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RESEARCH PAPER

Microstructural Investigation of Compressive Strength and Permeability of Concrete Containing Fly Ash in the Marine Environment of the Persian Gulf

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ABSTRACT: Investigating the impact of fly ash on concrete strength and durability in the challenging marine environment of the Persian Gulf is crucial due to sulfate attacks and salt effects. This study aims to enhance the lifespan of these structures by increasing strength and reducing permeability. The innovative approach involves microstructural assessment of fly ash's influence on Calcium Hydroxide (CH) and C-S-H nanostructure formation in concrete. Around 120 concrete samples with varying fly ash content were exposed to the Persian Gulf for three months, undergoing compressive strength, permeability, and microstructural analysis. Results reveal fly ash addition decreases permeability and boosts concrete strength. Notably, concrete containing 10% fly ash exhibited a 15.4% strength increase and reduced permeability from 22.4×10^{-7} cm/h to 8.98×10^{-7} cm/h after 90 days. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) analysis showcased CH reduction and enhanced C-S-H nanostructure, bolstering concrete durability. This study offers valuable insights for engineers constructing coastal Persian Gulf structures, indicating fly ash augmentation enhances microstructural properties, reduces permeability, and bolsters strength.

Keywords: Concrete, Fly Ash, Marine Environment, Permeability, Compressive Strength, Microstructure, Sulfate Attack, Calcium Hydroxide (CH), Pozzolanic Materials, SEM.

1. Introduction

The production of cement involves high-temperature calcination, which leads to the release of 5-8% CO_2 emissions (Afroz et al., 2023; Chaudhury et al., 2023). In light of environmental concerns and the adverse impacts of cement misuse on nature, the use of recycled materials in concrete or mortar has become more prevalent (Modarres and Ghalehnovi, 2023). Inorganic alum inosilicate materials (Abhishek et al., 2022) can be utilized in various chemical processes (Pan et al., 2014) to transform different industrial wastes, such as iron smelting furnace slag, fly ash, fuel ash, rice husk ash, met kaolin, natural pozzolans and any source containing amorphous alum

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inosilicates (Wang et al., 1995), into construction materials (Amiri and Tanide., 2020; Xu et al., 2014). The incorporation of industrial waste as a cement substitute in concrete not only helps to mitigate environmental pollution and address waste disposal issues, but also enhances concrete properties, leading to increased compressive (Jindal and RN, 2022).

Therefore, reducing the permeability of concrete is crucial for improving its durability and lifespan, especially in harsh environments such as coastal regions where concrete structures are exposed to saltwater and sulfate attacks. The addition of fly ash to concrete has been shown to be an effective method for reducing permeability and increasing durability, making it a viable solution for enhancing the performance of concrete structures in such environments (Junior et al., 2021). Chlorides can also cause the loss of bond strength between steel reinforcement and concrete (Amiri and Tanide., 2020), which further weakens the concrete structure.

Therefore, reducing the permeability of concrete is essential to improve its durability and increase its service life in chloride-rich environments (Rezaei et al., 2022). Moreover, the use of fly ash as a pozzolanic material in concrete has been reported to reduce the risk of Alkali-Silica Reaction (ASR) in concrete structures, which can lead to cracking and reduced durability (Taylor, 1997). ASR occurs when aggregates containing reactive silica come into contact with the highly alkaline environment of concrete, leading to the formation of an expansive gel that causes cracking and damage to the concrete (Mehta et al., 2014). Fly ash, when used as a partial replacement for cement, reduces the amount of reactive silica available in the concrete, thereby reducing the risk of ASR (Rigi and Ziaei, 2022).

Sulfate attacks on concrete structures in marine environments can cause extensive damage and decrease the strength and durability of the structure. The sulfate ions penetrate the concrete pores, resulting in chemical reactions that lead to cracking, expansion, and energy loss (Amiri and Tanide., 2020). This can eventually result in the failure of the structure, posing a threat to the safety of people and property. Therefore, it is important to study the effects of sulfate ions on concrete and find ways to improve the durability and strength of concrete in these harsh environments.

Concrete containing fly ash as a partial replacement for cement has shown significant improvement in its resistance to sulfate and chloride ions compared to concrete containing only ordinary Portland cement (Taylor, 1997). The presence of fly ash in the concrete mixture results in a denser pore structure, which reduces the permeability of the concrete and, consequently, limits the penetration of aggressive ions into the concrete (Mehta et al., 2014; Rigi and Ziaei, 2022).

Fly ash also has a pozzolanic reaction with the cement hydration products, which results in the formation of additional C-S-H nanostructure (Kang et al., 2019). The formation of C-S-H nanostructure in fly ash concrete can lead to increased strength and durability (Glosser et al., 2019; Jindal and RN, 2022). Additionally, the use of fly ash in concrete mixtures can also help to reduce the heat of hydration and improve the workability of the mixture (Behl et al., 2022; ACI Committee, 2005). It should be noted that the harmful effects of ettringite on the strength and durability of concrete are more pronounced in corrosive chloride and acidic environments (Mehta et al., 2014). Ettringite is formed in a needle-like shape after the reaction of tricalcium silicate, tricalcium aluminate (C_3A) and its formation is accompanied by the development of a nanostructure of C-S-H and Calcium Hydroxide $Ca(OH)_2$ during the hydration process (Taylor, 1997). The density of the C-S-H nanostructure is directly related to the strength of the concrete. However, the increase in the ettringite structure has been found to decrease the strength and durability of the concrete. Fly ash has a significant impact on the microstructure of concrete, particularly on the pore size distribution and shape. This results in the formation of more C-S-H bonds, which improves the strength and durability of concrete. High-calcium fly ash types are more reactive than low-calcium ones, as they contain crystallized reactive compounds such as C_3A and CS. The presence of C_3A in fly ash is beneficial because it reacts with chlorides and forms calcium aluminate chloride (Friedel's Salt), which enhances the chloride binding capacity of the cement system and delays the onset of corrosion.

