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The Effectiveness of Palm Oil Fuel Ash Cement Paste to Control Degradation in Ammonium Nitrate Solution

T Sadia[1], M E Rahman[2], A Raudhah[3] and S I Doh[4]

[1]Department of Civil Engineering, Curtin University Kent St, Bentley WA 6102, Australia
[2]Faculty of Engineering and Science, Curtin University Sarawak, CDT 250, 98009 Miri, Sarawak, Malaysia
[3]Department of Civil Engineering, University Malaysia Sarawak, 94300 Samarahan, Sarawak, Malaysia
[4]Faculty of Civil Engineering Technology, Universiti Malaysia Pahang, 26300 Gambang Kuantan, Pahang, Malaysia

Abstract. This paper presents the use of treated palm oil fuel ash (POFA) as a pozzolanic material in modified cement paste to control degradation in ammonium nitrate environment. The POFA used in this study had a mean diameter of 8.7µm. The treated POFA was used to replace cement in different percentage of 0%, 10%, 20% and 30% with a constant water to cement ratio of 0.4. 50mm cement cubes was prepared for mechanical, durability and micro-structural test. Mechanical test consisted of the compression strength test and durability test consisted of the Volume of Permeable Voids Test (VPV). Meanwhile, micro-structural test consisted of the Thermo-gravimetric analysis (TGA). After 28 days of full water curing, the 50mm cubes samples were immersed in 20% ammonium nitrate solution until 90 days. Based on the test results, it was observed that, cement cubes replaced with 20% POFA had good resistance against ammonium nitrate solution. However, in order to improve the current study, a number of recommendations had been suggested.

1. Introduction

Concrete is one of the oldest known man-made construction materials used for construction of various structures; such as bridges, dams, tunnels, buildings, sewerage systems, pavement, runways, roads and fertilizer plants. It is rare for concrete structures to fail since reinforced concrete structures are usually designed to a sufficiently high safety factor. However, over the last few decades, the lifespan of concrete structures has become a primary concern as many structures have collapsed, especially in buildings and transportation sectors. Failure of concrete structure happens due to various reasons. One particular reason is due to aggressive chemical solution attack. According to previous researchers, aggressive ammonium nitrate solution can cause failure of concrete structure by causing degradation to it **[1]**. A small amount of ammonium nitrate solution, approximately 0.5% by weight of cement, is sufficient to causes damage to concrete structures **[1].**

1.1. Research Gap
According to literature review, previous researcher have used POFA of various sizes as a cement replacement to study properties such as compression, tension, flexural, setting time, workability, heat evolution, dry shrinkage, water absorption, porosity, and permeability in aggressive solution such as chloride, carbon dioxide and sulfate. However, studies are yet to be done using POFA against aggressive ammonium nitrate solutions to control deterioration. The aim of this paper is to investigate the effect of using palm oil fuel ash (POFA) as a cement replacement material to control degradation of cement paste in ammonium nitrate environment. POFA is a pozzolanic material, which has a high percentage of alumino-silicate content **[2]**.

2. Methods

2.1. Material and Properties
The material used in this are OPC, POFA and ammonium nitrate. Potable tap water was used for mixing and curing throughout the research. The OPC used in this research had fulfilled the requirements set under ASTM C-150 Type 1 Ordinary Portland Cement (OPC) as well as meeting the Malaysian standard MS 522: Part 1-2007, ISO 9001 and 14001 quality requirements. Apart from that, based on the physical test, it was found out that, the OPC used had a mean diameter of 24.67 µm, specific gravity of 3.1 and surface area of 10667.40 cm^2/g. The chemical composition of the OPC is stated as in Table 1. POFA used in this study was collected from a local palm oil mill. The raw POFA was later further treated by burning 600^0degrees Celsius for one hour and grinding. Based on the test result, the treated POFA had mean diameter of 8.7 µm, specific gravity of 2.50 and surface area of 53206.33cm^2/g. The chemical composition of the treated POFA is shown in Table 1. The POFA in this study is classified as a class N pozzolanic according to **ASTM [3]**. Ammonium nitrate was obtained from local market in pellet form and 20% ammonium nitrate was prepared by mixing with water, **[4]**.

