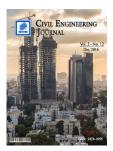


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# Effect of Natural Zeolite-Pozzolan on Compressive Strength of Oil-Polluted Concrete Marine Structures

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#### Abstract

Oil pollution into the concrete composed materials, leads to decrease the compressive strength of the constructed structure. In the present study, effect of using a natural pozzolan named Zeolite on concrete structures was tested in different marine conditions. A fixed amount of oil equal to 2% of sand weight was added as the pollution into the concrete composed materials. Natural Zeolite was added into the concrete instead of cement to the mix design with weight percentages of 10, 15 and 20. After preparing and curing, concrete specimens were placed into the three different conditions: fresh water, tidal, and sea water environments. Results of compressive strength tests showed that replacement of natural Zeolite instead of cement significantly increased compressive strength in comparison with control specimens, in all environments. Adding 20% natural Zeolite increased the compressive strength to its highest values about 60-85% higher than control specimens.

Keywords: Compressive Strength; Tidal and Sea Water Environments; Oil Polluted Sand; Natural Zeolite; Marine Concrete Structures.

#### 1. Introduction

Concrete is one of the most applicable materials in construction projects. Some effective factors on the compressive strength ( $f_c$ ) of concrete are W/C, compaction degree; type of cement, aggregate grade, mixing method, placement, curing method and presence of contaminates [1]. Oil polluted aggregates into the concrete leads to decrease the  $f_c$ . Oil pollution in concrete can be occurred in two major ways: Oil can be penetrated into the concrete as mixed by raw materials (along with fine and coarse aggregates) or in the case of being the oil around the concrete structure, it can penetrate into the pores of the concrete. Reducing the prosity of marine concrete structures is an effective way to increase the life time of the project [2-5]. To improve the mechanical properties and durability of the mortar and concrete, Natural Zeolite (NZ) can be selected as a concrete pozzolan. The important advantages of using on concrete properties, are high  $f_c$ , high tensile, modulus of elasticity, enhanced durability, low permeability to chloride and water intrusion, increasing abrasion resistance, resistance to chemical attacks from chlorides, acids, nitrates and sulfates. The positive effects of NZ on various properties of concrete were presented in several researches such as: Canpolat et al.; Albayrak et al.; Ikotun et al.; Perraki et al.; Ahmadi et al.; Karakurt et al.; Jitchaiyaphum et al.; Ramezanianpour et al. and Trník et al. [6-14].

Ayininual et al. examined the effects of diesel oil and bitumen on  $f_c$  of concrete. They made the concrete specimens, with marine sands with 2, 5 and 10% of diesel oil and bitumen also was used. W/C was assumed fixed. 28-day  $f_c$  of concrete was about 77.4% to 96.8% for diesel oil and for bitumen  $f_c$  was about 26.2% to 76.2% compared to conventional concrete specimens [15]. Al-Jalawi et al. examined the effects of oil and diesel on concrete properties with high efficiency. They observed that petroleum products have an unacceptable effect on the properties of high-performance concretes and found that slump, workability and  $f_c$  of specimens compared to Control Specimen (CS)

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decreases [16]. Ajagbe et al. investigated the effects of sand stained by crude oil on  $f_c$  of concrete specimens. They used oil, in amount of 2.5, 5, 10, 15, 20 and 25% of the weight of the sand. In their study, W/C was fixed. Their results showed that the  $f_c$  of concrete by increasing the percentage of oil reduced from 18% to 90% than the CS [3]. Diab also investigated the  $f_c$  and performance of low and high strength concrete soaked in mineral oil. Results showed a reduction in the  $f_c$  about 12% to 17% in the concrete specimens in the mineral oil compared to the clean potable water condition [1].

