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Comparison of chloride diffusion in nine months concrete specimens containing metakaoline and silica fume pozzolans.

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ABSTRACT: Chloride diffusion is one of the major causes of deterioration of concrete structures in Persian Gulf. A large amount of research has been conducted to study the chloride diffusion of concrete, both theoretically and experimentally. In this paper, chloride diffusion of concretes contain metakaoline (5%, 10%, 15%) and silica fume (5%, 7.5%, 10%) as a replacement of cement compared with control specimen after nine months exposure in tidal and splash zones in Persian Gulf. The results show replacements of cement with silica fume and metakaoline reduce the chloride penetration into concrete, significantly.

1 INTRODUCTION

The premature deterioration of reinforced concrete due to chloride-induced corrosion of reinforcement is a serious problem in Persian Gulf region. The most common form of deterioration is caused by chloride ingress through concrete, resulting in corrosion of the reinforcing steel. This situation is exacerbated for structures that are close to, or located in, a marine environment. When chlorides accumulate within the surface layer of concrete, a concentration gradient of chloride ions is established within the concrete cover with the result that chloride ions migrate toward the reinforcement in the concrete (Sreejith et al. 2008).

In this region, the use of silica fume as a supplementary cementitious material has increased substantially in concretes used for marine structures in the Persian Gulf. The reason for use of silica fume in these structures is claimed to be an increase in the durability of coastal structures. In recent years, there has been a growing interest in the use of MK as a mineral admixture for a similar purpose.

High reactive metakaoline, produced by controlled thermal treatment of kaolin, is the most recent mineral admixture to be commercially introduced to the concrete construction industry. Concrete incorporating of metakaoline has showed a faster strength development at early ages, but had similar strength after 28 days compared to concrete containing silica fume at the same amount of replacement of cement. It has been concluded that the resistance of concrete containing metakaoline to diffusion chloride was significantly higher than the ordinary concrete but similar to the concrete incorporating of silica fume (ACI 232.1R. 2000).

In this study, chloride diffusion of concretes contain metakaoline (5%, 10%, 15%) and silica fume (5%, 7.5%, 10%) as a replacement of cement compared with control specimen after nine months exposure in tidal and splash zones in Persian Gulf.

2 EXPERMENTAL PROGRAM

2.1 *Materials*

In this study, the cementitious materials were Hormozgan Portland cement type II (Iran), silica fume (SF) obtained from Azna ferro-silicon alloy manufacture and metalaoline. The chemical and physical properties of these are outlined in Table 1. A poly carboxylate superplasticizer was used for the mixes to achieve desirable slump at a water-to-binder ratio of 0.4.

2.2 *Mix properties*

Silica fume and metakaoline were incorporated to make concrete mixes. In addition to control type II cement mix, the replacement cement with 5%, 7.5%

and 10% silica fume and 5%, 10% and 15% metakaoline were used.

Concrete mixes set on site with water-cement ratio of 0.4 and approximately coarse and fine aggregate of 710 and 1140 kg/m3, respectively. Water content in all mixtures is 160 kg/m3. The concrete were cast in 150×150×150 mm cubes for compressive strength test and 150×150×600 mm which used for chloride diffusion test. The compressive strength test specimens were removed from the moulds after 24 hours and moist cured up to 7 and 28 days. But 150×150×600mm cubes were moist cured in baths for 3 days and after sealing all sides except one, were placed in exposure conditions.

Table 1. Chemical composition of cement, metakaoline and silica fume.

Components	Cement (%)	Silica Fume (%)	Metakaoline (%)
SiO_2	21	93.16	51.85
Al_2O_3	5	1.13	43.87
Fe_2O_3	3.5	0.72	0.99
CaO	63	---	0.2
MgO	1.8	1.6	0.18
SO_3	1.6	0.05	---
Na_2O	0.5	---	0.1
K_2O	0.6	---	0.12
L.O.I	2	1.58	0.57
Total	99	98.24	97.79

Table 2. Concrete mix proportions.

