Characterization of Particulate Matter in the Process of Manufacturing Titanium Metal Powder

Thingahangwi Madzivhandila, Nthabiseng Maledi, Shahed Fazluddin

Abstract—Working in the metal powder production environment may result in a high level of particulate matter, which might pose a health threat. The main objective of this study is to determine the amount and type of the particles that might be emitted at the main sections of the Titanium production process and evaluate and characterize the exposure risk and exposure variability within persons, between persons, and between groups to the community working in that environment and compare the results with the Occupational Health Limit. The samples were collected randomly using sampling pumps set at 2 l/min flow rate and 25 mm Polyvinyl chloride filters with a diameter of 0.8 microns. The weighing balance was to determine the amount of particulate matter loaded in the filter, X-ray powder diffraction to determine and quantify the crystalline particulate matter collected from the study area, X-ray fluorescence was used to determine the elemental composition of the particulate matter and Fourier-transform infrared spectroscopy was used to determine the arrangement of particulate matter through their movement. The assessment is computed from the location of the sample and variables. The results obtained by the weighing balance confirmed the low amount of the particulate matter loaded in the filters in all sample locations except at the $TiCl_4$ loading section. The same samples were analyzed by XRD and FTIR and the crystalline peak was identified confirming the presence of silicates and carbonate minerals. The analysis done by XRF confirms the presence of an oxide element. The association between variables and crystalline particulate matter concentration was assessed through linear regression modelling. This model was based on the calculation of mean, minimum and maximum and standard deviation values of each variable. The outcome variable respirable crystalline particulate matter concentration was log-transformed before the analysis. All the variables showed a non-significantly weak correlation with particulate matter concentration. The overall p-value for all variables showed statistically non-significant association with log-transformed average particulate matter concentration (p = 0.853). As the distance increased by 1 m, the particulate matter concentration decreased by 0.05% with significant differences (Coefficient: -0.0005; 95% CI: -0.00091; P = 0.050). As the wind speed increased by every 1 m/s^2, the mean of concentration particulate matter increased by 14% while every 1% increase in humidity showed a 0.2% decrease in average particulate matter concentration.

Keywords—Particulate matter, monitoring, characterization, concentration.

I. INTRODUCTION

CHARACTERIZING and maintaining the particulate matter at appropriate levels is one of the biggest challenges the world [1]. The characterization of particulate matter was done in occupational environment with the aim of identifying and quantifying exposure and comparing them with occupational health limit [1]. In order to be able to control the exposure and improve the quality of indoor environment, the quantification of particulate matter was of importance [2]. The anthropogenic and artificial are known sources that resulted to atmospheric pollution [3]. Particulate matter can cause health problems and environmental problems [2]. Human health problems caused by the emission of ultra-fine particles include breathing problems, oxidative stress, which can cause cardiovascular and neurological problems [4]. The particulate matters were measured in the same environment (Placeholder1)(using same materials and equipment to minimize the variation errors [5]. The determination of component of particulate matter was done using XRD and FTIR[6].

II. METHOD AND MATERIALS

A. Description of the Study Area

This study was conducted at the pilot plant of the CSIR. The CSIR is surrounded by the residential community and biodiversity community as shown in Fig. 1.

Fig. 1 Aerial photograph positioning the CSIR preferably Ti-Plant. Red colour is the whole of CSIR; green colour is the location of Ti-Plant within CSIR

The geographical location of the study area positioned at south gate of the CSIR with the following coordinates 28º16′36″E longitude and 25º45′18.5″S. The study area is comprised of 13 employees including contractors.

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B. Sample Selection

The samples were selected randomly with the characteristics of homogenous, known conclusive and unbiased results. The sample frame (target population) of this study was based on the existent population and part of population (sample) through sampling. To avoid the unbalanced sampling, the samples were duplicated and validated repeatedly. Sample size and related sampling error (precision) was determined using a target variance of an estimate sample to maintain the good precision and lowered the estimated variance. PVC filter papers were selected for the study with their properties of water vapour resistant, electrostatic and stable. The selection of cyclone was done to define the respirable particle sampling criteria and the importance of flow rate.
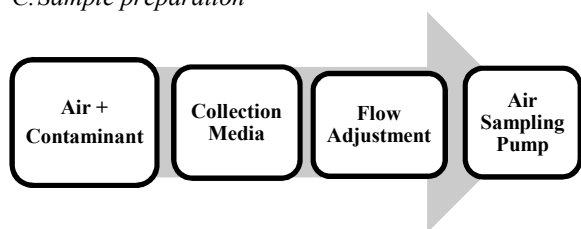
C. Sample preparation

