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Abstract: The present study investigated the compressive strength of periwinkle shell ash (PSA) blended cement concrete soaked in crude oil polluted water and portable water (control) media. Concrete cubes were prepared at 1:2:4 mix ratio by weight of cement with varying percentages of PSA replacement (0, 5, 10, 15 and 20%). Specimens were prepared from mix designed strength of 25 N/mm². One hundred and twenty (120) samples of concrete cubes were cast. Sixty (60) set of samples were each cured in potable water and crude oil contaminated water. The concrete cubes were crushed for compressive strength at curing ages of 7, 14, 21 and 28 days, respectively. The results indicated that different curing media led to significant changes in the compressive strengths of concrete made from PSA blended with Ordinary Portland Cement (OPC). The control specimen (0% PSA) had the highest value at all ages in both media. The rate of strength development is significantly low in the crude oil contaminated water medium. The compressive strength decreased with increased percentage PSA replacement and increased with increasing age of curing for all level of PSA replacement. The two way analysis of variance showed that variations in PSA/cement content and curing age had significant effects on the compressive strength of concrete for samples cured in both control (portable water) and crude oil polluted water media ($p < 0.05$).

Keywords: Analysis of variance, crude oil, periwinkle shell ash, potable water

Introduction

The effect of crude oil and crude oil related chemicals on concrete structures mainly within the coastal areas of the Niger Delta region of Nigeria has continued unabated. The situation is worse especially with the incessant attacks on crude oil pipelines coupled with activities of multinationals engaged in crude oil drilling along the coastal regions more intensively in the Niger Delta States of Nigeria. The need to evaluate the enormity of their effects on engineering infrastructure such as concrete structures has become necessary. Jasim and Jawad (2010) studied the effect of oil on strength of normal and high performance concrete and reported that the loss in mechanical properties (compressive and split tensile strengths) resulting from exposure to oil was relatively smaller for High Performance Concrete (HPC) compared with Normal Strength Concrete (NSC).

Crude oil is a compressive strength inhibitor in the production of concrete thus the higher the percentages of crude oil present in fine aggregates, the lower the compressive strengths (Osugi and Nwankwo, 2015). The use of oil contaminated sand in concreting should be avoided as much as possible because the higher the percentages of diesel oil and bitumen in sand, the lower the concrete compressive strength (Ayininiola, 2009). Concrete is highly susceptible to different level of aggressiveness in the solutions of crude oil concentrations. When in contact with crude oil, it causes deterioration as well as slow strength development (Ejeh and Uche, 2009; Diab, 2011; Abednego *et al.*, 2015). Corrosion rate is higher in undiluted crude oil than in crude oil. However, the mix of crude oil and water causes as much reductions in compressive strengths as are visible in the ratio 23:13 percent (Ejeh and Uche, 2009). Generally, major engineering research has shown that deterioration of reinforced concrete in the marine and offshore environment is more severe than in any other environment and this has led to more laboratory and field investigations on the causes, effects and remedies of concrete deterioration in similar environment (Daka and Ekweozor, 2004; Environmental Protection Agency EPA, 2006; Jonnesari and Moshref, 2005).

Meaningful efforts are being adopted globally on the use of pozzolanic materials to improve the strength and durability performance of concrete. The commonly utilized

pozzolans have been fly ash, silica fume, metakaolin and blast furnace slag. In the quest for more cost effective and environmentally friendly materials, there has been a growing interest in the use of agricultural wastes as pozzolans. Some of the pozzolans of agricultural origin include sawdust ash (Elinwa and Mahmood, 2002; Udoeyo and Dashibil, 2002; Elinwa and Ejeh, 2004), rice husk ash (Zhang and Malhotra, 1996; Khan *et al.*, 2012; Reddy *et al.*, 2013; Le *et al.*, 2016), corn cob ash (Adesanya and Raheem, 2009; Olafusi and Olutoge, 2012; Kamauet *et al.*, 2016), palm oil fuel ash (Tangchirapatet *et al.*, 2009; Bamagaet *et al.*, 2013; Oyejobiet *et al.*, 2015) and periwinkle shell ash (Dahunsi and Bamisaye, 2002; Job *et al.*, 2009; Koffi, 2008; Olusola and Umoh, 2012).