Jo et al. investigated material characteristics of Zeolite cement mortar. They observed that Zeolite cement has greater strength than existing normal Portland cement and has great potential to replace current construction materials [17]. Najimi et al. examined durability properties of concrete containing Zeolite as a highly reactive natural pozzolan. They constructed concrete specimens with 15% and 30% of NZ and results were compared with concrete without NZ. The results revealed considerable effectiveness of NZ application on water penetration, chloride ion penetration, corrosion rate and drying shrinkage of concrete. From the practical point of view, the incorporation of 15% NZ was found as an appropriate option for improving strength and durability properties of concrete [18]. Valipour et al. compared a natural pozzolan, Zeolite, metakaolin and silica fume in terms of their effect on the durability characteristics of concrete. In their laboratory study, effects of substituting cement with 10%, 20% and 30% NZ on concrete durability were compared to the effects of substituting 5%, 10% and 15% metakaolin and 5%, 7.5% and 10% silica fume, along with W/C of 0.35, 0.40, 0.45 and 0.50. Results showed that the Zeolite is not as active as silica fume or metakaolin, although it could be used as a substitute for pozzolans because it has better durability characteristics and is economical and environmentally friendly as well [19].

Also, Valipour et al. investigated chloride ingress in concretes containing NZ, metakaolin and silica fume exposed to various exposure conditions in a harsh marine environment. To achieve this objective, concrete specimens with W/B of 0.35, 0.40, 0.45 and 0.50 were fabricated. In addition, specimens with constant W/B of 0.40 containing 10% NZ, 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 NZ exhibits good performance in terms of improving the durability of concrete in harsh environments. Also, they concluded that splash zones affect concrete structures more harshly than tidal zones [20]. Attom et al. conducted an experimental study to assess the  $f_c$  mixed with sand contaminated by crude oil products. Their results showed that  $f_c$  of new concrete specimens decreased more than 42% compared to the control concrete. In mix design, they added oil and diesel to the sand in amount of 0.5%, 1% and 1.5% of the weight of sand, and then fine sand is added into the concrete mixture [4]. Sabet et al. published their findings about mechanical and durability properties of self-consolidating high performance concrete incorporating NZ, silica fume and fly ash. Their results showed that incorporation of mineral admixtures generally improve mechanical and durability characteristics of the mixes. However, silica fume is slightly more effective than NZ or fly ash in improving durability properties of self-consolidating high performance concretes, while NZ is much more cost effective [21].

Ranjbar et al. also investigated the effects of NZ on the fresh and hardened properties of Self-Compacted Concrete (SCC). They observed that SCC mixtures were prepared by inclusion of various amounts of NZ (0-20% by weight of cement) at different W/B. Their results showed that with the inclusion of NZ, SCC can successfully produce with satisfactory performance in flowability, passing ability and viscosity. For all mixtures, flow ability was lost with hauling time, although the rate of slump flow reduction was higher for mixes with higher amount of NZ. According to hardened properties, the effect of NZ on the compressive and splitting tensile Strength of SCC mixtures was generally related to its W/B. Moreover,  $f_c$  enhancement was seen for mixes with slump flow higher than 550 mm at prolonged mixing time. The ultrasonic pulse velocity (UPV) measurement showed that the effect of NZ of the UPV values at a high  $f_c$  is negligible. Compared to control SCC, absorption characteristics of SCC containing NZ significantly decreased with increasing ages [22].

Shahrabadi et al. investigated the effects of oil on the  $f_c$  of concrete in tidal and sea water environmental conditions. Oil percentages used in this study was, 0.5, 1, 2, 4, 6 and 8, respectively. The results represented a reduction about 27% in the  $f_c$  of concrete specimens with 2% oil weight, in all curing conditions. Also, reduced resistance in the sea water environments is more than other environments, but the maximum  $f_c$  occurs in clean potable water. Meanwhile, the maintain condition of clean potable water and immersed in oil, does not affect in the short term (28-day) on the  $f_c$  of normal concrete specimens (0% of oil) [5]. Vejmelkova et al. conducted an experimental study to assess engineering properties of concrete containing NZ as supplementary cementitious material. Their results showed that 20% Zeolite content in the blended binder is the most suitable option. The hydrothermal performance of hardened mixes containing 20% NZ, as assessed using the measured values of water absorption coefficient, water vapor diffusion coefficient, water vapor sorption isotherms, thermal conductivity and specific heat capacity is satisfactory [23].