Fig. 2 Particulate Matter Sampling preparation methodology

The materials used for air and contaminant sampling includes cassette with base, 25mm diameter PVC filters, forceps, blunt tipped, blue protective caps for filters (before sampling), red protective caps for filter cassettes (after sampling), yellow protective hose covers for field blank cassettes (blank), 47mm petri dishes, zip lock two quart plastic bags, sampling pumps, and tube pipe. Site and sampling date stickers for sampling cassette labelling, sampling sheets, and environmental conditions sampling sheets. The filters were labelled with a unique code each and acclimatized in an environmentally controlled for overnight (fig. 3).
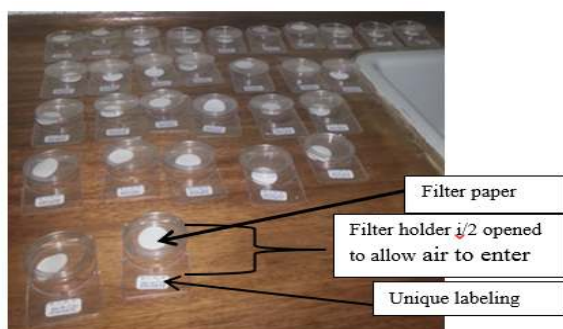

Fig. 3 Acclimatization of air samples in a stable environmental condition at weighing balance room where temperature range is 20°c-25°c and Humidity range of 45%-75% (HSL Guideline).

Forceps was used to place the filter support pad in the top tier of the cassette. The plug was removed from the outlet of the cassette; the end was attached to cassette using tygon tubing. The filter was placed on top of the support pad in the top tier

of the cassette and the middle tier was added and closed at the both ends of the cassettes with a protective cap. The cellulose shrink band was placed around the filter cassette and allowed to dry to prevent linkage (fig. 4).

Fig. 4 Sampling Train

Sampling pumps was calibrated using calibrator and operated properly to draw a constant flow [1]. To ensure this, the sampling pump was sufficiently charged, properly maintained, and calibrated with appropriate airflow meter instrumentation and calibrated before sampling and after sampling has been done. The calibration tubing was inspected for leaks, deformed tubing, and cracked rubber. To conduct calibration, sampling pumps were connected to the main calibrator through the bell jar and with appropriate flow cell of 20cc-6lpm. The initial reading to ascertain the current flow rate of the pump was recorded, and making an appropriate adjustments to the pump using a screwdriver to adjust the calibration screw and checking each adjustment with a reading. The sampling pumps were calibrated at a flow rate of 2 liter per minute (L/Min). Once acceptable readings are obtained, ten measurements were recorded and averaged. The averaged reading should be within the acceptable calibration range which is +/- 5% of target flow rate.
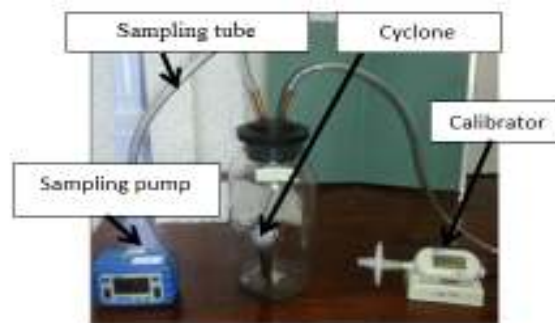

Fig. 5 Calibration set-ups

D. Sample Collection

The selection of study areas was determined by means of a face to face survey. For each selected study area, static samples (sampling from fixed location) were collected randomly.

Fig. 6 Sampling Strategy

The assessment of resources was conducted before sample collection to check if there is sufficient access to study population, sufficient time to conduct and complete the study, adequate qualified staff members to conduct the study and if the staff were adequately trained on protocol and their specific research related[7]. The sample was collected following OESSM sampling strategy designed by NIOSH publication no: 77-173 of 1977, United State of America. The three samples were collected before operation, during operation and after operation to compare the exposure to the days of operations. The samples were collected for eight hours shift[4]. Total number of 45 samples was collected. The filter was placed inside the cassette and to the sampling pump using the short flexible connecting tube. The sample collection trains were used based on the literature and experiments figure 7.

Fig. 7 Sampling Station

The samples in the cassettes were placed upside down and covered with a red cap to show that sampling has been completed (Fig. 8). The box was closed, locked securely packed in the upright position within purpose designed special cases designated for transporting equipment and transported to the laboratory together with sampling sheets.

Fig 8 Air samples inside the sample transportation box

E. Sample Analysis

The samples were analyzed at air and dust laboratory of CSIR. The Laboratory is ISO 17025:12017 SANAS accredited for both weighing balance and x-ray powder diffraction. Filters, cassettes, filter pads; forceps and cyclone were used to prepare the samples analysis. Chow and Watson, 1998 confirmed that during the analysis of particulate matter concentration depends on the mass, type and size of the material loaded. To determine the mass of material loaded, 5 decimal places weighing balance and ionizer for antistatic (Figure 2-8) was used following MDHS 14/3 (Method for Determination of Hazardous Substances).