Periwinkle Shell Ash (PSA) is obtained by burning periwinkle shell which is the by-product of periwinkle. Previous investigation on the incorporation of PSA in concrete production (Koffi, 2008; Dahunsi and Bamisaye, 2002; Olusola and Umoh, 2012) focused on its effect on the concrete compressive strength soaked in portable water medium. Inasmuch as pozzolanic reaction depends on the liberation of calcium hydroxide from cement hydration, the effect becomes much more beneficial to compressive strength development of concrete at later ages (Olusola and Umoh, 2012). From the foregoing, studies and literature abound on the effect of crude oil on the strength properties of cement based concrete structures as well as the effect of pozzolans such as PSA, PFA, RHA, CCA and SDA on strength properties of concrete. However, little or few studies are available on the effect of contaminated environment on strength properties of concrete produced from cement mixed with supplementary pozzolans. Therefore, the aim of this research is to investigate the compressive strength development of PSA blended cement concrete in simulated (crude oil contaminated water) and control (portable water) environment. The objective of this study is to evaluate the effect of crude oil contaminated environment on the compressive strength of PSA blended cement concrete cured up to 28 days and based on minimum structural design strength of 25 N/mm². The simulated medium represents a crude oil spill environment. It will help to assess the level of deterioration from strength development, strength reduction and design strength attained in comparison with the control medium. The outcome is proffering

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recommendation in consideration for its use in coastal areas where oil spillage is predominant.

Materials and Methods

Materials

The periwinkle shells used for this study were obtained from a dump site at IkotEbido Oku, Uyo, AkwaIbom State, Nigeria. The periwinkle shells were thoroughly washed, air dried in an open space before calcined (oven kilned) to a temperature of 1000°C. The calcined shell was brought out of the oven, allowed to cool and grinded to powdered form. It was sieved through BS sieve No 200 and stored in a sealed polythene bag. The cement used in this research was sourced from an open market at a shop in MkpatisEninL.G.A. X-Ray Fluorescence,XRF test was done on OPC and PSA specimen to determine their oxide composition (Table 1). The fine aggregate (sand) used in this study was sourced from a river bed in MkpatisEnin, AkwaIbom State, Nigeria, passing 4.75 mm sieve. The sand belongs to grading zone 2 according to the grading limits for fine aggregates (British Standard Institution, 1992) with a fineness modulus of 3.33 and specific gravity of 2.4. The water used throughout the duration of the research was portable tap water within AkwaIbom State University campus. The coarse aggregate was crushed granite of maximum size 20 mm with specific gravity of 2.65. The crude oil used for contamination was obtained from one of the oil fields within the locality. Two separate curing media considered in this study are the crude oil contaminated medium and the control medium. The crude oil contaminated medium was prepared in concentration of diluted 50:50% crude oil/water mix and the control medium (100% portable water) is based on zero contamination level. The crude oil/water mix is to represent oil spill/polluted environment which is common in the coastal regions of Niger Delta States, Nigeria.

Table 1: Chemical composition of Periwinkle shell ash and ordinary Portland cement

Elemental Oxides	Weight (%) PSA	Weight (%) OPC
CaO	42.32	61.14
MgO	42.32	1.35
K ₂ O	0.11	0.48
SiO ₂	29.54	21.40
SO ₃	0.31	2.53
Na ₂ O	0.43	0.24
Al ₂ O ₃	11.6	5.03
Fe ₂ O ₃	5.13	4.40
P ₂ O ₅	0.01	-
TiO ₂	0.042	-
LOI	8.5	1.29

Methods

Design mix

This is the process of selecting suitable ingredients and determining the specifiable characteristics of concrete mixture. Concrete mix design of 1:2:4 at water cement ratio of 0.6 was adopted and batched in weight in accordance with British Standards. The study was carried out using target mean strength of grade 25 N/mm². The concrete cubes were cured by both complete portable water, PW immersion taken as control medium and crude oil contaminated water, CCW regarded as simulated medium for 7, 14, 21 and 28 days curing. Periwinkle shell ash was used as cement replacement in concrete production. The levels of replacement for cement with PSA were at 0, 5, 10, 15 and 20 percent. A total of one hundred and twenty (120) samples of concrete cubes were cast, cured and tested. For each curing period, three (3) cubes

were produced and the results were recorded, the average value was computed and used.

Slump test

The slump test is a measure of the consistency or workability of fresh concrete. The test was carried out to determine the effect of PSA replacement on the workability of PSA-OPC blended concrete. The test was conducted in accordance with BS EN 12350: Part 2 (2009) Specifications.