Mix Code.	w/b	Cement kg/m^3	MK kg/m^3	SF $kg/\ m^3$
C	0.4	400	0	0
MK5	0.4	380	20	0
MK10	0.4	360	40	0
MK15	0.4	340	60	0
SF5	0.4	380	0	20
SF7.5	0.4	370	0	30
SF10	0.4	360	0	40

2.3 *xposure condition*

After 3 days of curing, the five sides of prism specimens were sealed with an epoxy coating to ensure that diffusion would occur in only one dimensional of the specimens. Then they were exposed to two different conditions in Persian Gulf region (Fig.1 and Fig.2).

The area between minimum and maximum height of water tide defines tidal zone. The above of this zone has been named splash zone in which seawater particles wash out concrete surface.

Figure 1. CMI exposure site in Persian Gulf-Tidal zone specimens.

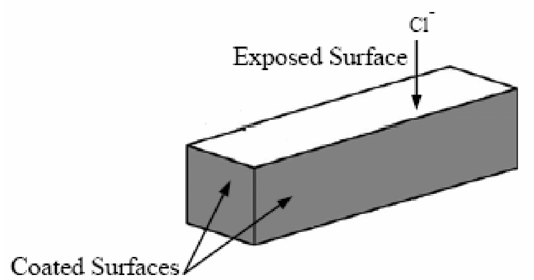

Figure 2. Typical concrete prism specimen and preparing the slice for powder sample.

2.4 *Sampling*

After nine months of exposure in seawater in Persian Gulf, powder samples for chloride analysis were ground off by Profile Grinder parallel to the exposed surface with the accuracy 0.1 mm at 9 different depths. The first 1mm powder was not included in calculations as it might be affected by actions such as skin effect (Fig.3). 10g sample at each depth was collected and analyzed separately for acid-soluble chloride according to ASTM C 114, part 19 (Shekarchi et al. 2009, Ghods et al. 2007).

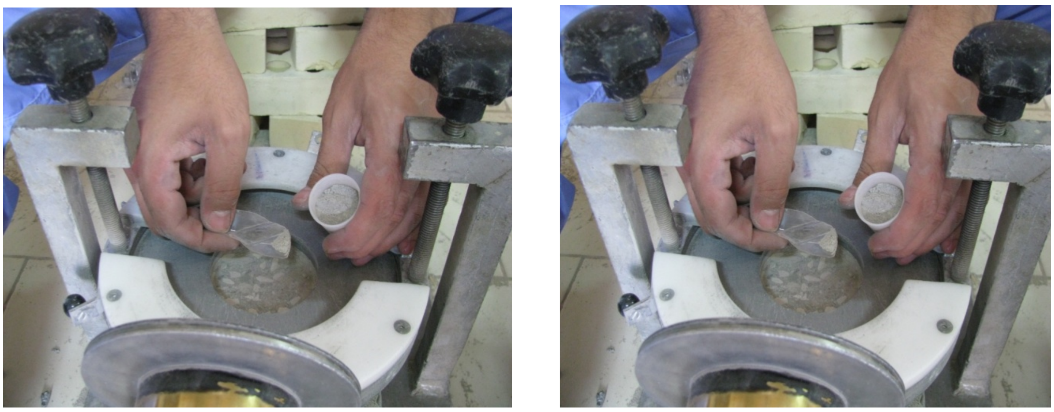

Figure 3. Sampling of concrete specimens using the Profile Grinder in exposure site.

3 TEST RESULTS AND DISCUTION

3.1 *Hardened concrete properties*

The compressive strength of hardened concrete specimens is given in Table 3, where each value is averaged from the results of three cubes. Specimens of 7 and 28 days old were cured in laboratory condition. As it was expected, the compressive strength increases with the use of silica fume and metakaoline compared with control mix. The compressive strength of cubes containing silica fume is more than metakaoline in 7 and 28 ages. Results of enhanced extent of compressive strength at 7 and 28 days show an optimum silica fume content of 7.5 to 10% and metakaoline content of 15% by weight of cement which corresponds to maximum enhanced extent of compressive strength. However, one can say the increase in the amount of MK might promote the compressive strength of MK concrete.

Table 3. Compressive strength of hardened concrete.

