

Air Quality Assessment of Cement Manufacturing Process: A Case Study in Khulna City

By

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DECLARATION

This is to certify that the thesis work entitled as “Air Quality Assessment of Cement Manufacturing Process: A Case Study in Khulna City” has been carried out by the Zerine Binte Alam in the Department of Civil Engineering, Khulna University of Engineering & Technology, Khulna, Bangladesh. The above research work or any part of this work has not been submitted anywhere for the award of any degree or diploma.

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To

My parents

Mentors of my life.....

ABSTRACT

Air pollution has deleterious impacts on human health and environment. Industrial sector has always led to increase the immense challenge of controlling this atmospheric pollution. Cement industry is one of the potential anthropogenic sources of air pollution and gradual substitution of traditional building patterns by modern high-rise ones has pushed up the use of cement in Bangladesh. It may cause an alteration on the air quality of Bangladesh in near future until any initiatives taken. Therefore, this study has made an attempt to determine the contribution level of a sampled cement manufacturing factory (CMF) on human health. With this consequence, this study has estimated the emission of air pollutant's by emission factor method, characterized existed materials by different micro analysis such as XRF, particle size analysis SEM-EDS, XRD, and FTIR to correlate them with the health risk exposure. In addition it has also assessed occupational health risks at sampled CMF.

The results of XRF analysis showed that the oxides such as CaO, SiO₂, Al₂O₃, MgO, SO₃, K₂O, Na₂O, and Fe₂O₃ are available in raw materials, products and by-products of CMF. SEM micrographs have evidently shown the existence of fine particles (<PM_{0.5}). The presence of heavy metals i.e. Ti and Mo are identified (Ti in clinker, gypsum and fly-ash, Mo in PCC, bag filter dust, clinker and slag) by EDS analysis. XRD analysis reveals the existence of carcinogenic substances i.e. α -quartz in sampled PCC, road dust, bag filter dust, fly ash and limestone. FTIR analysis also confirms the similar finding of XRD by bonding confirmation.

The study reveals the sampled CMF at Labanchara, Khulna executes a grinding based cement production where raw materials including clinker are being imported. Consequently, the CMF emits less gaseous pollutants and however, it produces a significant amount of dust. The CMF generates dust of approximately 50.31 metric ton/year to the surroundings. It signifies 51 g of dust is being discharged from per metric ton cement production or 2.57 g of dust from 1 cement bag. The CMF has the total annual emission of 162 kg, 157 kg, 33 kg, 13 kg and 11 kg of CO, NO_x, VOC_s, SO₂, and PM₁₀ respectively for vehicular movement.

The AQI of Labanchara CMF indicates moderate level of health concern. Annual number of premature deaths due to exposure to PM₁₀ is found for all cause mortality as 0.145 (95% CI: 0.115-0.178) at Labanchara CMF. Annual number of premature deaths due to exposure to PM_{2.5} is found as 0.135 (95% CI: 0.055-0.194) and 0.009 (95% CI: 0.004-0.012) for cardio-pulmonary diseases and lung cancer respectively there. The DALYs for study area has found as 6 hours per year per worker at CMF due to the exposure of PM which indicates the importance of imposing emission estimation and reporting policy for cement industries in Bangladesh.

The study concludes that the PCC is more hazardous than OPC regarding the health issue as it contains comparatively finer particles and carcinogenic substances such as crystalline silica originated from fly ash. Also the presence of very fine particles, heavy metals and crystalline silica making the cement dusts itself very hazardous substances. As a result it can cause harm on people upon inhalation staying within industry or in the vicinity of its surrounding. Even people working in or near construction site may be in alarming condition if no measure is taken when this cement product will be used for construction.

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ABBREVIATION

AQMP	Air Quality Management Project
ASTM	American Society for Testing Material
ATR	Attenuated Total Reflectance
AQI	Air Quality Index
BSE	Back Scattered Electrons
CAMS	Continuous Air Monitoring Stations
CEIDARS	California Emission Inventory Data and Reporting System
CASE	Clean Air and Sustainable Environment
CO	Carbon Monoxide
CO ₂	Carbon Dioxide
CMF	Cement Manufacturing Company
CI	Confidence Interval
DoE	Department of Environment
DALYs	Disability Adjusted Life Years
EET	Emission Estimation Technique
EBD	Environmental Burden of Diseases
FTIR	Fourier Transform Infra-Red spectroscopy
GoB	Government of Bangladesh
HSE	Health and Safety Executive
IR	Infra-red
KCC	Khulna City Corporation
NILU	Norwegian Institute for Air Research
NO _x	Nitrogen Oxides
NPI	National Pollutant Inventory
OPC	Ordinary Portland Cement
PCC	Portland Composite Cement
PM	Particulate Matter
PM ₁₀	Particulate Matter Having Diameter of 2.5 to 10 Micrometers
PM _{2.5}	Particulate Matter Having Diameter Smaller than 2.5 Micrometers

SEM - EDS	Scanning Electron Microscopy with Energy Dispersive Spectroscopy
SO ₂	Sulfur Dioxide
TDF	Tyre Derived Fuel
TSP	Total Suspended Particles
USAID	United States Agency for International Development
USEPA	United States Environmental Protection Agency
VOC	Volatile Organic Matter
VKT	Vehicle Kilometers Travelled
WHO	World Health Organization
XRD	X-ray diffractometry
XRF	X-Ray Fluorescence

UNITS OF MEASUREMENT

%	Percentage
t/yr	Ton per year
Kg	Kilogram
gm	Gram
m	Meter
m ³	Cubic meter
cm	Centimeter
µg/m ³	Microgram per cubic meter
cm ⁻¹	Per centimeter
g veh ⁻¹ km ⁻¹	Gram per vehicle per kilometer
g km ⁻¹	Gram per kilometer
kg yr ⁻¹	Kilogram per year
km day ⁻¹	Kilometer per day
hr/yr	Hour per year
m ³ /hr	Cubic meter per hour
mg/m ³	Milligram per cubic meter
°F	Degree Fahrenheit
°C	Degree Celsius
µm	Micrometer
mm	Millimeter
MJ/t	Mega joule per ton
t	Ton
kg/ha	Kilograms per hectore
ha	Hectore
kg/ha/hr	Kilograms per hectore per hour
kg/hr	Kilograms per hour
kJ/kg	Kilo joule per kilogram

Chapter 1

Introduction

1.1 General

Clean air is the basic necessity of human being and wildlife; however, the quality of air is increasingly deteriorating due to the pollution from anthropogenic sources. Cement industry is one of the most causative anthropogenic sources involved in air pollution and it has been listed in seventeen most polluting industries by the central pollution control board. The typical emissions to air from cement manufacturing plants include nitrogen oxides (NO_x), sulfur dioxide (SO₂), carbon oxides (CO and CO₂), dust and some trace elements (Pregger and Friedrich, 2009). Emissions of these pollutants have been found to have variety of detrimental effects on human health and the natural environment. Bangladesh cement industry holds a remarkable scope for its expanding growth in the long term, with current annual productivity of 33-35 million metric tons and a constant growth of 6% (Nahar, 2011). It may cause a tremendous degradation to the environmental air quality of Bangladesh in near future until any initiative taken. An attempt has been made in this study to determine the contribution level of deleterious impact by a sampled cement manufacturing factory (CMF) on environment and human health. With this consequence, this study has determined the estimation of air pollutant's emission, their concentration and occupational health risks at sampled CMF. Also all the raw materials, product and by product of cement has been characterized to make out the potential reason for causing air pollution. However, construction and development without cement is impossible to conceive (Potgieter, 2012). Therefore, this study essentially aims for the status and scope of implementation of efficient control strategies at CMF of Bangladesh to reduce its exposure to air pollution.

1.2 Rationale of the Study

Air pollution is hazardous to human health and environment. World Health Organization (WHO) reports that in 2012 around 7 million people died (one in eight of total global deaths) as a result of air pollution exposure (WHO, 2012). This finding also confirms that air pollution is now the world's largest single environmental health risk. Several studies reported significant correlations between air pollution and certain diseases including shortness of breath, sore throat, chest pain, nausea, asthma, bronchitis and lung cancer (Dockery and Pope, 1994; USEPA 1999a; USEPA 1999b; Jeff and Hans 2004). Extreme effects of air pollution include high blood pressure and cardiovascular problems (Sanjay, 2008). In addition to its destructive health impacts, air pollution is also catastrophic to animals, forests and vegetation, aquatic ecosystems, metals,

structures, leather, rubber etc. Hence reducing air pollution is mandatory to protect the total environment.

Mortality and respiratory diseases caused by air pollution are believed to be epidemic in major cities of Bangladesh. An estimated 15,000 deaths, as well as several million cases of pulmonary, respiratory and neurological illness occur every year due to the poor air quality of Dhaka, according to the Air Quality Management Project (AQMP), funded by the Government of Bangladesh (GoB) and the World Bank (Haque, 2015). In 2011, Norwegian Institute for Air Research (NILU) and the Department of Environment (DoE) started a three year collaboration to find out the level of pollution of Dhaka city. The researchers measured the concentration of sulphur dioxide, nitrogen dioxide, ozone as well as dust particles in the air and they found excessive concentration of dust which was three times from the standard level of Bangladesh and United States and five times of UK and Norway (Haque, 2015). Furthermore air pollution in other cities of Bangladesh is currently not seen as a serious difficulty like Dhaka due to the fact that there is no adequate data and information on the extent of air pollution. For instance, even after the installation of fixed Continuous Air Monitoring Stations (CAMS) by DoE; Khulna station has inadequate air pollutant's data due to poor data capture rate and malfunction of the analyzer or sensor (CASE, 2014).

Khulna is the third largest city of Bangladesh and an important hub of industry due to its seaport. However, industrial development always leads to degradation of environmental quality and it is estimated that 20-30% of air pollution in urban areas caused by industries. In case of Bangladesh it has been reported that industrial and transportation sectors are the principle sources of outdoor air pollution (Alam, 2009). Recently many cement production companies have been constructed their manufacturing factory in Khulna which may seriously affect the environmental air quality. Therefore, this study has assessed the sources of air pollutants and scenario of existing practices of air quality management at a CMF near Rupsha River (sampled area) in Khulna city. This study has also estimated the amount of emitted air pollutants per year by using Emission Factor Method for cement manufacturing. The raw materials, cement and dust particle at sampled CMF has been characterized by using particle size analysis, x-ray fluorescence (XRF), scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS), x-ray diffractometry (XRD) and fourier transform infra-red (FTIR) spectroscopy to determine the existence of

hazardous components or inhalable fine particles which may cause health hazard as well as air pollution. The study has assessed occupational health risks by monitoring the concentration level of the air pollutants at CMF. Some mitigation strategies have also been suggested for enhancing the air quality at sampled CMF.

1.3 Objectives of the Study

The specific objectives of this research work are as below:

- To assess the sources of air pollutants and quantify their annual emission from cement manufacturing factory located near Rupsha River in Khulna city.
- To characterize the raw materials (clinker, limestone, gypsum, slag, and fly ash), product (cement) and by-product (dust particles) of cement manufacturing factory in Khulna city.
- To perform the health risk assessment due to the exposure of air pollution from cement manufacturing factory in Khulna city.

1.4 Outline of the Dissertation

The dissertation is being presented in following seven distinct chapters comprising different aspects of study.

Chapter 1: It provides the problem statement, a general overview of background information, specific objectives and structure of dissertation.

Chapter 2: It reviews the previous literature encompassing the sources of air pollutants, their emission estimation techniques, control strategies for air pollutants, micro-analyses for characterization and effects on health and environment at CMF to understand the importance and application of the study.

Chapter 3: It describes the detailed methodologies adopted for emission estimation of air pollutants of CMF, sampling and testing protocol for characterization, monitoring the air pollution level, calculating air quality index and health risk assessment to accomplish the specific objectives.

Chapter 4: It represents the physical and environmental settings of the study area, the manufacturing process of cement at CMF, the assessment of sources of air pollution, the estimation of annual emission of air pollutants and their control management at CMF.

Chapter 5: It contains the oxide's concentration analysis by x-ray fluorescence, particle size analysis, scanning electron microscopy with elemental analysis and functional group analysis of the different collected samples of CMF.

Chapter 6: It describes the monitoring of pollution level of air pollutants, air quality index, occupational health risks and some mitigation measures to enhance the air quality management at sampled CMF.

Chapter 7: It includes the conclusions as the summery of findings and the recommendations of further studies.

References: Lists of relevant publications and reports cited in the texts are included in this section.

Appendices: This section provides the list of appendices used in this study.

Chapter 2

Literature Review

2.1 General

This chapter describes the relevant existing literature regarding the sources, pattern and control of emission of air pollutants and their environmental impact as well as associated health risks at CMF. This chapter explains some literature regarding techniques which have been employed in this study to quantify and characterize the existed air pollutants at sampled CMF. Some general information about the cement is included in this chapter to facilitate the understanding of the grounds of emission to air due to its ingredients and production process.

2.2 Cement

Concrete is the second most consumed substance on earth. Cement is the critical ingredient in concrete, locking together the sand and gravel constituents in an inert matrix; it is the "glue" which holds together much of modern society's infrastructure (Marlowe and Mansfield, 2002).

2.2.1 Different Types of Cement

Various types of cement are produced in Bangladesh but Portland cement and blended cement are by far the most common. Although they are primarily consist of a kiln fired and fused material known as clinker and addition of some materials make them applicable for different purpose. Portland cement primarily consists of clinker that is ground and combined with small amounts of gypsum or a similar material and is produced in several grades designed to provide certain properties to concrete. The major ingredients of blended cement are clinker, gypsum, fly ash, slag and limestone. Besides the Portland cement and blended cement, smaller amount of specialty cements are produced in Bangladesh i.e. masonry, off-white Portland cements etc.

2.2.2 Composition of Cement

The chemical composition of traditional Portland Cement can be classified basically into two categories:

- (i) Mineral composition
- (ii) Oxide composition

Table: 2.1 and Table: 2.2 are representing the typical mineral compositions and typical oxide compositions of traditional Portland cement respectively. The weight* in percentage shown in

tables are the representative weights of composition. However actual weight varies with the different types of cement.

Table: 2.1 Typical Mineral Composition of Traditional Portland Cement

Chemical Name	Chemical Formula	Shorthand Notation	By weight* (%)
Tricalcium Silicate	3 CaO.SiO ₂	C3S	55
Dicalcium Silicate	2 CaO.SiO ₂	C2S	18
Tricalcium Aluminate	3 CaO.Al ₂ O ₃	C3A	10
Tetracalcium Aluminoferrite	4 CaO.Al ₂ O ₃ .Fe ₂ O ₃	C4AF	8
Calcium Sulfate Dihydrate (Gypsum)	CaSO ₄ .2H ₂ O	CSH2	6
Others	-	-	3

(Source: Mindess et. al., 1981)

Table: 2.2 Typical Oxide Composition of Traditional Portland Cement

Oxide Name	Shorthand Notation	Common Name	By weight* (%)
CaO	C	Lime	64.67
SiO ₂	S	Silica	21.03
Al ₂ O ₃	A	Alumina	6.16
Fe ₂ O ₃	F	Ferric Oxides	2.58
MgO	M	Magnesia	2.62
K ₂ O	K	Alkalis	0.61
Na ₂ O	N	Alkalis	0.34
SO ₃	<u>S</u>	Sulfur Trioxide	2.03
CO ₂	C	Carbon Dioxide	-
H ₂ O	H	Water	-

(Source: Mindess et. al., 1981)

2.2.3 Manufacturing Process of Cement

The main stages in cement production can be discussed under the following sub-headings:

2.2.3.1 Raw material acquisition

Most of the raw materials used in cement production are extracted from the earth through mining and quarrying and can be divided into the following groups: lime, silica, alumina, and iron (Madsen et al., 2004). Quarry operations consist of drilling, blasting, excavating, handling, loading, hauling, crushing, screening, stockpiling, and storing. Naturally occurring calcareous deposits such as limestone, marl or chalk provide the source for lime whether silica, iron oxide and alumina are generally found in sand, iron ore, shale, and clay. Power station ash, blast furnace slag, and other process residues collected from different industry can also be used as partial replacements for the natural raw materials if they do not affect the cement properties.

2.2.3.2 Raw materials preparation

Raw milling involves mixing the extracted raw materials to obtain the correct chemical configuration, and grinding them to achieve the proper particle-size to ensure optimal fuel efficiency in the cement kiln and strength in the final concrete product (Karstensen, 2006). Three types of processes- the dry process, the wet process, or the semidry process may be obtained during raw milling. In the wet process, water is added to the raw materials during grinding where in dry process, the raw materials are ground in dry condition. The water used in the wet process is about 45% of the raw material (Aziz, 1995). In the semidry process the materials are formed into pellets with the addition of water in a pelletizing device.

2.2.3.3 Clinker burning

In pyro-processing, the mix after raw milling is heated into a rotary kiln to produce cement clinkers. A rotary kiln is a long steel cylinder used for pyro-processing, inclined about half to one foot, and is about 8 to 12 ft in diameter and 200 to 400 ft in length. The raw mix is supplied to the system as a slurry (wet process), a powder (dry process), or as moist pellets (semidry process). The pyro-processing system involves three steps: preheating, calcining (a heating process in which calcium oxide is formed), and burning. The obtained cement clinkers after

pyro-processing are hard, grey, spherical nodules with diameters ranging from 0.32 - 5.0cm created from the chemical reactions between the raw materials. The fuel to be used for this purpose is coal, oil or natural gas (Aziz, 1995). However the use of supplemental fuels such as waste solvents, scrap rubber, and petroleum coke has expanded in recent years to promote the environmental sustainability.

2.2.3.4 Clinker grinding

In this stage; the clinker is ground with other materials to form a fine powder which is actually the “cement”. The hot clinker obtained from rotary kiln need to be cooled before grinding. Gypsum is added to regulate the setting time of the cement. Other chemicals or mineral additives or air entrainment or cementitious materials may also be added to the ground clinker to achieve the particular properties.

2.2.3.5 Cement packaging and dispatch

The finished product is transferred using bucket elevators and conveyors to storage silos and then to packaging unit. After that cement can be delivered to customers in bags (normally having 50kg weight) or sometimes in loose amount by bulk conveyor.

Basic steps involves in cement manufacturing process are shown as flow chart in Fig 2.1.

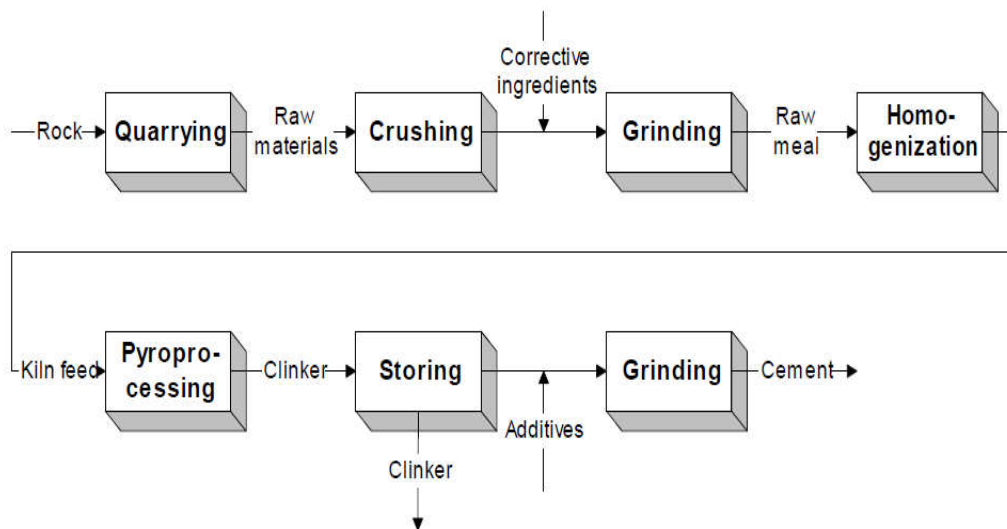


Fig 2.1: Principle drawing of the cement manufacturing process

2.3 Atmospheric Emission from CMF

The entire process of cement manufacturing involves emission of enormous pollutants which can affect the human health as well as the whole environment. Emissions from CMF include particulate matter and combustion gases from cement kiln and other production process; wastewater from the cooling of process equipment; slurries and sediments from wastewater; plant maintenance waste; and research and laboratory wastes.

However the air pollution from CMF has significant environmental impact and thus this industry has been enlisted as the third largest industrial source of air pollution (USEPA, 2016). Emission to air from CMF can be categorized into two groups:

- (i) Gaseous Pollutants
- (ii) Particulate Matter (PM)

Oxides of nitrogen (NO_x), sulfur dioxide (SO₂), and carbon oxides (CO₂ and CO) are the most likely listed substances emitted during the production of cement as gaseous pollutants. Trace quantities of volatile organic compounds (VOC) including benzene and phenol, ammonia, chlorine, some listed metals, and hydrochloric acid may also be emitted (EETs Manual, NPI, Australia, 1998). Gaseous pollutants emit generally during clinker production in rotary kiln and also from preheater and clinker cooler.

Particulate matters emit almost throughout total process flow of cement manufacturing including quarrying, crushing, grinding (only in dry process), blending (only in dry process), and transportation of raw materials, kilns operation, clinker cooling, stock piles and packaging. Also some of the gaseous pollutants and particulate matter may release due to the vehicular movement at CMF for the transportation of raw materials or to delivery final finished cement product. Although this vehicular emission may not be included in the emission from the core cement manufacturing process.

General emission sources for air pollutants in wet and dry process of cement production (Adapted from USEPA, 1995) are shown below in Fig 2.2:

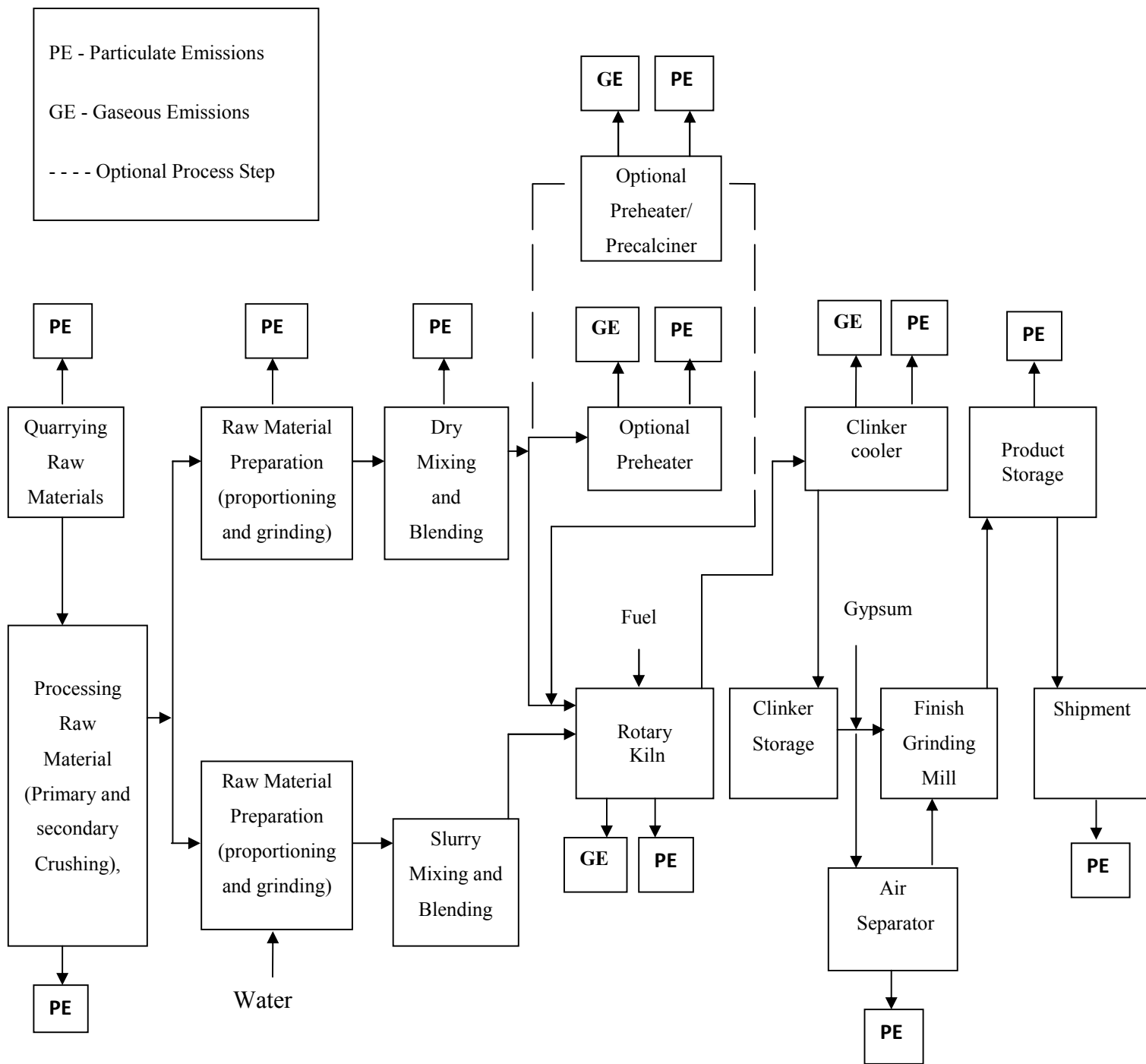
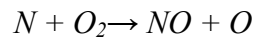
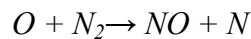


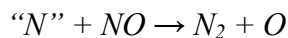
Fig 2.2: Air Pollutants Emission from Process Flow Diagram of Cement Production at CMF
 (Source: USEPA, 1995)

2.3.1 NO_x Emission

NO_x releases from combustion of fuel at high temperature in the cement kiln. Three types of NO_x form in the cement kiln- thermal, fuel, and feed NO_x. In kiln exhaust gases, more than 90% of NO_x is NO; with NO₂ generally makes up the remainder (Nielsen and Jepsen, 1990). Thermal NO_x is formed by oxidation of atmospheric nitrogen at high temperatures. The literature cites threshold temperatures for the formation of thermal NO_x ranging from about 1200–1600°C (2200–2900°F) (Nielsen and Jepsen, 1990). Since the flame temperature in a kiln is significantly above these temperatures, considerable amounts of thermal NO are generated in the burning zone. The thermal reaction between oxygen and nitrogen to form NO is named the Zeldovic reaction (Rother, 1997) and is simplified as follows:



NO_x emissions also result from the oxidation of nitrogen compounds in the raw material feed to the kiln (feed NO_x). It can also result from oxidation of nitrogen compounds in fuel (fuel NO_x). Higher concentration of volatiles in the fuel tends to reduce the percentage of fuel nitrogen converted into NO. An increase in the temperature of the secondary combustion zone will reduce net NO formation. At temperatures between about 815°C and 1100°C (1500°F and 2000°F), the following reactions may take place: “N” + O → NO



Where: “N” = nitrogen compounds originating in the fuel (Nielsen and Jepsen, 1990).

NO_x can contribute to a variety of health problems and adverse environmental impacts, such as formation of ground level ozone, acid rain, global warming, water quality deterioration, visual impairment, formation of photochemical smog etc.

2.3.2 SO₂ Emission

In process of cement manufacturing SO₂ are generated both from the sulfur compounds in the raw materials and from sulfur in fuels used to fire a preheater/precalciner kiln system. SO₂ is both liberated and absorbed throughout the pyroprocessing system, starting at the raw mill, continuing through the preheating/precalcining and burning zones, and ending with clinker production according to the reactions listed in Table 2.3.

Table 2.3: SO₂ Reaction Process in Cement Production

Process Description	SO₂ Formation	
Raw mill	SO ₂ Formation	Sulfides + O ₂ → Oxides + SO ₂ Organic S + O ₂ → SO ₂
	SO ₂ Absorption	CaCO ₃ + SO ₂ → CaSO ₃ + CO
Preheating zone	SO ₂ Formation	Sulfides + O ₂ → Oxides + SO ₂ Organic S + O ₂ → SO ₂
	SO ₂ Absorption	CaCO ₃ + SO ₂ → CaSO ₃ + CO
Calcining zone	SO ₂ Formation	Fuel S + O ₂ → SO ₂ CaSO ₄ + C → CaO + SO ₂ + CO
	SO ₂ Absorption	CaO + SO ₂ → CaSO ₃ CaSO ₃ + ½ O ₂ → CaSO ₄
Burning zone	SO ₂ Formation	Fuel S + O ₂ → SO ₂ Sulfates → Oxides + SO ₂ + ½ O ₂
	SO ₂ Absorption	Na O + SO ₂ + ½ O ₂ → NaSO ₄ K ₂ O + SO ₂ + ½ O ₂ → K ₂ SO ₄ CaO + SO ₂ + ½ O ₂ → CaSO ₄

(Source: Horkoss, 2008)

The SO₂ reacts with water vapor and other chemicals high in the atmosphere in the presence of sunlight to form sulfuric acids. The acids formed usually dissolve in the suspended water droplets, which can be washed from the air on to the soil by rain or snow. This is known as acid rain which is responsible for acidification of soils, lake and stream, corrosion of buildings and monuments and deforestation. Also SO₂ can form secondary particles like sulfates that cause haze and reduce visibility.

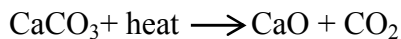
2.3.3 PM Emission

In cement industry, released PM is mainly cement dust. Heavy dust emits from quarrying, crushing, transportation of raw materials, grinding (in the dry process only), kiln operation, clinker cooling, stock piles, storage silos, packaging and during unloading of final cement

product in cement industry. The PM from kiln stacks is the largest emission stream from cement plants to the air (NPI, 1999). The constituents of PM are usually alumina, silica, calcium carbonate, and clay; the primary constituents of cement itself. Although it may contain heavy metals like chromium, nickel, cobalt, lead and mercury pollutants hazardous to the biotic environment with impact for vegetation, human health, animal health and ecosystem (Baby et al., 2008). The main environmental problem resulting from dust emission is reduced visibility and deteriorated ambient air quality. Even it can pollute water bodies when the dust is washed out with rain. It also acts as a contributory factor of acid deposition, ozone production and reflection of solar light and hence influence of climatic change.

2.3.4 CO₂ and CO Emission

CO₂ as a by-product is released during the production of clinker (occur in the upper, cooler end of the kiln, or a precalciner) in which CaCO₃ is heated at temperatures of 600-900°C in a rotary kiln and results in the conversion of carbonates to oxides. The simplified reaction is:



(Gibbs et al., 2015)

In cement production about 60% of CO₂ is released in unavoidable chemical reactions of limestone (calcination process). The indirect emissions of CO₂ and CO happen by burning the fossil fuel (natural gas, oil or coal) to heat the kiln and electricity consumption during cement production. Additional emission of CO₂ and CO depends on the presence of organic matter in raw material of cement. CO₂ is a green house gas and it is estimated that 5-6% of all CO₂ greenhouse gases generated by human activities originates from cement production (Rodrigues and Joekes, 2010). The estimated average carbon footprint is 0.83t CO₂/t of traditional Portland cement clinker (ranging from 0.7 to 1.4t). CO is weak greenhouse gas but its presence influences the concentrations of other greenhouse gases like methane, tropospheric ozone and CO₂ (carbon monoxide: its environmental impact, n.d., para 3).

2.3.5 VOC, Organic Matters and Heavy Metals Emission

Other cement related emissions in trace quantity include VOCs, dioxins, furans, methane, heavy metals etc. The main source of VOC emission from cement kiln is organic matter present in raw

material. Occurrence of VOCs is also associated with incomplete combustion. VOCs are precursor to ozone formation, which can also contaminate soil and ground water. It has been identified that VOCs can cause retardation of plant growth, chlorosis and necrosis in broad leaves plants. In cement manufacturing dioxins are also formed in the combustion system when chlorine and organic compounds are present and it contaminates soil and ground water. Some contents of fuel and raw material, which is naturally present in low concentration is liable for heavy metal emission i.e. lead, cadmium, nickel, titanium, molybdenum. Heavy metals contaminate soil and water and can adversely affect plant functions and cell structure. Bioaccumulation of heavy metal can cause poisoning in aquatic and terrestrial life through biomagnifications.

