DURABILITY ASSESSMENT OF WASTE TYRE ASH (WTA) CONCRETE

Supported by tetfund

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Received: September 27, 2020 **Accepted:** November 12, 2020

Abstract: This paper presents the findings of an investigation into the durability assessment of Waste Tyre Ash (WTA)-concrete in acid and salt media. The WTA used was obtained by open burning of waste tyre slices sieved through 75 µm BS sieve and characterized. The ash was subjected to chemical composition analysis using the X-Ray fluorescence (XRF) analytical method. The investigation was carried out using concrete of 29 N/mm^2 compressive strength, water-cement ratio (w/c) of 0.65 and slump range of 10 – 50 mm. The durability assessment was conducted for water absorption by WTA-mortar of (1:3) ratio and concrete at WTA replacement levels of 0, 5, 10, 15, 20, 25 and 30% of cement weight, respectively, to determine the influence of WTA on resistance of concrete to acids (H_2SO_4, HCL) and salt ($MgSO_4$) and also on the water absorption by mortar. A WTA-Cement: sand mortar of 1:3 mix by weight of cement and WTA was used with a water/cement ratio of 0.5. Mortar was cast in steel cube moulds of 100 mm and cured for 28 days. The WTA- concrete of mix 1:2:4 was also cast in steel cube moulds of 100 mm in accordance with BS EN 12390 – 3 (2009). At the end of every curing regime, three samples were air dried, then weighed before immersing in 5 percent concentration of diluted solutions of the stated acids and salty media at 7 days interval until the 28th day to determine the weight of the samples after the acid/salt degradation. Results indicated that water absorption increased with increase of WTA content implying that WTA-mortar absorbed more water as the ash content increased. The resistance to deterioration of WTA-concrete reduced with increase in the curing ages. The study demonstrated that concrete with WTA offered better resistance to deterioration by HCL than OPC concrete. Sulphuric acid was the most-aggressive to WTA-concrete followed by Magnesium Sulphate ($MgSO_4$) and lastly Hydrochloric acid (HCL). The use of WTA content as partial substitute of cement in concrete is recommended for enhanced resistance of concrete in hydrochloric acid and magnesium sulphate environments. However, this is not recommended in Acidic medium with H_2SO_4.

Keywords: Concrete, durability, waste tyre ash, deterioration, aggressive media

Introduction

Sourcing of alternative materials to supplement the conventional construction materials in view of their economic/environmental problems have continued to receive attention globally amongst researchers. It is evident today that the costs/environmental hazards of producing cement for instance is attracting good attention amongst construction experts. According to Heidari and Hasanpour (2013), Portland cement clinker production consumes large amounts of energy (850 kcal per kg of clinker) and has a considerable negative environmental impact. This involves massive quarrying for raw materials (limestone, clay, etc) as it takes 1-7 tones to produce 1 ton of clinker, as well as the emission of green house and other gases (NO_x, SO_2, CO_2) into the atmosphere (Gartner, 2004). Further states that around 850 kg of CO_2 is emitted per ton of clinker produced. Therefore, the replacement of cement in concrete by other waste products (or materials) represent a tremendous saving of energy and has important environmental benefits.

Besides, this can also have a major effect of decreasing concrete cost, since the cost of cement represents more than 45 percent of the concrete cost (Heidari and Hasanpour, 2013). It is thus evident today that the costs and environmental hazards of producing cement for instance, is attracting attention amongst construction experts. Further factors such as difficulties in accessing fund for construction works, the need to recycle wastes from other sectors of the economy such as agriculture, industries, etc., need for maintaining ecological balance are all reasons for sourcing of alternative materials for our construction work.

The disposal of waste or used tyre has been a thing of major concern to all and sundry because of its impact on waste management problems in the world. According to Xi *et al.* (2004) about 2-3 billion scrap tyres are stock piled in the United States alone, with almost 250 million more generated each year. In Nigeria, there is no known record of the amount of used tyres generated periodically (Oriakwu *et al.* 2013); they however do agree that used tyres constitute a disposal challenge. Felix *et al.* (2013) have opined that increased vehicle ownership and traffic volume has led to an increase in the quantity of waste tyres in Nigeria. That as the country's population and economy grow, so does the amount and type of scrap tyres generated. Accordingly, it is estimated that with an annual generation rate of 15%, between 700,000 and 850,000 scrap tyres are added to the scrap tyre waste stream in Nigeria each year (Aisien *et al.* 2013). Afolagboye and Talabi (2013) are also of the opinion that used car tyres are posing a disposal problem in Nigeria.

Eshmaiel *et al.* (2009) have suggested that one of the methods for utilization of these materials (wastes) is their use in concrete and other building products. And this is of interest to this research hence it borders on the expected savings that may be achieved if one of the constituent materials used to make concrete, such as cement, is substituted with tyre (ash).

Strength is a primary criterion in concrete application. The effect of any supplementary cementitious material on the strength of concrete depends on the pozzolana content and pozzolanic activity of the material during hydration. Supplementary cementitious materials (SCM) as mineral admixtures have been identified in literature as being essential towards achieving low cost construction materials with the main benefits of saving natural resources and energy as well as protecting the environment (Elinwa and Mahmoud, 2002).

Most research works done in the past on the use of scrap or used tyres in concrete have considered the effect of replacing either the coarse or fine aggregate in concrete, only, as in the works of (Rohit and Shalika, 2018; Ataria, 2015; Khalid and Mathew, 2012; Alan *et al.*, 2012; Prasad and Shubhad, 2012; Meyer, 2009). Mostly, reduction in strengths, density with increased durability and others have been reported. Not much works have been reported on the replacement of cement by Waste Tyre Ash in concrete as is the case in this study. However, the few cited cases of improved strengths and increased setting times achieved by using the tyre ash in mortar have increased the motivation for this research.

