Study of Microstructure of Waste Tyre Ash (WTA) Concrete Using the Scanning Electron Microscopy (SEM) and X – ray Diffraction (XRD) Techniques

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ABSTRACT

This paper reports the findings of an investigation into the microstructure of WTA – Concrete. The WTA was obtained by open burning of waste tyre slices to a temperature of about 5000C for about five (5) hours at the local open burning sites in Kano. And after allowing to cool, it was sieved through 75 µm BS Sieve and characterized. The ash was subjected to chemical composition analysis using the X-Ray fluorescence (XRF) analytical method using the X –Ray spectrometer machine. The investigation was carried out on a concrete of 29 N/mm2 compressive strength, Water – cement ratio (w/c) of 0.65 and slump range of 10 – 50mm. The microstructure assessment was conducted on the 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 the microstructure of WTA – Concrete using SEM and XRD techniques. Both SEM analysis and XRD results of WTA – concrete indicated the occurrence of pozzolanic reaction between WTA and cement and that the WTA has more porous micro-structure than OPC concrete especially at higher WTA concrete.

Keywords: Waste Tyre, Concrete, Microstructure, SEM, XRD

INTRODUCTION

The study of concrete microstructure has benefited greatly from the use of microscopic examination and in particular, Scanning Electron Microscopy (SEM). SEM imaging and X-ray microanalysis techniques have been developed and used for imaging the complex microstructure of concrete providing images with sub-microstructure definition. By combining the information provided in the backscattered electron and X-ray images, an accurate segmentation of the images into their constituent phases may be achieved. According to Stutzman (2001) [1], the application of SEM can enhance the possibility of characterizing cement and concrete microstructure and subsequently aid in the influence of supplementary cementing materials, concrete durability problems and in the prediction of service life.

Microstructure imaging have been adopted as an essential tool in the study of materials related to the construction sector such as concrete, cement paste, soils and rocks [2] (Hassan, 2009). Scanning Electron Microscope (SEM) which is the modern generation concept of the microstructure imaging has been described as a versatile analytical work station capable of providing several different types of images, quantitative data relating to porosity and cement paste composition and information about the microstructure of the matrix. Also, according to Hassan (2014) [3], in the last two to three decades the microscope imaging has become established as an essential tool in the study of concrete and its related materials. Referred to as the scanning electron microscope (SEM), it is a versatile analytical work station, capable of providing several different types of images, quantitative data relating to porosity and cement paste composition and information about the microstructure of the matrix. The morphology of a solid phase can be defined as its shape, form or structure at the microscopic scale, that is, the scale of nanometers and microns. The morphology of a material often has a greater impact on its microscopic properties than its chemical composition; this is certainly true of cement paste and concrete. The microstructure of cement paste revolves around the process of hydration.

The principal cementitious material in concrete and mortar is Portland cement, even though, nowadays, most concrete mixtures contain supplementary materials such as pozzolanas that make up a portion of the cementitious component in the concrete. These materials are generally by products from other processes or natural materials. They may or may not be further processed for use in concrete [4]. Pozzolanas by themselves do not have any cementitious properties, but when used with cement, react to form cementitious compound. But for these waste materials (used as Pozzolanas) to be utilized they need to meet requirements of established standards.

The performance of the Waste Tyre Ash as pozzolana for partial replacement of cement in concrete if positive and found to conform with the given standards would go a long way in providing a huge environmental benefit of disposing the ever-increasing scrap tyre nuisance in our environments and at the same time make our concrete more indigenous with less cost of production. According to Peter and John (2010) [5], well over 95% of cement used in concrete throughout the world is Portland cement in its various forms. So, any effort aimed at reducing the Portland cement content in our concretes will certainly be of interest.

A hydrous Portland cement cannot bind sand and stone; it acquires the adhesive property only when mixed with water. This is because the chemical reaction of cement with water referred to as the hydration of cement yields products that possess setting and hardening characteristics [6].

