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Enhancement of Concrete Mixed or Cured with Sea Water Using Fly Ash and Metakaolin

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ABSTRACT
Water plays an important role in the concrete industry. The research aims to study the effect of using seawater in mixing and curing concrete and indicating its effect on fresh properties of concrete such as slump and mechanical properties like compressive, tensile and flexural strength. The main variables of this paper are type of water (sea and fresh water), percentage of fly ash and metakaolin. The percentage of fly ash is 20%, 30% and 40% as a replacement of cement content. In addition, metakaolin with 3%, 5% and 7% as a replacement of cement content was used. Mineral admixtures are materials that have a softer degree compared to cement, and this leads to have denser concrete and less permeable concrete, which enhances the lower overall porosity of the system due to the filling of capillary pores. That leads to reduce the penetration of chloride and sulfate ions into the concrete. The results show that using mineral admixture gave the ability to use seawater in plain concrete, as a compressive strength of 49 MPa was achieved when seawater was used in mixing and curing concrete with 7% metakaolin and 30% fly ash. The results also showed an improvement in tensile and flexural strength.

Keywords: *seawater; slump; compressive strength; fly ash; metakaolin.*

1. Introduction

World is in urgent need to find an alternative to drinking water in the concrete industry, due to the increasing consumption. One of the most promising of these alternatives is seawater, where it represents 97.5% of water on the earth's surface [1, 2]. The concentration of salts in seawater varies from one to another with an average of 3.5%. Sodium chloride is the dominant salt in seawater [3]. Seawater contains sodium ions, carbonates, sulfates and magnesium that affect the penetration of chlorides [4], which leads to the corrosion of the reinforcing steel [4-5]. At early ages, sea water was found to improve the compressive strength, pore structure and makes concrete more homogeneous [6] .In addition, it gives both smaller crystals of calcium hydroxide (CH) and less amount of pores as the higher the amount of Calcium Silicate Hydrates (CSH), the smaller the voids become [6]. Seawater accelerates hydration of cement at early ages, which in turn increases the strength of concrete due to the increase of density [7]. This is because of the presence of chlorides that interact with calcium hydroxide CH resulting from the hydration of cement to produce calcium chloride $CaCl_2$. This compound, $CaCl_2$, accelerates hydration of cement [7].
A negative effect of using seawater regarding the compressive strength was reported after 28 days [2, 8]. Sulphates and chlorides lead to a decrease in the compressive strength of seawater concrete [9]. This is due to the pressure of the salt crystals inside the pores [8]. Corrosion of the reinforcing bars leads to reduce both the durability of the structure and life expectancy [10]. Mineral admixture usage enhances the long-term strength of concrete besides improving the durability of concrete, because of the pozzolanic reaction and its products. Mineral admixtures react with water and (CH) resulting from the cement hydration process to form (CSH) [11, 12].
Seawater Concrete with 5% metakaolin improves the compressive strength of concrete [13]. Metakaolin is one of the supplementary cementitious materials with high pozzolanic activity [13]. Metakaolin particle composition involves alumina and active silica [11]. Metakaolin addition can in turn consolidate concrete properties such as porosity, compressive strength, and resistance against chloride attack in addition to the enhancement of pore structure and reduction of permeability [13]. Metakaolin improves the concrete resistance to chloride attack as the pozzolanic reaction that leads to the formation of more CSH gel. Added to this formation, pozzolanic reactions improve the pore structure and forms friedel's salts leading to the obstruction of transfer of chlorides in concrete. On the other hand, concrete containing metakaolin and mixed with seawater includes less free chlorides due to the improvement of the restriction of chlorides in concrete

[13]. One of the ways to reduce the penetration of chlorides into concrete is to replace cement with mineral admixtures such as fly ash by 10%-50% [10]. Fly Ash converts CH into useful cementitious materials such as ($C_3S_2H_3$). This can promote the properties of concrete, for example, the resistance of concrete against aggressive water attack. Moreover, it reduces the leaching of CH released during the hydration of cement [12, 14].

2. Aim and Research Significance

The significance of the provided research is that it provides an alternative to fresh water, since the world suffers from a decline in the amount of ordinary water existing on the earth's surface, and the most readily available alternative is seawater. As a result, saltwater was employed in mixing and curing without any additives, resulting in concrete disintegration after 28 days. Mineral admixtures were utilized to mitigate the harmful effects of saltwater, and the findings revealed an improvement in the characteristics of concrete.

3. Experimental Program

The experimental program is concerned with studying the effect of seawater on the properties of concrete. The performance of using seawater for mixing and curing concrete is discussed. In addition, the effect of mineral admixture (fly ash and metakaolin) is studied to test their effect on seawater in concrete.

3.1-Material

Portland cement (CEM I 42.5N) (ELmomtaz) was used according to the Egyptian Standard Specification (E.E.S. 4756-1/2012) [15]. Natural siliceous sand as fine aggregates, which satisfies the Egyptian Standard Specification (E.S.S 1109/2008), was used [16]. Crushed Dolomite with a maximum size of 12 mm as coarse aggregates was used according to ASTM C-33 [17]. A chemical admixture with 1.2% of cement content was used according to ASTM C 494 types G & F [18]. Type F fly ash complying to ASTM C-618 [19] was used at 20, 30, 40% ratios as a replacement of cement content by weight and the chemical composition is shown in Table (1). Metakaolin was used with 3, 5, and 7% cement replacement and the chemical composition is shown in Table (2). Seawater used in mixing and curing was brought from the Mediterranean Sea, the chemical test for seawater was done in the Ministry of Water Resources and Irrigation (National Center for Water Research) as shown in Table (3).

