

Exposure to silica during the production of titanium dioxide from beach sand

MET Draai

20320361

*Mini-dissertation submitted in partial fulfilment of
the requirements for the degree Master of Science in
Occupational Hygiene at the Potchefstroom
Campus of the North-West University*

Supervisor: Prof FC Eloff

Co-Supervisor: Mr S J van Rensburg













November 2012

“And we know that in all things God works for the good of those who love him, who have been called according to his purpose.”

Rom 8:28

Authors Contribution

This study was planned and executed by a team of researchers. The contribution of each researcher is shown in the Table below:

NAME	RESPONSIBLE FOR
Prof FC Eloff	Supervisor  Assisted in the introduction, designing, planning and reporting of this study.  Approval of protocol.  Interpretation of results and documentation of this study.  Reviewing of the mini dissertation.
Mr S J van Rensburg	Co-Supervisor  Assisted with the designing, planning and the reporting of this study.  Interpretation of results and documentation of this study.  Reviewing of the mini dissertation.
MET Draai	 Planning and protocol of the study.  Respirable particulate sampling and the collection of bulk samples.  Literature study.  Statistical analysis and interpretation of results.  Writing of the article.

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

I declare that I have approved the 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 Maryda Draai's M.Sc. (Occupational Hygiene) mini-dissertation.

.....
Prof FC Eloff
(Supervisor)

.....
Mr S J van Rensburg
(Co-Supervisor)

Acknowledgements

I would like to extend my sincere gratitude to the following people and institutions for their help and support during the course of this study.

- All thanks to Almighty God for giving me the strength and courage to complete this study. All honour and glory to YOU.
- Prof FC Eloff for guidance, patience, motivation and support.
- Mr S J van Rensburg for guidance, patience, motivation and support.
- The employees at Richards Bay Minerals who assisted me in this study.
- Richards Bay Minerals for financing the study and providing the resources needed to complete this study.
- Mari van Reenen for her assistance with the statistical analysis of data.
- A special thanks to my parents Lisbe and Benjamin Draai. Thank you for your continued support and love, and for always believing in me.
- My friends and family in Potchefstroom and Oudtshoorn for all their motivation, love and support.
- Mr Theo and Mrs Kathleen Foutie for support and hospitality during this study.
- My friends and family in Richards Bay for all their love and support.
- Prof Schalk Vorster for all his help with language and technical editing.
- Mrs Anneke Coetzee for all her help with reference editing.

Preface

This mini-dissertation was written in article format. Chapter 1 is a general introduction to this study. It also stipulates the aims of the study and the hypothesis. In Chapter 2 a literature study is given with regard to the characteristics of silica, the effect of temperature changes on the silica structure, the route of exposure, the consequences of exposure, legislation in place to protect workers, the controls to minimize exposure and the prevention of exposure. Chapter 3 is written in article format according to the requirements of the Annals of Occupational Hygiene journal. The journal requires that references should be listed in alphabetical order by name of first author, using the Vancouver style of abbreviation and punctuation. Chapter 4 provides a final conclusion and recommendations.