This paper attempts to show how the combination of SEM and XRD procedures can be as effective in explaining the microstructure of a pozzolana – cement - concrete during the hydration process, with Waste Tyre Ash (WTA) as the pozzolana. Conventionally the SEM with EDS provides an easier and more readily applied procedure.

MATERIALS AND METHODS

Materials

Ordinary Portland cement manufactured in Nigeria branded as Dangote 3X Grade 42.5 and having specific gravity of 3.15 was used. The oxide composition of the cement 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, bulk density of 1500 kg/m^3 and average impact value of 20.87% was used. The particle size distribution curve for the fine aggregate, coarse aggregate and WTA is shown in Figure 1 and the oxide composition of WTA as obtained and that of OPC is compared and presented in Table 1.

Table 1. Chemical composition of Ordinary Portland Cement (OPC) and Waste Tyre Ash (WTA)

Oxide (%)	Al_2O_3	SiO_2	CAO	Fe_2O_3	K_2O	MnO	MgO	SO_3	Na_2O	P_2O_5	TiO_2
OPC	2.10	18.69	65.23	3.96	0.48	0.09	1.96	2.33	2.32	-	0.31
WTA	3.41	37.40	2.13	6.39	0.54	0.05	1.20	14.71	9.32	1.64	0.37
Oxide (%)	V_2O_5	Cr_2O_3	BaO	CuO	ZnO_2	CL	LOI				
OPC	-	0.03	0.07	0.03	0.03	-	1.3				
WTA	0.03	0.01	-	-	22.39	0.38	14.6				

Methods

Concrete used for this study was obtained using the Absolute Volume Method based on a mixed ratio of 1:2:4. Using trial mixes initially concrete with compressive strength of 29N/mm2 at 28 days of curing with w/c ratio of 0.65 and slump range of 50 mm was adopted. The slightly high w/c ratio of 0.65 was intentionally adopted because it is known that usually most mineral pozzolanic materials are known to be high water absorbers [7]. The formula for the Absolute Value Method used is given in equation 1 as;

$$\frac{W}{1000} + \frac{C}{1000\ Pc} + \frac{S}{1000\ Ps} + \frac{A}{1000\ PA} = 1m^3 \qquad (1)$$

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
Pc = Specific gravity of cement
Ps = Specific gravity of fine aggregate
PA = Specific gravity of coarse aggregate

Using the above formula, seven mixes as shown in Table 2 for the batched quantities of the concrete materials and WTA were obtained. COMP 0-B is the control mix 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 cement replacement levels of 5, 10, 15, 20, 25, and 30%, respectively.

Table 2. 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

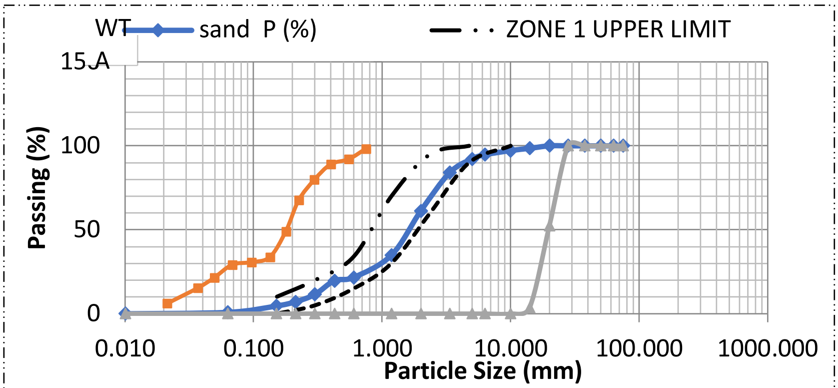

Figure 1. Particle Size Distribution of WTA, Fine Aggregates and Coarse Aggregates

The WTA was obtained by burning sliced pieces of waste tyres to ash through heating to a temperature of about 500°C in open burning for about five (5hrs) hours, at the local open burning site. The ash was allowed to cool and sieved through 75μm sieve. A chemical composition analysis of the waste tyre ash was conducted by use of X-Ray fluorescence (XRF) analytical method using X-Ray spectrometer.