Table 1- Chemical composition of fly ash [20]

Constituent compounds	FA
$_2O_3Al$	14.3
$_2SiO$	5.59
$_2O_3Fe$	4.8
CaO	11.5
$_2OK$	0.4
SO_3	1.1
$_2ONa$	0.6
LOI	2.4

Table 2- Chemical composition of metakaolin [21]

Constituent compounds	MK
$_2O_3Al$	40.26
$_2SiO$	54.3
$_2O_3Fe$	2.28
CaO	0.39
$_2OK$	0.5
$_2ONa$	0.12
MgO	0.08

Table 3- Chemical composition of seawater

Chemical	Concentration (mg/l))
Ca	533.33
K	400
Cl	19517.4
Mg	1477
$_4SO$	2629.1
Na	12000

3.2-Mix proportions

Concrete mixtures were prepared to study the effect of using seawater to mix and cure plain concrete. These mixtures were divided into four categories providing different combinations of using sea and fresh tap water in mixing and curing of concrete. These concrete categories were mixed and cured using fresh water (FF), mixed with seawater and cured with fresh water (SF), mixed with fresh water and cured with seawater (FS) and finally mixtures that are mixed and cured with seawater (SS). After 24 hours, all concrete specimens were cured at a temperature of 20°C. For reducing the harmful effect of seawater on concrete, mineral admixture such as metakaolin and fly ash were used in different proportions.

3.3- Concrete specimens

Cube, cylinder, and prism specimens having sizes of 10*10*10 cm, 10*20 cm and 10*10*50 cm were used to evaluate the compressive, tensile and flexural strength, respectively. A water to cement ratio of 0.35 and a chemical admixture dosage of 1.2% were fixed in all mixes with a cement content of 350kg/m3.

Fly ash replaced 20%, 30%, and 40% of cement by weight. Some mixtures combined fly ash and metakaolin so that MK ratios of 3%, 5% 7% of the cement weight were added as indicated in table (4)(

Table (4): Concrete Mix Proportions (kg/m^3)

Specimen name	C	Sand	Dolomite	MK	FA	Mixing water	Curing water
FF	350	673	1347	-	-	FW	FW
FS	350	673	1347	-	-	FW	SW
SF	350	676	1352	-	-	SW	FW
SS	350	676	1352	-	-	SW	SW
20FA	280	665	1330	-	70	FW	FW
		667	1335			SW	SW
30FA	245	660	1321	-	105	FW	FW
		663	1327			SW	SW
40FA	210	656	1313	-	140	FW	FW
		659	1318			SW	SW
AF20MK3	269.5	664	1328	10.5	70	FW	FW
		667	1334			SW	SW
AF30MK3	234.5	660	1320	10.5	105	FW	FW
		662	1325			SW	SW
AF40MK 3	199.5	655	1311	10.5	140	FW	FW
		658	1317			SW	SW
AF20MK5	262.5	663	1327	17.5	70	FW	FW
		666	1333			SW	SW
AF30MK5	227.5	659	1319	17.5	105	FW	FW
		662	1324			SW	SW
AF40MK5	192.5	655	1310	17.5	140	FW	FW
		658	1316			SW	SW
AF20MK7	255.5	671	1343	24.5	70	FW	FW
		666	1332			SW	SW
AF30MK7	220.5	659	1318	24.5	105	FW	FW
		661	1323			SW	SW
AF40MK 7	185.5	654	1309	24.5	140	FW	FW
		657	1315			SW	SW

Where: FA (Fly Ash), MK (Metakaolin), F (Fresh tap water), S (Sea water), C (cement)

4 Results

Slump:

The slump test was done directly after mixing on fresh concrete. Figure 1 depicts the slump of the investigated mixes. When compared to fresh water concrete, using saltwater in concrete minimizes slump. The proposed process in this case is that chloride ions in saltwater react with calcium hydroxide to generate calcium chloride, which is a powerful accelerator for cement hydration and so reduces the initial setting time. The slump of concrete containing mineral admixtures increased as compared to control mixes.

