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Short-Term Effect on Mechanical Strength and Water Absorption of Concrete Containing Palm Oil Fuel Ash Exposed to Chloride Solution

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Abstract: This research emphasises the short-term effects of mechanical strength and water absorption of concrete containing palm oil fuel ash (POFA) that is exposed to chloride solution compared to concrete exposed to normal water. The replacement of cement by POFA in concrete is one of the efforts to produce green concrete as well as to maintain environmental sustainability as the POFA always disposed off without any positive benefits. The POFA obtained from the mill was dried, sieved using 300 μm siever and refined using ball mill for two hours. The volume of 10%, 20% and 30% of cement were replaced by POFA with the same level of replacement. Hardened concretes were cured under normal water and 3.5% chloride solution until 28 days, respectively. Fresh concretes were tested by slump test while hardened concrete underwent compressive strength test, flexural strength test and water absorption test at the age of 7 and 28 days. By using the same w/b ratio, it was found that concrete workability and performances decreased with the increases of POFA replacement for both types of exposure. For short term effects, control concrete that exposed to chloride solution was found to have the highest chloride exposure with no deterioration as it achieved the highest compressive and flexural strength than control concrete exposed to normal water. The lowest percentage of water absorption also recorded by control concrete exposed to chloride solution. The overall results of the research found that increment of the percentage of POFA replacement with cement in concrete resulted in consistently decreased of compressive and flexural strength within 7 and 28 days. However, concrete containing 10% replacement of POFA was observed as having the potential as it achieved more than 80% compressive and flexural strength compared to control concrete exposed to water and chloride solution. Furthermore, it had a good percentage of water absorption.

Keywords: Palm oil fuel ash, chloride exposure, compressive strength, water absorption, flexural strength

1. Introduction

Concrete is one of the dominant building materials in construction. Various studies have been conducted to develop alternative materials for industrial construction with good strength, durability and permeability characteristics. Besides, various types of concrete have different advantages and are resistant to aggressive environmental attacks (Aitcin, 2000). One of the common drawbacks of concrete is the chloride attack, i.e., usually contained in seawater that results in the formation of Friedel salts due to the reaction of calcium, alumina, chloride and water (Zhang et al., 2019). The formation of these salts can affect the durability of the reinforced concrete as it would corrode the reinforcement. If high calcium content is found in concrete mixing, then concrete can potentially produce high salt when exposed to chloride. On the environmental side, concrete also could harm the environment, especially in the production of carbon dioxide (Deng et al., 2014).

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Palm oil fuel ash (POFA) is one of the pozzolan substances that can be used as a semi-cement substitute for its high chemistry composition of silica and alumina. Previous studies have noted the presence of POFA in concrete can help it to build better resistance to the penetration of chloride into concrete when a percentage of POFA in a concrete mix in the range of 15 to 35% is used (Sanawung et al., 2017). Besides, previous studies using approximately 20% of POFA have proven that the resistance to chloride decomposition is lower than using Portland cement completely when tested with the Rapid Chloride Penetration Test (RCPT) (Bamaga et al., 2010).

Studies on the commercialisation of further use of POFA in concrete should be carried out to ensure the effectiveness of this alternative. On the other hand, if these alternatives can be commercialised and used consistently, it can help in reducing environmental pollution levels while ensuring the health and well-being of the surroundings. The increase in productivity of the palm oil industry is seen to be economically advantageous. However, the impact of this productivity should be addressed as much as possible to ensure environmental sustainability.

2. Concrete Containing POFA

The use of POFA in concrete mixing can help in solving environmental problems. However, the use of POFA in concrete mixes is still non-commercial due to its lack of value. Efforts should be made to improve and enhance the value of POFA usages as a partial replacement of cement in concrete.

2.1 Pozzolanic Reaction

Pozzolanic activity is a reaction between active ingredients such as pozzolana, lime and water which pozzolana containing high levels of silica and alumina, that reacts with calcium hydroxide (CH) in the presence of water at room temperature (Franco, 2019). The pozzolanic activity would take a long time, which results in strong cement bonding. Hardening of this cement is permanent. Free calcium is essential for initiating and continuing the pozzolanic process (Cherian & Arnepalli, 2015).