2.4 Emission Estimation of Air Pollutants from CMF

In this study, the amount of emitted air pollutants per year has been estimated by using Emission Estimation Techniques (EETs) manual for cement manufacturing. This manual describes the procedures and recommended approaches for estimating emissions from facilities engaged in cement manufacturing activities. This manual was drafted by the National Pollutant Inventory (NPI) unit of the Queensland Department of Environment and Heritage on behalf of the Commonwealth Government of Australia.

There are four types of emission estimation techniques (EETs) described in the NPI Guide which can be used to estimate emissions from CMF. They are:

- (i) Sampling or direct measurement
- (ii) Mass balance
- (iii) Fuel analysis or other engineering calculations
- (iv) Emission factor

Selection of the EET (or mix of EETs) depends upon the purposes. For example, a mass balance is best estimate fugitive losses from pumps and vents, direct measurement for stack and pipe emissions, and emission factors when estimating the emission from storage tanks and stockpiles. This study has been used “Emission Factor” method. In “Emission Factor” method a tool is used called “Emission factor” to estimate emissions to the environment from a facility. Emission factors are obtained from US, European, and Australian sources and are usually expressed as the

weight of a substance emitted multiplied by the unit weight, volume, distance, or duration of the activity emitting the substance (for example: kilograms of sulfur dioxide emitted per ton of clinker produced).

2.5 Characterization of Materials

To determine the potential correspondence between raw materials, final product and by-product of cement and air pollution; it requires the application of material science which, in turn, requires the ability to resolve and describe their microstructures. Several microanalyses i.e. x-ray fluorescence (XRF), particle size analysis, scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM-EDS), x-ray powder diffraction (XRD) analysis and fourier transform infrared spectroscopy (FTIR) has been performed for characterization (size variation, surface topography, elemental or chemical composition, mineralogical composition, functional group analysis by atomic bonding etc.) of all the material of CMF.

2.5.1 XRF Analysis

XRF analysis is a fast, accurate and non destructive analytical method to determine the chemical composition of all kinds of materials and often applied for quality control in cement industry (Brouwer, 2010). X-Ray Fluorescence is the emission of characteristic secondary or fluorescent x-rays from a material that has been excited by bombarding with high-energy X-rays or gamma rays (Xrf and sem-eds icdd.eBook, 2016). When high energy photons (x-rays or gamma-rays) are absorbed by atoms, inner shell electrons are ejected from the atom, becoming “photoelectrons”. This leaves the atom in an excited state, with a vacancy in the inner shell. Outer shell electrons then fall into the vacancy, emitting photons with energy equal to the energy difference between the two states. Since each element has a unique set of energy levels, each element emits a pattern of X-rays characteristic of the element, termed “characteristic X-rays”. XRF is basically a reference method where calibration standards are required for quantitative analysis. The intensities of the characteristic X-ray of unknown samples are compared to those of known (calibration standards) by XRF instruments. The composition of standards must be similar to that of the sample.

2.5.2 Particle Size Analysis

Particle size influences many properties of particulate materials. For instance size and shape of the powder influences its flowing properties (Bumiller, n.d.) Sieving is probably the most widely used method of particle size analysis due the relative simplicity of the technique, low capital investment and low level of expertise required to carry out the analyses (Allen, 2003). Three ASTM standards define specifications for various types of sieves, E1 1-95, E161-96 and E323-80. E1 1-95 covers the requirements for woven wire sieves, E161-96 covers the requirements for electroformed sieves and E323-80 defines the specifications for perforated plate sieves (Allen, 2003). Woven wire sieves have been used in this study. These woven wire sieves having apertures ranging from 20 μm to 125 μm , are readily available in 100, 200, 300 and 450 mm diameters frames as well as 3, 8, 12 and 18 in diameters.

2.5.3 SEM-EDS Analysis

In SEM analysis an electron beam is scanned across a sample's surface. When the electrons strike the sample; a variety of signals are generated and they produce images or a sample's elemental compositions. The generated three signals i.e. secondary electrons, backscattered electrons, and X-rays usually provide the greatest information in SEM analysis. Secondary electrons are emitted from the atoms occupying the top surface and produce a readily interpretable image of the surface morphology of the sample. Backscattered electrons are the beam electrons which are 'reflected' from atoms in the solid. The contrast in the image produced is determined by the atomic number of the elements in the sample. The image will therefore show the distribution of different chemical phases in the sample. Interaction of the electron beam with atoms in the sample causes shell transitions which result in the emission of an X-ray and the emitted X-ray has an energy characteristic of the parent element. Detection and measurement of the energy permits elemental analysis which is called Energy Dispersive X-ray Spectroscopy (EDS).

EDS can provide rapid qualitative and quantitative analysis of elemental composition with a sampling depth of 1-2 microns. Qualitative analysis is done to identify the elements present in sample while quantitative analysis determines the mass fractions or weight percents of the elements present in the samples. Characteristic X-rays emitted from samples in SEM-EDS are compared with the data measured from standard reference materials in quantitative analysis. In

fully standardized quantitative analysis the spectra from the standards are collected on the same instruments where the samples are being analyzed. However in semi quantitative analysis, the obtained spectra of the samples are compared with the previously collected known spectra (“Quantitative EDS”, n.d., para 1). Suitable samples for SEM-EDS analysis include most solids which are stable under vacuum (metals, ceramics, polymers, minerals). Sample must be less than 2 cm in diameter and non-conducting samples have to be coated with a conducting thin layer like carbon or gold (“SEM/EDS: Scanning Electron”, n.d., para 7).

2.5.4 XRD Analysis

XRD is a tool that may afford greater understanding for identifying the atomic and molecular structure of a crystal, in which the crystalline atoms cause a beam of incident X-rays to diffract into many specific directions. By measuring the angles and intensities of these diffracted beams, a crystallographer can produce a three-dimensional picture of the density of electrons within the crystal. From this electron density, the mean positions of the atoms in the crystal can be determined, as well as their chemical bonds, their disorder and various other information. XRD is one the chief methods for characterizing the atomic structure of new materials and in discerning materials that appear similar by other experiments. The Cambridge Structural Database contains over 800,000 structures as of September 2016; over 99% of these structures were determined by X-ray diffraction (Revolv, 2016).

2.5.5 FTIR Analysis

FTIR is a technique which is used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. A FTIR spectrometer simultaneously collects high spectral resolution data over a wide spectral range. The term Fourier transform infrared spectroscopy originates from the fact that a Fourier transform (a mathematical process) is required to convert the raw data into the actual spectrum. The goal of this analysis is to measure how well a sample absorbs light at each wavelength. A molecule absorbs electromagnetic radiation with characteristic frequencies and this ‘characteristic frequencies’ is used to identify molecules or specific groups present in a compound or sample. Sending electromagnetic radiation of known frequency through the sample and measuring the change in intensity of the radiation provides the characteristic wave numbers of an infrared (IR) spectrum. The IR spectra are usually presented as plots of intensity versus

wave number. Two substances absorbing at the same wave numbers are most likely identical. An IR spectrum represents a fingerprint of a sample. As each different material is a unique combination of atoms and no two compounds produce the exact same infrared spectrum. In addition; the size of the peaks in the spectrum is a direct measurement of the amount of material present. Therefore infrared spectroscopy is an excellent tool for quantitative analysis with modern software algorithm.

2.6 Monitoring of Air Pollutants

Air quality monitoring is useful in better understanding the sources, levels of different air pollutants, effects of air pollution control policy, and exposure of various substances in the air. The EPA has established ambient air monitoring methods for the criteria pollutants as well as for toxic organic compounds and inorganic compounds. The methods specify precise procedures that must be followed for any monitoring activity related to the compliance provision of the clean air act. These procedures regulate sampling, analysis, calibration of instrument and calculations of emissions level i.e. concentration.

The number of monitoring stations should be minimum three. The location of station is dependent upon the area of coverage and the wind rose diagram which gives the predominant wind direction and speed. One station must be upstream of predominant wind direction and other two must in downstream of predominant wind direction. Gaseous pollutants should be monitored continuously while PM should be once every three days. PM monitoring is usually accomplished with manual measurements and subsequent laboratory analysis. A quantitative analysis of PM uses gravimetric measurement principles. Then chemical analysis of PM can be done by Automatic Absorption Spectrometry (AAS), Atomic Florescence Spectrometry (AFS), and X-Ray Florescence (XRF) spectroscopy. Gaseous pollutant monitoring can be quantified and analyzed gaseous pollutants include: Spectrophotometry, Chemiluminescence, Gas Chromatography-Flame Ionization Detector (GC-FID), Gas Chromatography-Mass spectrometry (GC-MS), and Fourier Transform Infrared spectroscopy (FTIR).

2.7 Air Quality Index

Air Quality Index (AQI) is an indicator which helps in understanding the level in which air is polluted and the associate health effects that might concern. AQI values are derived from air

quality data reading of a specific area and standard ambient air quality data which allows more meaningful comparison of pollutants. In addition; if the AQI increases it means the population likely to be experienced severe adverse health effects. In Bangladesh the AQI is calculated by based on five criteria pollutants, such as: PM (PM₁₀ and PM_{2.5}), NO_x, CO, SO₂ and O₃. The DoE of Bangladesh has set national ambient air quality standards for these pollutants given as below:

Table 2.4: Approved Air Quality Index for Bangladesh

AQI Range	Category	Colour
0-50	Good	Green
51-100	Moderate	Yellow Green
101-150	Caution	Yellow
151-200	Unhealthy	Orange
201-300	Very Unhealthy	Red
301-500	Extremely Unhealthy	Purple

(Source: CASE, 2015)

2.8 Health Risks due to the Exposure of Air Pollutants from CMF

Exposure to cement dust and different gaseous pollutants contributed by cement plants can severely affect the human health besides environmental degradation. UK Health and Safety Executive(HSE) in 1994 noted evidence that repeated exposure of humans to Portland cement produced rhinitis, chronic productive cough (chronic bronchitis), slight abnormalities on chest radiography and impaired pulmonary function. The adverse effects of exposure of air pollutants from CMF are described below:

2.8.1 NO_x

NO_x has a pungent odor, and can cause eye, nose and throat irritation, can lead to respiratory illness such as chronic inflammation and irreversible structural changes in the lungs and can destroy living tissue. Affected population with lung diseases such as asthma and exposure to NO_x at cement industry can cause damage to lung tissue (USEPA, 2016). Exposure to high concentration of NO_x can make living organisms more susceptible to bacterial infection and lung cancer. NO_x reacts in the atmosphere in the presence of sunlight to form ground-level ozone,

which causes respiratory disease when breathed and other health problems (USEPA, n.d.). Studies indicate positive relation between NO_2 concentrations and heart disease and cancer cases (Najjar, 2011).

2.8.2 SO_2

SO_2 is a colorless gas with a pungent and suffocating odor and irritates the eyes, nose and can cause respiratory illnesses like chronic bronchitis, asthma. This gaseous pollutant is also responsible for lung cancer. SO_2 can react with other compounds in the air to form small particles which penetrate deeply into sensitive part of the lungs and can cause the respiratory, heart diseases and premature death.

2.8.3 Cement Dust

Exposure to cement dust for a short period may not cause serious problem, however prolonged exposure can cause serious irreversible damage to plants and animals (Heather, 2003). Cement dust particle may contain potentially harmful toxic metals and compound such as lead, chromium, nickel, barium etc which can pose serious health impact on human health. Inhalation of the cement dust particle can affect the lungs (inflammation, oxidative stress, accelerated progression and exacerbation of COPD, increased respiratory symptoms, effected pulmonary reflexes, reduced lung function), heart (altered cardiac autonomic function, increased dysrhythmic susceptibility, altered cardiac repolarization, increased myocardial ischemia), blood and brain of the human body. It can also cause eye, throat and skin irritation and increase mortality rates (OSHA, 2004). Other reported effects of cement dust on plants include reduced growth, reduced chlorophyll, clogged stomata in leaves, cell metabolism disruption, interrupt absorption of light and diffusion of gases, lowering starch formation, reducing fruit setting (Lerman, 1972), inducing premature leaf fall and leading to stunted growth (Darley, 1966) thus causing suppression in plants (Iqbal and Shafug, 2001).

The main route of entry of cement dust particles in the body is the respiratory tract and/ or the gastrointestinal tract by inhalation or swallowing respectively (Green, 1970). Both routes, especially the respiratory tract are exposed to numerous potentially harmful substances in the cement mill environment (Mehraj and Bhat, 2013). The aerodynamic size of cement particles is

respirable in size and this size distribution would make the trachea-bronchial respiratory zone, the primary target of cement deposition (Mehraj and Bhat, 2013). Physical properties of such particles determine the extent of their effect on human health. Coarse particulate ($>PM_{10}$) are considered to cause local nuisance than creating health hazard while fine particles ($<PM_{10}$ - $PM_{2.5}$) are majorly big concern for health hazard due to their repairable nature. Particles $<PM_{10}$ penetrates deeply into the respiratory system through inhalation. Particles $<PM_{2.5}$ is so small and $1/30^{\text{th}}$ of average width of human hair can lodge to the lungs directly after being inhaled and passes into the blood stream (USEPA, 2016).

2.8.4 CO₂ and CO

Recent study shows that CO₂ increases surface ozone, carcinogens and particulate matters resulting in increase cases of asthma, death, hospitalization and cancer cases (Jacobson, 2008). CO can cause harmful health effects by reducing oxygen delivery to the body's organs and tissues, as well as adverse effects on the cardiovascular and central nervous systems. CO can also contributes to the formation of smog (ground-level ozone), which can cause respiratory troubles.

2.8.5 VOC, Organic Matter and Heavy Metals

Heavy metals can cause damage to brain and nervous system, increased blood pressure, affect on gastrointestinal functions and reproduction. VOCs is known as potential carcinogen and can cause potential health hazard like irritations in respiratory tract and eyes, headache, nausea, damage to liver, kidney and central nervous system. VOCs like NO_x reacts in the atmosphere in the presence of sunlight to form ground-level ozone, which causes respiratory disease when breathed and other health problems. Dioxins and furans can also cause health impact like Skin rashes, liver damage, weight loss and reduction in immunity (USAID, 2008).

2.9 Control Strategies of Emission of Air Pollutants at CMF

Different control strategies of emission of air pollutants at CMF are stated below:

2.9.1 Control of NO_x

NO_x control approaches applicable to the CMF may be grouped as below:

- (i) Process modifications

- (ii) Combustion control approaches
- (iii) NO_x reduction controls

(USEPA, 2000)

Process Modifications: Raw materials with greater alkali content need to be burned longer to meet alkali requirements and thus may produce greater NO_x emissions. Also an experimental test on a cement kiln showed that by reducing excess air from 10-5%; NO_x emissions per unit time can be reduced by approximately 15% (Miller, 1977). In addition a small amount of steel slag to the raw kiln feed can reduce NO_x emissions by 30% (Andover Technology, 2000). Since NO_x formation is directly related to the amount of energy consumed in cement-making, alternative or low-nitrogen fuels can also reduce emission of NO_x. Recycling cement kiln dust from the dust collectors would reduce the energy requirement per ton of a clinker as well as NO_x emissions (Andover Technology, 2000).

Combustion Control Approaches: Combustion modifications can be accomplished by modifying the way oxygen or fuel is provided for combustion. Technical literature and industry publications report NO_x reduction rates of 23-47% with the installation of low-NO_x burners, depending on the baseline emissions, type of kiln, type of low-NO_x burner, and operating conditions (USEPA, 2000). Use of tire derived supplemental fuel at a preheater/precalciner has been shown to decrease NO_x emissions by 30-40% (Biggs, 1999).

NO_x reduction controls: NO_x removal controls destroy NO_x that is formed in the combustion process. Selective catalytic reduction (SCR) and selective non catalytic reduction (SNCR) are two types of NO_x removal controls. SCR uses ammonia in the presence of a catalyst to selectively reduce NO_x emissions from exhaust gases. SNCR relies on the reduction of NO_x in exhaust gases by ammonia or urea without using any catalyst and can achieve NO_x emission reductions of 30-70 %.

2.9.2 Control of SO₂

The highly alkaline conditions of the kiln system can capture up to 95% of the possible emissions of SO₂. But this absorption rate may decline to as low as 50% if sulphide (pyrites) is present in the kiln feed and therefore, careful selection of raw materials is needed. Using of oil or

gas fuel instead of coal fuel can contribute in considerably lowering of SO₂. The raw mill and preheater/precalciner use kiln exhaust gases to dry, heat and calcine the raw feed before it enters the kiln. The counter flow of raw materials and exhaust gases in the raw mill and preheater act as an inherent semi-dry (raw mill) and dry scrubber (preheater) to control SO₂ emissions. Some SO₂ may also be dry scrubbed in the baghouse particulate control system. Depending on the process, and the source and concentration of sulfur, SO₂ absorption in preheater/precalciner kiln systems has been estimated to range from approximately 70-95%. Dry reagent injection of quicklime/hydrated lime into the duct between the two upper cyclones in the preheater tower or Ca(OH)₂ injection at various points can result in SO₂ reduction of 50-70%.

2.9.3 Control of Dust

In cement industries, the control of dust resulting from different steps throughout the total manufacturing process can be a difficult challenge. However well-planned management of activities in total operation can lessen the generation of dust significantly and with relatively little additional cost. The use of covered or enclosed conveyers, crushers, material transfer points and storage areas; installation of mechanical equipments where needed; paved roads; vacuum sweepers and water sprinklers for plant roads; latex stabilizing sprays for storage piles; and site landscaping and vegetation may be the effective dust control measures for CMF. Besides all the measures; installation of mechanical equipments has turned out to be indispensable because of high efficiency for heavy dust control. Some of them are described below:

A dust collector (bag house) is a typically low strength enclosure consists of fabric bags separates dust from a gas stream by passing the gas through a media filter. Dust becomes trapped in the fiber mesh on the fabric bags, as well as the filter cake which is subsequently formed. The dust is collected on either the inside or the outside of the filter. A pulse of air or mechanical vibration removes the layer of dust from the filter. This type of filter is typically efficient when particle sizes are in the 0.01 to 20 micron range.

In an electrostatic precipitator, particles suspended in the air stream are given an electric charge as they enter the unit and are then removed by the influence of an electric field. A high DC voltage is applied to the discharge electrodes to charge the particles, which then are attracted to

oppositely charged collection electrodes, on which they become trapped. An electrostatic precipitator can remove particulates as small as 1 μm with an efficiency exceeding 99 %.

In Flexible Pulse Jet Filters raw gas enters the filter compartments via inlet ducts equipped with guide vanes that distribute the gas uniformly across the filter bags. This arrangement creates a downward gravimetric gas flow along the filter bags, precipitating the dust into the hopper below. In contrast to filters where raw gas enters through dampers located in the hoppers, the design of the flexible pulse jet filter gas distribution system prevents the creation of high can velocities (or vertical, upward gas flow). High gas velocities prevent fine particulate from settling into the hoppers during on-line cleaning cycles. The raw gas is filtered by the fabric from the outside and the clean gas exits at the top of the bag (Alstom, 2011).

In a wet scrubber, the polluted gas stream is brought into contact with the scrubbing liquid by spraying it with the liquid or by forcing it through a pool of liquid to remove the pollutants. Scrubbers can be designed to collect PM or gaseous pollutants. It removes dust particles by capturing them in liquid droplets and pollutant gases by dissolving or absorbing into the liquid.

2.9.4 Control of CO₂ and CO

To lessen CO₂ emissions from cement plants, some ways for improvement have been identified:

- (i) Increasing energy efficiency in order to consume less energy
- (ii) Using of alternative fuels to replace conventional fuels
- (iii) Using of alternative raw materials and addition of cementitious material.

Cement production basically consumes thermal energy and electric energy and both directly emit CO₂ to the atmosphere. Thermal energy consumption greatly depends upon the selection of raw milling during cement manufacturing process. Wet-process kiln system with thermal energy consumption is up to 6000 MJ/t of clinker whereas dry-process kiln system with multi-stage cyclone preheaters and precalciners, consumes approximately 3000 MJ/t of clinker. Cement production consumes a high amount of electric energy; equivalent to 90,000-130,000 t CO₂ per 1Mt of cement if the electricity is coal-generated. To reduce electricity energy consumption during the grinding processes as well as the CO₂ emission; chemical processing agents like

grinding aids (example: poly carboxylate polymers) can be used during cement production (Schraback, 2010).

Using of alternative fuels can reduce significantly CO₂ emission. Biomass, municipal solid waste, tyre derived fuel (TDF) etc are being used as alternative fuels in cement production. CO₂ emissions from biomass are climate neutral (CEMBUREAU, 2009) and the high calorific value of tires (approximately 31,400 kJ/kg) makes TDF an effective supplemental fuel for cement kilns (Pipilikaki et al., 2004). Subsequently, when using TDF instead of coal, a kiln operator can reduce coal by 1.25 t for every ton of TDF used (Constans and Gossman, 1997).

The clinker causes the main CO₂ emissions during cement production. Alternative raw materials i.e. contaminated soil; waste from road cleaning, coal fly ash and blast furnace slag can be used to replace the traditional raw materials extracted from quarries to produce clinker. The chemical suitability of alternative raw materials is important to ensure that they provide the necessary constituents for the formation of clinker. Each percentage of reduced clinker content lowers the CO₂ emission by 8300 t per 1 Mt of blended cement (Schraback, 2010).

2.9.5 Control of VOC, Organic Matters and Heavy Metals

Choice of raw material and fuel with low organic matter, with low content of volatile and semi-volatile heavy metals can reduce these emissions. Implementation of efficient dust control measures can capture this metal compounds emissions. Depending on the type of metal compounds presents in raw material and flue gas, control options may include wet scrubbers and activated carbon absorption (NPI, 1999).

Chapter 3

Research Methods

3.1 General

This chapter presents the required methods those have been employed in this study to accomplish the research objectives as stated in section 1.3. This chapter describes the techniques for emission estimation of air pollutants for the sampled CMF. The methodology of oxides concentration analysis by XRF, elemental and surface morphology analysis using SEM-EDS, particle size analysis, mineralogical components identification by XRD and functional group analysis by FTIR will be explained here. Also the methods of air quality analysis, air quality index, DALYs and mortality cases calculations due to the exposure of PM at sampled CMF are described in this chapter.

3.2 Study Location

Khulna is south-western divisional city in Bangladesh situated between 21.38° north altitude and 88.58° east longitude. The CMF selected for this study is situated at Labanchara in Khulna City (Figure: 3.1). Khulna is located on a natural levee of the Rupsha and Bhairab Rivers, characterized by Ganges tidal floodplains with low relief, criss-crossed by rivers and water channels, and surrounded by tidal marshes and swamps. The populations of Khulna city were about 1.5 millions in 2005.

The annual rainfall ranges from 1650 to 1800 mm here. In Khulna southerly wind blows from the bays of Bengal during the monsoon and north westerly wind from Himalayas during winter. Khulna's climate is classified as tropical. Ambient air quality of Khulna city is satisfactory according to DoE, Khulna Divisional Office, 1998 (Table: A-1 in Appendix). The summers here has moderate rainfall, while the winters have very little. The yearly average wind rose suggests that wind prevails flowing from south to north direction in most of the time in a year. During November to February, maximum prevailing wind flows from north and northwest to south and south-west direction. During March to April, wind mostly flows from south and south-west to north and north-east and during May to October, it flows from south to north and southeast to northwest direction (Weather and climate, 2015).

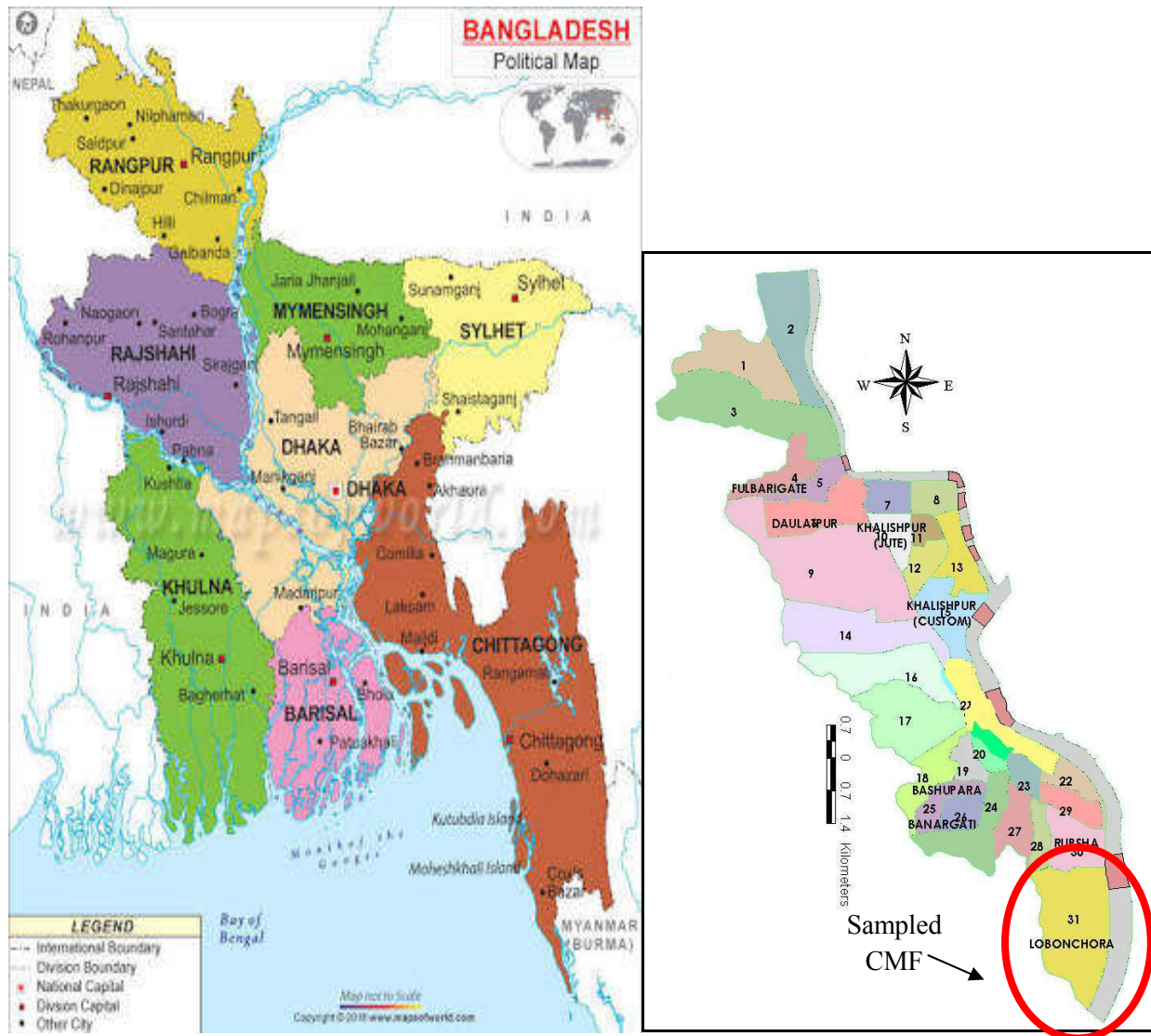


Fig 3.1: The Sample Location in Khulna City

3.3 Emission Estimation of Air Pollutants at Labanchara CMF

- Several field surveys have been conducted to study the total mechanism of existing process of cement production at sampled CMF which helped to determine the sources of air pollutants and the current practice of air quality management at sampled CMF.
- ‘Emission factor’ method from Emission Estimation Techniques manual accredited by National Pollutant inventory (NPI) of Australia 1998 for cement manufacturing has been adopted to estimate the annual emission of air pollutants by weight.

- In this study; annual emissions of particulate matter from CMF at Labanchara due to the production of cement has been calculated by these equations (Equation 3.1 and 3.2):

(i) From material handling and storage: $E_{kpy, PM10} = E_{PM10} * OpHrs \dots\dots 3.1$

Here;

$E_{kpy, PM10}$ = Annual emissions

E_{PM10} = hourly emissions of PM_{10} , kg/hr

$E_{PM10} = EF_{PM10} * Area * ER_{PM10}$

EF_{PM10} = emission factor of PM_{10} , kg/ha/hr

Area = area of base of stockpile, ha

ER_{PM10} = emission reduction of PM_{10} , %, (Table: A-2 in Appendix)

NB: In the absence of available PM_{10} data use the default $EF_{PM10} = 0.3$ kg/ha

(ii) When bag filter outside-venting: $E_{kpy PM10} = EF_{PM10} * A * OpHrs * 10^{-6} \dots\dots 3.2$

Here;

$E_{kpy PM10}$ = annual emissions of PM_{10} , kg/yr

EF_{PM10} = emission factor for PM_{10} , mg/m^3

A = activity rate (hourly flow of air exhausted through the bag filter), m^3/hr

OpHrs = operating hours, hr/yr

10^{-6} = conversion factor mg to kg

- Also motor vehicle emissions from CMF at Labanchara have been estimated in this study by using Emission Factor method from Emission Estimation Technique manual for aggregated emission from motor vehicles which is under NPI of Australia 2000.
- Motor vehicle emissions is calculated for a grid cell from data on spatial Vehicle Kilometers Travelled (VKT) by road type and fleet composition, and the relevant emission factors as the following equation:

$$E_c = 365 * 0.001 * \sum_r \{ V_{r,c} * \sum_m \sum_r \sum_p (X_{r,m,f} * e_{r,m,f,p}) \} \dots\dots 3.3$$

Here,

E_c = Annual emissions from motor vehicles in grid cell c, $kg yr^{-1}$

0.001 = conversion factor g to kg

365 = Days in year

$V_{r,c}$ = Average VKT for road type r in grid cell c, km day⁻¹

$X_{r,m,f}$ = Relative VKT of vehicle type m and fuel type f on road type r,

$e_{r,m,f,p}$ = Emission factor for vehicle type m, fuel type f and emission process type p on road type r, g km⁻¹

- Emission rates (g veh⁻¹ km⁻¹) suggested by Alam, 2015 for different types of vehicles for CO, NO_x, VOC_s, SO₂ and PM₁₀ simplifies the calculation for motor vehicle emissions from Labanchara CMF in this study. Emission rates are shown in Table: A-2 at appendix and with the accordance of Table: A-2; Equation: 3.3 can be simplified as follows:

$$E_c = 365 * 0.001 * \text{Emission Rate} * \text{VKT} \dots\dots 3.4$$

Where, VKT can be calculated for specific typed vehicles by the following equation:

$$\text{VKT} = 2 * \text{average no. of trip} * \text{vehicle traveling path} \dots\dots 3.5$$

3.4 Testing Protocol

The methodologies of sample collection, x-ray fluorescence (XRF) tests, scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM-EDS), particle size analysis, x-ray diffractometry (XRD) and fourier transform infrared spectroscopy (FTIR) are described below.

3.4.1 Sample Collection

At the start samples were collected cautiously in some air tight plastic bottles from the CMF of Labanchara to accomplish these analyses. The collected samples were the raw materials (clinker, gypsum, slag, limestone, fly ash) final products (OPC and PCC) and by-products of cement (bag filter's dusts and deposited road dusts). The collected samples were ground (especially the coarser materials i.e. clinker, gypsum and limestone) into fine powder as like they remain in final cement product which helped to obtain a better understanding of sample's micro structures if they become inhalable particles. Also most of these analyses (XRF, XRD, and FTIR) require the samples mandatorily in fine powdered state.

3.4.2 XRF Analysis

Clinker, gypsum, slag, limestone, fly ash, OPC and PCC were collected from CMF at Labanchara for XRF analysis. The collected fine materials each weighing 10g were ground again into a fine powder to obtain a grain size of less than 1 μm and then mixed them with a binding aid for 1-2 minutes at 600 rpm by using a Minimill2 by PanAlytical grinding machine. Cellulose wax mixture was used as binding aid here and it was combined with the samples in a proportion of 20-30%. The resulting mixture were pressurized into circular discs to make a homogeneous sample pellets. Each disc pellet was analyzed by using PanAlytical Epsilon 3^X XRF analyzer to get the oxide concentrations of the collected samples.