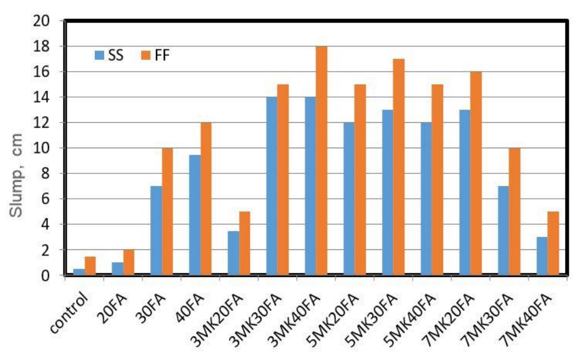

Figure 1- Slump of ordinary water mixtures and seawater mixture

Compressive strength:

The compressive strength of 10*10*10 cm cubes was tested. The use of a low water/cement ratio strengthens concrete against sulphate attack. According to Ref. [8,] high cement content integration improves the workability of concrete and increases the strength between concrete components. Figure (2) illustrates the development of compressive strength of mixtures containing seawater and ordinary water during mixing and curing. SS mixture had the highest compressive strength values compared to FF, FS, and SF at 7 age and 28 days, whereas sea water mixture has an increase of 24.25%, 8.46%, and 2.7% at 7 days and 10%, 10.97%, and 16.87% at 28 days compared to FF mixes. The use of saltwater in mixing and curing enhances compressive strength at early ages. These results was founded by Tiwari et al. (2014) [3] and Kumar et al (2020)[5]. However, after 28 days, saltwater reduces compressive strength.

Compressive strength in (SS) mixture reduces by 15.78% at 180 years compared to FF mixture and this agrees with M. M. Islam et. al (2010) [22]. The presence of sulphates causes this decrease in compressive strength.

Ettringite ($CaO.Al_2O_3.CaSO_4.H_2O$) and gypsum $CaSO_4$ are created. In saltwater, magnesium sulphate interacts with CH to create gypsum [22, 23]. Ettringite is formed when gypsum combines with tricalcium aluminate, and the amount of gypsum and ettringite after crystallisation is more than the volume of the compounds they occupy [22]. This might put a lot of pressure inside the concrete pores, causing the concrete to deteriorate. If the sulphate ions react completely before the hydration of C_3A is complete, it interacts with ettringite to create Calcium Monosulfoaluminate hydrate. Chlorides attack concrete where Friedel's salts occur because Friedel's salt has a low to medium expansion characteristic. The more the formation of calcium chloride, the greater the permeability of concrete [22]. Magnesium chloride combines with the CH produced by cement hydration to make calcium chloride, which dissolves and leaks. This causes material leakage and loss, resulting in poor strength [22]. The use of mineral admixtures in concrete reduces the damaging effects of saltwater on concrete.

The results indicate that the presence of two types of mineral additive has a greater influence on the compressive strength of mixed and cured concrete with sea water at 90 days. Figure (3) demonstrates that using both MK and FA in compressive strength, such as 3%MK. with different proportions

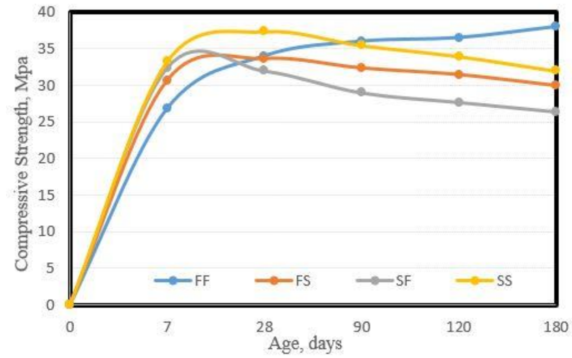

Figure 2- Compressive strength of control specimen

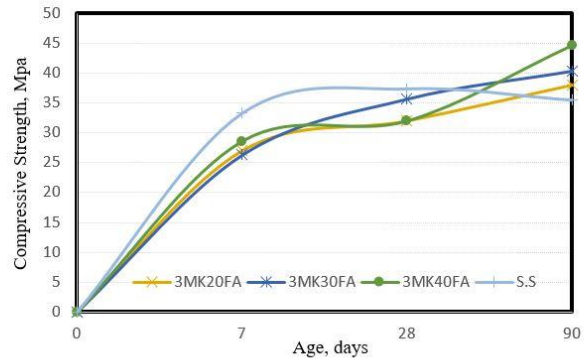

Figure 3- Compressive strength for seawater mixes using 3%metakaolin and fly ash as mineral admixtures

like 20%FA, 30%FA, and 40%FA mixes, outperforms saltwater combinations by 7.04%, 13.8%, and 25.6%, respectively, at 90 days. Figure (4) shows that compressive strength of 5%MK with 20%FA and 40%FA rises by 7.88% and 9.01%, respectively, over saltwater mixes after 90 days. Figure (5) shows that at 90 days, mixes of 7%MK with 20%FA, 30%FA, and 40%FA had a rise in compressive strength of 18.3%, 38.8%, and 9.85%, respectively, above saltwater solutions without admixture.