2.2 Aggressive Chloride Environment

Concrete is potentially exposed to hazardous chemicals that may be found in groundwater, industrial waste and seawater. Among the hazardous substances in wet or damp compositions is carbon dioxide for carbonation, oxygen for staining, chloride that promotes drying and sulfate that can cause the growth of cement and alkali, which can expand the aggregation. The most dangerous chemicals that can affect the durability of concrete are chloride and sulfate. Concrete that is exposed to these two chemicals has the potential to cause micro-fractures. This problem is due to the decomposition of chloride that causes the formation of Friedel salts and changes in the composition of the corrosion, which causes the cracking to concrete (Imbin et al., 2013).

In the seawater environment, concrete resistance is based on the degree of corrosion that occurs on reinforced steel. There are two possible mechanisms for concrete exposed to seawater, i.e., chloride deposition to the position of reinforced steel and the level of reinforcement of steel to seawater. In addition to concrete that is not directly exposed to seawater, it is also potentially exposed to evaporated air containing chlorides in the seawater environment, that occurs in the spray zone (waves) where the wind carries the chloride through the air (Costa & Appleton, 2001).

2.3 Palm Oil Fuel Ash (POFA)

Palm oil fuel ash is a waste product of kernels, fibres and bunches in the manufacturing industry to produce energy as an effort to extract palm oil. After the combustion process, it was found that 5% of the palm oil was derived from the overall weight of the material burned. The ash produced from these burns would appear grey to black in colour (Hamada et al., 2019). Table 1 below describes the previous research chemical composition of POFA. The dominant chemical composition affecting POFA is silica, followed by calcium oxide, magnesium oxide, kalium oxide and lastly by aluminium oxide and ferric oxide (Khalid et al., 2018).

Table 1 - Previous chemical composition of POFA

Chemical Composition (%)	Zeyad *et al.*, 2013	Sanawung *et al.*, 2017	Khalid *et al.*, 2018
Silicon Dioxide (SiO_2)	51.18	55.40	53.30
Aluminium Oxide (Al_2O_3)	4.61	9.1	1.90
Ferric Oxide(Fe_2O_3)	3.42	5.5	1.90
Calcium Oxide (CaO)	6.93	12.4	9.20
Magnesium Oxide (MgO)	0.81	4.6	4.10
Sulphur Trioxide (SO_3)	0.19	2.3	-
Sodium Oxide (Na_2O)	0.056	-	-

Potassium Oxide(K_2O)	5.52	-	6.10
Loss of Ignition (LOI)	21.6	7.9	-

2.4 Properties of Concrete Containing POFA

The compressive strength of concrete containing POFA is based on the fineness and percentage of cement replacement. The use of POFA in concrete does not alter the elastic modulus of concrete. Concrete containing POFA has about 10% to 30% reduced concrete shrinkage value by 10% -17% compared to concrete using Portland cement. Also, it can help improve the water's permeability depending on the percentage of concrete and concrete age (Tanchirapat & Jaturapitakkul, 2010).

POFA can be used as a partial replacement of cement in concrete without degradation of compressive strength at a mature age. The rate of decomposition of chloride to concrete decreases when using palm oil fuel ash (Bamaga *et al.*, 2011). The addition of POFA would cause the workability and the hardening rate of the concrete to decrease due to the decrement in hydration heat. The hardening rate slows down is due to the size of the POFA particles, and it absorbs more water that slows down the hydration process. At the extension of times, silicon dioxide (SiO_2) reacts with calcium hydroxide (CH) and produces calcium silicate hydrate that enhances bonding between aggregates and thereby increasing the strength of concrete. Tensile strength decreases when concrete is mixed with POFA; however, it can be overcome by the use of reinforced steel (Thomas *et al.*, 2017).

POFA acts as fillers in the early stages of concrete fixation. However, at an extension age, POFA begins to react with the hydration process to become solid concrete. There is an increase in resistance to chloride and sulfate increased with an increase of 20% in a concrete mix containing POFA (Bamaga *et al.*, 2010).

3. Materials and Methods

The entire research was conducted in relevant laboratories, i.e., Materials Engineering Laboratory, Advanced Materials Laboratory and Jamilus Research Center at Universiti Tun Hussein Onn Malaysia.

3.1 Material Preparation

The materials that have been used for this research are Portland cement, coarse and fine aggregates, water, palm oil fuel ash (POFA) and 3.5% chloride solution. The POFA was further sieved passing through 300 µm and 2 hours of refinement in the ball mill. In this research, POFA containing of total SiO_2+Al_2O_3+Fe_2O_3 between 50% to 70% and its loss of ignition (LOI) is between 6% to 12 %, refer to ASTM C618, POFA in this research is classified as in between class C and F. The POFA is used as a partial cement replacement, while 3.5% chloride solution is used as a curing solution for specimens. Table 2 to Fig 3 below describes the properties, chemical composition and sieve analysis of the material that have been used for this research.

