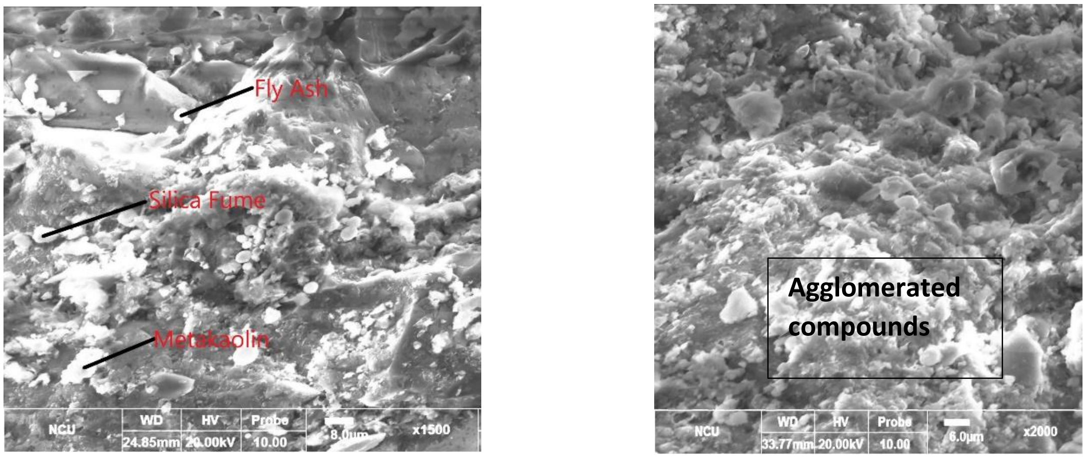
3. Results and discussion

The workability of the mix prepared 100% cement was found to be 112 mm and the mix with 70% cement+20% FA+5% SF+5% MK was found to be 142 mm. It can be noted from here that the quaternary cement blend has resulted in higher slump value. The compressive strength values of the prepared mixes are shown in Table 7. Marginal increase in the strength at all curing days can be observed after the addition of different percentage of sea water to the mix. The 100% replacement with sea water have resulted in 10% strength increase. This may be due to the acceleration of cement hydration due to the presence of chlorides in concrete. It is observed here that the SCMs when mixed with seawater refines the pore structure of concrete and hydration acceleration

Table 7. Compressive Strength Test for Different Mixes.

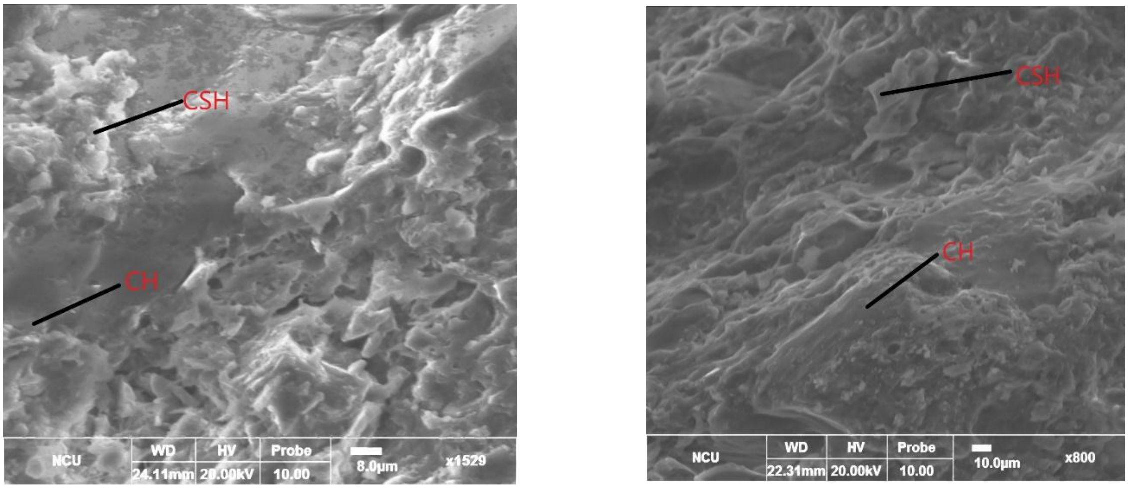
Mix (↓)	Compressive strength, (N/mm^2)			
Age (days) →	7	28	56	90
100% Fresh Water – M0	20.74	38.81	44.15	48.29
5% Sea Water – M1	20.59	38.22	44	48.44
10% Sea Water – M2	20.74	38.07	44.74	48
15% Sea Water – M3	20.89	38.37	43.56	48.59
20% Sea Water – M4	20.14	38.52	44.29	48.44
25% Sea Water – M5	20.29	38.96	44.59	49.18
100% Sea Water – M6	21.78	39.7	47.11	53