2.2. Curing and Mix Proportion
The curing ages for the testing was 3, 7, 28, 56 and 90 days. The method of curing used in this research was water curing. Fresh cement paste was cast in 50mm moulds and demolded on the next day. The cement cubes were then immersed in water for 27 days for full water curing. After the desired cuing age was achieved, some of the samples were left at room temperature and some were placed in an ammonium nitrate solution for 90 days. Table 2 and 3 shows the curing condition and mix proportion of the samples.

2.3. Compressive Strength
Compressive strength test is a type of test which determines the maximum amount of load which can be applied to a material before fracturing. Compressive strength tests were carried out in accordance with **Australian Standard [5]**. Five samples were tested and an average result was calculated. The calibrated compression machine was used for a 50 mm cube test at a loading rate of 700 N/sec., which was within a loading range between 0.2 N/mm2 /sec and 0.4 N/mm2 /sec. Mechanical properties test consisted of the compressive strength test. The tests were carried out at 3, 7, 28, 56 and 90 days for 0%, 10%, 20% and 30% POFA samples. The compressive strength test was carried out in room temperature and in ammonium nitrate solution and comparison was made. 50mm samples were cast and cured in water until 28 days, after which samples were treated in room temperature and in ammonium nitrate solution until 90 days.

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Table 1. Chemical Properties of Treated POFA and OPC

Type	SiO_2	AL_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	LOI
Treated POFA (%)	58.1	2.6	1.67	10.8	6.1	0.7	6.45	6.83
OPC (%)	19.28	4.67	3.3	65.9	1.7	0.3	0.5	n/a

Table 2. Curing Condition

Moulds	Waters	Ammonium Nitrates	Room Temperatures
1 day in mould	27 days curing in water	50% immersed till 90 days	50% left in room temperature till 90 days

Table 3. Mix Proportion

Mix. No	Symbol	OPC (gram)	POFA (gram)	W/C ratio	Water (gram)
1	0%POFA	200	0	0.4	80
2	10%POFA	180	20	0.4	80
3	20%POFA	160	40	0.4	80
4	30% POFA	140	60	0.4	80

2.4. Volume of Permeable Voids

Volume of permeable voids is a type of test which determines the amount of voids present in a sample. Volume of permeable void test was carried out according to ASTM C642 Standard. According to the standards, the VPV test was carried out in three steps. In the first step, samples were oven dried, in the second steps, the sample were immersed in water and in the third step, samples were immersed again in water to calculate the apparent mass. The VPV test was carried out for the 0%, 10%, 20% and 30 %POFA samples POFA samples treated in room temperature and in ammonium nitrate solution.

2.5. Thermo-gravimetric analysis (TGA)

Thermo-gravimetric analysis (TGA) test determines the mass gain or loss of a material due to oxidation, decomposition or losses of volatiles. The TGA test was carried out using STAR Software (METTLER TOLEDO) and test was carried out according to the procedure stated in the test machine manual. The micro-structure studies consisted of the Thermo-gravimetric Analysis (TGA). The test was carried out for 0%, 10%, 20% and 30% POFA samples treated in room temperature and in ammonium nitrate solution.

3. Result and discussion

3.1. Compressive strength of the modified cement paste

The compressive strength of the samples is stated as in Table 4 and in Figure 1 and 2. Based on Table 4 and Figure 1, for samples treated in room temperature, the compressive strength increased with an increase in the curing time. This is due to the fact that with an increase in the curing time, the cement matrix had been modified. There had been an addition formation of calcium silicate hydrate(C-S-H) and calcium hydroxide formed in the cement paste, as a result, the cement paste became denser and stronger.

Table 4. Comparison of compressive strength treated in room temperature and in ammonium nitrate solution

Mixes	Compressive strength (MPa)- Normalized compressive strength (%)				
	3 days	7 days	28days	56days	90days
Control	37.7 - 100	47.8 - 100	50.2 - 100	57.5 - 100	60.4 - 100
Control (AN)	37.7-100	47.8 - 100	50.2 - 100	42.7 - 74	39.2 - 65
10%POFA	26.2 - 100	41.9 - 100	52.7 - 100	57.9 - 100	63.7 - 100
10%POFA (AN)	26.2 - 100	41.9 - 100	52.7 - 100	47.4 - 82	37.4 - 59
20%POFA	20.9 - 100	34.4 - 100	52.0 - 100	60.7- 100	69.5 - 100
20%POFA (AN)	20.9 -100	34.4 - 100	52.0 - 100	44.2 - 73	42.4 - 61
30%POFA	20.0 - 100	24.4 - 100	41.8 - 100	45.7 - 100	57.0 - 100
30%POFA (AN)	20.0 - 100	24.4 - 100	41.8 - 100	36.1 - 79	31.8 - 56