Fig. 9 A-Weighing Balance and **B**-Ionizer

The weighing balance is installed in optimized working conditions to obtain the results that are within a specified tolerance of sample weight variation, accuracy of technological processes and others. Before weighing is conducted, the environmental condition (humidity and temperature) was checked and recorded (MDHS 14/4). To prepare the equipment to analyze the samples, the reference weights ($1000\mu g$, $2000\mu g$ and $5000\mu g$) were verified to assess the accuracy of the weighing balance. The operation principle of the weighing balance is movement of the weighing dish assembly in an electromagnetic field[8]. When the samples is placed on the weighing dish, the change in position of the weighing dish changes the electronic characteristics of those magnetic fields in proportion to the mass. The translated mass value is displayed on the balance. The samples were weighed before sampling and after sampling to determine the weight gain or loss of the air samples during air sampling and to

determine the moisture percentage content in the soil samples. The workstation was located far away from air conditioning devices to prevent air drafts (Fig. 10).
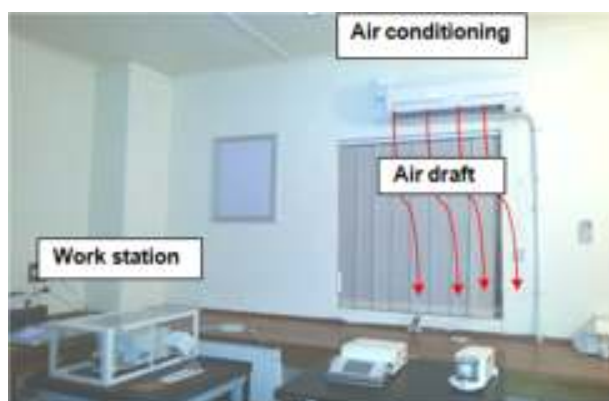

Fig. 10 Position of a weighing balance workstation.

The PM concentrations were determined as per table 1. The volume of air passing through the sampler was calculated by multiplying the average volumetric flow rate in litres per minute by sampling time in minutes. The net weight/ mass correction gain (has been converted into mg by multiplying by 1000) of the samples and divided by air sampled (m³) to give the average dust concentration in milligram per cubic meter of air (mg/m³).

TABLE 1
FORMULA USED TO DETERMINE THE
CONCENTRATION OF PM LOADED BY
GRAVIMETRIC ANALYSIS

The type of material was determined by Rietveld method of XRD and MDHS 101/2. The Analytical X'Pert PRO powder diffractometer was used to determine the chemical composition of the PM. XRD is a versatile, non-destructive analytical technique for identification and quantitative determination of a various crystalline forms. The condition of the samples were checked and declaimed well. After receipt, the cassettes holders were opened and filter papers were taken out using a forceps and placed in the labelled filter holder (Fig. 11).

Fig. 11 Air samples analysis preparation

The bragg Law was used to quantify the results with the correct angle (2θ) to fulfil the Bragg condition with the following equation:

$$n \lambda = 2dsin\theta. \qquad (a)$$

Where: d = is the spacing between diffracting planes
θ = is the incident angle
n = is any integer
λ = is the wavelength of the beam.

The filter diameter (25mm), filter pore size (0.8μm), standard flow rate of 2L/Min and cyclone type used during the sample collection determined the respirable particle size which is best suited for PM_{10} and $PM_{2.5}$ (EPA,2006). The portable handled XRF DP6000 was used to determine the elemental

VARIABLE	FORMULA
Mass of PM (μg)	Post Mass-Pre Mass
Volume of sample air (m³)	$\dfrac{\text{flow rate (l.m}^{-1})\text{ x Sample time (min)}}{1000}$
PM Concentration (mg/m³)	$\dfrac{\text{Mass of PM(mg)}}{\text{Volume of air sampled (m}^3)}$

composition of the material. The analyses were based on US-EPA 6200 method of determination for element in the air using XRF (revision 2007) fig. 12.

Fig. 12 IN-SITU analysis of particulate matter by X-rays Fluorescence

The X-ray fluorescence radiation was emitted from the sample to receiver where the element started to be analysed. The rays from the sample source strike an inner shell electron in the sample and remove it from the atom. As the atom consists of a nucleus (protons and neutrons) and electrons, the electrons spin in the shells at specific distances from the nucleus and separate energy in the inner shell where the electrons are bound more tightly and are harder to be removed from the atom fig. 13.
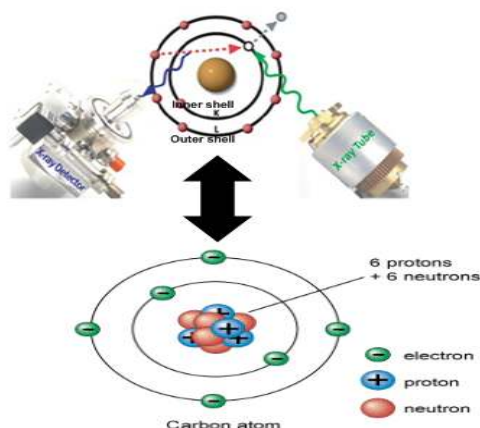