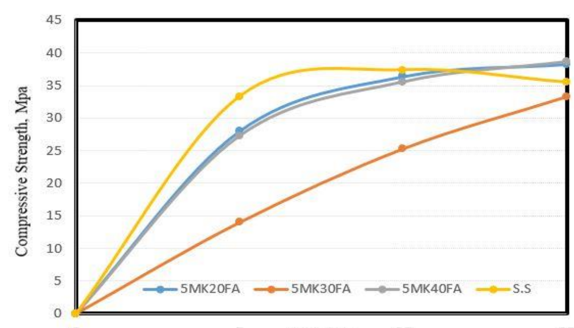

Figure 4- Compressive strength for seawater mixes using 5%metakaolin and fly ash as mineral admixtures

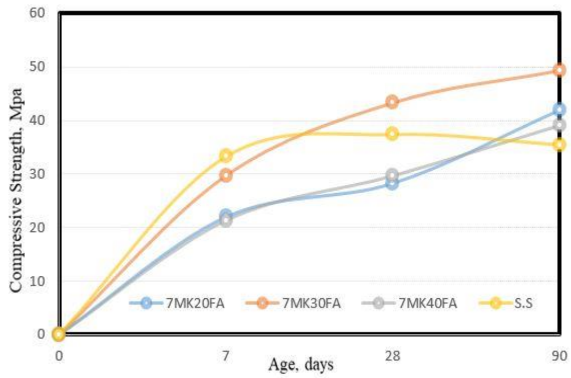

Figure 5- Compressive strength for seawater mixes using 7%metakaolin and fly ash as mineral admixtures

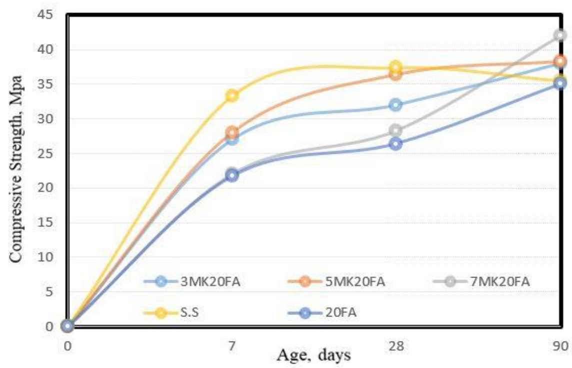

Figure 6- Compressive strength for seawater mixes using metakaolin and 20%fly ash as mineral admixtures

Figure (6) compares compressive strength increases of 7%, 7.88%, and 18.3% after 90 days for mixes containing 20% FA with varying amounts of MK and saltwater, as 3%MK20%FA, 5%MK20%FA, and 7%MK20%FA. Figure (7), on the other hand, shows that the combinations containing 30% fly ash alone or with 3%, 5%, and 7%MK. Except for 5%MK with 30%FA, they all had better compressive strength increases than seawater combinations. Furthermore, 30%FA results in a 15.49% increase, while 3%MK with 30%FA and 7%MK with 30%FA result in 13.8% and 38.87% increases in compressive strength after 90 days, respectively. Figure (8) depicts the combinations of 40% fly ash alone or with 3%, 5%, or 7% MK. Except for 40% FA, all of them show an increase in compressive strength as compared to seawater mixture. At 90 days, 3%MK with 40%FA produces the largest rise of 25.6%. As shown in figure 9, mixes of 30% FA have a greater compressive strength than combinations of seawater without admixtures, with a 15.49% increase.

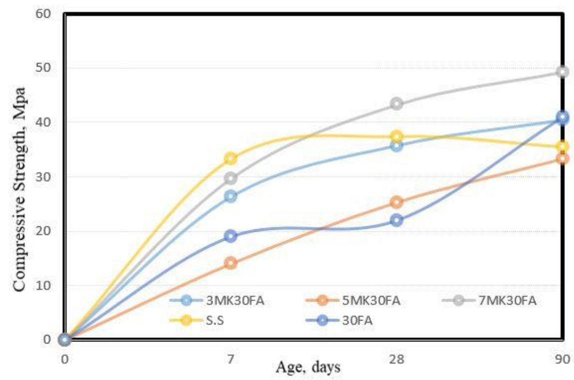

Figure 7- Compressive strength for seawater mixes using metakaolin and 30%fly ash as mineral admixtures

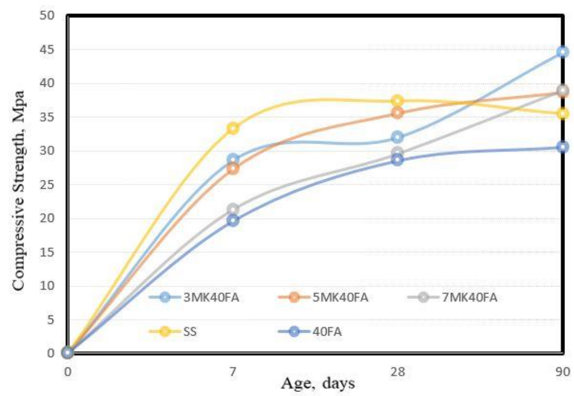

Figure 8- Compressive strength for seawater mixes using metakaolin and 40%fly ash as mineral admixtures

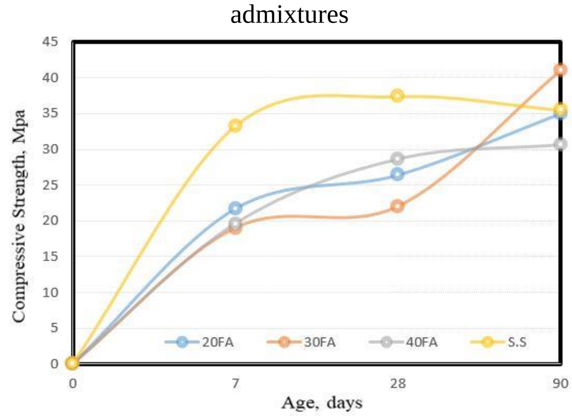

Figure 9- Compressive strength for seawater mixes using different percentages of fly ash as mineral admixtures