The amount of Friedel and Kozel salts formed due to the inclusion of fly ash increases the amount of bound chlorides in the system, thereby reducing the amount of free chlorides and the risk of corrosion of steel reinforcement (Ortiz-Salcedo et al., 2022; Saffari and Firuzi, 2011). In addition to reducing the risk of corrosion, the use of fly ash in concrete can also improve its strength and reduce its permeability. Fly ash particles can fill in the gaps and voids in the concrete matrix, resulting in a denser and more compact structure. This, in turn, can reduce the permeability of concrete, making it more resistant to the penetration of aggressive agents such as water, sulfate and chloride ions (Khankhaje et al., 2023; Supit and Shaikh., 2015; Thomas and Matthews, 1992). Furthermore, fly ash is a sustainable alternative to traditional cement, as it is a waste product that would otherwise be sent to landfills. By using fly ash in concrete, the amount of cement required can be reduced, thereby reducing the carbon footprint of the construction industry (Rigi and Ziaei, 2022).

The use of natural pozzolans as a replacement for cement is a popular and cost-effective solution, as it can reduce concrete heat generation, lower permeability, and increase chemical resistance, which can improve the durability of the concrete mixture. When fly ash is added to concrete, pozzolanic reactions occur, leading to a reduction in permeability and increased durability in sulfate and chloride environments.

The reaction of fly ash plays a key role in determining the durability of the concrete mixture, influencing parameters such as the amount of CH, type and amount of C-S-H, and pH of the pore solution. In this study, the effect of adding different percentages of fly ash as a substitute for part of cement on the microstructural level of concrete durability and strength in the marine environment of the Persian Gulf was evaluated, with a focus on changes in the amount of CH and C-S-H.

The samples were naturally preserved in the sea of the Persian Gulf, and the study's innovative aspect lies in its detailed microstructural investigation of the compressive strength and permeability of concrete containing fly ash in the harsh marine environment. The results of this study can provide valuable insights into the development of durable concrete mixtures suitable for marine environments.

2. Materials and Methods

An innovative approach was taken to investigate the compressive strength and permeability of concrete containing fly ash in the aggressive marine environment of the Persian Gulf. Ordinary Type II Portland cement, obtained from Hormozgan Cement Company in Bandar Khamir, and fly ash produced at the Bandar Abbas power plant were used to prepare the concrete samples.

The tests were conducted in accordance with ASTM standards. The chemical analysis of the ordinary Portland cement Type II and fly ash Class F (ASTM, 2018) were performed through X-Ray Fluorescence (XRF) analysis, and the results are presented in Table 1. Additionally, some characteristics of the Persian Gulf seawater are provided in Table 2. It is noteworthy that any environment with a PH lower than 12.5 can be aggressive, and acidic ions such as SO_4^{-2} and Cl present in seawater can often lower the PH.

Table 1. Chemical characteristics of Portland cement Ttype II and fly ash

Materials	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	Na_2O	SO_3	L.O.I
Cement II	22.00	5.30	4.00	65.00	0.70	0.50	2.50	2.50
Fly ash	56.70	28.20	5.30	2.80	1.73	0.78	0.68	3.70

Table 2. Characteristics of seawater in the Persian Gulf

Properties	pH	SO_4^{-2}(mg/L)	Cl(mg/L)	NaCl	TDS (g/L)	Ec (mS/cm)
Persian golf	7.9	2541	23491.77	3.5%	39	59

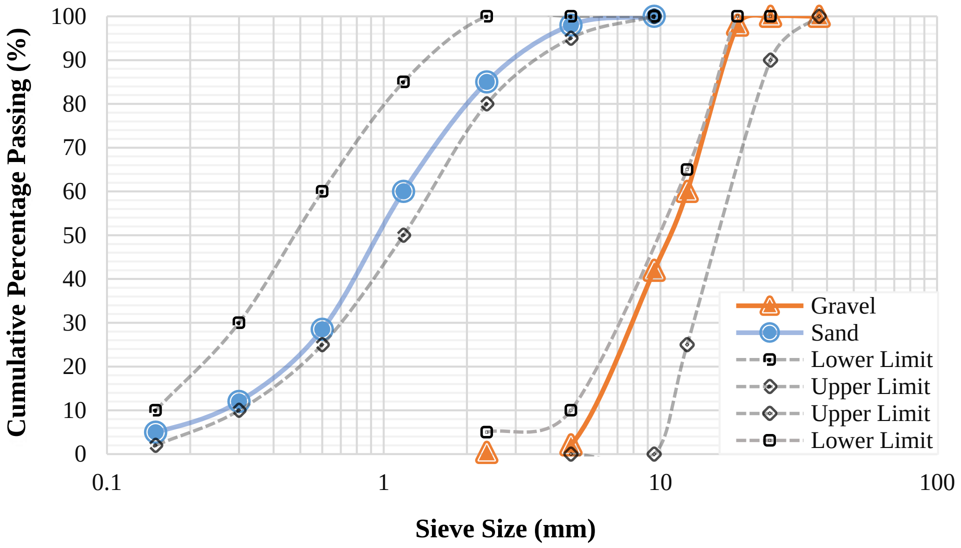


Fig. 1. Granulometry curve of the materials used (sand and gravel) based on ASTM C33 standard

The Persian Gulf environment is classified as moderate according to the ACI 318-19 standard with a sulfate level of 2541 mg/L (ACI Committee, 2005). The chloride content of 23491.77 mg/L in the Persian Gulf environment is harmful to Portland cement concrete, as the limit value of chloride ions to initiate corrosion has been reported in the range of 600-900 mg/L for a conventional sample of concrete mixture (Mehta et al., 2014). To investigate the impact of fly ash on the compressive strength and durability of concrete samples exposed to the sulfate and chloride environment of the Persian Gulf, varying amounts of 5%, 10%, 15% and 20% of fly ash were used as a partial substitute for cement. The aggregates used in this research included gravel and sand. The granulomere curve of the sand used, based on ASTM C33 standard, is presented in Figure 1 (ASTM, 2009).

