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In situ study of chloride ingress in concretes containing natural zeolite, metakaolin and silica fume exposed to various exposure conditions in a harsh marine environment

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HIGHLIGHTS

- It is concluded that splash zones affect concrete structures more harshly than tidal zones.
- Natural zeolite performed as well as metakaolin and silica fume in terms of improving the durability of concrete.
- The use of pozzolans to have more durable concrete is more efficient than reducing w/c ratio.

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ABSTRACT

The Persian Gulf is well known as one of the most aggressive environments in the world because of its high relative humidity, temperature and concentration of chloride ions. Therefore, studying the deterioration processes, such as the chloride ion penetration process, that lead to severe reinforcement corrosion in aggressive environments is necessary. To improve the durability and serviceability of concrete structures in such environments, several investigations have been conducted that address the addition of silica fume and metakaolin, while less attention has been given to the newly introduced pozzolan called natural zeolite. In this paper, the performance of concretes containing natural zeolite, metakaolin and silica fume and that of concretes with different water-to-binder ratios under various exposure conditions in terms of chloride ion diffusivity were investigated. To achieve this objective, concrete specimens with water-to-binder ratios (w/b) of 0.35, 0.40, 0.45 and 0.50 were fabricated. In addition, to examine the performance of three different pozzolans, other specimens with constant water-to-binder ratios of 0.40 containing 10% natural zeolite, 5% metakaolin and 5% silica fume were prepared. All of the specimens were subjected to four exposure conditions (tidal, splash, atmosphere and soil). The results were obtained from a field exposure site and indicate that natural zeolite exhibits good performance in terms of improving the durability of concrete in harsh environments. In addition, it is concluded that splash zones affect concrete structures more harshly than tidal zones.

1. Introduction

The deterioration of concrete structures due to reinforcement corrosion has become a major problem in marine environments such as the Persian Gulf. One of the distinct characteristics of the Persian Gulf that leads to it having a higher concentration of salt than any other sea waters in the world is its closed nature [1]. Due to this and other characteristics, concrete structures in this specific region are more vulnerable to deterioration, premature failure and reduced service life.

Investigators have claimed that reinforcement corrosion is the main reason for such deterioration and reduction of concrete's durability and serviceability [2,3]. Several studies have indicated that lowering the w/b ratio and adding different types of pozzolanic materials to the mix can improve the compressive strength, durability and permeability of concrete. Lowering the w/b ratio reduces the porosity, which thereby reduces chloride ingress during the exposure period by as much as 25% [4–8]. Moreover, pozzolanic materials are being used widely as mineral admixtures to enhance the mechanical properties of concrete and thereby improve the concrete's microstructure. These admixtures, either natural or artificial, reduce the $Ca(OH)_2$ content produced during the cement hydration process and instead form C–S–H gel through the secondary reactions. This process retards the hydration process, significantly reducing the porosity and permeability of the concrete [9–12].

Among the mineral admixtures used for this purpose, silica fume (SF) and metakaolin (MK) have been observed to noticeably

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reduce chloride ingress into concrete in marine environments [11–13]. The effect of SF on concrete microstructure is well reported in the literature. SF is an artificial pozzolan that increases the compressive strength of concrete by strengthening the transition zone and increasing the rate of hydration early in the life of the concrete [12,14]. MK is a silica-based, active pozzolan that improves the mechanical properties of concrete in both the short and long terms [15–20]. In this context, the prefix *meta* refers to the calcination of kaolinite at certain temperatures and the production of MK [21,22]. According to some research studies, applying 10% MK replacement to cement with a w/b ratio of 0.3 yields a higher compressive strength and lower chloride permeability than that of SF [23,24]. In addition, the rate of the pozzolanic reaction of MK is higher than that of SF early in the life of the concrete [21,24]. Reducing the w/c ratio by 10% and adding 5% SF may reduce the chloride diffusion by a factor of up to 10, as indicated by Sandberg et al. [25].

However, another admixture is available that has not received sufficient attention, and certain aspects of its ability to improve the performance of concrete in aggressive environments remain almost unknown. Natural zeolite(NZ) is a crystalline mineral that contains silicon and aluminum oxide; similar to other mineral admixtures, natural zeolite produces more C–S–H gel through pozzolanic activity [26,27]. Zeolite replacement of 5–20% can lead to the production of high-quality concrete with a lower chloride ion diffusivity coefficient, water absorption and permeability; however, using a superplasticizer to achieve the required workability is necessary [28]. According to research conducted by Poon et al., porosity reduction is only possible with a limited amount of zeolite replacement, which is reported to be approximately 15% [29]. However, zeolite is not as effective as SF in decreasing chloride ion diffusivity or increasing compressive strength and initial surface absorption[29,30]; its performance improves slightly when used with a low w/b ratio and is comparable to or better than that of fly ash [15–20]. When concrete is affected by an alkali-aggregate reaction that causes an expansion, zeolite can be advantageous in improving the durability of concrete structures [27,31,32].