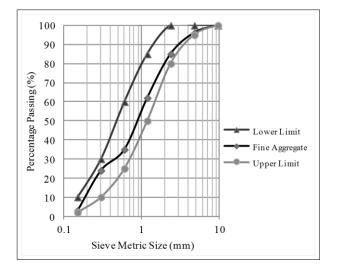
Markiv et al. examined the mechanical and durability properties of concretes incorporating NZ. In their studies, the mechanical and durability properties of concretes containing 10% of NZ and super plasticizer, as well as 10% of NZ, super plasticizer and an air-entraining agent in comparison to concretes without NZ. Their results also reveal the considerable effect of using a super plasticizer and an air-entraining agent in Zeolite incorporating concretes on water penetration, drying shrinkage and freeze-thaw resistance of concretes [24]. Nagrockiene et al. investigated the

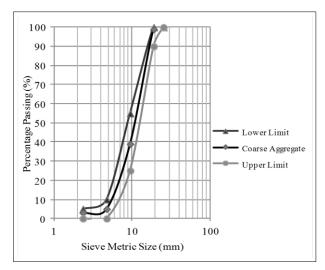
properties of concrete modified with NZ addition. The results showed that Substitution of up to 10% of cement with NZ increases the  $f_c$  of concrete by 15%, reduces water absorption 2.3 times, increases density and ultrasonic pulse velocity. Substitution of up to 10% of cement with NZ increases closed porosity and subsequently improved the freeze-thaw resistance of concrete. The predicted freeze-thaw resistance calculations revealed 3.3 times higher resistance of concrete modified with up to 10% of NZ [25].

In the present experimental research, improvement of  $f_c$  of oil polluted marine concrete structures by adding NZ to the concrete specimens was studied. To do so, the amount of oil in all mix designs was considered about 2% of sand weight. W/C was constant for all specimens and equal to 0.6. NZ was induced as a replaced material, into the concrete mix design by replacing the cement in different percentages. Weight percentages of NZ for three considered mix designs were equal to 10, 15 and 20%. Specimens were cured in three different marine conditions representing fresh water, tidal and sea water environments. To collect required data,  $f_c$  of 3, 7, 14 and 28-day specimens were tested. Based on obtained data from experiments,  $f_c$  were plotted and analyzed in different scenarios.

## 2. Materials and Experimental Methods

Ordinary Portland Cement (OPC) of Type 2 was used in this study which is the most common cement used in fresh water, tidal and sea water [21]. Fresh water used for concreting in mix design. Both the fine and coarse aggregates were air dried to reach the Saturated–Surface–Dry (SSD) condition to ensure that the W/C had not been affected. The particle size distribution of the fine and coarse aggregates which were well graded were shown in Figures 1 and 2, respectively. The sieve analysis of aggregates was performed in accordance with ASTM C136 [26].





#### Figure 1. Particle size distribution curve of fine aggregate



The properties of used oil in this study were summarized in Table 1.

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Tests	Limit	Test Method
Corrosion 3hr @ 100°C	max 1	ASTM D130
Density @ 15°C (Kg/m <sup>3</sup> )	max 820	ASTM D1298
Flash Point (°C)	min 38 °C	ASTM D93
Total Sulphur (wt %)	max 0.15	ASTM D1266

The source of used NZ (Clinoptilolite Type) was the mines, from north of Semnan province in Iran. NZ has a specific gravity of 2.20. The chemical properties of the NZ and used cement are shown in Table 2.