Code	Compressive strength (MPa)			
	7days	Enhanced extent (%)	28days	Enhanced extent (%)
C	27	100	38	100
SF5	34	126	45	118
SF7.5	41	152	50	132
SF10	38	141	52	137
MK5	32	119	43	113
MK10	36	133	45	118
MK15	39	144	47	124

3.2 *Chloride profiles*

The chloride penetration rate as a function of depth from the concrete surface and time can reasonably be represented by Fick's second law of diffusion according to the following expression (Crank 1975):

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

The solution for this differential equation is:

$$C(x,t) = C_0\left(1 - erf\left(\frac{x}{2\sqrt{D \cdot t}}\right)\right)$$

where x is distance from concrete surface (m); t is time (s); Dc is diffusion coefficient (m^2/s); Cs is equilibrium chloride concentration on concrete surface; C(x,t) is chloride concentration at the depth of x from the surface at time; and erf is error function.

Using a computer statistical analysis program, the regression was carried out on the experimental data and by curve fitting of Fick's second law of diffusion, the values of Dc and Cs were determined. Also the chloride threshold concentration of 0.07% by weight of concrete has been obtained for this investigation (Pargar et al. 2007, Shekarchi et al. 2009).

The evolution of the diffusion coefficient for different silica fume and metakaoline mixes at sampling age of 9 month is represented in Figures 4 and 5, respectively. Table 4 presents depth corresponds to chloride value of 0.07% by weight of concrete. The chloride profile of control mix is transverse by chloride value of 0.07 at the depths of 29.5 mm and 33.5 mm in splash and tidal zones, respectively. While SF10 and MK15 have the lowest depths in both zones.

Table 4. Depth of corresponding to chloride of 0.07% by weight of concrete (mm).

Code	Splash zone	Tidal zone
C	29.5	33.5
MK5	23	20.2
MK10	16.3	15.5
MK15	14.3	13.6
SF5	22.7	21.8
SF7.5	20.4	17.4
SF10	17	14.4

The values of diffusion coefficient (D) and surface chloride concentration (Cs) are given in Table 5. It is clear that the diffusion coefficient of concrete incorporating 15% metakaoline decreases up to 86% in the splash zone and 90% in the tidal zone. While diffusion coefficient of concrete containing 10% silica fume decreases up to 77% in the splash zone and 87% in the tidal zone compared to the control mix. Also, it can be found that using higher percentage of metakaoline decrease the diffusion coefficient significantly in splash and tidal zones. On the other hand, silica fume and metakaoline concretes at the same replacement (5%, 10%) have similar diffusion coefficient in splash and tidal zones. The surface chloride content at the splash zone is higher than tidal zone. The wetting and drying cycles in both zones, especially in splash zone, caused the large amount of surface chloride content.

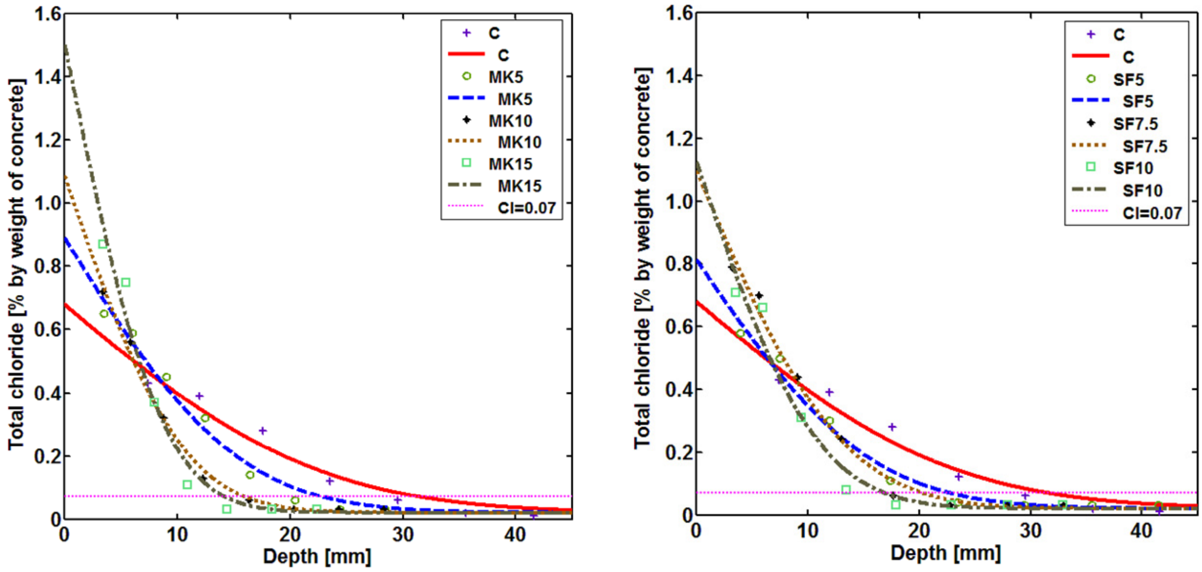

Figure 4. Chloride concentration profiles in splash zone.