Table 2 - Properties of material

Material	Type/Properties	Density (kg/m^3)	Specific surface area (m^2/g)	Particle size mean (µm)
Cement	Normal Portland Cement	1164	1.16	16.4
Palm Oil Fuel Ash	POFA passing sieve 300µm and refined for 2 hours in ball mill	564	0.87	35.3
Coarse Aggregate	Passing sieve 14 mm	-	-	-
Fine Aggregate	Passing sieve 5mm	-	-	-
Water	Tap Water	-		-

Table 3 - Chemical composition of materials

Chemical composition	OPC %	POFA %
Silicon Dioxide (SiO_2)	20.57	45.5
Aluminium Oxide (Al_2O_3)	4.93	11.7
Ferric Oxide (Fe_2O_3)	3.8	4.5
Calcium Oxide (CaO)	63.85	9
Magnesium Oxide (MgO)	0.9	5
Sulphur Trioxide (SO_3)	2.4	2.6
Sodium Oxide (Na_2O)	0.05	0.4
Potassium Oxide (K_2O)	0.9	5
Phosphorus Pent Oxide (P_2O_5)	0.12	6
Loss of Ignition (LOI)	2.48	10.3
SiO_2+ Al_2O_3+ Fe_2O_3	29.3	61.7

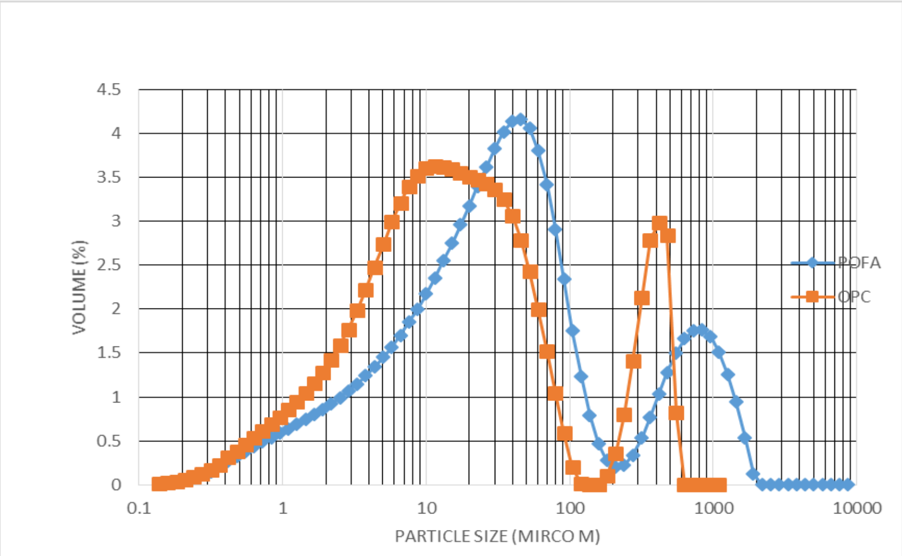


Fig. 1 - Particle size analysis of OPC and POFA

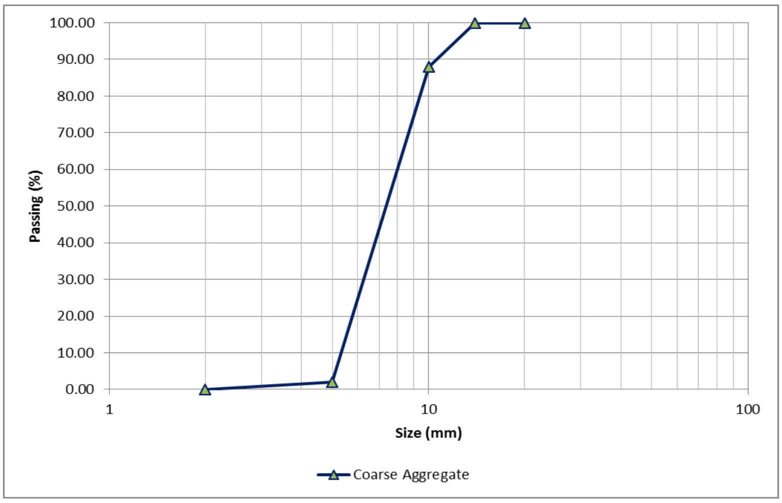


Fig. 2 - Sieve analysis of coarse aggregate

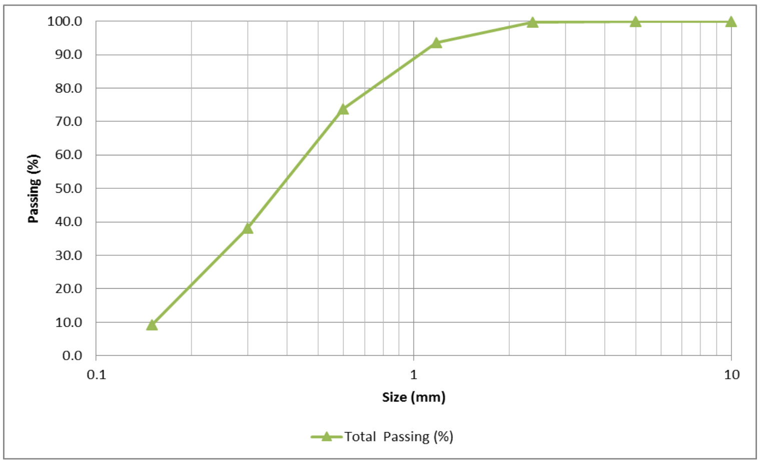


Fig. 3 - Sieve analysis of fine aggregate

3.2 Specimens Preparation

Total of 144 specimens consisting of 96 specimens of 100 mm × 100 mm × 100 mm cube and 48 of 500 mm × 100 mm × 100 mm prism specimens were produced. The grade 30 mixture design was used in this research. The volume of cement has been replaced by the same volume of POFA to maintain the volume of total binder in concrete. The replacement of cement has been made by 10%, 20% and 30% of volume of POFA. The water-cement ratio for fresh mixes of 0.0558m³ was 0.64 to achieve the ranges of target slump.

Table 4 - Design mix proportions

Term	Replacement	OPC (kg/m³)	POFA (kg/m³)	Coarse Aggregate (kg/m³)	Fine Aggregate (kg/m³)	Water (kg/m³)
P0	0%	390	0	1170	625	250
P10	10%	351	19	1170	625	250
P20	20%	312	38	1170	625	250
P30	30%	273	57	1170	625	250

The curing method used was full immersion using 3.5% chloride solution and water. The curing process is up to the concrete age of 7 and 28 days. After that, the concrete specimen was ready for testing.

3.3 Testing

Fresh concrete was tested using a slump test to identify the workability of the concrete after it is constantly mixed. The slump value of control concrete was ensured to be in the range of 75 ± 25 mm. All of mixes types were subjected to slump test. Workability test was in accordance with the BS EN 12350-2: 2019.