The consumption of CH results in an increase in the compressive strength of mixes including mineral admixtures. CH can impact the durability of concrete and the pore structure, causing it to transform into C-S-H, which is one of the bindings between the concrete's components. This is due to the pozzolanic interaction of MK and FA, both of which have a high aluminate concentration. The aluminate concentration rises as the two materials contact. They have a function in increasing compressive strength when saltwater is used, and this has an influence on the effect of different supplemental cementitious materials SMCS [24]. MK and FA increase concrete strength because they include a high percentage of SO3/Al2O3, which influences the interaction and hydration products. Furthermore, this serves to protect concrete against sulphate attack and to minimise permeability [25]. Early in life, saltwater enhances the shape of the pores and lowers the size of capillary holes larger than 100 nm [24]. Because of chemical interactions with hydration products, the amount of free chloride and sulphate ions decreases with age, resulting in a loss in compressive strength [6]. Because fly ash may fill cavities, the compressive strength of concrete combined with saltwater is improved [26]. Fly ash contributes to concrete resistance to chloride and enhances concrete durability as a result of the interaction of fly ash granules with Ca(OH)2 to create C-S-H filling gaps in concrete [10,11, and 27]. One of the properties of fly ash is that it gives concrete strength; nevertheless, it diminishes the compressive strength of concrete at early ages because it slows the setting time and the hydration of cement [10, 28]. The effect of saltwater on concrete diminishes with age because fly ash increases compressive strength with age [24.[

The findings show the impact of adding mineral admixtures and saltwater in concrete, such as 20% FA, 30% FA, and 40% FA. When combinations combined and cured with potable water (FF), 30%FA has a 13.8% improvement in compressive strength compared to FF after 90 days, as shown in figure (10). Figure (11) shows that when comparing 20%FA, 30%FA, and 40%FA with 3%MK after 90 days, the compressive strength increases by 5.55%, 12.22%, and 23.88%, respectively, over FF.

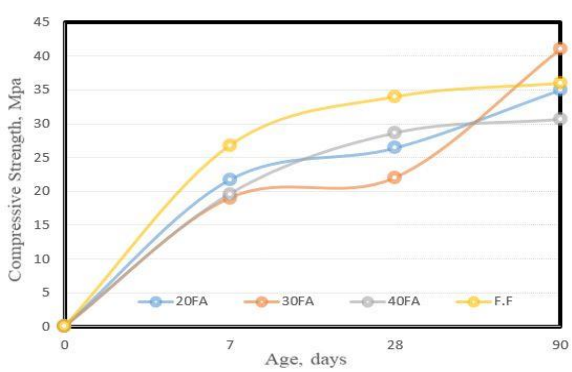

Figure 10- Compressive strength for seawater mixes using different percentages of fly ash as mineral admixtures with the ages and fresh water mixes.

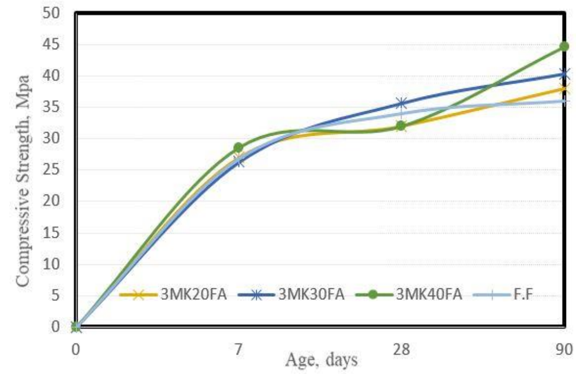

Figure 11- Compressive strength for seawater mixes using 3%metakaolin and fly ash as mineral admixtures with the ages and fresh water mixes

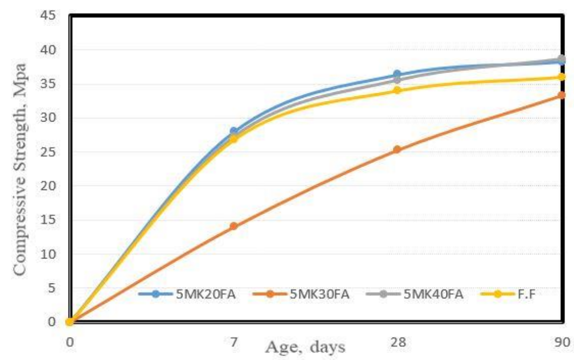

Figure 12- Compressive strength for seawater mixes using 5%metakaolin and fly ash as mineral admixtures with the ages and fresh water mixes

Figure (12) shows that 5%MK with 20%FA and 40%FA have a higher compressive strength than FF at 90 by 6.38% and 7.5%, respectively.

As demonstrated in figure (13), 7%MK with 20%FA, 30%FA, or 40%FA has a higher compressive strength than FF at 90, with percentages of 16.6%, 36.9%, and 8.33%, respectively.