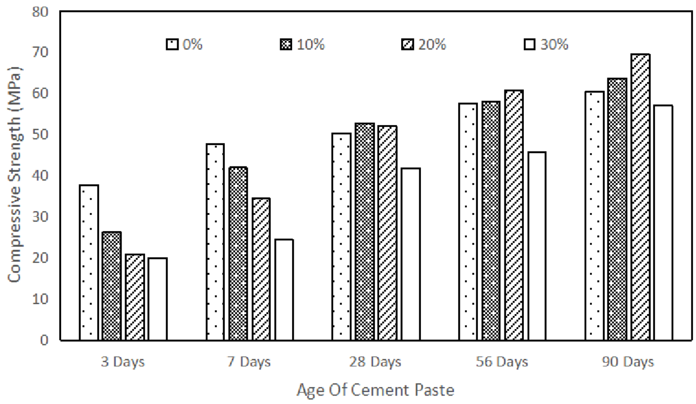

Figure 1. Compressive strength of cement paste in room temperature

For samples treated in room temperature, it was observed that, at 56 and 90 days, samples replaced with 20% POFA had the highest compressive strength. The compressive strength was 60.7MPa and 69.5MPa respectively for 20%POFA sample at 56 and 90 days. The highest compressive strength for 20%POFA samples is due to the pozzolanic reaction between the SiO_2 in the POFA with $Ca(OH)_2$ in the cement paste. However, based on Table 4 and Figure 2, for samples treated in ammonium nitrate solution, it was observed that the compressive strength of the samples shows a decrease after 28 days. This is due to the decalcification reaction, which had leached the $Ca(OH)_2$ out from the cement paste. Consequently, it was observed that, the percentage decrease in compressive strength at 56 days in an ammonium nitrate solution was almost 25% compared to samples at room temperature. The strength however continued to decrease to about 50% at 90 days in an ammonium nitrate solution. Findings, similar to this test results were also reported by other author **[4, 6, 7, 8, 9].** It was therefore concluded that, samples replaced with 20% POFA had good performance in room temperature and against ammonium nitrate solution.

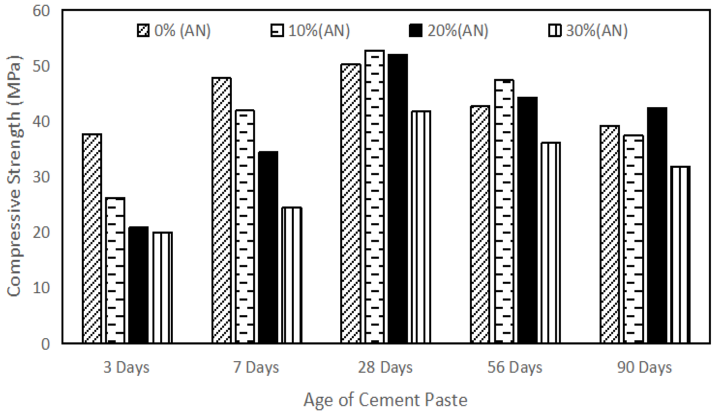

Figure 2. Compressive strength of cement paste in ammonium nitrate solution

3.2. Volume of Permeable Void (VPV) of the modified cement paste

The durability properties test consisted of volume of permeable voids (VPV) test. The VPV test was carried out to determine the amount of voids in a sample. The permeable void affects the transport properties and durability of concrete. The VPV test was carried out for the 0%, 10%, 20% and 30 %POFA samples POFA samples treated in room temperature and in ammonium nitrate solution. At 28 days, the VPV for 0%, 10% 20% and 30% POFA samples were 20.98%, 20.47%, 20% and 20.41% respectively. At 56 days, for sample treated in room temperature, the VPV for 0%, 10%, 20% and 30% were 20.77%, 19.63%, 18.01% and 20.35% respectively. At 56 days for samples treated in ammonium nitrate solution, the VPV for 0%, 10%, 20% and 30% POFA were 22.36%, 22.27&, 20.61% and 20.72%. Consequently, at 90 days for samples treated in room temperature, the VPV were 19.96%, 18.68%, 16.67% and 20.25% for 0%, 10%, 205 and 30% POFA samples. The VPV at 90 days for samples treated in ammonium nitrate solution were 23.5%, 25.84%, 23.85% and 23.72% for 0%, 10%, 20% and 30% POFA.