Material	$SiO_2$	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>
Cement (Type II)	20.68	13.18	4.32	64.14	2.38	2.06	0.42	0.56	
Natural Zeolite	69.28	10.43	0.49	3.56	0.50		0.73	1.27	0.17

Table 2. Chemical compositions of binders (% by mass)

As presented in Table 2, the total Content of  $Sio_2$ ,  $Al_2O_3$  and  $Fe_2O_3$  in the Zeolite were found to be approximately 80% more than the minimum requirement (70%) in ASTM C618 [27] for natural pozzolans.

#### 3. Mix Design and Preparation of Specimens

The proportion design was conducted according to the ACI guide lines [28]. To produce Oil Polluted Sand (OPS), Fresh uncontaminated sand was contaminated with 2% oil (by weight). Resulted OPS was air-dried for about five days to allow proper reaction of the mixture and simulate the oil spill environment [5]. Used NZ in the mix design was 10, 15 and 20% by weight of cement. To compare the effects of added NZ on the mix design of concrete, non- NZ specimens were also prepared. Dimensions of cube specimens were selected as  $150 \times 150 \times 150 \times 150$  mm. Details of various mixing plans of the concrete specimens and compressive test condition were shown in Table 3.

		Tubi	с <b>С</b> . типл	proporti	on and compressiv	ve test condition			
Materials (kg/m <sup>3</sup> concrete)									
		Cement Water		Cement	Water	Aggregate Oil Natural Zeolite	er Agg	Natural Zeolite	
Specimen Name			Fine	Coarse	(2% by weight of fine aggregate)	(by weight of cement)			
CS (0% NZ)	315	190	840	1030	16.8	0			
A (10% NZ)	315	190	840	1030	16.8	31.5			
B (15% NZ)	315	190	840	1030	16.8	47.25			
C (20% NZ)	315	190	840	1030	16.8	63			

Table 3. Mix proportion and compressive test condition

Where CS specimens are considered CS without NZ; *A*, *B* and *C* were specimens which had NZ with 10, 15 and 20% by weight of cement, respectively. It should be noted that in this research the NZ had been substituted with equal amount of cement to make the results more reliable and practical.

Studied environments to maintenance the specimens in this research include Fresh Water, Tide and Submerged in water of India Ocean (Figures 3-5).

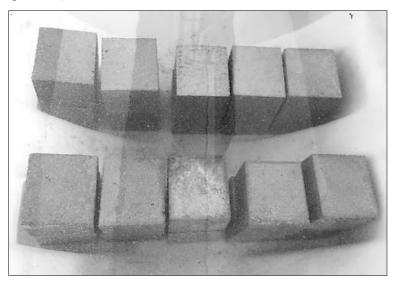


Figure 3. Specimens in Fresh Water (FW) environment



Figure 4. Specimens in Tide of India Ocean (TIDAL) environment

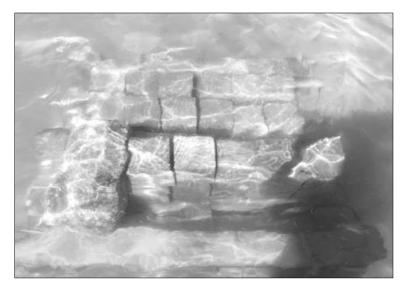
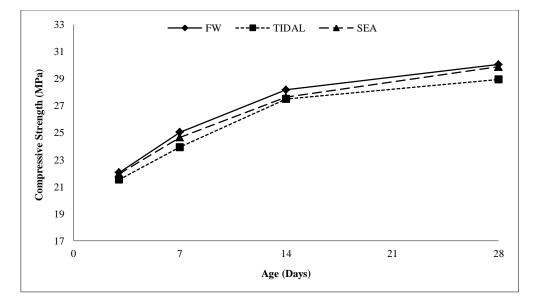


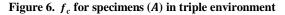
Figure 5. Specimens in Water of India Ocean (SEA) environment

Compressive strength tests on 3, 7, 14 and 28-day, are done for all three specimens in the triple environments. In this research, totally 144 different specimens (according to the Table 3) were prepared and tested. In all experiments, three cube specimens were tested for  $f_c$  at the age of 3, 7, 14 and 28-day, according to ASTM guideline [29]. Using the specified mix designs, concrete specimens were made and after the initial curing, each of the specimens was transferred to the desired preservation environments (Fresh water, tidal and sea water).