All fresh specimens were left in formwork for 24 hours before being demolded and then subjected to curing process using water and chloride solution. Specimens that achieved curing ages of 7 and 28 days were tested by compressive, flexural and water absorption. Density test of hardened concrete was conducted when concrete achieved 28 days. All of the test procedures were following the BS EN 12390-3:2019, BS EN 12390-5: 2019 and BS 1881-122: 2011.

4. Results and Discussions

4.1 Workability of Fresh Concrete

The result of the slump test is shown as in Fig 4 below. The slump value of the control concrete is in the 75 ± 25 mm range with a slump value of 68 mm, which is the workability accepted for concrete work. As increment of percentage POFA replacement, a decrease in workability of 30.8%, 47.1% and 69.1% was recorded by P10, P20 and P30. From the findings of Zeyad et al. (2013, 2016 & 2017), POFAs that have a larger particle size and are not heat-treated contain higher values of carbon and loss of ignition (LOI) than cement. Zeyad et al. also found that POFAs with smaller particle sizes than cement enhance the workability of fresh concrete. The carbon content of concrete can also affect the workability of a fresh concrete. The low carbon content of concrete reduces water demand and increases the workability of fresh concrete. Ul Islam (2015) used POFA particle size smaller than cement in his research and much smaller than the POFA particle size in this research. Ul Islam also did not treat POFA with heat in his research. Therefore, the carbon and LOI content in the POFA of the research is higher than cement. Ul Islam uses more water reducers in every mixture to improve concrete workability. Ul Islam found that the use of high and untreated POFA requires more water reducers to improve the workability of fresh concrete containing POFA. This is because untreated POFA has a high LOI value, greater use of the POFA will increase the LOI content of the concrete and resulting in greater water absorption and porosity of the concrete compared to the control concrete.