Based on the test results, for samples treated in room temperature, the void percentages in the cement paste decreased as the curing age increased. This is because more calcium silicate hydrate and calcium hydroxide is produced during the cement hydration process. Calcium silicate hydrate is responsible for decreasing the void percentages as the cement paste becomes denser. A lower void percentage is an indication the sample has a denser matrix and would increase durability. However, it was observed, that the VPV decreases as the curing age increases for samples treated in ammonium nitrate solution after 28 days. This is due to the dissolution of the calcium hydroxide. Calcium hydroxide is a hydrated product, which fills the pore system within the cement paste. Removal of the calcium hydroxide from the pore increases voids within the cement paste. As a result, the concrete becomes more permeable. According to previous research, similar test results were reported. The lower void percentage in samples with 10% and 20% POFA is due to the pozzolanic reaction, which produced additional calcium silicate hydrates. Previous author reported the VPV values decreased with an increase in the duration of the curing age **[4]**. However, the VPV values increased when immersed in an ammonium nitrate solution. According to literature review, the VPV value is influenced by the paste/aggregate ratio **[10]**. As the paste/aggregate ratio increases, the void ratio in the hardened concrete decreases. Previous researchers reported that the VPV value was lower for the 56 days samples compared to the 28 days samples **[11]**. In addition, the author also stated the VPV values decreased as the cement replacement percentage with pozzolanic material increased. Based on the test results, it is recommended to replace OPC with 20% of POFA if at room temperature and in an ammonium nitrate conditions.

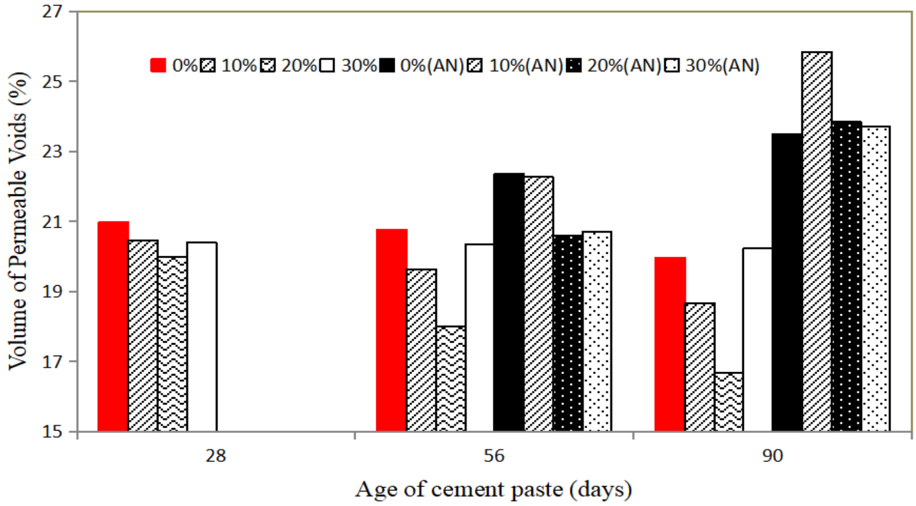

Figure 3. Volume of Permeable Voids (VPV) of the modified cement paste in room temperature and in ammonium nitrate solution