To achieve the research objectives, an appropriate mixing plan related to the research subject was presented based on the ACI-211 standard, as shown in Table 3. In this regard, the materials were first weighed according to each mixing plan in a workshop environment. Then, the desired sample was made using a mixer, and after conducting the slump test, the concrete was poured into standard molds with dimensions of 15 × 15 × 15.

The mold was filled and compacted three times. The samples were removed from the molds after 24 hours, and then 12 specimens from each mixing design (four specimens for the 7-day test, four for the 28-day test, and four for the 90-day test) were stored under normal environmental conditions (water) and the marine environment of the Persian Gulf. The compressive strength of the samples was measured in the laboratory at 7-day, 28-day, and 90-day intervals (ASTM, 2009). The mixing plan used for cement samples had a water-to-cement ratio of 0.45.

Table 3. Concrete mix design using type 2 portland cement according to ACI-211 standard

Constituents	Gravel (kg/m^3)	Sand (kg/m^3)	Water (kg/m^3)	Cement (kg/m^3)	Fly ash (kg/m^3)
Concrete	693.6	1069	157.5	350	0
Concrete + %5 fly ash	693.6	1069	157.5	332.5	17.5
Concrete + %10 fly ash	693.6	1069	157.5	315	35
Concrete + %15 fly ash	693.6	1069	157.5	297.5	52.5
Concrete + %20 fly ash	693.6	1069	157.5	280	70

The water used to make the samples was water from Bandar Abbas with a pH of 7.5. To perform the compressive strength test, the samples were made according to the ASTM C39 standard at laboratory temperature and based on the mixing scheme in Table 3 (ASTM, 2009). It is worth noting that the samples were in the Persian Gulf, and the tests were conducted from the beginning of September to the end of November when the water temperature ranged between 18 and 28 degrees Celsius. To analyze the microstructure of the concrete samples, Scanning Electron Microscopy (SEM) was employed.

3. Discussion and Results Analysis

3.1. Microstructure of Samples in Seawater and Tap Water Conditions

Figure 2 displays SEM images of the control sample and samples containing 5%, 10%, 15% and 20% fly ash stored in tap water and seawater for 90 days. The concrete microstructure changes with an increase in the percentage of fly ash, as seen in Figures 2a to 2e. Figure 2a shows the morphology of the control sample after being exposed to tap water.