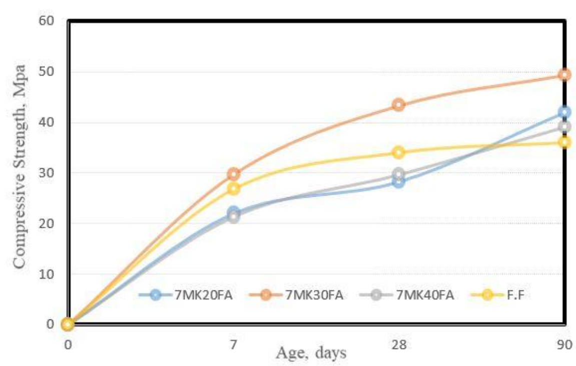

Figure 13- Compressive strength for seawater mixes using 7%metakaolin and fly ash as mineral admixtures with the ages and fresh water mixes.

Tensile strength:

Tensile strength is examined on 10*20 cm cylinders, and figure (14) shows the relationship between tensile strength and age's test of mixes containing saltwater and potable water in mixing and curing concrete. At 28 days, the SS mixture has the highest tensile strength values compared to the FF,FS,SF mixtures, with an increase of 15% compared to the combination (FF), while at 90 and 180 days, all mixes have a drop in tensile strength save the mixture (FF). This is in accordance with [1]. Meanwhile, figure (15) demonstrates that employing both MK and FA in tensile strength mixes like 3%MK with 20%FA, 30%FA, and 40%FA gives a better value than saltwater mixtures by 0.46%, 15%, and 49.2% at 90 days, respectively. Figure)16 (shows that 5%MK with 20%FA and 40%FA combinations had greater tensile strength values at 90 days than saltwater mixtures by 23.47% and 6.1%, respectively.

Figure (17) shows that 7%MK with 20%FA, 30%FA, and 40%FA mixes had greater tensile strength values after 90 days than saltwater combinations by 25.35%, 59.62%, and 11.73%, respectively.

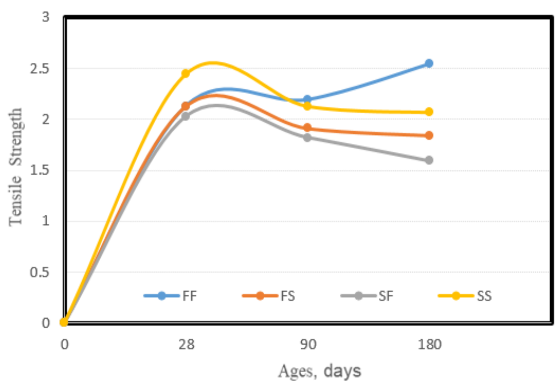

Figure 14- Tensile strength of control specimen.

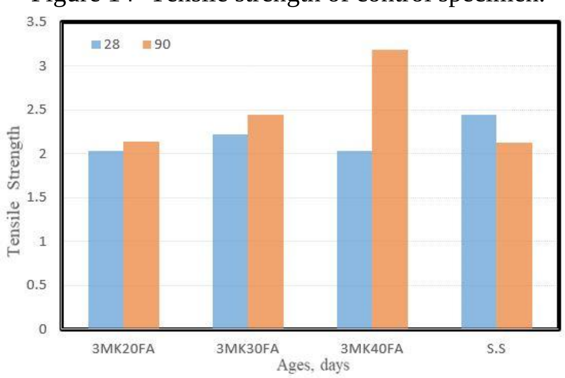

Figure 15- Tensile strength for seawater mixes using 3%metakaolin and fly ash as mineral admixtures

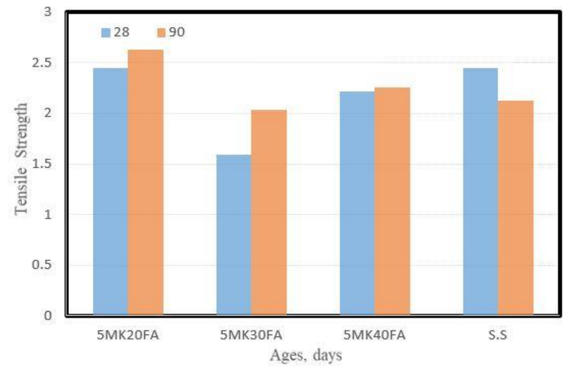

Figure 16- Tensile strength for seawater mixes using 5%metakaolin and fly ash as mineral admixtures

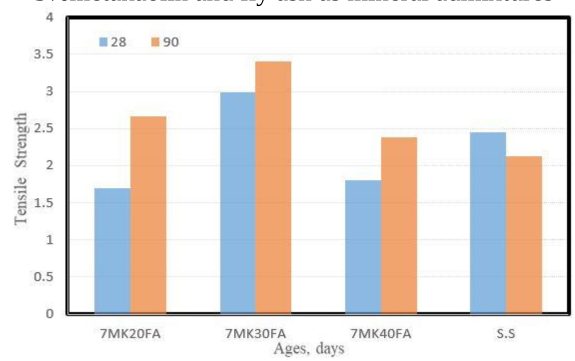

Figure 17- Tensile strength for seawater mixes using 7%metakaolin and fly ash as mineral admixtures

Figure (18) shows that mixes containing 20%FA with 3%MK, 5%MK, and 7%MK all had larger tensile strength increase than sea water mixtures with 0.46%, 23.47%, and 25.35%, respectively, at 90 days. Except for the 5%MK with 30%FA, where 30%FA and 3%MK with 30%FA report increases of 19.24% and 15.02%, respectively, the mixes containing 30%FA solo or with 3%MK, 5%MK, and 7%MK all recorded a larger tensile strength gain than sea water combinations after 90 days, Figure (19).