In this research, the POFA used was not heat-treated and had a larger particle size than cement. The LOI content of the POFA used was also higher than that of cement. Therefore, the POFA used has a higher carbon value than cement. The high carbon content in concrete causes an increase in water demand and causes a decrease in the workability of fresh concrete. Excessive use of water reducer in each mixture is required to obtain better workability.

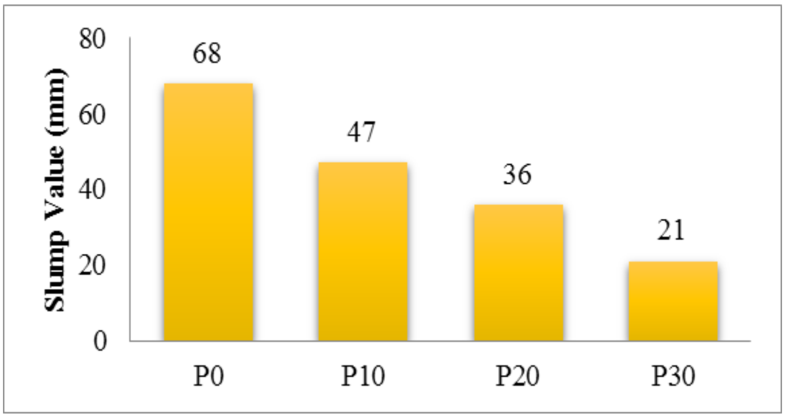


Fig. 4 - Workability of concrete containing POFA

4.2 Density of Hardened Concrete

The density test was conducted when the specimens achieved curing ages of 28 days. It was found that concrete densities for both exposures at 28 days resulted in a consistently decreasing density with an increment of POFA replacement. Total concrete densities decreased when the replacement of POFA was made because POFA has lesser particles density compare to normal cement particles density (Sofri *et al.*, 2015). Consequently, the replacement of POFA by volume would result in a lower total density of concrete than control concrete.

P0 that exposed to chloride solution has the highest density amongst all the specimens. This data shows that an increment of density happened within the concrete. P0 has the highest calcium content among all specimens, which lead to higher production of salt in concrete when exposed to chloride. It may be due to calcium hydroxide (CH) from cement hydration reacts with chloride and free alumina in chloride solution and produces Friedel salt that fills the cavity of the concrete and tends to increase the density of the concrete.

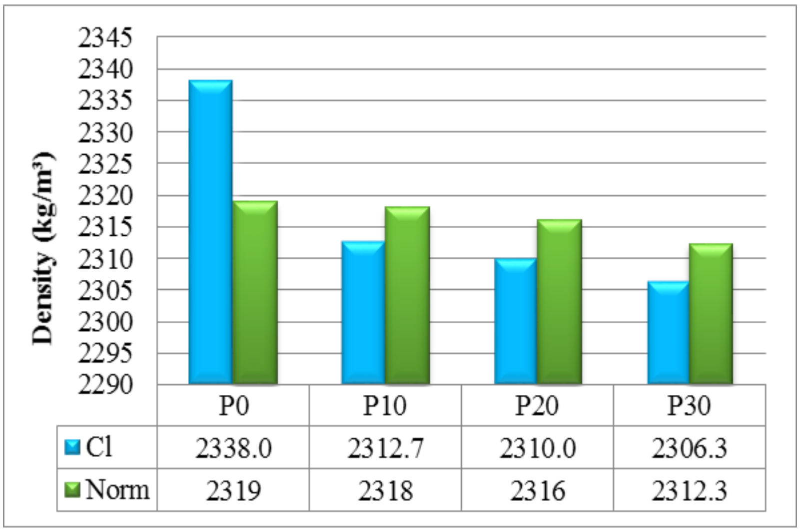


Fig. 5 - Density of concrete for both exposures

4.3 Compressive Strength

In Fig 6, for normal water exposure, the highest reading was recorded on P0 concrete where it was the control concrete with a reading of 30.2 MPa and P10 concrete reached 98% of the control concrete's compressive strength at 7 days. Concrete containing POFA has experienced a reduction in cement content that has led to a reduction in the production of calcium silicate hydrate (CSH) in the early state of concrete strengthening (Tangchirapat & Jaturapitakkul, 2010). This statement indicated that there was a constant declination of compressive strength when the increment of POFA replacement was made. At 28 days, the positions of P0, P10, P20 and P30 were still the same where P0 recorded the highest compressive strength.