Sustainable development is an emerging political and social issue of global significance. The increasing need for the concrete industry to comply with the fundamental goals of sustainable development and to reduce its impact on the environment, has led scientists and researchers to improve upon the properties of concrete products and at the same time to develop material and technologies that can recycle the various wastes for their effective and economical use in cement based products and thus ultimately making these materials as commodity products. Over the years, many waste materials like fly ash, ashes produced from various agricultural wastes such as palm oil waste, rice husk ash, wheat straw ash, have been tried as pozzolana or alternate cementitious materials in cement based products (Ajayi *et al.* 2013).

Thus, use of WTA which is an ash produced from the incineration of abandoned or wasted stock of scrap tyres, as a supplementary cementitious material in concrete will be an attempt to find an alternative way of disposing the material with more benefit. However, the burning of tyres is reported to cause the emission of particulates such as SO_2, NO_2 and HCL, organic emissions, dioxins and furans (Gray, 1996; STMC, 1992). Also the production of heavy metal concentrations. But that emissions data from test burns at several pulp and paper mills where scrap tyres were used as fuel in their kilns showed that while particulate emissions increased, releases were still within permitted values (Barlez *et al.* 1993).

It is also reported that Tyre Derived Fuel (TDF) which indicates the use of waste tyre as fuel for energy to power the cement/paper and pulp kilns has no adverse effect upon the emissions, i.e. the use of TDF has not caused a facility to exceed its operating limits (Gray, 1996; Environmental Agency, 1998).

In recent time, cement based concrete design have become more complicated due to factors of resource conservation, waste recovering and durability challenges. And though cement cannot be fully eliminated in concrete, pozzolanas have however been employed to lower cement consumption in concrete (Aliyu, 2019; Ogork, 2014; Ramezanlapour *et al.* 2009; Heru, 2004). Nabil and Mohammed (2004) also studied durability aspects of mortar to accelerated cycles of freezing and thawing damage using mortar containing 5 and 10% Tyre Rubber Ash (TRA) replacement. The freezing and thawing damage was assessed using the relative dynamic modulus of elasticity and durability factor, respectively. To accelerate these tests, mortar specimens were subjected to freezing and thawing cycling after 7 days of moist curing. Their results indicated that mortar specimens containing 5 and 10% TRA showed higher durability to freezing and thawing damage. Mortar specimens containing 5% TRA reached 55% relative dynamic modulus of elasticity of 150 cycles of freezing and thawing and the durability factor of 28%. While mortar specimens containing 10% TRA reached 60% relative dynamic modulus of elasticity at 225 cycles of freezing and thawing and the durability factor was 40%. This was compared to the control mortar which showed little durability to freezing and thawing for which the relative dynamic modulus of elasticity reached 55% at only 50 cycles of freezing and thawing and the durability factor was only 9%.

Again the findings of Nabil and Mohammed (2004) on the durability of mortar to chloride ion penetration was also encouraging using mortar containing 5% and 10% TRA replacement. In this study, the control mortar showed the highest value of electrical charge of 3200 coulombs at 28 days (indicating low resistance to chloride-ion penetration) when compared to the mortar containing 5 and 10% TRA which were 870 and 420 coulombs, respectively. This indicated higher resistance to chloride-ion penetration than the control mortar. After 10 days of moist curing, the electrical change passed through all three types of mortar was reduced for the control mortar it was reduced to 1875 coulombs. This was significantly higher than that of the mortar containing 5% TRA (at 520 coulombs) and mortar containing 10% TRA (at 350 coulombs) (Nabil and Mohammed, 2004).

According to ASTM C 1202-03, when the electrical charge passed through mortar is below 1000 coulombs, the mortar has high resistance to chloride-ion penetration. This according to Nabil and Mohammed (2004) may be attributed to the effect of TRA filler packing, which reduces the air content of mortar and consequently increases the resistance of mortar to chloride-ion penetration.

Portland cement concrete usually does not have good resistance and is vulnerable to acid attack because of its alkaline nature (Nuruddeen, 2012). The components of the cement paste break down during contact with acids depending on the type and concentration of the acid. Acids attack concrete by dissolving both hydrated and unhydrated cement compounds as well as calcerous aggregate. In most cases the chemical reaction forms water-soluble compounds, which are then leached away (Beddoe and Dorner, 2005).

Certain acids such as oxalic acid and phosphorus acids are harmless but the most vulnerable part of the cement hydrate is $Ca(OH)_2$, but C-S-H gel can also be attacked (Beddoe and Dorner, 2005). Concrete can be attacked by liquids with PH value less than 6.5. But the attack is severe only at a PH value below 5.5. At a PH value below 4.5, the attack is very severe (Steve, 2003). As the attack proceeds, all the cement compounds are eventually broken down and leached away, together with any carbonate aggregate material. With the sulphuric acid attack, calcium sulphate becomes formed and can proceed to react with calcium aluminate phase in cements to form calcium sulphoaluminate, which on crystallization can cause expansion and disruption of concrete (Shetty, 2006). Against this background, the research is aimed at investigating the effect of WTA used as a pozzolana in concrete exposed to acidic and salty attack, respectively.

The objective of this study will be achieved by considering durability factors such as water absorption of WTA – mortar and the rate of decrease of weight of WTA – concrete immersed in 5% concentration of hydrochloric acid (HCL) sulphuric acid (H_2SO_4) and magnesium sulphate ($MgSO_4$), respectively.