Compressive strength test

Two sets of 60 cubes were cast and cured separately in two different media; control media (portable water) and simulated media (50:50% crude oil/water mix; i.e., crude oil contaminated water). They include concrete mixes 0 % PSA (cement based) and with replacement of 5, 10, 15 and 20% of PSA. Three cubes were tested at the ages of 7, 14, 21 and 28 days of the different mixes respectively. The compressive strength test was carried out on the hardened cured concrete cubes. The cubes were tested using compression machine. The test was conducted in accordance with BS EN 12390, Part 3 (2009) specifications.

Results and Discussion

Physical properties of materials

The specific gravity of PSA, Ordinary Portland Cement, sand (fine aggregate) and coarse aggregate were found to be 2.56, 3.13, 2.4 and 2.65, respectively. The particles size distribution of coarse and fine aggregate are shown in Tables 2 and 3. The specific gravity of PSA and cement implies that PSA is lighter than cement and more volume of PSA will be required for replacing equal weight of cement in concrete.

Table 2: Sieve analysis for fine aggregate

Sieve (mm)	Weight of material retained (g)	Percentage of material retained (%)	Cumulative percentage of material retained (%)	Percentage passing (%)
9.5	0	0	0	100
4.75	14	2.8	2.8	97.2
2.36	84	16.8	19.6	80.4
1.18	180.5	36.1	55.7	44.3
0.6	175	35	90.7	9.3
0.3	37	7.4	98.1	1.9
0.15	9	1.8	99.9	0.1
Total	499.5	99.9	—	—

Table 3: Sieve analysis for coarse aggregate

Sieve (mm)	Weight of material retained (g)	Percentage of material retained (%)	Cumulative percentage of material retained (%)	Percentage passing (%)
38.1	0	0	0	100
20	235	15.67	15.67	84.33
14	495	33	48.67	51.33
9.5	676.5	45.1	93.77	6.23
4.75	81.5	5.43	99.2	0.8
2.36	11	0.73	99.93	0.07
Total	1499	99.93	—	—

Workability of PSA-OPC Blended Concrete

The results of the slump test carried out on the fresh concrete with varying percentage of PSA as cement replacement are presented in Table 4. The results also show that the slump decreases with increase in the amount of PSA used, which indicates that more water is required to maintain the same consistency as PSA content increases. This was consistent with the finding of Olusola and Umoh (2012) who reported a decrease in workability with an increase in PSA replacement. For instance at 0, 5, 10, 15 and 20% PSA content, the slump values were 29, 28, 25, 23 and 21 mm, respectively. This

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implies that PSA absorbs more water than ordinary Portland cement in concrete.

Table 4: Slump test result of PSA-OPC blended concrete

Percentage replacement (%)	Slump(mm)
0	29
5	28
10	25
15	23
20	21

Compressive strength

Effect of periwinkle shell ash content on the compressive strength of specimens cured in portable water and crude oil contaminated water

The variation of compressive strength of periwinkle shell ash, PSA blended cement concrete with PSA content cured for 7, 14, 21 and 28 days in control media (portable water) and simulated media (crude oil contaminated water) respectively, are presented in Figs. 1 to 4. The results show that at first the compressive strength of each of the replacement of PSA is low compared with that of the higher values obtained from cement based (0% PSA) at 7, 14, 21 and 28 curing age, respectively. Generally, the compressive strength decreased with increase in percentage replacement of PSA for both media compared with the higher strengths of cement base (0% PSA) specimens at 7, 14, 21 and 28 days curing period, respectively. This is so, because the pozzolanic activity is slow due to the possible influence of PSA content which leads to reduction of tri-calcium silicates (C3S), a contributing compound from cement. This also describes the attribute that the pozzolanic reaction depends on the release of calcium hydroxide from cement hydration thus the hydration potential of cement in the blend reduced with time (Olusola and Umoh, 2012).

At the 7-day of testing the cubes (Fig. 1), the compressive strengths of cement based mix (0% PSA), 5, 10, 15, and 20% PSA content specimens cured/soaked in crude oil contaminated water media are 17.9, 16.14, 15.19, 13.32 and 13.01 N/mm², respectively compared to cubes cured/soaked in portable water media having compressive strengths 19.29 N/mm², 18.88, 17.23, 15.74 and 15.20 N/mm² obtained at 7, 14, 21 and 28 days, respectively. This shows that the curing media have effect on the compressive strength of concrete cubes. Similar trend were observed for specimens cured at 14, 21 and 28 days in portable water and crude oil contaminated water respectively (Figs. 2, 3 and 4).