Fig. 13 Atomic structure after Georg Siegbahn, 1924

The enough energy of 20 keV was used to remove atom from the inner shell (K) to outer shell (N). The electrons were then start move through the gas and create a current, which raises some electrons in other atoms to higher energy levels; this level is x-ray emission lines for a heavy element including Au and Pb [9]. Once the energy level increases, the electrons turn back in the atoms and release electromagnetic radiation (light). The amount of light released at different wavelengths, called the emission spectrum to detect a light elements (such as Mg, Al, Si, Ca) or medium elements (such as Cr, Fe, Cu, Ag) which are located at 1st energy level [2].
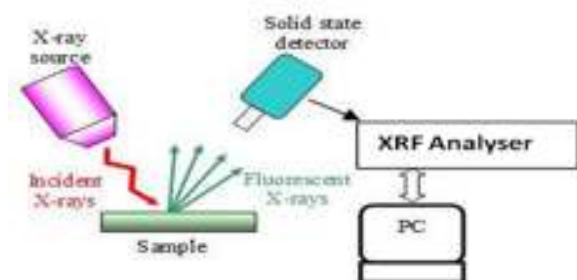

Fig. 14 Detailed how the PM samples are analysed by X-rays Fluorescence after (D.C Harris, 2007)

The fig 14 explained that the source X-rays irradiates the sample, and the sample detector measures the X-ray fluorescence radiation emitted from the sample. To stimulate the emission of characteristic X-rays from a specimen, a high-energy beam of charged particles such as electrons or protons were determined into the sample. The X-rays were emitted from a specimen and measured by an energy-dispersive spectrometer and produce photoelectric effect in a XRF

spectrum form.

Fig. 15 Showing Fourier Transform Infrared Spectrometry instrument to analyze respirable particulate matter.

The FTIR was used to analyze organic and in-organic particulate matter on a filter media. The FTIR is a non-dispersive probing in the mid-IR range radiationThe materials were thin enough to allow the absorbance spectrum in a sample without sample preparation at 400-4000cm vibrational frequencies [10]. The electromagnetic wavelength range from 400cm⁻1-400cm⁻1 was used to determine the particulate matter of 2.5µm to 25µm (Figure 2-16).
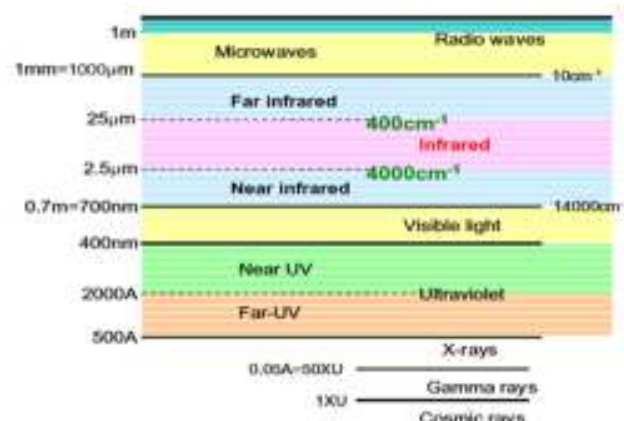

Fig. 16 Electro-magnetic radiation used to analyse particulate matter FTIR

When the sample analysed, the infrared spectroscopy transform the IR radiation passed through a sample, the molecular bonds absorbs and transmits frequency of the vibration models of electric dipole and electric field [6] and resulting to spectrum which represents the molecular absorption and transmission, creating a molecular fingerprint of the sample[11] .

