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# Long-term field study of chloride ingress in concretes containing pozzolans exposed to severe marine tidal zone

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## HIGHLIGHTS

- Long-term field effectiveness of pozzolans on the chloride ingress into concrete.
- Comparing the performance of pozzolans on the compressive strength & chloride ingress.
- Chloride diffusivity & surface chloride content changes over the time in tidal zone.

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## ABSTRACT

Chloride ingress in concrete is the most deteriorating factor for reinforced concrete structures exposed to marine environment. This phenomenon depassivates reinforcing steel in concrete and causes steel corrosion. To improve the durability and serviceability of concrete structures in harsh environments with high relative humidity, temperature and concentration of chloride ions such as in the Persian Gulf, the addition of silica fume and other pozzolans have been recommended by several investigations. In this paper, the chloride ion diffusivity and mechanical performance of concretes containing silica fume, metakaolin and natural zeolite, and those of concretes with different water-cement ratios (w/c) under in-situ tidal exposure condition were investigated. To achieve this objective, concrete specimens with w/c of 0.35, 0.40, 0.45 and 0.50 were fabricated. In addition, to examine the performance of pozzolans, other specimens with constant water-binder ratio (w/b) of 0.40 containing 5% silica fume, 5% metakaolin and 10% natural zeolite were prepared. All of the specimens were subjected to laboratory and tidal exposure in the field conditions. The results indicate that 10% natural zeolite, 5% metakaolin and 5% silica fume have similar effects on concrete strength and durability in harsh marine environments. In addition, it is concluded that at long time field exposure, chloride diffusion coefficient and surface chloride content of different mixtures reach to relatively similar amounts.



## 1. Introduction

Chloride ingress in concrete is the most deteriorating factor for reinforced concrete structures exposed to marine environment. This phenomenon depassivates reinforcing steel in concrete and causes steel corrosion. Chloride penetration intensifies with the warm climate and high salinity of the sea water, i.e. the Persian Gulf region. The deterioration rate related to temperature in the Persian Gulf region should be about 8 times faster than that in Nordic region, as the average yearly temperature of the former region is 30 °C higher [1].

It is shown that for non-steady state condition, the chloride transport into saturated concrete obeys Fick's second law of diffusion (Eq. (1)).

$$\frac{\partial C}{\partial t} = \frac{\partial \left(D \frac{\partial C}{\partial x}\right)}{\partial x} \tag{1}$$

where C is chloride concentration at the location x and time t, and D denotes chloride diffusion coefficient of concrete.

For constant D, the solution of Eq. (1) for the boundary condition of $C = c_s$ (for $x = 0$ and $t \geqslant 0$) and actual initial condition of $C = c_i$ (for $x > 0$ and $t = 0$) is given by Eq. (2a) or (2b) [2].

$$C(x,t) = c_s - (c_s - c_i) \cdot erf\left(\frac{x}{\sqrt{4D \cdot t}}\right) \tag{2a}$$

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or

$$C(x,t) = c_i + (c_s - c_i) \cdot erfc\left(\frac{x}{\sqrt{4D \cdot t}}\right) \tag{2b}$$

where erf is the error function which generally can be written as Eq. (3) and erfc is the complementary error function which can be written as Eq. (4).

$$erf(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-u^2)du \tag{3}$$

$$erfc(z) = 1 - erf(z) \tag{4}$$

Several studies have shown that w/b ratio and using cement replacement materials such as pozzolans affect greatly on the mechanical strength, permeability and durability parameters of the concrete. Decreasing the w/b ratio reduces porosity of concrete, and this reduction causes increase in compressive strength and also decrease in concrete permeation [3–5]. In general, the use of pozzolans such as silica fume, metakaolin and natural zeolite enhance concrete permeability and durability [6]. This enhancement is because of improving the distribution of pore size and structure of concrete matrix, improving interfacial transition zone of the interface between aggregates and the matrix, reducing chloride ingress, and increasing chloride binding [3,4,7–9].

Silica fume and metakaolin are commonly used pozzolans in construction projects. According to studies, these two pozzolans can sharply increase the compressive strength of concrete and decrease its permeability, at the same cement replacement level [3,6,10]. However, recent tendency to use natural pozzolans because of lower cost and accessibility have been led to use natural zeolite, one of the most common natural pozzolanic material [11].

Natural zeolite is a crystalline mineral that contains silicon and aluminum oxide. Similar to other pozzolans, natural zeolite produces C–S–H gel through pozzolanic activity. Natural zeolite as cement replacement of 5–30% can lead to concrete with a lower permeability and higher compressive strength. However, natural zeolite is not as effective as silica fume in decreasing chloride ion diffusivity or increasing compressive strength [11,12].