The SEM works by aiming an electron beam at the surface of the Specimen. When the electron beam strikes a solid object, the electrons are either scattered or absorbed. The collection of these responses is what forms the SEM image. Crushed samples of WTA-Concrete cubes used for the compressive strength test were labeled and preserved (wrapped in foil paper and sealed in small polythene bags) for microstructure analysis of the concrete to study the effect of WTA on concrete.

X-ray Diffractometer is the equipment used to scan samples for XRD analysis. A small amount of powder sample is put into an aluminum sample holder and the surface is finished smoothly. The holder is then placed into the X-ray diffractometer. The samples are scanned by an X-ray diffractometer using CUK radiation at 40KV/20mA. CPS = 1k, width 2.5, speed 20/min and scanned with an angle of 2Ө from 3 – 70 0. The analysis is stepped at 0.04-degree increments and continued for a period of 3 seconds. In X-ray diffraction, X-rays are scattered by atoms in a pattern that indicates lattice spacing of elements present in the material analyzed. Once the X-ray analysis is completed, the scans are analyzed using Jade 7-Xray Diffraction (XRD) software. Using Jade, peak intensities at different angles are compared with a database of different minerals and compounds. Compounds with peak intensities matching those of the scans are identified and the compounds present in the samples are also determined.

RESULTS AND DISCUSSIONS

Microstructure of WTA Concrete

As already stated, SEM has become a useful tool in the study of concrete and its related materials. It has been described as a versatile analytical tool capable of providing several different types of images, qualitative data relating to porosity and cement paste composition and information about the microstructure of the concrete matrix [8]. For this study, the WTA – concrete matrix.

Accordingly, Figure 2 shows our SEM image of the control concrete (0% WTA) at seven days indicating large clusters of the light grey or brightest spots of anhydrous cement/ or calcium hydroxide crystals reflecting the early period of hydration of Ordinary Portland Cement (OPC).

OPC concrete sample at 28 days shown in Figure 3 on the other hand shows more areas of dark grey articles indicating sheet like habit of C-S-H, hexagonal habit of $Ca(OH)_2$, aggregate and the dark particles at the extreme points indicating voids. The SEM image also indicates some anhydrous cement particles through the brightest spots on the image. Overall the SEM photograph of the OPC concrete sample at 28 days (Figure 3) showed more C-S-H and $Ca(OH)_2$ than that at 7 days resulting from the hydration process. This is consistent with the Grey Image ranking analysis as presented by [2,9] respectively.

For concrete with 5 % WTA, the morphology at 28 days curing shown in the SEM picture in Figure 4 indicated observed WTA – Cement hydrated paste with large voids as evidenced by the dark patches of black areas indicating voids and the visible cracks seen consistent with the explanation of [3]. The voids here appear larger than the OPC concrete, residual cement grains appear brightest but with less hydration products of calcium hydroxide (CH) and C-S-H due to the dilution of OPC and low pozzolanic reaction of WTA at 28 days of hydration.

Figure 5 gives the SEM image of WTA concrete replacement at 10% for 28 days curing. The effect is similar to that of 5% at 28 days but with more formation of C-S-H and CH hydration products as evidenced by the presence of light gray irregular shape areas indicating calcium hydroxide crystals and dark grey areas representing calcium silicate hydrate. This observation is consistent with the explanation of [2] and [9] in their respective works on SEM image analysis.

Generally, the microstructure of WTA-concrete improved with curing age, but was more porous and exhibited more cracks with increase in WTA content.