3.4.3 SEM – EDS Analysis

The surface morphological image and the chemical composition of collected samples (clinker, gypsum, slag, limestone, fly ash, OPC, PCC, bag filter's dusts and deposited road dusts) were determined by means of a scanning electron microscope (JEOL JSM 6490 LA) equipped with a system of chemical compositional analysis based on energy dispersive x-ray analysis (JEOL JED 2300 Analysis Station). Samples were mounted into stubs and introduced into the vacuum chamber. High voltage was applied in the vacuum chamber to turn on the electron beam for providing the best Back Scattered Electrons (BSE) and BSE provided the micrographs of the sample's surfaces. Digital images were acquired with an electron microscope image scanner. The chemical composition of samples was then analyzed by semi quantitative method through energy dispersive x-ray spectroscopy.

3.4.4 Particle Size Analysis

A considerable amount of deposited road dusts and the bag filter's dusts were collected from CMF at Labanchara with the aim of particle size analysis. This analysis was carried out by means of sieving. American standard sieve series with specification of ASTM E11:95 ranging from 20 μm to 125 mm were employed in this study. The analysis involved a nested column of sieves placing in a mechanical shaker according to their decreasing size. Then the sampled dusts were poured in top sieve and the shaker shook the column of sieves for 5 minutes. The particles of the samples were then graded in certain range of size.

3.4.5 XRD Analysis

The collected samples (clinker, gypsum, slag, limestone, fly ash, OPC, PCC, bag filter's dusts and deposited road dusts) were examined for mineralogical composition using X-Ray Diffractometry (XRD). Ultima-IV multipurpose diffractometer by Rigaku was used as diffractometer in this study. The fine powdered samples were placed into ground glass depression of a sample holder and positioned onto the X-ray powder diffractometer. The scan range was 10° to 80° at 2 θ angle and the scan was done by using a copper anode X-ray source with fixed optics and a graphite monochromator with a power of 40 kV. Finally XRD patterns provide the mineral identifications according to the “signals” in a diffractogram are called (Bragg or diffraction) peaks. The mineralogical compositions of the samples were then determined by comparing the scanned data with the data obtained from “RRUFF database” (data obtained from “RRUFF database” are presented in appendix). RRUFF database is a project of University of Arizona of USA which provides a complete set of high quality spectral data by using Raman spectra, XRD and FTIR analysis from well characterized minerals.

3.4.6 FTIR Analysis

At the start; a mixer was prepared with an appropriate quantity of an infrared transparent soft salt i.e. potassium bromide (KBr) and collected nine powdered samples by grinding in an agate mortar during this analysis. The pellets were then made with about 100 mg of this mixture. Attenuated Total Reflectance (ATR) technique was applied by using FT-IR 8400s Shimadzu spectrophotometer to analyze the collected samples. 32 scans with 4 cm⁻¹ spectral resolution over the range of 4000–500 cm⁻¹ were used to prepare the FTIR spectra. The bonding as well as components of the collected samples was found from the scanned FTIR spectra by comparing with the FTIR spectra from RRUFF database.

3.5 Health Risk Assessment

The methods obtained for calculation of DALY and mortality cases due to the exposure of air pollutants at Labanchara CMF for this study are described in this part. Also the process of computation of AQI is included here.

3.5.1 Concentration and Monitoring of Atmospheric Dust

Monitoring of the presence of TSP and its characterization by pollutants analyzer within the Labanchara CMF for the purpose of study was not permissible by authority. Therefore; the concentration of TSP monitored by DoE of Khulna Divisional Office at CMF had to collect to determine the presence and level of existed TSP. DoE of Khulna Divisional Office used gravimetric principals for TSP measurement at this CMF. In this method; a filter based high volume sampler (a vacuum type device that draws air through a filter or absorbing substrate) retains atmospheric pollutant for further laboratory weighing and chemical analysis. Particles are trapped or collected on filters, and the filters are weighed to determine the volume of the pollutant. The weight of the filter with collected pollutant minus the weight of the clean filter gives the amount of particulate matter in a given volume of air.

3.5.2 Air Quality Index

According to USEPA; the air quality index can be derived from the following formula:

$$AQI_{\text{pollutant}} = (\text{Pollutant Data Reading} / \text{Standard}) * 100 \dots\dots 3.6$$

In this study existed concentration ($\mu\text{g}/\text{m}^3$) of TSP found from DoE of Khulna Divisional Office was used as pollutant data reading. The standard for TSP in 24 hours has been prescribed by DoE for Bangladesh as $200\mu\text{g}/\text{m}^3$.

3.5.3 DALY due to the Exposure of PM

This study has used the data of World Health Organization (WHO) for DALY (Disability Adjusted Life Years) calculation due to the exposure of PM. WHO has worked to determine Environmental Burden of Diseases (EBD) for various countries and this organization has calculated EBD for Bangladesh in terms of DALYs for the outdoor pollution due to the exposure of PM.

3.5.4 Mortality Rate due to the Exposure of PM

This study has followed a WHO report, 2004 on “Outdoor air Pollution” by Bart Ostro for the calculation of mortality cases. This report has basically assessed the environmental burden of

diseases due to the exposure of PM. By following this WHO report; the expected number of mortality cases of due to the exposure of PM for various health outcome has been calculated with this following Equation:

$$E = AF \times B \times P \dots\dots\dots 3.7$$

Here;

E = Expected number of mortality case of due to the exposure of PM

B = the population incidence of given health effects (deaths per 1000 people)

P = the relevant exposed population for the health effects

AF = Attributable factor based on Relative Risk function (RR) = (RR - 1) / RR

RR for different outcomes and exposure metric is described in Table 3.4 as below.

Table 3.1: Recommended Health Outcomes and Relative Risk Function

Outcomes And Exposure Metric	Relative Risk Function (RR)	Suggested β Co-Efficient (95% CI)	Subgroup
All-cause mortality and short-term exposure to PM ₁₀	$RR = \exp \{ \beta(X-X_0) \}$	0.0008 (0.0006-0.0010)	For all ages
Cardiopulmonary mortality and long-term exposure to PM _{2.5}	$RR = \{ (X+1)/(X_0+1) \}^\beta$	0.15515 (0.0562-0.2541)	Age > 30 years
Lung cancer and long term exposure to PM _{2.5}	$RR = \{ (X+1)/(X_0+1) \}^\beta$	0.23218 (0.08563-0.37873)	Age > 30 years

Where; X = Annual mean concentration of PM

X₀ = Background or lowest concentration of PM

X₀ is the level which would exist without anthropogenic pollution and it is assumed as 10µg/m³ and 5µg/m³ in case of PM₁₀ for PM_{2.5} respectively.

β is a co-efficient suggested with 95% confidence interval (CI)

Background or lowest concentration (X₀) is the level which would exist without anthropogenic pollution and it is assumed as 10µg/m³ and 5µg/m³ in case of PM₁₀ for PM_{2.5} respectively for

computation of relative risks function. The total persons working at sampled industry older than 30 years (P) are currently 250 (personal communication). All cause mortality rate (B) in Bangladesh in 2016 is 5.3 per one thousand of people (CIA, 2016). In Bangladesh cardiopulmonary diseases are treated separately as respiratory and cardiovascular disease. Respiratory and cardiovascular mortality rates are 11% and 17% of the total death rate respectively (WHO, 2014). Therefore cardiopulmonary mortality rate (B) has been taken as 28% of the total death rates in this study by doing average of respiratory and cardiovascular mortality rates. The mortality rate for lung cancer (B) has been found as 1.33% of the total death rates (WHO, 2014).

Chapter 4

Emission Estimation of Air Pollutants at Labanchara Cement Manufacturing Factory in Khulna

4.1 General

This chapter describes physical and environmental settings of the selected CMF at Labanchara, Khulna and manufacturing process of cement to identify the sources of air pollution at CMF. The existing control strategy of air pollution is also described here. The annual emission of air pollutants from Labanchara CMF is estimated in this chapter. Emission estimation can facilitate to understand the pollution level in air and can be useful to manage the emission related environmental pollution.

4.2 Physical and Environmental Settings of Labanchara CMF

The selected CMF is situated in the bank of Rupsha river at Labanchara, the ward no 31 (Figure 4.1 and Figure 4.2) of Khulna City Corporation (KCC). The CMF at Labanchara was founded in 2014 and the total land area of this CMF is 826.95 decimal i.e. 3.343 hectares (DoE, 2014). Labanchara is mainly an industrial zone assembled with different industries such as fish processing industries, Bangladesh Oxygen Company, Khulna Shipyard, Bangladesh Match Factory and Dhaka Match Factory and so on.



Figure 4.1: Labanchara CMF in Khulna from Google Earth

4.3 Manufacturing Process at Labanchara CMF

The maximum production capacity of CMF at Labanchara is designed for about 1.3 million metric ton, however, the CMF at Labanchara has produced 0.98 million metric ton cement in average by the last three years. Two types of cement such as Portland Composite Cement (PCC) and Ordinary Portland Cement (OPC) are produced here and the production rate of PCC and OPC is about 75% and 25%, respectively, of the total annual production. The clinker; the key quality factor of cement comes straight from China, Japan and Thailand and the gypsum comes from Thailand quarry for cement production at this CMF (Company Website, 2017). According to the questionnaire survey other raw materials are also imported from different foreign countries i.e. China, Japan, Vietnam, India and Thailand.

The Labanchara CMF has a closed circuit grinding system which can resist the direct emission of cement dust to air. It has two roller ball mills (movable and fixed) where the raw materials are crushed. The clinker is usually conveyed by a conveyor belt from jetty to roller ball mill directly for grinding without keeping in storage. The other imported cementitious materials are kept for storage in closed space unless they are moist and then they are conveyed by conveyor belt to roller ball mill according to their requirement. Sometimes materials can be moist due to the entrance of water during shipping. In that case they are dried up naturally in open space of industry or jetty; which is a very unusual phenomenon.

During the manufacturing of OPC; only 5% gypsum is added to the 95% clinker and in PCC 8.5% slag, 4% limestone, 3.5% gypsum and 22% fly ash are added to 62% clinker controlled by computerized operating system. The raw materials are weighed by weight feeder prior to crushing to obtain the prescribed proportion. After crushing the grinded materials are sent to a separator for segregation the coarser particles (the particles larger than 90 micron) from the finer portion. The coarse particles are returned to the roller ball mill and the finer particles are separated to obtain uniform particle sized product. Fly ash, very finer in size, and is added lastly without being ground to the fine ground mixture of clinker, slag, limestone, gypsum. The finished product is transferred by using conveyors to storage silos where it can be stored up to 1 month before packaging. All the processes throughout the different stages of manufacturing operation in this CMF are automated controlled.

The final product (Cement) of Labanchara CMF is tested using X-Ray Fluorescence (XRF) analysis for quality control. XRF analysis provides the percentage of oxide compositions such as CaO, SiO₂, Al₂O₃, Fe₂O₃, MgO and SO₃ which are essential for sustaining the properties of cement. Finally, cement is delivered to consumers in suitable paper or PVC bags normally weighed as 50 kg or sometimes loose cement by bulk carrier.

The total manufacturing process of cement production in sampled CMF is described below as flow diagram (Fig: 4.3):

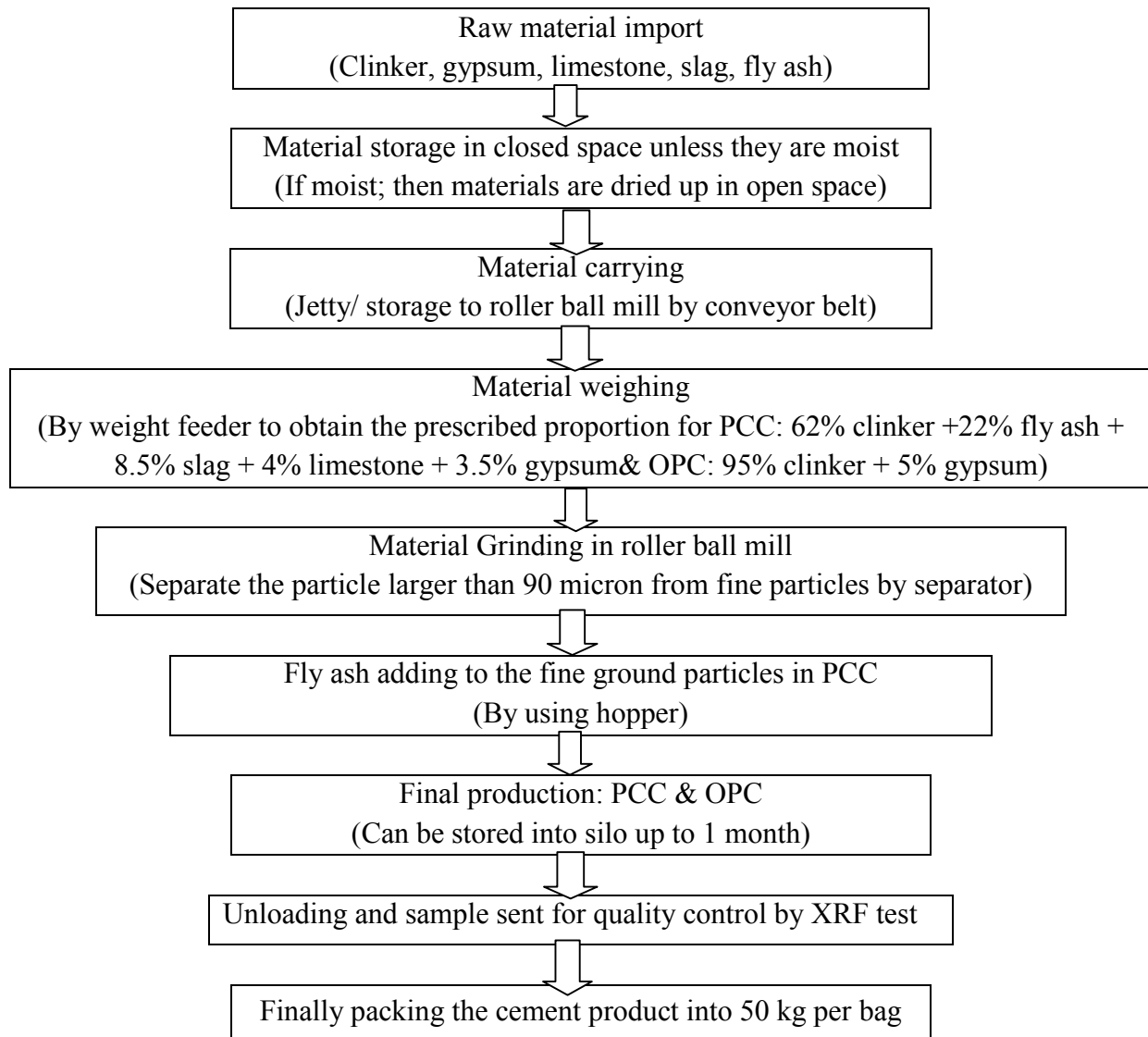


Figure 4.3: Process Flow Diagram of Labanchara CMF

4.4 Sources of Air Pollution at Labanchara CMF

In cement industry, a significant amount of cement dust is generated and emitted to the surrounding atmosphere during the handling, storing of imported materials, conveying, weighing, grinding, packaging and transport of cement. However, emission of gaseous pollutants at this CMF is relatively lesser as the clinker and other additives are being imported from other foreign countries. A small amount of gaseous pollutants may emit through the vehicular movement within the industrial area due to transportation of raw materials and final cement products by motor vehicles and other motor engines.

To control the cement dust at CMF of Labanchara; dust collectors (bag filters) are provided in necessary points to reduce dust emission. The roller ball mills are major dust generating points of CMF which are equipped with reverse jet bag typed dust collector. Other dust collectors are also provided at belt conveyor discharge points, clinker and gypsum feeding units, silo extraction, unloading units and packing plant. The specific number of bag filters and their installation points is shown in Table 4.1. The dust arising due to vehicular movement within CMF is prevented by constructing paved internal roads and many of belt conveyors are covered with hoods to resist the trapping of material in wind stream. Although each conveyor needs to be provided with conveyer hoods and sprinkling of water or using of any chemical suppression should be applied regularly in 2-3 days along the internal roads in the plant in order to control the dust entirely. In addition a thick greenbelt can be developed around the plant to arrest the fugitive emissions.

4.5 Emission Estimation of Air Pollutants at Labanchara CMF

Cement dust generated at Labanchara CMF from material handling and storage and from dust collectors beyond its control efficiency and gaseous pollutants released from vehicular movement at CMF has been estimated by using emission factor method and are described in the following sub-sections.

4.5.1 Emission Estimation of Dust from Manufacturing Process

The daily operating hours of CMF at Labanchara is about 18 hours which results approximately total 6570 operating hour per year. The total generated amount of dust from 34 nos of installed bag filters ahead of its control efficiency has been calculated by using Equation 3.2 (Chapter 3)

is shown in Table 4.1. Air flow rate (m³/hour) of the bag filters were collected from the CMF. A sample calculation for emission estimation of dust from bag filter is given in appendix.

Table: 4.1 Dust Emissions from Bag Filters at Labanchara CMF

System Name	No. of Bag filter	Air flow rate (m³/hour)	Estimated dust emission (kg/year)
1. Clinker silo top (bucket side)	01	4,500	358.78
2. Clinker silo top	03	11,160	2,639.56
3. Clinker silo bottom	03	6,900	1,631.99
4. Clinker silo middle	01	4,500	358.78
5. ID fan main motor ball mill	01	4,500	358.78
6. Clinker jetty (hopper side)	03	4,500	1,064.34
7. Clinker jetty (belt side)	01	4,500	358.78
8. Gypsum, limestone and slag unloading point (hopper side)	01	2,000	157.68
9. Gypsum, limestone and slag unloading point (bucket side)	01	2,000	157.68
10. Gypsum, limestone and slag unloading point (belt side)	02	2,000	315.36
11. Pre feeding silo top	02	4,500	717.56
12. Fly ash silo top	01	16,200	12,777.20
13. Fly ash silo bottom	01	1584	124.88
14. Mill main outlet bag filter	01	40,000	6,307.20
15. Main mill bag filter	01	2,40,000	18,921.60
16. Cement silo (air slide)	01	3,500	275.94
17. Cement silo (top)	02	6,900	1087.99
18. Feeding belt- pre feeding silo	02	4,500	717.56
19. Bulk loading carrier	02	6,900	543.99
20. Packing (second floor)	02	4,500	717.56
21. Packing (top floor)	02	4,500	717.56
Total =			<u>50310.77</u>

4.5.2 Emission Estimation of Dust from Material Handling and Storage

Raw materials are stored in enclosed structure at CMF after shipping and are carried out usually within some closed boxes when conveyed by conveyor belt. All the procedures of handling, feeding and crushing are done within buildings. Also the finished cement products are stocked into enclosed silos before packaging. Cement Industry Federation Limited in 1998 (Table: A-2 in appendix) reported that the material handling and storage in enclosed stockpiles provides 100% control efficiency for PM₁₀ emission (NPI, 1998). It denotes less PM₁₀ emission from Labanchara CMF since material handling and storage operations are executed inside the building.

The total generated amount of dust beyond the control efficiency of bag filters at sampled CMF is found approximately 50310.77 kg/year (50.31 metric ton/year) and from material handling and storage is nil. It indicates that 0.051 kg of dust is discharged from per metric ton of cement production or 2.57 g cement dust from 1 cement bag. It has been reported that 1 kg of cement manufactured in Egypt generates about 0.07 kg of dust in the atmosphere (Hindy et al., 1990). Therefore, it signifies that the Labanchara CMF contributes less amount of dust comparing with other CMF. The reasons behind the lower dust emission can be that the CMF mainly does only grinding of the imported clinker with other materials. Another reason can be the newly set up of industry and as a result the dust collectors are performing with their preeminent condition. Moreover it was visibly observed that the dusts at CMF were better controlled with respect to other CMF in Bangladesh. Generated amount of dust at Labanchara CMF is summarized as below in Table 4.2:

Table 4.2: Dust Emission from CMF at Labanchara

	Per Year	Per metric ton of cement production	Per bag of cement production
Dust Emission	50310.77 kg (50.31 metric ton)	51g	2.57 g

4.5.3 Emission from Motor Vehicles at Labanchara CMF

The emission in air from motor vehicles used for cement loading has been estimated using the Equation 3.4 and 3.5 described in chapter 3. Several types of vehicle are being used at CMF of

Labanchara for loading and unloading of cement bags and to deliver to the consumers. Bulk carried typed (9 Nos.) and ten wheelers (9 Nos.) trucks are used here to transport with carrying capacity of 728 cement bags. In addition; 10 Nos. of six wheelers small trucks with different carrying capacity and a pickup van are used in this mill for hauling of cement bags on regular basis. The pickup van has been included in small group. Besides these some of the private cars (2 Nos) and micro-buses (3 Nos) are used by the employees of CMF. The emissions in air from motor vehicles being used at Labanchara CMF are represented in Table 4.3 and a sample calculation is stated in appendix. However, the emission of loading and unloading of cement and its imported raw materials using waterway transport as not been included in calculation.

Table: 4.3 Emissions in Air from Motor Vehicles at Labanchara CMF

Air pollutants	Annual emission (kg/yr)				Total emission
	Private car	Micro-bus	Pick-up van/ Small truck	Large truck	
CO	8.62	15.51	27.11	110.89	162
NO _x	1.42	2.54	30.07	123.03	157
VOC _s	1.08	1.91	7.36	21.98	33
SO ₂	0.05	0.075	2.53	10.34	13
PM ₁₀	0.04	0.063	2.07	8.45	11

Table 4.3 is showing the total annual emission of CO, NO_x, VOC_s, SO₂, and PM₁₀ from the motor vehicles used at the CMF as 162 kg, 157 kg, 33 kg, 13 kg and 11 kg respectively. The Table 4.3 also represents the gaseous emissions from Labanchara CMF are less in amount with comparing the dust emission during cement production here.

Chapter 5

Characterization of Raw Materials, Product & By-Product of Cement Manufacturing

5.1 General

This chapter presents the XRF, particle size analysis, SEM-EDS, XRD and FTIR analysis for characterization of raw materials, product & by-product of cement manufacturing to correlate them with the health risk assessment.

5.2 Implication of the Characterization

Total Suspended Particle (TSP) is very significant as it can be inhaled by the human body and therefore it needs to be characterized to verify whether it may have any possibility to cause harm upon inhalation. However, TSP characterization by pollutants analyzer within the CMF at Labanchara for the purpose of study was not permissible by the authority. Since TSP can deposit when wind flows with a moderate velocity and therefore the deposited dust on road pavements within the sampled industrial area were collected to make an idea about the nature of the TSP.

A number of laboratory tests were performed to discover a reasonable correlation between the exposure of TSP and the materials obtainable in the sampled industry. At the start XRF test was accomplished for cement products and all the raw materials to achieve their definite percentage of oxides. XRF analysis facilitates the initial understanding of compositional status of raw materials and produced cements in the sampled industry. The cement products (OPC and PCC), raw materials (clinker, gypsum, slag, limestone and fly ash), cement dust captured through bag filter and deposited road dust were analyzed by SEM-EDS to obtain the microscopic images of surface morphology as well as their elemental distribution.

Dust collectors can escape cement dust particles to the surroundings beyond its control efficiency and afterward it can unite with the TSP. Thus particle size of deposited road dust and bagfilter dust were analyzed to reveal the potential hazards due to their particular size. The SEM micrographs also helped to depict the dimension of particles of sampled materials in micrometer scale. XRD analysis was performed to identify mineral constituents of all samples and FTIR was accomplished to resolve the presence of composition through their bonding confirmation. The outcome of the XRD and FTIR facilitated to reaffirm the outcome of SEM-EDS and XRF analyses.

5.3 XRF Analysis

XRF analysis was carried out for the raw materials (clinker, gypsum, slag, limestone, fly-ash) and for the final products of cement (OPC and PCC) to get their oxide compositions i.e. CaO, SiO₂, Al₂O₃, Fe₂O₃, MgO, SO₃. XRF analysis OPC, PCC and their raw material are discussed below:

Table 5.1: XRF Analysis of Raw Materials of Sampled Cement

Compound	Concentration (%)				
	Clinker	Gypsum	Slag	Fly Ash	Limestone
CaO	65.364	33.747	38.339	5.86	51.683
SiO ₂	21.994	0.770	33.715	50.20	3.012
Al ₂ O ₃	4.701	-	18.119	28.70	-
Fe ₂ O ₃	3.860	0.419	1.691	5.72	-
MgO	2.512	4.900	6.893	1.74	-
SO ₃	0.418	43.922	-	-	-

Clinker is the core ingredient of Portland cement. The standard limit of concentration of the compounds in Portland cement clinker according to ASTM are specified as CaO: min 64%, SiO₂: 20-22.5%, Al₂O₃: 4.6 – 7%, Fe₂O₃: 3-5%, MgO: max 4%, SO₃: max 1%, loss on ignition: max 1% and total alkali: max 0.9% (TANDIS, 2015). The analysis illustrates that the concentration of compound in clinker are within their standard limits. The concentration of loss on ignition and total alkali in sampled clinker are not determined here. Although the remaining % concentration is 1.15% which is less than 1.9% (loss on ignition: max 1%+ total alkali: max 0.9 = 1.9%).

OPC constitutes of 95% clinker with 5% gypsum. In this sampled industry 3.5% gypsum is added to 62% of clinker to produce PCC with slag (8.5%), limestone (4%) and fly ash (22%). The function of gypsum is to slow down the setting action of cement paste. The sampled gypsum contains SO₃ 43.922% as SO₃ acts as a retarding compound in cement. Al₂O₃ is entirely absent in gypsum here as it imparts quick setting property to the cement.

Slag and fly ash are the industrial co-products and are added to Portland cement as a partial replacement due to its similar compositional status to Portland cement. Adding co-products are economic and sustainable for environment. From this XRF analysis it can be observed that the compounds of sampled slag are nearly similar with the compounds of Portland cement. Although this sampled slag contains 33.715% of SiO₂ and 18.119% of Al₂O₃ whereas silica (SiO₂) more than 30% and alumina (Al₂O₃) more than 8% can weaken cement. It also contains 6.893% MgO while amount of MgO exceeding 2% makes cement unsound. Fly ash also contains silica (50.20%), alumina (28.70%) beyond the limit and very less amount of lime (CaO = 5.86%). Therefore slag and fly ash should to be added to the composite cement in such amount unless they affect the properties of cement. However the absence of SO₃ in slag and fly ash is beneficial as it reduces the total amount of presence of SO₃ in cement as well as the sulfate attack in reinforced cement concrete.

In PCC, limestone acts as filler between clinker grains and gives a denser end-product (Oates, 1998) According to the test it is found that the limestone provides a considerable amount of CaO (51.683%) and some lesser amount of SiO₂ (3.012%) which are the key strength imparting ingredients of Portland cement. Substantial amount of CaO in limestone might be useful to PCC to balance the deficiency of lime (CaO) in slag and fly ash.

Table 5.2: XRF Analysis Final Product of Cement: OPC and PCC

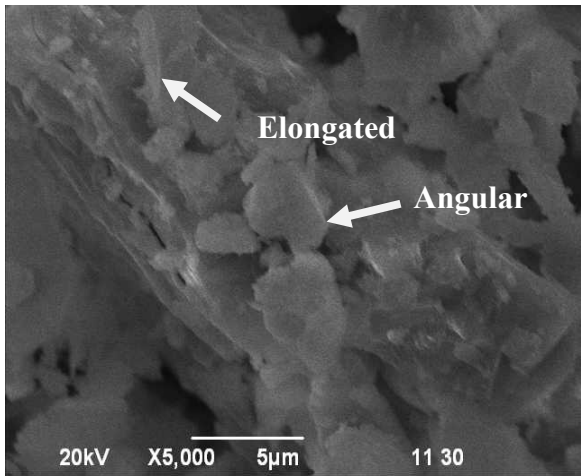
Compound	Concentration (%)	
	OPC	PCC
CaO	61.189	52.654
SiO ₂	22.538	26.422
Al ₂ O ₃	6.304	13.52
MgO	2.259	2.121
SO ₃	2.842	1.128
K ₂ O	0.867	0.679
Na ₂ O	0.206	0.161
Fe ₂ O ₃	2.070	3.009

In addition to Na_2O , MgO , Al_2O_3 , SiO_2 , SO_3 , K_2O , CaO and Fe_2O_3 ; other oxides can be present in cement. However this XRF analysis has only revealed the essential oxides those should be presented in cement. From XRF analysis; lime (CaO) has been found more in OPC (61.189%) than PCC (52.654%). Although the presence of SiO_2 is 22.538% in OPC and 26.422% in PCC; indicates that the key strength imparting ingredients of cement i.e. CaO & SiO_2 are being nearly balanced by their percentage. The percentage of concentration of alumina (Al_2O_3) in sampled OPC is 6.304%. But in PCC; alumina (13.52%) has notably crossed the typical range of alumina (3% - 8%) which can affect the strength of cement. Fe_2O_3 content in PCC (3.009%) is slightly more than the content of Fe_2O_3 in OPC (2.07%) due to the adding of fly ash in PCC; but both are within typical range (0.5%-6%). MgO found 2.259% in OPC and 2.121% in PCC are within the typical range (1%-3%). From this analysis; the percentage of Na_2O and K_2O in PCC (Na_2O : 0.161% and K_2O : 0.679%) have slight lower value than OPC (Na_2O : 0.206% and K_2O : 0.867%). This might be good as it is stated that alkali content (Na_2O , K_2O etc) of Portland cement with no supplementary cementing materials has a significant value on expansion of concrete (Shehsta & Thomas, 2010). SO_3 has been found 1.128% in PCC and 2.842% in OPC and PCC contains less SO_3 results less corrosion in reinforced cement concrete.

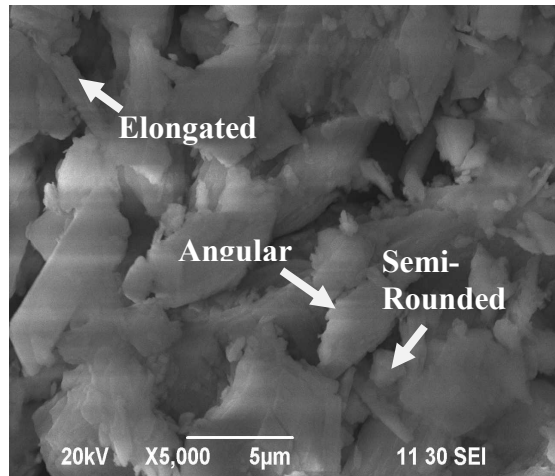
According to this analysis; the amount of typical strength imparting ingredients of cement are slight lesser in PCC than OPC. Nevertheless PCC has some additional quality; for instance: diminution of corrosion of reinforcement in RCC construction due to less SO_3 content, reduction of expansion and efflorescence in concrete due to less alkalis etc. As well using of industrial co-products as raw materials (slag, fly ash etc.) eases the waste management as well as promotes sustainable environment. The most vital observation is that attenuation of use of clinker in PCC is substantially lowering the production of pollutants to the air which may lead towards the air pollution control strategy.

5.4 SEM-EDS Analysis

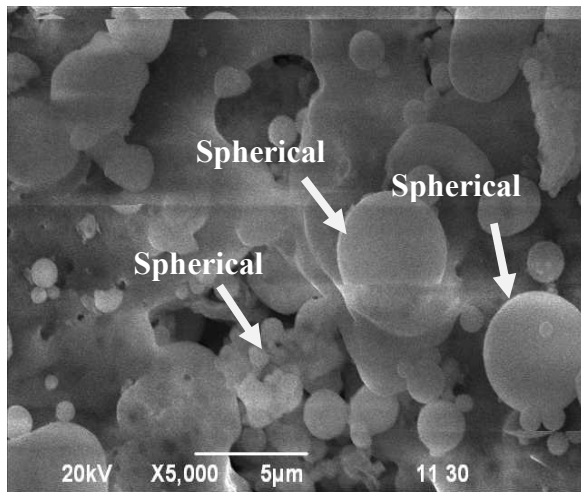
SEM-EDS analysis has been performed for raw materials, OPC and PCC; bagfilter dust and deposited particulate matters on road pavements. This analysis has given the scanning electron microscopic images of surface morphology in different magnification as well as the elemental composition of all the samples.