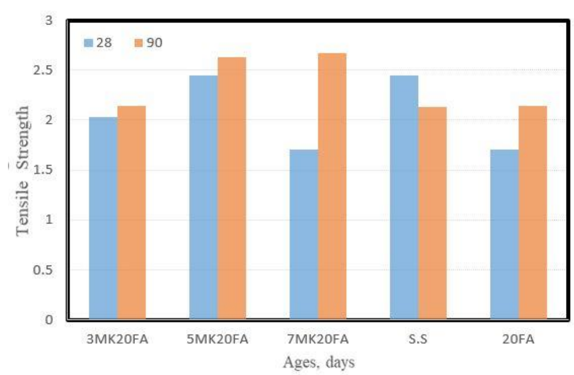

Figure 18- Tensile strength for seawater mixes using metakaolin and 20%fly ash as mineral admixtures

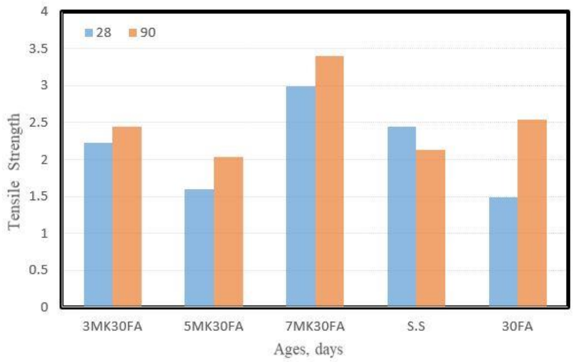

Figure 19- Tensile strength for seawater mixes using metakaolin and 30%fly ash as mineral admixtures

Figure (20) depicts the impact of combining MK and FA in tensile strength, with 3%MK with 40%FA, 5%MK with 40%FA, and 7%MK with 40%FA mixes outperforming saltwater counterparts by 49.29%, 6.1%, and 11.73%, respectively.

Figure (21) shows the tensile strength of fly ash mixes, with 30%FA increasing by 19.24%. The addition of mineral admixtures to boost tensile strength, which correlates to [29].

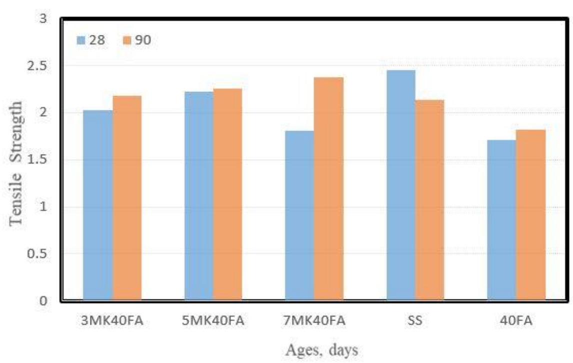

Figure 20- Tensile strength for seawater mixes using metakaolin and 40%fly ash as mineral admixture

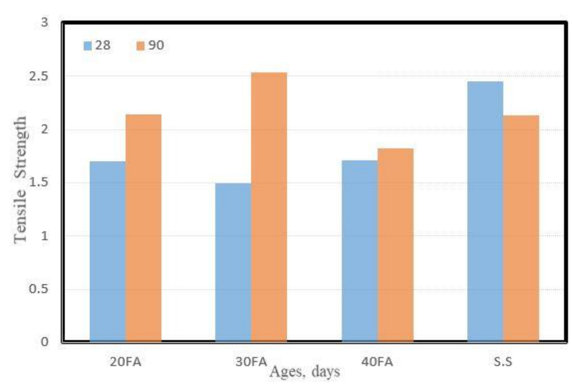

Figure 21- Tensile strength for seawater mixes using different percentages of fly ash as mineral admixtures and seawater mix

Flexural strength:

Flexural strength is tested on prisms 10*10*50 cm in size. In order to do so, investigate the link between flexural strength and the age's test.

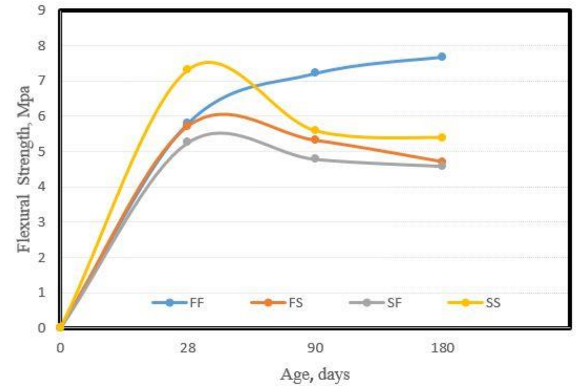

Figure 22- Flexural strength of control specimen

Figure (22) shows a mixture of saltwater and potable water used in mixing and curing concrete. The SS combination has the highest flexural strength values at 28 days, with a 26.2% gain over the mixtures (FF), whereas all mixes except (FF) had a reduction in flexural strength at 90 and 180 days. This is in accordance with [1]. In addition, Figure (23) shows the good effect of combining MK and FA in flexural strength, with 3%MK with 20%FA, 30%FA, and 40%FA mixes outperforming seawater combinations by 13.21%, 31.25%, and 60.17%, respectively, after 90 days.