Materials and Methods

Materials

Ordinary Portland cement manufactured in Nigeria known as Dangote 3X, Grade 42.5N brand, having specific gravity of 3.15, Fineness (% Passing 90 µm Sieve) of 97 and Loss on Ignition of 1.3 was used. The oxide composition of the cement as compared to that of WTA, the waste tyre ash used in this study is shown in Table 1.

Sharp sand from river Challawa, Kano, Nigeria, with specific gravity of 2.80 and classified as zone 1 was used. Crushed granite coarse aggregate of 20 mm nominal diameter and 2.85 specific gravity was used. The particle size distribution curve for the fine aggregate, coarse aggregate and WTA is shown in Fig. 1.

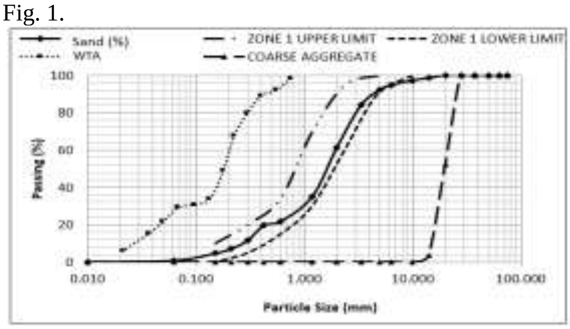

Fig. 1: Particle size distribution of WTA, fine aggregates and coarse aggregates

WTA used in this study has a specific gravity of 1.87 is dark grey (black) in colour with fineness of 100 (% passing 90 µm sieve)

Methods

Concrete mix design

The prescribed mix for concrete used for this study was conducted using the Absolute Volume Method. The formula for the Absolute Volume Method is given in Equation 1.

$$\frac{W}{1000}+\frac{C}{1000P_C}+\frac{S}{1000P_S}+\frac{A}{1000P_A}=1m^3 \quad (1)$$

Where: W = Weight of water/m^3 of concrete; C = Weight of cement/m^3 of concrete; S = Weight of fine aggregate/m^{3}of concrete; A = Weight coarse aggregate/m^3 of concrete; P_c = Specific gravity of cement; P_s = Specific gravity of fine aggregate; P_A = Specific gravity of coarse aggregate

A target mean strength of 25 N/mm^2 at 28 days was set. Trial water – cement ($^w/_c$) ratios of 0.50, 0.55, 0.60, 0.65, 0.70 and 0.75, respectively were used to produce three trial concrete mixes each, using a mix ratio of 1:2:4 of cement, fine aggregate and coarse aggregate, respectively. The Trial concrete mixes were produced and cured for each of the w/c ratios given and cured for 3, 7, and 28 days, respectively.

For the normal concrete mix with target cube strength of 25 N/mm^2 at 28 days, the water – cement ratio of 0.65 gave the closest value of 29 N/mm^2. And because generally pozzolanic materials are known to be high water absorbers and consequently need more water, it was thus chosen and adopted to be used in the Waste Tyre Ash concrete.

Concrete used for this study therefore has a compressive strength of 29 N/mm^2, Water – cement ratio (w/c) of 0.65 and slump range of 10 – 50 mm. Quantities of concrete materials used for this study are shown in Table 3. Seven mixes as shown in Table 3 were used, COMP 0-B is the control mix (% WTA) and COMP 5-B, COMP 10-B, COMP 15-B, COMP 20-B, COMP 25 - B and COMP 30-B are mixes containing WTA at replacement levels of 5, 10, 15, 20, 25 and 30%, respectively.

Table 3: Quantity of materials for WTA-concrete production

Mix No.	WTA %	Cement (kg/m^3)	WTA (kg/m^3)	Sand (kg/m^3)	Crushed granite (kg/m^3)	Water (kg/m^3)	W/C
COMP 0 – B	0	324.12	0	648.24	1296.48	210.68	0.65
COMP 5 – B	5	307.91	16.21	648.24	1296.48	210.68	0.65
COMP 10 – B	10	291.71	32.41	648.24	1296.48	210.68	0.65
COMP 15 – B	15	275.5	48.62	648.24	1296.48	210.68	0.65
COMP 20 – B	20	259.3	64.82	648.24	1296.48	210.68	0.65
COMP 25 – B	25	243.09	81.03	648.24	1296.48	210.68	0.65
COMP 30 – B	30	226.88	97.24	648.24	1296.48	210.68	0.65

The WTA was obtained by burning sliced pieces of waste tyres to ash through heating to a temperature of 500^{0}C in open burning for about 5 h at the local open burning site off the Eastern bye-pass ring road adjacent to Unguwa Uku Ward in Tarauni Local Government Area of Kano – Nigeria. The temperature of burning was realized using a thermocouple instrument which was inserted directly into the burning tyre slizes on one end and the other end was connected to a thermometer to read the temperature accordingly. The fire was maintained to keep the temperature reading at 500^{0}C continuously and this was monitored at 30 min interval.

The ash was allowed to cool and sieved through BS Sieve No. 200 (75 µm). A chemical composition analysis of the Waste Tyre Ash was conducted by use of X–Ray fluorescence (XRF) analytical method using X–Ray spectrometer at the Multi-User Research Laboratory at Ahmadu Bello University, Zaria, Nigeria. The oxide composition of WTA used is presented in Table 1.

Slump of waste tyre ash (WTA)-concrete

Slump test was conducted on WTA concrete whose preparation was earlier described in accordance with BS EN 12350 – 2: 2009 and whose material quantities were given in Table 3.