III. RESULTS

A. X ray fluorescence results

TABLE II
RESULTS FOR THE ELEMENT IDENTIFED IN
THE STUDY AREA

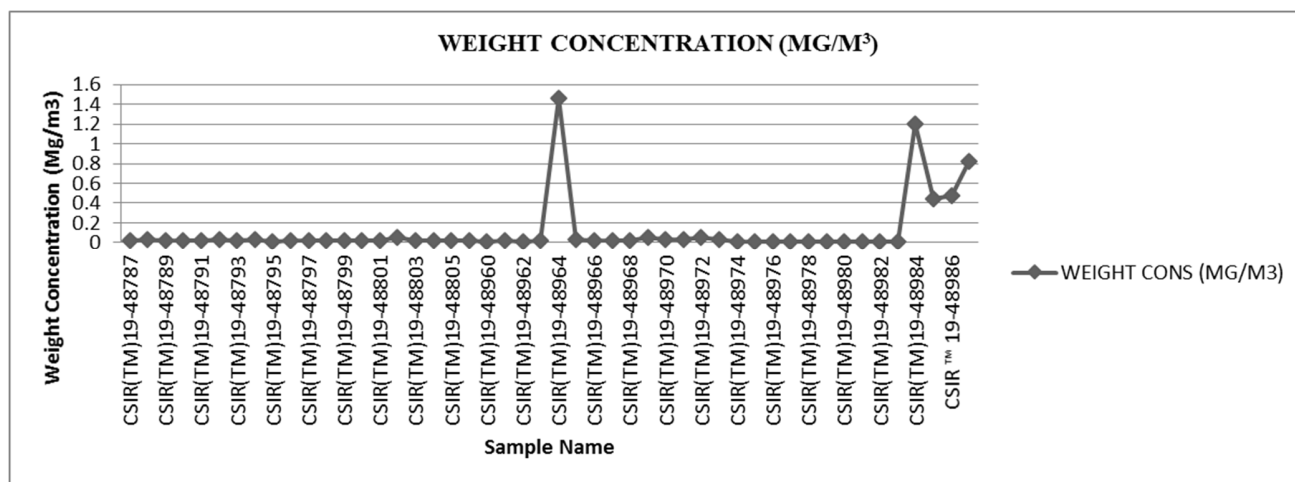| name of the element	LODS (PPM)	Pilot Plant (avrg cons %)	Crusher (Average Concentration in %)
LE		65.3	23.14
Cu	5	<LoD	<LoD
Fe	450	<LoD	<LoD
Al	10	<LoD	<LoD
Ag	5	<LoD	<LoD
Ti	5	<LoD	<LoD
S	20	<LoD	<LoD

B.   Weighing Balance Results

Fig. 17 Particulate Matter weight concentration versus the sample name

The high weight concentration of PM was obtained by sample number CSIR™-19-48964 and followed sample number CSIR™-19-48984 with the concentration of above 1mg/m³. The sample position of these samples was at the $TiCl_4$ loading section. The sample CSIR™-19-48964 was taken on the 13th of March 2019 and sample number CSIR™-19-48984 was collected on the 14th of March 2019. The sample number CSIR™-19-48985, CSIR™-19-48986 and CSIR™-19-48987 were also loaded slightly high PM concentration.
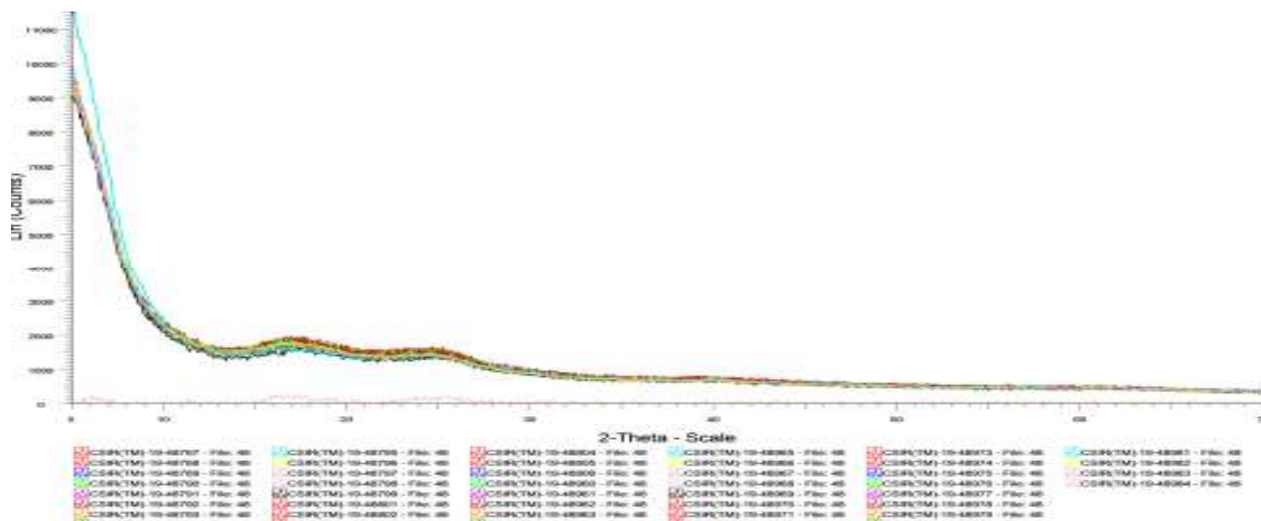
C.   X-ray diffraction Results

Fig. 17 Full scan of all samples collected from the study areas being analyzed by X-ray powder diffraction.