Summary

Silica is a common silicon dioxide (SiO_2) that can be crystalline or non-crystalline (amorphous). Amorphous silica is considered to be less hazardous than crystalline silica. Three dominant crystalline polymorphs exist, with silica quartz being the most common. Exposure to respirable crystalline silica (quartz) causes silicosis, a lung scarring disease. The aim of this study was to identify and quantify the silica exposure in respirable dust personal exposure samples, as well as in representative bulk samples which are large samples taken from the sources of airborne dust obtained from different mining and production plants involved in the production of titanium dioxide from beach sand. This is needed to determine the degree of risk of developing silicosis. Forty five workers employed in different mining and production plants participated in this study. Their eight-hour personal exposure to respirable particulate was determined. Personal respirable dust exposure samples and bulk samples were analyzed for silica by an accredited laboratory by means of X-ray diffraction based on NIOSH method 7500. Silica quartz was detected in personal respirable dust samples and bulk dust samples obtained from the mining and production plants, but amorphous silica was only detected in three personal exposure samples at the Slag plant and in the bulk sample obtained from the Roaster plant. All the silica quartz and amorphous silica concentrations in personal exposure samples were well below their respective exposure limits of 0.1 mg/m^3 (quartz) and 3 mg/m^3 (amorphous). No significant differences were found between the silica quartz concentrations in personal respirable exposure samples obtained from the mining ponds and the production plants, although a practical significance was found between some mining and production area personal exposure samples. The non-significant differences found between exposure concentrations and a practical significance suggest the necessity of involving a larger sample group in future. Other studies done in non-mining industries showed that some workers were over exposed to respirable silica dust. Compared to these findings the results of the present study showed the opposite, with respirable silica dust levels being below the South African action level and OEL. Further research, involving more samples, spread over a longer period of time, would probably be able to show a clear trend as to how quartz structures and exposure profiles change from the mining to the various production processes. Overexposure to silica quartz anywhere at the mine and production processes is considered unlikely, with the risk of developing silicosis being low.

Keywords: Silica, respirable dust, beach sand, titanium dioxide

Opsomming

Silika is 'n silikondioksied (SiO_2) wat algemeen voorkom en wat kristallyn of nie-kristallyn (amorf) kan wees. Amorfe silika is minder gevaarlik as kristallyne silika. Drie dominante kristallyne silikastrukture bestaan, waarvan silikakwarts die meeste voorkom. Blootstelling aan respireerbare kristallyne silikakwarts veroorsaak silikose, 'n siekte wat die longe beskadig. Die doel van die studie was om die silikastruktuur te identifiseer en te kwantifiseer in persoonlike respireerbare monsters en grootmaatmonsters, wat 'n groot monster is, wat verkry is van die die stofbronne van die verskillende areas betrokke in die vervaardiging van titaandioksied uit seesand. Dit is nodig om die graad van risiko vas te stel vir die ontwikkeling van silikose. Vyf en veertig werkers is uit die verskillende myn- en produksie-areas gekies. Die agt-uur blootstelling aan respireerbare partikels is bepaal. Die persoonlike blootstelling en grootmaatmonsters is geanaliseer vir silika deur middel van X-straaldiffraksie volgens NIOSH-metode 7500. Silikakwarts is gevind in persoonlike respireerbare monsters asook in grootmaatmonsters wat verkry is in die verskillende myn- en produksie-areas. Amorfe silika was slegs teenwoordig in drie persoonlike respireerbare monsters by die Slak-area en in een grootmaatmonster in die Rooster-area. Al die konsentrasies kwarts en amorfe silika in die persoonlike respireerbare blootstellingsmonsters was onder hul onderskeie blootstellingsdrempels van 0.1 mg/m^3 (kwarts) en 3 mg/m^3 (amorfe). Geen betekenisvolle verskille is tussen die silikakwartskonsentrasies in persoonlike respireerbare blootstellingsmonsters en grootmaatmonsters gevind nie, alhoewel 'n praktiese beduidenheid gevind is tussen sommige myn- en produksie-area persoonlike respireerbare monsters. Praktiese beduidendheid naas die voorkoms van geen betekenisvolle verskille, dui op die noodsaak van 'n groter monstergroep vir toekomstige navorsing. Ander studies wat gedoen was in die nie-myn industrieë het getoon dat sommige werkers oormatig blootgestel was aan respireerbare silikastof. In vergelyking met hierdie bevindinge toon die huidige studie die teenoorgestelde, met die die respireerbare stof vlakke onder die Suid-Afrikaanse aksie vlak en beroepsblootstellingsdrempel. In toekomstige studies sal meer monsters, versprei oor 'n langer tydperk, moontlik 'n duideliker tendens toon ten opsigte van hoe die kwartsstruktuur en blootstellingsprofile verander vanaf die myn en in die produksieprosesse. Dit wil voorkom of oormatige blootstelling aan silikakwarts in enige deel vanaf die myn deur die verskillende produksieprosesse nie waarskynlik is nie, en daarom is die risiko om silikose te ontwikkel ook laag.

