Characterisation of airborne dust in a South African opencast iron ore mine. A pilot study.

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Preface

For the aim of this mini-dissertation it was decided to use article format. The whole dissertation is according to the guidelines of the Annals of Occupational Hygiene which is the chosen journal for potential publication. The journal requires that the references in the text should be in the form Jones (1995), or Jones and Brown (1995), or Jones *et al*. (1995) if there are more than two authors. References should be listed in alphabetical order by name of first author, using the Vancouver Style of abbreviation and punctuation.

Chapter 1 contributes a brief introduction to the airborne dust associated with the opencast iron ore mining industry which up until now has not been clearly characterized. Furthermore, it includes the problem statement, research question, and hypothesis. Chapter 2 consists of an in-depth discussion of airborne dust as found in the iron ore mining industry, the characteristics of dust, the dangers of airborne iron ore dust including the health aspects, the role of nanoparticles and the sampling methodologies used in this study. Chapter 3: Characterisation of airborne dust in a South African opencast iron ore mine: a pilot study, is written in article format. All tables and figures are included here, along with text, to present the findings of this study in a readable and understandable format. The article will be submitted to the Annals of Occupational Hygiene for peer reviewing and publication. Chapter 4 includes a final summary and conclusion, as well as recommendations for future studies.

In order to prevent confusion, the following definitions are explained below:

> Inhalable dust: Dust particles with an aerodynamic diameter up to 100 µm, with a 50 % cut-point of 100 µm.
>
> Nanoparticles: Airborne dust particles with an aerodynamic diameter smaller than 0.1 µm (or 100 nm).
>
> Opencast mining: A surface mining technique of for extracting rock or minerals from the earth by their removal from an open pit.
>
> Respirable dust: Dust particles with an aerodynamic diameter up to 10 µm, with a 50 % cut-point of 4 µm.
>
> Ultrafine particles: are particles with at least one dimension smaller than 0.1 µm (or 100 nm).

Author's Contribution

The study was planned and executed by a team of researchers. The contribution of each researcher is listed below

Name	Contribution
Mr R Badenhorst	• Designing and planning of the study; • Literature searches, interpretation of data and writing of mini dissertation; • Execution of all monitoring processes.
Mr PJ Laubscher	• Supervisor; • Assisted with designing and planning, approval of protocol, interpretation of results and documentation of the study; • Review of the dissertation. • Giving guidance with scientific aspects of the study.
Mrs A van der Merwe	• Co-Supervisor; • Review of the dissertation.

The following is a statement from the co-authors that confirms each individual's role in the study:

I declare that I have approved the above- mentioned article and that my role in the study as indicated above is representative of my actual contribution and that I hereby give my consent that it may be published as part of R Badenhorst M.Sc (Occupational Hygiene) mini-dissertation.

Mr PJ Laubscher	Mrs A van der Merwe
(Supervisor)	(Co-Supervisor)

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- Mr PJ Laubscher
- Mrs A van der Merwe
- Prof. FC Eloff

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Abstract

The iron ore mining industry makes use of various processes that result in the release of airborne dust into the surrounding atmosphere where workers are exposed, to produce a final product. The deposition in the lung and toxicological influences of airborne dust can be determined by their physical- and chemical characteristics. The Occupational Health and Safety Act (OHSA) regulations for hazardous chemical substances have no current system of how the physical- and chemical properties of particulates originating from specific areas will influence a worker's exposure and health, especially for ultrafine particles (UFP). It is therefore imperative to characterise airborne dust containing micrometer and UFP size particles originating from specific areas to determine if there are physical- and chemical characteristics that may or may not have an influence on the workers' health.

Aim: This pilot study is aimed at the physical- and chemical characterisation of the airborne iron ore dust generated at the process areas of an opencast iron ore mine. **Method:** Sampled areas included the Primary-secondary crusher, Tertiary crusher, Quaternary crusher and Sifting house. Gravimetric sampling was conducted through the use of static inhalable- and respirable samplers in conjunction with optical- and condensation particle counters that were placed near airborne dust- emitting sources. Physical- and chemical characterisation was done with the use of scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). **Results:** The results found in the study indicate high mass concentration levels of inhalable dust at all four process areas, as well as high levels of respirable dust found at the primary- secondary crusher area. Particle size distribution optical particle counter (OPC) results indicate that the majority of particles at all four process areas are in the region of 0.3 µm in size. Condensation particle counter (CPC) results integrated with OPC results indicate that at the primary-secondary and Tertiary crushers the majority of particles are found to be in the size fraction <0.3 µm. SEM analysis indicates that particle agglomeration largely occurs in the airborne iron ore dust. Particle splinters originating from larger particle collisions and breakages are present in the airborne dust. EDS analysis indicates that the elemental majority of the airborne iron ore dust consists of iron, oxygen, carbon, aluminium, silicon, potassium and calcium. The elemental percentages differ from each process area where an increase in iron and decrease in impurities can be seen as the ore moves through the beneficiation process from the Primary-secondary crusher to the Sifting house. **Conclusion:** The results obtained from the physical- and chemical properties of the airborne iron ore dust indicate high risk of over-exposure to the respiratory system, as well as possible ultrafine particle systemic exposure, that may overwhelm the physiological defense mechanisms of the human body and lead to reactive oxygen species (ROS) formation and the development of pathologies such as siderosis, silicasiderosis and lung cancer.

Key words: airborne, mine, characterisation, particle size, nanometer, micrometer, ultrafine, physical, chemical.

Opsomming

Titel: *Die karakterisering van luggedraagde stof in ‘n Suid Afrikaanse oopgroef ysterertsmyn: ‘n Loodsstudie.*

Die ysterertsmyn industrie maak gebruik van verskeie prosesse vir die ontginning van hul finale produk. Tydens die verskeie ontginningsprosesse word luggedraagde stof in die omliggende atmosfeer vrygestel waar die werkers daaraan blootgestel word. Die deponering en toksikologiese invloede van die luggedraagde stof kan slegs bepaal word deur die stof se fisiese- en chemiese eienskappe. Die Beroepsgesondheid en Veiligheidswet (BGVW) regulasies vir gevaarlike chemise substanse het huidiglik geen sisteem van hoe die fisiese- en chemiese eienskappe van partikels wat onstaan vanuit spesifieke areas, die werker se blootstelling en gesondheid sal beïnvloed nie, veral waneer daar gefokus word op ultrafyn partikels (UFP). Dit is dus noodsaaklik dat karakterisering van luggedraagde stof wat mikrometer en UFP grote partikels bevat en voortkom uit spesifieke areas uitgevoer word om te bepaal of daar fisiese- en chemiese eienskappe is wat die werker se gesondheid kan beïnvloed al dan nie.

Doel: Hierdie loodsstudie is gemik op die karakterisering van die fisiese- en chemiese eienskappe van luggedraagde ysterertsstof wat gegenereer word by die prosesareas van ‘n oopgroef ysterertsmyn. **Metode:** Die monsterneem areas sluit die Primêre-sekondêre breker, Tersiêre breker, Kwantienêre breker en Sifhuis areas in. Gravimetriese monsterneming het geskied deur die gebruik van statiese inasembare- en respireerbare monsters in samewerking met optiese- en kondensasie partikeltellers wat naby die stofbronne geplaas is. Fisiese- en chemiese karakterisering van die luggedraagde stof het geskied deur die gebruik van ‘n skandeer elektron mikroskoop (SEM) en energieverspreiding X-straal spektroskopie (EDS). **Resultate:** Die resultate gevind in die studie toon hoë massa konsentrasievlakke van inasembare stof aan by elk van die vier prosesareas, asook hoë vlakke van respireerbare stof by die Primêre-sekondêre breker area. Optiese partikelteller (OPT) partikel grootte verspreiding- resultate toon aan dat die meerderheid van die partikels by al vier prosesareas ‘n grootte het van 0.3 µm. Kondensasie partikelteller (KPT) en OPT geïntegreerde resultate wys dat by die Primêre-sekondêre breker en Tersiêre breker brekerareas die meerderheid van die partikels inderwaarheid kleiner is as 0.3 µm. SEM analise toon aan dat partikel agglomerasie grootliks voorkom in die luggedraagde stof. Partikelsplinters wat onstaan vanuit botsing tussen groter partikels kan ook waargeneem word. EDS analise wys dat die meerderheid van die elementele samestelling van die luggedraagde stof bestaan uit yster, suurstof, koolstof, aluminium, silikoon, natrium en kalsium. Die elementele persentasies verskill tussen elk van die prosesareas waar daar ‘n verhoging in yster en ‘n verlaging in onsuiwerhede waargeneem is soos die ystererts deur die ontginnings-proses beweeg vanaf die Primêre-sekondêre breker area tot by die Sifhuis area. **Gevolgtrekking:** Die resultate wat verkry is vanuit die fisiese -en chemiese eienskappe van die luggedraagde ysterertsstof toon aan daar ‘n hoë risiko is van oormatige blootstelling aan die respiratoriese stelsel, asook moontlike UFP sistemiese blootstelling, wat die beskermings- meganismes van die liggaam kan oorkom en lei tot die formasie van reaktiewe suurstofspesies (RSS) en die ontwikkeling van patologieë soos siderosis, silicasiderosis en longkanker

Sleutelwoorde: Luggedraagde, oopgroefmyn, partikel grootte, nanometer, mikrometer, ultrafyn, fisiese, chemiese.

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List of Symbols and Abbreviations

Symbols

%	Percentage
<	Less than
>	Greater than
Al	Aluminium
C	Carbon
Ca	Calcium
cm/sec	Centimetre per second
Fe	Iron
g/cm3	Grams per cubic centimetre
K	Potassium
mg/m^3	Milligrams per cubic meter
nm	Nanometer
O	Oxygen
p/cm^3	Particles per cubic centimeter
p/m^3	Particles per cubic meter
Si	Silica
µm	Micrometer

Abbreviations

ACGIH	American Conference of Governmental Industrial Hygienists
AD	Aerodynamic diameter
CPC	Condensation particle counter
EDS	Energy dispersive X-ray spectroscopy
FP	Fine particles
IL	Interleukin
IOM	Institute of Occupational Medicine

ISO	International Organisation for Standardization
OEL	Occupational exposure limit
PM	Particulate matter
PM_{10}	Particulate matter of 10 µm
$PM_{2.5}$	Particulate matter of 2.5 µm
$PM_{0.1}$	Particulate matter of 0.1 µm
ROS	Reactive oxygen species
SEM	Scanning Electron Microscope
SSA	Specific surface area
TNF	Tumor necrosis factor
TSP	Total suspended particulate matter
UFP	Ultrafine particles
WHO	World Health Organisation

CHAPTER 1

INTRODUCTION

1.1. Overview

Airborne particulate matter (PM) is an ever present occurrence in the atmosphere, with many studies indicating that airborne PM as environmental pollutants may lead to various health effects (Valavanidis *et al.*, 2008). Cheremisinoff (2002) states that airborne PM consists of a combination of organic- and inorganic substances that is small enough to be suspended in the atmosphere in the form of dust, dirt, soot, smoke and liquid droplets. Airborne PM can originate from various processes such as blasting, drilling, crushing, transportation and handling of material that will lead to airborne PM respiratory exposure. Characterisation of PM involves the identification of the physical- and chemical properties of the particles. The physical properties determine the transportation and deposition of the particles and the chemical composition will have an influence on the possible health effects that may arise due to overexposure (Cheremisinoff, 2002). Through the use of particle characterisation, the particle morphology, concentrations and elemental compositions can be determined to better our understanding of the role that airborne PM can play on human health.

Airborne PM exposure to the human body is predominantly achieved through the inhalation process of the respiratory tract (Mark, 2005). Particles that are deposited in the respiratory tract can enter the circulation system where they can then be distributed to various sites in the body. The origins of aerosol sampling consisted mainly of sampling particles over the entire size range with 100 % sampling efficiency, referred to as total aerosol sampling. In the mid 1900s, aerosol sampling progressed to focusing on sampling of particles that can be inhaled into the respiratory system leading to sampling that will reflect human exposure to aerosols more accurately (Vincent, 2007). Human exposure to airborne particulates by means of total aerosol sampling is considered inefficient due to the size and nature of the particles being the determining factor concerning respiratory tract deposition. This led to the establishment of criteria for occupational hygiene exposures by the Occupational Safety and Health Administration (OSHA) in 1970, based on the American Conference of Governmental Industrial Hygienists (ACGIH) size selection curve that was later improved and accepted by European Committee for standardisation (CEN), International Organisation for Standardization (ISO) and ACGIH. The criteria were introduced as a curve that illustrates the deposition of particles of different size ranges at different areas of the respiratory tract (McDermott, 2004).The mass concentration size selective criteria of airborne particles can be expressed by three different size fractions which are called inhalable, thoracic and respirable particulate mass fractions. The inhalable size fraction (<100 µm) refers to the total airborne particles inhaled through the nose and mouth. The thoracic size fraction (<10 µm) is the fraction of inhaled particles that are deposited along the respiratory system beyond the larynx. The respirable fraction (<4 µm) refers to the particulate mass fraction that is deposited in the uncilliated airway regions of the lung (Mark, 2005; Belle and Stanton*,* 2007). Particle size selective sampling thus enables us to better determine the site of particle deposition in the respiratory system, which can be enhanced by taking other physical characteristics of particles such as size, mass concentration and agglomeration into account. Particle deposition in the respiratory tract, however, is not only dependent on the physical characteristics of airborne particulates but the physiological- and biological composition of an individual as well as deposition mechanisms such as sedimentation, impaction and diffusion.

To truly understand the effects that the deposited particles will have on the health response of the human body, the physical aspects of the particles should be studied along with the chemical aspects such as the aerosol elemental composition (Hinds, 1999; Volkwein *et al.,* 2011). This will enable us to understand the deposition of the specific particles that individuals are exposed to, as opposed to a generalised view of particle deposition. Thus by subjecting airborne particles to characterisation on the basis of physical- and chemical aspects, we will enhance our knowledge of not only where specific particles will be deposited in the human body, but also how these particles will elicit a health response due to their composition.

1.2. Aims and objectives

The aim of this study is to characterise static airborne iron ore dust concentrations (physical- and chemical properties of dust) at a South African opencast iron ore mine to improve our understanding of the possible health risks it may hold.

1.3. Hypothesis

Particulate matter found in airborne dust at four different process areas of an iron ore mine may yield different results as to their physical- and chemical properties.

1.4. References

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CHAPTER 2

LITERATURE STUDY

In the literature study the important key points will be discussed. A more in depth look will be focused on airborne particulates, the sampling of airborne particulate matter and airborne particle characterisation. The aspects of airborne particle deposition in the respiratory tract and hematite iron ore particles will be investigated.

2.1. Airborne particulates

Airborne particles, also called atmospheric particulate matter (PM) or aerosols, are one of the biggest occupational hazards that originate in almost all forms of the mining industry (Petavratzi *et al*., 2005), where machines, crushing and screening plants, transport equipment and unpaved haul roads are especially problematic in opencast mines (Sinha and Banerjee, 1997). Aerosols are defined as particles suspended in a gaseous medium, usually air in context with occupational hygiene, and originate in the form of airborne dusts, sprays, mists, smokes and fumes (WHO, 1999). Davidson *et al.* (2005) states that atmospheric particles consist of a variety of complex mixtures of particles and gasses where the primary particles are discharged directly from their source, while secondary particles are formed in the atmosphere from gaseous emissions. For the purpose of this study, the focus will be on the aspects of dust, especially in terms of the characterisation of iron ore dust.

The International Standardization Organization (ISO 4225 – ISO, 1995) defines dust as *“small solid particles, conventionally taken as those particles below 75 micron (µm) in diameter, which settle out under their own weight but which may remain suspended for some time”*. The “Glossary of Atmospheric Chemistry Terms” (IUPAC, 1990) broadens the definition by adding that dust constitutes *“small, dry, solid particles projected into the air by natural forces, such as wind, volcanic eruption, and by mechanical or man-made processes such as crushing, grinding, milling, drilling, demolition, shoveling, conveying, screening, bagging, and sweeping. Dust particles are usually in the size range from about 1 to 100 µm in diameter, and they settle slowly under the influence of gravity.”*

There are a variety of dust types found in the working environment. Some examples include:

- **Mineral dusts**, such as coal, cement, and silica quartz
- **Metallic dusts**, such as iron, nickel, lead and cadmium
- **Chemical dusts**, such as pesticides and bulk chemicals
- **Organic dusts**, such as wood, cotton, flour and pollen
- **Biohazards**, such as spores

For the purpose of occupational hygiene studies concerning dust, the particle size measurement is conducted by concentrating on the particle aerodynamic diameter (AD), the reason being that it relates to the sampling devices and respiratory tract depositions of the airborne particles (WHO, 1999). The particle AD is defined as the diameter of a hypothetical sphere of density 1 g/cm^3 having the same terminal settling velocity in calm air as the particle in question, regardless of its geometric size, shape and true density.

Airborne PM is divided into different categories which are dependent on the particle size or AD. Coarse particles are defined as airborne particles with an AD ranging from 2.5 µm to 10 µm ($PM_{10-2.5}$). Fine particles (FP) are airborne particles which are smaller than coarse particles, having an AD of 2.5 µm ($PM_{2.5}$) or less and ultrafine particles (UFP) are particles with at least one dimension < 100 nanometer (nm) ($PM_{0.1}$) (WBG, 1998; Brown *et al.*, 2002; Oberdorster *et al.*, 2005; Katsnelson *et al.* 2012). Particles with a physiochemical structure larger than that of the atomic- or molecular dimensions, but smaller than 100 nm, which still adhere to their physical-, chemical- and biological properties, are referred to as nanostructured particles.

Aerosol science indicates that particles with AD larger than 50 µm have a terminal velocity of >7cm/sec and do not remain airborne very long, but depending on the conditions, even particles larger than 100 µm can become airborne but only remain so for a short period. For the settling of particles with an AD smaller than 1 µm and a settling velocity of 0.003 µm/sec, movement with the airstream is more important than gravity sedimentation.

Fibrous dust particles are defined by the WHO as particles with a diameter of < 3 µm and the length of >5 µm. These dust fibers have an aspect ratio of greater than or equal to 3 to 1 (WHO, 1999).

2.1.1. Dust generation

Generation of dust is potentially hazardous to various aspects of the mining industry such as human health, the environment and the productivity of the mine itself (Sinha and Banerjee, 1997). Dust is usually generated through mechanical breakdown processes of the same material, i.e. crushing, grinding, cutting, drilling, explosion or material friction. The dust generated through these mechanical breakdown processes is referred to as primary airborne dust and may not necessarily be of the same composition as the parent rock because different minerals may be broken down or removed at different rates (WHO, 1999).

2.1.2. Dust classification

There are various classifications for dust pertaining to certain fields of study.

Some classifications for dust in the environmental- and occupational hygiene field include total suspended particulate matter (TSP), nuisance dust and fugitive dust. TSP refers to all airborne dust particles that by means of breakdown processes are suspended in the air. The particle size fraction usually has an AD of 40 -50 µm (Petavratzi *et al*., 2005; Slanina, 2006).

Nuisance dust refers to any coarse particles that may lower environmental quality, damage machinery or functions as a physiological irritable substance in the atmosphere.

Fugitive dust describes dust particles often generated from unconfirmed sources that escape capture and is often found outside the boundaries far from the generation sources. This phenomenon usually occurs in the mining industry.

2.2. Sampling of airborne particulate matter

Airborne particulate matter (PM) sampling in the field of occupational hygiene is carried out to determine the concentration of PM inhalation exposure of a worker during the work shift. Originally airborne PM sampling consisted of only total mass sampling but in the early 1990’s the criteria for size-selective sampling became internationally accepted for sampling that focuses on specific regions of the respiratory tract (CEN, 1993; ISO, 1995). This led to a more accurate understanding of the effect that particle characteristics may have concerning respiratory deposition and the accompanying health effects that may occur.

2.2.1. Particle size-selective sampling

Airborne particles are easily inhaled into the respiratory tract where they are deposited along the tract depending on their size.

When dealing with micro particles in terms of occupational hygiene, their deposition along the respiratory tract is currently expressed in three different size fractions: inhalable, thoracic and respirable particulate mass (PM) (Mark, 2005; Petavratzi *et al.*, 2005; Belle and Stanton, 2007).

Inhalable PM refers to the amount of particles in a cloud of dust that can be inhaled through the nose and mouth with an aerodynamic diameter (AD) of up to 100 µm. Inhalable particles result in adverse health effects when deposited anywhere along the respiratory tract. Sampling criteria for Inhalable PM states that the sampler has a 50% cut point of 100 µm as illustrated in Figure 1.

Thoracic PM refers to the particles with an AD of < 30 µm that can penetrate the airways of the head and the lungs and show adverse health effects when deposited in the lung airways and gas exchange processes in the alveoli. Thoracic PM has a 50% cut point of 10 µm sampling criteria as illustrated in Figure 1.