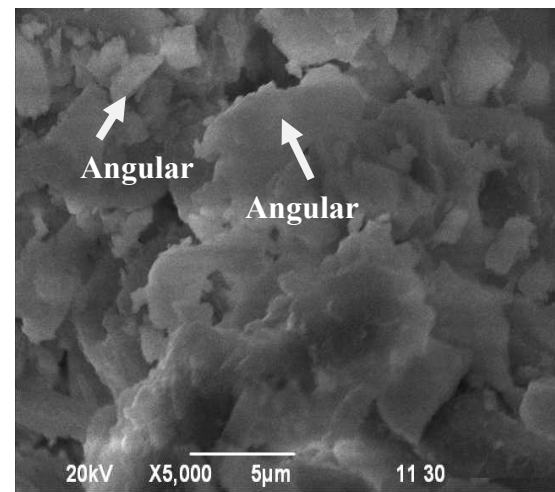
(a) : Clinker



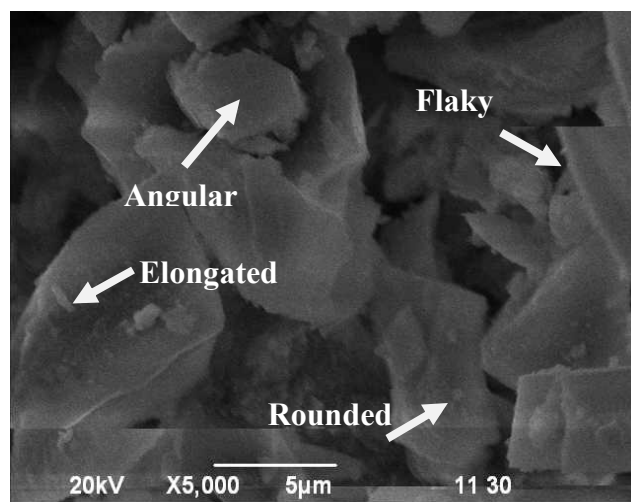
(b): Gypsum



(c): Fly ash



(d): Limestone



(e): Slag

Fig 5.1 (a-e): SEM Micrographs of Sampled Raw Materials

The SEM images of sampled raw materials were captured by magnifying 5,000 times than the regular magnitude. Fig 5.1 (a) is representing the microscopic image of clinker while Fig 5.1 (b), Fig 5.1 (c), Fig 5.1 (d) and Fig 5.1 (e) are of gypsum, fly ash, limestone and slag respectively. The views of Fig 5.1 illustrate some of the brighter zone combined with darkened portion of surface morphology of these raw materials as the elements of heavy molecular weight in samples are generally caught evidently in SEM micrograph whether the elements of lighter molecular weight may create darkened images. Also lighter molecular weighted elements sometimes can be damaged by X-Ray so that surface morphology of them cannot be recognized clearly. The surface morphology of clinker (Fig 5.1-a) is showing the micro-particles having no definite shape. Some angular and elongated shaped particles are seen from microscopic image of clinker. SEM micrograph of gypsum (Fig 5.1-b) is viewing some elongated, semi-rounded and angular shaped particles whether fly ash (Fig 5.1-c) is accumulated of only spherical shaped particles. The surface morphology of limestone (Fig 5.1-d) is presenting some flaky and semi-angular shaped particles and microscopic image of slag (Fig 5.1-e) is showing particles of some semi-elongated, angular and rounded shaped.

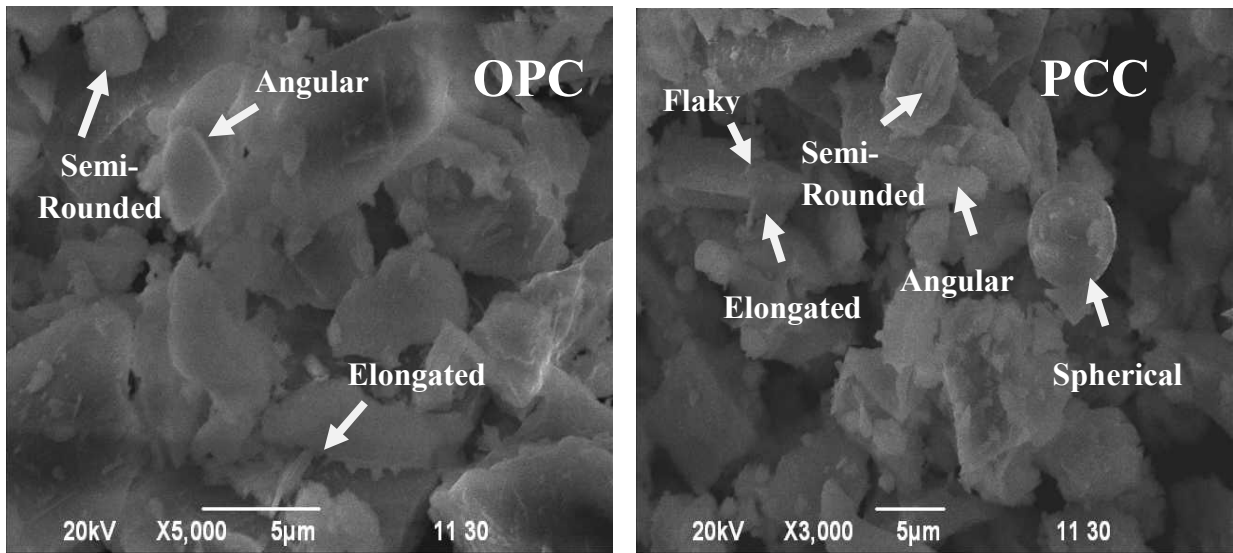


Fig 5.2: SEM Micrographs of OPC and PCC

OPC of this sampled industry is manufactured with clinker (95%) and gypsum (5%). The surface morphology of OPC (Fig 5.2) is presenting some elongated, semi-rounded, angular shaped particles which are previously found from microscopic images of clinker and gypsum (Fig 5.1-a

and Fig 5.1-b). Sampled PCC is made of grinded clinker, fly ash, slag, limestone and gypsum and its surface morphology is showing the flaky, semi-rounded, elongated, angular and spherical shaped particles. Slag and fly ash might be the source of flaky and spherical shaped particles respectively in PCC. Elongated, angular are commonly seen in clinker, gypsum and slag. Limestone contains only angular typed particles (Fig 5.1-d) and gypsum contain some semi-rounded particles in addition.

SEM micrograph of bagfilter dust (Fig 5.3-a) shows semi-angular typed particles and deposited road dust (Fig 5.3-b) shows some semi-rounded, angular shaped particles.

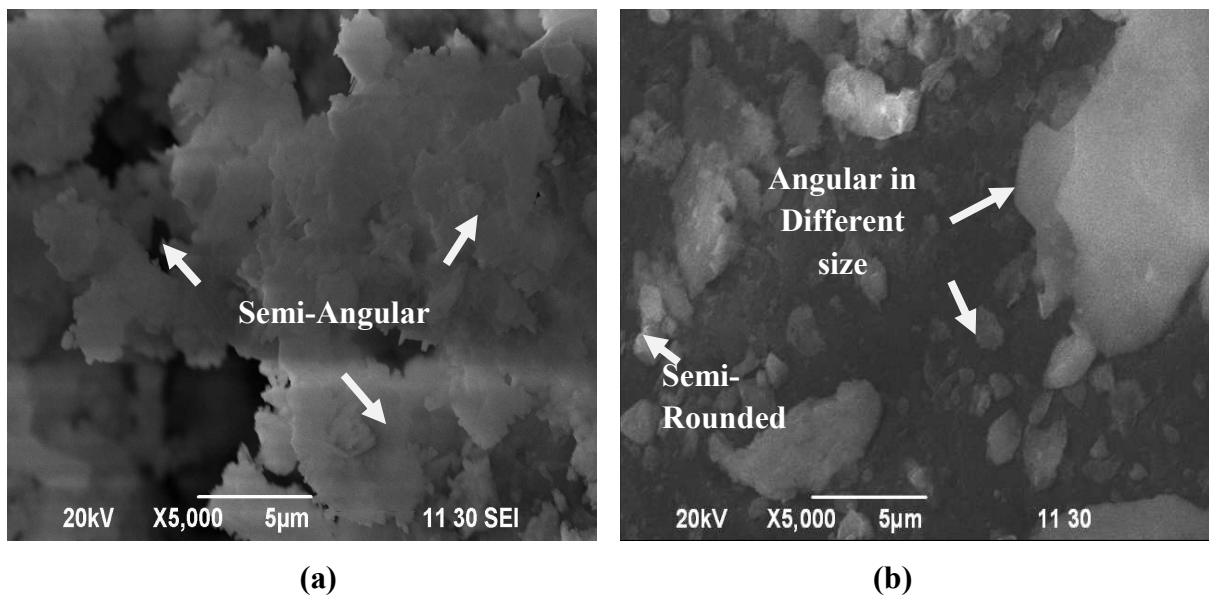


Fig 5.3: SEM Micrograph of (a) Bagfilter's Dust and (b) Deposited Road Dust

Energy Dispersive X-ray Spectroscopy (EDS) was done for nine samples simultaneously with SEM to attain elemental distribution of samples. The study has also included the quantitative analysis of elements present in the samples. The elemental analyses of clinker, OPC, PCC, bagfilter dust and deposited road dust are shown below. However the EDS analysis was accomplished with some specific points or of the surface of the samples; thus higher altitude of any peak in graph does not always signify the higher concentration of that element's presence. The analyses of other samples i.e. gypsum, fly ash, limestone, slag are given to the appendix (Figure: A-10 to A-13).

From Fig 5.4; it is obtained that sampled clinker and sampled gypsum are containing Ca, Si, Al, Fe, O, C, Mo, Ti and Ca, Si, Al, O, S, K, Mo, Ti respectively (Fig A-10 in appendix). The Fig 5.5 is showing that the sampled OPC is consisted of Ca, Si, Al, Fe, O, C, S and Mg. The EDS analysis represents the sampled OPC are not comprised of all elements contained by their sampled raw materials i.e. clinker and gypsum. For instance Ti and Mo are present in sampled clinker and gypsum but not in OPC. Also Mg is absolutely absent in sampled clinker and gypsum whether it is present in OPC. The reason might be the EDS analysis was accomplished with some specific points or of the surface of the samples or collected OPC was not made with the batch of sampled clinker or gypsum or the very lower concentration of Ti and Mo in OPC.

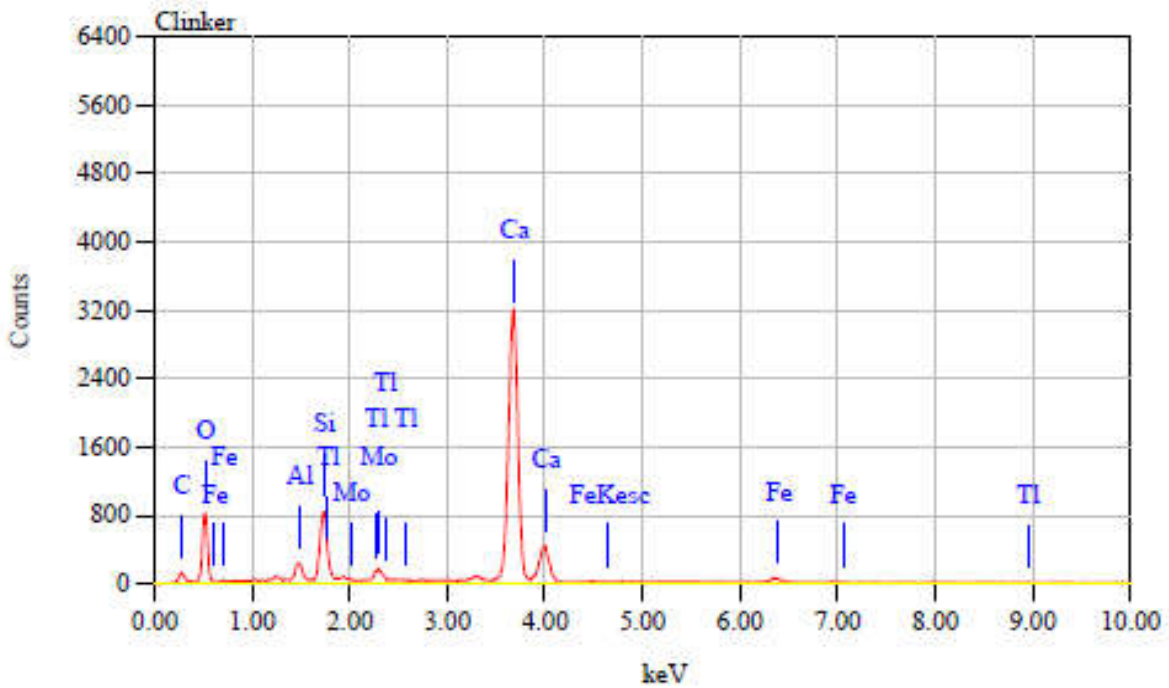


Fig 5.4: Energy Dispersive X-ray Spectroscopy of Clinker

The sampled fly ash(Fig A-11 in appendix), slag (Fig A-12 in appendix) and limestone (Fig A-13 in appendix) are containing Si, Al, O, C, Ca, Si, Al, Mg, O, Mo and Ca, Si, Al, Mg, O, C respectively. Fig 5.3.7 is viewing that the sampled PCC is consisted of Ca, Si, Al, Fe, O, C, Mg, K and Mo. But sulfur (S) is not seen in EDS analysis of PCC though gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is one of the raw materials of it. Also the sampled clinker contains Ti and Mo which are not present in PCC. Since the samples collected for the test were taken at different time; so the sampled PCC

might be made with raw materials other than the samples. Another reason might be the lower concentration of the absent elements (Ti or Mo) or as stated before EDS analysis was accomplished with some specific points or of the surface of the samples.

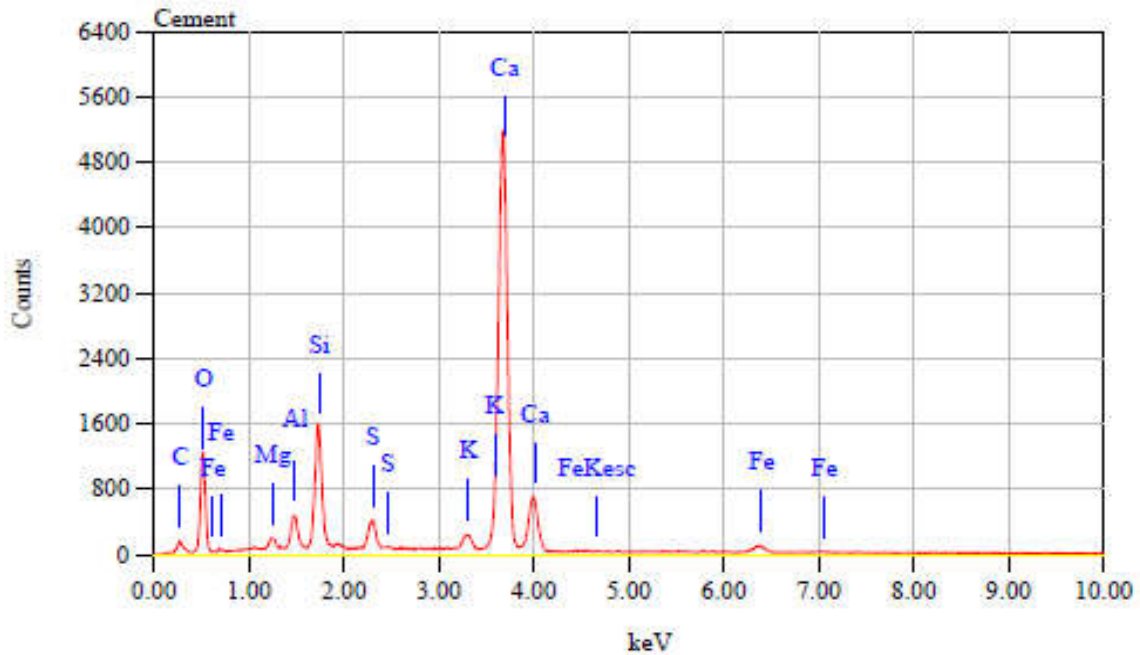


Fig 5.5: Energy Dispersive X-ray Spectroscopy of Cement Sample (OPC)

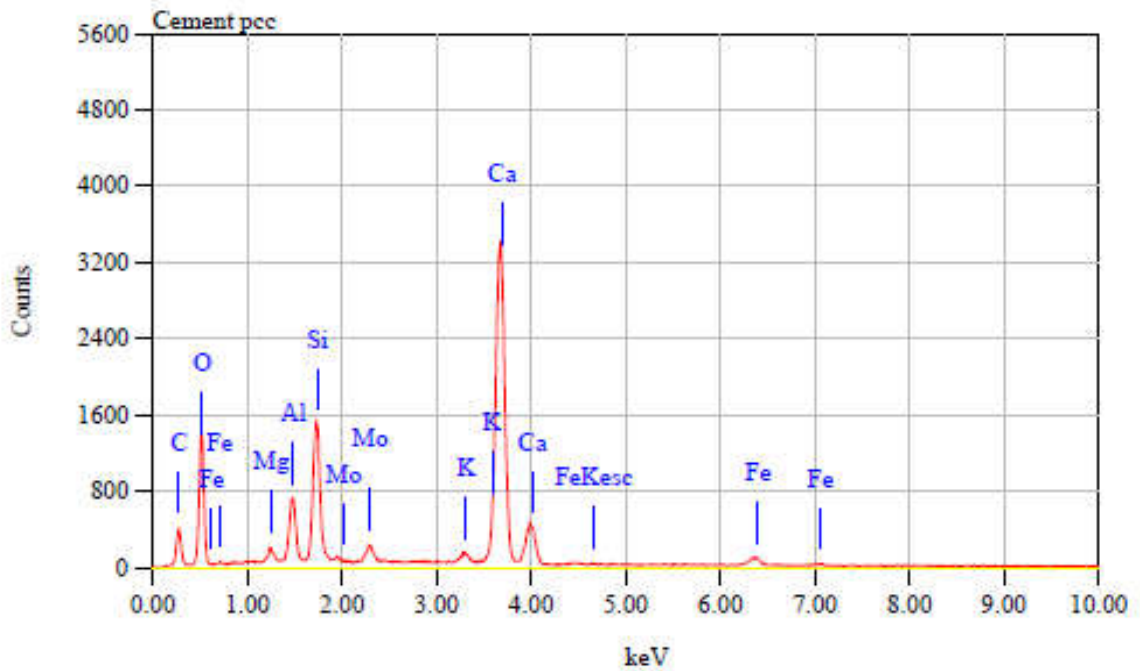


Fig 5.6: Energy Dispersive X-ray Spectroscopy of Cement Sample (PCC)

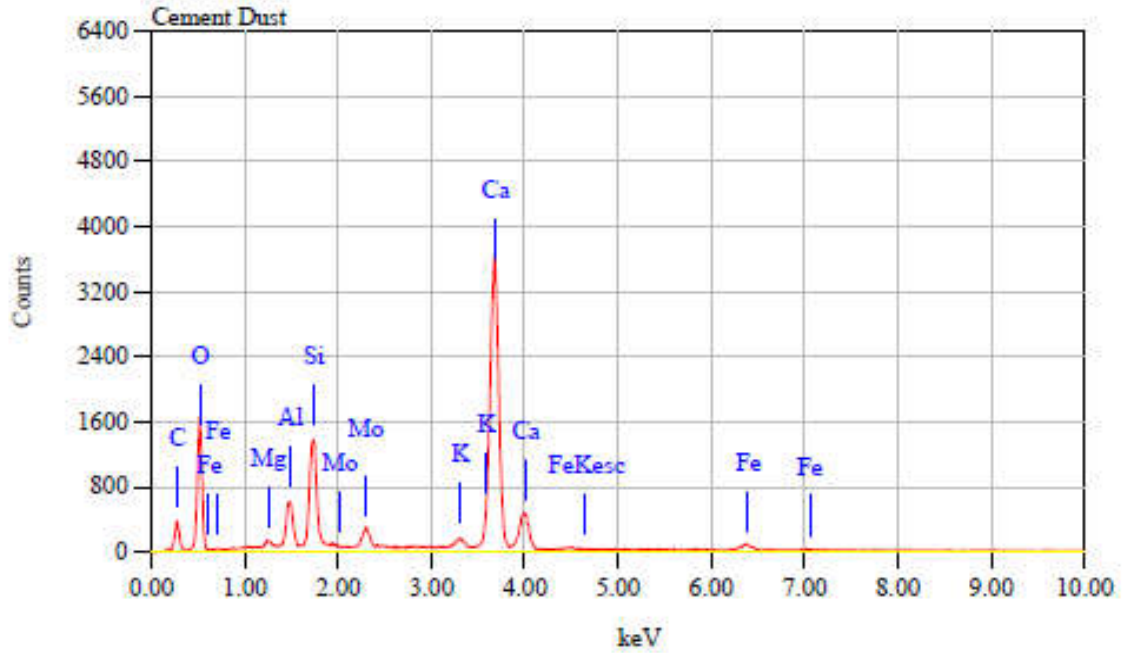


Fig 5.7: Energy Dispersive X-ray Spectroscopy of Bagfilter dust

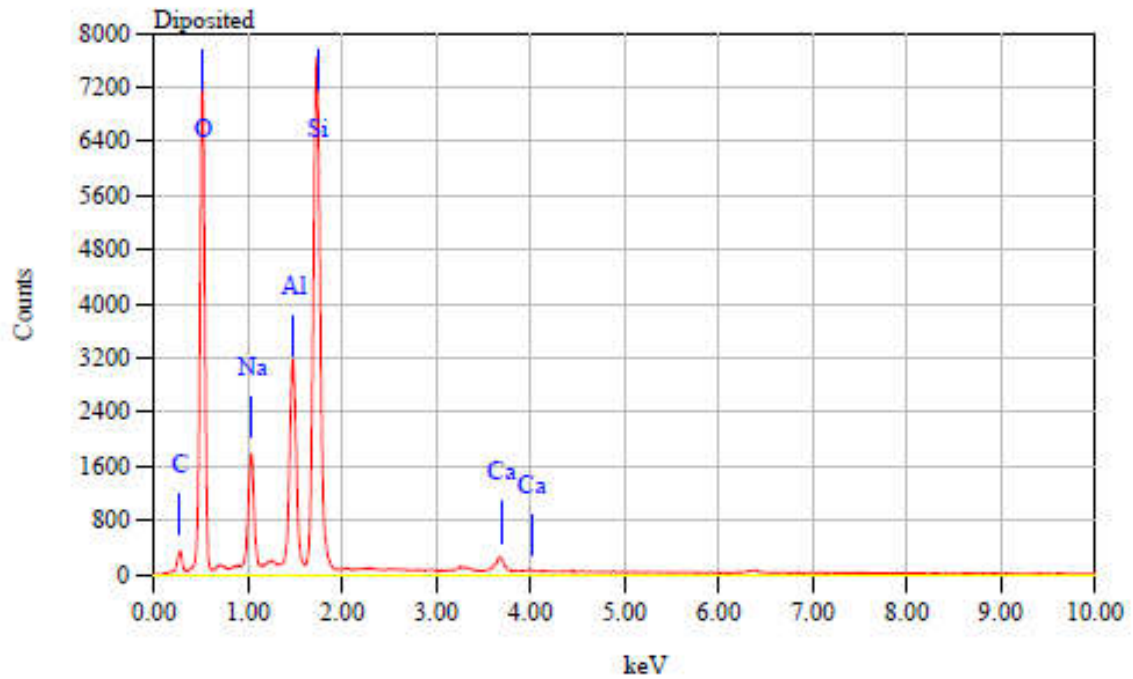


Fig 5.8: Energy Dispersive X-ray Spectroscopy of Deposited Road Dust

As stated before the bagfilter dust of dust collector can emit to surroundings and can unite with TSP and the deposited road dust remains in contact with human being. In this sense; cement dust

captured at dust collector and deposited road dust are the most crucial samples among all of these and their EDS analyses are showing the presence of Ca, Si, Al, Fe, O, C, Mg, Mo and Ca, Si, Al, Fe, O, C, Na respectively (Fig:5.7 and Fig:5.8).

Table 5.3 is representing the quantitative analysis of elements present in the sampled raw materials, final products and co- products in definite mass concentration.

Table 5.3: Quantitative Analysis of Elements Present in Samples

Name of the Samples	Mass (%)											
	Ca	Si	Al	Mg	Fe	O	C	S	K	Na	Mo	Ti
Clinker	31.30	5.46	1.44	-	1.30	50.31	7.11	-	-	-	3.09	2.29
Gypsum	13.89	1.47	1.13	-	-	62.33	-	8.60	1.10	-	12.5	1.14
Fly Ash	-	17.39	14.64	-	-	45.81	9.83	-	-	-	-	10.1
Slag	19.96	11.31	6.88	3.90	-	55.47	-	-	-	-	2.47	-
Limestone	27.42	0.61	0.33	0.60	-	54.68	16.3	-	-	-	-	-
Cement Product- OPC	32.48	6.50	1.85	0.72	1.65	48.25	5.59	1.71	1.24	-	-	-
Cement Product- PCC	52.72	12.23	5.09	1.04	2.48	11.24	6.81	-	1.55	-	6.84	-
Bagfilter dust	21.21	5.55	2.47	0.39	1.28	50.51	14.7	-	0.72	-	2.29	-
Deposited Road Particles	1.74	37.99	14.42	-	-	35.27	3.48	-	-	7.09	-	-

5.5 Particle Size Analysis

The physical properties of particulate matter determine the extent of their effect on human health (Ibrahim et al., 2012). The dimension of particulate matter is one of the significant factors which determine how and when it is going to deposit in the air passages of the respiratory system of a human being (CCOHS, 2012). The CMF at Labanchara provides enclosed building for raw material handling and storage and it increases control efficiency for PM₁₀ emission according to the Cement Industry Federation Limited, 1998 (Table: A-2 in appendix). However, bag filter emit dust beyond its control efficiency thus the bagfilter dust can contribute to TSP. Also deposited road dust is directly contacted with the individuals at industrial zone. Therefore, it is imperative to examine the particle size distribution of bagfilter dust and deposited road dust for their further settling pattern within the air passages of the respiratory system of a human being.

Table 5.4: Particle Size Analysis of Bagfilter dust and Deposited Road Dust

Sample	particle size analysis (µm)
Bagfilter dust	25-150
Deposited Road Dust	35-250

Table 5.4 illustrates the particle size of bagfilter dust and deposited road dust is ranging between 25-150 µm and 35-250 µm respectively. The particle size analysis of these two samples was done by using woven wire sieving. Woven wire sieves are generally available of ranging in size from around 125 mm down to 20 µm (Allen, 2003). Therefore outcome of this particle size analysis limits prior to 20 µm. However according to the SEM micrograph of bagfilter dust (Fig 5.9) and deposited road dust (Fig 5.10); it is evidently revealed that the particles of them are very fine and even many particles are less than 2.5 micrometers in diameter (PM_{2.5}).

The SEM micrograph of bagfilter dust is showing numerous particle of size less than 2.5 µm and 1 µm or even less than that. PM_{2.5} is so small and one 30th of average width of human hair and can lodge deeply into the lungs (USEPA, 2016). SEM micrograph of deposited road dust is viewing the existence of particles less than 2.5 µm and 1 µm abundantly. Also particles less than 0.1 µm exists in deposited road dust sample as shown in Fig 5.10.

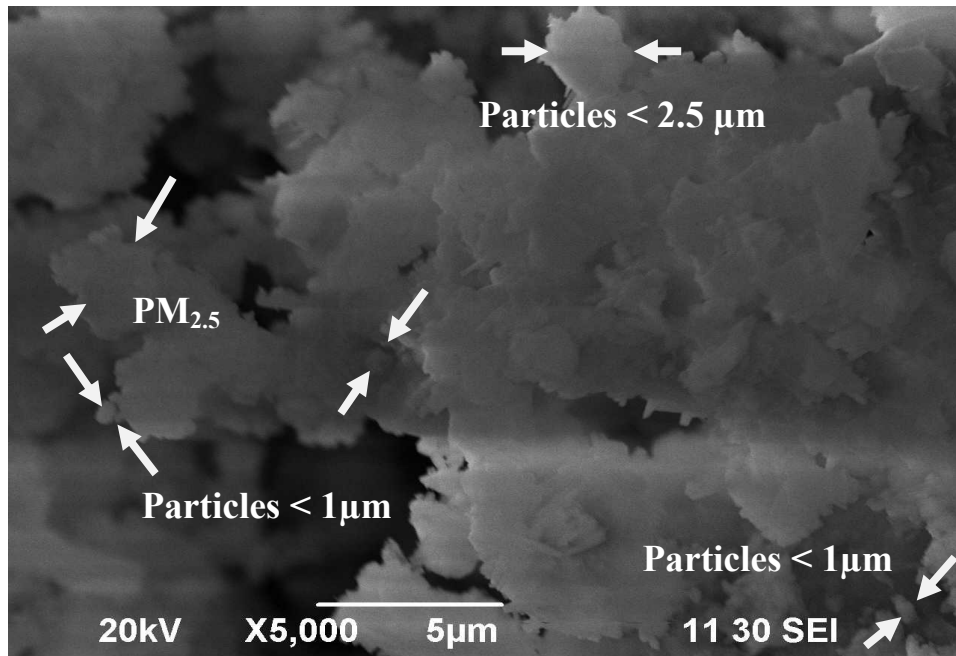


Fig 5.9: Particle Size Identification by SEM Micrograph of Bagfilter dust

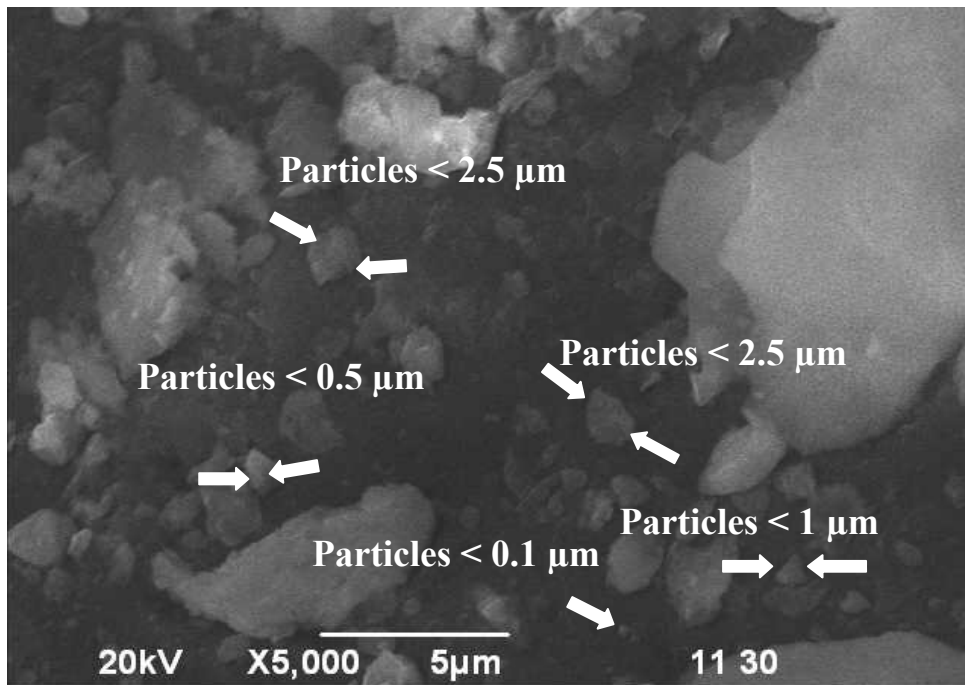


Fig 5.10: Particle Size Identification by SEM Micrograph of Deposited Road Dust

5.6 XRD Analysis

The XRD analysis was performed for the clinker, gypsum, slag, fly ash, limestone, OPC, PCC, bagfilter's dust and deposited road dust to discover their mineral constituents. Different figures are showing below the XRD pattern of the collected nine samples from Labanchara CMF. The predominant presence of alite, belite, quartz and calcite minerals was found in XRD analysis of collected OPC, PCC, cementious supplements (slag, fly ash) and bagfilter dust. The collected samples of limestone and gypsum confirmed their typical mineral existence. The XRD pattern of deposited road dust illustrated the presence of quartz, alumina, sodium oxide and limestone mineral as shown in fig 5.16. In addition XRD analysis confirmed the presence of molybdenum (Mo) in PCC, clinker, gypsum, slag, bagfilter dust and titanium (Ti) in clinker, gypsum, and fly ash. It also revealed the existence of α -quartz i.e. crystalline silica in sampled PCC, gypsum, fly ash, limestone, bagfilter dust and deposited road dust.