The addition of pozzolans to concrete reduces the chloride diffusion coefficient, but it is reported that partial replacement of cement by pozzolans reduces the alkalinity of the pore solution mainly due to pozzolanic reactions and then reduces chloride binding capacity and chloride threshold value of steel corrosion in concrete. But most of researchers observed that the addition of the pozzolans especially silica fume leads to improvements in the corrosion-resisting performance of reinforced concrete [7].

Exposure condition of concrete affects greatly on chloride diffusion coefficient. Studies showed that tidal zone and splash zone are the most severe conditions in the case of chloride ingress and steel corrosion in concrete, in comparison to atmosphere and immerged zone [3,13].

When the durability is considered, long-term measurements can be more valuable than short-term ones, and they provide better estimations of long-term performance of concrete structures. These estimations are necessary for chloride ingress modeling in concrete.

In this study, long-term in situ observations are presented to investigate the effect of the different w/b ratios and pozzolan replacement on chloride ion penetration under laboratory tests and tidal exposure in the field conditions. For this purpose, plain concrete specimens with different w/c ratios (0.35, 0.40, 0.45 and 0.50) were molded. In addition, concrete specimens containing silica fume, metakaolin and natural zeolite with cement replacement levels of 5%, 5% and 10%, respectively, with a constant w/b ratio of 0.40 were prepared under laboratory and tidal exposure in the field conditions, and the chloride ingress of all the specimens were examined.

**Table 1**
Composition of cement, silica fume, metakaolin and natural zeolite (%).

| | Cement | Silica fume | Metakaolin | Natural zeolite |
|---|---|---|---|---|
| $SiO_2$ | 21 | 93.16 | 51.58 | 67.79 |
| $Al_2O_3$ | 5 | 1.13 | 43.87 | 13.66 |
| $Fe_2O_3$ | 3.5 | 0.72 | 0.99 | 1.44 |
| CaO | 63 | N/A | 0.2 | 1.68 |
| MgO | 1.8 | 1.6 | 0.18 | 1.20 |
| $Na_2O$ | 0.5 | N/A | 0.01 | 2.04 |
| $K_2O$ | 0.6 | N/A | 0.12 | 1.42 |
| $SO_3^{2-}$ | 1.6 | 0.05 | N/A | 0.50 |
| Loss on ignition | 2 | 1.58 | 0.57 | 10.32 |

## 2. Experimental investigations

### 2.1. Materials

The cementitious materials used include Type II Portland cement, silica fume, metakaolin and the natural zeolite. The chemical and physical properties of the cement and other pozzolanic materials are listed in Table 1. Crushed limestone with maximum size of 19 mm was used as the coarse aggregate (62%), and the fine aggregate (38%). In addition, polycarboxylate-based superplasticizer was used to achieve the desired workability.

### 2.2. Mixture proportions

Mix designs contain four ordinary concretes with w/c ratios of 0.35, 0.40, 0.45 and 0.50, and three other ones with 5% silica fume (SF), 5% metakaolin (MK) and 10% natural zeolite (ZE) as cement replacement and all with the constant w/b ratio of 0.4. Table 2 lists the mix proportions details.

### 2.3. Specimens & exposure conditions

To determine the chloride penetration profile, two sets of specimens were considered. For laboratory specimens (compressive

**Table 2**
Concrete mixtures details.

| Code | w/b | Water ($kg/m^3$) | Binder, ($kg/m^3$) | | | | Superplasticizer ($kg/m^3$) | Slump (cm) | $c_i$ (%) |
|---|---|---|---|---|---|---|---|---|---|
| | | | PC | SF | MK | ZE | | | |
| C1 | 0.35 | 140 | 400 | – | – | – | 0.35 | 8 | 0.015 |
| C2 | 0.40 | 160 | 400 | – | – | – | 0.2 | 7 | 0.015 |
| C3 | 0.45 | 180 | 400 | – | – | – | 0.1 | 15 | 0.015 |
| C4 | 0.50 | 200 | 400 | – | – | – | 0 | 18 | 0.015 |
| SF5 | 0.40 | 160 | 380 | 20 | – | – | 1.2 | 6 | 0.01 |
| MK5 | 0.40 | 160 | 380 | – | 20 | – | 0.8 | 5 | 0.01 |
| ZE10 | 0.40 | 160 | 360 | – | – | 40 | 4 | 6 | 0.015 |

w/b is water-binder ratio, PC is Portland cement, SF is silica fume, MK is metakaolin, ZE is natural zeolite and $c_i$ is initial chloride content.