#### 4. Results and Discussions

According to the specified time table, concrete specimens were broken under increasing compressive loads at a constant speed equal to 675 (kgf/s) according to the ASTM C39. In Figures 6-9.  $f_c$  curves were drawn for A, B and C concrete specimens in fresh water, tidal and sea environments by age of them.





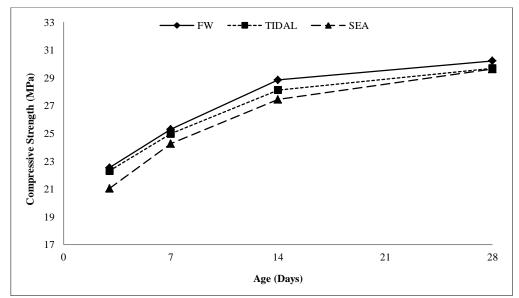


Figure 7.  $f_c$  for specimens (B) in triple environment

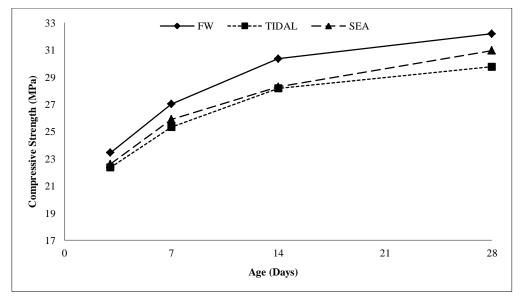


Figure 8.  $f_c$  for specimens (C) in triple environment

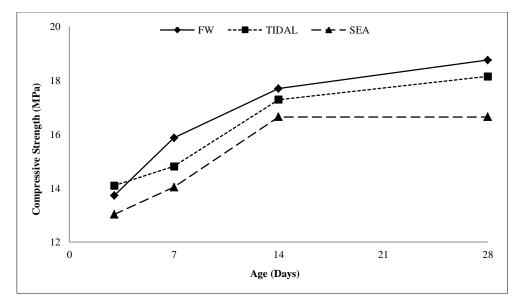


Figure 9.  $f_c$  for specimens (CS) in triple environment

Based on Figures 6 to 9, it was indicated that in all days, the highest  $f_c$  of specimens was observed in fresh water environment. However, for specimens A and C, the minimum  $f_c$  was observed in the tidal environment and for specimens B,  $f_c$  in sea water environment. In terms of maximum  $f_c$ , CS was almost similar to those mixed with NZ (specimens B) and the maximum  $f_c$  of CS was occurred in the fresh water environment. However, the minimum  $f_c$  for CS was observed in the sea water environment that was not equal to the results of NZ-containing specimens  $f_c$ .

3-day  $f_c$  of specimens in fresh water and tidal environment were higher than specimens in sea water environment. However, the results of  $f_c$  of specimens in first days (3-day) in tidal and sea water conditions were closer to each other. For specimens in 7, 14, 28-day,  $f_c$  of specimens in fresh water environment were more than two other environments. However, the minimum  $f_c$  was observed in 7 and 28-day specimens in tidal environment and in 14-day in sea water environment. The  $f_c$  of concrete specimens were equal in 7 and 14-day for tidal and sea water environments. Along the time,  $f_c$  of specimens in tidal environment was decreased rather than other specimens and conditions. So that, in 28day,  $f_c$  of specimens in tidal environment was smaller than other specimens.

Due to constant amounts of NZ, it can be found that the most important factors in reduction of  $f_c$  in tidal environment compared to the other ones were wetting, drying and erosion caused by the collision of sea waves.

In Figures 10-13,  $f_c$  in 3, 7, 14 and 28-day in different environments and NZ were drawn.