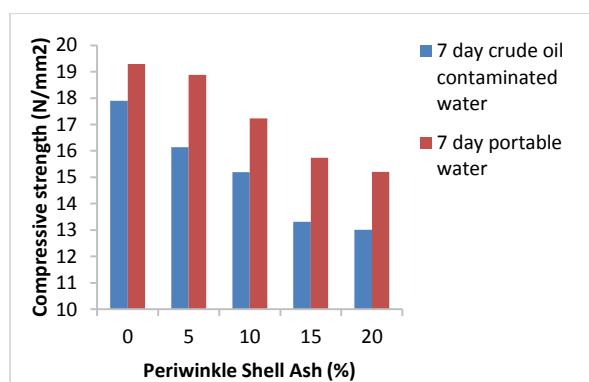


Fig. 1: Variation of compressive strength of periwinkle shell ash blended cement concrete cubes with periwinkle shell ash content cured for 7 days in portable water and crude oil contaminated water

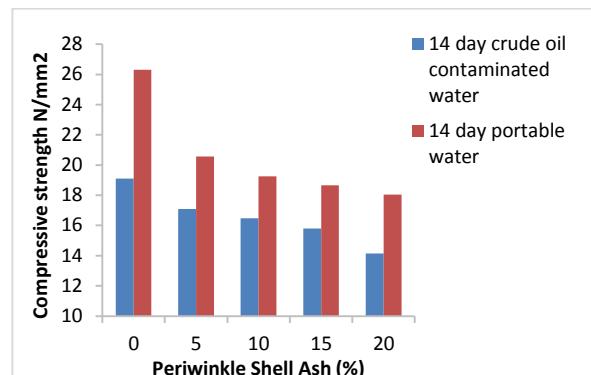


Fig. 2: Variation of compressive strength of periwinkle shell ash blended cement concrete cubes with periwinkle shell ash content cured for 14 days in portable water and crude oil contaminated water

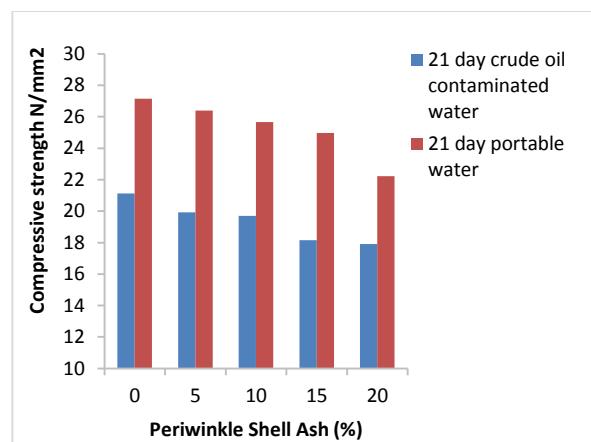


Fig. 3: Variation of compressive strength of periwinkle shell ash blended cement concrete cubes with periwinkle shell ash content cured for 21 days in portable water and crude oil contaminated water

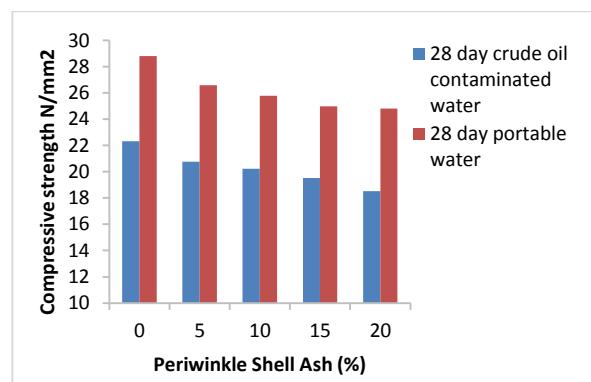


Fig. 4: Variation of compressive strength of periwinkle shell ash blended cement concrete cubes with periwinkle shell ash content cured for 28 days in portable water and crude oil contaminated water

Effect of curing age on the compressive strength of specimens cured in portable water and crude oil contaminated water.