The effect of chloride diffusivity on multi-zone concrete structures in marine environments differs from one exposure condition to another. Among all the exposure conditions, tidal and splash zones have been reported to be the most severe conditions in terms of durability [33]. Due to the wetting and drying cycles and subsequent evaporation, splash and tidal zones tend to have the highest chloride content, while atmospheric zones undergo the least deterioration due to the low chloride penetration [8,33].

In this research, in situ studies were initiated to investigate the effect of different w/b ratios and pozzolan replacement percentages on chloride ion penetration under various exposure conditions (tidal, splash, atmospheric and soil). For this purpose, plain concrete specimens with different w/c ratios (0.35, 0.40, 0.45 and 0.50) were produced. In addition, concrete specimens containing zeolite, MK and SF with replacement levels of 10%, 5% and 5%, respectively, under various exposure conditions with a constant w/b ratio of 0.40 were prepared, and the chloride permeabilities of all the specimens were examined at a field exposure site. These replacement percentages were selected based on previous research results [28].

2. Experimental program

2.1. Materials

Type II Portland cement was used throughout the investigations. The chemical and physical properties of the cement and other pozzolanic materials are listed in Table 1. To achieve more consistency, materials were selected from the field. Crushed limestone with a maximum grain size of 19 mm was used as a coarse aggregate (62%), and the fine aggregate (38%) was river sand. In addition, to achieve the desired workability, the use of a polycarboxylate-based superplasticizer was necessary.

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

	Cement	Silica fume	Metakaolin	Zeolite
Silicon dioxide (SiO_2)	21	93.16	51.58	67.79
Aluminum oxide (Al_2O_3)	5	1.13	43.87	13.66
Ferric oxide (Fe_2O_3)	3.5	0.72	0.99	1.44
Calcium oxide (CaO)	63	–	0.2	1.68
Magnesium oxide (MgO)	1.8	1.6	0.18	1.2
Sodium oxide (Na_2O)	0.5	–	0.01	2.04
Potassium oxide (K_2O)	0.6	–	0.12	1.42
Sulfur trioxide (SO_3)	1.6	0.05	–	0.5
Loss on ignition	2	1.58	0.57	10.32

2.2. Mixture proportions

Seven mix designs – four plain concretes with different w/c ratios of 0.35, 0.40, 0.45 and 0.50 (without pozzolans) and three with 5% SF, 5% MK and 10% NZ cement replacement with constant w/b ratio of 0.4 – were investigated. Table 2 lists the mix proportion details.

2.3. Specimen preparation, casting and curing

To determine the chloride penetration, $150 \times 150 \times 600\ mm^3$ concrete prisms were prepared, and to analyze the compressive strength, $150 \times 150 \times 150\ mm^3$ concrete cubes were prepared. The specimens were compacted on a vibrating table, and after being demolded, the specimens were moist-cured for 2 days. Then, the specimens that were subjected to tidal and splash zones were sealed on five sides using epoxy coating; for the specimens subjected to soil and atmosphere zones, only four sides were coated, leaving the top and bottom sides uncoated, as illustrated in Fig. 1.

2.4. Exposure conditions

Table 3 provides the mean monthly temperature and relative humidity of Qeshm Island (located in Persian Gulf). The specimens were exposed to four different exposure conditions, including tidal, splash, atmosphere and soil conditions, on Qeshm Island (Fig. 2). The location of the specimens in the tidal zone was selected such that the total time required for the specimens to undergo the wetting and drying cycles was equal. In other words, the specimens were fully submerged at the half time exposure. For further protection against sea waves, the samples were placed inside latticed plastic boxes with the uncoated side facing up. In the splash zone, the specimens were placed at a higher elevation than in the tidal zone to prevent immersion during the exposure period; thus, only sea water drops sprayed the concrete surface. For the soil and atmospheric zones, the specimens were uncoated on both the bottom and top sides of the concrete, with the intention of evaluating the chloride ion penetration at the bottom from the soil and at the top from the atmosphere. The specimens were placed far enough from the sea to avoid exposure to any sea water drops.

2.5. Sampling and testing

The total chloride concentration profiles were analyzed after nine months of exposure in the Persian Gulf. Powder samples were obtained from the concrete specimens at 9 different depths with an accuracy of 0.5 mm. The powder samples at the first 1 mm were discarded. At each depth, 10-g samples were analyzed separately to determine their acid-soluble chloride content according to ASTM C 114, part 19 [34]. The chloride concentrations at different depths were determined using the method presented in [14].

Table 2
Details of the concrete mixtures.

Code	w/b	Water (kg/m^3)	Binder (kg/m^3)				Superplasticizer (kg/m^3)	Slump (cm)
			Cement	SF	MK	NZ		
C1	0.35	140	400	–	–	–	0.35	8
C2	0.40	140	400	–	–	–	0.2	7
C3	0.45	140	400	–	–	–	0.1	15
C4	0.50	140	400	–	–	–	0	18
SF5	0.40	140	380	20	–	–	1.2	6
MK5	0.40	160	380	–	20	–	0.8	5
ZE10	0.40	160	360	–	–	40	4	6