Sleutelwoorde: silika, respireerbare stof, seesand, titaandioksied

Table of Contents

Authors Contribution	i
Acknowledgements.....	ii
Preface	iii
Summary	iv
Opsomming	v
List of Abbreviations.....	ix
List of Tables	x
List of Figures	xi
CHAPTER 1	1
GENERAL INTRODUCTION.....	1
1.1 Introduction.....	2
1.2 Aims and objectives of the study	3
1.3 Hypothesis.....	4
1.4 References	5
CHAPTER 2	7
LITERATURE STUDY.....	7
2.1 The chemical and physical properties of silica	8
2.2 The effect of temperature on silica structure.....	9
2.3 The human respiratory system	10
2.4 Health effects of amorphous silica	11
2.5 Toxicology	12

2.5.1	Route of exposure.....	12
2.5.2	Important factors that contribute to biological toxicity of crystalline silica.....	12
2.5.2.1	Chemical components and composition	12
2.5.2.2	Size and structure.....	12
2.5.2.3	Surface reactivity and age.....	13
2.5.2.4	Mechanism of crystalline silica pathogenicity.....	14
2.6	Crystalline silica exposure and disease development.....	14
2.7	Crystalline silica and lung cancer.....	16
2.8	History of silicosis.....	17
2.9	Factors that influence the development of silicosis.....	18
2.9.1	The pathological features of silicosis	18
2.9.1.1	Alveolar lipoproteinosis (Acute silicosis).....	18
2.9.1.2	Accelerated silicosis	19
2.9.1.3	Chronic silicosis.....	19
2.9.1.4	Simple silicosis	19
2.9.1.5	Complicated silicosis	19
2.9.2	Symptoms of silicosis.....	20
2.9.3	Silicosis and its diagnosis.....	20
2.10	Prevention and treatment of silicosis	20
2.11	Occupational exposure to silica.....	21
2.11.1	Industries where silica exposure occurs	21
2.11.2	Silica exposure in mining	23
2.11.3	Silica exposure in a heavy mineral processing mine.....	24
2.12	Occupational exposure limits	26
2.12.1	General monitoring of airborne particulates.....	27
2.12.2	Personal airborne particulate exposure sampling of silica	28
2.12.3	Bulk sampling	28
2.12.4	Quality assurance programme for crystalline silica for sampling	29
2.12.5	Environmental exposure to silica at the mines	29
2.13	Control measures to lower silica exposure.....	29
2.14	References	31

List of Abbreviations

ACGIH	American Conference of Governmental Industrial Hygienists, USA
AIDS	Acquired Immunodeficiency Syndrome
AIOH	Australian Institute of Occupational Hygienists
ANOVA	Analysis of Variance
CEN	European Standardization Committee
EQA	External Quality Assurance
HIV	Human Immunodeficiency Virus
HMC	Heavy Mineral Concentrate
HSE	Health and Safety Executive
IARC	International Agency for Research on Cancer
ILO	International Labour Organization
IR-AS	Infra-Red Absorption Spectrophotometry
ISO	International Organization for Standardization
NIOH	National Institute for Occupational Health
NIOSH	National Institute for Occupational Safety and Health, USA
OEHHA	Office and Environmental Health Hazard Assessment
OEL	Occupational Exposure Limit
OSHA	Occupational Safety and Health Administration, USA
PEL	Permissible Exposure Limit
PMF	Pulmonary Fibrosis
PMN	Polymorphonuclear Leukocytes
PPE	Personal Protective Equipment
ROS	Reactive Oxygen Species
TLV	Threshold Limit Value
TWA	Time Weighted Average
WASP	Workplace Analysis Scheme of Proficiency
XRD	X-Ray Diffraction

List of Tables

Chapter 2

Table 2.1:	Physical properties of quartz, cristobalite and tridymite	9
Table 2.2:	Main industries and activities around the world in which silica exposure has been reported	22