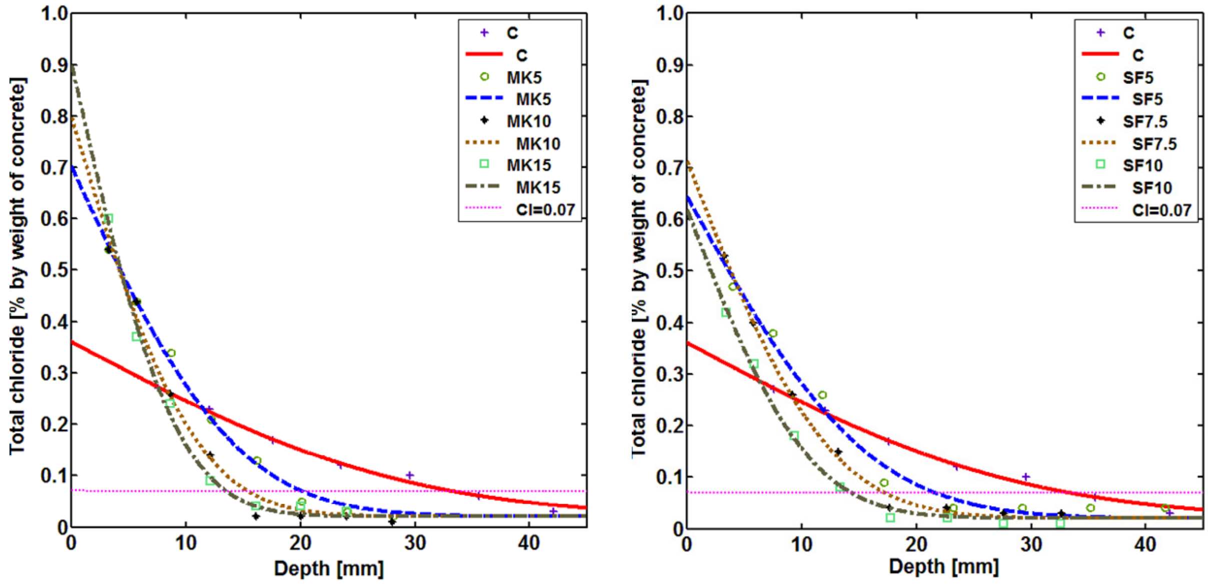

Figure 5. Chloride concentration profiles in tidal zone.

Table 5. Values of diffusion coefficient and surface chloride concentration after nine months of exposure.

Zon e	Code	Cs	$Dc \times 10^{12}$	Reduction in Dc vs. control mix
		% wt. of concrete	m^2/s	%
	C	0.66	6.66	0
	MK5	0.87	3.09	54
	MK10	1.1	1.38	79
	MK15	1.48	0.95	86
	SF5	0.79	3.2	52
	SF7.5	1.08	2.2	67
Splash	SF10	1.1	1.5	77
	C	0.34	11.07	0
	MK5	0.69	2.68	76
	MK10	0.78	1.47	87
	MK15	0.88	1.06	90
	SF5	0.63	3.23	71
	SF7.5	0.69	1.94	82
Tidal	SF10	0.59	1.44	87

4 CONCLUTION

(1) Results of compressive strength show an optimum silica fume content of 7.5% to 10 % and metakaoline content of 10% to 15% by weight of cement.
(2) Depth of chloride penetration reduces as the replacement of admixture increases.
(3) Cs value increases as the replacement of pozzolans increases. But the diffusion coefficient decrease with the increase in the replacements of pozzolans.
(4) The surface chloride content of concrete in splash zone is more than tidal zone
(5) At the same replacement, concretes containing metakoaline have similar diffusion coefficient and chloride in depth to those of silica fume. But the surface chloride content of metakaoline is more than silica fume.

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