Respirable PM refers to the particles with an AD up to 10 µm that pass through the terminal bronchioles of the lungs and into the gas- exchange regions or alveoli and mainly induce adverse health effects at the gas exchange processes. Respirable PM has a 50% cut point of 4 µm sampling criteria as illustrated in Figure 1.

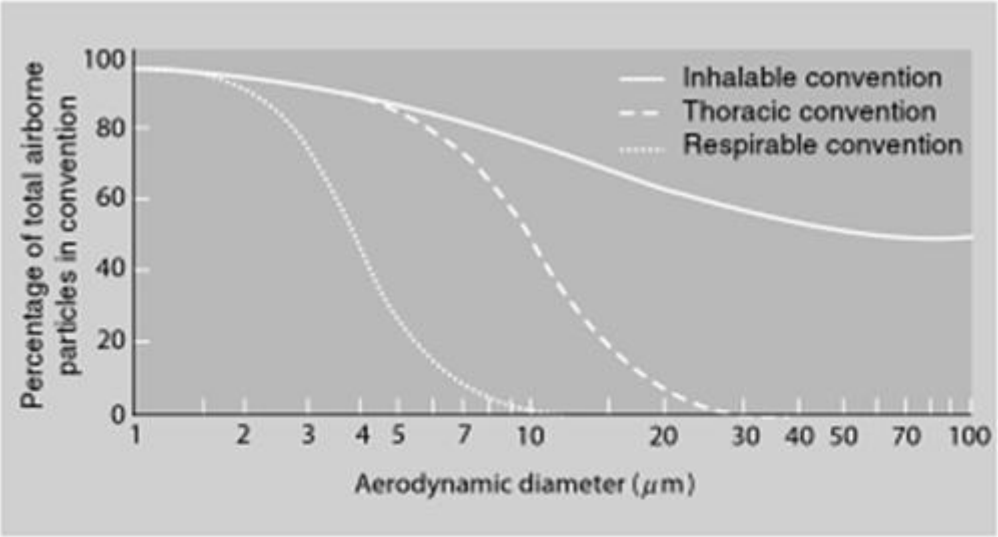

Figure 1: The ISO/CEN/ACGIH sampling conventions for health- related aerosols (Mark, 2005).

2.2.2 *UFP size-selective sampling criterion*

Currently the field of occupational hygiene tends to only focus on the inhalable, thoracic and respirable PM when dealing with airborne particle sampling but the increase of new scientific development creates a need for a fourth airborne particle sampling method. This new category will focus on UFPs that have the ability to not only accumulate in the lung alveolar regions, but that may also transverse the alveolar boundary and enter the pulmonary systemic blood circulation (Buzea *et al.* 2007). Characterisation of UFPs will enable us to determine the chemical- and physical properties of UFPs in order to identify the effects that these particles will have on the deposition and penetration of the physiological system.

2.3. Airborne particle characterisation

Dust generated through mechanical breakdown processes usually consists of a variety of particles, each of which adheres to their own specific properties. Characterisation of airborne dust particles through the use of a Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Spectrometry (EDS) enables us to have a better understanding concerning the composition, physical- and chemical properties of these particles which in turn will provide the necessary information for more in -depth evaluation and classification of the dust particles (Petavratzi *et al*., 2005).

2.3.1. Physical properties

The physical properties of airborne PM will influence the transport and deposition of the particles (Hinds, 1999). When dealing with the physical properties for particle characterisation there is a variety of aspects which could be included in the primary focal point. There are however a few norms, such as particle size and shape, which are considered as a necessity when dealing with the characterisation of the physical properties. Other properties that will be focused on for this study will include the mass concentration and agglomeration.

2.3.1.1. Particle size and shape

Particle size is stated as the most important parameter for particle characterisation as many particle properties are dependent on the particle size (Hinds, 1999; Petavratzi *et al*., 2005). In the field of occupational hygiene, particle size is especially important as it will give an indication of particle deposition in the physiological system and thus the biological influences with which it is associated (Oberdorster *et al.,* 1994; Maynard and Kuempel, 2005). Particle shape entails the form, habit and features (such as convexity and surface roughness) of particles (Pabst and Gregorova, 2007). Although some particle shapes are regular and simple, the majority of particle shapes are irregular and complex. The shape of the particle is determined from its source of origin or formation process. Mechanical force on larger particles may contribute to breakages or fractures. This phenomenon, coupled with factors such as particle agglomeration, will lead the complexity and irregularity of the particulate shape (Morawska and Salthammer, 2003). Particle size and shape may be defined as the linear length measured in SI unit and is usually described as the aerodynamic diameter of a particle; however, since particles are three dimensional they cannot be sufficiently characterized by only a single dimension such as in perfect spheres, where only the radius or diameter has to be taken into account (Pabst and Gregorova, 2007). This process can be modified for more convenient particle size characterisation through the use of an equivalent sphere concept. The concept for equivalent spheres refers to defining the particle size and shape with the diameter of an equivalent sphere that has the same properties as the actual particle in question, such as volume or mass.

2.3.1.2. Mass concentration

The mass concentration of dust is defined as the mass of particulate matter in a unit volume of air, normally expressed in milligrams per cubic meter (mg/m^3) (Cheremisinoff, 2002).

2.3.1.3. Agglomeration

Agglomeration of particles refers to the collision of particles with one another due to the relative motion between them resulting in the particles adhering to form larger particles. Magnetic nanoparticles tend to attract each other, banding together and forming an agglomerate state which, depending on the size, may behave as larger particles (Buzea *et al.,* 2007). Figure 2 illustrates examples of particle agglomeration pertaining to same- size particles (isometric) and different- sized particles (inhomogeneous).

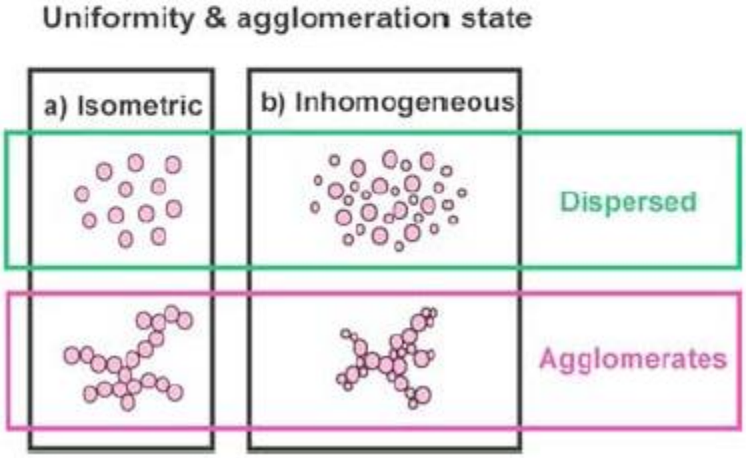

Figure 2: Illustration of dispersed- and agglomerated particles in isometric and inhomogeneous states (Buzea *et al.,* 2007).

2.3.2. Chemical properties

The chemical properties of airborne dust will give an indication of the type of possible health effects that may occur due to particle over exposure. By determining the elemental composition of airborne dust, speculations can be made as to determine the possible hazardous chemical compounds, and their toxicological properties can be studied to determine the possible effects of the compounds on the physiological system.

2.3.2.1. Composition

Airborne PM, as previously stated, consists of a variety of major components that can each be represented by a percentage of the total particulate mass (Harrison and Yin, 2000). Bulk chemical composition is a term that can be used to describe airborne PM that consists of major elements. In reference to iron ore airborne PM, the bulk chemical composition can be the same for a number of different iron ore mining areas, however the concentration percentage of the elemental composition may differ between individual areas.

2.3.3. Nanoparticles

Nanoparticles have two specific properties (Kreyling *et al.,* 2006). Firstly, any particle smaller than 50 nm adheres to the laws of quantum physics, meaning that they are distinguished from larger particles because of their optical-, magnetic- or electrical capabilities. Secondly, as the particle size decreases, the mass and surface area ratio, or specific surface area (SSA) rapidly increases (Maynard and Pui, 2007), thus meaning that the ratio of the atoms or molecules at the surface and the total molecules at the surface increase with declining particle size. The small size of the solid nanoparticles combined with the large SSA bestows specific properties to these nanoparticles, such as enabling them to catalyse chemical reactions at the surface (Oberdorster *et al.,* 2005), making them much more reactive than larger particles with the same mass, provided that the particles are not solute. This may lead to either desirable- or undesirable biological activity, or both, when solid nanoparticles come into contact with cells.

The curvature of the surface, due to breakages of the crystal structure, leads to the atoms trying to change their bindings, enabling them to be reactive to their environment. Thus the inhalation or ingestion of these particles can easily lead to harmful effects in the physiological system.

2.4. Deposition of airborne particulates in the respiratory tract

2.4.1. Respiratory regions and particle deposition

Airborne dust particles are able to enter the respiratory pathway by inhalation of the particles through the nose and mouth. The physical and chemical properties of inhaled airborne particulates play an important role in determining the particle penetration, deposition, retention time and rate of clearance in the respiratory tract, as well as the rate of absorption into the pulmonary circulatory system and accompanying tissues (IRCP, 1994). Other physiological properties can also influence these factors, including the breathing pattern at the time of inhalation and the state of health of the tissues in the respiratory tract (if healthy or deteriorated as result of disease or unhealthy habits like smoking).

There are several important factors that influence particle deposition in the respiratory tract: the characteristics of the particles, such as size, shape and surface properties, the biological- and physiological aspects of an individual, such as the individual's breathing pattern and lung morphology, and the physical deposition mechanisms (Hinds, 1999; Heyder, 2004; Gehr and Heyder, 2005). In order to determine the deposition of particles throughout the respiratory tract, modelling of the respiratory tract through multi-disciplinary fields including mathematics, physics and biology, is undertaken to provide substantial information regarding particle deposition (Hoffman, 2011). Various particle deposition models are constructed and generally state that the respiratory tract is divided into three regions.

The head airways region (HAR), also called the extra-thoracic (ET) or nasopharyngeal region, is the primary area for particle inhalation, consisting of the nose and mouth and serves as the entrance of the trachea (Lazaridis and Colbeck, 2010). Under circumstances of normal breathing patterns, air is inhaled through the nose and pharynx into the larynx. When circumstances leading to nasal obstructions come into effect, additional air will be inhaled through the mouth which may lead to particle impaction of the mouth and throat area. The principal task of the ET region is to clean the inspired air before it moves further down the respiratory tract. Cleansing of the inspired air is regulated through temperature and humidity adjustment by use of the respiratory mucosa and ciliated epithelium lining the nasal wall. The stages of cleansing begin with the impaction or diffusion at the anterior unciliated nares, leading to particle filtration at the hairs (vibrissae) behind the nasal entrance. Impaction of particulates occurs behind the vestibule in the horizontal chambers formed by the nasal septum and turbinates. The inspired air moves through the posterior nares down towards the pharynx and then towards the larynx and trachea.

The trachea-bronchial (TB) region ranges from the trachea to the terminal bronchioles.

The acinar, alveolar-interstitial or pulmonary region entails the region of the lower pulmonary system where gaseous exchange takes place between the alveoli and pulmonary circulatory system.

Deposition of airborne particles in the respiratory tract is dependent on 5 deposition mechanisms: impaction, gravitational sedimentation, Brownian diffusion, interception and electrostatic diffusion (Lippmann and Chen, 1998; Gehr and Heyder, 2005).

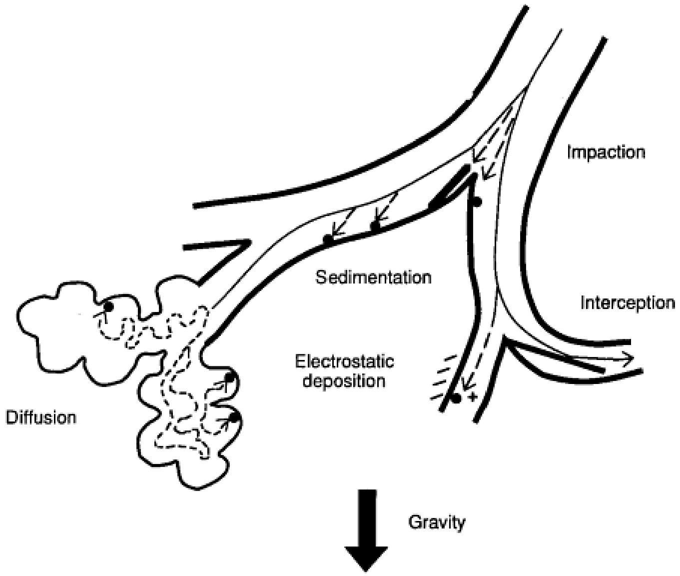

Figure 3: The primary deposition mechanisms influencing inhaled particles in the respiratory tract (Gehr and Heyder, 2005).

Airborne particles larger than 1 µm are primarily deposited in the upper regions of the respiratory tract where deposition mainly occurs through sedimentation and impaction. An increase in particle size will result in an increase of particle deposition in the mouth and throat regions (Finlay, 2001). As the particulates decrease in size smaller than 0.5 µm, sedimentation and impaction are no longer relevant and the deposition occurs through Brownian diffusion. Interception is mainly important only for fibres as they tend to align with the airstream lines. This leads to fibres being resistant to sedimentation and impaction. Turbulence can occur which will lead to a rotational flipping movement of the fibres that will inevitably impact on the lung wall lining causing fibre collection at the area. The small size of UFPs enables them to behave like a gas, inferring that they are easily exhaled and thus less likely to be deposited than particles with a greater AD. UFP deposition can largely occur in the upper airways of the respiratory tract depending on particle size, however it is seen that UFPs with a particle size of 20 nm have a 50 % deposition rate in the alveolar region (Webster, 2009; van Berlo *et al.*, 2012).

2.4.2. Respiratory defence mechanisms (particle clearance)

The retention of airborne particles in the pulmonary system can be countered through pulmonary clearance mechanisms. The clearance mechanisms in the upper airways of the pulmonary system are attributed to the mucociliary escalator and the clearance of the lower pulmonary system airways is attributed to phagocytosis and passive uptake.

2.4.2.1. Mucociliary escalator

When particles are deposited in the respiratory tract, clearance of these particles is carried out through physical translocation of the non-soluble particles or by chemical clearance of soluble particles. Soluble particles deposited in the airways can interact with the lung wall lining mucus and dissolve, and can then be transported out of the respiratory tract; or the particles can be absorbed by the epithelial cells where they are then transported into the lymphatic or circulatory system (Lippman *et al.,* 2003). Non-soluble particles undergo a much slower form of clearance from the airways than the soluble particles. When particles are deposited in the respiratory tract, they will make contact with the lining fluid which is primarily composed of proteins and phospholipids (Lippmann and Chen, 1998). This will lead to the particles being moistened and moved towards the epithelium by the forces that occur at the surface, attributed to the liquid-air interface. The epithelium cells of the bronchia have cilia which will move the covering mucous layer, consisting of trapped particles, up through the upper airways away from the lungs and to the pharynx where the mucous layer can then enter the gastro-intestinal tract. This process can take up to several hours and is known as the mucociliary escalator. Particle uptake by esophageal epithelial cells is possible if they are in the presence of pre-existing inflammation.

2.4.2.2. Phagocytosis and passive uptake

Inhaled airborne particles that are smaller than 10 µm can be deposited at the alveoli of the lower pulmonary system. Clearance of these particles will be carried out through macrophage phagocytosis. The clearance rate of macrophage phagocytosis is dependent on particulate size. Particles in the size range between 1.5 µm and 3 µm are considered to be optimal for macrophage clearance efficiency. A decline in particle size smaller than 1 µm will lead to a decrease in the clearance efficiency (Ruzer and Harley, 2013). Macrophages are cells that help initiate defence mechanisms by acting as transport vesicles to remove foreign- or benign particles out of the physiological system. Macrophage cells engulf, or phagocytose, and break down pathogens, apoptotic- or damaged cells and inert particles through use of dedicated receptors that are able to recognize various molecules such as those of pathogens that have different molecules from those found in the physiological system (Hinds, 1999). These receptors can either cause particle adhesion or internalization. Phagocytosis of particles can be sped up through the use of a labelling process known as opsonisation. Opsonins are present in the lining fluid of the lungs and can label foreign particles with special molecules such as antibodies or complement molecules which will enable faster phagocytosis through macrophage cells (Ellis, 1998). Macrophages in the lung alveoli will transport particles to the mucociliary escalator or through the epithelium to the lymph nodes in the lungs or associated areas, where the particles can then be removed from the physiological system. If the lungs are subjected to prolonged- or chronic exposure, white blood cells (leucocytes) may be recruited to help with the particle clearance.

Nanoparticles smaller than 100 nm deposited in the lower pulmonary airways are less likely to be subjected to macrophages phagocytosis (Simeonova *et al*., 2007). The size of human alveolar macrophages range between 14 to 21 µm and can engulf particles of a size similar to their own dimensions, thus being less effective when dealing with larger or smaller particles. This phenomenon will increase the likelihood of nanoparticles interacting with epithelial cells to gain access to the circulatory- and lymphatic systems. However, agglomeration of particles occurring due to large concentrations form agglomerates usually larger than 100 nm which stand a better chance to undergo macrophage phagocytosis, thus lowering the risk of particle uptake in the circulatory- and lymphatic systems. Particles that reach the circulatory- and lymphatic systems can be distributed to organs, such as the kidneys, where clearance may occur through the organ-specific mechanisms.

In situations where chronic exposure to inhaled particles lead to the capacity of the clearance mechanisms of the pulmonary systems being overwhelmed, the excess particles induce lung burden which can initiate a range of toxicological responses that will result in damage of the lung tissue (Lippmann and Chen, 1998). The degree of these adverse health effects depends on the rate of particle deposition and clearance (lung burden) and the residence time of particles in the pulmonary system.

2.4.3. Adverse health effects and toxicity

No foreign particles entering the pulmonary system are completely harmless. Adverse health effects can be initiated through even low particle concentrations, depending on the residency time in the respiratory tract. Smaller particles, such as nanoparticles, are subjected to having a higher level of toxicity than larger particles of the same elemental composition and structure due to the SSA increasing with decreasing particles size, thus making the nanoparticles more reactive which will generate oxidative stress between the particles and the fluid of the lung wall lining, as well as particle contact with cells, thus leading to an increase of inflammatory reactions in the lungs (Gilmour *et al.,* 1996*;* Kreyling *et al.* 2006).

Adverse reactions in accordance with nanoparticles include inflammation, impaired macrophage clearance and epithelial cell proliferation that will lead to pathologies such as fibrosis, emphysema and tumour development. The extent of the adverse health effects on the physiological system may be dependent on genetic susceptibility and health status of an individual.

2.5. Hematite iron ore dust

2.5.1. Overview

Iron ores are represented as rocks and minerals from which iron can be extracted through mining processes for commercial use. The iron found in iron ore mainly occurs in iron-oxide compound forms. The principle sources of iron-oxide compounds are hematite, magnetite, goethite and limonite (Beukes *et al., 2002;* Figueroa *et al.*, 2011*)*. Hematite (Fe_2O_3) is red in colour and occurs in all forms, from solid rock to loose earth. Magnetite (Fe_3O_4) is black in colour, Goethite (Fe_2O_3) is brown in colour and Limonite ($Fe_2O_3.H_2O$) is a yellow-brown ore which is a mixture of impure goethite and hydrated iron oxides.

Hematite originates in a variety of rock forms, but is most abundant in sedimentary banded-iron formations. The iron extracted from hematite ore is used for the production of steels and alloys like ferroalloys, ferrosilicon and ferromanganese (Cairncross, 2004).

Airborne iron ore dust particulate exposure may lead to various adverse health effects in the physiological system, however the health effects experienced may differ between iron ore mining sites due to the difference of the elemental composition of the dust and the chemical compounds that these elements form (Banerjee *et al.,* 2006). Iron ore is usually composed of compound mixtures rich in iron, with some level of compounds that contributes to impurities (Anon, 2002). The chemical compounds that are the principle contributors of iron-ore dust toxicology are iron oxide and silica (Banerjee *et al.* 2006). There are often impurities found in iron ore such as chemical components of phosphorous, sulphur, sodium, potassium, aluminium, silica and sometimes titanium. Other chemical components such as manganese and calcium are also present, but may only be considered as desirable depending on the composition of the other raw materials used in the iron producers' process.

2.5.2. Iron-oxide

Some trace elements in the physiological system, such as iron (Fe), that occur in high doses are highly toxic (Harrison and Yin, 2000). Iron as a transition metal can contribute to the production of free radicals, hydroxyl radicals, through non-classical mechanisms which can generate reactive oxygen species (ROS) in biological tissue and lead to adverse health effects (Gilmour *et al.,* 1996; Chen and Lippmann, 2009).

2.5.2.1. Toxicology

Transition metals, in this case Fe, have the ability to catalyse one electron reduction of molecular oxygen (O) needed to produce ROS (Plummer *et al*, 2011).