Chapter 3

Table 3.1:	The mean silica quartz and amorphous exposure concentrations (mg/m^3) and standard deviation for the mining (MPA, MPC, MPD, MPE) and production areas	47
Table 3.2:	The percentage of silica quartz or amorphous silica content of total bulk samples obtained from the mining and production areas	50
Table 3.3:	The percentage of silica quartz or amorphous silica content of total bulk samples obtained from the mining and production areas	53
Table 3.4:	Effect sizes for silica quartz and amorphous silica for mining ponds (MPA, MPC, MPD, MPE) and production areas	56
Table 3.5:	Effect sizes for silica quartz and amorphous silica for the six mining (combined) areas and production areas	57

List of Figures

Chapter 2

Figure 2.1: The polymorphs of crystalline silica	8
Figure 2.2: Silica transitions with temperature changes	10
Figure 2.3: The human respirator system	11
Figure 2.4: Process overview of a heavy mineral processing mine	26

Chapter 3

Figure 3.1: The mean % silica quartz content in respirable dust exposure samples for production streams 1 and 2	48
Figure 3.2: The mean % amorphous silica content in respirable dust exposure samples for production streams 1 and 2	48
Figure 3.3: The mean TWA concentration of silica quartz in the different mining and production areas	49
Figure 3.4: The mean TWA concentration of amorphous silica in the different mining and production areas	49
Figure 3.5: The % silica quartz or amorphous silica in bulk samples obtained from the different mining and production areas – Stream 1	51
Figure 3.6: The % silica quartz or amorphous silica in bulk samples obtained from the different mining and production areas – Stream 2	52

CHAPTER 1

GENERAL INTRODUCTION

1.1 Introduction

Silica is a common silicon dioxide (SiO_2) that occurs naturally and is the second most abundant mineral in the earth's crust (Yassin *et al.*, 2005; Mason and Thompson, 2010). Silica can be both crystalline and non-crystalline (amorphous). Three crystalline forms exist, with quartz being most abundant. All three forms may become respirable size particles when crystalline silica containing objects are chipped, cut, drilled or grined (Gottesfeld *et al.*, 2008).

Inhalation of silica-containing dust has historically been associated with silicosis, a lung-scarring disease. It is characterised by three pathological phases which are dose-dependent, and are referred to as acute, accelerated and chronic silicosis. Silicosis has fatal consequences and may progress even after exposure has ceased (Gottesfeld *et al.*, 2008; Mason and Thompson, 2010). Diseases associated with silica exposure include, tuberculosis (TB), autoimmune respiratory disease, non-malignant renal disease and cancer. It is also known that silica exposure contributes to a high incidence of TB, with the presence of HIV in individuals with an already compromised immune system (Swanepoel and Rees, 2011).

Crystalline silica dust has been classified as a known human carcinogen (class I) by the International Agency for Research on Cancer (IARC) after numerous epidemiological studies and reviews have been published on this subject (IARC, 1997; Sherson, 2002; Thompson and Kelley, 2010).

Many workers are still excessively exposed to crystalline silica dust, both in developing and developed countries. Past exposures to silica has recently been estimated to be nearly 800 deaths per year in the United Kingdom (HSE, 2012). It was recorded that 3 030 foundry workers were exposed to silica dust in Vietnam (Lan *et al.*, 2003). Industries where crystalline silica is mechanically handled and released include mining, construction, foundries, stone and sand production, as well as clay and glass manufacturing. Mechanical handling and release of silica poses a high exposure potential ('T Mannetje *et al.*, 2002; Collins *et al.*, 2005).

Exposure to airborne crystalline silica is measured by using a cyclone fitted with a cassette to collect the respirable fraction of the aerosol connected to a sampling pump, where the cyclone is attached in the worker's breathing zone. These samplers are required to conform to the criteria of the International Organization for Standardization

(ISO), the European Standardisation Committee (CEN), and the American Conference of Governmental Industrial Hygienists (ACGIH) for collecting particles of the correct sizes (NIOSH, 2003). Analysis methods include X-ray diffraction (XRD) and infrared absorption spectrophotometry (IR-AS).