Water absorption of WTA-mortar

The quantity of materials for mortar in Table 5 was used to determine the water absorption of WTA-mortar. Seven mixes were used and Mix WAM 0-B is the control mix containing 0% WTA while mixes WAM5-B, WAM10-B, WAM15-B, WAM20-B, WAM25-B and WAM30-B are mixes containing WTA at replacement levels of 5 to 30%, respectively. A WTA-Cement: sand mortar of 1:3 mix by weight of cement and WTA was used with a water/cement ratio of 0.5. Mixing was done manually and cast in steel cube moulds of 100 mm. The mortar was cured in water for 28 days, then air dried for 24 h and weighed. The cubes were further cured for 7 days in water to determine amount of water absorbed. A total of twenty one (21) cubes were cast and three cubes tested for an average for each curing regime and the results are shown in Table 6.

Effect of acids and salt on WTA-concrete

The relative weights of concrete cubes shown in Table 7 were used to determine the effect of acidic and salty media on WTA-concrete. Seven mixes were used, CONCID – 00 to CONCID-30. CONCID – 00 is the control mix containing 0% WTA while CONCID-05 to CONCID – 30 are mixes with various proportions of WTA replacement by weight of cement, ranging from 5 to 30%, respectively. Mixing was done manually and cast in steel cube moulds of 100 mm during the casting of cubes for compressive strength test. A total of sixty three cubes were cast and cured in water for 28 days in accordance with BS EN 12390 – 3(2009). At the end of every curing regime, three sample were air dried, then weighed before immersing in 5 percent concentration of diluted solutions of sulphuric acid (H_2SO_4), Hydrochloric acid (HCL) and magnesium sulphate ($MgSO_4$), respectively.

Their pH values determined were 2.5, 2.4 and 7.4, respectively. The pH values were measured using a handy pH electronic meter which was directly inserted into the concrete shortly after being mixed before casting into the moulds. The concrete cubes were then weighed after immersion in the acid and salt solutions at 7 days interval until the 28th day to determine the weight of the samples after the acid/salt degradation. Acid and salt resistance were then evaluated by determining the weight loss (WL) and compressive strength loss (CSL) of the specimens using Equation 2 adopted from (Nuruddeen, 2012):

$$WL(\%) = \frac{W_1 - W_2}{W_1} \text{ X100} \quad (2)$$

Where: w_1 = Weight of the concrete specimen before immersion in acid/or salt medium; w_2 = Weight of the concrete specimen after immersion in acid/salt medium

The results of WTA-concrete resistance to acidic and salty solutions are given in Table 8.

Results and Discussion

Cement and waste tyre ash

Table 1 shows the comparison of the 3X Dangote cement used for the study with BS EN 197-1:2000 chemical specifications for cement. Also the composition of the 3X Dangote cement used for this study as compared with BS EN 197 – 1:2000 being the chemical specification for cement, is presented in Table 2. The result indicates that the oxide composition and physical properties of the Dangote 3X used in this study has satisfied the specifications of BS EN 197-1(2000) for Ordinary Portland Cements. The results also show that the cement has satisfied the physical properties of ordinary Portland cements. From Table 1, it can be seen that waste tyre ash has a very low CaO content which is far lower than 20% composition for cementitious materials (Ljubica *et al.,* 2005) and thus, has no cementing characteristics. From the chemical composition of waste tyre ash result, the sum of the total percentage composition of iron oxide (Fe_2O_3 = 6.39%), Silicon dioxide (SiO_2 = 30.40%) and Aluminum oxide (Al_2O_3 = 3.41%) was found to be 40.2%. This value is below the required value of 70% minimum for class F and N pozzolanas and 50% for class C pozzolanas (ASTM C618, 2005). The magnesium oxide content was 1.2 percent. This satisfied the required value of 4 percent maximum (ASTM C618, 2005). The content of MgO is usually limited to 4 – 5%, because quantities of this component in excess of about 2% can occur as periclase (magnesium oxide), which through slow reaction with water can cause destructive expansion of hardened concrete (Nuruddeen, 2012). Free lime (calcium oxide) can behave similarly (Taylor, 1997).

Table 1: Chemical composition comparison of ordinary portland cement (OPC) with waste tyre ash (WTA)

Elemental Oxides	% Composition of Ordinary Portland Cement (OPC)	% Composition of Waste Tyre Ash(WTA)
Al_2O_3	2.10	3.41
SiO_2	18.69	30.40
Cao	65.23	2.13
Fe_2O_3	3.96	6.39
K_2O	0.48	0.54
MnO	0.09	0.05
MgO	1.96	1.20
SO_3	2.33	10.71
Na_2O	2.32	4.32
P_2O_5	–	1.64
TiO_2	0.31	0.37
Cr_2O_3	0.03	0.01
BaO	0.07	–
CuO	0.03	–
ZnO_2	0.03	22.39
CL	–	0.38
LOI	1.3	14.6

Table 2: Cement chemical composition comparison with BS EN 197-1:2000 specifications

Elemental Oxides	3X Dangote Cement Composition (%)	BS EN 197-1:2000
Al_2O_3	2.10	Max 6.3%
SiO_2	18.69	Max 35.5%
CaO	65.23	Limit not specified
Fe_2O_3	3.96	Max 6.5%
K_2O	0.48	Less than 0.6
Na_2O	2.32	Limit not specified
MnO	0.09	Limit not specified
SO_3	2.33	Max 3.5%
TiO_2	0.31	Limit not specified
MgO	1.96	Limit not specified
Cr_2O_3	0.03	Limit not specified
BaO	0.07	Limit not specified
CuO	0.03	Limit not specified
ZnO_2	0.03	Limit not specified

The SO_3 content is 10.71%. As per ASTM C618 (2005) the maximum SO_3 content should not be more than 5.0%. The SO_3 content has been reported to affect to some degree the early age compressive strength of mortar and concrete specimens. The higher the SO_3 content, the higher is the resultant strength (Nuruddeen, 2012).