The generation of ROS in the physiological system can be expressed through several chemical reactions, as illustrated below (Chen and Lippmann, 2009). The Haber-Weiss reaction indicates the interaction of iron with super oxide ($O_2^{\bullet -}$). The Fenton reaction indicates the interaction of iron with hydrogen peroxide (H_2O_2).

The hydroxyls are formed through Haber-Weiss/Fenton reactions as illustrated by the following equations:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + OH^-$$

$$Fe^{2+} + O_2 + H^+ \longrightarrow Fe^{3+} + O_2^-$$

$$HO_2^- + O_2^- + H^+ \longrightarrow O_2 + H_2O_2$$

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + OOH^{\cdot} + H^+$$

$$\text{Reductant}^{n} + Fe^{3+} \longrightarrow \text{Reductant}^{n+1} + Fe^{2+}$$

The redox cycle will continue as long as there are O_2 and H_2O_2 reductants. The hydroxyl radicals (OH, **.**OOH) and super oxide (O_2^-) react with various biological molecules, which in turn will activate cellular signals and lead to cellular damage (Chen and Lippmann, 2009).

2.5.2.2. Adverse health effects

Iron ore miners over-exposed to hematite iron ore dust may develop the pulmonary pathologies of siderosis and diffuse fibrosis-like pneumoconiosis (Winder and Stacey, 2005; Smedley *et al.,* 2013)

2.5.3. Silica

Silica or silicon dioxide (SiO_2) is the most abundant mineral on earth (Lippmann and Chen, 1998; Naghizadeth *et al.,* 2011;) and is extremely hazardous to the pulmonary system when the exposure limit is exceeded. Silica occurs naturally in various forms such as crystalline-(quartz), cryptocrystalline- and amorphous silica, with crystalline silica being the most abundant form (Stellman, 1998). Minerals containing silica are known as silicates, but silica can also be found unbound to other minerals. Unbound silica is usually called free silica or silica quartz. Inhalation of airborne dust containing respirable crystalline silica will lead to the development of silicosis, a potentially fatal pulmonary disease. The level of silicosis is dependent on the exposure period (acute, accelerated or chronic) as well as the intensity level at which the exposure occurs. Chronic silicosis may develop into progressive fibroses even if an individual is no longer exposed to airborne silica dust.

2.5.3.1. Toxicology

The inhalation of respirable crystalline silica leads to particle deposition in the pulmonary alveoli. The exact mechanism of silica pathology is still unknown, but certain theories have been formulated (Muetterties *et al., 2003)*.

One such theory states that after alveolar entry, the alveolar macrophage will ingest the silica particle and terminates, resulting in the release of proteolytic enzymes along with the silica particle. The released particle will then be ingested by another macrophage, thus resulting in a repetitive cycle (Johnson, 2008). This is a simplistic view as other fibrogenic factors like interleukin (IL) 1; IL B-4 and tremor necrosis factor (TNF) are also involved.

Another theory states that the macrophage is in fact activated by silica particle ingestion, and not terminated. This theory is supported by electron microscopic examination of the bronchiolar fluid of silica exposed individuals that show an increase of particle containing macrophage activity. An increase of macrophage activation will lead to production of collagenase and thus parenchymal lung destruction. Pulmonary fibroblasts have been identified as targets for silica particles in the pulmonary system. As silica particles are absorbed there are no signs of cellular damage, however there are increases in collagen synthesis, fibroblast proliferation, growth factor down-regulation and IL1 up-regulation. Crushed silica contains more free radicals than stored silica and is more cytotoxic, and will thus contribute to silica lung injury development.

2.5.3.2. Adverse health effects

Long term inhalation of excessive respirable crystalline silica will lead to the development of silicosis, a pulmonary disease that decreases lung function and for which there is no effective treatment (Muetterties *et al., 2003;* Smedley *et al*., 2013). Silicosis arises in the pulmonary system through three types of exposure: acute-, sub-acute- and chronic exposure. Acute silicosis is diagnosed through an early onset of dyspnoea, or breathlessness and a dry cough within months of exposure to a large quantity of silica- containing dust and can progress over 1 – 2 years to respiratory failure.

Sub-acute silicosis symptoms include a gradual onset of dyspnoea and dry cough over years of moderate exposure to silica- containing dust. Upper and middle nodular fibroses will occur with hilar lymph node calcification. Lung function will eventually become restrictive.

During chronic silicosis nodular development will decrease after many years of low exposure to silica-containing dust.

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CHAPTER 3

ARTICLE

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Characterisation of airborne dust in a South African opencast iron ore mine. A pilot study.

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Abstract

The iron ore mining industry makes use of various processes to produce a final product that results in the release of airborne dust into the surrounding atmosphere where workers are exposed. The deposition and toxicological influences of airborne dust can be determined by their physical- and chemical characteristics. The Occupational Health and Safety Act (OHSA) regulations for hazardous chemicals have no current system of how the physical- and chemical properties of particulates originating from specific areas will have an influence on worker exposure and health, especially for ultrafine particles (UFP). It is therefore imperative to characterize airborne dust containing micrometer and UFP size particles originating from specific areas to determine the influence that the physical- and chemical properties will have on the workers' health.

Aim: This pilot study was aimed at the physical and chemical characterisation of the airborne iron ore dust generated at the process areas of a South African opencast iron ore mine. **Method:** Sampled areas include the Primary-secondary crusher, Tertiary crusher, Quaternary crusher and Sifting house. Gravimetric sampling was conducted through the use of static inhalable- and respirable samplers in conjunction with optical- and condensation particle counters that were placed near airborne dust- emitting sources. Physical- and chemical characterisation was done through the use of scanning electron microscopy (SEM) and energy dispersive X-ray (EDS) spectroscopy. **Results:** The results found in the study indicate high mass concentration levels of inhalable dust at all four process areas, as well as high levels of respirable dust found at the Primary-secondary crusher area. Particle size distribution optical particle counter (OPC) results indicate that the majority of particles at all four process areas were 0.3 µm in size. Condensation particle counter (CPC) results integrated with OPC results indicate that at the primary- secondary- and Tertiary crushers the majority of particles were found to be in the size fraction <0.3 µm. SEM analysis indicates that particle agglomeration largely occurs in the airborne iron ore dust. Particle splinters originating from larger particle collisions and breakages are present in the airborne dust .EDS analysis indicates that the elemental majority of the airborne iron ore dust consists of iron, oxygen, carbon, aluminium, silicon, potassium and calcium. The elemental percentages differ from each process area, where an increase in iron and decrease in impurities can be seen as the ore moves through the beneficiation process from the primary- secondary crusher to the Sifting house. **Conclusion:** The results obtained from the physical- and chemical properties of the airborne iron ore dust, indicate a high risk of over- exposure to the respiratory system, as well as possible ultrafine particle systemic exposure that may overwhelm the physiological defense mechanisms of the human body and lead to reactive oxygen species (ROS) formation and the development of pathologies such as siderosis, silicasiderosis and lung cancer.

Key words: airborne, mine, characterisation, particle size, nanometer, micrometer, ultrafine, physical, chemical.

Introduction

Iron ore is a mined product that after various stages is broken down through crushing processes where it is then washed and separated into coarse, medium or fine pieces by wet screening. During these processes a vast amount of dust containing iron, oxygen, silica, aluminium and carbon is released into the surrounding atmosphere. These airborne particles vary in size from as small as nanometers (nm) up to several micrometers (µm), and contribute to adverse health effects that can be detected in the mining workforce. Spellman and Bieber (2012) stated that there are four factors which will influence the degree that airborne particle exposure will contribute to adverse health effects. These factors include particulate size, exposure time, the chemical nature of the particles and the particle concentration in the affected persons breathing zone during exposure. These factors will give an indication of airborne particle exposure leading to acute health effects such as coughing and difficulty breathing that may lead to the development of chronic obstructive pulmonary diseases (COPD) such as fibrosis, pneumoconiosis, emphysema and lung cancer if exposure persists over longer time periods (Boyd *et al.,* 1970; Greim and Snyder, 2008).

Recently the toxicological influences of nanoparticles became known. Because of the current lack of occupational exposure levels (OEL) concerning nanoparticle exposure in the occupational hygiene setting, it is important to improve the current knowledge of airborne dust nanoparticle exposure through physical- and chemical characterisation.

Daily worker- exposure to airborne dust particles over an extended period will lead to adverse health effects if the workers are not properly protected through engineering-, administrative- and personal protective measures. These measures can currently be effectively incorporated for worker protection concerning exposure ranging in size as small as micro particles. Recent studies however have shown that UFP exposure (particles in nanometer range classified as particles with at least one linear dimension (< 100 nm) of the same element differ greatly concerning their physiological effects (Brown *et al.*, 2002; Oberdorster *et al.*, 2005; Balbus *et al*., 2007; Katsnelson *et al., 2012*). Characterisation of micro- and nanoparticles through the use of a scanning electron microscope (SEM), energy dispersive x-ray spectroscopy (EDS) and the counting of particulates of various aerodynamic diameters (AD) may enable a better understanding of the influence of iron ore airborne dust particles on physiological systems, which can lead to a better overall understanding of what airborne dust entails, and thus improve the implementation of protective measures concerning the workers' health (Petavratzi *et al*., 2005; Buzea *et al*., 2007; Schmoll, 2009).

Particle size and shape can have a major influence on physiological functions, an example being on the effectiveness of mucociliary clearance of sub-micron particles and the transition of these particles over the pulmonary barrier, enabling the particles to be systemically distributed (Buzea *et al*., 2007; Maynard and Pui, 2007). In order to lower the effect that these particles have on not only the respiratory system but also other physiological processes due to systemic ultra fine particle (UFP) uptake, an in- depth study has to be carried out concerning the characterisation of micro-particles and UFPs. Ultrafine particles (UFP) are particles with at least one dimension < 100 nanometer (nm) ($PM_{0.1}$) (WBG, 1998; Brown *et al.*, 2002; Oberdorster *et al.*, 2005; Katsnelson *et al.* 2012).

Airborne particles are easily inhaled into the respiratory tract where they are deposited along the tract depending on their size. When dealing with micrometer size particles, their aerodynamic diameter can be divided into three size ranges according to the area of deposition in the respiratory system: inhalable -, thoracic - and respirable particulate mass (Petavratzi *et al*., 2005; Belle and Stanton*,* 2007).

UFPs may institute a fourth form of respiratory tract exposure which can be called systemic particulate mass, the reason being that their miniscule size enables them to bypass the pulmonary barrier of the lungs and enter the systemic circulation of the body (Balbus *et al.,* 2007). As the size of nanoparticles decrease, the specific surface area (SSA) rapidly increases (Maynard and Pui, 2007; Araujo, 2011). This enables these particles to catalyze chemical reactions at the surface, making them more reactive than larger particles with the same mass, thus leading to nanoparticles having different toxicological properties than particles of the same nature in micrometer size. The inhalation or ingestion of these particles can easily lead to harmful effects in the physiological system (Sioutas *et al., 2005;* Kreyling *et al.*, 2006).

Particle characterisation includes the study of the physical- and chemical properties by analyzing airborne dust samples through SEM and EDS analysis. The physical properties include the particle size, shape, distribution, surface area and level of agglomeration. Condensation particle counters (CPC) and optical particle counters (OPC) are used to determine the particle count size distribution (Schmoll, 2009). The chemical properties entail the chemical analysis of particles to determine their elemental composition and percentage concentration (Sobanska *et al.,* 2002; Petavratzi *et al.*, 2005).

Iron ore is usually composed of compound mixtures rich in iron, with some level of compounds that contribute to impurities (US dept. of energy, 2002). The iron found in iron ore mainly occurs in iron-oxide compound forms. The principal sources of iron-oxide compounds are hematite, magnetite, goethite and limonite (Beukes *et al., 2002;* Figueroa *et al.*, 2011*)*. Hematite (Fe_2O_3) is red in color and occurs in all forms, from solid rock to loose earth. There are often impurities found in iron ore such as chemical components of phosphorous, sulfur, sodium, potassium, aluminium, silica and titanium. Chemical components such as manganese and calcium are also present but may be considered as desirable depending on the composition of the other raw materials used in the iron producers' process.

The Occupational Health and Safety Act 85 of 1993: Regulations for Hazardous Chemical Substances states that in terms of dust, if there is no specific exposure limit for a specific dust: the personal exposure should be kept below 10 mg/m^3 TWA for inhalable dust and 5 mg/m^3 TWA for respirable dust.

The miniscule size of UFP and micro particles enable them to be easily inhaled into the respiratory system all the way to the alveoli in the lungs (Walter, 2007). Total deposition of UFP's in the respiratory tract increases as the particle size decreases and the respiratory time increases (Jaques and Kim, 2000; Wang, 2005). Thus, lung morphology, respiratory physiology, air flow and particle characteristics are key factors in determining UFP particle deposition.

Over exposure to inhalable and respirable particles over an extended period may lead to the development of chronic obstructive pulmonary diseases (COPD) such as fibrosis, pneumoconiosis and emphysema, as well as lung cancer (Boyd et al., 1970; Greim and Snyder, 2008). Because of the bio-stability of the particles, complex biochemical processes can take place which could lead to an increased probability for inflammation and high risk for lung cancer. Pulmonary toxicity studies have revealed that exposure to UFPs induce more enhanced inflammatory responses compared to larger particles of the same elemental composition, due to their larger SSA (Warheit *et al.*, 2008; Araujo, 2011). Nanoparticles accumulating in the alveoli cannot be removed by mucociliary clearance, where nanoparticles smaller than 200 nm have an increased probability to avoid macrophages phagosytosis. This will lead to the nanoparticles entering the pulmonary interstitial sites and interacting with the epithelial cells to gain access to the circulatory- and lymphatic systems (Buzea *et al.,* 2007). When the interstitium is penetrated, the nanoparticles will be systemically distributed, causing pulmonary- and systemic inflammation which can lead to various adverse health effects, including cardiovascular diseases (Gwinn and Vallyathan, 2006), altered cell mechanical properties due to reactive oxygen species (ROS) formation (Buyukhatipoglu, 2011), as well as translocation and toxicity of other organs such as the liver and the brain. Nanoparticles can also penetrate the cellular barriers, inducing toxicological effects on the organelles and the cell nucleus (Balbus *et al.,* 2007).

Methods

The sampling protocol was designed to monitor real time atmospheric dust particles as well as gravimetric area dust samples.

Sampling methodology and equipment:

Real time particle counting of various sizes was done with an TSI AeroTrak™ Portable Counter Model 9310 optical particle counter (OPC) and the TSI™ Condensation Particle Counter Model 3007 (CPC). Static inhalable and respirable dust was sampled gravimetrically with the Institute of Occupational Medicine (IOM) inhalable samplers and SKC respirable dust aluminum cyclone samplers.

The TSI™ Condensation Particle Counter Model 3007 (CPC) is a hand held battery powered device capable of measuring the particle number concentration between size ranges of 10 nm and 1 µm. Particle concentrations were sampled every 1 second for a sampling period of 1 hour after which the average particle concentration was automatically calculated to the value of particles per cubic centimetre (p/cm^3).

The AeroTrak™ Portable Counter Model 9310 optical particle counter (OPC) is a hand- held battery powered device which measures airborne particles number concentration from 0.3 to 25 µm. Particle concentrations were sampled every 1 second for a sampling period of 1 hour after which the average particle concentration was calculated to the value of particles per cubic meter (p/m^3).

The IOM samplers were used to collect inhalable dust. Three samples were taken at each area using the NIOSH 7300 method, sampling at 2 l/min. 25 mm mixed cellulose ester (MCE) filters with a pore size of 0.8 µm were used.

The SKC respirable dust aluminium cyclone was used to collect respirable dust. The SKC cyclones are conductive and will not develop an electrostatic charge and will thus not influence charged particles. Three samples were taken per area using the NIOSH 0600 method. 37 mm mixed cellulose ester (MCE) filters with a 0.8 µm pore size were used.

Each area was sampled through the use of a sampling station, the layout of which is represented in Figure 1. The sampling station layout consists of a base plate on top of a tripod which measures 1.8 meters above the floor to ensure adequate sample exposure to airborne dust. The gravimetric sampling trains and the direct reading apparatus were placed on top of the sampling station base plate throughout the sampling time period. For each sampling period 3 IOM sampling trains and 3 cyclone sampling trains were used in conjunction with both direct reading apparatus. Each sampling train was spaced more than 30 cm apart to ensure the quality of the sampling that was conducted. The IOM and cyclone samplers were initiated at the start of each daily sampling period and ran continuously throughout the duration of the sampling period. The direct reading apparatus each ran for two - one hour periods during the course of the sampling period.

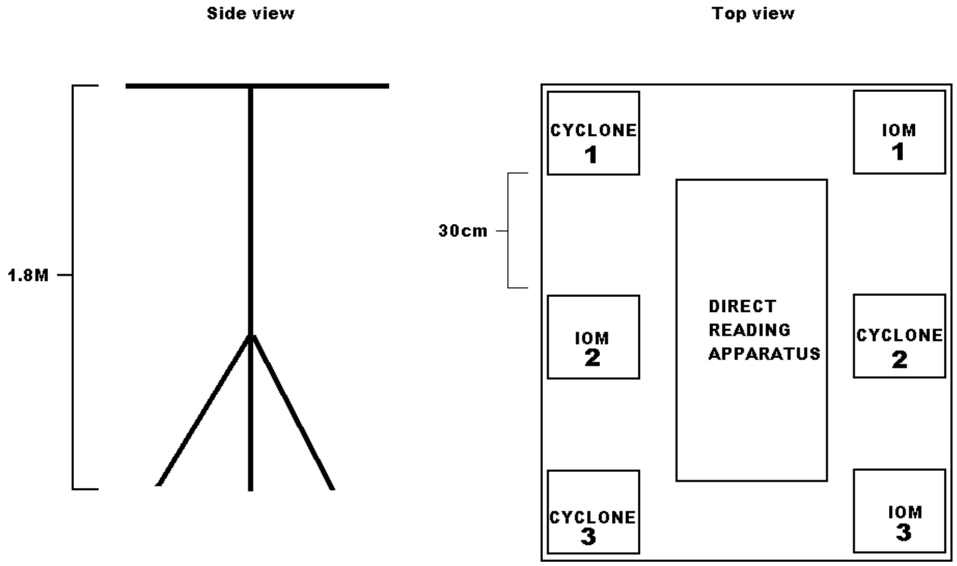

Figure 1: Illustration of the airborne dust sampling station.

The sampled areas are illustrated in Appendix B and included the Primary-secondary-, Tertiary-, and Quaternary crusher areas as well as the Sifting house. These are key dry process areas that represent worker exposure to airborne dust, throughout the flow of the beneficiation process from the mining sites to the final product at the mixing beds. Sampling conducted at the Primary-secondary crusher, Tertiary crusher and Quaternary crusher took place by setting up the sampling station between 2 crushing machines for sufficient dust capture. The sampling station at the Sifting house area was placed on the top floor which consists of a grid floor above a shuttle that deposits ore from a feeder that is fed by an ore belt originating from the Quaternary crusher area. Sampling conducted at the Primary-secondary crusher area took place in a small room below ground that is isolated from natural ventilation and relies on mechanical ventilation. The Tertiary crusher, Quaternary crusher and Sifting house sampling areas are all situated above ground inside mechanically ventilated buildings.

Electron microscopy

After determining the gravimetrical mass concentration, the samples were prepared for SEM and EDS analysis.

Through the use of a scanning electron microscope (SEM), a model FEI Quanta 250 FEG, the size and shape of the captured particles were determined. The dust samples were mounted on SEM stubs with double- sided carbon tape. The SEM can determine the size of particles down to between 50 nm and 100 nm. The SEM also identified the dimensionality, morphology, uniformity and state of agglomeration of the particles. To make it possible to view the nanoparticles, some of the samples were spatter- coated with gold/palladium and viewed with a model FEI Quanta 250 SEM.

The integrated Oxford X-max Energy Dispersive X-ray Spectroscopy (EDS) is attached to the SEM to determine the elemental composition and concentration percentage of the gravimetrical samples.

Results

Results obtained from the IOM and cyclone sampling media was used to determine the airborne dust concentrations. The concentrations were calculated by following the first six steps to calculate TWA concentrations as set out in the South African Mines Occupational Hygiene Programme (SAMOHP) codebook. These steps are illustrated in Appendix 1. The results of the mass concentration calculations are represented in Table 1 and Table 2.

Table 1: Average static respirable airborne dust concentrations as sampled with the use of the SKC cyclone sampler.