Crystalline silica, commonly known as silica quartz, occurs in numerous rock types and is a common mineral in most beach sands. Heavy minerals are extracted from beach sand by means of dredge mining in order to obtain titanium which is found in minerals such as rutile and ilmenite. Titanium is needed for the production of titanium dioxide, which is a very important commercial product used in sunscreens, toothpaste and paints. Rutile deposits are most typically found in beach sand where they are mined, concentrated and separated to obtain ilmenite that acts as a titanium dioxide raw material. After the roasting process, the roasted ilmenite is cooled and transferred via a conveyor to storage silos in the form of iron ore. The roasted ilmenite and dry char are transferred from silos via the conveyors to the furnaces for smelting (Zhang *et al.*, 2011).

By means of the above-mentioned mining, concentration, separation and smelting processes, silica is expected to transform from a crystalline structure into a non-crystalline/amorphous structure, by being exposed to temperatures above silica's melting point of 1600 °C (Samal *et al.*, 2010). One can thus reasonably expect employees involved in sand mining and subsequent titanium dioxide extraction processes to be exposed to these different structural forms of silica, depending on the specific phase of the process in which they work. Titanium dioxide, which is obtained through industrial processing such as roasting or smelting, can further be treated to produce different grades of titanium dioxide.

The study sets out to investigate the different forms of crystalline silica and to quantify its occupational exposure at a heavy mineral surface mine located in the north-eastern region of Kwa-Zulu Natal.

1.2 Aims and objectives of the study

The aims and objectives of the study were to:

- investigate the different forms of crystalline silica and amorphous silica at the different production phases of titanium dioxide from beach sand;

- quantify personal airborne dust exposure at different production phases of titanium dioxide and evaluate the risk of developing silicosis;
- identify the structure of silica, as well as the quantification thereof in bulk samples collected from different phases in the production of titanium dioxide; and
- identify and quantify silica by means of X-ray diffraction (XRD).

1.3 Hypothesis

Changes in the structure of silica in the airborne dust inhaled during the course of titanium dioxide production from beach sand does not pose a risk for developing silicosis.

1.4 References

- Collins JF, Salmon AG, Brown JP *et al.* (2005) Development of a chronic inhalation reference level for respirable crystalline silica. *Regul Toxicol Pharmacol*; 43: 292-300.
- Gottesfeld P, Nicas M, Kephart JW *et al.* (2008) Reduction of respirable silica following the introduction of water spray applications in Indian stone crusher mills. *Int J Occup Environ Med*; 14: 94-103.
- HSE (HEALTH AND SAFETY EXECUTIVE). (2012) Coal worker's pneumoconiosis and silicosis. Available from URL: <http://www.hse.gov.uk/statistics/causdis/pneumoconiosis/pneumoconiosis-and-silicosis.pdf>. Accessed 25 Aug 2012.
- IARC (INTERNATIONAL AGENCY FOR RESEARCH ON CANCER). (1997) Monographs on cancer on the evaluation of carcinogenic risks to humans. Silica, some silicates coal dust and para-aramid fibrils. Available from: URL: <http://monographs.iarc.fr/ENG/Monographs/vol68/volume68.pdf>. Accessed 25 Aug 2011.
- Lan TN, Son PH, Trung LV *et al.* (2003) Distribution of silica- exposed workers by province and industry in Vietnam. *Int J Occup Environmental Health*; 14: 128-133.
- Mason E, Thompson SK. (2010) A brief overview of crystalline silica. *J Chem Health Saf*, 7: 6-8.
- NIOSH (NATIONAL INSTITUTE FOR OCCUPATIONAL HEALTH AND SAFETY). (2003) Manual of analytical methods. Determination of airborne crystalline silica. Available from: URL: www.cdc.gov/niosh/docs/2003-154/pdfs/chapter-r.pdf. Accessed 25 Aug 2011.
- Samal S, Mohapatra BK, Mukherjee PS. (2010) The effect of heat treatment on Titania slag. *J Min Mat Char Eng*; 9: 795-809
- Sherson D. (2002) Silicosis in the twenty first century. *Occup Environ Med*; 59: 721-2.
- Swanepoel AJ, Rees E. (2011) Silica exposure in South-African farming. *Occup Health Southern Africa*; 17 (6): 14-11.