The alkali content (Na_2O) was found to be 4.32%. This value is higher than the maximum alkali content of 1.5% required for pozzolana. The alkali content is important where pozzolana is to be used with reactive aggregate (Rafat, 2008). In such case, the Pozzolana will not be suitable for construction work where reactive aggregate is to be used.

The loss on ignition obtained was 14.6%. This value is more than 10% maximum as required for pozzolanas (ASTM C 618, 2005). Higher LOI means higher unburnt carbon which will reduce the pozzolanic activity of the ash. Unburnt carbon itself is not pozzolanic but its presence may serve as filler to the mixture (Nuruddeen, 2012).

Water absorption of WTA-mortar

The result of water absorption of WTA – mortar is presented in Table 6 and Fig. 2, respectively.

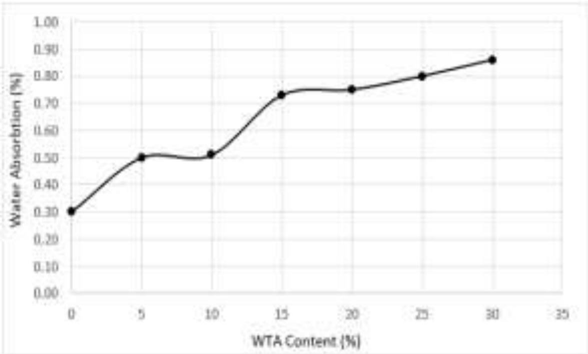

Fig. 2: Water absorption of WTA-mortar

The Figure showed that water absorption increased with increase in WTA content. This implies that the WTA-mortar absorbed more water as the ash content increased. The water absorption at 5 percent WTA content was 0.50% and this increased to 0.86% at 30 percent WTA content. However, these values are less than 10% which is the percentage water absorption value accepted for most construction materials (Ogork *et al.,* 2015; Rafat, 2008; Ogork and Rimi, 2009).

As explained by Ogork *et al.* (2015) in their work on Groundnut shell ash mortar, this behaviour of WTA mortar may be attributed to the incomplete formation of calcium silicate hydrate gel during hydration. Also, that for a constant water-binder ratio, the flow of mortar reduced with increase in percentage substitution with WTA and this reduced compaction of mortar which results in porosity of the mortar. The high carbon content of WTA may also be responsible for the high water absorption behaviour as observed.

Table 4: Slump of WTA-concrete

Mix. No	WTA (%)	Average Slump (mm)
COMP 0-B	0	25.0
COMP 5-B	5	24.0
COMP 10-B	10	19.7
COMP 15-B	15	15.0
COMP 20-B	20	13.3
COMP 25-B	25	9.5
COMP 30 –B	30	5.0

Table 5: Mix roportion of WTA-cement mortar

Mix No	WTA (%)	Cement (kg/m^3)	WTA (kg/m^3)	Sand (kg/m^3)	Water (kg/m^3)	W/C
WAM 0-B	0	529.1	0	1,587.3	264.6	0.5
WAM 5-B	5	502.6	26.5	1,587.3	264.6	0.5
WAM 10-B	10	476.2	52.9	1,587.3	264.6	0.5
WAM 15-B	15	449.7	79.4	1,587.3	264.6	0.5
WAM 20-B	20	423.3	105.8	1,587.3	264.6	0.5
WAM 25-B	25	396.8	132.3	1,587.3	264.6	0.5
WAM 30-B	30	370.4	158.7	1,587.3	264.6	0.5

Table 6: Water absorption of WTA-mortar

Mix No.	WTA (%)	Mean Water Absorption (%)
WAM 0-B	0	0.30
WAM 5-B	5	0.50
WAM 10-B	10	0.51
WAM 15-B	15	0.73
WAM 20-B	20	0.75
WAM 25-B	25	0.80
WAM 30-B	30	0.86

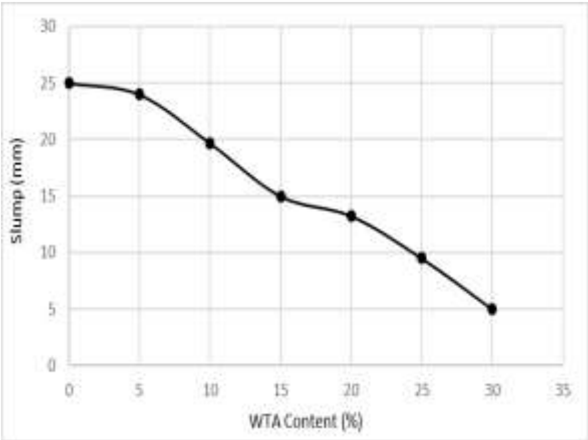

Fig. 3: Slump of WTA-concrete

Slump of WTA-concrete

The result of concrete slump of WTA Concrete is presented in Table 4 and Fig. 3, respectively. This gives the variation in slump value when cement in the concrete is partially replaced with Waste Tyre Ash. It shows that concrete slump decreased with increase in WTA replacement. There was gradual decrease in slump with the use of WTA as partial substitute of cement in concrete over that of control mix which became significant as the WTA content become highest. The slumps of WTA-concrete ranged from 20.0 - 96.0% of control concrete, with least slump of 5.0 mm observed at 30% WTA replacement and maximum slump of (24.0 mm) at 5% WTA replacement. The decrease in slump with increase in WTA content may be attributed to the higher specific surface area and high carbon content of the WTA. This explanation is supported by Ogork *et al.* (2015), in their work on the slump of Groundnut Husk Ash (GHA) and Cordeiro *et al.* (2009), and Bui *et al.* (2005), in their reports on workability of RHA. The high demand for water as the ash content increases gives rise to low workability at higher value WTA content. The higher the WTA content after the optimum value, the lower the workability/slump.