For chloride exposure specimens, the compressive strength of P0 at 7 days was 36 MPa, which was the highest among the four specimens. P10, P20 and P30 recorded lower compressive strength compared to P0 by 25%, 32.2% and 45.8%, respectively. At 28 days, the results of the compressive strength show the same pattern as compressive strength at 7 days, which P0 still leads. The compressive strength pattern results consistently in line with the density test, where higher density produces high compressive strength.

It can be seen that at 7 and 28 days, the P0 concrete exposed to chloride solution reached the highest compressive strength among all specimens. P0 compressive strength increased because of the formation of Friedel salts in P0 concrete that involves the exchange of ions between the hydroxide ions that interact with calcium and the chloride ions, which are the breakdown of sodium chloride (Suryavanshi *et al.*, 1996). Concrete containing POFA recorded lower compressive strength compared to P0 due to lower amount of calcium content, which led to less formation of salt when exposed to chloride and lesser formation of CH during hydration reactions due to lower calcium content. Thus, it leads to lower calcium silicate hydrate in concrete exposed to normal water. Concrete containing POFA is potential to have greater compressive strength due to pozzolanic reaction after 28 days of curing (Zeyad *et al.*, 2016).

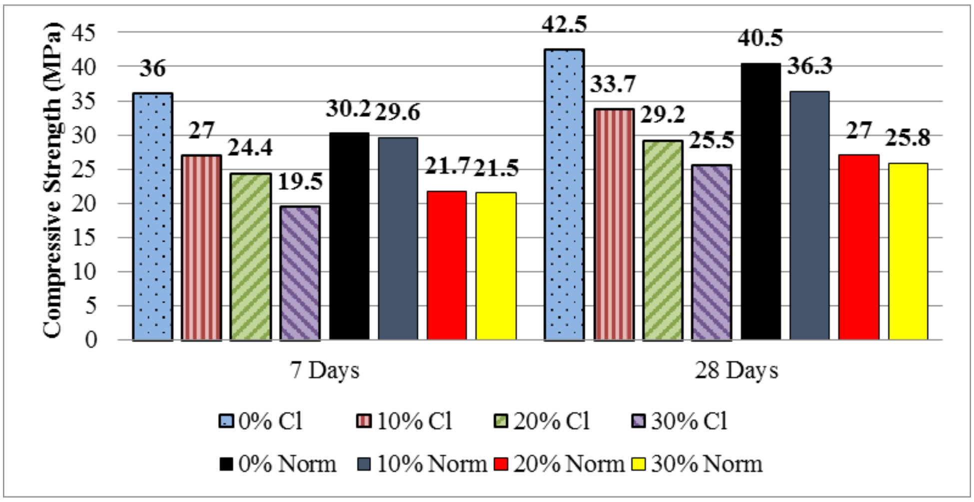


Fig. 6 - Compressive strength of concrete for both exposures

4.4 Flexural Strength

Fig 7 pattern shows that the replacement of POFA caused a decrease in the flexural strength of concrete for both exposures. This decrease is seen in a consistent state where it is parallel with a declination of compressive strength. On day 28, P0 exposed to chloride still recorded higher flexural strength values compared to other concrete specimens.

Based on a research conducted by Sofri *et al.* (2015), the decrease in flexural strength occurred consistently with the increment of a POFA replacement in concrete exposed to water. Therefore, the 9.9 MPa value obtained from P30 exposed to normal water should not occur.

P20 exposed to chloride showed slightly higher flexural strength values compared to P10. Altwair *et al.* (2013) conducted a research, where concrete containing POFA replacement exposed to chloride solution recorded the highest flexural strength value compared to control specimen on day 88. They proved that pozzolanic processes occur slowly over a period of time.

It can be concluded that P0 exposed to chloride recorded the highest flexural strength readings on days 7 and 28 compared to all other concrete specimens. The highest flexural strength mechanism focuses on the reaction of Friedel salt formation, which gives the concrete a better strength in 7 days, but believed that the strength would begin to decline after concrete age reached 28 days.