- Thompson CR, Kelley TR. (2010) A brief review of silicosis in the United States. *Environ Health Insights*; 4: 21-26.
- ‘T Mannelje A, Steenland K, Attfield M *et al.* (2002) Exposure-response analysis and risk assessment for silica and silicosis mortality in a pooled analysis for six cohorts. *Occup Environ Med*; 59: 723-8.
- Yassin A, Yebesi F, Tingle R. (2005) Occupational exposure to crystalline silica dust in the United States, 1988-2003. *Environ Health Perspect*; 113: 255-60.
- Zhang W, Zhu Z, Cheng CY. (2011) A literature review of titanium metallurgical processes. *Hydrometallurgy*; 108: 177-188.
-

CHAPTER 2

LITERATURE STUDY

The overview presented in the literature study that follows, presents a discussion of the characteristics of silica, the effect of temperature changes on the silica structure, the route of exposure to humans, and the consequences of exposure. In addition, legislation that is in place to protect workers against the hazardous effects of silica exposure and controls aimed at minimising and preventing exposure is also discussed.

2.1 The chemical and physical properties of silica

Silica exists in both crystalline and non-crystalline (amorphous) forms (TCEQ, 2009). It has a melting point of 1600 °C and is a colourless, odourless and non-combustible solid granule (Yassin *et al.*, 2005). Amorphous silica can be natural, can be produced as a by-product or synthetically created and is considered less pathogenic than quartz. In amorphous silica the molecules are randomly arranged and not in a repetitive three dimensional pattern (NIOSH, 2003a; Mbatha, 2009). The crystalline polymorphs are forms in which the silicon SiO_4 tetrahedra molecules are arranged in repetitive three dimensional patterns that have a unique spacing configuration, a lattice structure and an angular relationship to its atoms. Quartz, cristobalite and tridymite are the most frequently found crystalline polymorphs (RSA DOL, 2006; TCEQ, 2009). Figure 1 shows the layer and pattern arrangements of these crystalline polymorphs. Quartz has a rhombohedral structure, tridymite consists of layers of paired tetrahedrals, and with successive layers alternating in stacking and cristobalite also consists of layers of paired tetrahedra, except that these alternate in a cubic pattern. Table 1 lists prominent physical properties of these polymorphs.

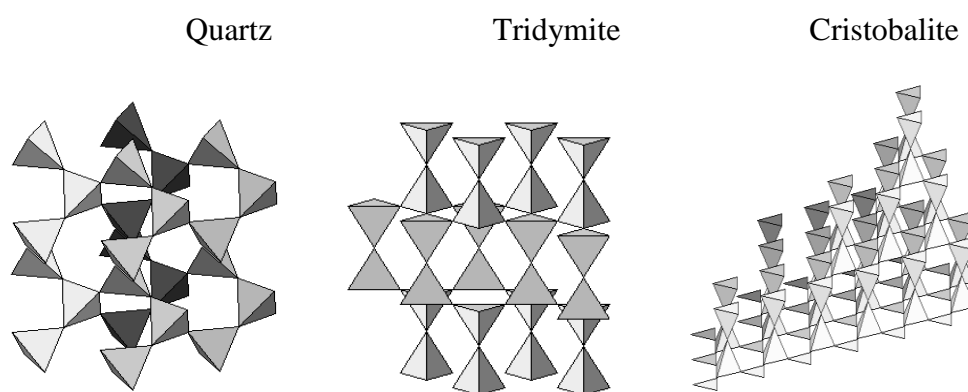


Figure 2.1: The polymorphs of crystalline silica

Available from: Dutch, (2009)

Table 2.1: Physical properties of quartz, cristobalite and tridymite.