Effects of acids and salt on WTA-concrete

The effect of 5% concentration of hydrochloric acid (HCL), sulphuric acid (H_2SO_4) and magnesium sulphate ($MgSO_4$) media respectively on WTA-Concrete is shown in terms of weight retained and presented in Table 8. These values are then used to plot the graphs of the effect of the acids and salt on WTA concrete for varying curing ages after the concrete cubes were cured for the initial 28 days in normal water. The graphs are then presented in Figs. 4, 5 and 6 representing the effect of HCL, H^2SO_4 and $MgSO_4$ on WTA-concrete, respectively. Generally, from the figures it is observed that for all the media used (HCL, H_2SO_4 and $MgSO_4$) the resistance to deterioration reduced with increase in the curing age. The results further showed that concrete with WTA offered better resistance to deterioration by HCL than OPC concrete. While OPLC concrete performed better than WTA concrete in magnesium sulphate media. Fig. 4 shows the percentage changes in weights of the control OPC concrete and the WTA-concrete at specified WTA-contents and exposed to different curing regimes as explained earlier.

Table 7: Raw data on weight of WTA-concrete immersed in hydrochloric acid, sulphuric acid and magnesium sulphate solutions after initial 28 Days of curing in water

% Replac.	Acid type	Initial weight	Weight in acid solution (kg) 7 Days	14 Days	21 Days	28 Days
0		2490	2255	2115	2088	2010
		2488	2218	2188	2058	1895
		2498	2233	2126	2044	1911
5		2367	2117	2018	1932	1821
		2377	2123	2088	1964	1863
		2463	2231	2186	2050	1930
10		2420	2256	2164	2020	1891
		2433	2212	2111	2014	1864
		2453	2231	2110	2023	1885
15		2461	2257	2132	2021	1936
		2466	2259	2153	2033	1847
		2455	2260	2174	2044	1960
20		2515	2322	2262	2122	1923
		2550	2080	2263	2172	1905
		2541	2364	2244	2223	2106
25		2534	2377	2242	2134	1900
		2514	2333	2248	2143	2005
		2571	2377	2282	2161	2054
30		2523	2368	2262	2150	2020
		2434	2218	2139	2097	2184
	HCL	2389	2172	2041	1968	1834
0		2572	2361	2151	1985	2064
		2643	2288	2199	2015	1821
		2544	2326	2152	1974	1740
5		2542	2317	2014	1917	1787
		2572	2291	2122	2019	1934
		2478	2225	2068	1917	1791
10		2588	2316	2099	1964	1841
		2538	2282	2124	1946	1818
		2489	2149	2090	1938	1816
15		2537	2240	2154	1982	1849
		2571	2300	2023	1862	1726
		2534	2238	2110	1972	1813
20		2478	2151	1979	1914	1781
		2518	2243	2069	1914	1741
		2517	2270	2060	1882	1775
25		2471	2242	2019	1918	1755
		2578	2202	1997	1976	1725
		2571	2307	2118	1852	1724
30		2566	2276	2085	1838	1837
		2461	2139	1971	1854	1817
	H_2SO_4	2432	2149	1963	1835	1358
0		2421	2155	2021	1936	1891
		2488	2122	2085	1961	1871
		2498	2212	2057	1932	1808
5		2467	2117	2114	1932	1812
		2477	2123	2088	1909	1826
		2463	2174	2009	1936	1813
10		2420	2116	2061	1974	1837
		2433	2087	1988	1921	1809
		2453	2102	2022	1928	1819
15		2461	2012	1978	1904	1826
		2466	2008	1984	1910	1800
		2455	2018	1982	1922	1815
20		2415	1944	1956	1898	1814
		2450	2024	1973	1879	1763
		2441	1979	1952	1900	1793
25		2434	1989	1935	1846	1788
		2414	2003	1907	1868	1808
		2471	2010	1955	1856	1776
30		2385	1930	1902	1823	1744
	$MgSO_4$	2434	1988	1905	1876	1744
		2389	1957	1887	1801	1758

Replac. = Replacement

Table 8: Retained relative weight of WTA-concrete (in %) immersed in acidic and salty solution after initial 28 Days of curing in water

Mix No.	WTA (%)	Medium	Initial Weight (%)	Mean weight in acidic and salty solution (%)			
				7 Days	14 Days	21 Days	28 Days
COM 0-B	0	HCL	100	89.7	86.0	82.8	77.8
COMP 5-B	5		100	89.8	87.3	82.8	77.9
COMP 10-B	10		100	91.7	87.4	82.9	77.9
COMP 15-B	15		100	91.8	87.5	82.6	77.9
COMP 20-B	20		100	92.9	89.0	85.7	78.2
COMP 25-B	25		100	93.0	88.9	84.5	78.2
COMP 30-B	30		100	92.0	87.7	84.6	78.0
COMP 0-B	0	H_2SO_4	100	89.9	83.8	77.0	72.5
COMP 5-B	5		100	90.0	83.0	77.1	72.6
COMP 10-B	10		100	88.6	82.9	76.8	71.9
COMP 15-B	15		100	88.7	82.3	76.1	70.5
COMP 20-B	20		100	88.7	81.3	76.0	70.5
COMP 25-B	25		100	88.6	80.7	75.4	68.3
COMP 30-B	30		100	88.0	80.5	74.1	67.2
COMP 0-B	0	$MgSO_4$	100	87.6	83.2	78.7	75.2
COMP 5-B	5		100	86.6	82.5	78.0	73.6
COMP 10-B	10		100	86.3	83.1	79.7	74.8
COMP 15-B	15		100	82.0	80.5	77.7	73.7
COMP 20-B	20		100	81.8	80.5	77.7	73.5
COMP 25-B	25		100	81.5	79.2	76.3	73.4
COMP 30-B	30		100	81.0	79.0	76.1	73.2