In figure 17 there is no peak observed for most of the samples analyzed by the X-ray powder diffraction qualitatively. The noise background was overruling the spectra scan. Sample CSIR™-19-48964, CSIR™-19-48984, CSIR™-19-48985 and CSIR™-19-48986 experienced a small peak. The detailed information about the peaks are summarized in figure 18 and 19.
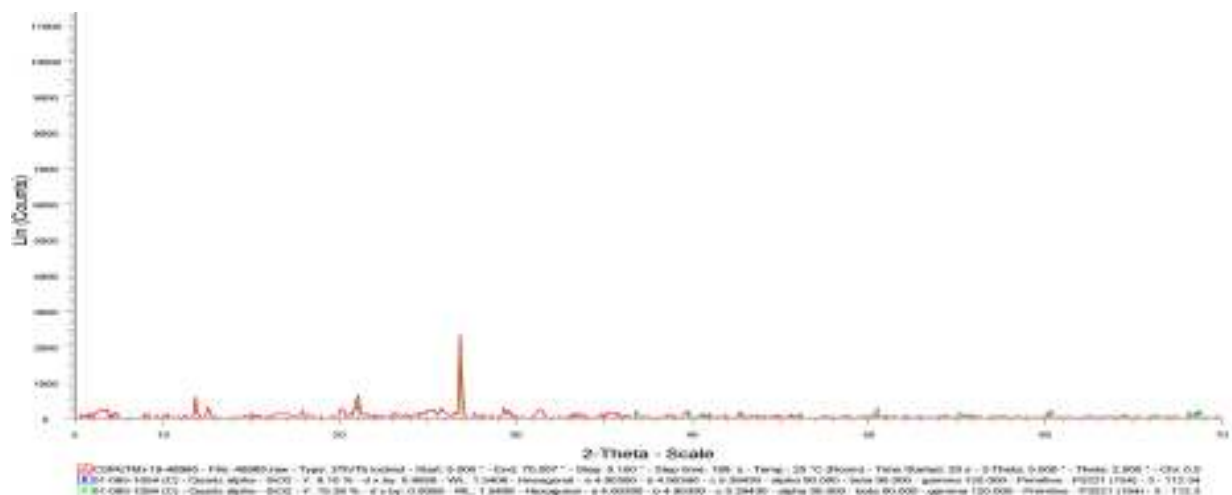

Fig. 18 Showing the full scan of all samples collected from the study areas being analyzed by X-ray powder diffraction.

In this figure there is no peak observed for most of the samples analyzed by the X-ray powder diffraction qualitatively. The noise background was overruling the spectra scan. Sample CSIR™-19-48964, CSIR™-19-48984, CSIR™-19-48985 and CSIR™-19-48986 experienced a small peak. The detailed information about the those peaks are summarized at figures below
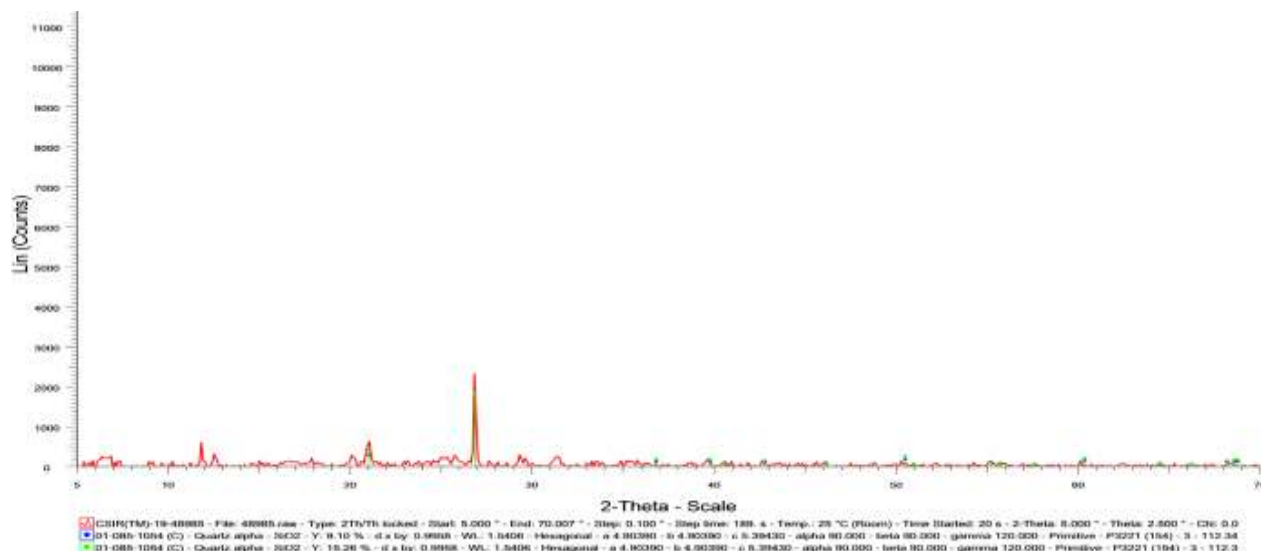
Fig. 19 Detailed analysis for sample CSIR™-19-48985 by X-ray powder diffraction