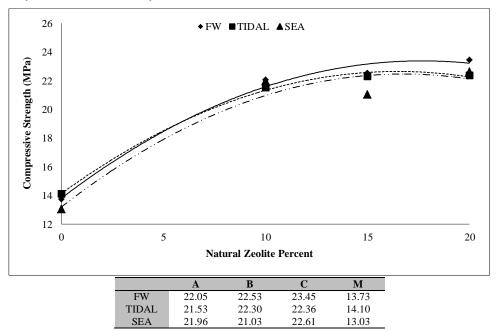


Figure 10. f<sub>c</sub> (3-day) in triple environment

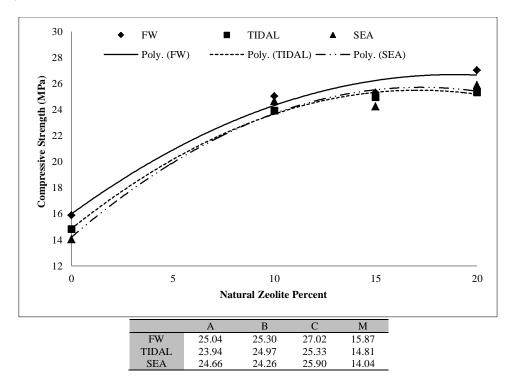


Figure 11.  $f_c$  (7-day) in triple environment

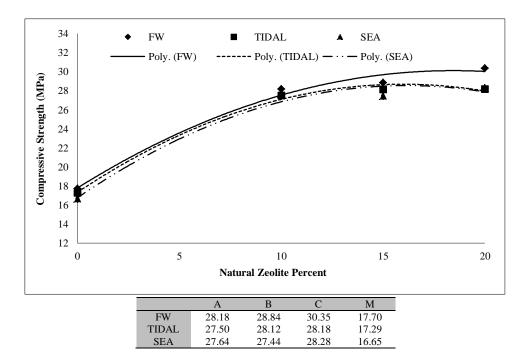


Figure 12.  $f_c$  (14-day) in triple environment

(1)

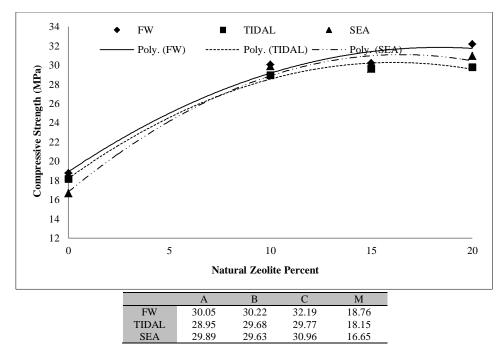


Figure 13.  $f_c$  (28-day) in triple environment

The maximum  $f_c$  in different environments was for specimens containing 20% NZ. In fresh water and tidal environments, specimens with 15% and 10% NZ were ranked next but in sea water environment, specimens with 10% and 15% NZ were ranked next. The minimum  $f_c$  was observed in CS without NZ.

With over 144 set tests of  $f_c$  for the variables E (Different Environments), NZ (Percent of natural Zeolite) and D (Days of concrete age), an equation was developed for  $f_c$  with a correlation factor of about 0.972 as:

$$f_c = 12.113E^{-0.039}(NZ+1)^{0.177}D^{0.137}$$

Where, E = 1, 2 and 3 for FW, SEA and TIDAL conditions, respectively. If NZ = 0 (without using NZ in mix design), therefore, an ordinary concrete strength will be concluded.

Figures 14-16, show the  $f_c$  in different environmental conditions.