Generally, the weight of concrete retained decreased with increase in exposure duration in HCL media. But increased with increase in WTA content up to 25% with a maximum weight retained at 28 days of 78.2% compared to 77.8% for the control specimen. The improvement in resistance to Hydrochloric acid of WTA up to 25% in concrete could be attributed to the pozzolanic reaction of WTA with lime in the paste matrix. Another explanation for the improved resistance of WTA-concrete to HCL acid may be explained from the reaction of WTA with lime in the paste mix which consequently reduced the free lime present in the concrete matrix. Hence lime is considered as a harmful compound because it reacts with many chemicals causing concrete degradation as observed by (Elinwa and Abdulkadir, 2011). This is consistent with the view of Ogork and Ayuba (2014) in their treatise on the influence of sawdust ash (SDA) as admixture in cement paste and concrete.Also, the additional calcium silicate hydrates formed from WTA pozzolanic reaction improved the concrete pore structure with greater impermeability than that of Ordinary Portland cement concrete, and would slow down the penetration of water and chemicals into the concrete.

But at higher percentage addition of WTA, above 25%, the other WTA oxides such as phosphorus oxide and potassium oxide will inhibit further formation of $CaSiO_4$ hydrates and may lead to the formation of voids in WTA-concrete due to the formation of potassium silicates that displace more calcium oxide in cement with a consequent reduction in resistance to hydrochloric acid aggression.

The effect of hydrochloric acid on WTA-concrete shown as weight retained in Fig. 4 shows that WTA – concrete offered better resistance to HCL than OPC concrete. The average weight loss of WTA – concrete after 28 days of exposure was 22.02% compared to the OPC concrete weight loss of 22.2%. Fig. 5 shows the effect of sulphuric acid attack on plain and WTA-concrete, respectively.

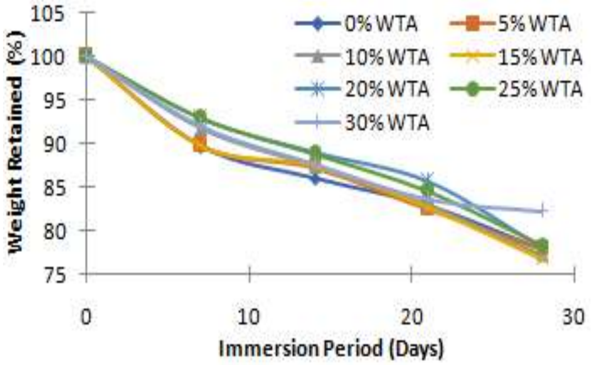

Fig. 4: Percentage weight of WTA-concrete immersed in HCL medium (HCL)

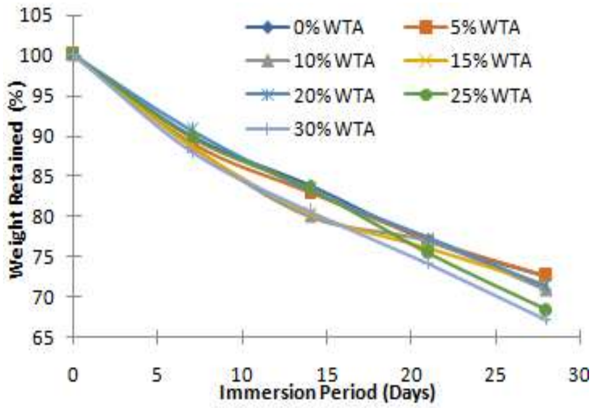

Fig. 5: Percentage weight of WTA-concrete immersed in H_2SO_4

As observed in Fig. 5, the effect of H_2SO_4 on both the OPC concrete and the WTA-Concrete seems to be more aggressive than the HCL. Generally also, there appears to be an apparent increase in the percentage weights of WTA-concrete over the control OPC concrete initially at 5% WTA replacement which later at higher WTA level decreases as observed. This may be explained in the fact that the reaction between sulphuric acid and the cement constituents of concrete have influenced the conversion of calcium hydroxide to calcium sulfate (gypsum) which in turn, may have been converted to calcium sulfoaluminate (ettringite). And that each of these reactions involves an increase in volume of the reacting solids by a factor. This is consistent with the findings of Attiogbe and Rizkalla (1988), who have confirmed the factor as two. The formation of calcium sulfate leads to softening (Moradian *et al.* 2011); leading to decrease in density of the concrete. And since weight depends on both volume and density, the initial gain of the concrete weight as observed above becomes probably due to the relative increase in volume being greater than the relative decrease in density.

The weak resistance of WTA – concrete to H_2SO_4 acid attack when compared with plain OPC concrete could be attributed to the incomplete pozzolanic reaction of WTA after 28 days of curing in water. This is consistent with the explanation of (Ogork *et al.*, 2014) in their work on Groundnut Husk Ash (GHA) – concrete under acid attack.