The major essential mineral constituents of Portland cement i.e. Alite (Ca_3SiO_5), belite (Ca_2SiO_4), aluminite ($\text{Ca}_3\text{Al}_2\text{O}_6$), ferrite ($\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) were commonly identified in XRD analysis of OPC (Figure A-14) and PCC (Fig 5.11). The primary diffraction line for α -quartz is 26.66° at 2θ (3.343 D) (NIOSH, 2003). The XRD analysis of PCC showed peaks at 26.58° at 2θ which signified the presence of crystalline silica in PCC. The presence of molybdenum was also found in PCC by this analysis. Clinker (Fig 5.12) also showed similar mineralogical constitutions as OPC and PCC excluding gypsum. Some trace amounts of titanium and molybdenum were identified in sampled clinker and quartz (SiO_2), alumina (Al_2O_3), hematite (Fe_2O_3), magnesia (MgO) and calcite (CaCO_3) were also found in OPC, PPC and clinker samples.

The sampled gypsum illustrated the typical XRD pattern which coincided with the XRD analysis of gypsum performed by RRUFF Database collected from university of Arizona Mineral Museum 4884. The XRD pattern of sampled gypsum (Fig A-15 in appendix) confirmed the occurrence of pure gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) at peak of 11.587° , 20.68° , 23.327° and 28.052° and also molybdenum at peak of 40.598° and 58.103° at 2θ . It also confirmed the presence of crystalline silica at peak of 26.589° at 2θ .

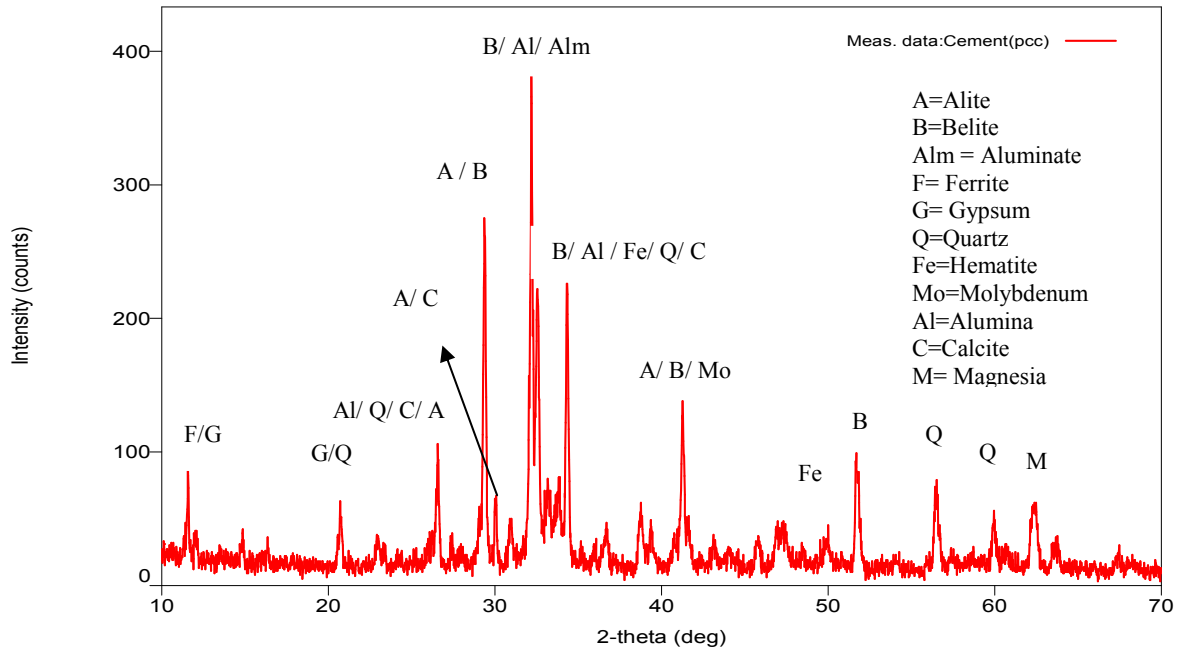


Fig 5.11: XRD Analysis of PCC

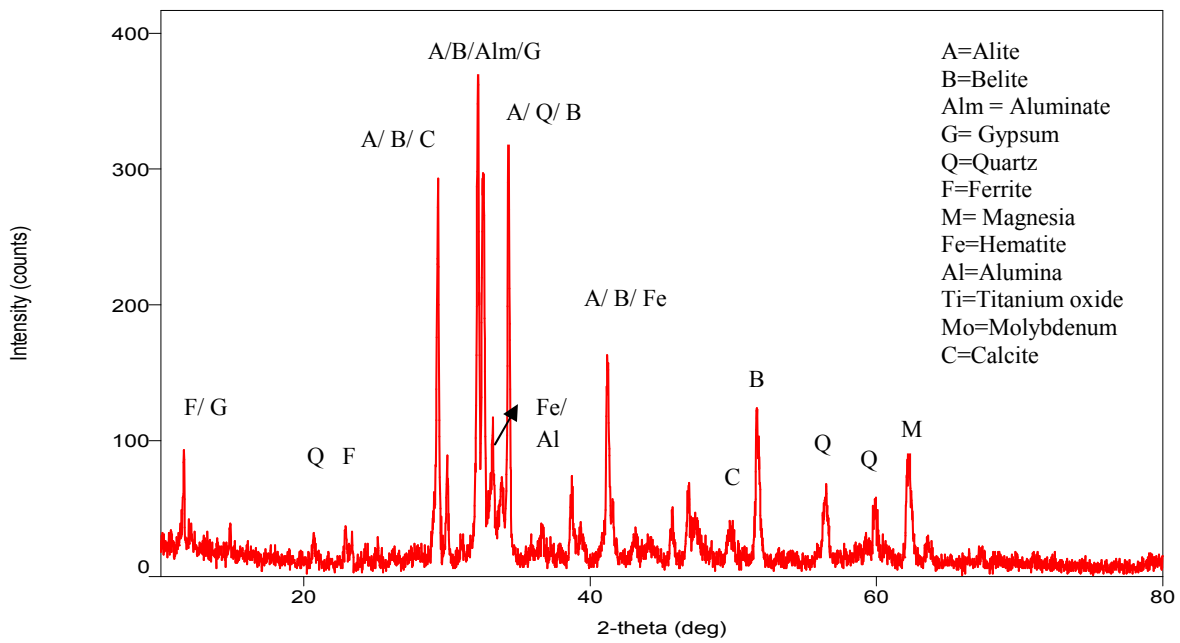


Fig 5.12: XRD Analysis of Clinker

Sampled fly ash analyzed by XRD showed the presence of mullite ($\text{Al}_2\text{O}_3 \cdot \text{Si}_2\text{O}_3$) at 16.413 and quartz at the peak of 20.835, 26.606, 39.30, 49.372 at 2-theta respectively. Existence of alumina (peak at 35.15 and 53.79 at 2-theta) and hematite (peak at 33.18, 36.50 and 49.72 at 2-theta) was also found in XRD analysis of fly ash. In addition peaks at 26.606 at 2-theta revealed the occurrence of crystalline silica in sampled fly ash.

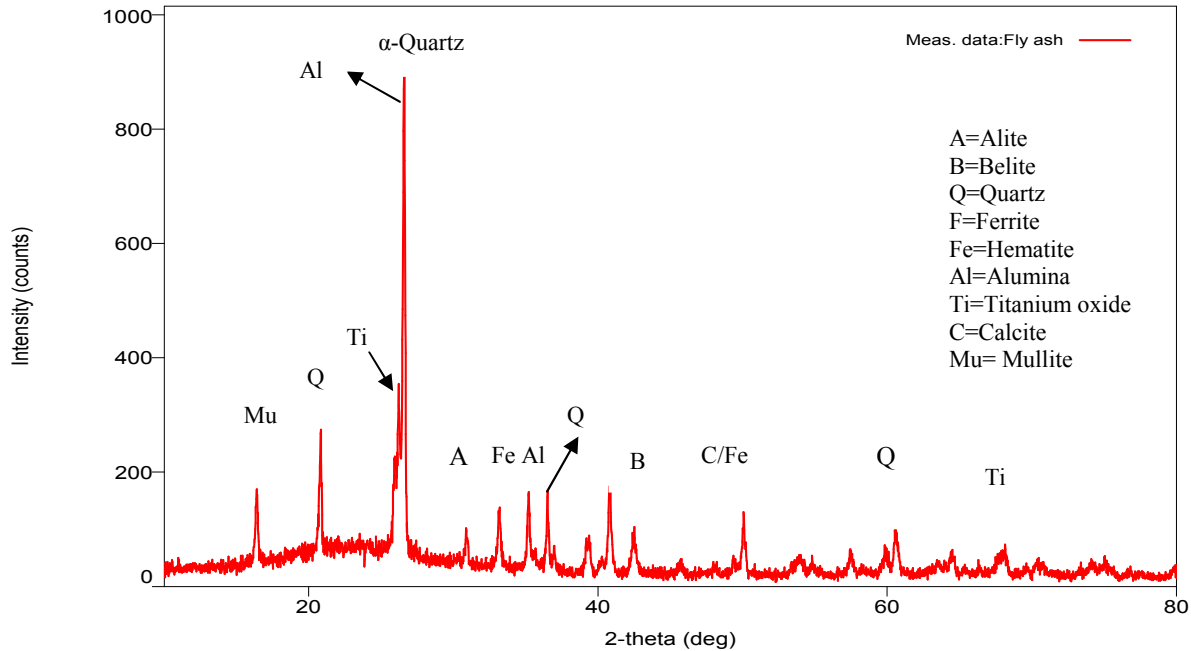


Fig 5.13: XRD Analysis of Fly Ash

Sampled slag showed two major peaks at 30.5 and 42.7 at 2-theta as in Fig 5.14. Peak at 30.5 and 32 at 2-theta specified the existence of alite or belite and 42.7 at 2-theta ferrite or belite respectively. XRD analysis of sampled limestone showed the governing presence of calcite and small amount of quartz, alumina and magnesia (Fig A-16 in appendix). Calcite gave various peaks at 23.044, 30.939, 35.967, 39.486, 47.118, 48.509 whereas quartz, alumina and magnesia showed peak at 26.626, 44.91 and 62.158 respectively at 2-theta (deg). The existence of crystalline silica was found at peaks of 26.626 at 2-theta in XRD analysis of limestone.

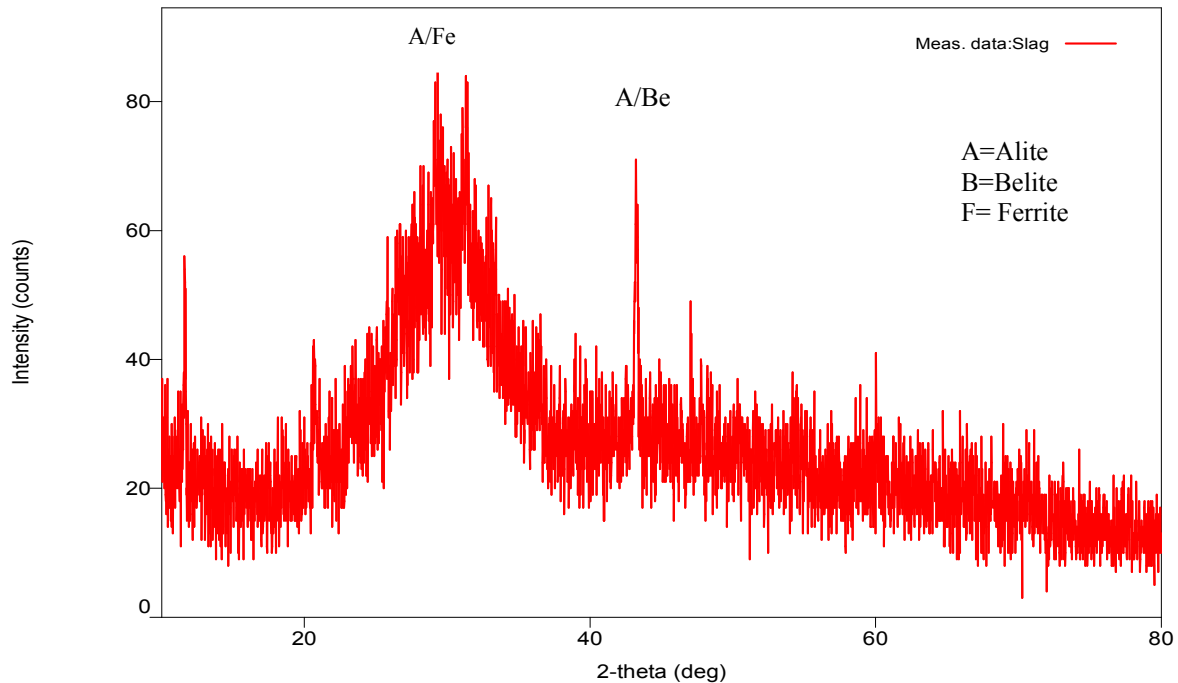


Fig 5.14: XRD Analysis of Slag

Dust captured from the bag filter during manufacturing of both OPC and PCC therefore it is supposed to include the mineral of OPC and PCC. Accumulated bagfilter dust at bag filter contained alite, belite, quartz, calcite, hematite, alumina, molybdenum and gypsum according to the Fig 5.15. Deposited road dust contained quartz, alumina, sodium oxide and limestone according to its XRD analysis. The source of quartz and alumina could be cement products and vehicular movement at CMF. As the study area is situated in a coastal area, sodium oxide can be presented in samples. Limestone was obtainable as deposited dust were accumulated from the road near to the limestone storage. The peaks at 26.602 and 26.679 at 2-theta in XRD analysis of bagfilter dust captured from the bag filter and deposited road dust respectively revealed the presence of crystalline silica.

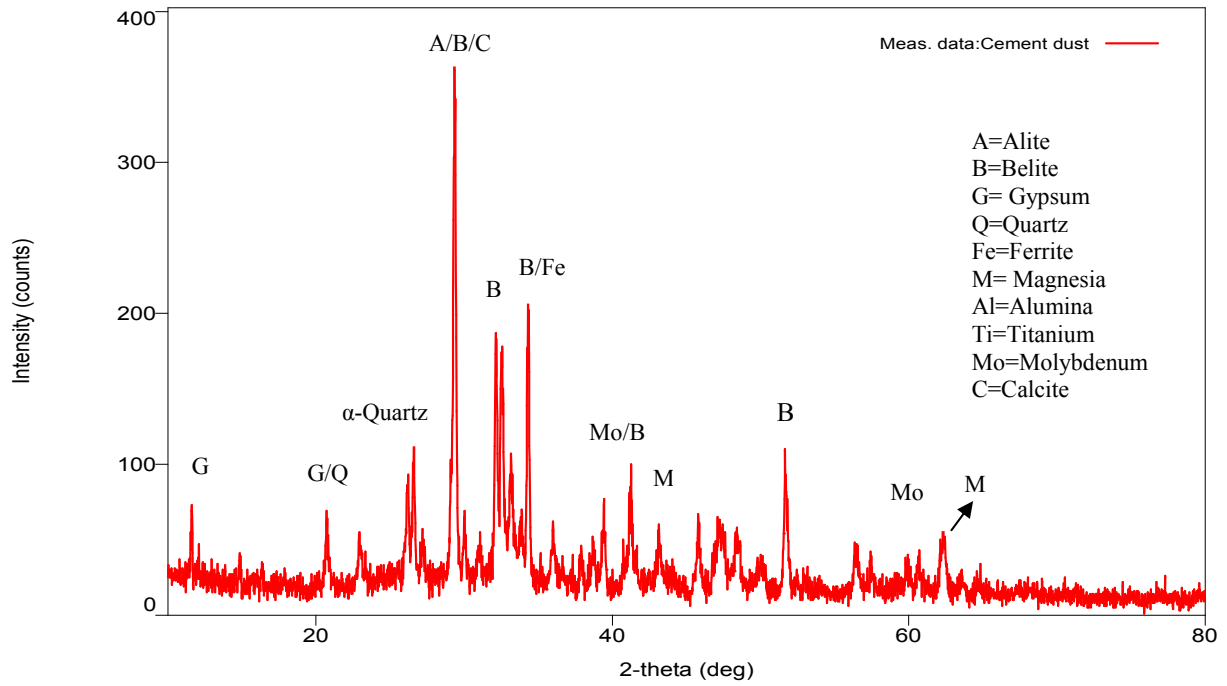


Fig 5.15: XRD Analysis of Bagfilter dust

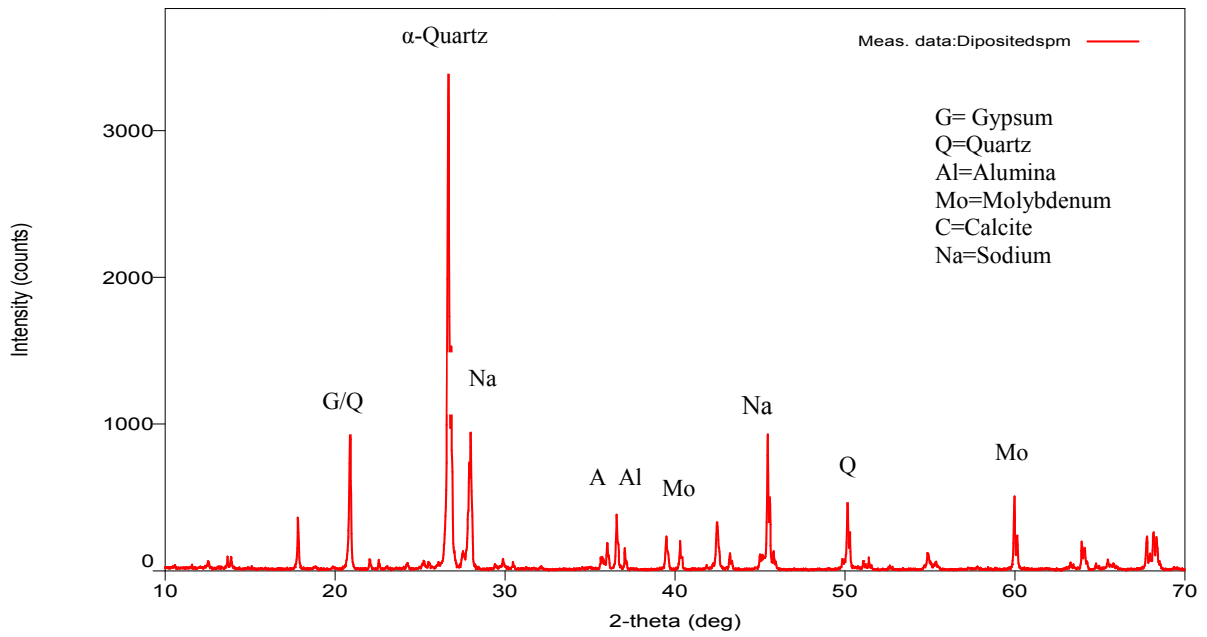


Fig 5.16: XRD Analysis of Deposited Road Dust

5.7 FTIR Analysis

The FTIR analysis was also performed for the collected nine samples i.e. clinker, gypsum, slag, fly ash, limestone, OPC, PCC, bag filter's dust and deposited road dust. The FTIR analysis aims here to determine their chemical compositional analysis according to their absorption capacity of infra-red light of a sample at each wavelength.

Quartz has the primary absorption strong asymmetric Si-O-Si stretching band near 1100 cm^{-1} (Marlene et. al.,1981) and it also gives peak near at 474, 956, 1632, 3246 and 3437 cm^{-1} (RRUFF Database). The α -quartz exhibits a unique characteristic but small doublet at 798-790 and $779\text{--}780\text{ cm}^{-1}$ and secondary peaks at 694, 512, 460, 397 and 370 cm^{-1} in FTIR spectra (NIOSH, 2003). In calcite, the band is smooth, symmetrical, and broad and show at least one strong absorption band from C-O stretching in the region of $1550\text{--}1350\text{ cm}^{-1}$. Carbonate bending vibrations produce sharp bands in the region of $900\text{--}650\text{ cm}^{-1}$. These bands show measurable frequency deviations corresponding to the attached cation. For example, the out-of-plane bending vibration for calcium carbonate (calcite) occurs near at 872 cm^{-1} . Additionally, small, sharp O-H bending vibrations occur at $1100\text{--}1000\text{ cm}^{-1}$ for the hydrated carbonates (Marlene et. al., 1981).

Sulfates, such as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) shows a strong S-O stretching vibration band in the region of $1200\text{--}1050\text{ cm}^{-1}$. Another small band occurs near 1000 cm^{-1} , because of an S-O bending vibration, along with sharp, slightly stronger bands at $700\text{--}600\text{ cm}^{-1}$. Gypsum has also bands near at 3555 and 1690 cm^{-1} (Marlene et. al., 1981). The anhydrous iron oxide (hematite) provide strong band near 555 cm^{-1} and also band occurs near 620 cm^{-1} broad in nature and 472 cm^{-1} sharp in nature with medium intensity. Additionally hematite presents some weak and broad bands occur near 1052 and 1093 cm^{-1} .

Alumina (Al_2O_3) shows strong and broad band at $500\text{--}400\text{ cm}^{-1}$, doublet peak at $500\text{--}600$ and sharp peak at 650 cm^{-1} . Molybdenum (Mo) and Magnesia (MgO) show band at 2850, 2910, 1221, 1074, 722, 633 cm^{-1} and 436, 1451, 1632, 3440, 3700 cm^{-1} respectively (RRUFF Database). Bands at 579, 670, 1040, 1384, 1459, 1558, 1638, 1739, 2337, 2854 cm^{-1} associated to carbon bonding. A strong broad band at 3440 cm^{-1} are intensified with hydration, indicating that the increase of hydrated products associated with water. Sharp band at 3630 cm^{-1} associated

to O-H stretching vibrations of portlandite ($\text{Ca}(\text{OH})_2$) and the peaks at 3410 and 1610 cm^{-1} are correspond to stretching and bending modes of water of crystallization particularly from gypsum. The carbonates peak at 1425 cm^{-1} , 717 cm^{-1} and 875 cm^{-1} are observed due to the reactions of atmospheric CO_2 with calcium hydroxide. FTIR spectra of specific molecules can be tabulated as below (Table: 5.5).

Table: 5.5 FTIR spectra of minerals and bondings

Name of the minerals and bondings	Infra Red Absorption Frequencies (cm^{-1})
Quartz	474, 956, 1100, 1632, 3246, 3437
α -quartz	798-790, 779-780, 694, 512, 460, 397, 370
Calcite	872, 900-650, 1550-1350
Hydrated carbonates	717, 875, 1100-1000, 1425
Gypsum	500-700, 1000, 1200-1050
Anhydrous iron oxide (hematite)	472, 555, 620, 1093, 1052
Alumina	500-400, 500-600, 650
Molybdenum	633, 722, 1074, 1221, 2850, 2910
Magnesia	436, 1451, 1632, 3440, 3700 cm^{-1}
C-C bonding	579, 670, 1040, 1384, 1459, 1558, 1638, 1739, 2337, 2854
O-H bonding	1610, 3410, 3440, 3630

(Source: RRUFF database)

Table: 5.6 represent the assignment of bonding on different peaks at FTIR spectra of the collected samples which can give the assurance of presence of compounds. The Fig: 5.17, Fig: 5.18, Fig: 5.19 and Fig 5.20 are viewing the FTIR spectra of PCC, OPC, deposited road dust and fly ash respectively. The FTIR spectra of clinker, gypsum, limestone, slag and bagfilter dust are shown at appendix on Fig: A-17, Fig: A-18, Fig: A-19, Fig: A-20 and Fig: A-21 respectively.

Table: 5.6 Assignment of Infra Red Absorption Frequencies of the Collected Samples

Name of the samples	FTIR spectra at Peak	Assignment
OPC	457.13	Si-O-Al
	522.71	Si-O-Al
	1111	Highly intense C-O bonding
	1631.78	-C=C- and C=O stretching vibration
	2868.15	C-H stretching vibration
	2927.15	C-H stretching vibration
	3441.01	Strong O-H stretching vibration
PCC	462.92	In- plane and out of plane aromatic ring deformation vibration for activated carbon
	779.24	Si-O-Si (α -quartz)
	1080.14	Strong S-O stretching vibration band
	1409.96	C-H deformation band
	1624.06	C-N stretching band
	2854.65	Aliphatic C-H stretching vibration
	2924	Aliphatic C-H stretching vibration
	3435.22	Water absorption Band
	3691.75	Stretching vibration of O-H
Deposited road dust	459.06	Si-O-Si
	881.47	Amine C-N stretch
	925.83	O-H stretching
	1431.18	C-O stretching
	1625.99	C=N strong bend
	2858.51	C-H stretching
	2924.09	C-H stretching
	3427.51	-OH bounded

Fly ash	464.84	S-S stretching band
	790.81	Si-O-Si (α -quartz)
	1379.1	C=C or C=H
	1089.78	SO ₃ ²⁻
	1631.78	C=C- and C=O stretching vibration
	2864.29	C=H stretching
	3454.51	Stretching vibration of O-H
	3695.61	Al-OH
	3772.76	Al-OH
Gypsum	466.77	Ti-O-Ti
	601.79	Stretching and bending mode of sulfate
	669.3	Stretching and bending mode of sulfate
	1126.43	Stretching and bending mode of sulfate
	3404.36	Stretching vibration of O-H
	3545.16	Stretching vibration of O-H
Limestone	474.49	Si-O-Si
	875.68	Bending mode of the carbonate calcite
	1111	Highly intense C-O bonding
	1427.32	C-O Stretching mode of Carbonate band
	1620.21	Stretching and bending mode of O-H
	1801.51	Stretching vibration of C-O group
	3444.87	Stretching vibration of O-H
	3697.54	Stretching vibration of O-H
Bag filter's's dust	470.63	Ti-N
	1109.07	Out of plane O-H deformation and C-O stretching
	1477.47	C-C
	1633.71	C-N
	2935.66	C-H stretching
	3454.51	O-H stretching
Clinker	460.99	Si-O-Si

Clinker	522.71	Si-O-Al
	931.62	C-H stretching
	1107.14	C-N stretching band
	1433.11	C-H bending
	1631.78	C=C- and C=O stretching vibration
	2860.43	C-H stretching
	2926.01	C-H stretching of Alkanes
Slag	3450.65	Stretching vibration of O-H
	881.47	Si-O-Si
	1705.07	C=O
	2860.43	C-H
	2926.01	C-H
	3446.79	Stretching vibration of O-H