In figure 18, two peaks has been observed. About 9.10% of alpha quartz was determined at 20º 2θ whereas about 15.26% of alpha quartz was observed at 26.6º2θ. Both identified alpha quartz has a hexagonal structure. The other small peaks were also identified with less than 0% PM concentration.
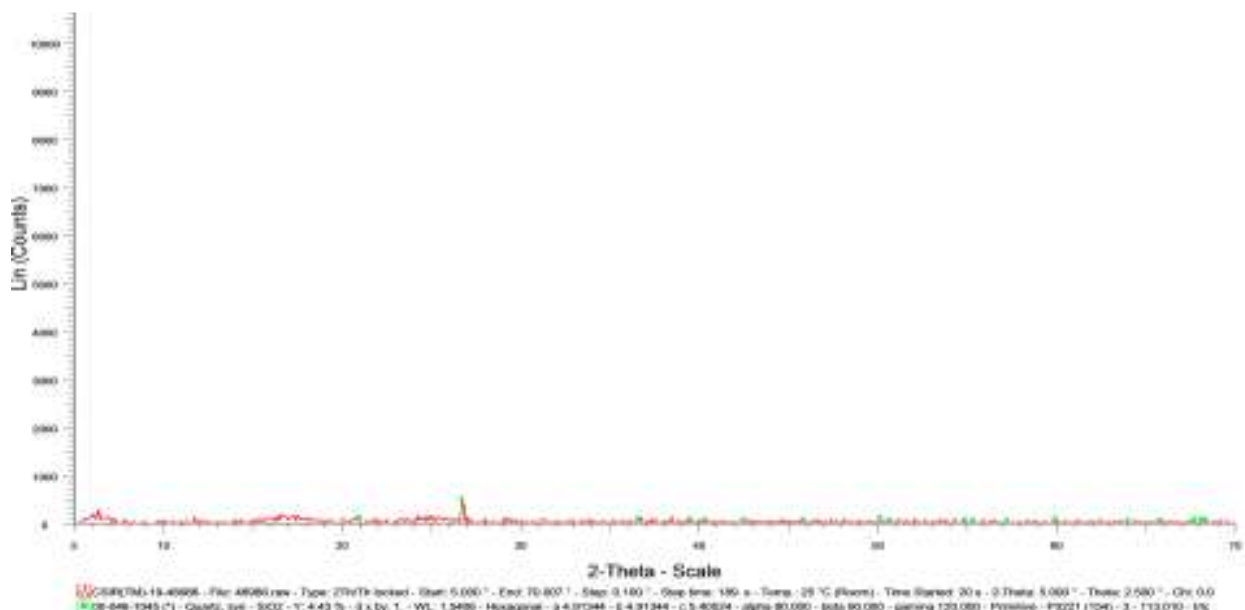

Fig. 20 Detailed analysis for sample CSIR™-19-48986 by X-ray powder diffraction

In figure 19, one peak was observed with 4.43% of quartz syn quartz at 27º 2θ. The structural form of this sample was hexagonal structure. The other small peaks were also identified with less than 0% PM concentration.
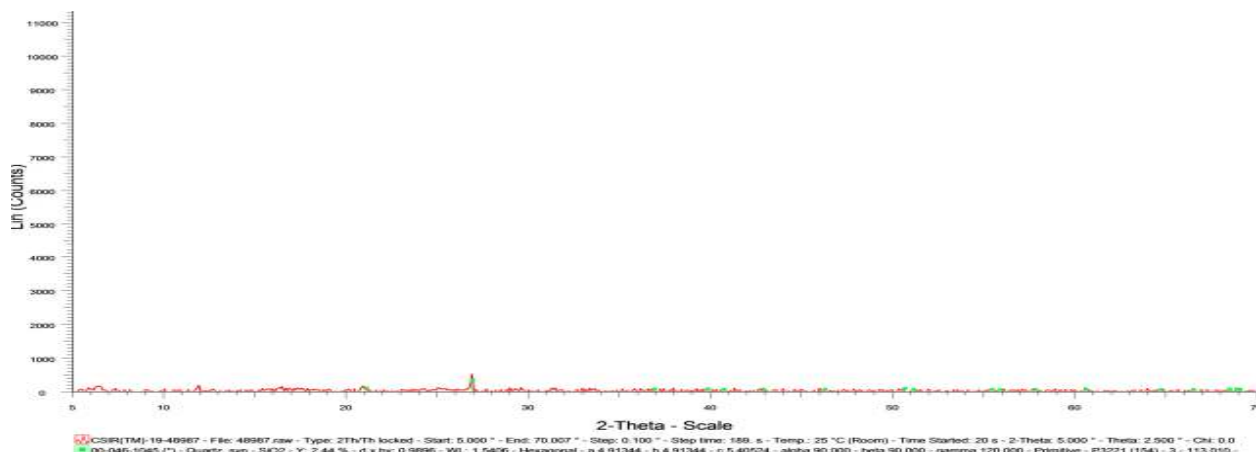
Fig. 21 Detailed analysis for sample CSIR™-19-48987 by XRD

In figure 20, one peak was observed with 2.44% of quartz syn quartz at 27º 2θ. The structural form of this sample was hexagonal structure. The other small peaks were also identified represented by green colour with less than 0% PM concentration.