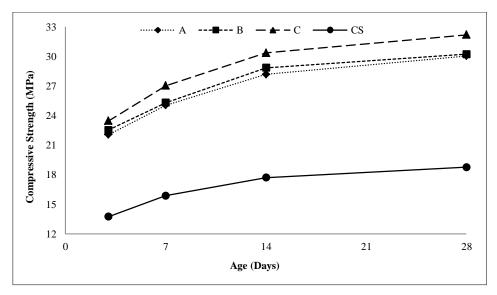


Figure 14. f<sub>c</sub> in Fresh Water (FW) environment

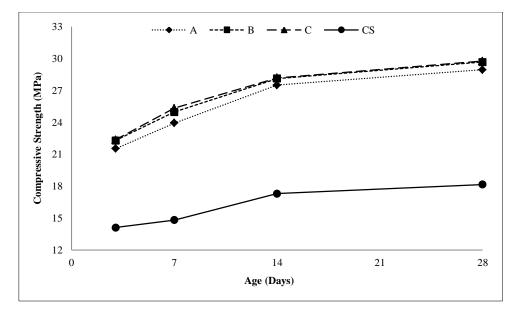


Figure 15.  $f_c$  in TIDAL environment

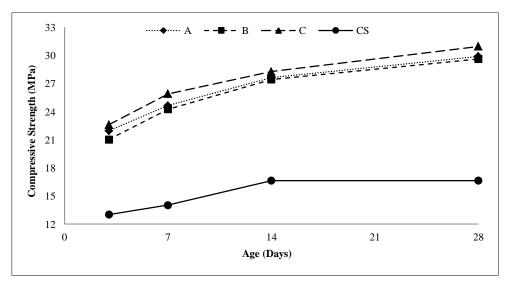


Figure 16.  $f_c$  in SEA environment

In Figures 17-19, increment percent in  $f_c$  in comparison with *CS* had calculated for different ages and environments. According to Figure 17, in fresh water, the maximum percent of increasing in  $f_c$  was happened for specimens *C* in 28-day in comparison with *CS* in most of ages about 72%. Moreover, the minimum percent of increasing in  $f_c$  was happened for specimens *A* in 7-day about 58%. On average, in different ages,  $f_c$  increased about 71% in fresh water environment. In tidal environment (Figure 18), the maximum percent of increasing in  $f_c$  was happened for specimens *C* (in 7-day about 71%. However, the minimum percent of increasing in  $f_c$  was happened for specimens *A* in 3-day about 53%. In this environment, percent of  $f_c$  increased considerably about 64%, on average.

In sea water environment, the maximum percent of  $f_c$  increment was related to specimens *C* about 86% for 28-day. However, the minimum percent of increasing in  $f_c$  was happened for specimens *B* in 3-day about 61%. Overall, in different ages,  $f_c$  increased about 78% in sea water environment.