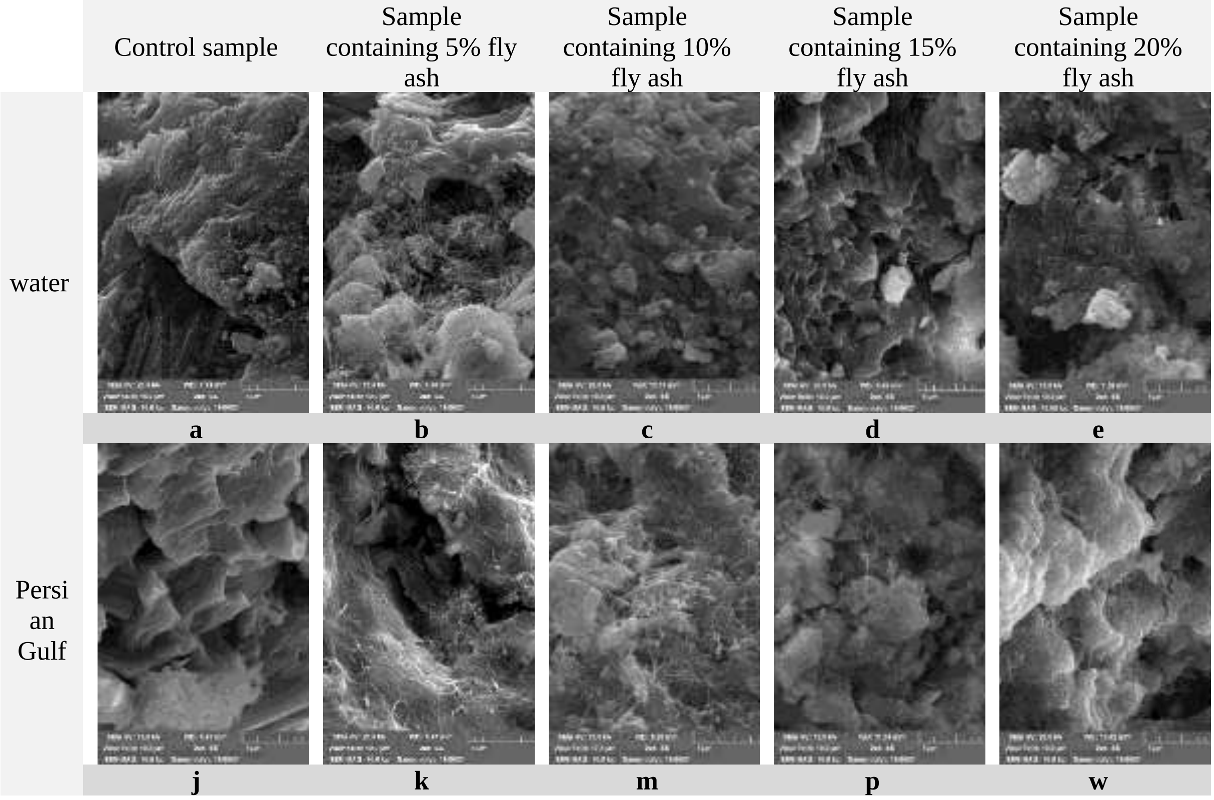


Fig. 2. SEM images of concrete samples, including: a) Control sample stored in water; b) Sample containing 5% fly ash stored in water; c) Sample containing 10% fly ash stored in water; d) Sample containing 15% fly ash stored in water; e) sample containing 20% fly ash stored in water; j) Control sample stored in the Persian Gulf; k) Sample containing 5% fly ash stored in the Persian Gulf, m) Sample containing 10% fly ash stored in the Persian Gulf; p) Sample containing 15% fly ash stored in the Persian Gulf; and w) Sample containing 20% fly ash stored in the Persian Gulf.

The completion of the hydration process and the growth of the nanoscale sponge-like structure of calcium silicate hydrate (C-S-H) reduces the porosity and enhances the cohesion in the cement paste of this sample. The amount of Calcium Hydroxide $Ca(OH)_2$ or CH, in the cement paste without fly ash is not visible. Typically, CH appears as distinct hexagonal crystals that vary in shape depending on the available space in the cement paste. Due to its low Van der Waals force, the role of CH in the strength of concrete is limited.

Additionally, the effect of CH on the chemical durability of concrete against acids is undesirable because of its high solubility. Figures 2b to 2e show the morphology of samples containing different percentages of fly ash, stored in potable water for 90 days. The amount of CH in samples containing fly ash has decreased. In fact, fly ash has less CaO in its chemical composition, and its pozzolanic activity consumes CH significantly. When C_3S (tricalcium silicate) comes into contact with water, the calcium silicate minerals separate into calcium and silicate ions. This loaded ions deposit as a thin layer on the surface of C_3S to delay the reaction between C_3S and water. The nucleation and growth of CH crystals fill the empty spaces between the particles. In addition, C-S-H particles in water precipitate as a silicate-rich layer on C_3S grains and gradually transform into needle-like ettringite-like compounds. In cement paste containing fly ash, the amount of nanostructure C-S-H has increased, and a limited amount of ettringite has formed.

Therefore, these processes can reduce porosity and potentially decrease permeability. Figures 2j to 2w show SEM micrographs of control samples and samples containing 5%, 10%, 15%, and 20% fly ash maintained in the Persian Gulf environment for 90 days. Figure 2j shows the morphology of the control sample treated in the Persian Gulf environment.

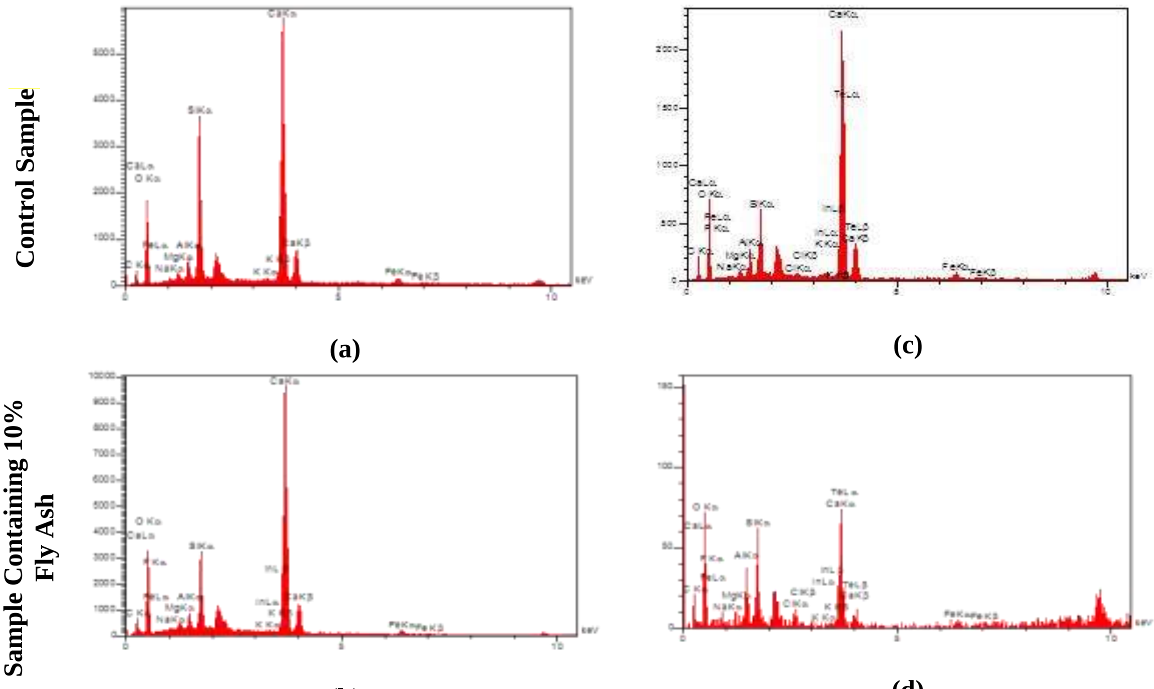
Due to the penetration of sulfate and chloride ions present in the Persian Gulf waters, gypsum crystals and needle-like ettringite structures have occupied a large volume, which is why this sample is associated with more destructive effects than the sample maintained in water (Figure 2a). Figure 2k shows the microstructure of the concrete sample containing 5% fly ash treated in a chloride and sulfate environment of the Persian Gulf for 90 days.