The variation of compressive strength of PSA blended cement concrete cubes with curing age in portable water and crude oil contaminated water medium are presented in Figs. 5 and 6, respectively. Generally, the average compressive strength increased with curing age up to 28 days maximum curing period for cement based (0 %), 5, 10, 15 and 20% PSA replacement in portable water and crude oil contaminated water, respectively.

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The average compressive strength of cement based cubes (0% PSA content) cured in control medium (portable water) at 7, 14, 21 and 28 days are 19.29, 26.31, 27.15 and 28.80 N/mm², respectively (Fig. 5). These values maintained a consistent increase in compressive strength as the curing ages increased. This is expected as the strength of cement - based materials cured in water increases with age (Ejeh and Uche, 2009; Jasim and Jawad, 2010; Abednego *et al.*, 2015). Similarly, on the 7, 14, 21 and 28 days of testing, the average compressive strengths of cement based specimens (0% PSA content) cured in simulated media (crude oil contaminated water) are 17.9, 19.11, 21.12 and 22.32 N/mm², respectively (Fig. 6). These results show that compressive strength increased with curing age for crude oil media but at low strength development rate. Similar trend were obtained for the two media; PW and CCW with 5, 10, 15 and 20% PSA replacement, respectively.

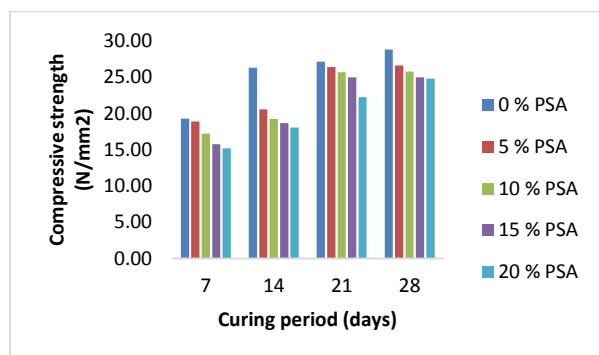


Fig. 5: Variation of compressive strength of periwinkle shell ash blended cement concrete cubes with curing period for specimen cured in portable water.

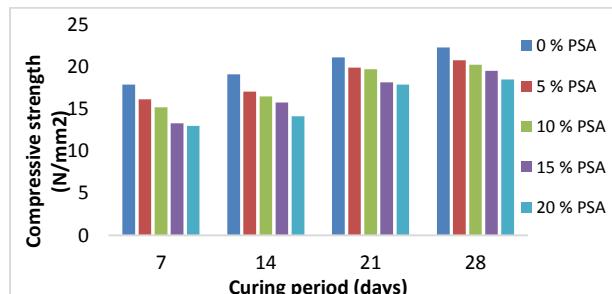


Fig. 6: Variation of compressive strength of periwinkle shell ash blended cement concrete cubes with curing period for specimen cured in crude oil contaminated water.

The results of compressive strength of concrete cubes cured in PW and CCW displayed in Table 5 and Fig. 7 shows that the simulated curing media (CCW) have effect on the compressive strength of concrete cubes (Fig. 7). The compressive strength of specimen cured in PW showed a consistent increase as the curing age increases, whereas the cubes cured in crude oil contaminated media showed a slow rate increase in compressive strength. The clear difference in compressive strength results under the two conditions of soaking may be attributed to effect of chemical reaction taking place in crude oil/water solution but absent in control medium (portable water) (Ejeh and Uche, 2009; Ogbonna *et al.*, 2013). The chemical reaction effect brings about delayed strength development and subsequently low compressive strength when hardened as well as leading to concrete early rotting (Ogbonna *et al.*, 2013; Abednego *et al.*, 2015). The reductions in strength can be linked to the likelihood and vulnerability of

crude absorption, which is about 50% concentration in water (crude oil contaminated water). The adsorption of crude oil onto C-S-H gel termed ‘wetting - weakening effect’ may have contributed to the reduction in compressive strength of the surface material. This is consistent with the result of Ejeh and Uche (2009). The absorption of crude oil into the microstructure of the matrix of concrete may have caused vulnerable effect of dilation of the gel and weakening of the cohesive forces in the paste and hence low strength development of the concrete cured in CCW.