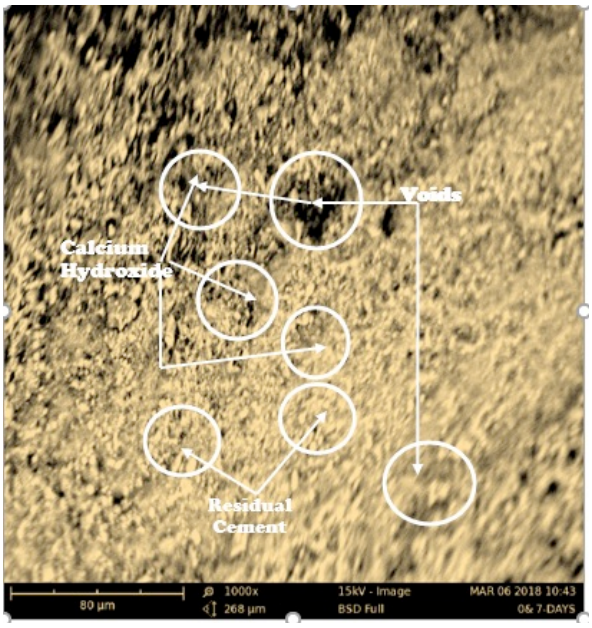

Figure 2: SEM of OPC Concrete at 7 Days

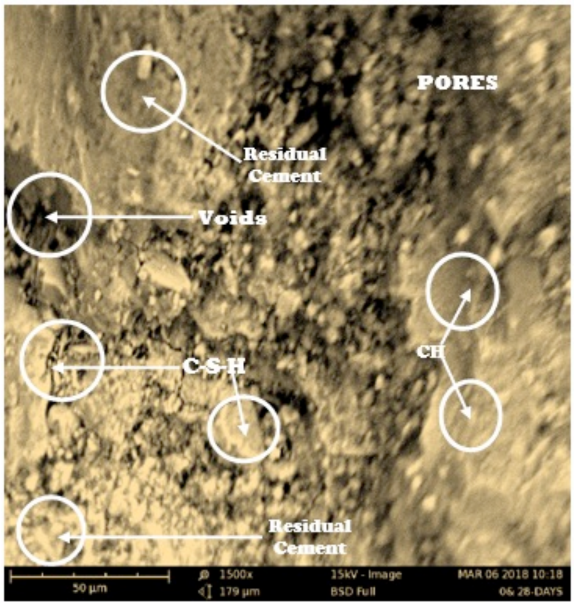

Figure 3: SEM of OPC Concrete at 28 Days

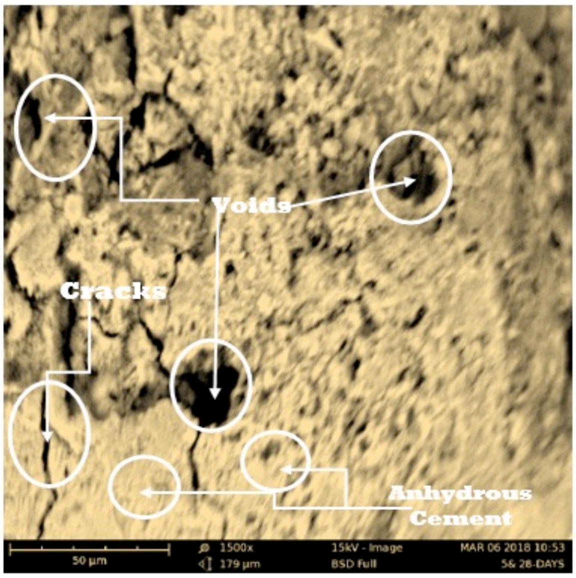

Figure 4: SEM of 5% WTA Concrete at 28 Days

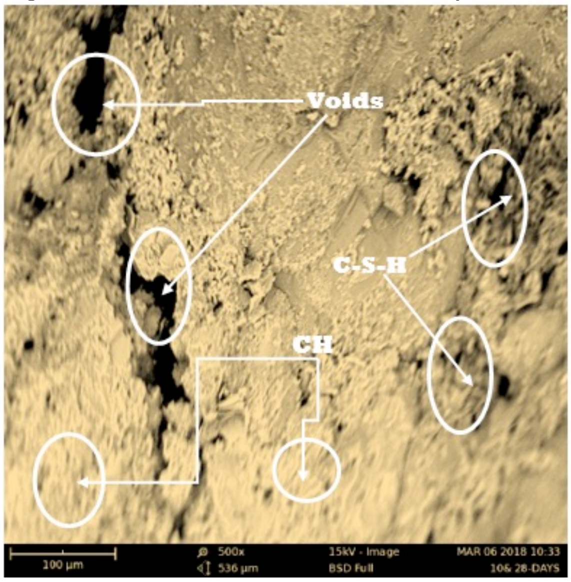

Figure 5: SEM of 10% WTA Concrete at 28 Days

XRD Result

Researchers have so far supported the combination of SEM and XRD techniques in explaining the microstructure of cement pastes and concrete materials [8, 10, 11].

In line with this approach, XRD analysis was carried out on the concrete used in this study to reveal the microstructure of WTA – concrete.

Figure 6 shows the XRD pattern indicating the development of reaction products in the control plain OPC concrete at day 7. At 7 days as shown in the Figure, the crystalline phases identified are Portlandite, Quartz and calcite. However, the focal point of interest here is the Portlandite content since it indicates the progress of cement hydration and pozzolanic reactions [10,11]. As expected, the concentration of Portlandite as observed in Figure 7 is seen to have considerably reduced for the OPC concrete curing age of 28 days. This may be attributed to the progressive hydration process expected. This further explains the increase in strength as the age of curing of the concrete increases.