Date	**Sample train number**	**Number of samples taken (n)**	**Average sampling time (minutes)**	**Sample train concentrations (mg/m^3)**			**Area average concentration (mg/m^3)**
				Ave.	**Min.**	**Max.**	
Primary-secondary crusher							
27/08/2012	CYCSTE	2	334	11.6	9.445	13.755	6.855
28/08/2012	CYCSTF	2	434	2.110	2.035	2.185	
Tertiary crusher							
10/08/2012	CYCSTA	2	389	0.428	0.814	0.897	0.632
13/08/2012	CYCSTB	3	430	0.596	0.576	0.608	
24/08/2012	CYCSTD	1	407	0.259	0.259	0.259	
29/08/2012	CYCSTG	2	434	1.245	1.010	1.390	
Quaternary crusher							
3/09/2012	CYCSTJ	3	371	3.337	2.253	4.714	3.106
4/09/2012	CYCSTK	3	370	3.655	3.055	4.101	
5/09/2012	CYCSTL	3	445	2.325	1.920	2.550	
Sifting house							
30/08/2012	CYCSTH	2	421	1.882	1.729	2.035	1.424
31/08/2012	CYCSTI	2	366	0.965	0.580	1.350	

Table 1 and Figure 2 indicate the respirable mass concentrations sampled with the use of the SKC cyclone. The highest average airborne particulate mass concentration was found at the Primary-secondary crusher area with a value of 6.855 mg/m^3. The lowest average airborne particulate mass concentration was found at the Tertiary crusher area with a value of 0.632 mg/m^3. The maximum mass concentration was 13.755 mg/cm^3, found at the Primary-secondary crusher area. This is more than 675 % the minimum concentration and indicates that the airborne dust released at this area is not a constant concentration but varies with 675% over time.

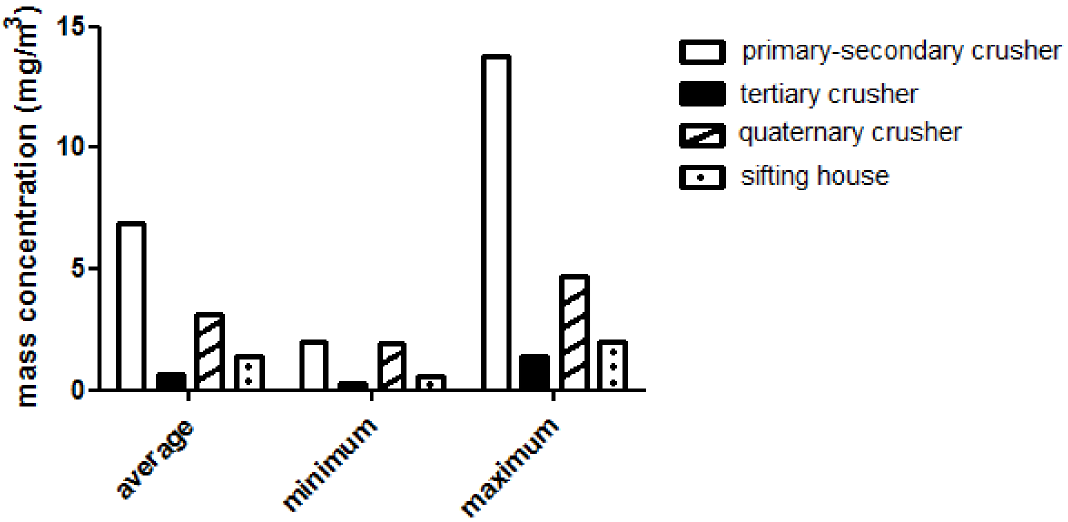

Figure 2: An illustration of the respirable mass concentrations as sampled through the use of the SKC cyclone sampler.

Table 2: Average static inhalable airborne dust concentrations as sampled through the use of the plastic IOM sampler.

Date	**Sample train number**	**Number of samples taken (n)**	**Average sampling time (minutes)**	**Sample train concentrations (mg/m^3)**			**Area average concentration (mg/m^3)**
				Ave.	**Min.**	**Max.**	
			Primary-secondary crusher				
27/08/2012	IOMST5	3	333	175.582	169.832	178.883	143.638
28/08/2012	IOMST6	2	433	111.693	111.173	122.213	
			Tertiary crusher				
10/08/2012	IOMST1	3	388	68.734	52.093	81.554	51.603
13/08/2012	IOMST2	3	429	30.227	25.746	33.726	
24/08/2012	IOMST4	2	406	32.910	31.466	34.353	

Date	Sample train number	Number of samples taken (n)	Average sampling time (minutes)	Sample train concentrations (mg/m^3)			Area average concentration (mg/m^3)
				Ave.	Min.	Max.	
Tertiary crusher							
29/08/2012	IOMST7	2	433	74.539	65.632	83.446	
Quaternary crusher							
3/09/2012	IOMST10	3	370	41.371	29.696	53.056	40.114
4/09/2012	IOMST11	3	369	45.862	37.728	51.320	
5/09/2012	IOMST12	3	443	33.110	25.454	38.023	
Sifting house							
30/08/2012	IOMST8	3	420	76.637	64.641	91.727	59.004
31/08/2012	IOMST9	2	365	41.371	31.044	52.878	

Table 2 and Figure 3 indicate the inhalable mass concentrations as sampled through the use of the IOM sampler. The highest average area airborne particulate mass concentration was found at the primary-secondary crusher area with a value of 143.638 mg/m^3. The lowest average area airborne particulate mass concentration was found at the Tertiary crusher area with a value of 40.114 mg/m^3.

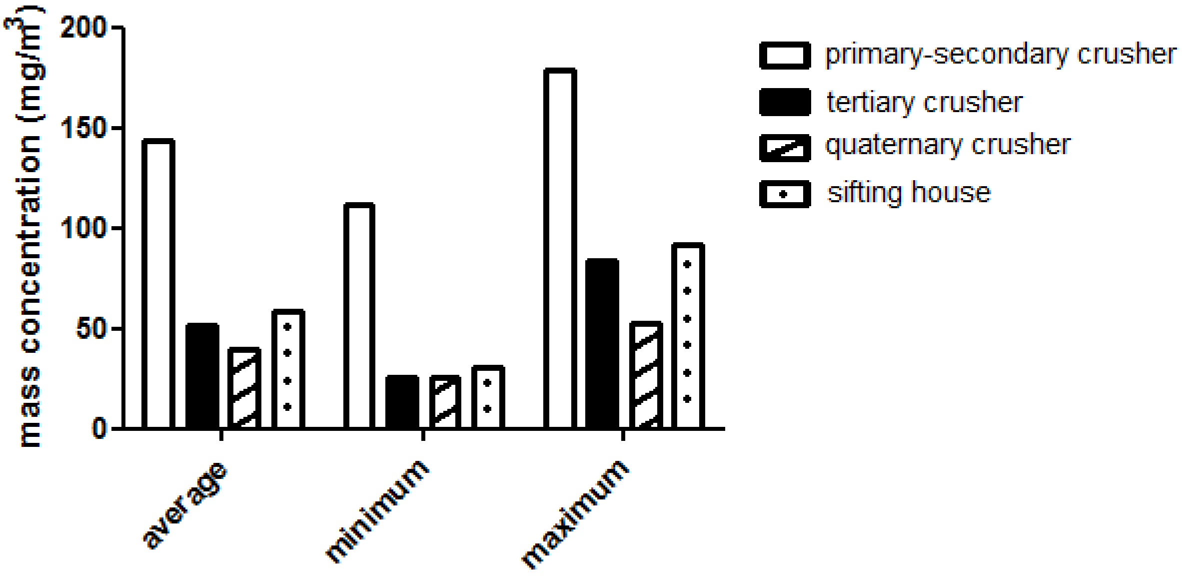

Figure 3: an Illustration of the inhalable airborne dust concentrations as sampled through the use of the plastic IOM sampler.

Table 3: The particle count concentration within the size range of 10 nm and 1 µm as sampled at the Primary-secondary crusher and Tertiary crusher areas with the CPC.

Area	**CPC measurements (p/m^3)**		
	Average	**Minimum**	**Maximum**
Primary- secondary crusher	2.62E+10	3.85E+09	9.22E+10
Tertiary crusher	2.5E+10	1.15E+10	3.99E+10

Table 3 and Figure 4 indicate the particle size distribution as sampled with the CPC. Only the Primary-secondary crusher and Tertiary crusher areas could be sampled with the CPC as the particle counter experienced a malfunction when sampling was conducted at the Sifting house areas and was thus unable to operate for the sampling of the Sifting house and Quaternary crusher areas. The area with the highest average number of particles released in the 10 nm to 1 µm size range was at the Primary-secondary crusher area with a concentration of 2.62E+10 p/m^3. This average concentration is only slightly higher than the average concentration of 2.5E+10 p/m^3 found at the Tertiary crusher. The maximum particles found at the Primary-secondary crusher area was 9.22E+10 p/m^3 which is 25 times more than the minimum concentration, indicating that the Primary-secondary crusher area undergoes time periods of higher and lower airborne dust released into the surrounding atmosphere.

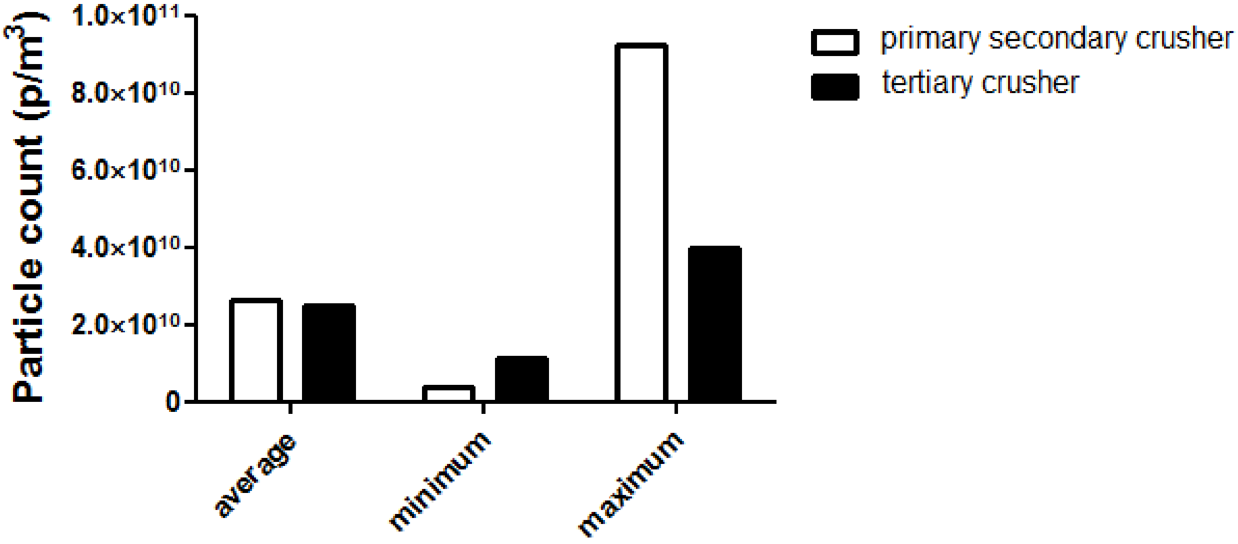

Figure 4: An illustration of the CPC measurements as sampled at the primary- secondary crusher and Tertiary crusher areas.

Table 4: Optical particle counter (OPC) measurements indicating the particle count within the size range of 300 nm and 10 µm as sampled at the Primary-secondary crusher, Tertiary crusher, Quaternary crusher and the Sifting house areas.

OPC measurements (p/m^3)						
Primary-secondary crusher area						
Particle size range (µm)	**0.3**	**0.5**	**1**	**3**	**5**	**10**
Average	9.7E+07	7.9E+07	6.4E+07	1.4E+07	4.0E+06	9.4E+04
Minimum	4.2E+07	1.9E+07	1E+07	7.0E+05	1.17E+05	1.5E+04
Maximum	1.9E+08	1.8E+08	1.7E+08	5.1E+07	1.5E+07	4.7E+05

OPC measurements (p/m^3)						
Tertiary crusher area						
Particle size range (µm	**0.3**	**0.5**	**1**	**3**	**5**	**10**
Average	9.8E+07	7.7E+07	5.6E+07	1.2E+07	4E+06	4E+05
Minimum	5.9E+07	3E+07	1.6E+07	1E+06	1E+05	4E+03
Maximum	1.3E+08	1.2E+08	9.6E+07	2.6E+07	1E+07	9E+05
Quaternary crusher area						
Particle size range (µm	**0.3**	**0.5**	**1**	**3**	**5**	**10**
Average	1.2E+08	1.1E+08	8.7E+07	1.6E+07	3E+06	5E+03
Minimum	9.2E+07	9E+07	4.1E+07	1E+06	8.2E+04	8E+02
Maximum	1.5E+08	1.5E+08	1.5E+08	3.1E+07	6.2E+06	1.4E+04
Sifting house area						
Particle size range (µm	**0.3**	**0.5**	**1**	**3**	**5**	**10**
Average	1.6E+08	1.4E+08	1.1E+08	1.6E+07	4.4E+06	3.5E+05
Minimum	9.4E+07	7.8E+07	6E+07	5.5E+06	7.2E+05	6E+04
Maximum	1.8E+08	1.8E+08	1.5E+08	2.8E+07	8.6E+06	6.6E+05

Table 4 and Figure 5 indicate the particle size distribution as sampled with the OPC. It is seen that the largest particle count was found to be in the 0.3 µm size range with a steady decrease through the 0.5 µm and 1 µm size ranges and a dramatic drop in the 3 µm, 5 µm and 10 µm size ranges. The highest concentration of particles was found at the Sifting house area with 1.6E+08 p/m^3 at a 0.3 µm size range. It is seen that the particle count more or less increases for all size ranges for each area following the beneficiation process.

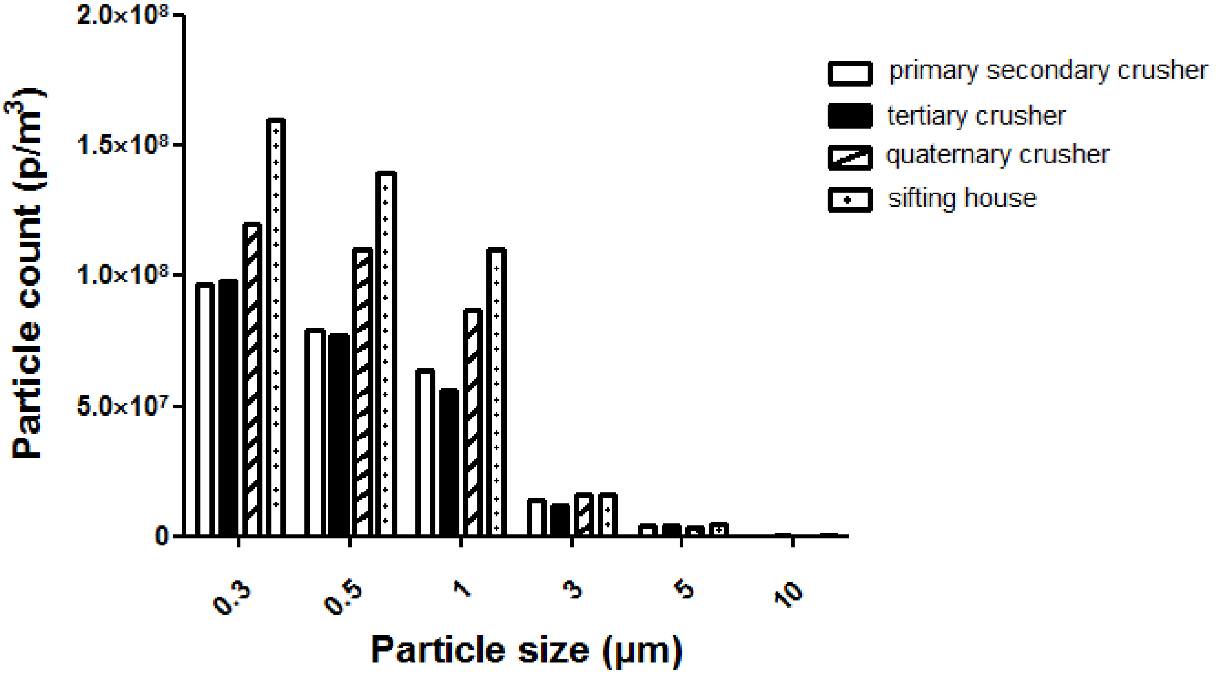

Figure 5: An illustration of the OPC measurements as sampled at the primary- secondary crusher, Tertiary crusher, Quaternary crusher and the Sifting house areas.

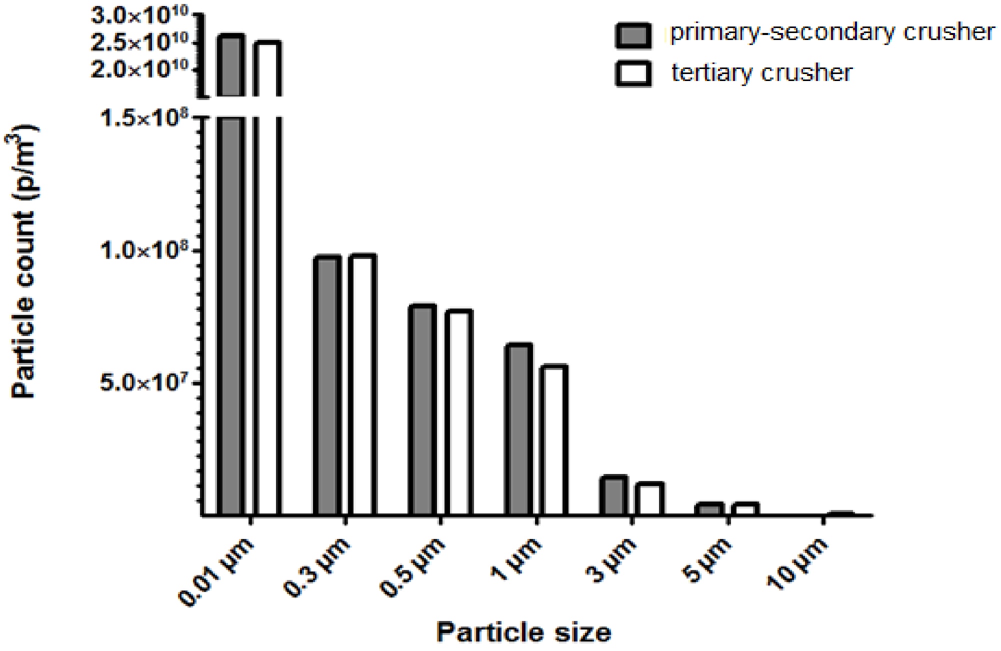

Figure 6: Integrated OPC and CPC measurements as sampled at the primary- secondary crusher and Tertiary crusher areas.

By subtracting the 0.3 µm OPC count from the 1 µm OPC count to get a value which will then be subtracted from the CPC count, the particle count for the size range between 0.01 µm and 0.3 µm can be determined. This data can then be used to combine the CPC and OPC counts as seen in Figure 6. It is clear that the highest dust particle exposure at both the Primary-secondary crusher and Tertiary crusher areas were in the sub-micrometer particle range between 0.01 µm and 0.3 µm.

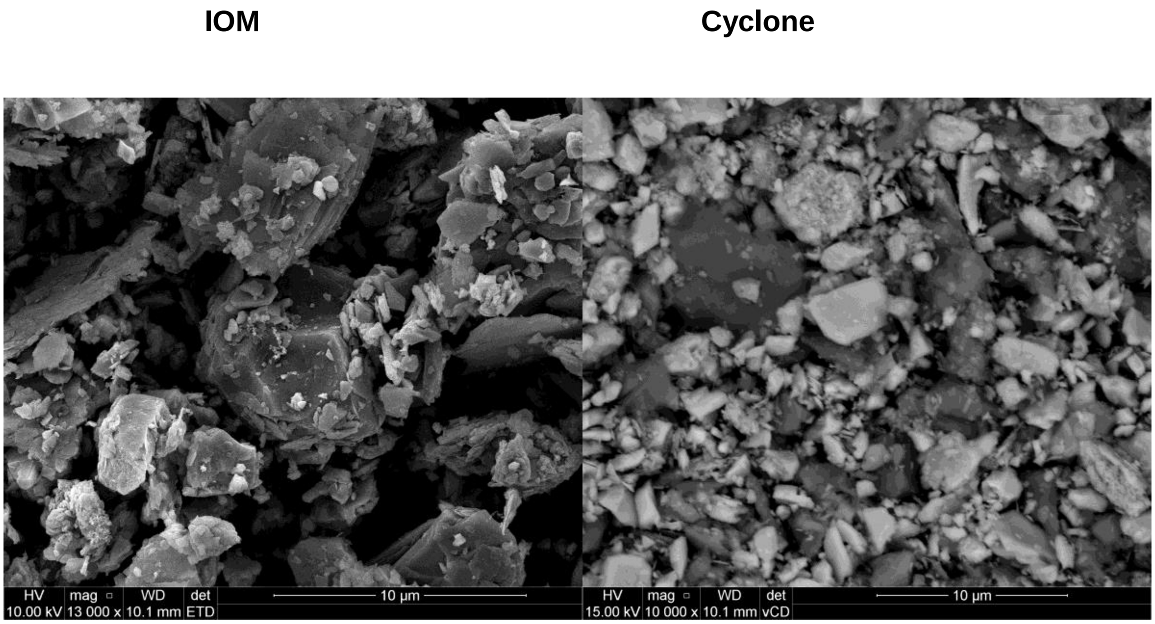
IOM **Cyclone**

Figure 7: Electron microscopy photo illustrating airborne dust at the primary- secondary crusher area taken from IOM sample IOMST5.1 (left) and cyclone sample CYCSTE.3 (Right).