Silica polymorph	Crystal structure	Index of refraction	Specific gravity	Molecular Weight	Melting point (°C)
Quartz	Hexagonal	1.544	2.645-2.660	60.08	1610
Cristobalite	Cubic or tetragonal	1.487	2.32	60.08	1723
Tridymite	Rhombohedral	1.469	2.26	60.08	1703

Adapted from NIOSH, 2003b

Quartz commonly refers to crystalline silica dust and is the most abundant of the crystalline polymorphs (NIOSH, 2003b; Yassin *et al.*, 2005). Quartz is present in most rocks, soils and concrete (Mbatha, 2009). It is the most thermodynamically stable polymorph under those ambient conditions where igneous rocks at the earth's surface crystallise. Occupational exposure to quartz occurs where grinding, blasting, fracturing and earth movement (such as mining and construction) take place (NIOSH, 2003b; RSA DOL, 2006). Cristobalite and tridymite are abundant in volcanic rock and soils, but cristobalite is typically associated with ceramic, refractory and diatomaceous earth industries and foundry processes (NIOSH, 2003b). Other crystalline forms such as keatite, coesite, stishovite and mognite are less commonly found in nature and is of limited occupational interest. These polymorphs are components of rocks and crystallise at high temperatures. This can be observed when amorphous silica formed by skeletons of diatoms is converted to cristobalite when heated (Rees and Murray, 2007).

2.2 The effect of temperature on silica structure

Silica, both amorphous and crystalline, can transform at extreme heat or at very slow-cooling conditions (NIOSH, 2003b). Amorphous silica can transform into crystalline silica at temperatures higher than 1 000 °C (OSHA, 2009). Silica quartz can transform into amorphous silica when high temperatures are used in industrial processes; this leads to changes in the crystalline structure (RSA DOL, 2006; Rees and Murray, 2007). This transformed crystalline structure is considered to be more toxic than the original quartz structure. Alpha and beta quartz are sub-polymorphs of quartz. Of these two forms, alpha quartz is the most common and stable under ambient conditions. Beta quartz is only stable above temperatures of 570 °C. When temperatures are below 570

°C, cooling takes place and beta quartz quickly reverts back to alpha quartz. Trace elements like aluminium and iron influence the transformation rates. When the heating process exceeds 578 °C, tridymite will be formed at 870 °C. At temperatures above 1 470 °C cristobalite will be formed. These two crystalline polymorphs cannot convert back to alpha quartz, and require the breaking of SiO bonds which results in the tetrahedral structure being rearranged. Cristobalite and tridymite exposures are rare and can only be encountered when silica-containing materials are exposed to extreme temperatures (Guthrie and Driscoll, 2010). Figure 2.2 demonstrates the silica transitions with temperature changes.

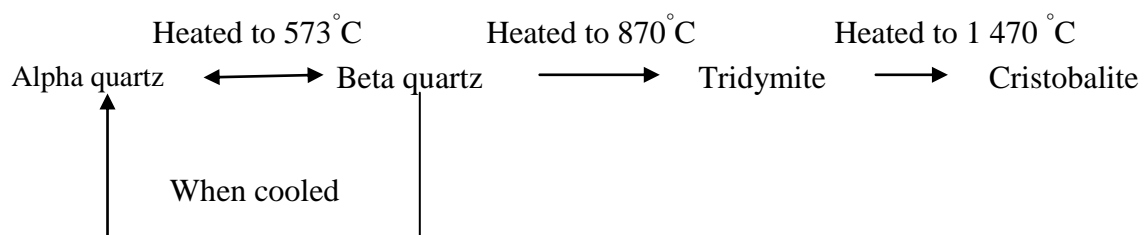


Figure 2.2: Silica transitions with temperature changes

Available from OSHA, (2009)