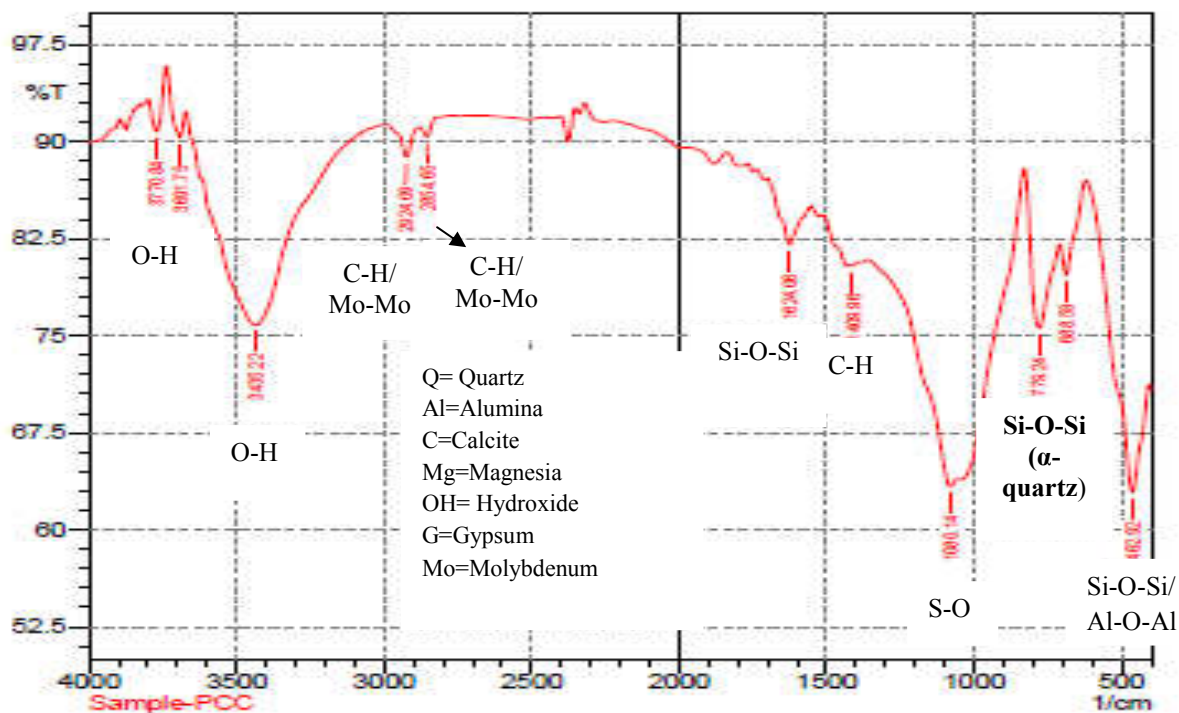


Fig 5.17: FTIR Analysis of PCC

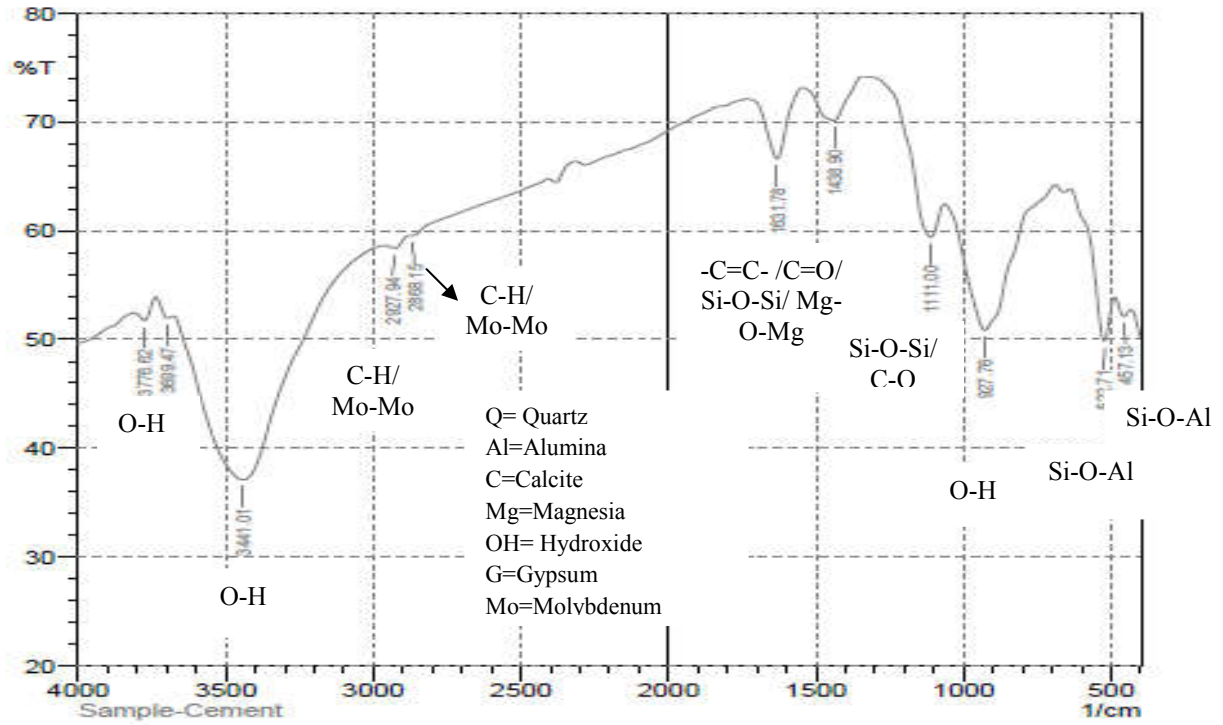


Fig 5.18: FTIR Analysis of OPC

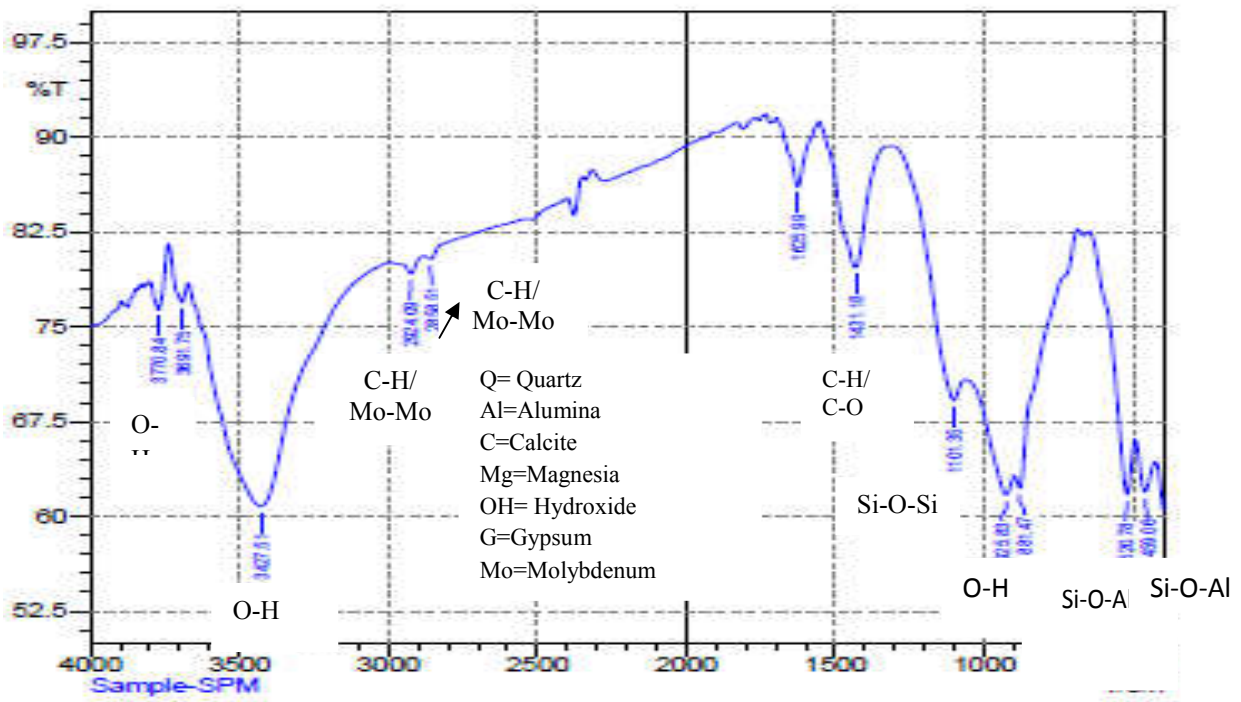


Fig 5.19: FTIR Analysis of Deposited Road Dust

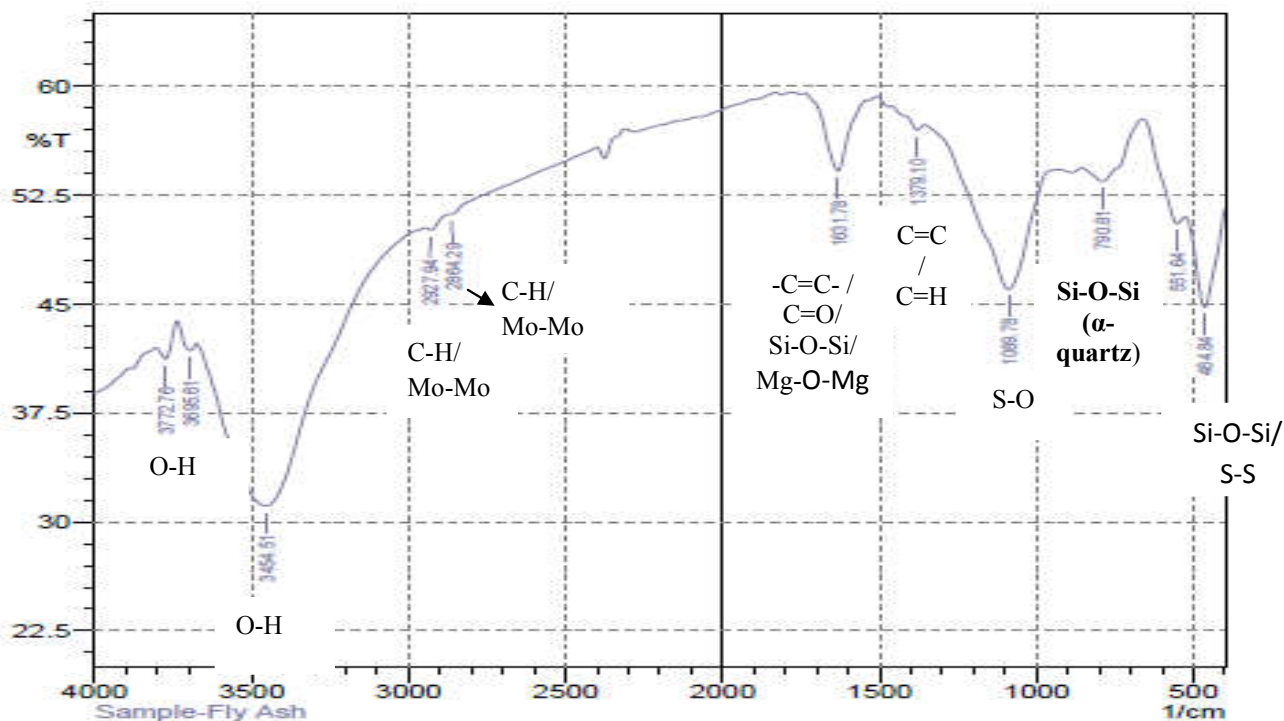


Fig 5.20: FTIR Analysis of Fly Ash

5.8 Effects of Harmful Elements on Human Health found from Micro-Characterization

Bagfilter dust is considered itself a health hazard if it is inhaled by a human body as it may contain potentially harmful compounds i.e. silica (specially crystalline silica), alumina, iron oxide and heavy metals etc. These micro analyses have found the presence of these hazardous substances in different samples of Labanchara CMF which can cause harm upon people staying within industry or in the vicinity of its surrounding. Even people working in or near construction site may be in alarming condition if no measure is taken when this cement product will be used for construction. Moreover the analyses has found PCC more hazardous than OPC regarding the health issue as it contains comparatively finer particles and carcinogenic substances such as crystalline silica originated from fly ash.

Although Silica is the essential components of cement; it is considered as immense health hazard currently if crystalline silica presents. There are many epidemiological studies of occupational cohorts exposed to respirable silica dust. Silicosis, lung cancer, and pulmonary tuberculosis are associated with occupational exposure to quartz dust. IARC classified inhaled crystalline silica

(quartz or cristobalite) from occupational sources as a Group 1 carcinogen. Statistically significant increases in deaths or cases of bronchitis, emphysema, chronic obstructive pulmonary disease, autoimmune-related diseases (scleroderma, rheumatoid arthritis, systemic lupus erythematosus), and renal diseases have been reported due to crystalline silica exposure. Regarding exposure to ambient quartz in the general environment, a benchmark dose analysis predicted that the silicosis risk for a continuous 70-year lifetime exposure to 0.008 mg/m³ (estimated as high crystalline silica concentration in US metropolitan areas) is less than 3% for healthy individuals not compromised by other respiratory diseases or conditions and for ambient environment (USEPA, 1996).

Contact with alumina can cause eyes and skin irritation. Inhalation of alumina can irritate the nose, throat and lungs and repeated exposure can lead to lung damage. Exposure to iron oxides fume can cause metal fume fever. This is a flulike illness with symptoms of metallic taste, fever, chills, aches, chest tightness and cough. Repeated exposure to iron oxide fume can cause pneumoconiosis (siderosis) with cough, shortness of breath and changes in x-ray.

Inhalation of heavy metals has undesirable health effects on human and animals. The micro analyses have found the presence of Mo, Fe and Ti in some samples of CMF. Although Fe is an essential elements for the human body but not in the form of inhalable particles as Fe-bearing particles can simulate reactive oxygen species on the lung surface, which may further lead to scarring of the lung tissue (Knaapen *et. al.*, 2004). It has been reported that exposure of titanium powder and its inhalation may cause tightness and pain in chest, coughing and difficulty in breathing. Also its contact with skin or eyes may cause irritation. Molybdenum is generally considered to be of low human toxicity. However; chronic exposure of molybdenum may result in higher serum uric levels and gout like illness (Kovalskii et al., 1961). It affects more to animals than human and chronic exposure defined as the administration of total single dose of 2.365 to 24.497 micrograms of molybdenum results in a rise in the number of death rates from 14.2% to 57.2% in exposed animals. Thus these heavy metals should be examined in raw materials by quality control test (as for instance Ti and Mo are redundant in cement) before grinding at CMF.

Existence of fine particles (PM_{10} and $PM_{2.5}$) in materials is toxic for human health upon inhalation and very fine particles (particles $< PM_{0.5}$) have been already found in the SEM micrographs of different collected samples of CMF. The study has revealed the surface morphology (angular, semi-rounded, flaky, spherical, and elongated) of particles available in different samples of CMF. Particle deposition in the lung is governed primarily by three mechanisms: Impaction, Sedimentation and Diffusion. Particle slip, shape and density affect deposition of particles in the human lung by contributing to at least one of these mechanisms (Timothy *et. al.*, 2002). Particle deposition from inertial impaction and sedimentation is directly dependent upon the relaxation time of the aerosol particle and relaxation time depends on particle diameter, particle density, aerodynamic particle diameter unit density and aerodynamic diameter is dependent upon both density and shape of a particle (Timothy *et. al.*, 2002). Therefore this study recommends the further study on surface morphology of particles on their deposition pattern.

Chapter 6

Health Risk Assessment

6.1 General

Cement industry is a potential anthropogenic source of air pollution (Allaban and Qudais, 2011) and these air pollutants can pose threats to human health as well as environment. However, from chapter 4 it is clearly evident that SO_x, NO_x, CO₂ or VOC may not exist in a significant quantity at sampled industry while Particulate Matter (PM) may exist in a considerable degree which can create health hazards. Hence, this chapter will describe the air quality index and the occupational health risks associated with the exposure of PM at sampled industry.

6.2 Air Quality Analysis

For the purpose of study monitoring of PM in air and its characterization by pollutants analyzer within the CMF was not permissible by authority. Therefore an air quality analysis of sampled factory performed by DoE of Khulna divisional office was collected to obtain the concentration of existed PM. PM is measured usually as PM₁₀; however DoE has measured PM as Total Suspended Particles (TSP) for CMF at Labanchara. TSP includes all sizes of PM those are suspended in the air and can be inhaled by human body. The air quality analysis (Table 6.1) of CMF is presenting below.

Table 6.1: Air Quality Analysis of Labanchara CMF

Sample Location	24 hours TSP Concentration ($\mu\text{g}/\text{m}^3$)	Remarks
East Side of Industry	166	
West Side of Industry	158	
North Side of Industry	164	All concentrations are within range
South Side of Industry	186	
Bangladesh Standard	200 ($\mu\text{g}/\text{m}^3$)	

(Source: DoE, 2016)

Table 6.1 is viewing the 24 hours TSP concentrations; measured as 166 $\mu\text{g}/\text{m}^3$, 158 $\mu\text{g}/\text{m}^3$, 164 $\mu\text{g}/\text{m}^3$ and 186 $\mu\text{g}/\text{m}^3$ from east side, west side, north side and south side of the industry respectively in month of February of 2016. All TSP concentrations are found within the standard range (200 $\mu\text{g}/\text{m}^3$) prescribed by DoE of Bangladesh. Although the location for measuring

concentration of air pollutants should be selected according to the intensity of discharge and for instance; packaging zone, stockpiles of raw materials etc.

6.3 Air Quality Index

Air Quality Index (AQI) provides the understanding of air pollution level at which air can be polluted and the associated health effects might concern. Equation 3.6 of chapter: 3 has been used to determine AQI for this factory. DoE of Bangladesh has set ambient air quality standards for different air pollutants and $200\mu\text{g}/\text{m}^3$ has been prescribed as standard for 24 hours TSP concentration. Sample calculation of AQI for this CMF is added to appendix. The Table 6.2 is presenting the AQI value as shown below. According to Table 6.2; AQIs of sampled industry are found as 83, 79, 82 and 93 for the TSP concentration of $166\mu\text{g}/\text{m}^3$, $158\mu\text{g}/\text{m}^3$, $164\mu\text{g}/\text{m}^3$ and $186\mu\text{g}/\text{m}^3$ respectively. These AQIs have fallen in yellow green colored group; ranging from 51 to 100 and hence in moderate level of health concern. AQI ranging between 51 and 100 indicates the air quality is acceptable but it may be a moderate health concern for a very small number of people susceptible to exposure of particular matter.

Table 6.2: Air Quality Index of Labanchara CMF

24 Hours TSP Mean Concentration ($\mu\text{g}/\text{m}^3$)	Bangladesh Standard Pollutants Data ($\mu\text{g}/\text{m}^3$)	AQI Value	AQI Range	Level of Health Concern	Color
166	200	83	51-100	Moderate	Yellow Green
158	200	79	51-100	Moderate	Yellow Green
164	200	82	51-100	Moderate	Yellow Green
186	200	93	51-100	Moderate	Yellow Green

6.4 Environmental Burden of Disease

The impact of health problem due to environmental pollution; as measured by morbidity or mortality is defined as Environmental Burden of Disease (EBD). Health Risks has been determined in terms of EBD in this study. EBD can also be expressed in terms of DALYs (Disability Adjusted Life Years). DALYs is the sum of years of potential life lost due to

premature mortality and years of productive life lost due to disability (WHO, 2016). In other word; DALYs give an indication of the equivalent number of healthy life years lost in a population due to premature mortality and morbidity (Murray and Lopez, 1996). The DALYs for sampled industry due to the exposure of PM are calculated in Table: 6.3. Premature mortality due to some selected disease associated with the exposure of PM_{2.5} and PM₁₀ has been calculated in terms of annual number of deaths (Table: 6.4 and Table: 6.5) in this study by using equation 3.7 of chapter: 3. Sampled calculations for premature mortality cases counts are shown in appendix.

6.4.1 DALYs Calculation for Labanchara CMF due to Emission of PM

According to World Health Organization DALY for Bangladesh was found as 0.7 per 1000 capita/year in case of outdoor pollution (WHO, 2009). The outdoor pollution was accounted for particulate matter in this WHO report. Total 275 Nos. employees is working at Labanchara CMF currently and the DALYs for study area is found as 0.193 per 275 capita/year or total 70.5 days for all workers (Table 6.3). It indicates a worker at Labanchara CMF can lose his life expectancy by 6 hours in a year due to PM exposure. Therefore the using of mask by the employee should be employed mandatorily and taking of shower by the workers before leaving the workplace should be encouraged to lessen the extent of dusts hazard.

Table 6.3: Calculation of DALYs for Labanchara CMF due to the Exposure of PM

DALYs for Outdoor Pollution for Bangladesh	Population at Sampled Industry	DALYs for Sampled Industry
0.7 per 1000 capita/year	275	0.193 per 275 capita/year or 70.5 days for all workers or 6 hours for a single worker

6.4.2 Premature Mortality Associated with the Exposure of PM

TSP can be accumulated with different sized particulate matter. Therefore; PM₁₀ and PM_{2.5} has been assumed for certain percentage of mean concentration of existed TSP (168.5µg/m³) to

determine the EBD. CEIDARS (California Emission Inventory Data and Reporting System) suggests that PM₁₀ and PM_{2.5} fraction of TSP are 0.92 and 0.62 respectively for cement manufacturing factory. This section has calculated annual number of death due to long term exposure to PM_{2.5} and short term exposure to PM₁₀.

Table: 6.4 Annual Numbers of Premature Deaths from Long-Term Exposure to PM_{2.5} at Labanchara CMF

Outcome and Exposure Metric	PM _{2.5} concentration (µg/m ³)	Mortality rate of disease group (B) (No. of deaths /1000/year)	Attributed factor (AF)	Worker of sampled industry as population (P)	Deaths from Exposure to PM _{2.5} at Sampled Industry (Deaths/Year)	
					Best Estimate	95% CI
Cardio-pulmonary mortality	104.5	0.0015	0.359	250	0.135	0.055-0.194
Lung cancer mortality	104.5	0.00007	0.486	250	0.009	0.004-0.012

Table: 6.5 Annual Numbers of Premature Deaths from Short-Term Exposure to PM₁₀ at Labanchara CMF

Outcome and Exposure Metric	PM ₁₀ concentration (µg/m ³)	Mortality rate of disease group (B) (No. of deaths /1000/year)	Attributed factor (AF)	Worker of sampled industry as population (P)	Deaths from Exposure to PM ₁₀ at Sampled Industry (Deaths/Year)	
					Best Estimate	95% CI
All cause mortality	155.02	0.0053	0.109	275	0.159	0.115-.178

Annual number of premature death due to long term exposure to $PM_{2.5}$ is found as 0.135 (best estimate) with confidence interval 0.055 to 0.194 for cardio-pulmonary diseases at sampled industry (Table: 6.5) whereas 0.009 (best estimate) with confidence interval 0.004 to 0.012 due to lung cancer. Annual numbers of premature deaths due to short-term exposure to PM_{10} at sampled industry by using equation 3.7 of chapter: 3 are found as 0.159 (best estimate) with 95% confidence interval 0.115 to 0.178 for all cause mortality (Table: 6.4). Sample calculation is added to appendix. Premature death due to $PM_{2.5}$ and PM_{10} emission has been found less than a one person annually. Otherwise a person in about 7 years will be found as expected premature deaths due to PM_{10} exposure for all cause mortality. In case of $PM_{2.5}$ exposure a person in 8 years and a person in 111 years will be found as expected premature deaths for cardio-pulmonary diseases and lung cancer respectively. In addition the cumulative TSP concentration is found as 60 mg/m^3 ($168.5 \text{ } \mu\text{g/m}^3 * 355 \text{ days}$) which is less than 300 mg/m^3 which indicates a better control for air pollution at sampled CMF. It has been reported that the risk of developing a notable obstructive impairment of respiratory system significantly increases for the cumulative total dust exposures in excess of 300 mg/m^3 in a year (HSE, 2005).

Chapter 7

Conclusions and Recommendations

7.1 Conclusions

The summary of the results and discussion of this research work is as below:

- The DALY was found as 6 hours per worker per year due to the exposure of dust particles at Labanchara CMF which indicates the importance of imposing emission estimation and reporting policy for cement industries in Bangladesh.
- The study has confirmed the presence of carcinogenic substances such as crystalline silica (α -Quartz) in PCC, road dust and bag filter dust at Labanchara CMF. The existence of crystalline silica in PCC was originated from raw materials such as fly ash and limestone.
- The study has found the presence of very fine particles ($< PM_{0.5}$) in PCC, OPC, road dust and bag filter dust at Labanchara CMF and their presence can have severe negative impact on human health and surrounding environment.
- The study has revealed the existence of redundant heavy metals such as Ti and Mo in PCC and OPC which can affect the quality of cement and human health as well.
- The PCC was found more hazardous than OPC regarding the health issue as it contains comparatively finer particles and carcinogenic substances such as crystalline silica originated from fly ash.
- The study has estimated that the Labanchara CMF emits about 50.3 metric ton dust per year (2.57g dust per cement bag) to the atmosphere.
- The study has also identified more flaky and spherical shaped particles in PCC which could be originated from slag and fly ash.

7.2 Recommendations for Further Studies

From the above given conclusions the recommendations can be implied for the further studies as below:

- Determining the emission factors intended for cement industry as well as other industry in respect of Bangladesh.
- Establishing the national reporting process and threshold limit for emission from industrial sector in Bangladesh.
- Determining the effect of surface morphology of particulate matter on their deposition pattern.
- Long term monitoring of air pollutants at the downwind and upwind areas of sampled CMF and their dispersion pattern.
- Comprehensive assessment of environmental and health risks due to exposure of criteria pollutants generating from cement industry.

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Appendix-A

SUPPLEMENTARY TABLES

Table: A-1 Emission Reduction Factors for Materials Handling and Storage

Reduction Method	Reduction Factors (ER_{PM10})	Control Efficiency (CE_{PM10})
Wind breaks	0.7	30%
Water sprays	0.5	50%
Chemical suppression	0.2	80%
Enclosure (2 or 3 walls)	0.1	90%
Covered stockpiles	0.0	100%

(Source: Cement Industry Federation Limited, 1998)

Table: A-2 Emission Factors Considered for Different Types of Vehicles

Air pollutants	Emission rate (g veh⁻¹ km⁻¹)			
	Private Car/Jeep	Micro-Bus	Pick-up Van/ Small Truck	Large Truck
	Petrol	Petrol	Diesel	Diesel
CO	5.500	6.600	3.148	7.870
NO _x	0.902	1.082	3.492	8.730
VOC _s	0.676	0.811	0.857	1.560
SO ₂	0.027	0.032	0.294	0.734
PM ₁₀	0.0224	0.0268	0.240	0.600

(Source: Alam, 2015)

Appendix-B

SAMPLE CALCULATION

Sample Calculation: 01

Annual emissions of PM₁₀ from bag filter installed at clinker silo top (bucket side) is,

$$\begin{aligned} \text{Ekpy, PM}_{10} &= \text{EFPM}_{10} * A * \text{OpHrs} * 10^{-6} \\ &= 12\text{mg/m}^3 * 4,500\text{m}^3/\text{hr} * 6570\text{hr/yr} * 10^{-6} \\ &= 358.78\text{kg/year} \end{aligned}$$

Here,

Emission factor for PM₁₀ in this case, EFPM₁₀ = 12mg/m³ (NPI, 1999)

Air flow rate, A = 4,500m³/hr

Operating hours, OpHrs = 6570hr/yr

10⁻⁶ = conversion factor mg to kg.

No of bag filter installed at clinker silo top (bucket side) is 1

So, Ekpy, PM₁₀ = 358.78kg/yr

Sample Calculation: 02

Annual emission of CO from large truck is,

$$\begin{aligned} E_c &= 355 * 0.001 * \text{Emission rate} * \text{VKT} \\ &= 355 * 0.001 * 7.870 * 2.205 \\ &= 6.16 \text{ kg/yr} \end{aligned}$$

No of large truck at CMF is 18,

So total emission = 110.89 kg/yr

Here;

355 = working days per year

0.001 = conversion factor g to kg

Emission Rate = 7.870 g veh⁻¹ km⁻¹ (Table: 3.2)

VKT = 2 * average no. of trip * vehicle traveling path

Average no. of trip = 3.5

Vehicle traveling path at CMF = 315 m (Obtained from Google Earth)

2 = for incoming and outgoing

So, VKT for large truck = 2.205 km

Appendix-C

SUPPLEMENTARY FIGURES

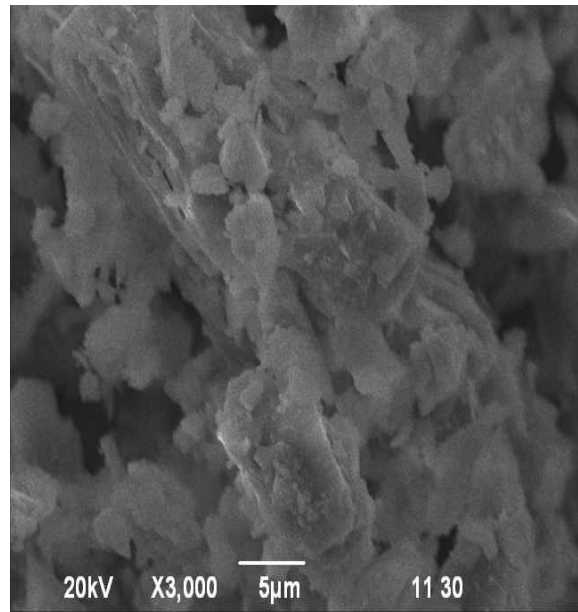
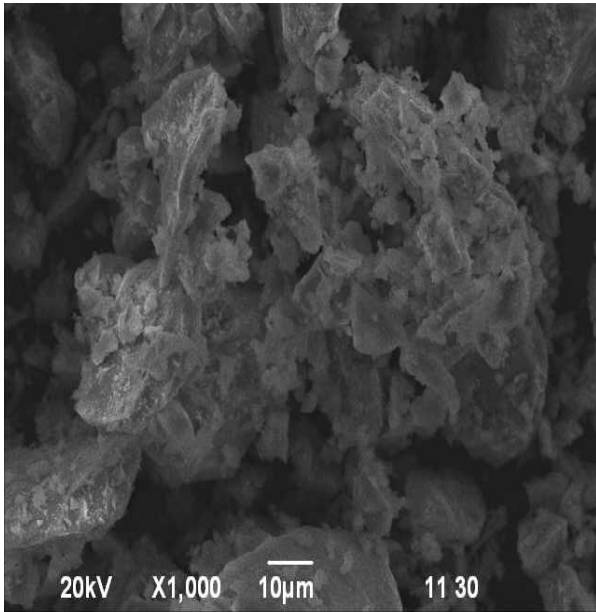


Fig A-1: Scanning Electron Microscopic Images of Clinker

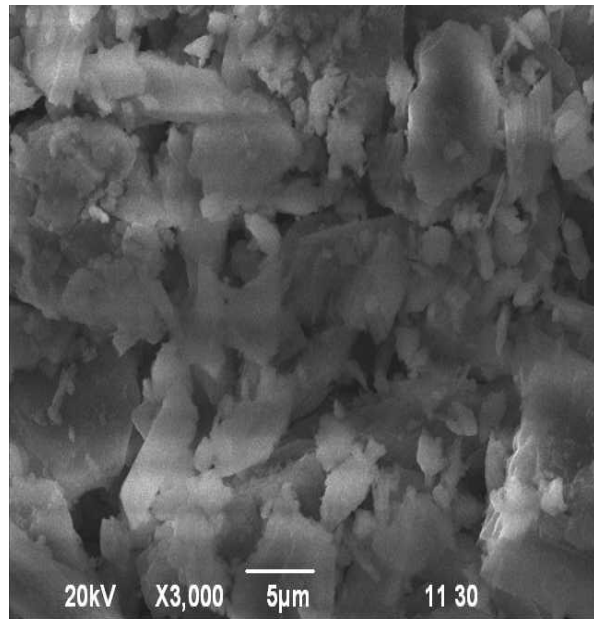
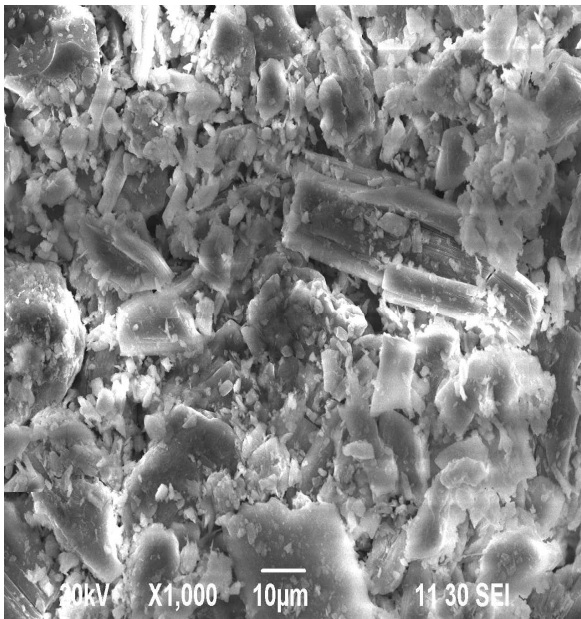


Fig A-2: Scanning Electron Microscopic Images of Gypsum

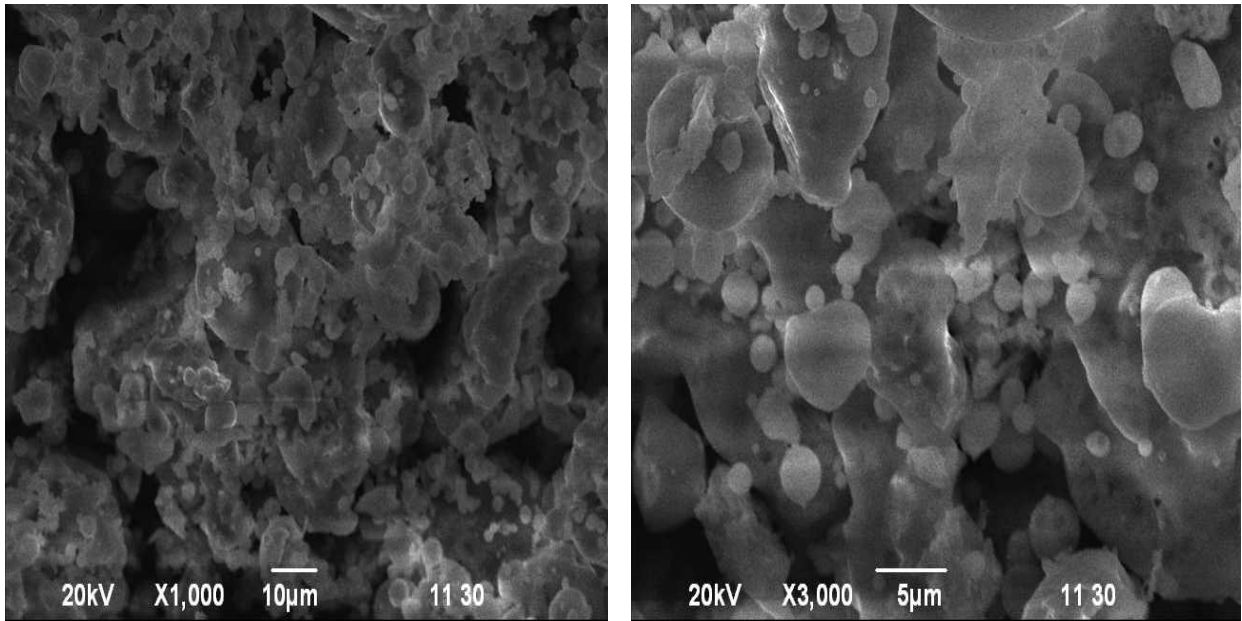


Fig A-3: Scanning Electron Microscopic Images of Fly Ash

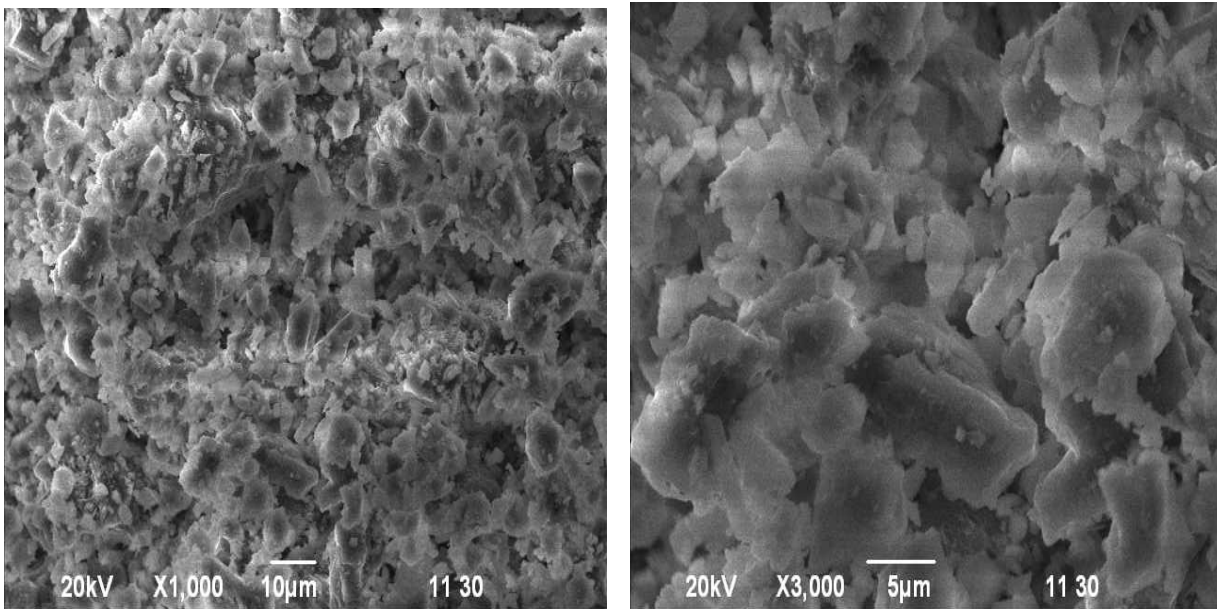


Fig A-4: Scanning Electron Microscopic Images of Limestone

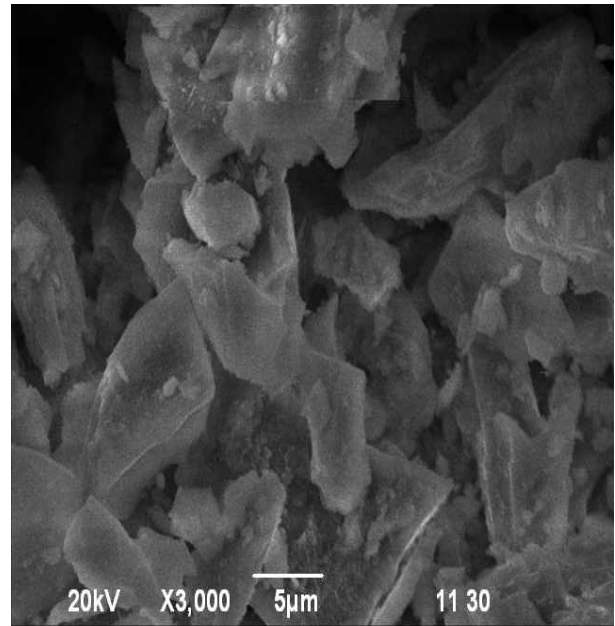
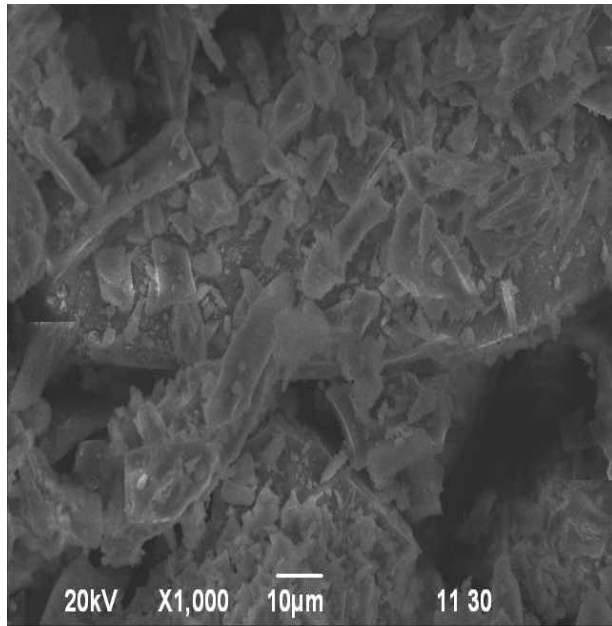