Considering the control medium (portable water) as base, the values at control media are subtracted from the values of the simulated media (crude oil contaminated water) to see the effect of each medium on the specimens. It is evident that soaking in crude oil contaminated water is aggressive to concrete material as the resistance of the concrete cubes reduces with time as the compressive strength drops. However, a variability of the resistance was observed at various curing ages due to the replacement of PSA. This may not be unconnected with the quality of concrete mixture obtained at various PSA replacement as well as the curing media effect. Putting the reduction in compressive strength in percentage using the control medium as base, showed that the reduction in compressive strength of 0 – 20 % PSA blended concrete ranges from 7.2 to 15.4%; 14.4 to 27.4%; 19.4 to 27.3% and 21.5 to 25.3% at 7, 14, 21 and 28 days of curing, respectively (Table 5). It therefore can be said that 50% diluted crude oil medium generally has a detrimental effect on concrete at short, medium and longer duration. The trend of variations in aggressiveness of CCW medium may not be unconnected with the concentration and conductivity of Sulphur ions in crude oil and other chemical reactions thereby creating overall loss in concrete strength (Ejeh and Uche, 2009).

In consideration of design strength attained at various curing age, the results at 7 days show that in all the replacement levels of PSA the attainment of the design strength ranges from 60.8 to 77.16% for PW and from 52.04 to 71.06% for CCW; at 14 days in all replacement level it ranges from 72.2 to 105.24% for PW and from 56.6 to 76.44% for CCW; at 21 days in all replacement level, it ranges from 88.88 to 108.6% for PW and from 71.6 to 84.48% for CCW; at 28 days for all replacement level, it ranges from 99.2 to 115.2% for PW and from 74.12 to 89.28% for CCW (Table 6). These values satisfied the requirement of normal concrete strength development which is stipulated to be between 50 – 66% (British Standard Institution, 1985; Illston, 1994). The results obtained for control medium is consistent with the report of Olusola and Umoh (2012) who considered PSA at 10, 20, 30 and 40% replacement. Although the designed strength was satisfactory (British Standard Institution, 1985; Illston, 1994) however, its applicability in a harsher environment will not suffice in the long term. Therefore, the effect of crude oil contaminated environment on the strength and durability of concretes structures over time as observed from the diminishing design strength compared to it designed strength obtained from uncontaminated environment (portable water media) is significant. This should be incorporated in design considerations of PSA blended cement concrete for use in structures or buildings in coastal areas where crude oil spillage is predominant.

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Table 5: Compressive strength, reduction in compressive strength and attainment of design strength of PSA blended cement concrete in portable water and crude oil contaminated media respectively

Curing age	PSA content	PW (N/mm ²)	CCW (N/mm ²)	Compressive strength reduction (%)	Design strength PW (%)	Design strength CCW (%)
7	0	19.29	17.9	7.2	77.16	71.6
	5	18.88	16.14	14.5	75.52	64.56
	10	17.23	15.19	11.8	68.92	60.76
	15	15.74	13.32	15.4	62.96	53.28
	20	15.2	13.01	14.4	60.8	52.04
14	0	26.31	19.11	27.4	105.24	76.44
	5	20.56	17.08	16.9	82.24	68.32
	10	19.26	16.48	14.4	77.04	65.92
	15	18.65	15.79	15.3	74.6	63.16
	20	18.05	14.15	21.6	72.2	56.6
21	0	27.15	21.12	22.2	108.6	84.48
	5	26.4	19.92	24.5	105.6	79.68
	10	25.67	19.71	23.2	102.68	78.84
	15	24.97	18.15	27.3	99.88	72.6
	20	22.22	17.9	19.4	88.88	71.6
28	0	28.8	22.32	22.5	115.2	89.28
	5	26.6	20.77	21.9	106.4	83.08
	10	25.79	20.24	21.5	103.16	80.96
	15	24.98	19.53	21.8	99.92	78.12
	20	24.8	18.53	25.3	99.2	74.12