This image shows the formation of six-sided calcium hydroxide crystals (CH) and C-S-H nanostructure. The formation of ettringite in the sample is limited. Figure 2w shows the morphology of the concrete sample containing 20% fly ash treated in the Persian Gulf environment. In this image, the C-S-H nanostructure has grown in the samples treated in seawater, and six-sided CH are also observed. In this sample, the needle-like ettringite structure is observable but is not the dominant structure. In this study, the presence of needle-like ettringite structures in the samples was observed, although they were not the predominant structures.

Generally, it can be concluded that the addition of fly ash resulted in a decrease in the amount of CH and a relative increase in the amount of calcium silicate hydrate (C-S-H) in the samples. Furthermore, in samples exposed to the marine environment of the Persian Gulf, the addition of fly ash resulted in a reduction in ettringite formation, as well as a decrease in CH content.

3.2. Structural Analysis by Energy Dispersive X-ray Spectroscopy (EDX)

Energy Dispersive X-ray spectroscopy (EDX) is an analytical method used for the structural and chemical analysis of a sample. Figure 3 displays the results obtained from EDX spectroscopy for the samples at 90 days. Figure 3a shows the EDX pattern of the control sample maintained in water at 90 days. The peak corresponding to CaKα is observed at 3.7 Kev.



(a) (c)

(b) (d)

Water **Persian Gulf**

Fig. 3. EDX images of concrete samples, including: a) Control sample stored in water; b) Sample containing 10% fly ash stored in water; c) Control sample stored in the Persian Gulf; and d) Sample containing 10% fly ash stored in the Persian Gulf.

Figure 3b shows the EDX pattern of the sample containing 10% ash maintained in water. The peak corresponding to CaKα is observed at 3.7 Kev, and a peak corresponding to SiKα is observable at 1.7 Kev. Figure 3c shows the EDX pattern of the sample without ash maintained in the environmental conditions of the Persian Gulf at 90 days. As shown in Figure 3c, a peak for CaKα is observable at 3.7 Kev. Figure 3d shows the EDX pattern of the sample containing 10% ash maintained in the Persian Gulf seawater at 90 days. The peak for CaKα in this sample is at 3.7 Kev.

Furthermore, the EDX spectra in samples containing ash indicate the presence of a Ca ion peak. The changes in the weight percentage of elements present in concrete samples obtained from EDX analysis show that the Ca/Si and Ca/ (Al + Si) ratios in the control sample maintained in water are 5.313 and 4.148, respectively. These ratios indicate that the sponge-like nanostructure of C-S-H is formed to a large extent, and the volume of small pores at the micro and nano level is very small.

The EDX results of the sample containing 10% fly ash maintained in water also show Ca/Si and Ca/ (Al + Si) ratios of 2.816 and 2.405, respectively. The addition of nano silica results in a decrease in CH, an increase in C-S-H, and consequently, a decrease in Ca/Si ratios. The weight percentage of Si and Al ions in the sample containing 10% fly ash maintained in the Persian Gulf seawater has decreased compared to the control sample. The Ca/Si and Ca/ (Al + Si) ratios obtained from the EDX results for the control sample maintained in the Persian Gulf seawater are 1.943 and 1.072, respectively.

In addition, the Ca/Si and Ca/ (Al + Si) ratios for the sample containing 10% fly ash maintained in the Persian Gulf seawater are 5.941 and 3.970, respectively. As observed, the Ca/Si and Ca/ (Al + Si) ratios in the sample containing 10% fly ash maintained in the Persian Gulf seawater have increased compared to the control sample. In general, it can be stated that the amount of cations in all samples maintained in water and Persian Gulf seawater increases with an increase in fly ash percentage. The results of the EDX test show that the Ca/Si and Ca/ (Al+Si) ratios in the control sample maintained in the Persian Gulf marine environment have reached the lowest values compared to other samples.

This ratio indicates the severe penetration of chloride and sulfate ions from seawater into the sample and also indicates the formation of a destructive structure of ettringite and gypsum and the destruction of C-S-H nanostructures in the samples, which is well matched with the results shown in the SEM images in Figure 2. As chloride and sulfate attacks progress, the calcium content within the C-S-H nanostructure decreases, leading to a decrease in the molar ratio of Ca/Si. The molar ratio of Ca/Si serves as an indicator for identifying the C-S-H nanostructure, with the minimum and maximum ratios observed in the C-S-H phase being 1.943 and 5.941, respectively. However, the use of fly ash as an additive has been found to increase the Ca/Si ratio in the samples. This suggests that incorporating fly ash into concrete mixtures may improve the performance of the material in marine environments. The literature supporting this finding is derived from authentic journals in the field of concrete technology.

3.3. Investigation of Changes in Compressive Strength in the Marine Environment of the Persian Gulf

The compressive strength changes in concrete specimens containing various percentages of fly ash in contact with two different environments, water and Persian Gulf seawater, at the ages of 7, 28 and 90 days are presented in Figures 4 and 5.