Figure 7 illustrates a SEM photo taken at a 13 000x magnification for the IOM sample, and 10 000x magnification for the cyclone sample. The figure shows how the sizes of airborne dust particles differ between IOM (inhalable) and cyclone (respirable) samples. It is clearly visible that the IOM airborne dust sample contains a higher variety of particle sizes. The cyclone airborne dust sample illustrates smaller- and more even sized particles.

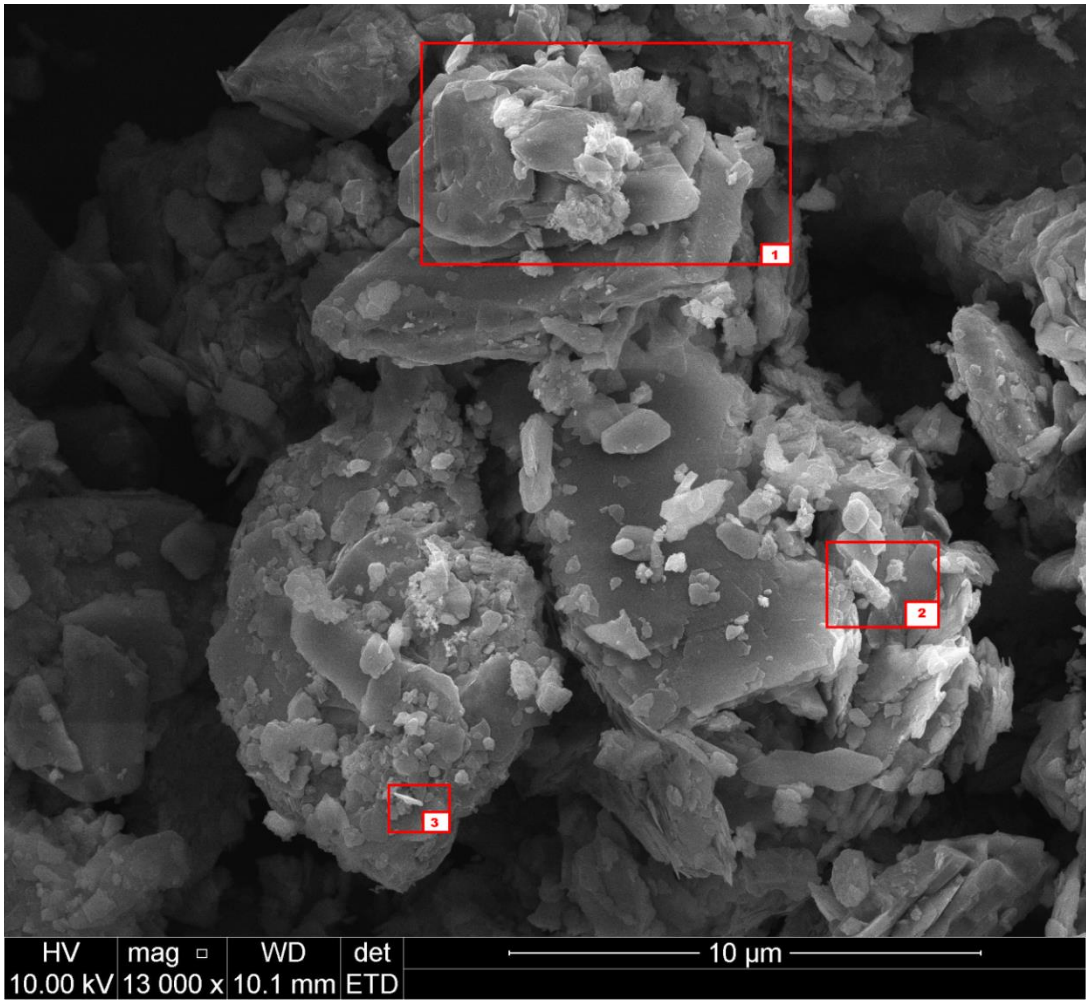

Figure 8: Electron microscopy photo illustrating airborne dust at the primary- secondary crusher area taken from IOM sample IOMST5.1. The highlighted areas represent physical properties such as particle agglomeration (1) and elongated particles (2 and 3).

Table 5: EDS chemical composition of airborne dust at the Primary-secondary crusher area as analysed from IOM sample train IOMST5 and cyclone sample train CYCSTE

Sample media	**Element percentage (%)**							**Total (%)**
	C	**Al**	**Si**	**K**	**Ca**	**Fe**	**O**	
IOM	3.245	4.125	7.06	1.23	0.515	48.97	34.855	**100**
Cyclone	4.27	3.42	6.34	1.09	0.45	48.49	35.94	**100**

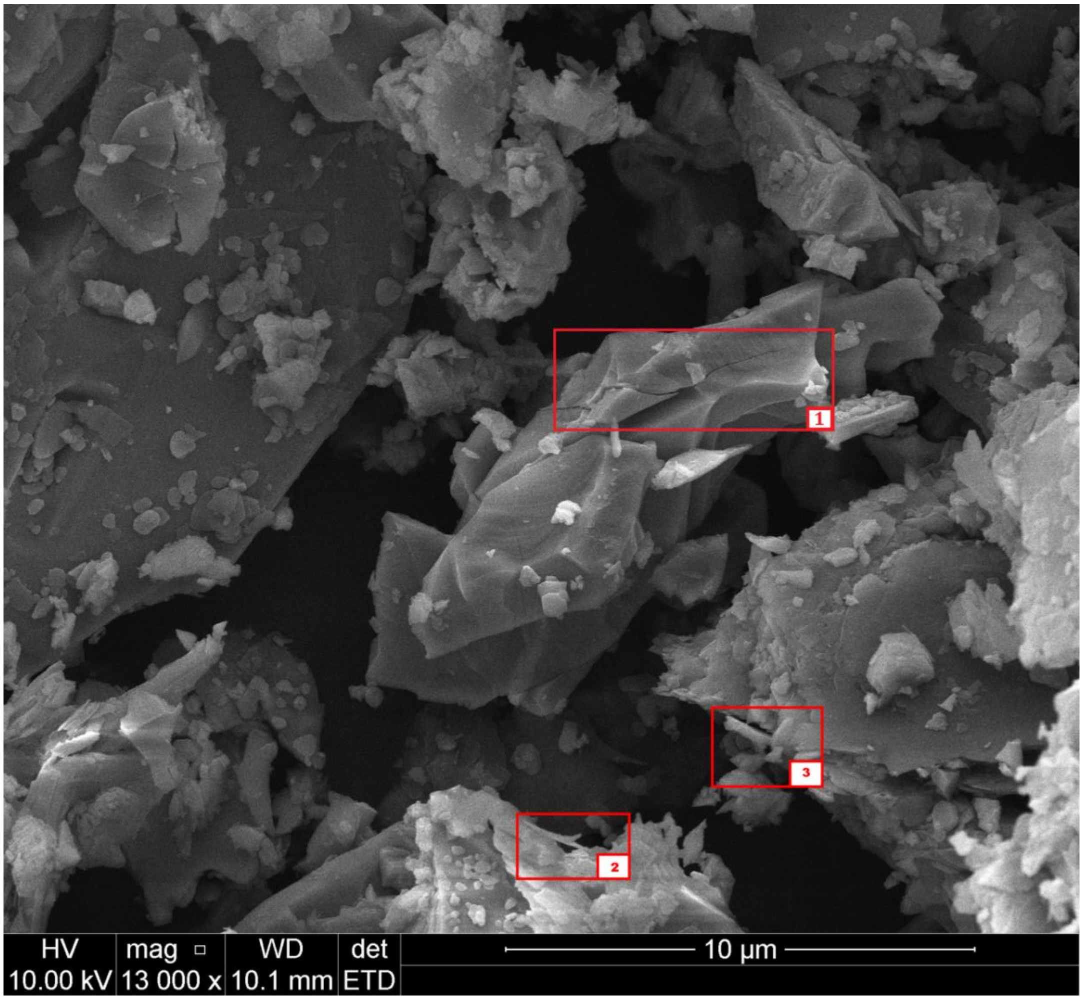

Figure 9: Electron microscopy photo illustrating airborne dust at the Tertiary crusher area taken from IOM sample IOMST1.1 (number 1 represents a hairline fracture in the particle). The highlighted areas represent evidence of breakages of a larger particle by illustrating a hairline fracture (1) and elongated particles (2 and 3).

Table 6: EDS chemical composition of airborne dust at the Tertiary crusher area as analysed from IOM sample train IOMST1 and cyclone sample train CYCSTD.

Sample media	**Element percentage (%)**							**Total (%)**
	C	**Al**	**Si**	**K**	**Ca**	**Fe**	**O**	
IOM	3.94	4.415	9.04	1.24	0.415	43.39	37.565	**100**
Cyclone	3.8	4.63	7.56	1.44	0.61	45.54	36.43	**100**

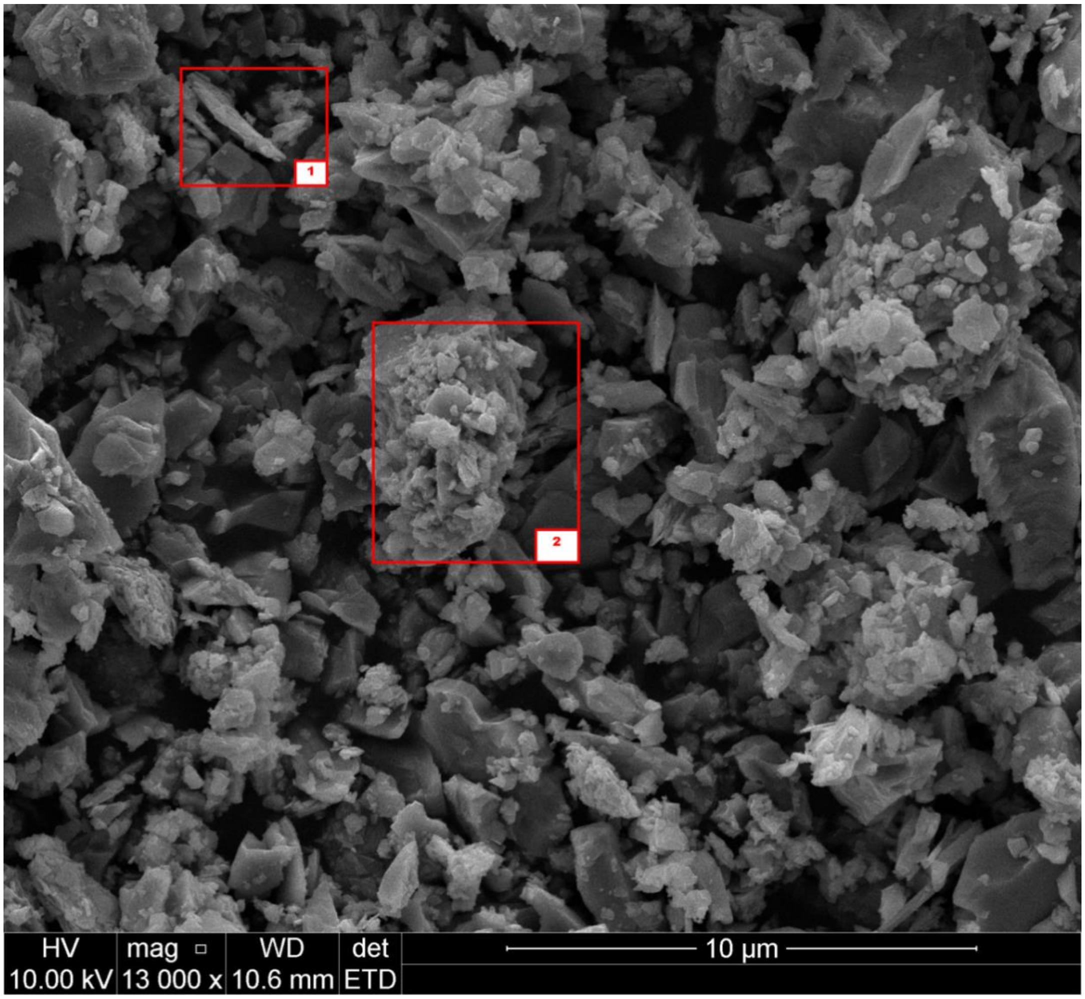

Figure 10: Electron microscopy photo illustrating airborne dust at the Quaternary crusher area taken from IOM sample IOMST10.1. The highlighted areas represent elongated particles (1) and particle agglomeration (2).

Table 7: EDS chemical composition of airborne dust at the Quaternary crusher area as analysed from IOM sample train IOMST10 and cyclone sample train CYCSTJ.

Sample media	**Element percentage (%)**							**Total (%)**
	C	**Al**	**Si**	**K**	**Ca**	**Fe**	**O**	
IOM	3.915	0.925	2.9	0.25	0.22	59.925	31.86	**100**
Cyclone	4.29	4.74	8.93	1.26	0.49	41.98	38.3	**100**

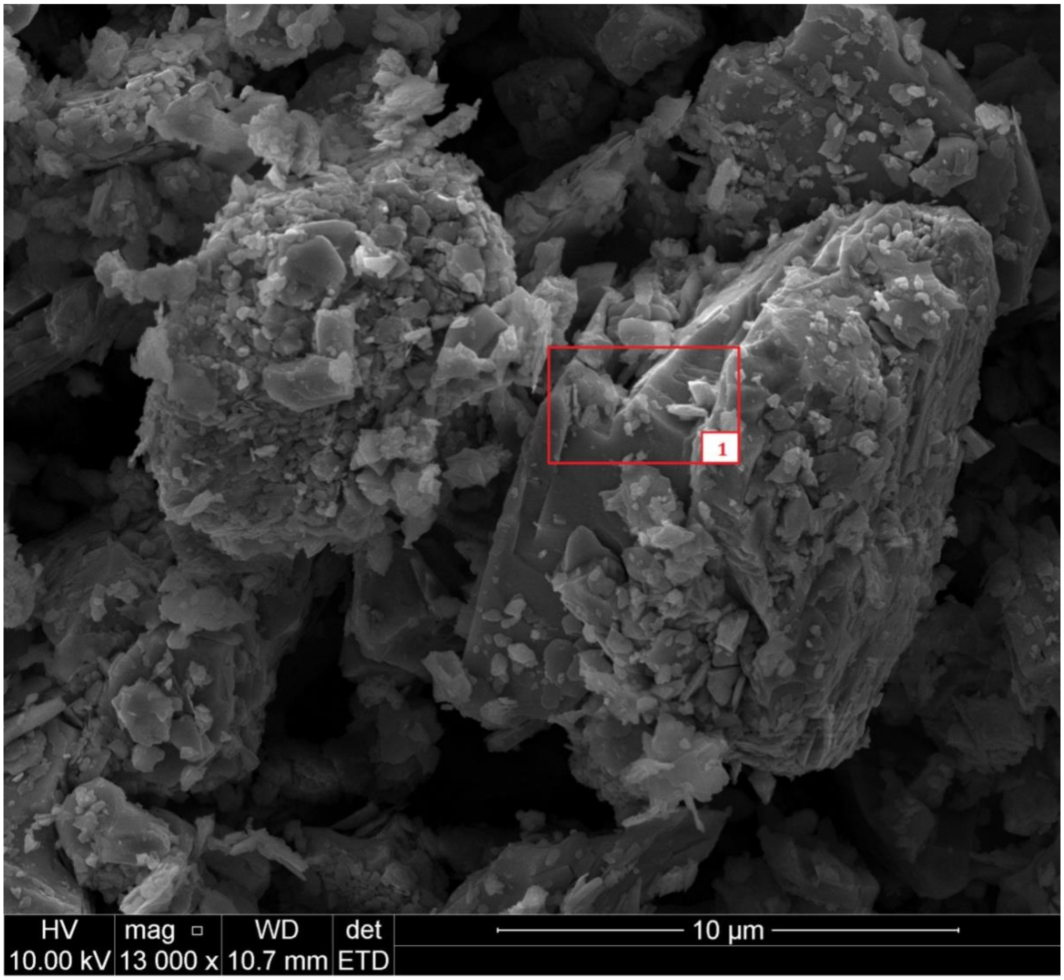

Figure 11: Electron microscopy photo illustrating airborne dust at the Sifting house area taken from IOM sample IOMST8.1 The highlighted area (1) represents a large particle with evidence of particle breakages having occurred.

Table 8: EDS chemical composition of airborne dust at the Sifting house area as analysed from IOM sample train IOMST8 and cyclone sample train CYCSTH.

Sample media	**Element percentage (%)**							**Total (%)**
	C	**Al**	**Si**	**K**	**Ca**	**Fe**	**O**	
IOM	2.805	1.43	2.485	0.425	0.195	62.905	29.755	**100**
Cyclone	18.4	0.42	0.78	0.09	0	23.32	56.99	**100**

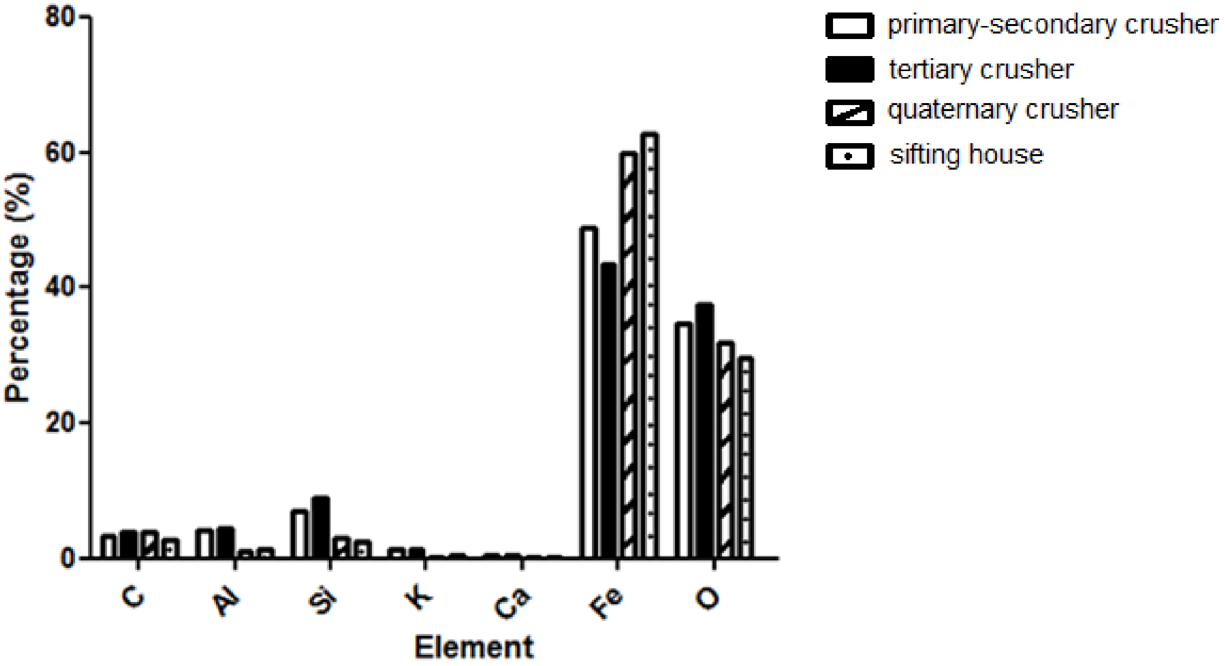

Figure 12: EDS analysis representing the inhalable IOM samples taken at the Primary-secondary crusher, Tertiary crusher, Quaternary crusher and Sifting house areas.

Tables 5 to 8 and Figure 12 illustrate that the majority of the elemental composition found in the IOM inhalable dust samples were iron and oxygen, where iron constitutes more than 40% and oxygen more than 30% at all areas. The highest percentage of iron was found at the Sifting house area where the composition of iron is 62.905 %. It is seen that the iron composition slightly decreases from the Primary-secondary crusher area to the Tertiary crusher area and then increases at the Quaternary crusher and the Sifting house areas. The composition of impurities, such as silica, oxygen, carbon and aluminium, can be seen to decrease at the areas that show an increase in iron composition.