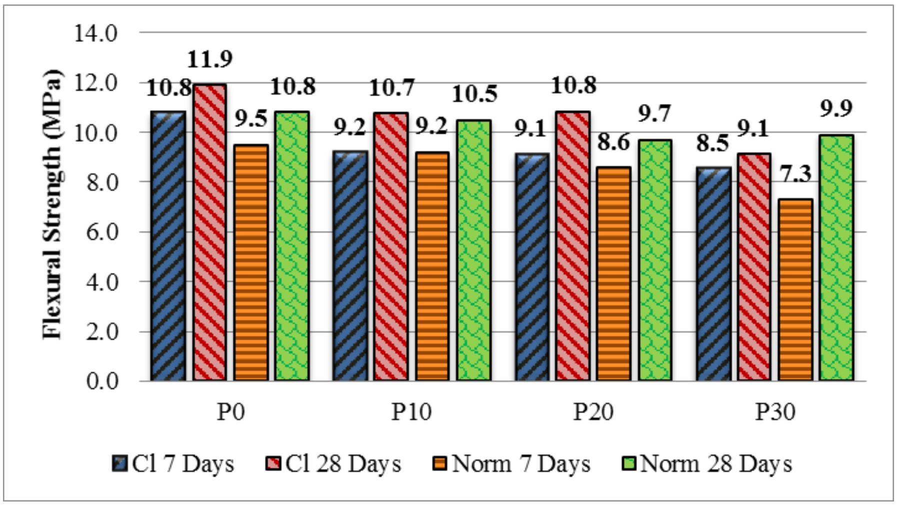
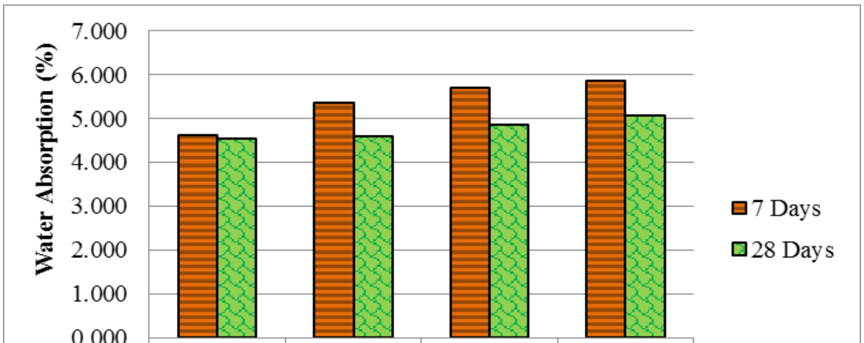


Fig. 7 - Flexural strength of concrete in both exposures

4.5 Water Absorption

Figs 8 and 9 show the water absorption test results. Water absorption tests were performed on concrete specimens of 100 mm × 100 mm × 100 mm at 7 and 28 days. The cubes were dried using an oven and cured in water for 24 hours and then analysed using differences of weight method.



	P0	P10	P20	P30
7 Days	4.631	5.369	5.713	5.869
28 Days	4.547	4.593	4.850	5.080

Fig. 8 - Water absorption in 7 and 28 days in the water

Water absorption patterns appear to decrease consistently at 7 and 28 days with the increment of POFA replacement in specimens exposed to water. Concrete at 28 days have lower water absorption compared to concrete at 7 days because continuous curing of the concrete aided the hydration process of the concrete as well as pozzolanic reaction to form C-S-H in the POFA-blended mixes and these helped to reduce the pores within the concrete (Ul Islam, 2015). The lowest recorded water absorption held by P0 for both durations. P30 recorded the highest water absorption amongst all of the specimens. Based on Sofri *et al.* (2015) POFA absorbs water at high rates during the early stage of concrete hardening. High water absorption in concrete containing POFA could be due to the presence of voids in the concrete which allowed greater absorption of external water (Ul Islam, 2015).

The water absorption patterns of specimens exposed to chloride solution are seen to consistently decrease too, as specimens exposed to water for both durations. P30 experienced the most significant decrease in water absorption. The lowest of recorded water absorption of specimens exposed to chloride held by P0.