At 5% WTA replacement as shown in Figure 8 for 28 days of curing respectively, the Portlandite content is either almost similar to or slightly lower than that of plain OPC indicating little or no contribution of WTA via pozzolanic reaction at early ages. The presence of calcite in all the mixes can be attributed to the secondary reaction of Portlandite with atmospheric carbon dioxide (CO2). This is consistent with the explanation of [10] in their work on Palm Oil Ash and metakaolin ternary blend cement mortar at elevated temperatures. At later age, 28 days and for higher WTA content, as shown in Figure 9, the amount of Portlandite and unreacted alite and belite progressively and significantly reduced, marking the progress of hydration and pozzolanic reaction. At 30% WTA replacement, however, as seen in Figure 10, the reduction in strength of WTA - Concrete may be due to dilution effect of cement at that level.

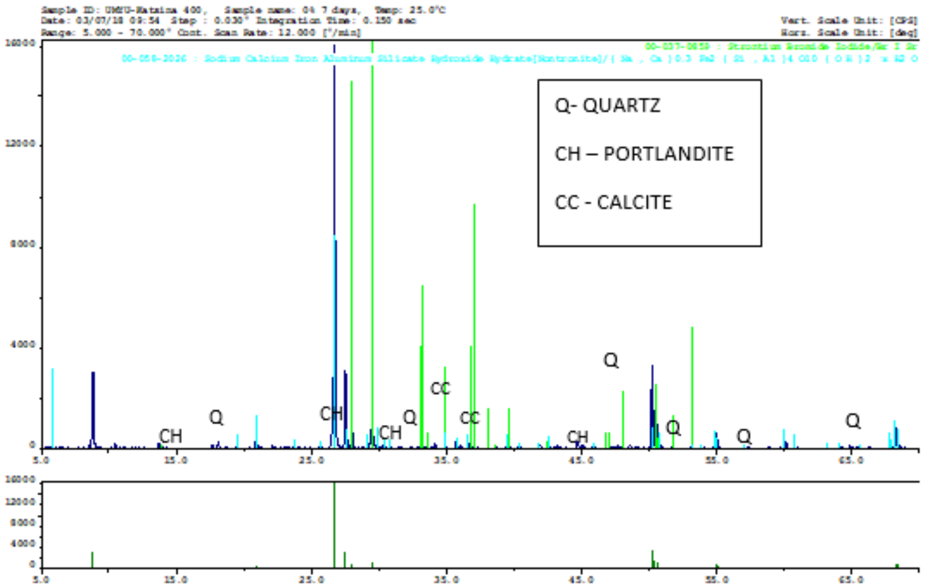

Figure 6. XRD Pattern of Control(OPC) Concrete Specimen for 0%WTA at 7 Days.