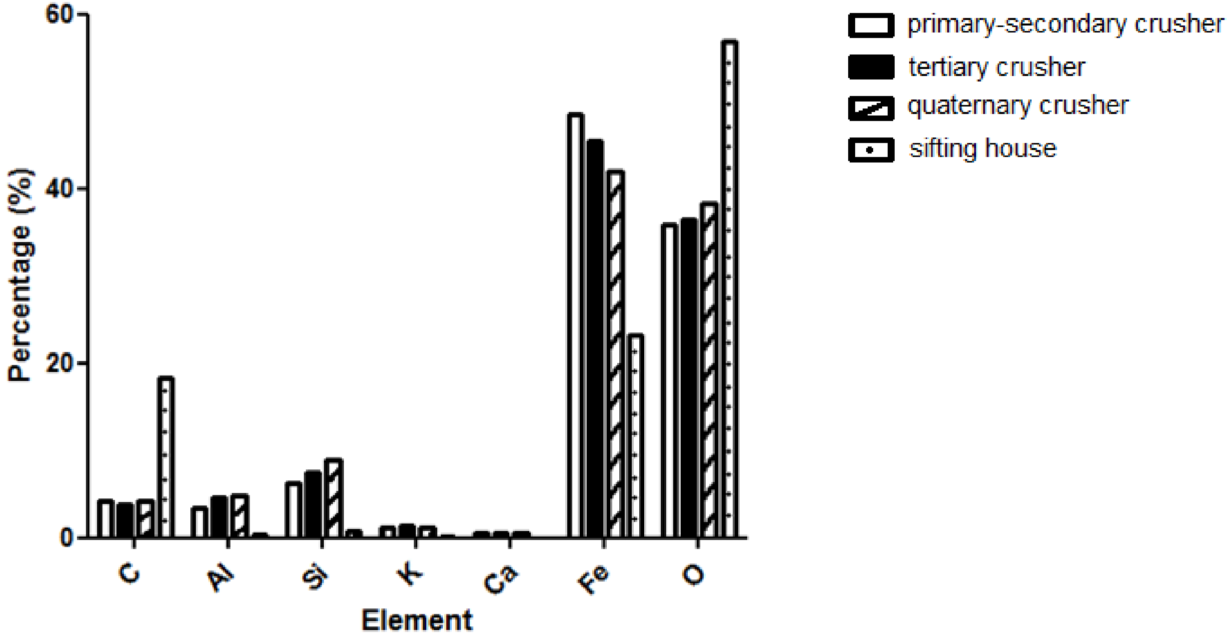

Figure 13: EDS analysis representing the respirable cyclone samples taken at the Primary-secondary crusher, Tertiary crusher, Quaternary crusher and Sifting house areas.

Figure 13 illustrates that the majority of the elemental composition found in the respirable dust samples are iron and oxygen. The respirable elemental composition indicates results proportionate to the results found for the inhalable elemental composition with the only variation found at the Sifting house. The Sifting house illustrates higher elemental percentages for oxygen (56.99%) and carbon (18.4%) as well as lower percentages for iron (23.32%) compared to the other process sites.

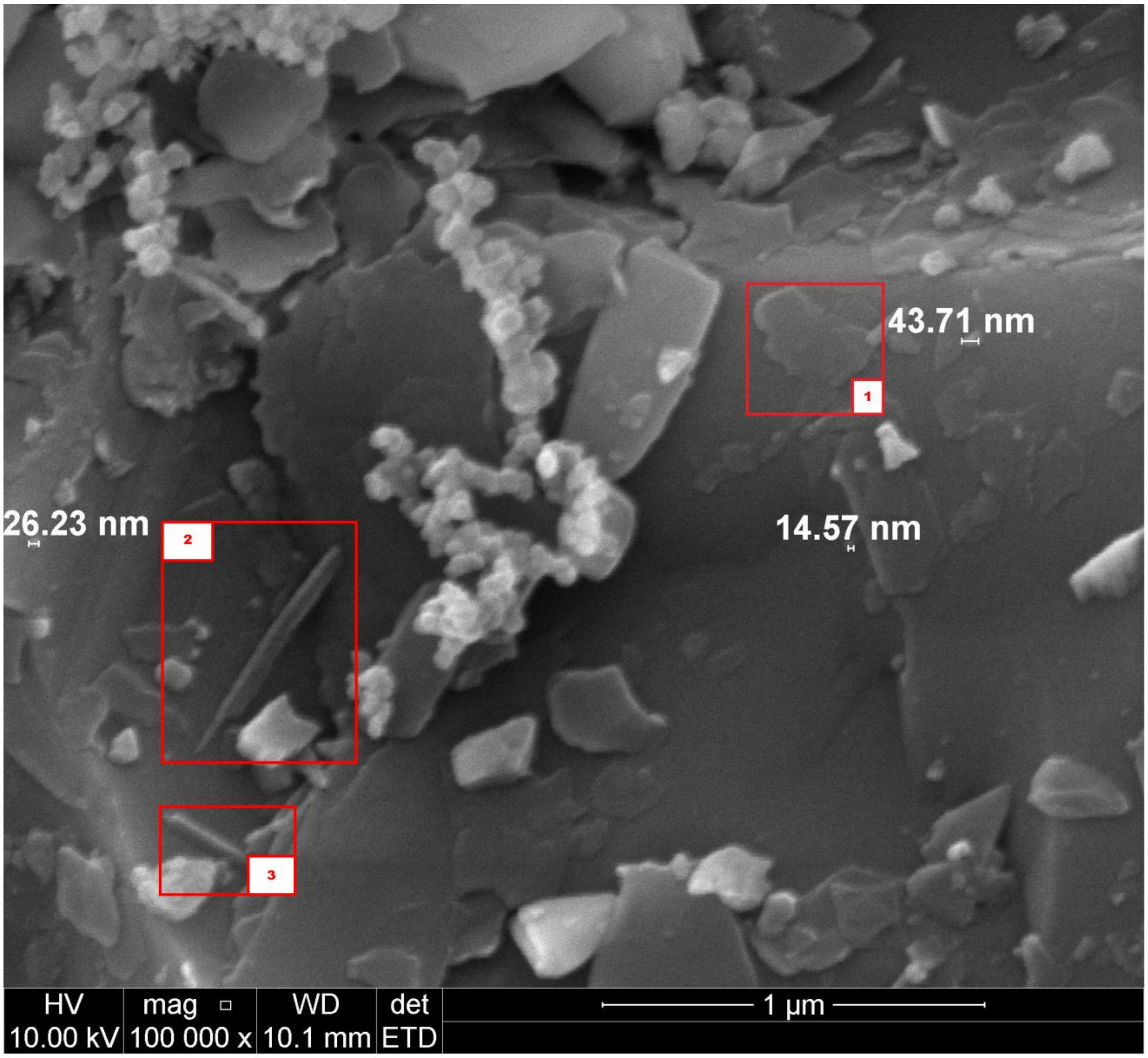

Figure 14: Electron microscopy photo illustrating airborne dust ultrafine particles at the Primary-secondary crusher area taken from IOM sample IOMST5.1. The highlighted areas represent a clay platelet (1) and elongated particles (2 and 3).

Figure 14 represents a SEM photo at 100 000x magnification taken from an IOM airborne dust sample which is coated with a gold-palladium coating. The photo clearly illustrates that there are numerous ultra-fine particles, almost all of which are smaller than 1 micron, some even as small as 14.57 nm. The shape of these particles is irregular; some showing triangular sharp edges – the points of which are slightly rounded. Even though there are independent particles, the photo clearly illustrates particles bonded together in an agglomerated state as can be seen in the centre of the photo. Highlighted area 1 shows a clay platelet. Highlighted areas 2 and 3 illustrate elongated particles.

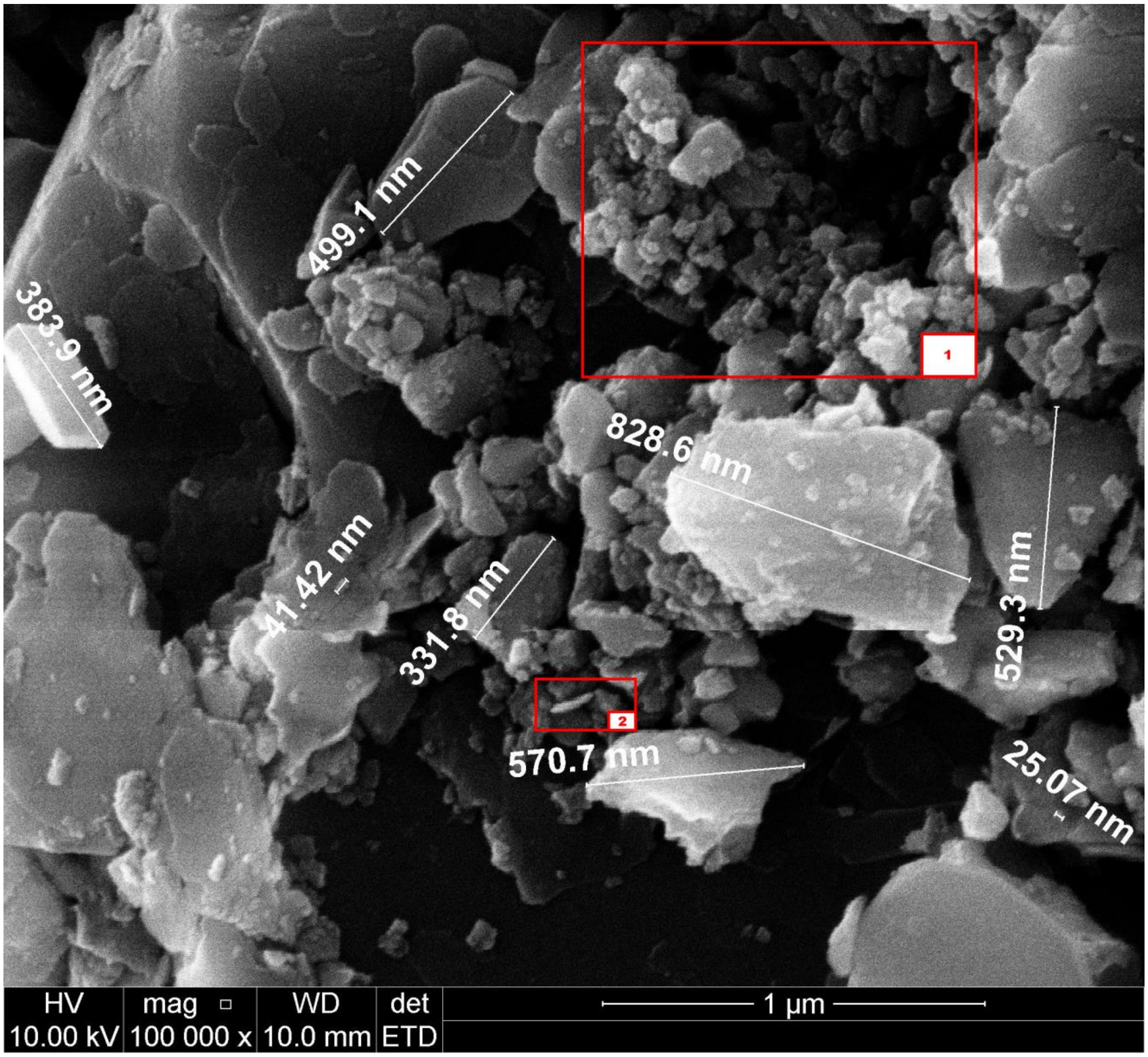

Figure 15: Electron microscopy photo illustrating airborne dust nano and ultrafine particles at the Tertiary crusher area taken from IOM sample IOMST1.1.

Figure 15 represents a SEM photo at 100 000x magnification taken from an IOM airborne dust sample which is coated with a gold-palladium coating. There are numerous nano and ultrafine particles, ranging in sizes from as large as 829.6 nm to 25.07 nm. The shapes of the particles are irregular, with most particles having blunted edges. There are a small number of independent particles, but most of the particles are in an agglomerated state as seen by highlighted area 1. Highlighted area 2 illustrates an elongated particle.

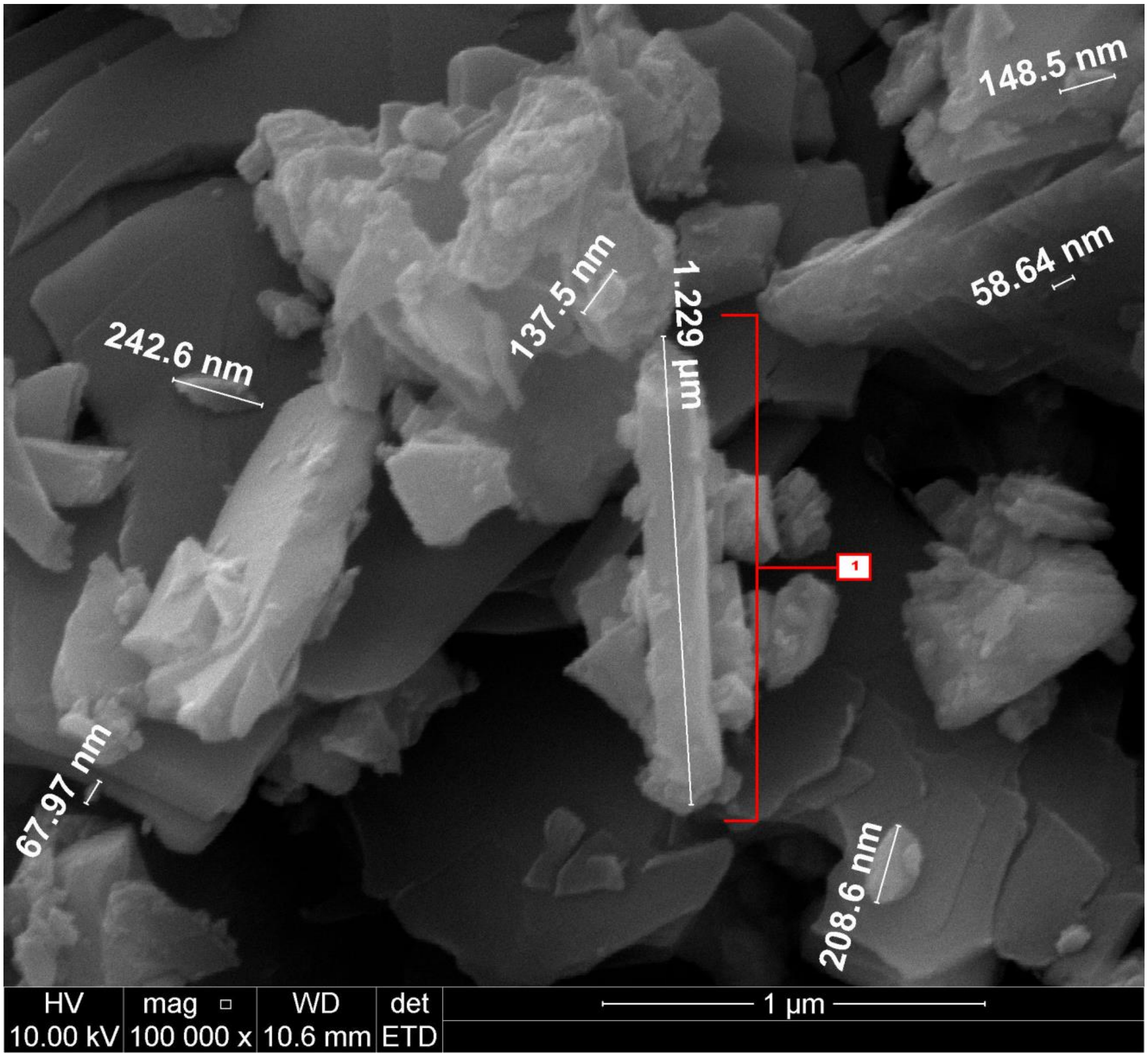

Figure 16: Electron microscopy photo illustrating airborne dust nano and ultrafine particles at the Quaternary crusher area taken from IOM sample IOMST10.1.

Figure 16 represents a SEM photo at 100 000x magnification taken from an IOM airborne dust sample which is coated with a gold-palladium coating. The particles represented in the photo range in sizes between 1.229 µm and 67.97 nm. The shapes of the particles are irregular, some of which are elongated and others more rounded. There are some independent particles, but most are in an agglomerated state. Highlighted area 1 illustrates a large elongated particle.

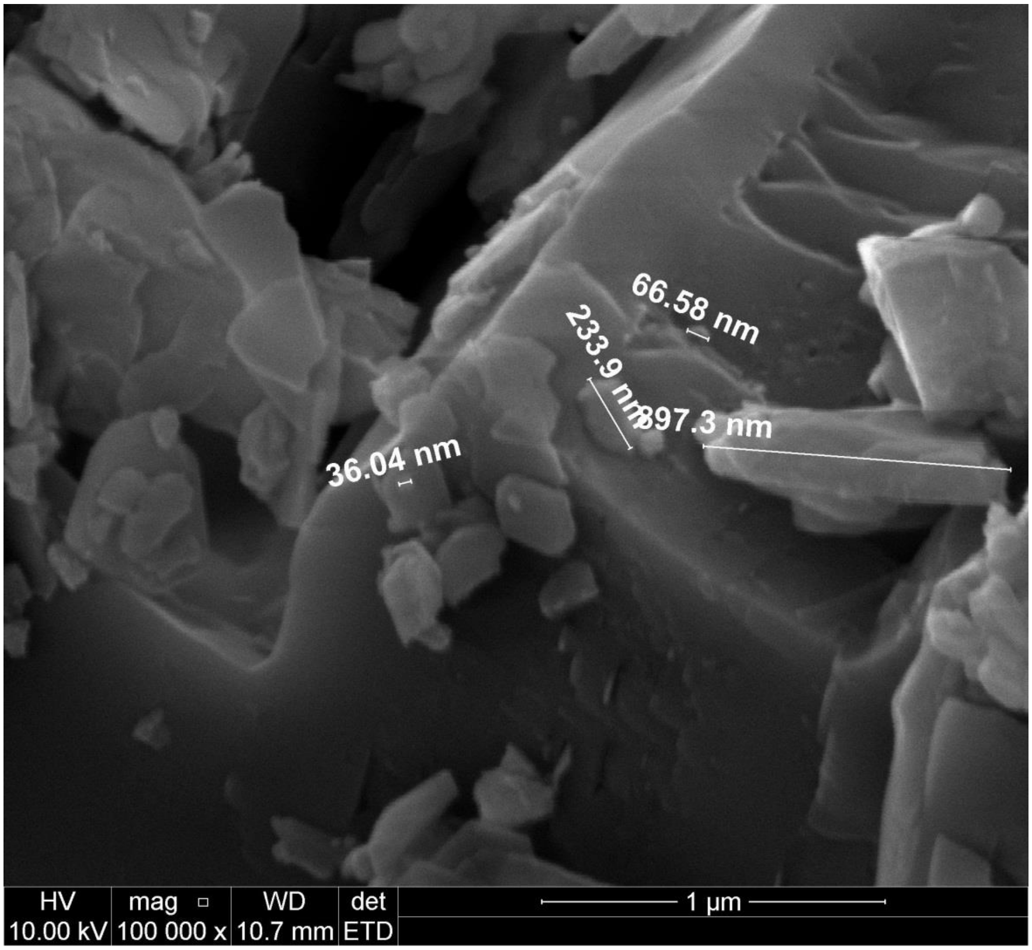

Figure 17: Electron microscopy photo illustrating airborne dust nano and ultrafine particles at the Sifting house area taken from IOM sample IOMST8.1.

Figure 17 represents a SEM photo at 100 000x magnification taken from an IOM airborne dust sample which is coated with a gold-palladium coating. The photo clearly illustrates one large particle in the centre that, near to the top right hand side of the photo, shows evidence of areas where smaller pieces have broken off. There are smaller particles ranging in sizes of 897.3 nm to 36.04 nm that are in an agglomerated state with each other as well as the larger micron particle. The particles have irregular shapes, most having rounded edges.

Discussion

Gravimetrical data

Table 1 represents the mass concentrations for respirable airborne dust sampled at the four process areas. The Occupational Health and Safety Act 85 of 1993: Regulations for Hazardous Chemical Substances states that the occupational exposure limit (OEL) for respirable airborne dust is 5 mg/m^3. The results indicate that the mass concentration of the samples taken at the Tertiary crusher, Quaternary crusher and Sifting house process areas is lower than the OEL, with only the Primary-secondary crusher area rendering concentrations that exceed the OEL. The sampling was conducted to obtain airborne dust concentrations through static sampling, not personal sampling. Thus the results indicate that even for maximum exposure, the respirable airborne dust generated at three of the four areas has acceptable exposure lower than the OEL.

Table 2 represents the mass concentrations for inhalable airborne dust sampled at the four process areas. The Occupational Health and Safety Act 85 of 1993 states that the OEL for inhalable/total airborne dust is 10 mg/m^3. As previously stated, the sampling was conducted with the aim of obtaining the maximum airborne dust samples, thus static sampling and not personal sampling was conducted. Unlike the results obtained from the respirable airborne dust samples, the inhalable dust samples present mass concentrations that surpass the prescribed OEL to a great extent. The reason for such high inhalable mass concentrations at the process areas can be attributed to the open faced IOM cassettes that were placed in areas that would yield a maximum concentration of airborne dust over an extended period of up to 8 hours. The exposure of the airborne dust to the static sampling equipment for such an extended time period will probably yield results that will be higher than the recommended OEL for personal sampling.