3.3. Thermo-gravimetric Analysis (TGA) of the modified cement paste

Thermo-gravimetric Analysis (TGA) is a widely accepted technique to assess $Ca(OH)_2$ content in hydrated cement paste. For this study, the TGA test was carried out to determine the total percentage of $Ca(OH)_2$ present in the 0%, 10%, 20% and 30% POFA samples at different curing ages and conditions. At 28 days, the $Ca(OH)_2$ content in 0%, 10%, 20% and 30% POFA was 21.07%, 18.92%, 16.82% and 19.37%. The $Ca(OH)_2$ content in 0%, 10%, 20% and 30% at 56 days for sample cured in room temperature was noted to be 23.61%, 21.05%, 17.82% and 16.81%. Consequently, the $Ca(OH)_2$ content in 0%, 10%, 20% and 30% at 56 days for sample treated in ammonium nitrate solution was noted to be 22.97%, 19.38%, 16.82% and 16.25%. The $Ca(OH)_2$ content at 90 days for sample cured in room temperature in 0%, 10%, 20% and 30% POFA was noted to be 27.99%, 22.25%, 18.40%, 15.78% respectively. At 90 days, the $Ca(OH)_2$ content in 0%, 10%, 20% and 30% POFA treated in ammonium nitrate solution was noted to be 23.86%, 19.79%, 18.06% and 15.21% respectively. According to Figure 4, it was observed the Ca(OH)2 content in the 0% POFA samples was the highest compared to samples containing POFA. This is attributed to the fact that there is a high amount of $Ca(OH)_2$ present in the paste due to the absence of the pozzolanic reaction. Based on the test results, it was observed that, the percentage of $Ca(OH)_2$ in 10%, 20% and 30% POFA was lower than sample containing 0%POFA. This is attributed to the fact that the $Ca(OH)_2$ content decreases as the replacement of POFA increases. Hence, the higher the amount of cement replaced with POFA, the higher the consumption of the $Ca(OH)_2$ due to the pozzolanic reaction. As a result, the $Ca(OH)_2$ content in the paste decreases with an increase in the percentage replacement of POFA. Apart from that, it was observed the $Ca(OH)_2$ content for samples in an ammonium nitrate solution were lower compared to samples at room temperature. This is attributed to the decalcification reaction, which caused some of the $Ca(OH)_2$ to reacted with the ammonium nitrate solution and hence its percentage is lower. Therefore, based on the test results, it is recommended to replace OPC with 20% POFA if at room temperature and in ammonium nitrate solution.

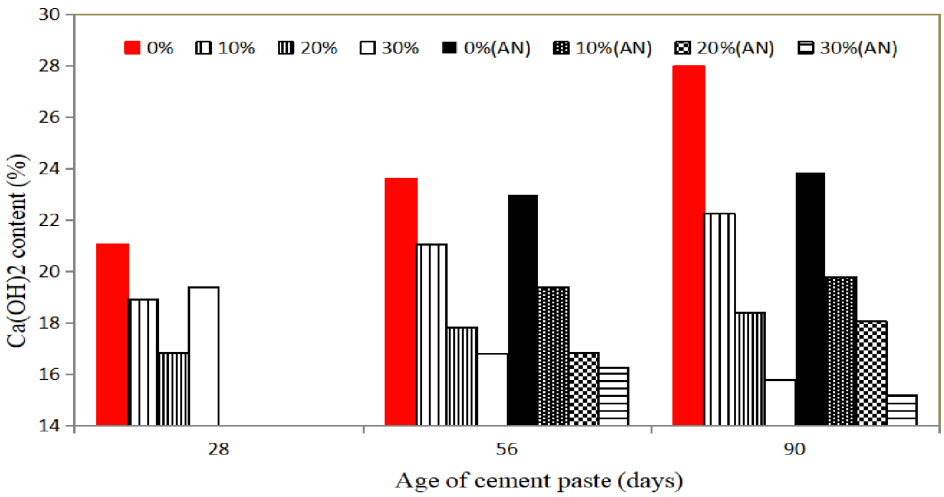

Figure 4. Calcium Hydroxide content of the cement paste in room temperature and in ammonium nitrate solution

4. Conclusion

Based on the test results, the following conclusions were drawn:

a. The compressive strength of the sample cured in room temperature increases with increase in the curing age. However, for sample immersed in ammonium nitrate solution, the compressive strength decreases after 28 days. Based on the test results, it is recommended to replace OPC with 20% POFA for good performance in room temperature and in ammonium nitrate solution.

b. The VPV value for sample cured in room temperature decreases with an increase in the curing time due to the modification of the cement matrix. The VPV of the samples treated in ammonium nitrate solution increases with curing time due to the decalcification reaction. It is suggested to replace OPC with 20% POFA for resistance against ammonium nitrate solution

c. According to the TGA test results, it was observed the calcium hydroxide content decreases as the percentage of POFA replacement increases in the cement paste. However, it was notice that, the calcium hydroxide content for sample immersed in ammonium nitrate solution was much lower than sample cured in room temperature.

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