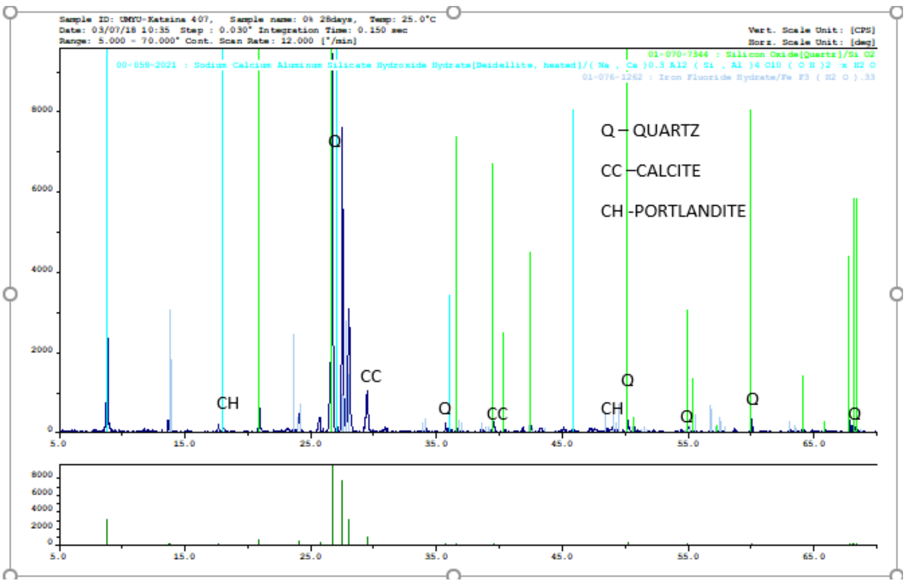

Figure 7. XRD Pattern of Control (OPC) Concrete Specimen at 28 days.

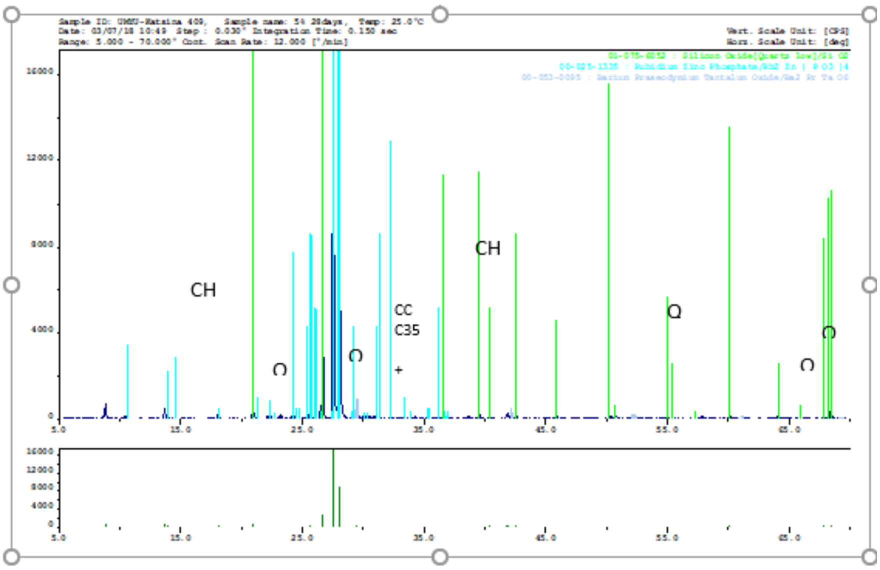

Figure 8. XRD Pattern of 5% WTA Replaced Concrete Specimen at 28 days.