The results obtained from the respirable- and inhalable static samples indicate that there is a possibility of the workers in the process areas being over exposed to airborne dust, and thus the possibility that fine particles and UFPs may affect the workers' health.

SEM and EDS analysis

The SEM and EDS analyses of the sampled airborne dust at the process areas of the iron ore mine brought forth a large amount of information concerning airborne iron ore dust characterisation. As seen in Figures 4 to 8 and 11 to 14, the results obtained from the SEM revealed that there is a vast concentration of airborne particles with the majority ranging in size between 14.57 nm and < 50 µm. Figure 3 represents a comparison between SEM photos taken from both IOM and cyclone samples at a higher magnification to indicate the difference in size between the airborne dusts sampled. There is a clear indication of larger particles in the IOM samples as to the smaller, more even sized particles of the cyclone samples. This can be attributed to the cyclone samples being more biased concerning the sampling sizes as the cyclone sampling train is designed to capture respirable particles at a 50% cut point of 4 µm as to the inhalable particle IOM sampling train having a 50% cut point of 100 µm. As stated in the methodology, the 2 different sampling trains were used for the purpose of comparing the inhalable dust samples with the respirable dust samples to see if their elemental composition would yield different results when undergoing SEM and EDS analysis. Tables 5 – 8 and Figures 12 and 13 represent the EDS analysis of both the IOM and cyclone samples at the 4 process area sites. These tables clearly indicate that even though the samples were obtained from different sampling trains, there are no substantial differences concerning the elemental composition between the inhalable and respirable samples. The data does show that there is a rise in inhalable iron elemental percentage and a decrease in respirable iron elemental percentage as the ore moves through the beneficiation process. This indicates that the majority of the iron is found in the larger micrometer particles and that the smaller micrometer and sub-micrometer particles contain more impurities. Table 8 does yield different results between the inhalable- and respirable samples compared to the consistency found in Tables 5 to 7. Relating to the inhalable samples of Table 8, it is clear that the results obtained from the respirable samples at the Sifting house area do not adequately represent the iron ore airborne dust. Currently this phenomenon can only be explained by the very low concentrations of dust on the cyclone filters that caused a poor transfer of dust to the SEM stubs and consequently opening up the carbon on the double- sided carbon tape for the analysis by the EDS. Table 8 clearly illustrates a higher elemental percentage of carbon than can be found in Tables 5 to 7 which may be an indication of insufficient coating of the carbon coated stub due to the insufficient amount of airborne dust captured by the cyclone sampling train.

The particle characterisation through SEM and EDS analysis rendered valuable information concerning the airborne iron ore dust. Characterisation of physical- and chemical aspects of airborne iron ore dust was conducted at 4 process area sites. These aspects will be discussed separately in accordance to the data obtained from these sampled areas.

Physical aspects

Particle size and distribution

SEM photos taken from samples obtained at the primary crusher area, as illustrated in Figure 8, indicate that most of the individual particles found, are smaller than 10µm. The same results have been found for the Tertiary crusher, Quaternary crusher and Sifting house areas, as illustrated in Figures 9, 10 and 11.

Table 3 and Figure 4 illustrate the measurements taken with the CPC particle counter and table 4 and Figure 5 illustrate the measurements taken with the OPC particle counter. These results indicate that there are a number of particles present between the size ranges of 10 nm to 10 µm. Figure 5 illustrates that the highest concentration of particles found, at all process areas, to be of sizes smaller than 0.3 µm, with the lowest concentration at 10 µm. This finding opens up new challenges for measuring dust exposure during the processing of mined iron ore and may well have ramifications into the physiological influences of exposure to iron ore dust, as iron is a transition metal that can increase cellular free radicals and subsequently the risk of DNA damage and cancer.

There are as yet no official standards for air quality concerning particle counts. However, a comparison can be made to cleanroom standards such as the ISO 14644 cleanroom standards. The ISO 14644 cleanroom standard states that a Federal Standard 290E class 100 000, the least clean of all the classes, represents a particle count of no more than 1.02E+07 p/m^3 for particles ≥ 0.3 µm (Whyte, 2010; Ensor and Dixon, 2011). If this value is compared to the results found at the four process areas which all exceed the class 100 000 standard threshold, it is clear that the particle count at these areas is considered very high and will lead to over- exposure of sub-micron particulates and UFPs to workers in these areas.

Figure 6 shows that as the ore moves through the processes, the size distribution curve shifts to the left, indicating that there are a higher number of particles in the UFP size range than particles in the micron size range. This can be contributed to the crushing processes giving rise to finer dust as the ore quality of the dust becomes higher. This information is consistent with the results obtained by EDS analysis, which will be discussed later on. As illustrated by Figures 14 to 17 of the SEM analysis, as well as Figures 4 to 6 detailing the results of the particle counters, there are UFPs smaller than 100 nm present in the dust samples, some as small as 14.57 nm. The small size of UFPs causes these particles to behave like a gas, which means that UFP can more easily be exhaled than particles of a larger size (Webster, 2009). This also leads to the majority of UFP deposition taking place in the upper respiratory tract, however UFPs with a particle size of 20 nm have an alveolar deposition of 50% as seen in Figure 18 (Buzea *et al.,* 2007; van Berlo *et al*., 2012).

Clearance mechanisms of the pulmonary system are able to clear the deposited particles from these sites, however over- exposure to airborne dust over extended periods may prove to overwhelm the pulmonary clearance mechanisms, leading to the generation of lung pathologies (Maynard and Kuempel, 2005; Buzea *et al.,* 2007).

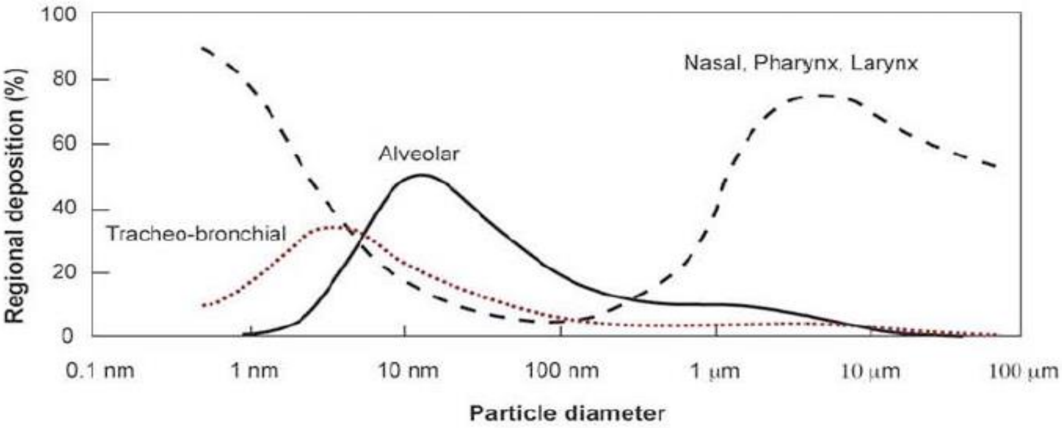

Figure 18: Deposition of inhaled particles in the human respiratory tract versus the particle diameter (Buzea *et al.* 2007).

Particle shape and agglomeration

Through use of SEM analysis it was found that the particle shapes were irregular and not consistent. The Figures representing the SEM photos indicate that the particle shapes range from spherical to rectangular, some portraying sharp edges while others portray more rounded edges. This phenomenon can probably be contributed to constant particle collision leading to mechanical breakdown of particle size and edges. Figure 11 and 17 represent large particles that show clear signs of breakage, as well as Figure 9 which illustrates one of the larger particles having a hairline fracture, which would eventually lead to particle breakdown (WHO, 1999). The clay platelets found in the dust samples as seen in Figure 14, have the ability to envelop smaller particles, thus covering the particles completely which may possibly explain the rounded edges. This can especially be seen in Figures 14 to 17 which focus on UFPs.

Figures 8 to 11 illustrate that particle agglomeration largely occurs with smaller particles clinging not only to each other, but to the larger particles as well, almost entirely coating some of the larger particles. The particle agglomeration can be attributed to the magnetic properties of the particles' chemical compounds. The level of agglomeration can have a positive effect on the physiological system where smaller particles that can enter the lung alveoli individually, are clustered together to form a larger particle which will have a lower SSA and thus a lower surface reactivity (Maynard and Pui, 2007; Asmatulu *et al.*, 2013). When clustered to form an agglomerative state, nanoparticles may behave as larger particles depending on the size of the agglomeration (Maynard and Kuempel, 2005; Buzea *et al.,* 2007). The larger agglomerated particle can then be excreted through the pulmonary mucociliary clearance mechanism. Particle agglomeration may thus lower the risk for the individual particle toxicity on the physiological system.

However, not all particles are bonded together, as individual particles can be seen in Figures 8 to 11.

Figures 8 to 10 and 14 to 16 illustrate the presence of elongated particles in the airborne iron ore dust. These elongated particles are possibly splinters that originate from breakages due to collision of the dust particles.

Chemical properties

Characterisation of the airborne iron ore dust chemical properties will include the elemental composition through use of EDS analysis, as well as the possible compounds that these elements might form.

EDS analysis

The EDS analysis carried out on samples collected at the 4 process areas all yield the exact same elemental composition, but at different percentages of quantity. It is found that the majority of airborne iron ore dust contains the following elements:

- Carbon (C)
- Aluminium (Al)
- Silicon (Si)
- Potassium (K)
- Calcium (Ca)
- Iron (Fe)
- Oxygen (O)

Figure 12 and figure 13 represent an illustration of the quantity percentage of elements found at the four process areas. It is clearly visible that the elemental bulk of the airborne iron ore dust consists of Fe and O. The analysis of the dust rendered data that can probably indicate an increase in the quality of the iron ore as the ore progresses through the process areas by the increase of the desirable Fe content when comparing the sites from the primary crusher to the Sifting house. There is however a slight decrease in airborne dust Fe content at the Tertiary crusher. This finding may be due to uncontrollable environmental conditions, such as strong shifting winds that could have blown non- process airborne dust into the sampling area. This finding, coupled with the possibility of the crusher not constantly running throughout the shift, as well as the high silicon content found in the dust sample, contribute to the conclusion that there was non-process dust mixed with the process dust in the sample.

Possible chemical compounds

Before continuing with the discussion on possible chemical compounds, it should be stated that the results obtained from the SEM and EDS analysis enables us to determine the elements found in the airborne iron ore dust but does not enable us to determine the chemical compounds of these elements. This information can only be based on previous research done on such subjects, which is why only possible chemical compounds can be discussed.

The iron ore mined at the site primarily consists of hematite (Fe_2O_3), also called iron oxide. As can be seen by the chemical formula, hematite consists of the elements Fe and O. This is consistent when observing the results obtained in Figures 12 and 13 which illustrate that the majority of the airborne dust consists of Fe and O. Acute effects of overexposure to iron oxide include irritation of the nose, throat and lungs. Overexposure to iron oxide particles over extended periods will lead to iron particles accumulating in the lungs which may lead to iron pneumoconiosis, or siderosis (Karmis, 2001, Fishwick, 2011; Ratney, 2011).

Another possible chemical compound that can be found in the airborne iron ore dust is crystalline silica (SiO_2), also called silicon dioxide. Figures 12 and 13 of the EDS analysis illustrate that the Si content in the dust samples is third highest in quantity, next to Fe and O. Even so, the Si quantity of the dust samples still accounts for less than 10 % at all the sampled process areas. Exposure to SiO_2 can lead to the development of silicosis (Lippmann and Chen, 1998; Absher, 2012; Acton, 2013). The aluminium present in the sample dust can bind with silicon to form aluminosilicates, which is a typical compound of natural clay. Clay platelets can be seen in the photos taken by the SEM, as illustrated in Figure 14.

Health impact

Over- exposure to airborne iron ore dust could lead to various negative physiological impacts. The results found through EDS analysis clearly indicate that the airborne dust found at the iron ore mine consists largely of iron. As stated by Buzea *et al.* (2007), metal- rich dust has the capacity to generate reactive oxygen species (ROS) on the surface of the lungs which can lead to scarring of the lung tissue. ROS have the ability to damage cells through various mechanisms such as by peroxidising cell membrane lipids, altering proteins, disrupting DNA, interfering with signalling functions and modulating gene transcriptions (van Berlo *et al.,* 2012). Scarring of the lung tissue due to ROS generation can also have effects on cell respiration, metabolism, ischemia/reperfusion, inflammation and the metabolism of foreign compounds.

UFPs found at the sampled areas have the ability to cross the pulmonary barrier and enter the lung circulatory- and lymphatic system (Oberdorster *et al.,* 2005; van Berlo *et al.,* 2012). Once the UFPs are in these afore mentioned systems, they can be distributed to various body tissues and organs.

The deposition and accumulation of the iron oxide particles in the lung tissue (macrophage uptake) is known as the pathology siderosis. Siderosis is a form of pneumoconiosis that can be associated with silicosis among iron ore miners if there is over- exposure to silica, termed sidero-silicosis, leading to fibrotic changes and deterioration of the pulmonary function.

Conclusion

The pilot study concerning the characterisation of airborne iron ore dust particles at a South African opencast iron ore mine gave rise to valuable information pertaining to the physical- and chemical aspects of the airborne iron ore dust. It is clear that there are differences between the physical- and chemical aspects of the airborne iron ore dust sampled at the four different process sites.

The physical characterisation of the airborne dust indicates high mass concentration levels of inhalable airborne dust found at the four process areas as well as high levels of respirable dust at the primary- and secondary crusher area. The particle size distribution sampling conducted with the use of the particle counters indicates that the majority of the particles in the airborne dust range in size smaller than 0.3 µm, with the highest concentration of particles found at the Sifting house area. SEM analysis indicates that the airborne iron ore dust is greatly affected by particle agglomeration where smaller individual particles group together to form larger particles. SEM analysis also indicates the presence of particle splinters that have fibre like qualities. These splinters originate as a result of particle collisions leading to breakages as evidenced by photos taken with the SEM that clearly represent this phenomenon.

Chemical characterisation of the airborne particles through the use of EDS analysis indicates that the majority of the airborne dust consists of the following elements: carbon, aluminium, silicon, potassium, calcium, iron and oxygen. However the percentage amount of each element differs from each process area sampled. The elemental percentage of iron increases and the percentages of the silicon, aluminium and carbon impurities decrease as the ore moves through the beneficiation process from the primary- and secondary crusher to the Sifting house.

This phenomenon coupled with the chemical- and physical aspects of the dust indicates a high level of exposure to the lower areas of the human pulmonary system, which in turn may overwhelm the mucociliary clearance mechanisms of the lungs, generate ROS, and lead to the development of pulmonary pathologies such as siderosis, silicasiderosis and even lung cancer. The UFPs found through SEM analysis show that the size of these particles found in the samples is a clear indication that these particles have the ability to cross into the pulmonary-, circulatory- and lymphatic systems where they can spread through the body and cause oxidative stress and organelle damage. This however is only speculation as to the effects that airborne iron ore dust may have on the physiological system. For more accurate results of the role the dust may play in physiological pathology of workers operating in such areas, personal sampling of airborne iron ore dust should be conducted and a biological sampling program should be implemented to determine the respiratory- and systemic exposure of workers working at the opencast iron ore mine.

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CHAPTER 4

CONCLUDING CHAPTER

4.1. Further discussion and final conclusion

The aims and objectives of this study were to characterize and compare the physical- and chemical aspects of airborne particulate matter at the primary- secondary crusher, Tertiary crusher, Quaternary crusher and Sifting house process areas of an opencast iron ore mine with the use of inhalable- and respirable particle samplers, particle counters, SEM microscopy and EDS analysis. The results concerning physical characterisation of the airborne particles indicate high mass concentration levels of inhalable dust at all four process areas, with the highest mass concentration level found at the primary- secondary crusher having a concentration of 143.638 mg/m^3. High levels of particle mass concentration for respirable airborne dust were only found at the primary- secondary crusher area with a value of 6.855 mg/m^3. If comparing these results to the OHSA threshold for respirable and inhalable dust, which is 5 mg/m^3 and 10 mg/m^3 respectively, it is clearly seen that over- exposure to airborne dust is a concern. Particle size distribution results showed that the majority of particles found at all four process areas are <0.3 µm in size indicating that workers are mostly exposed to sub-micrometer particulate fractions. SEM analysis indicates that particle agglomeration largely occurs in the airborne iron ore dust. Particle splinters were also detected which may originate as a result of particle collisions leading to breakages and thus splinter formation. Chemical characterisation through EDS analysis showed that the majority of the elemental makeup of the airborne dust consists of iron, oxygen, carbon, aluminium, silicon, potassium and calcium. The elemental percentage at each process area differs, resulting in an increase of iron and a decrease in silicon, aluminium and carbon impurities as the ore moves through the stages of the beneficiation process starting at the primary- secondary crusher and ending at the Sifting house. When taking these physical- and chemical characteristics into account, it is clear that there is a high risk of over exposure to the lower areas of the human pulmonary system that may render the physiological defence mechanisms of the lungs ineffective, leading to the formation of ROS (Buyukhatipoglu and Clyne, 2011) and the development of pathologies such as siderosis, silicasiderosis and lung cancer. UFP SEM analysis indicates that the particles have the ability to cross over to the pulmonary- circulatory- and lymphatic systems (Oberdorster *et al.,* 2005; van Berlo *et al.,* 2012), thus leading to the particles spreading through the body and causing oxidative stress and organelle damage (Buzea *et al.,* 2007).

4.2. Addressing of hypothesis

In chapter 1 the hypothesis stated that particulate matter found in airborne dust at four different process areas of an iron ore mine will yield different results as to their physical- and chemical properties. From the results obtained it is seen that airborne dust at the four different process areas do show differences in their physical- and chemical properties, although they do not differ completely, as physical- and chemical similarities were also found. This is seen by the physical properties of the airborne dust having different mass concentrations and particle size majorities at each process site, but sharing the same physical properties of particle agglomeration and shape. It is also seen that the airborne dust at each process area has the same chemical composition but yields different elemental percentages. Given these results, the hypothesis of the particulate matter found in airborne dust at four different process areas of an iron ore mine yielding different results as to their physical- and chemical properties, is confirmed. However the hypothesis should be improved by including that the physical- and chemical properties do not differ completely and share some similarities.

4.3. Potential hazards and health effects

The results obtained from the inhalable- and respirable mass concentration data indicate that the airborne iron ore dust may lead to potential worker over-exposure to airborne iron ore dust that can lead to adverse health effects, such as the development of COPDs like pneumoconiosis and siderosis. This pilot study however, has revealed results obtained through the use of particle counters, SEM and EDS analyses which indicate that sub-micron particles are largely present in the airborne iron ore dust found at the process areas of an opencast iron ore mine. These results indicate that sub-micrometer particle exposure of workers is a great concern regarding adverse health effects, as these particles may not only have an influence on the human respiratory tract but can transverse into the systemic circulation of the body where it can lead to the development of ROS, causing oxidative stress and organelle damage (Oberdorster *et al.,* 2005; Buzea *et al.,* 2007; van Berlo *et al.,* 2012). This pilot study thus shows the need for more in-depth studies to be conducted concerning sub-micron particles found in airborne dust and their impact on human health, so that the protective measures concerning worker health can be optimized.

4.4. Challenges in this study

As the focus on nanoparticulates in the occupational hygiene setting is still relatively new, the literature and other studies concerning nanoparticle exposure are still in short supply, especially as there are currently no OELs concerning sub-micrometer particles due to the lack of knowledge concerning sub-micrometer and nanoparticle toxicology. This is the reason for the launch of this pilot study: to act as a foundation for the development of future studies.

The equipment that was used in this pilot study gave rise to various difficulties, such as spoiled samples obtained due to the numerous malfunctions of some of the Gilian® pumps - failing to operate or not operating for the duration of the scheduled sampling periods. Even though enough backup samples were taken in case of such an event, these malfunctions may prove to be problematic in future studies. Sampling conducted with the use of the CPC was also affected by the device malfunctioning during the sampling of the Sifting house area, which led to data obtained from only two process areas being used in the study. Environmental factors such as rain, strong winds and changing wind directions led to the inability of some of the cyclone- and IOM samplers to capture sufficient airborne dust for the transfer of the dust from the filters to the SEM stubs.

The sampling conducted could have been improved if there were no financial limitations. Expensive devices such as low pressure impactors would have improved the sampling process by acquiring samples with more ease, as well as giving more accurate results by improving the capturing and particle size analysis.

4.5. Future investigations on characterisation of airborne iron ore dust

The characterisation of airborne iron ore dust can be improved through future studies by focussing on the following aspects:

It is recommended that the sampling be intensified and conducted throughout the year to adequately compare results to seasonal changes which will thus lead to an improved understanding of the workers' health which may be affected by airborne dust micrometer- and sub-micrometer exposure.

Future studies should include static sampling integrated with personal sampling and personal biological sampling, (particle concentrations in blood and urine samples) to adequately represent the workers' exposure to airborne dust, and the effect that the dust may have on the workers' health.