IV. DISCUSSION OF THE RESULTS

The results obtained by XRD indicated the decrease in the concentration of PM as the sampling days increased. With the evidence given by the weight concentration of gravimetric analysis, the high amount of PM loaded in the samples were also experienced at the same samples as the XRD find. The Both light and heavy elements were identified by XRF were below limit of detection. The results obtained by XRF confirmed the different sources of the materials for example the presence of Al, Ca, Cu, Fe, Mg, Mn,Na, K, Pb, V, Zn represented the industrial source [12]. The presence of Fe, Zn, Ni, Cr and Ti confirmed the metal containing particulate matter that contain more than two or more metals [12]. Cr, Fe, Ni, Pb, Ti, V, Mn, Co and Zn are trace metals in the atmosphere [5]. EPA's National Ambient Air Quality Standard is designed to protect against exposures of the entire group of oxides, carbonates and toxic chemicals[13]. Particulate Matter concentration was also computed for sample positions and distance between the sample positions. Pearson correlation coefficient for linear relationship between the dependent variable and predicator variables was established as per table Ⅲ

TABLE Ⅲ

AVERAGE SUMMARY OF PARTICULATE MATTER CONCENTRATION BY SAMPLE POSITION AND SAMPLE DISTANCE

Sample Positions	Mean($\mu g/m^3$)	(SD)
Ticl₄ Loading Section	6.6	±8.0
Reduction Section	1.9	±3.1
Operator Section	1.7	±2.0
Surrounding	2.4	±2.3
Outside the Pilot plant	3.8	±5.1
Sample Distance	**Mean($\mu g/m3$)**	**(SD)**
0m away from the crusher	1.3	±1.3
500m away from the crusher	2.8	±3.1
1000m away from the crusher	3.1	±2.2
1500m away from the crusher	2.2	±2.6
2000m away from the crusher	3.8	±7.0

SD: Standard deviation

In Table Ⅲ the summary of Particulate Matter concentration was determined according to position of the samples and distance between them. The highest average concentration of Particulate Matter was almost 7 $\mu g/m^3$ with standard deviation of ±8.0 and was found in Ticl₄ lading section, followed by nearly 4 $\mu g/m^3$ carried standard deviation of ±5.1 in outside the Pilot plant, and the lowest Particulate Matter concentration was observed in operator section. Much of the Particulate Matter

concentration was obtained during crushing in all sample distances. The average concentration of Particulate Matter at 2000m away from the crusher was about 4 μg/m^3 while at 1000 m away from the crusher was 3.1 μg/m^3. At 500m away from the crusher was low 2.2 μg/m^3 and standard deviation of ±2.6.

To assess association between variables and Particulate Matter concentration, linear regression modelling was conducted for unadjusted analysis[14]. This model was based on the calculation of mean, minimum and maximum and standard deviation values of each variable[15]. Five variables were assessed (study locations, seasons, humidity, wind speed and distance). The outcome variable of Particulate Matter concentration was log transformed before the analysis as per table IV.

TABLE IV

RELATIONSHIP BETWEEN STUDY CHARACTERISTICS AND PM CONCENTRATION

Study Characteristics	Coefficients	P values	95%
Location of samples	0.0522	0.6134	1.614
Temperature	0.0554	0.5920	0.750
Humidity	-0.0938	0.3631	0.017
Wind Speed	0.0704	0.4954	0.293
Distance	-0.1073	0.2983	-3.06^0

Table IV indicates measure of the strength of the linear relationship between the explanatory factors and the outcome variables. All the variables showed non-significantly weak correlation with PM concentration[16]. The location of samples, Distance between the sample position and wind speed showed a positive correlation, Particulate Matter concentration decreased as humidity and distance increases (negative correlation) [17]. The overall p value for season showed statistically non-significant association with log transformed [18]average Particulate Matter concentration (p=0.853). For a 1 metre increase in distance, the average concentration of PM decreased by 0.05% with marginally significant differences (Coefficient: -0.0005; 95% CI: -0.00091   -3.06-7; P= 0.050). As the wind speed increased by every 1 m/s2, the mean of concentration PM increased by 14% while every 1% increase in humidity showed a 0.2% decrease in average articulate Matter concentration[19].

V. CONCLUSION

Environmental Protection Agency "National Ambient Air Quality Standard" is designed to protect against exposures of the entire group of oxides, carbonates and toxic chemicals. The study indicated the presence of oxides, carbonate and toxic chemicals in less than occupational Health Limit. The study determine presence of low temperature particulate matter at the beginning of the process and high temperature particulate matter at the end of the process shows the variation in the process was also determined, so the Health and Safety Management Tool is required to control and maintain the process.

ACKNOWLEDGEMENT

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