PW- Portable water; CCW- Crude oil contaminated water

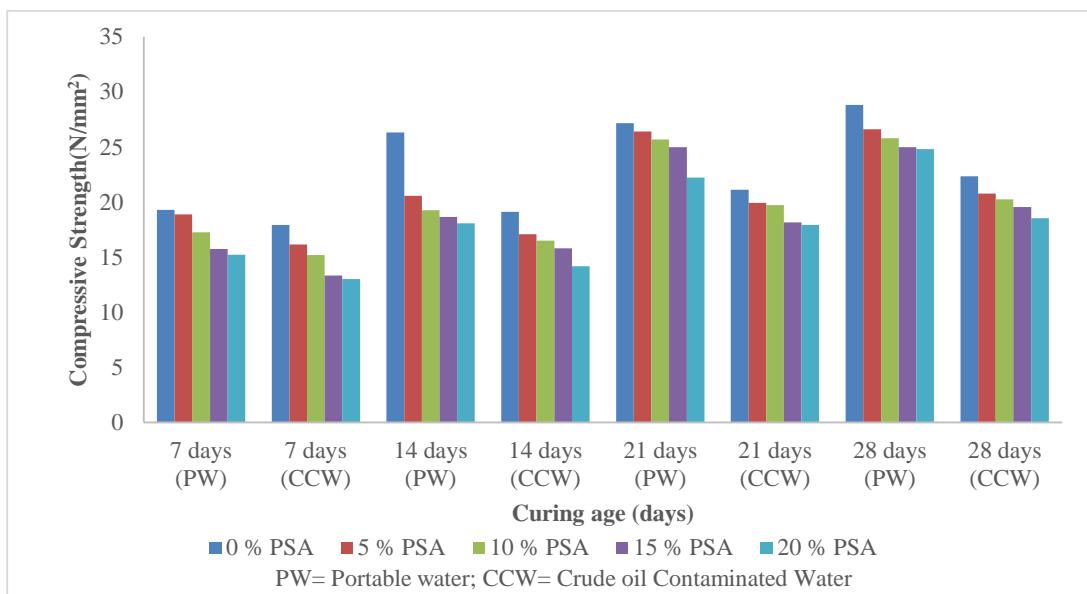


Fig. 7: Variation of compressive strength of periwinkle shell ash blended cement concrete cubes with curing age for specimens cured separately in portable water and crude oil contaminated water.

Table 6: Results for two – way analysis of variance for compressive strength of PSA/cement concrete cured in portable water (PW) and crude oil contaminated water (CCW)

Parameter	Source of variation	df	F _{CAL}	P-value	F _{CRIT}	Remark
Compressive strength (PW)	PSA/Cement	4	12.61	0.00029	3.26	F _{CAL} > F _{CRIT} , SS
	Curing period	3	65.77	1.02E-07	3.49	F _{CAL} > F _{CRIT} , SS
Compressive strength (CCW)	PSA/Cement	4	58.31	9.20E-08	3.26	F _{CAL} > F _{CRIT} , SS
	Curing period	3	159.05	6.32E-10	3.49	F _{CAL} > F _{CRIT} , SS

Statistical analysis of variance

The two-way statistical analysis of variance (ANOVA) of the compressive strength results at 95% confidence level (i.e., $\alpha = 0.05$) showed that it was statistically significant, SS within curing range. This implies that variations in PSA/cement content and curing age had significant effects on the compressive strength of concrete cubes cured in water and crude oil contaminated water respectively. The results of F_{CAL} was observed to be more than three times greater the F_{CRIT} and p-values far less than 0.05 (Table 6).

Conclusion

PSA contains all the main chemical constituents of cement though in varying quantities compared to that of OPC; this means it is a good replacement as pozolana. The strength of concrete for all level of PSA replacement increased with curing age and decreased with increasing percentage of PSA replacement for both control and simulated media respectively. The simulated curing medium has one form of compound or the other which is considered deleterious and hinders the bond formation between constituent materials thus bringing about segregation of cubes made from PSA - cement blend and cement-based materials. All concrete specimens cured in control medium (water) increased steadily incompressive strength at age 7, 14, 21 and 28 days, respectively. The design strengths were generally higher for control than for simulated media signifying deterioration of strength in the simulated medium. The Ordinary Portland cement - PSA concrete have weak resistance to chemical and environmental aggressions as they displayed low as well as slow compressive strength development in all ages of exposure in crude oil contaminated environment when compared to the control medium. Generally, the effect of the aggressive media (crude oil contaminated water) on concrete is such that it causes deterioration. This is characterized by the cement paste matrix being chemically altered and ultimately, leading to compressive strength loss due to the structure not been able to exhibit properties consistent with cementitious characteristics often shown in concrete. Two way analysis of variance was statistically significant on the variation of PSA/cement and curing media on both compressive strength obtained for control and crude oil contaminated environment respectively. For structural sustainability purpose, it is recommended that cement-PSA blended concrete structures be kept free from crude oil contaminated environment.

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