This increase can be confirmed from the microstructural changes as observed from the scanning electron microscopy images as shown in figure 4 and 5. After 7 days of curing period, the M0 mix with 100% fresh water shows the unutilized particles of fly ash, silica fumes and metakaolin, however the M6 mix with 100% sea water shows the agglomerated compounds. The SEM images after 90 days of curing shows the formation of CSH and CH gel and responsible to higher strength.



(a) M0 with 100% fresh water (b) M6 with 100% sea water

Figure 4. SEM Image after 7 days of curing.



(a) M0 with 100% fresh water (b) M6 with 100% sea water

Figure 5. SEM Image after 90 days of curing.

The long-term effect of strength was evaluated by checking the durability of the mixes. Rapid chloride permeability test was adopted to check the durability. The charge passed by various mixes after 7, 28, 56 and 90 days of curing is shown in Table 8. For all the mixes, the charge reduces with the curing age which confirms the gain of strength at higher curing periods. The addition of sea water in concrete does not show a particular pattern of the passing charge. But, 100% addition of sea water increases the passage of charge and thus reduces the durability of the mix. However, the charge passed through the M6 mix (100% sea water) after 90 days of curing is LOW as per the prescribed limits of ASTMC1202 [17]. It has been reported that the addition of SCMs in concrete increases the chloride resistance of concrete in comparison to the conventional concrete [4]. The present study shows the reduction in strength upon the addition of sea water.

Table 8. Test Result of Rapid Chloride Permeability Test for Different Mixes.

Mix (↓)	Charge passed (Coulombs)			
Age (days) →	7	28	56	90
100% Fresh Water – M0	2120.1	1901.5	1234.44	581.78
5% Sea Water – M1	1400.38	1806.12	1410.57	863.89
10% Sea Water – M2	7.15	1951.16	1586.26	1100.11
15% Sea Water – M3	4039.72	2507.65	1623.21	1143.65
20% Sea Water – M4	6174	2221.51	1716.67	1162.83
25% Sea Water – M5	5469.72	2336.91	1847.61	1198.55
100% Sea Water – M6	3874.11	3105.56	1622.36	1455.02

Table 9. Charge range as per ASTM C1202.

Charge passed (coulombs)	Chloride ion permeability
> 4,000	High
2000 – 4000	Moderate
1000 – 2000	Low
100 – 1,000	Very Low
< 100	Negligible

5. Conclusions

1-The concrete mix M6 i.e. the concrete mixed with 100% seawater had the highest compressive strength when compared to other mixes with 100% freshwater and 5%, 10%, 15%, 20% and 25% replacement of freshwater with seawater at 90 days of hydration age.

2-The SEM images showed that concrete mixed with seawater had a denser structure when compared to the concrete mixed with fresh water. This is due to the presence of seawater which accelerates the cement hydration.

3-From the Rapid Chloride Permeability Test (RCPT) it was observed that the total charge passed through concrete decreased with the increase in hydration age. At 90 days of hydration age the highest charge passed was in 100% seawater mixed concrete and the lowest was in 100% freshwater mixed concrete.

4-The present studies show the potential of using sea water in place of fresh water in concrete.

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