Based on the results presented in Figure 4, the compressive strength of the control sample reached 278 kg/cm^2 after 7 days of exposure to tap water. After 28 days, the compressive strength of the control sample increased to 285 kg/cm^2 and reached 304 kg/cm^2 after 90 days. The results show that the control sample exposure to tap water at the age of 28 and 90 days had a 2.27% and 9.09% increase in compressive strength compared to the 7-day sample, respectively. The SEM images in Figure 2 show that this increase in strength is due to the completion of the hydration process and the evolution of C-S-H nanostructures, as well as a reduction in the porosity of the samples over time. The compressive strength of 7-day-old specimens containing 5%, 10%, 15%, and 20% fly ash and treated with tap water were 319 kg/cm^2, 293 kg/cm^2, 258 kg/cm^2, and 231 kg/cm^2, respectively.

Samples containing 5%, 10%, 15% and 20% of fly ash processed with water showed an increase in compressive strength compared to the control sample of 25.98%, 31.48%, 19.0 % and 0.65%, respectively, at the age of 90 days. Samples containing 10% fly ash exposure to tap water at the ages of 7, 28 and 90 days obtained compressive strength of 293 kg/cm^2, 369 kg/cm^2 and 399 kg/cm^2, respectively. The results show that the sample containing 10% fly ash exposure to tap water at the age of 28 and 90 day had a 25.59% and 36.04% increase in compressive strength compared to 7-day sample, respectively. Samples containing 20% fly ash exposure to tap water at the ages of 7, 28 and 90 days obtained compressive strength of 231 kg/cm^2, 257 kg/cm^2 and 306 kg/cm^2, respectively. The results show that the sample containing 20% fly ash exposure to tap water at the age of 28 and 90 days had an 11.51% and 32.41% increase in compressive strength compared to 7 days samples, respectively.

The use of fly ash led to an increase in the long-term strength of the concrete. According to the SEM images shown in Figure 2, with the passage of time, the C-S-H nanostructure in the samples treated with water grew, creating a high specific surface area that improves adsorption characteristics and fills the pores (Hong and Glasser, 2002; Amiri and Tanide, 2020). During the hydration of concrete in the presence of fly ash, there are two possible mechanical reactions.

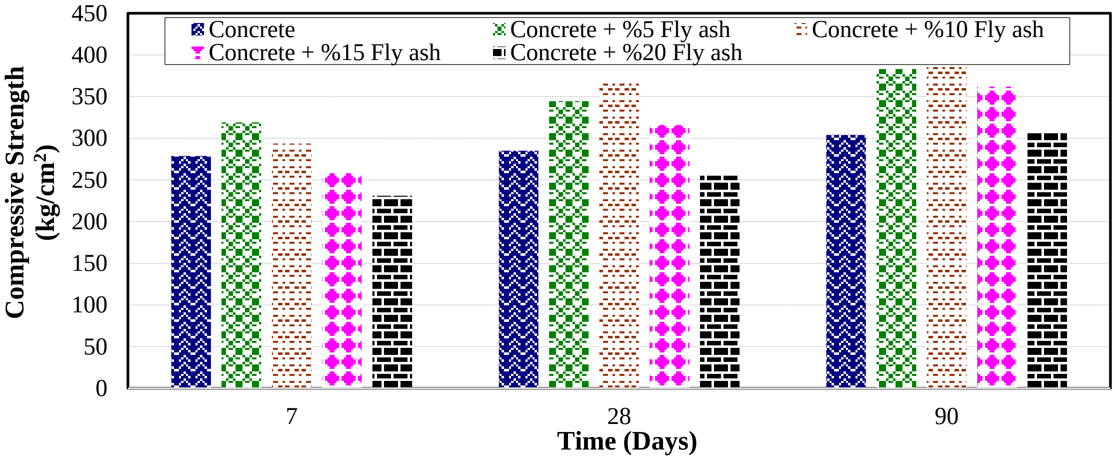


Fig. 4. Changes in compressive strength of concrete samples stored in water

Fly ash particles can accelerate cement hydration by forming $H_2SiO_4^{-2}$ which reacts with Ca^{+2} present, producing additional calcium-silicate-hydrate (C-S-H) (Singh et al., 2013). C-S-H constitutes approximately 75% of the weight of hydrated cement and forms at temperatures near ambient conditions, contributing to the increased strength of the concrete (Wang et al., 2019).

Based on the results presented in Figure 5, the control sample stored in seawater in the Persian Gulf achieved compressive strengths of 258 kg/cm^2, 284 kg/cm^2 and 300 kg/cm^2 at ages of 7, 28, and 90 days, respectively. The control sample stored in seawater at the age of 28 and 90 days had a 10.07% and 16.27% increase in compressive strength, respectively, compared to the 7-day sample. The compressive strengths of 5%, 10%, 15%, and 20% fly ash concrete samples stored in seawater for 7 days were 297 kg/cm^2, 284 kg/cm^2, 277 kg/cm^2, and 194 kg/cm^2, respectively. The results showed that at the age of 90 days, the samples containing 5%, 10%, 15%, and 20% fly ash had an increase in compressive strength of 15.34%, 15.4%, 13.16%, and 0.74%, respectively, compared to the control sample.

Samples containing 10% fly ash stored in seawater at the ages of 7, 28 and 90 days obtained compressive strength of 284 kg/cm^2, 357 kg/cm^2 and 346 kg/cm^2, respectively. Sample stored in seawater at the age of 28 and 90 days had a 25.85% and 21.79% increase in compressive strength compared to 7-day samples, respectively.

Samples containing 20% fly ash stored in seawater at the ages of 7, 28 and 90 days obtained compressive strength of 194 kg/cm^2, 365 kg/cm^2 and 302 kg/cm^2, respectively. Sample stored in seawater at the age of 28 and 90 day had an 87.46% and 55.77% increase in compressive strength compared to 7-day sample, respectively.