When concrete is exposed to environment containing sulphuric acid, it becomes exposed to severe deterioration due to neutralization reactions. Sulphuric acid reacts with free lime ($Ca(OH)_2$) in the concrete to form gypsum ($CaSO_4$. $2H_2O$). Also there is the reaction between calcium aluminate and the gypsum crystals. These two products form the less soluble reaction ettringite given as (3Cao. Al_2O_3. $3CaSO_4$. $32H_2O$) [40]. And both of these two i.e. gypsum and ettringite cause expansion which results in cracking of concrete

(Bonakdar and Mobasher, 2010). Perhaps this explains why sulphuric acid is often described as very aggressive to OPC concrete.

Consequently, the corroded concrete surface becomes soft and white, and when this continues, the corroded concrete structure loses its mechanical strength according to Monteny *et al.* (2001). But Tumadajski *et al.* (1995) have stated that the rate of deterioration of concrete exposed to sulphuric acid environment depends on: the concentration of the acid, ambient temperature, cement type, water to cement ratio, porosity and presence of admixtures. Thus, the application of a pozzolana in OPC concrete may result in a concrete with a denser structure and better ability to withstand sulfate attack but it also reduces or eliminates the free, leachable calcium hydroxide (Pavlik and Uncik, 1997).

The loss of durability by the attack of aggressive chemicals can be either due to the decomposition of cement paste or due to the destructive internal expansion caused by chemical reactions in the paste or by both combined actions. Deleterious chemicals such as acid solutions can react with $Ca(OH)_2$ to form water soluble salts that can leach out of the concrete, hence increasing the permeability of the concrete thus aggravating the attack by increased and faster ingress of harmful chemicals (Zivica and Bajza, 2001). Also according to Ramachadran (1976) sulfates can react with $Ca(OH)_2$ to form calcium sulfoaluminate (ettingrite) that can cause swelling and internal disruption of concrete.

These actions may explain the poor resistance of WTA-Concrete to sulphuric acid attack when compared with plain OPC concrete. Also according to Aboshio *et al.* (2009) and Ogork *et al.* (2014), the action could be attributed to the incomplete pozzolanic reaction of WTA after 28 days curing in water.

Chloride, sulfate, or bicarbonate of magnesium are frequently found in ground waters, seawater and some industrial effluents. The magnesium solutions react with the calcium hydroxide present in Portland cement paste to form soluble salts of calcium. $MgSO_4$ solution is very aggressive because of sulfate attack on alumina bearing hydrates present in the Portland cement paste. A characteristic feature of the magnesium ion attack on Portland cement paste is that the attack eventually is extended to the calcium silicate hydrate which is the principal cementitious constituent. Upon prolonged contact with a magnesium solution, the C-S-H in the hydrated Portland cement paste gradually loses calcium ions, which are partially or sometimes completely replaced by the magnesium ions. The ultimate product of this substitution reaction is magnesium silicate hydrate, the formation of which is associated with loss of the cementitious characteristic. This perhaps explains the behavior of the magnesium sulphate solution on the WTA- concrete as observed in Fig. 6. The weight of concrete retained decreased both with increase of WTA content and curing ages, respectively.

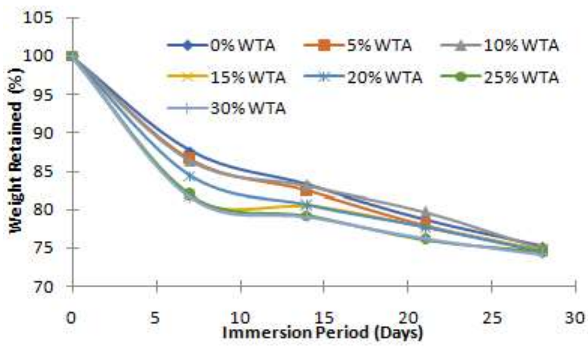

Fig. 6: Percentage weight of WTA-concrete immersed in $MgSO_4$

Generally, it was noted that 5% concentration of solution of sulphuric, hydrochloric acids and magnesium sulphate, respectively, were very aggressive media with significant detrimental effect on WTA-Concrete. The results have also shown that Sulphuric acid (H_2SO_4) is the most aggressive to OPC concrete, then Hydrochloric acid (HCL) and Magnesium Sulphate ($MgSO_4$) being the least aggressive of the three.

Conclusions

In this study, influence of waste tyre ash as a supplementary cementitious material in concrete, on the durability of concrete, was investigated. Based on the findings, the following conclusions are made:

i. WTA has low reactivity, with a combined SiO_2, Al_2O_3 and Fe_2O_3 content of 40.2% which indicate that it does not satisfy the minimum value of 70% recommended in ASTM C618 for a good pozzolana.
ii. The water absorption of WTA-motar increased with increase in WTA content.
iii. The workability of concrete significantly decreased with increase in WTA content at constant water–binder ratio.
iv. For all the media used (H_2SO_4, $MgSO_4$ and HCL), the resistance to deterioration of WTA – concrete reduced with increase in the curing age. Also concrete with WTA offered better resistance to deterioration by HCL than OPC concrete. Sulphuric acid (H_2SO_4) was the most aggressive to OPC concrete, followed by Hydrochloric acid (HCL) and lastly Magnesium Sulphate ($MgSO_4$). Sulphuric acid was again the most aggressive to WTA-concrete, then $MgSO_4$ and lastly HCL.
v. The use of WTA content as partial substitute of cement in concrete is recommended for enhanced resistance of concrete in hydrochloric acid and magnesium sulphate environments. However, this is not recommended in sulphuric acid environments.

Conflict of Interest

Author has declared that there is no conflict of interest.

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