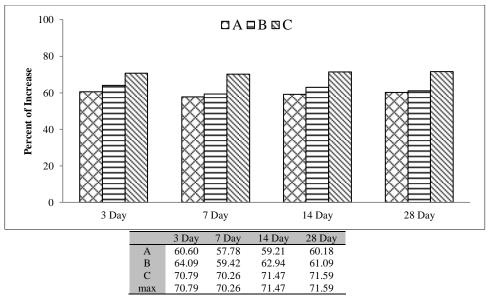


Figure 17. Percent of increasing  $f_c$  to CS in FW

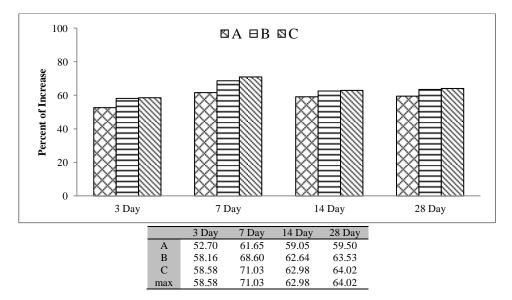


Figure 18. Percent of increasing  $f_c$  to CS in Tidal

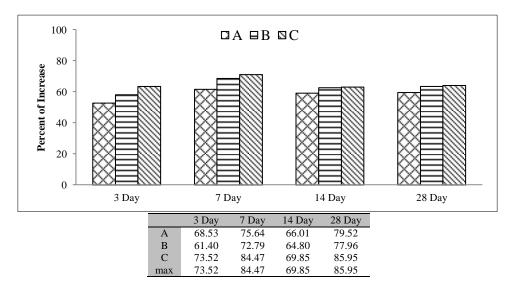


Figure 19. Percent of increasing  $f_c$  to CS in SEA

Figure 20 compares the 28-day  $f_c$  of NZ-containing specimens and CS in different environments. According to this figure, in all three environments, the highest increment in  $f_c$  compared to the CS was observed in specimens C (in sea water environment) which was equal to 86%. The minimum increment in  $f_c$  was observed in specimens A in tidal environment (about 60% increment).

According to Figure 20, there was at least 60-85% increment in the strength of all specimens made with NZ - containing mix design.

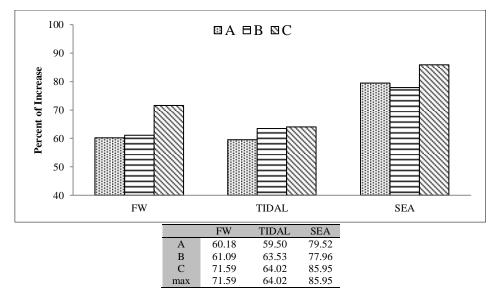


Figure 20. Percent of increasing  $f_c$  to CS for 28-day in triple environments

In reviewing the results, it had been found that the maximum effect of adding NZ to the oil polluted concrete on  $f_c$  was happened for specimens *C* (with 20% NZ) in all environments. Results of this study show that adding NZ to the mix design of polluted concrete to the oil was caused a very significant increment in the  $f_c$  of concrete specimens in all studied environmental conditions. Moreover, the failure mode of the tested specimens as observed due to the experimental time was fitted on the Type 3 regarding to the ASTM C39.

#### 5. Conclusion

According to the experimental results and analyzing data, the most important obtained results were as follows:

- Among various specimens in different conditions, the maximum  $f_c$  was observed in fresh water environment and the minimum  $f_c$  was observed in tidal and sea water environments.
- In the majority of specimens, the maximum  $f_c$  in 3, 7, 14 and 28-day, was observed in fresh water environment and the minimum value was observed in tidal or sea water environment.
- In fresh water, tidal and sea water environments, the maximum  $f_c$  was observed in specimens containing 20% NZ (specimens *C*), followed by 15% (specimens *B*) and 10% (specimens *A*) NZ:
  - ✓ In fresh water environment:  $f_c C > f_c B > f_c A$
  - ✓ In tidal environment:  $f_c C > f_c B > f_c A$
  - ✓ In sea water environment:  $f_c C > f_c A > f_c B$
- For all studied environments, adding different values of NZ to the polluted sands with oil increased their  $f_c$  at least 60-85% more than CS. The highest increment in strength for 28-day (about 86%) was observed in sea water environment and for specimens C (20% NZ). The minimum increment in strength for 28-day (about 60%) was observed in tidal water environment and for specimens A (10% NZ).
- Although adding oil as much as 2% of sand weight to the concrete specimens led to about 20 to 30% reduction in  $f_c$  in different environments, adding NZ at least as much as 10% of cement weight can eliminate this problem in different environmental conditions. As a result, for improving  $f_c$  of concrete specimens, adding NZ as much as 20% of cement weight to the mix design can be considered as the best recommendation.

#### 6. Acknowledgement

The authors gratefully acknowledge the Department of Civil Engineering, Chabahar Maritime University for their kindly cooperation.

## 7. Notation

The following symbols are used in this paper:

$f_c$	Concrete Compressive Strength	W/C	Water/Cement ratio
W/B	Water/Binders ratio	FA	Fine Aggregates
CA	Coarse Aggregates	FW	Fresh Water
ОРС	Ordinary Portland cement	OPS	Oil Polluted Sand
SCC	Self-Compacted Concrete	NZ	Natural Zeolite
CS	Control Specimen	Ε	Environmental Condition
D	Days of concrete age		

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