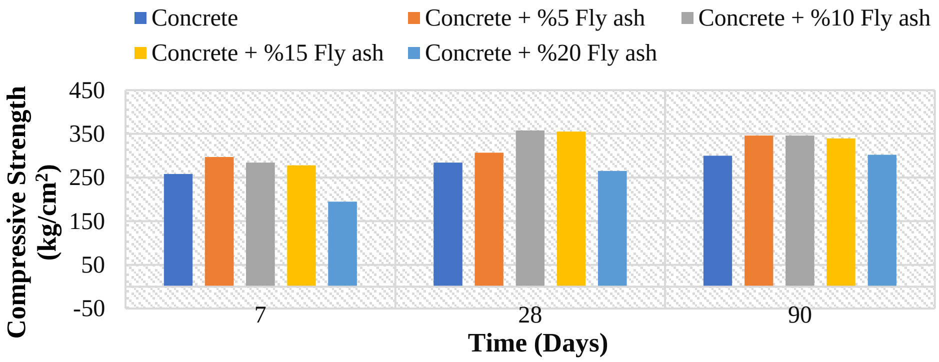


Fig. 5. Changes in compressive strength of concrete samples stored in Persian Gulf sea water

These results indicate that adding fly ash improves the mechanical properties and durability of concrete in the Persian Gulf seawater at later ages. However, concrete samples stored in seawater showed a reduction in compressive strength compared to samples stored in water at ages of 7, 28, and 90 days, with reductions of 7.41%, 0.35%, and 1.32%, respectively.

This reduction in strength is due to the penetration of sulfate and chloride ions into the concrete structure. For the concrete samples stored in seawater, the effect of the sulfate and chloride environment is intensified by the consumption of hydration products such as CH and C-S-H. Therefore, the dissolution of hydration products and the formation of Friedel’s salt, the needle-shaped structure of ettringite, and gypsum crystals due to attacks by sulfate, chloride, and acid in the seawater have occurred, which is consistent with the SEM image results shown in Figure 2 and leads to the breakdown of the concrete structure. The result of these destructive effects is the destruction of the nanostructure of C-S-H and CH, causing a decrease in the compressive strength of the concrete samples.

In addition, the EDX test results show that the Ca/Si and Ca/ (Al + Si) molar ratios in the concrete samples stored in the Persian Gulf environment have reached their lowest values compared to other samples. Generally, with the progress of sulfate and chloride attacks, the calcium present in the C-S-H nanostructure is lost, and the Ca/Si and Ca/ (Al + Si) molar ratios decrease.

The 28-day concrete samples stored in seawater showed a reduction in compressive strength of 10.8% and 3.25%, respectively, compared to the samples stored in water containing 5% and 10% fly ash. Increasing the percentage of fly ash used in concrete samples can help improve concrete impermeability, resulting in increased resistance of concrete samples to sulfate and chloride-containing water and a denser sample structure. An increase in compressive strength in concretes containing fly ash even after long-term exposure to marine environments was observed by Supit and Shaikh (2015) and Lopez-Calvo et al. (2012).

3.4. Effect of Fly Ash on Permeability Coefficient in the Persian Gulf Marine Environment

The chart depicting the permeability coefficient and depth of water penetration for concrete samples containing varying percentages of fly ash in two environments, namely water and the Persian Gulf marine environment, is presented in Figure 6.

Based on the results, the permeability coefficient of the control sample in water was 18.3×10^{-7} cm/h. The permeability coefficients of samples containing 5%, 10%, 15%, and 20% fly ash treated in water were 6.45×10^{-7} cm/h, 5.70×10^{-7} cm/h, 4.90×10^{-7} cm/h, and 3.19×10^{-7} cm/h, respectively. The results indicate that the sample containing 20% fly ash in water showed an 82.56% reduction in permeability coefficient compared to the control sample. The depth of water penetration of samples containing 5%, 10%, 15%, and 20% fly ash treated in water decreased by 41.66%, 46.5%, 50%, and 60%, respectively, compared to the control sample.

Overall, the results showed that with increasing dust deposition, the permeability coefficient and the depth of water penetration decreased. According to the presented results, the permeability coefficient of the control sample maintained in the Persian Gulf was 22.4×10^{-7} cm/h. The permeability coefficients of samples containing 5, 10, 15, and 20% dust deposition and treated in the Persian Gulf were 12.38×10^{-7} cm/h, 8.98×10^{-7} cm/h, 7.75×10^{-7} cm/h, and 5.84×10^{-7} cm/h, respectively. The results indicate that the sample containing 20% dust deposition maintained in the Persian Gulf showed a 73.92% decrease in permeability coefficient compared to the control sample.