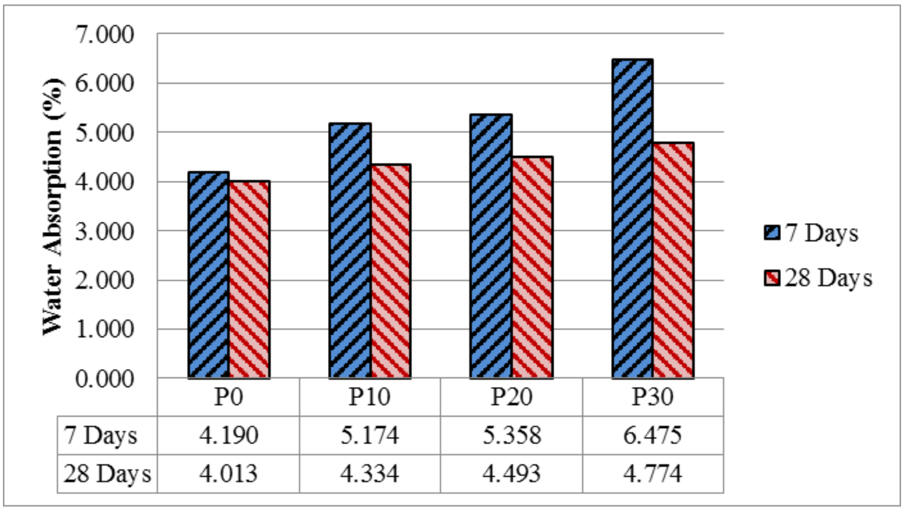


Fig. 9 - Water absorption in 7 and 28 days in chloride

A comparison of the water absorption of concrete exposed to chloride and water throughout 7 and 28 days has been made. On day 7, the highest percentage of water absorption was at P30 concrete exposed to chloride solution while the lowest percentage of water absorption was P0 concrete exposed to chloride solution. On day 28, the highest percentage of water infiltration was P30 exposed to normal water while the lowest percentage of water infiltration was maintained by P0 exposed to chloride. It can be seen that a drastic declination of water absorption occurred in specimens exposed to chloride, especially P10, P20 and P30. At 28 days, the pozzolanic reaction caused by the presence of POFA producing calcium silicate hydrate (CSH) filled the cavity in the concrete causing a decrease in the percentage of water absorption (Suryavanshi *et al.*, 1996).

4.6 Influences of Density and Water Absorption to Compressive and Flexural Strength

Reduction of the concrete density affects the compressive strength and the flexural strength of the concrete. From the perspective of concrete exposed to chloride solution, P0 exhibits the highest compressive strength and flexural strength compared to other concrete, either exposed to chloride or water. When the density of P10 exposed to chloride solution, it begins to decrease compared to P10 exposed to water, which the value of compressive and flexural strength P10 exposed to chloride solution begins to decrease. The concrete density plays an important role in producing concrete strength. The higher the concrete density, the higher the strength obtained.

For both types of exposures, it was found that the percentage of water absorption that occurred for both periods of 7 and 28 days increased when there was an increase in POFA replacement in the concrete. As the water absorption increases, it is found that there is a decrease in compressive and flexural strength of concrete. However, when the 28th day for the concrete exposed to the chloride solution was reached, the difference in the percentage of water absorption for the concrete exposed to the chloride became smaller, and this could be attributed to the flexural strength narrowing the gap with the P0 concrete exposed to the chloride.

5. Conclusions

In conclusion, concrete mixed with POFA caused a decrease in workability in line with the increment of POFA replacement with cement. The decrease in workability is because of POFA has a high carbon and LOI value, which indicates that the water absorption rate is high. The light properties of POFA also affected the concrete density, which lowers the density value when the increment of POFA replacement has been made. The compressive and flexural strength found to be decreased consistently as well since the POFA replacement percentage was increased. The opposite phenomenon occurred for water absorption, which water absorption started to increase when the increment of POFA replacement has been made. It is found that P0 exposed to chloride solution stated the highest value for all types of tests, i.e., density, compressive strength, flexural strength test and water absorption. The high value in density, compressive strength, flexural strength and water absorption can be attributed to the mechanism of chloride attack that has taken place on the concrete. Cement hydration produces calcium silicate hydrate (CSH) and calcium hydroxide (CH). Then, chloride reacts with the calcium hydroxide (CH) in the process of forming Friedel salts, which result in an increase of the initial strength of the concrete at 7 and 28 days. Also, other specimens exposed to chloride solution other than P0 are likely to have less chloride attack due to the reduction in cement used that affects the production of calcium hydroxide (CH) for the reaction of formation of Friedel salt to take action. P10 was found to have the potential as it achieved more than 80% of the control's compressive strength within 28 days for both types of exposure. It can be observed that the exposure to chloride did not have a significant impact on the mechanical properties of the POFA concrete compared to the control concrete exposed to the chloride, which has received a drastic chloride attack. In the end, it has slightly increased value of POFA usage in concrete to produce better green concretes.

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