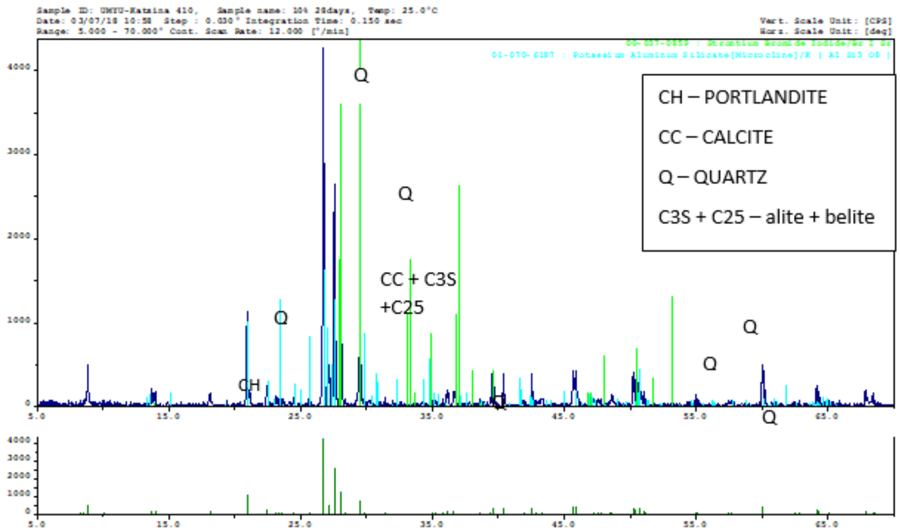

Figure 9. XRD Pattern of 10% WTA Replaced Concrete Specimen at 28 days.

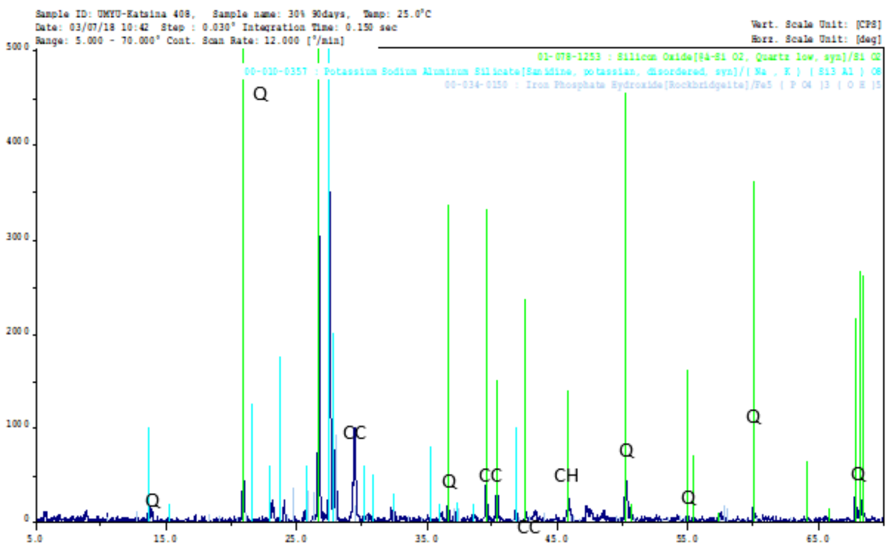

Figure 10. XRD Pattern of 30% WTA Replaced Concrete Specimen at 90 days

CONCLUSION

Both SEM analysis and XRD results of WTA – concrete indicated the occurrence of pozzolanic reaction between WTA and cement and that the WTA – concrete has more porous microstructure than the OPC concrete especially at higher WTA.

It also shows that the pores in the WTA concrete increase with increase in the waste tyre ash in the mix.

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