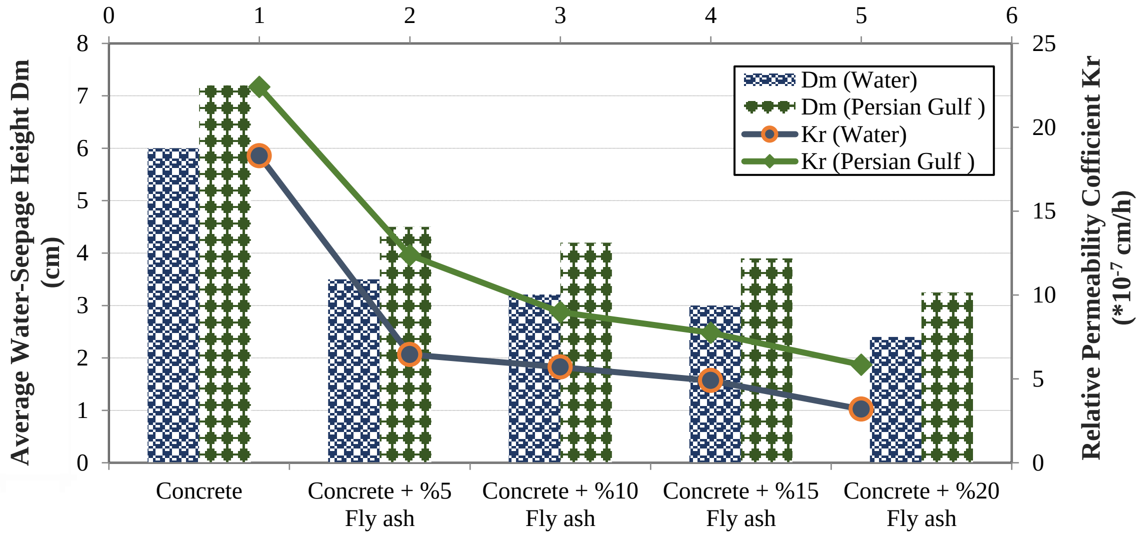


Fig. 6. Permeability coefficient and depth of water penetration of concrete samples containing different percentages of fly ash stored in water and the Persian Gulf environment

The depth of water penetration in concrete samples containing 5%, 10%, 15%, and 20% dust deposition and treated in the Persian Gulf exhibited significant reductions of 37.5%, 41.66%, 45.83% and 54.86%, respectively, compared to the control sample. SEM images in Figure 2 demonstrated that the utilization of dust deposition improved the microstructure of concrete, leading to a substantial reduction in permeability coefficient and depth of water penetration. This is attributed to the small particle size and low specific surface area of dust deposition, which fills the pores and reduces porosity. As a result, the permeability of chloride and sulfate ions in concrete decreases, leading to enhanced durability against attacks by these ions in the Persian Gulf environment (Abedi, 2021).

However, the permeability coefficient of concrete samples containing 5%, 10%, 15%, and 20% dust deposition stored in the Persian Gulf increased by 91.93%, 57.54%, 58.16%, and 83.07%, respectively, compared to the samples stored in water. This increase is due to the penetration of sulfate and chloride ions in the concrete structure by seawater in the Persian Gulf.

The reaction between fly ash particles and calcium hydroxide produces C-S-H nanostructure, which fills the pores and enhances the fine structure of concrete (Abedi, 2021). This improvement in the fine structure of concrete results in reduced permeability and water penetration depth, leading to increased durability against sulfate and chloride attacks in the Persian Gulf environment.

A decrease in permeability and depth of penetration in concrete containing fly ash was also observed in the research of Moffatt et al. (2017); Thomas and Matthews (1992); Supit and Shaikh (2015) and Chalee et al. (2010)

4. Conclusions

In this study, the effect of the Persian Gulf marine environment on concrete containing different percentages of fly ash as a cement substitute was investigated from the perspective of microstructure. The laboratory studies revealed the following key findings:

- Scanning Electron Microscopy (SEM) images indicated that the hydration process and the growth of a sponge-like C-S-H nanostructure in samples immersed in water reduced permeability and increased compressive strength.
- EDX and SEM results demonstrated that in samples exposed to the aggressive Persian Gulf marine environment, the Ca/Si

and Ca/ (Al + Si) ratios reached their lowest values. This emphasizes the pronounced influence of chloride attack, while sulfate attack had a comparatively minor impact. The penetration of chloride and sulfate ions from the Persian Gulf waters led to the formation of destructive compounds, including ettringite and gypsum, and the degradation of the C-S-H nanostructure, ultimately diminishing the strength of the samples.

- The sample containing 10% fly ash, kept in the Persian Gulf, exhibited a 25.70% and 15.4% increase in compressive strength compared to the sample without additives after 28 and 90 days, respectively.
- The sample containing 10% fly ash displayed the highest compressive strength after 90 days of exposure to the Persian Gulf environment and tap water, with values of 346 kg/m² and 399 kg/m², respectively. Incorporating 10% fly ash, particularly at a water-cement ratio of 0.45, not only improved compressive strength but also reduced permeability and penetration depth.
- Increasing the percentage of fly ash as a cement substitute for samples immersed in the aggressive Persian Gulf environment increased the durability and compressive strength of the samples and reduced the porosity and permeability of the concrete over time. Fly ash increased the hydration process over time and the pore structure was gradually modified with more processing time, increasing density and resulting in a denser sample structure. Concrete containing fly ash had higher strength than concrete without fly ash at older ages.
- Adding fly ash reduced the amount of CH and increased the relative amounts of C-S-H in the samples. In samples immersed in the Persian Gulf’s marine environment, adding fly ash reduced the destructive effects of chloride and sulfate ions and increased the durability of concrete. In general, the results suggested that adding fly ash as a cement substitute can improve the durability of concrete in the Persian Gulf marine environment.
- In the Persian Gulf’s marine environment, chloride attack is the primary cause of concrete erosion, expansion, and cracking, while sulfate attack has a limited impact. Incorporating fly ash as a supplementary cementitious material can enhance concrete's resistance to chloride-induced deterioration.

Overall, the microstructural investigation demonstrated that fly ash is an effective cement substitute for enhancing the durability and compressive strength of concrete in the aggressive marine environment of the Persian Gulf. In marine environments, the significance of chloride attack in concrete deterioration takes precedence over sulfate attacks, emphasizing its dominant role.

The findings of this study could be useful in designing and constructing durable concrete structures in coastal regions with similar marine environments.

5. Availability of Data and Materials

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

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