Fig A-5: Scanning Electron Microscopic Images of Slag

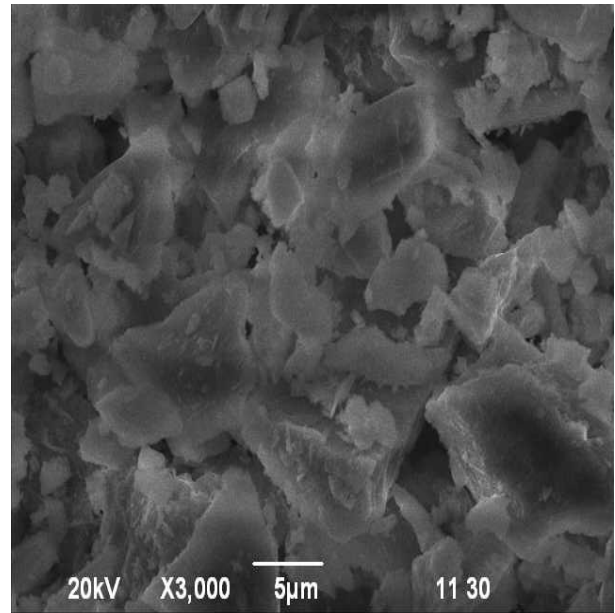
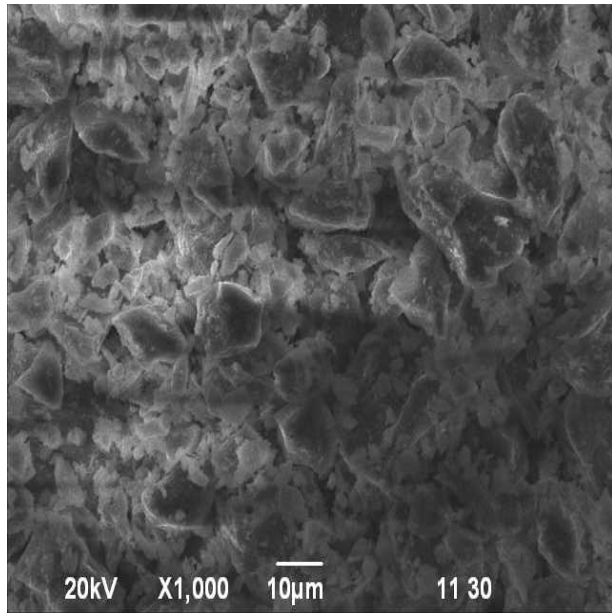


Fig A-6: Scanning Electron Microscopic Images of Cement Sample (OPC)

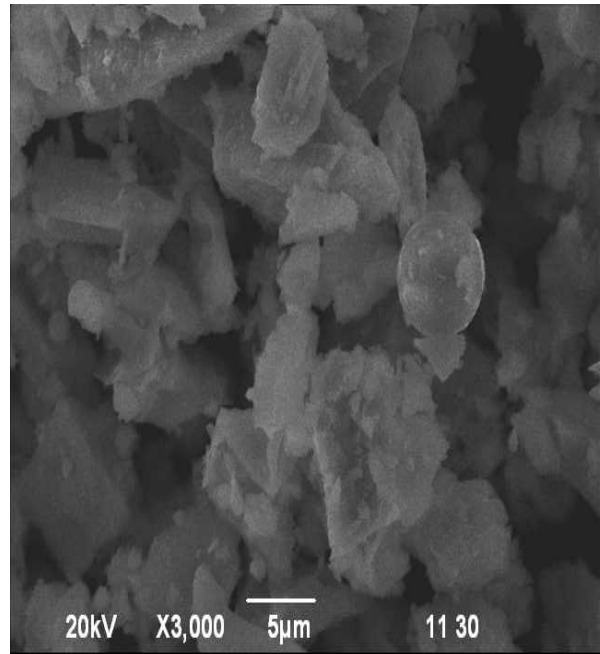
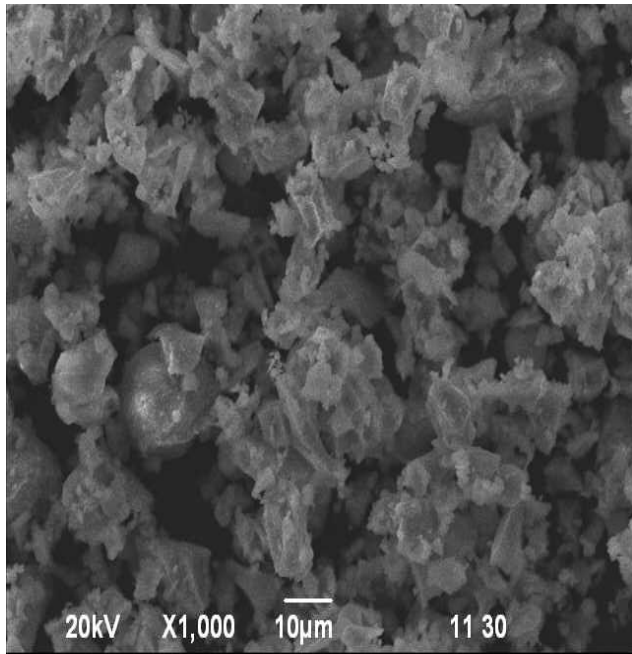


Fig A-7: Scanning Electron Microscopic Images of Cement Sample (PCC)

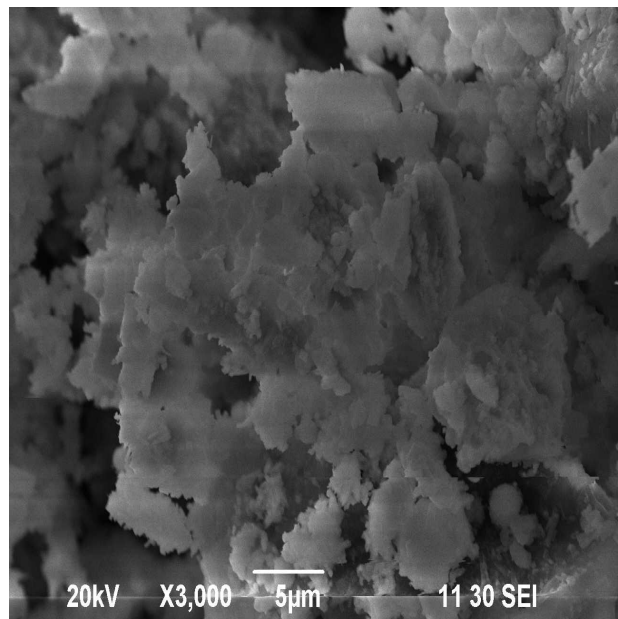
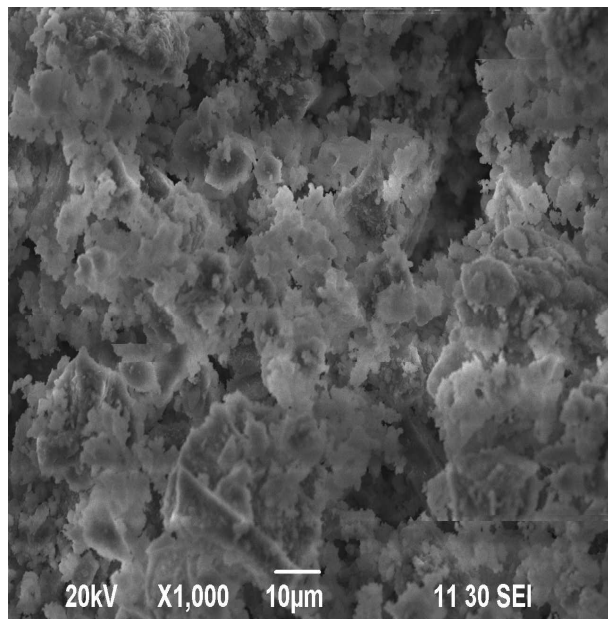


Fig A-8: Scanning Electron Microscopic Images of Cement Dust

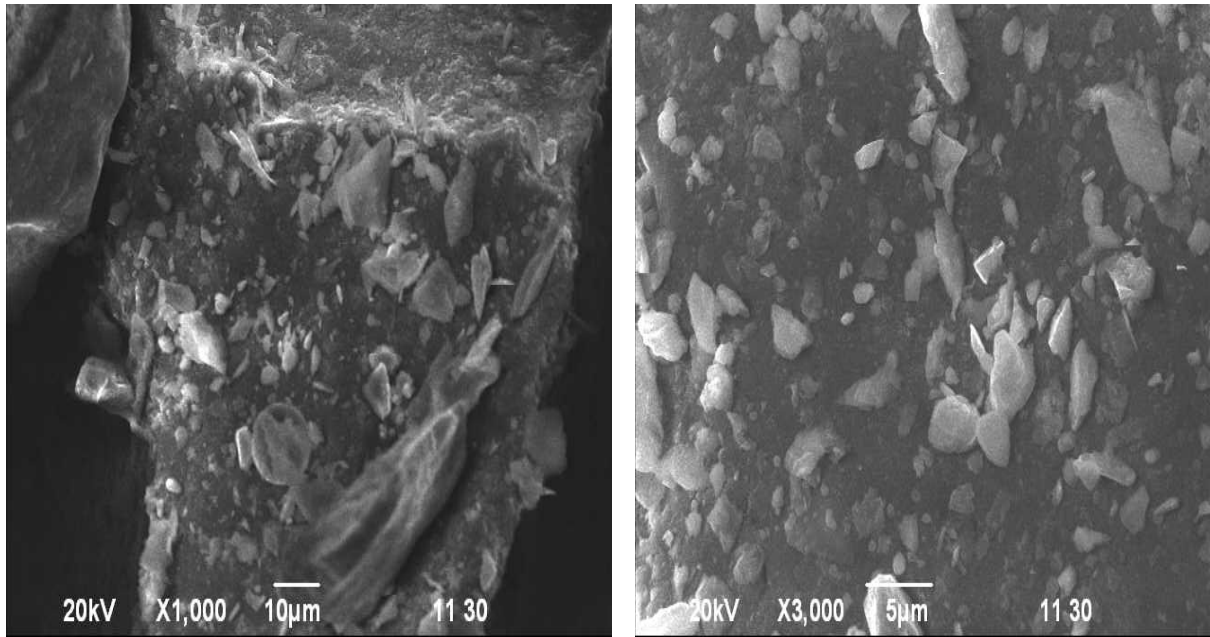


Fig A-9: Scanning Electron Microscopic Images of Deposited Road Dusts

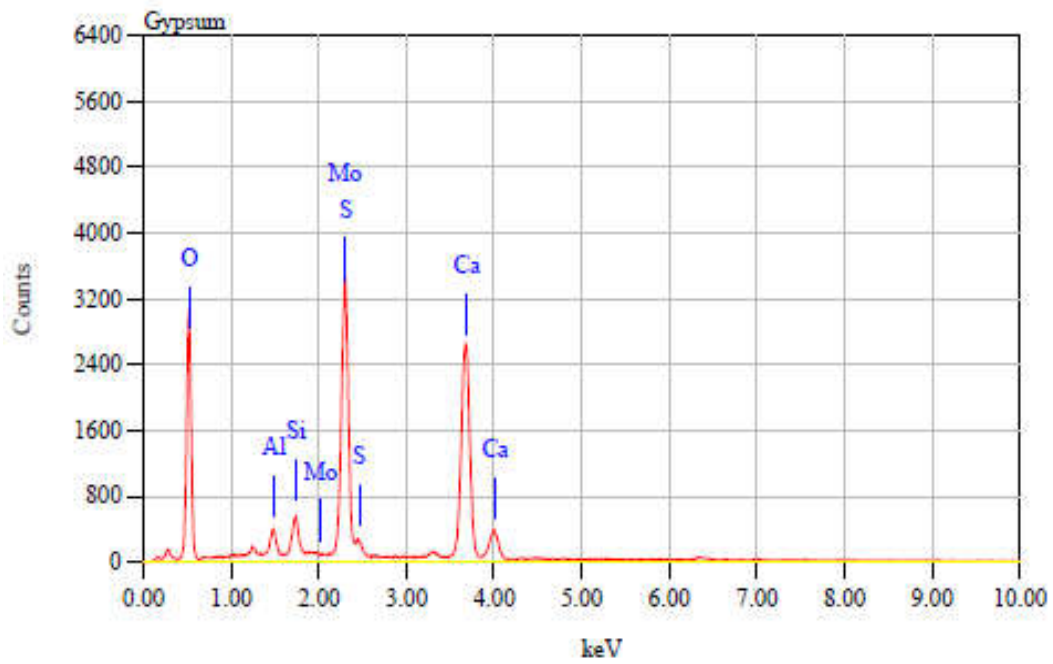


Fig A-10: Energy Dispersive X-ray Spectroscopy of Gypsum

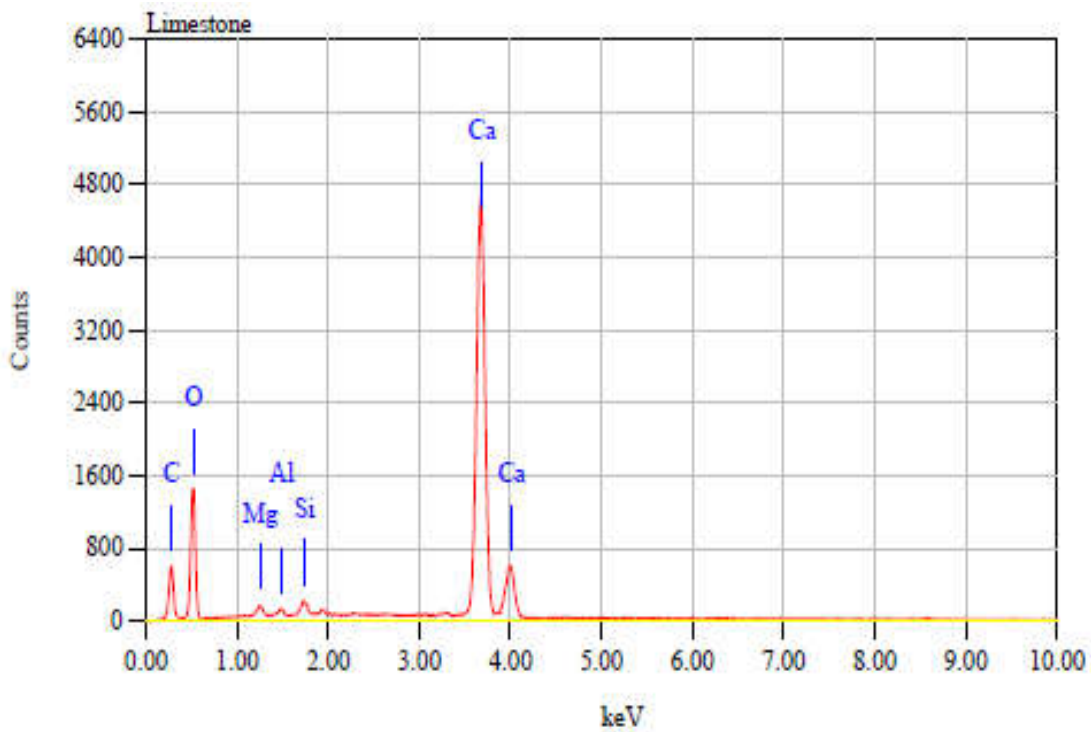


Fig A-11: Energy Dispersive X-ray Spectroscopy of Limestone

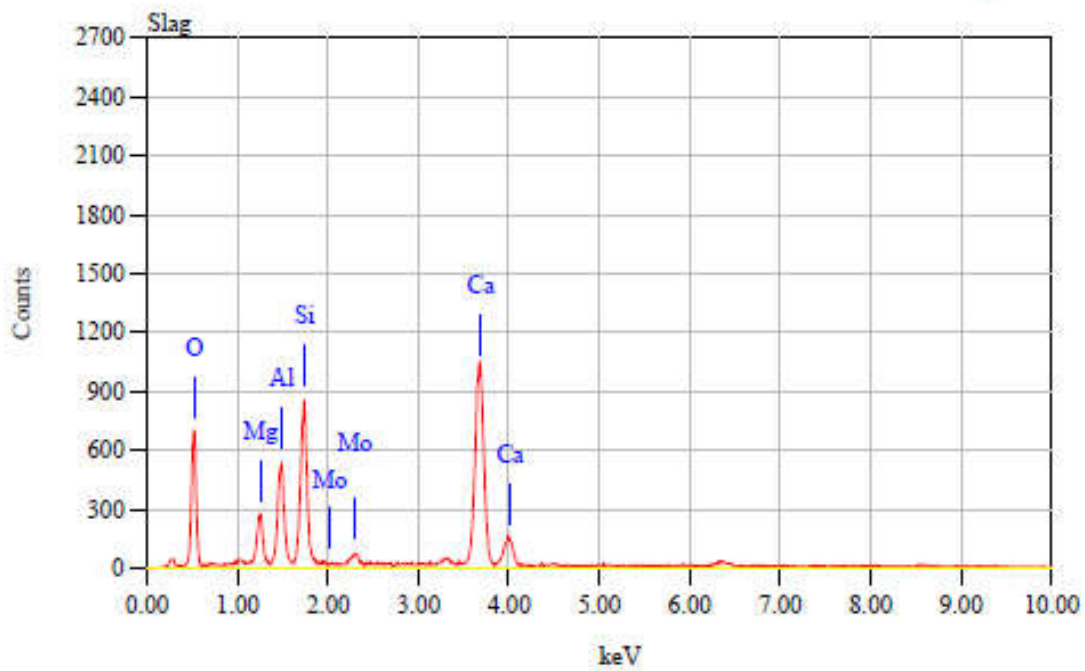


Fig A-12: Energy Dispersive X-ray Spectroscopy of Slag

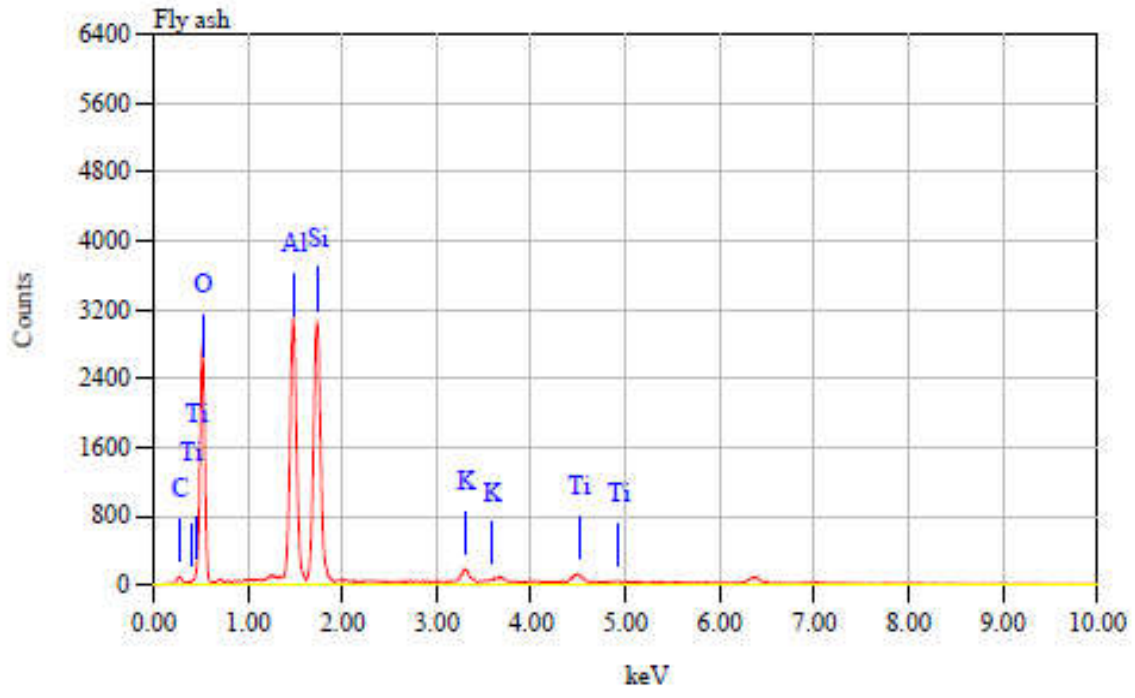
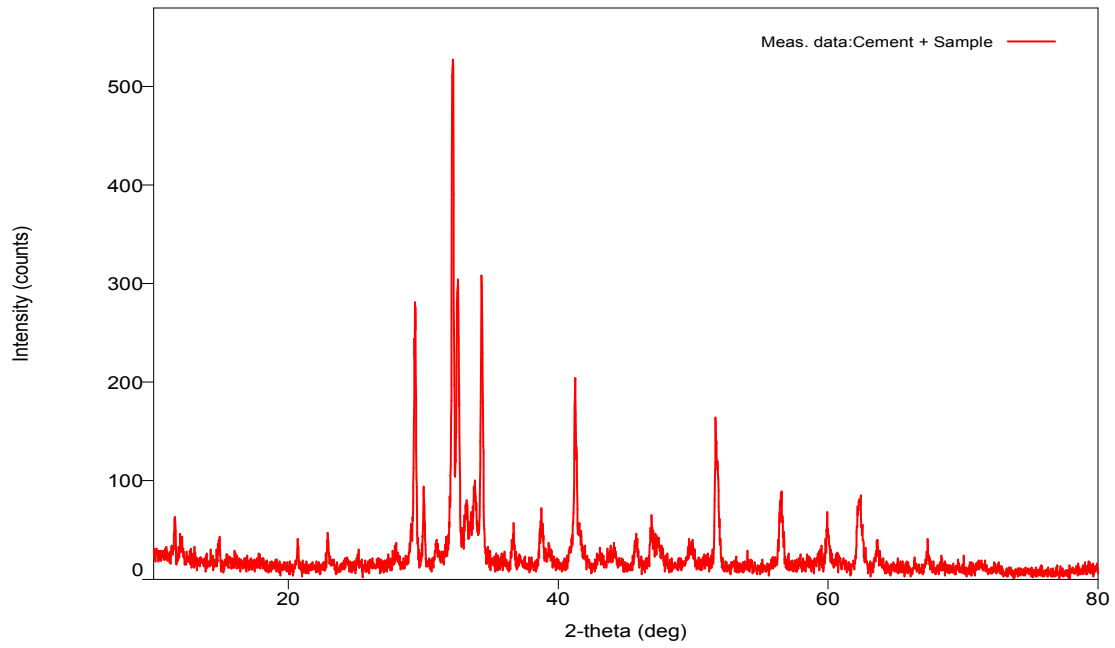


Fig A-13: Energy Dispersive X-ray Spectroscopy of Fly ash



14: XRD Analysis of OPC

Fig A-

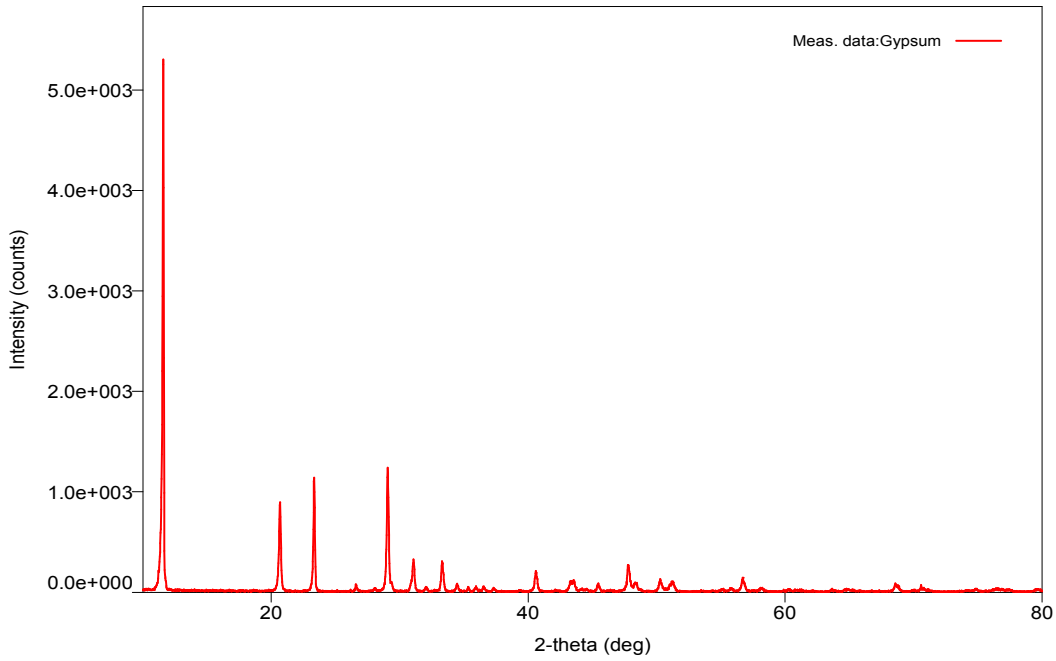


Fig A-15:

XRD Analysis of Gypsum

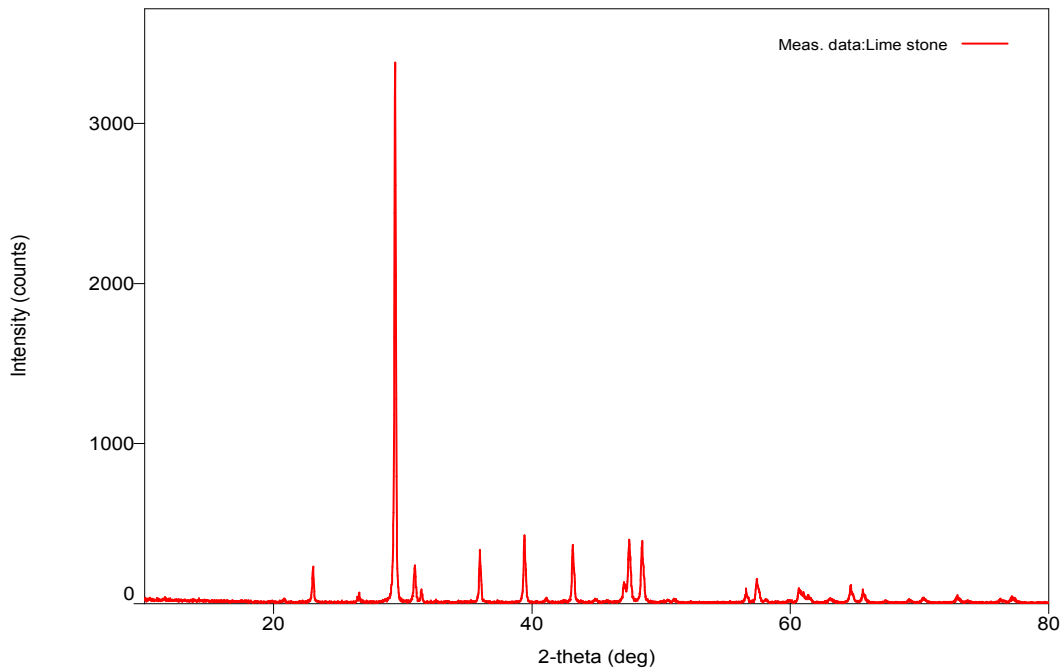


Fig A-16:

XRD Analysis of Limestone

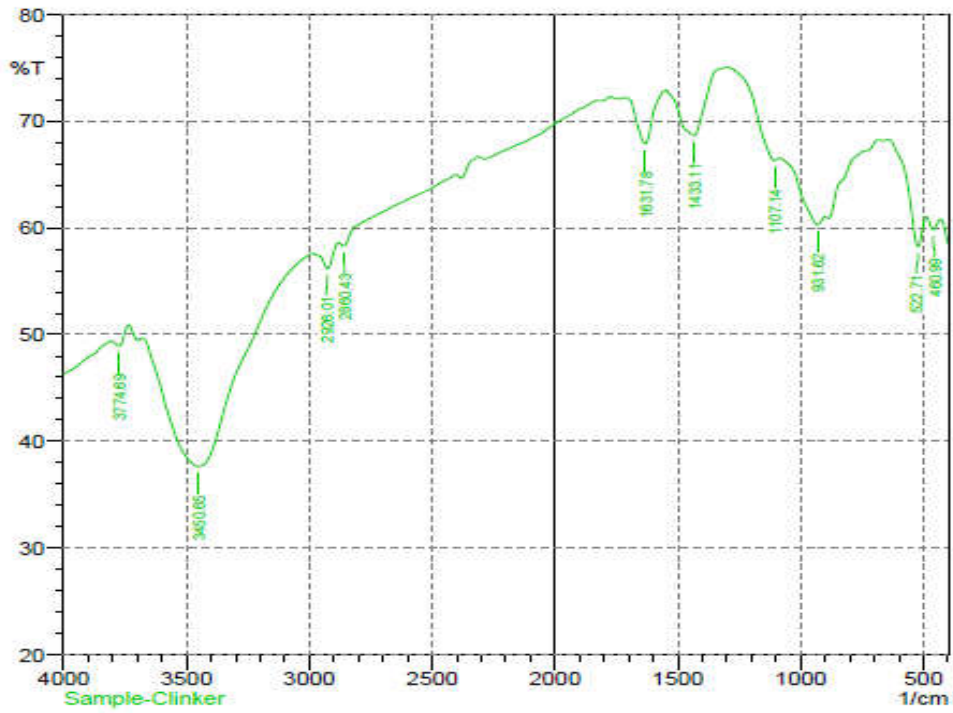


Fig A-17: FTIR Analysis of Clinker

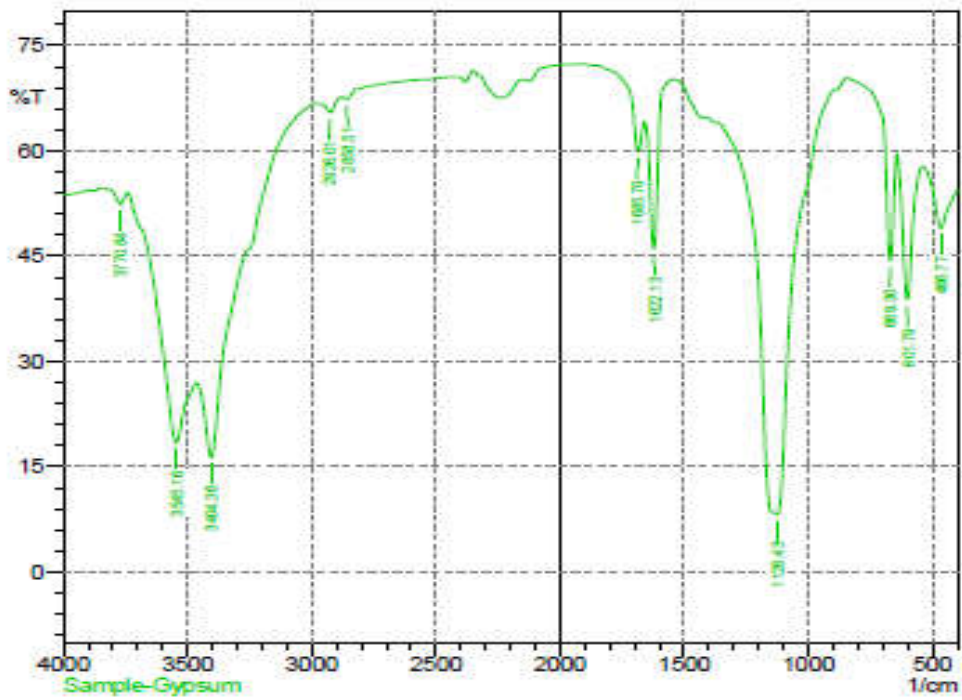


Fig A-18: FTIR Analysis of Gypsum

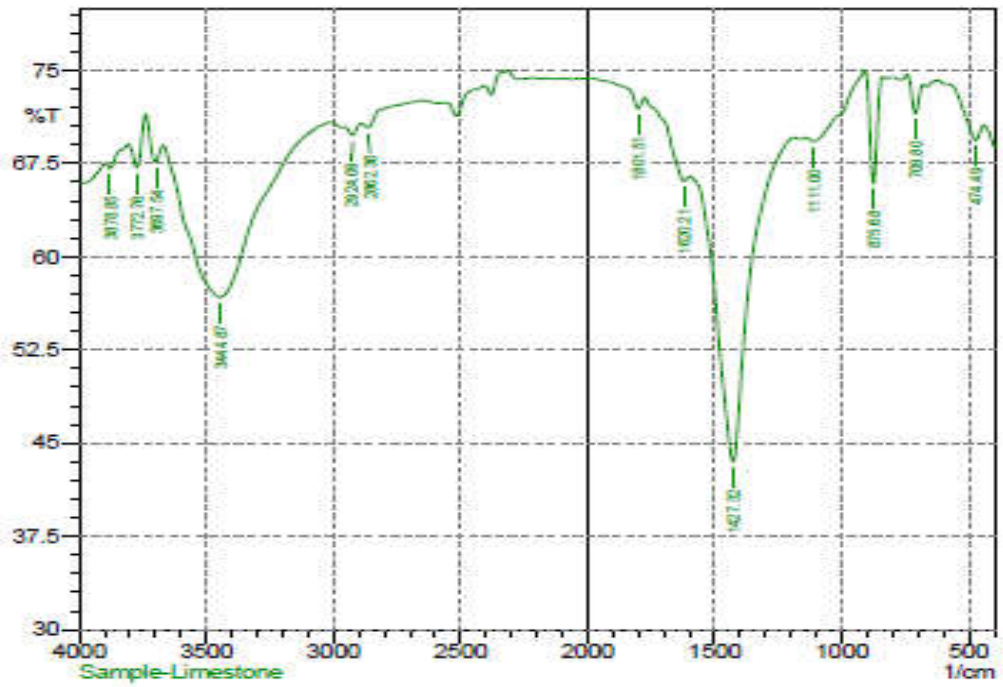


Fig A-19: FTIR Analysis of Limestone

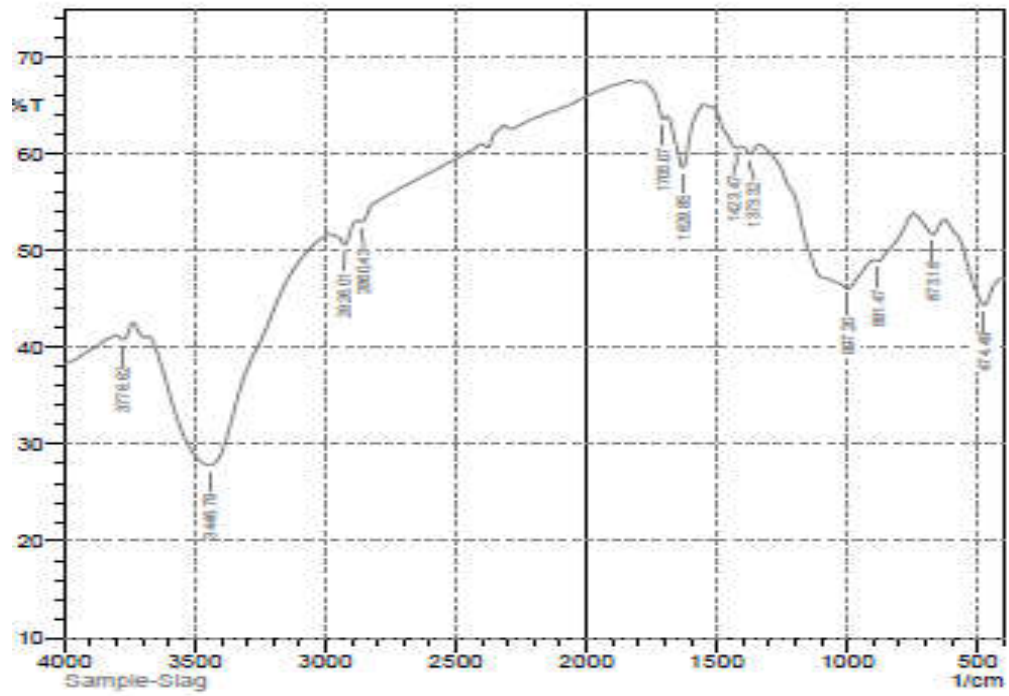


Fig A-20: FTIR Analysis of Slag

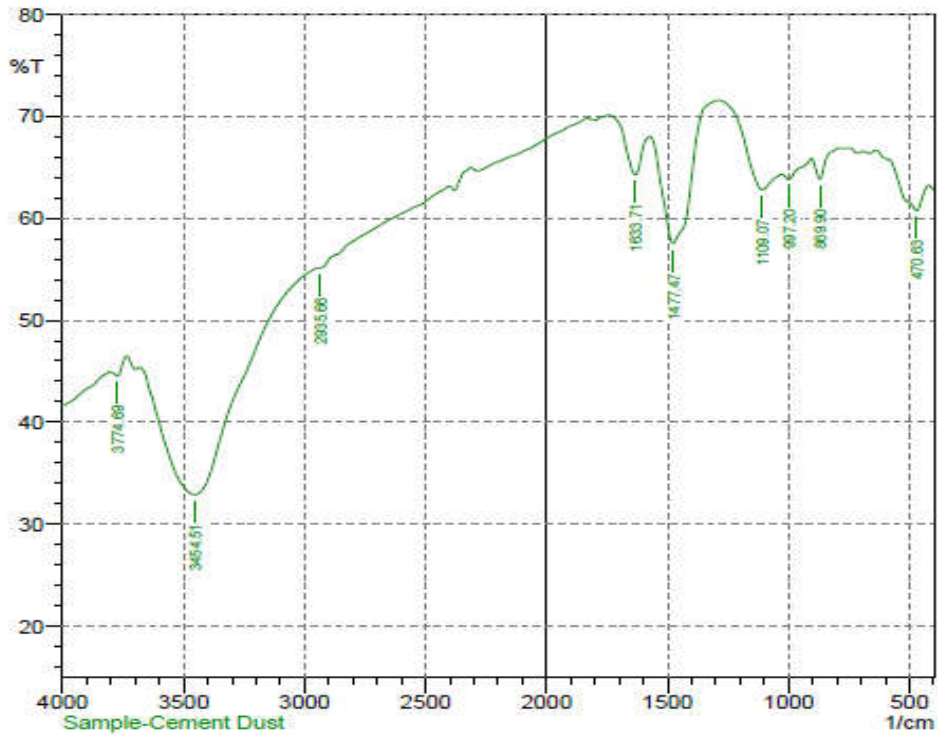


Fig A-21: FTIR Analysis of Bag Filter's Dusts

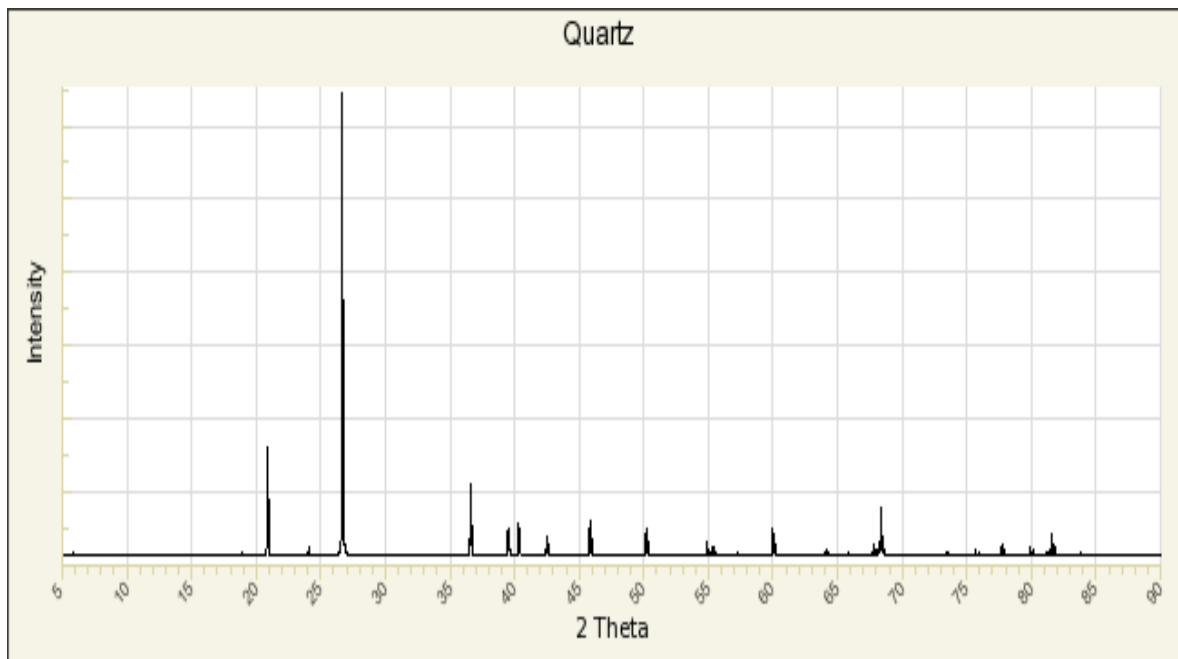


Fig A-22: XRD Analysis of Quartz Obtained from RRUFF database (RRUFF ID: R040031)

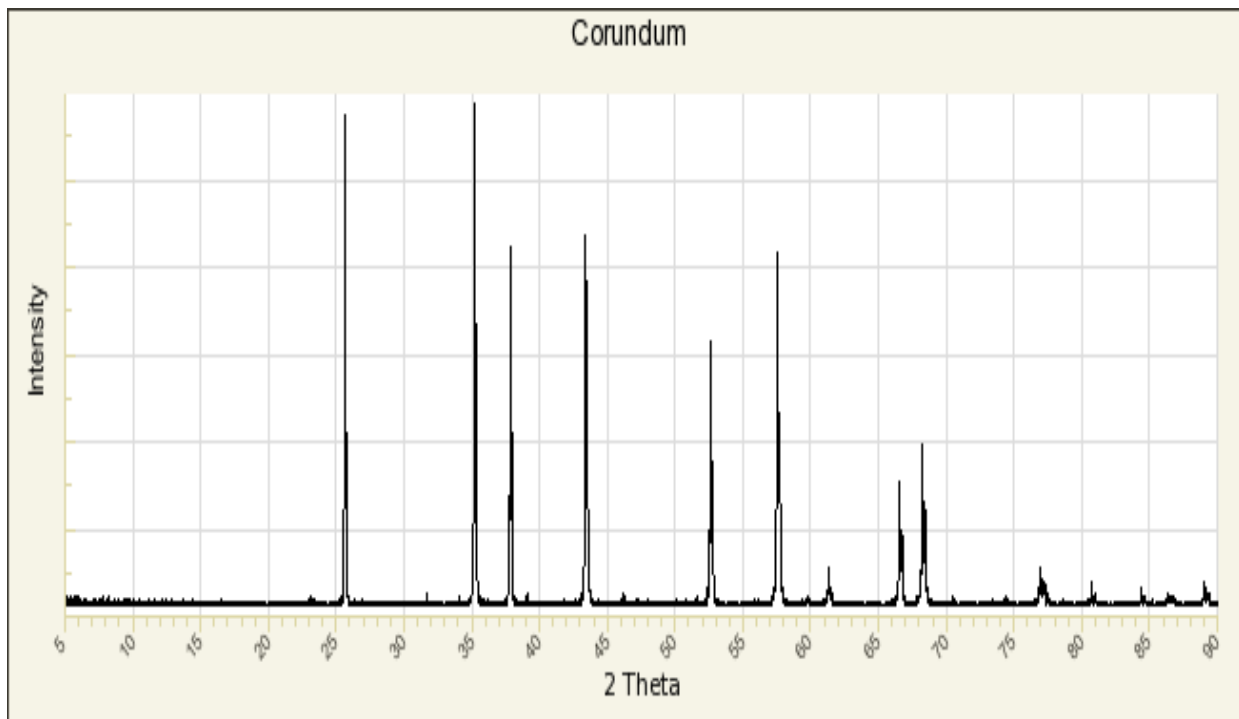


Fig A-23: XRD Analysis of Alumina Obtained from RRUFF database (RRUFF ID: R040096)

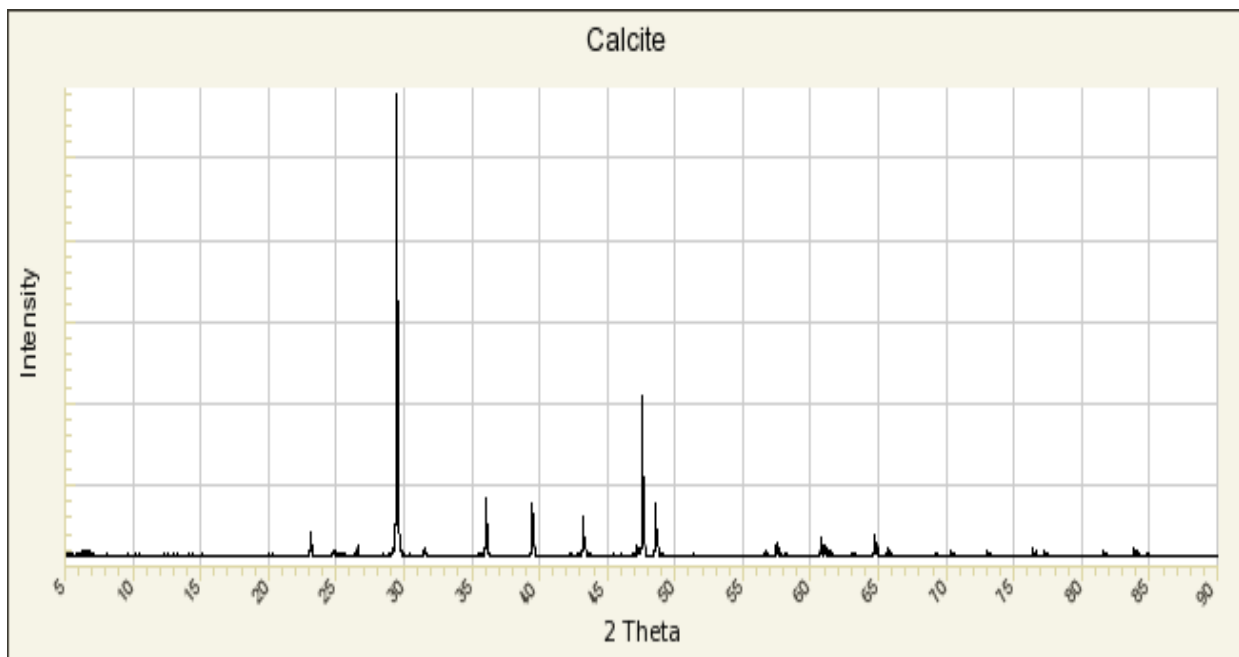


Fig A-24: XRD Analysis of Calcite Obtained from RRUFF database (RRUFF ID: R040070)

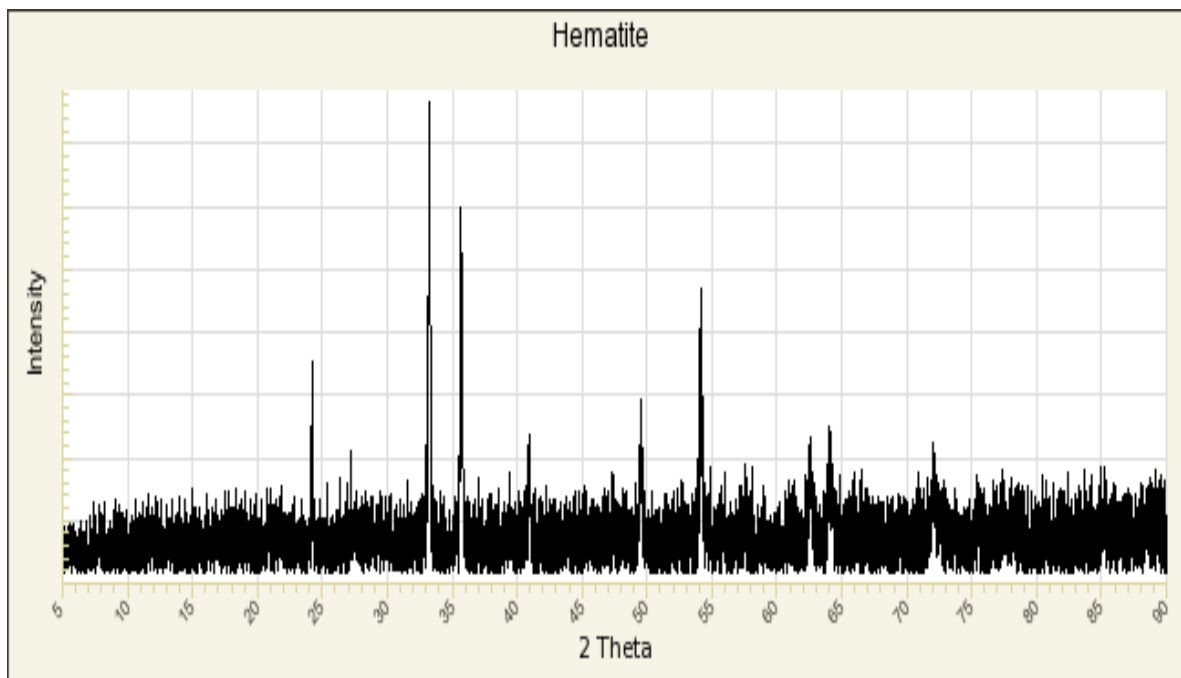


Fig A-25: XRD Analysis of Iron oxide Obtained from RRUFF database (RRUFF ID: R040024)

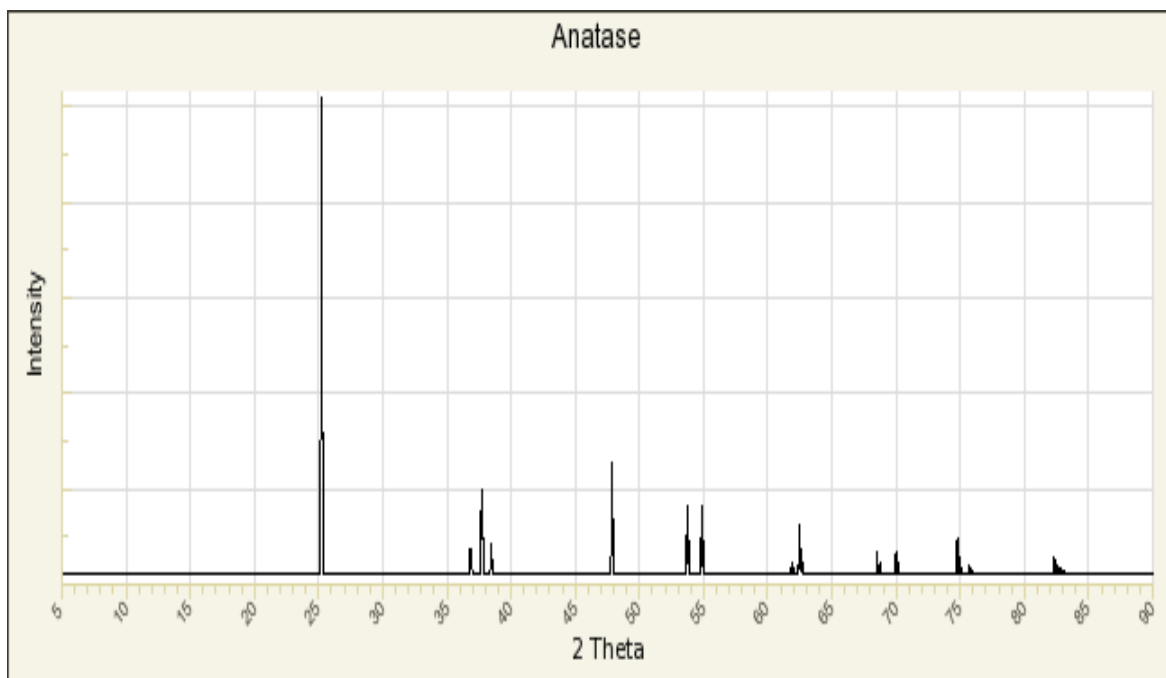


Fig A-26: XRD Analysis of Titanium oxide Obtained from RRUFF database (RRUFF ID: R040029)

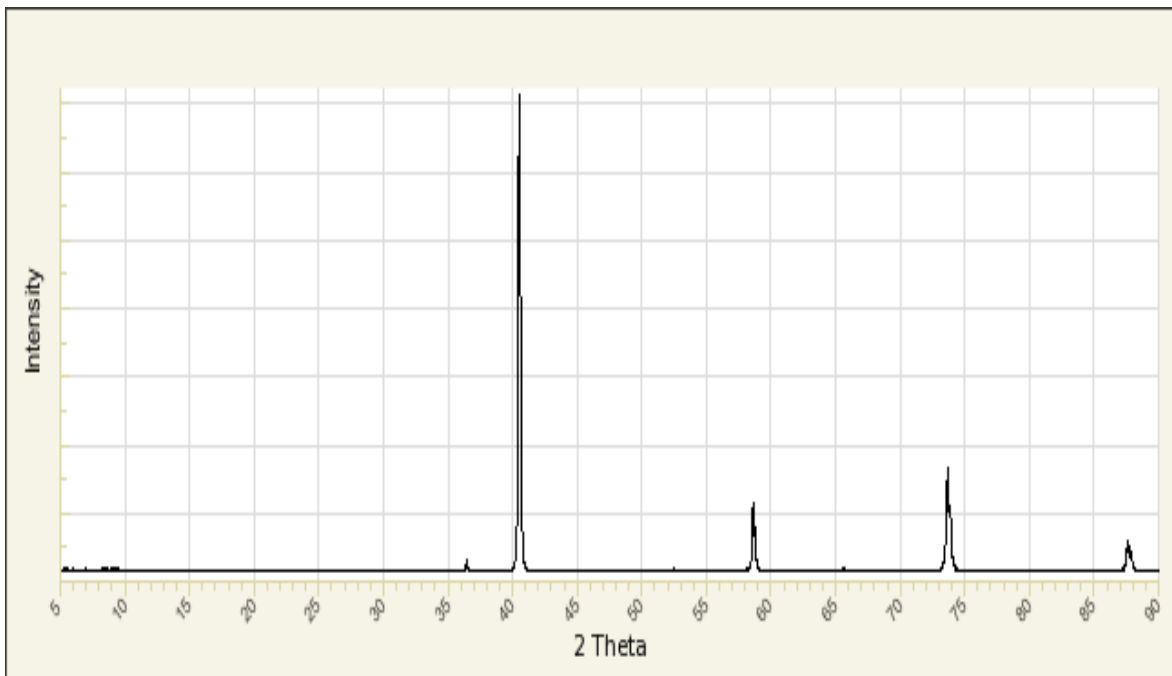


Fig A-27: XRD Analysis of Molybdenum Obtained from RRUFF database (RRUFF ID: R100216)

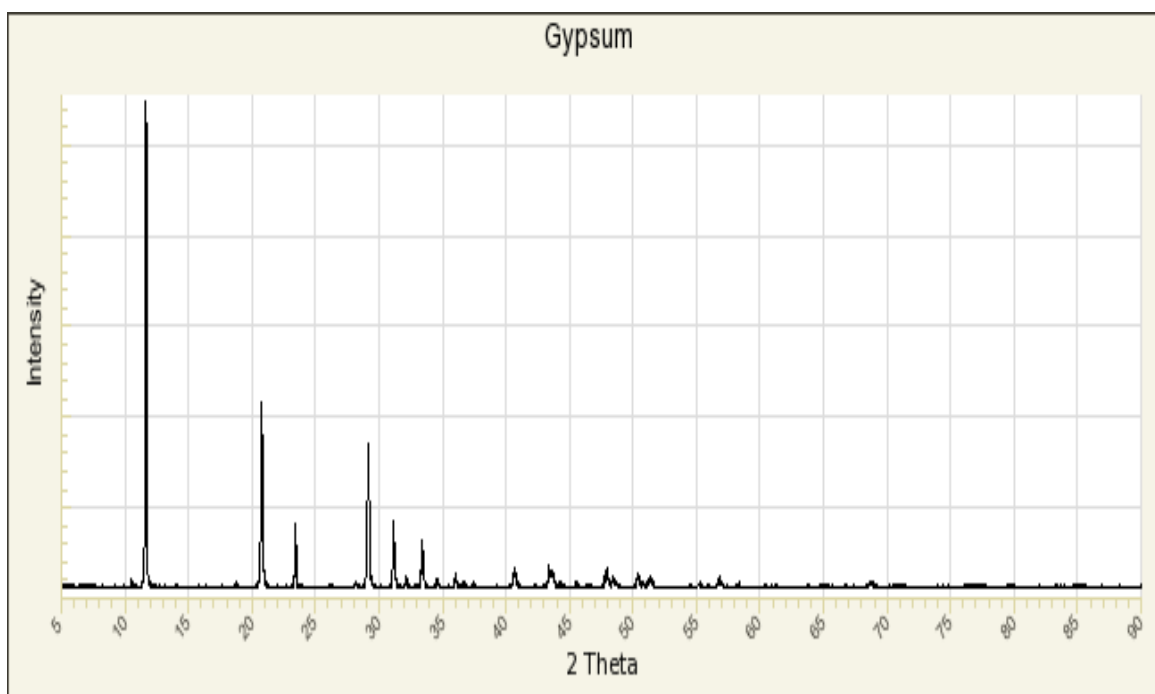


Fig A-28: XRD Analysis of Gypsum Obtained from RRUFF database (RRUFF ID: R040029)

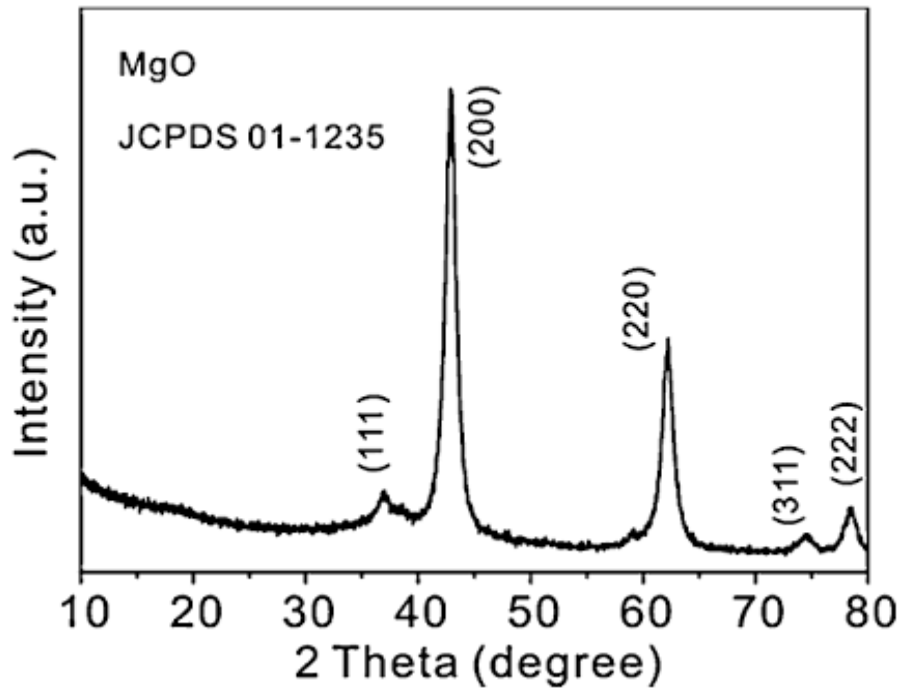


Fig A-29: XRD Analysis of Magnesia (Lian-Xiang *et. al.*, 2014),

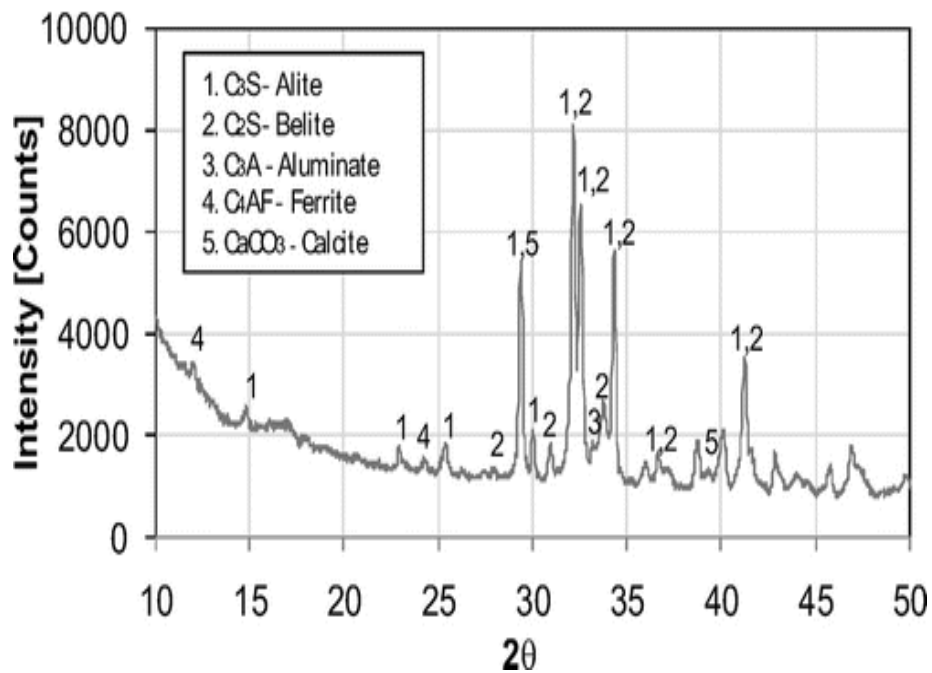


Fig A-30: Identification of alite and belite by XRD Analysis of OPC