Studies conducted with better sampling equipment will yield more accurate results. The use of low pressure impactors, such as the Dekati® Low Pressure Impactor, will enable the user to divide the particulate sizes into 13 categories ranging from 30 nm to 10 µm. This will lead to an improvement of physical- and chemical particle characterisation (Marjamäki *et al.,* 2000; Van Gulijk *et al.* 2004).

4.6. Recommendations

The information obtained in this pilot study provides a foundation for the importance of particle characterisation coupled with a particle size selective sampling program in the iron ore mining industry, which can be utilized for determining a better, more updated, sampling strategy to effectively reduce airborne particulate exposure of workers. This information can also be used to establish an updated risk assessment for the process areas.

The training of workers needs to be updated to include particle- size exposure education which will inform the workers on exactly what the air they breathe contains and how the exposure influences their physiological system and affects their health. This will lead to better informed workers who will understand the principle of the sampling and PPE systems, thus giving the worker cause to adhere to these systems instead of only being instructed to do so.

4.7. References

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CHAPTER 5

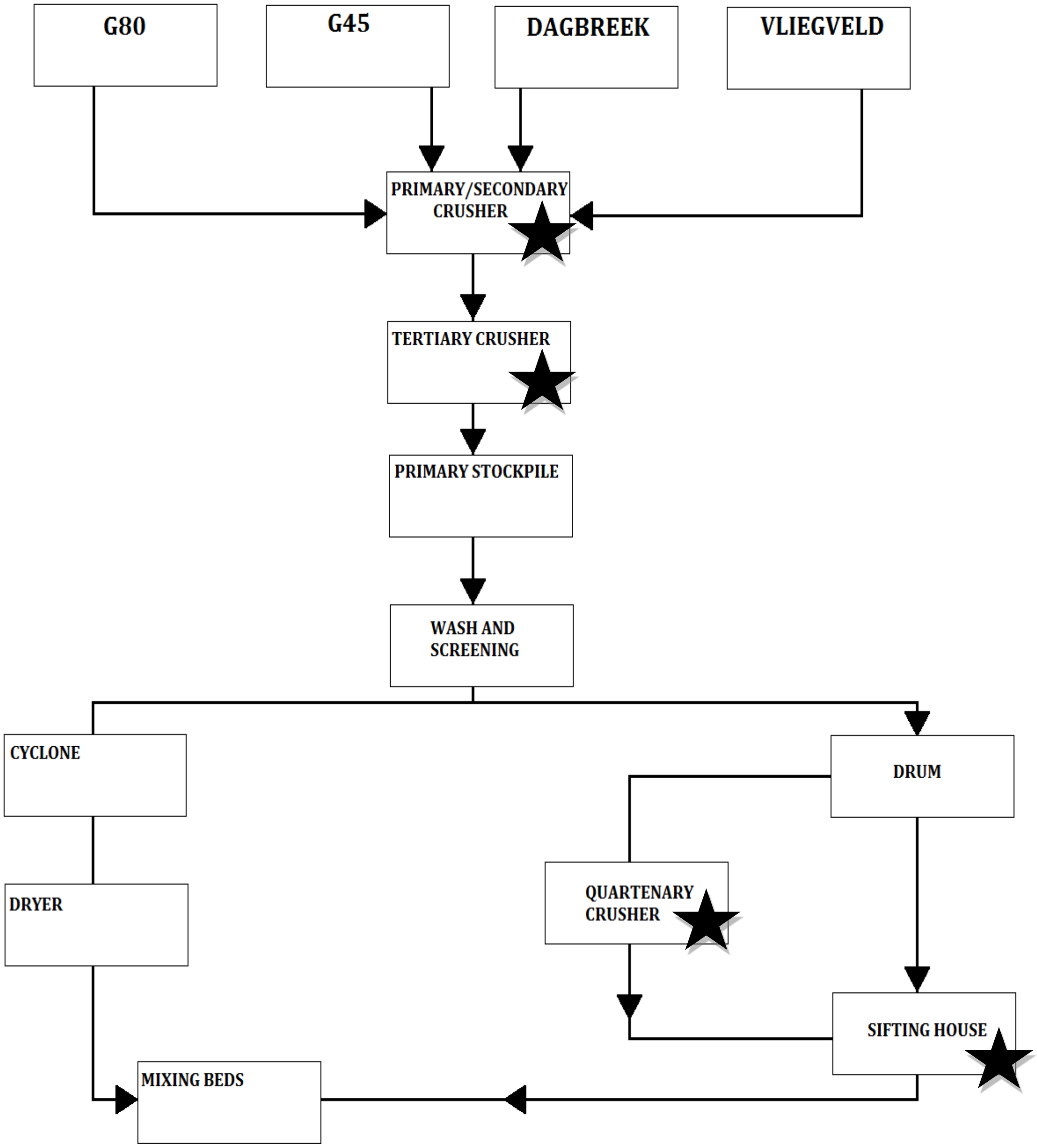
APPENDICES

5.1. Appendix A: Floor plans of monitored areas

Key Index

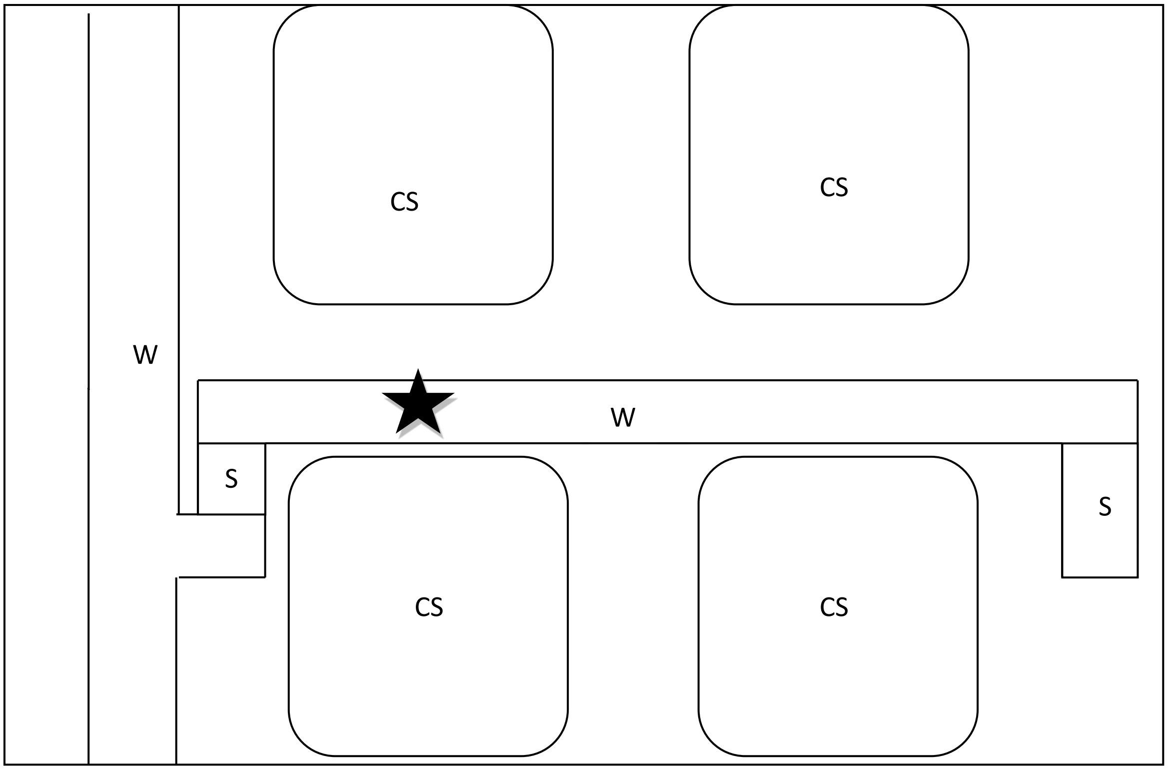
★	Placement of sampling station
C	Crusher
CS	Crusher chute
MA	Maintenance area
F	Feeder
S	Stairway
W	Walkway

Simplistic layout of the process areas



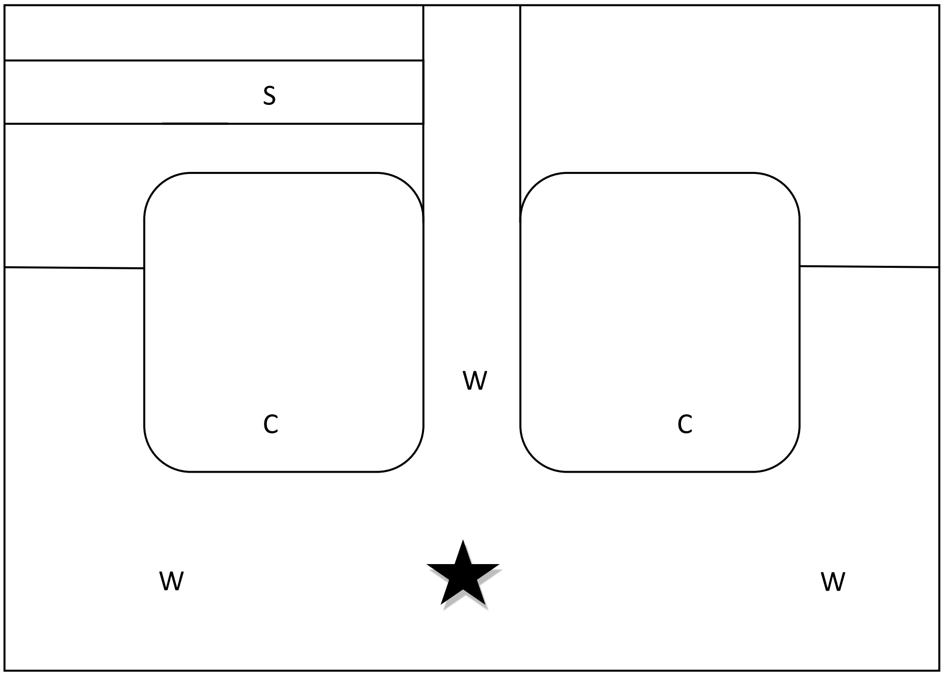
Primary- and secondary crusher

6th Floor



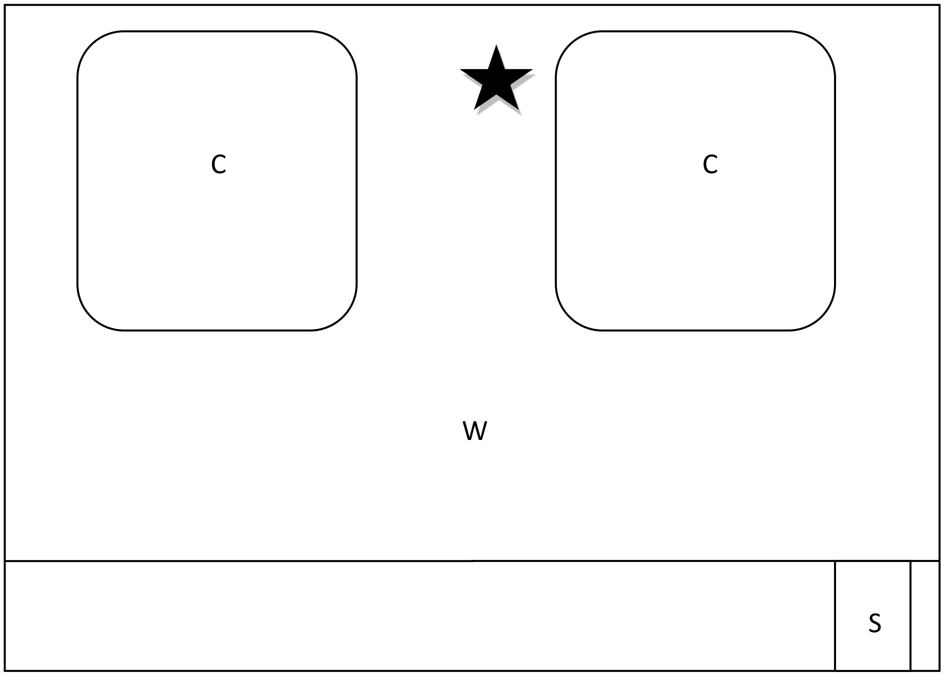
Tertiary crusher

3rd Floor



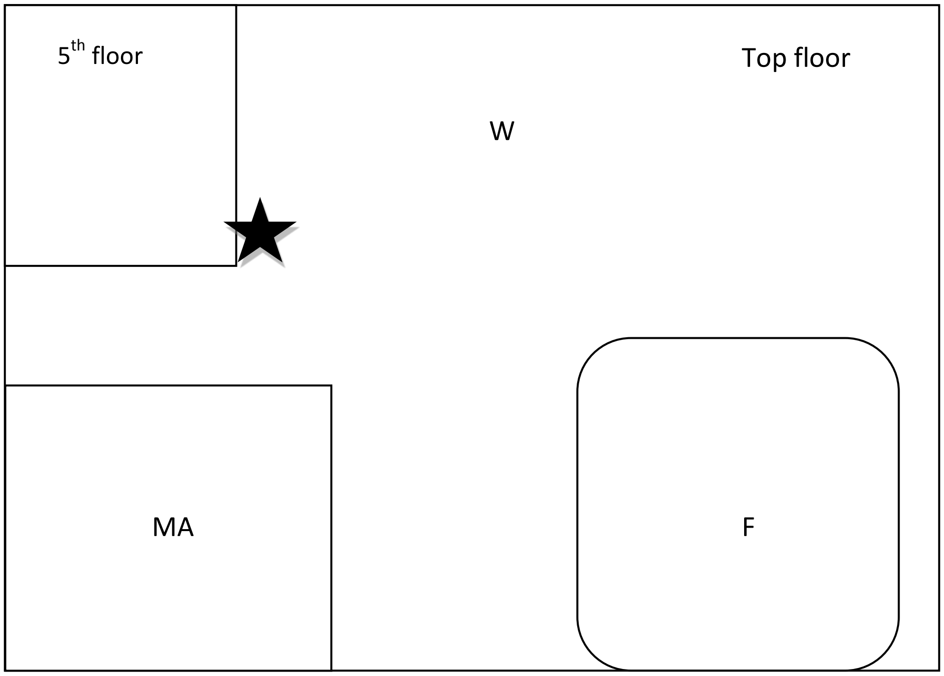
Quaternary crusher

3rd Floor

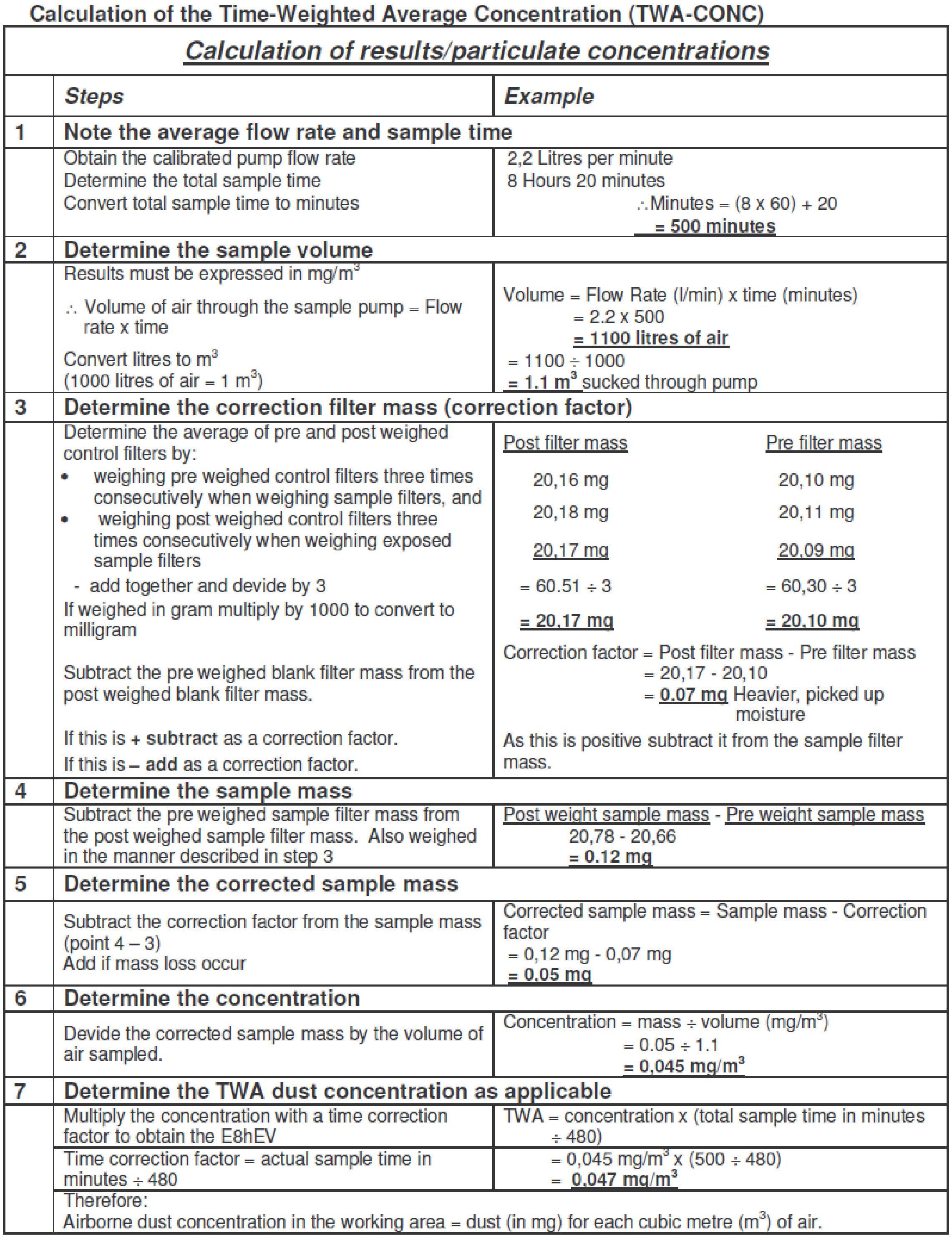


Sifting house

Top floor



5.2. Appendix B: Method for calculation of particle concentrations as set out in the South African Mines Occupational Hygiene Programme (SAMOHP) codebook



Calculation of the Time-Weighted Average Concentration (TWA-CONC)

	Calculation of results/particulate concentrations	
	Steps	***Example***
1	**Note the average flow rate and sample time**	
	Obtain the calibrated pump flow rate Determine the total sample time Convert total sample time to minutes	2,2 Litres per minute 8 Hours 20 minutes ∴Minutes = (8 x 60) + 20 **= 500 minutes**
2	**Determine the sample volume**	
	Results must be expressed in mg/m^3 ∴ Volume of air through the sample pump = Flow rate x time Convert litres to m^3 (1000 litres of air = 1 m^3)	Volume = Flow Rate (l/min) x time (minutes) = 2.2 x 500 **= 1100 litres of air** = 1100 ÷ 1000 **= 1.1 m^3** sucked through pump
3	**Determine the correction filter mass (correction factor)**	
	Determine the average of pre and post weighed control filters by: • weighing pre weighed control filters three times consecutively when weighing sample filters, and • weighing post weighed control filters three times consecutively when weighing exposed sample filters - add together and devide by 3 If weighed in gram multiply by 1000 to convert to milligram Subtract the pre weighed blank filter mass from the post weighed blank filter mass. If this is + **subtract** as a correction factor. If this is – **add** as a correction factor.	Post filter mass 20,16 mg 20,18 mg 20,17 mg = 60.51 ÷ 3 **= 20,17 mg** Pre filter mass 20,10 mg 20,11 mg 20,09 mg = 60,30 ÷ 3 **= 20,10 mg** Correction factor = Post filter mass - Pre filter mass = 20,17 - 20,10 = **0.07 mg** Heavier, picked up moisture As this is positive subtract it from the sample filter mass.
4	**Determine the sample mass**	
	Subtract the pre weighed sample filter mass from the post weighed sample filter mass. Also weighed in the manner described in step 3	Post weight sample mass - Pre weight sample mass 20,78 - 20,66 **= 0.12 mg**
5	**Determine the corrected sample mass**	
	Subtract the correction factor from the sample mass (point 4 – 3) Add if mass loss occur	Corrected sample mass = Sample mass - Correction factor = 0,12 mg - 0,07 mg **= 0,05 mg**
6	**Determine the concentration**	
	Devide the corrected sample mass by the volume of air sampled.	Concentration = mass ÷ volume (mg/m^3) = 0.05 ÷ 1.1 **= 0,045 mg/m^3**
7	**Determine the TWA dust concentration as applicable**	
	Multiply the concentration with a time correction factor to obtain the E8hEV	TWA = concentration x (total sample time in minutes ÷ 480)
	Time correction factor = actual sample time in minutes ÷ 480	= 0,045 mg/m^3 x (500 ÷ 480) = **0,047 mg/m^3**
	Therefore: Airborne dust concentration in the working area = dust (in mg) for each cubic metre (m^3) of air.	