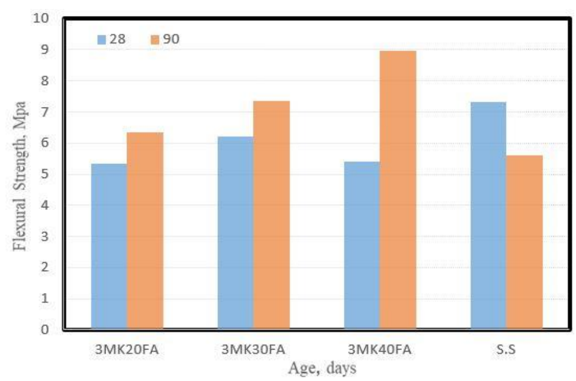

Figure 23- Flexural strength for seawater mixes using 3%metakaolin and fly ash as mineral admixtures

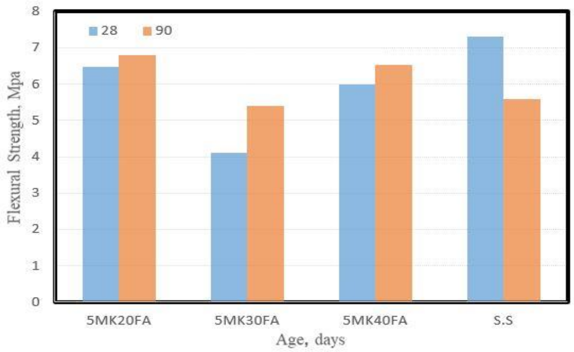

Figure 24- Flexural strength for seawater mixes using 5%metakaolin and fly ash as mineral admixtures.

Figure (24) shows that 5%MK with 20%FA or 40%FA combinations had a greater flexural strength after 90 days than seawater mixtures by 21.42% and 16.78%, respectively. Figure (25) shows that 7%MK with 20%FA, 30%FA, and 40%FA mixes had a greater flexural strength after 90 days than saltwater combinations by 37.32%, 61.42%, and 16.78%, respectively. Figure (26) examines the flexural strength of mixes having different proportions of fly ash such as 20%, 30%, 40% FA, and 30%FA at 90 days. The use of mineral admixtures to increase flexural strength, as described in [29].

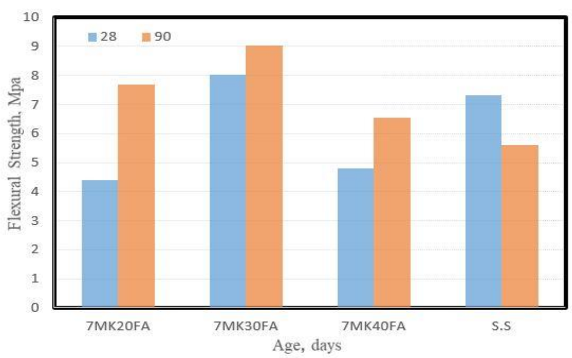

Figure 25- Flexural strength for seawater mixes using 7%metakaolin and fly ash as mineral admixtures

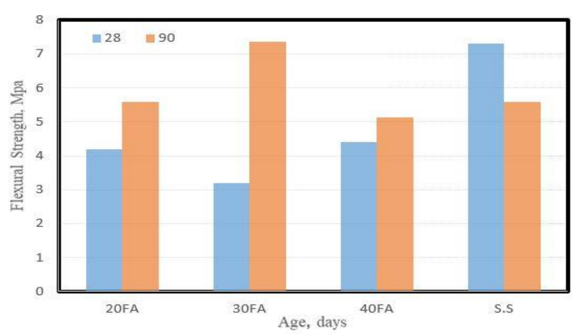

Fig 26: Flexural strength for seawater mixes using different percentages of fly ash as mineral admixtures and seawater mix

5. Conclusions

1- Using sea water in mixing lowered consistency when compared to fresh water.

2- Mineral admixtures have the greatest influence on the workability of sea water concrete at 3%MK with 30%FA or 40%FA.

3- When compared to fresh water mix, the compressive strength of sea water mix improves by 24.25% at early ages. However, the compressive strength has decreased by 15.78% after 180 days.

4- The mineral admixtures increased the compressive strength of the sea water mixes after 90 days, with an increase of 38.87% for 7%MK and 30%FA compared to the compressive strength of the control sea water mix.

5- The use of sea water in concrete develops tensile and flexural strength at an early age, however there is a decline compared to fresh water combinations at 180 days by 18.5%, 29.7%.

6- The presence of mineral additive increases the tensile and flexural strength of sea water concrete at 90 days for 7%MK and 30%FA with an increase 59.6%, 61.4% respectively.

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