Titanium dioxide is commonly found in nature in ilmenite ores in association with various amounts of oxide purities of elements such as iron, silicon, magnesium and others. Ilmenite can be commercially upgraded into titania slag. Titania slag is an odourless black solid that is produced through electro-arc smelting at 1 700 °C, which is above the melting point of silica. Titania slag is composed of an abundance of the crystal phases known as pseudobrookite-karooite (>97%); it also consists of a glassy amorphous silica phase (<3%). Titania slag is rapidly cooled by air after smelting and then cooled by water by means of a water spray system. By these heating and rapid cooling processes, the silica structure changes from solid crystalline (quartz) into liquid and then into an amorphous solid state (Samal *et al.*, 2010).

2.3 The human respiratory system

Under certain circumstances, individuals are exposed to hazardous chemical substances which can be inhaled and deposited in different areas of the respiratory tract. Due to silica being an inhalation hazard it is important to look at the respiratory tract and region which is most affected by respirable fractions of silica.

The respiratory tract can be divided into three regions. The extra thoracic region includes the nasal passage, nasopharynx, and the oral pharynx down to the larynx. The tracheobronchial region covers the trachea, bronchi, while the alveolar region consists of bronchioles and the alveoli (Lange, 2008). When inhaled, larger particles will deposit in the upper airways while the respiratory fraction smaller than 10 μm will penetrate deeper into the alveolar region. The bronchi are lined with cilia that move deposited particles and mucus upward to the trachea. Macrophages are located in the alveolar cavities and are mobile scavengers that engulf foreign particles in the lungs (Makinson, 2008). Figure 2.3 shows a diagram of the human respiratory system.

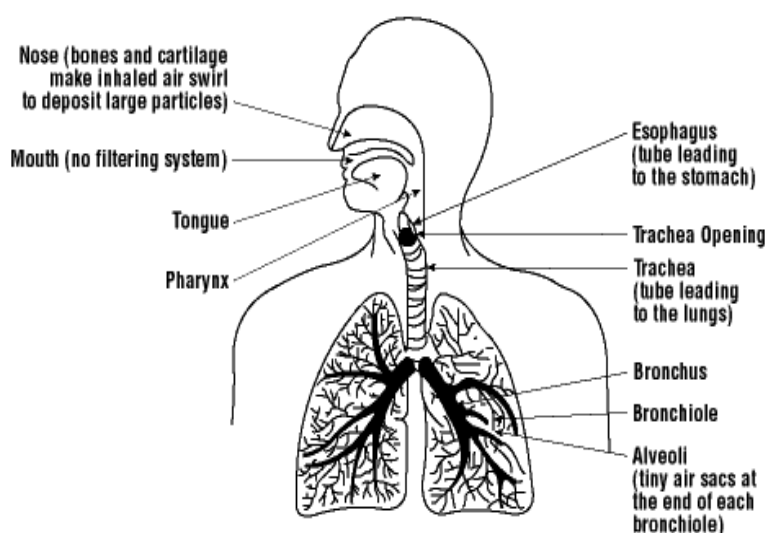


Figure 2.3: The human respiratory system

Available from CCOHS, 2011

2.4 Health effects of amorphous silica

Amorphous silica exhibits a non-crystalline formation and can be (1) naturally occurring; (2) produced as a by-product of power stations and metallurgical processes; or (3) synthetically produced (NIOSH, 2003c). There are several types of amorphous silica, including fumed silica and diatomaceous earth, while synthetic amorphous silica is encountered more frequently. Amorphous silica is considered to be less hazardous than crystalline silica. Animal inhalation studies on synthetic amorphous silica have shown reversible inflammation, granuloma formation, emphysema and alveolar hyperinflation (Keawamatawong *et al.*, 2005; Cho *et al.*, 2007). In humans, epidemiological studies have shown no evidence of silicotic and inflammatory effects and no potential of carcinogenicity. This is observed from the lower recruitment of

leukocytes and neutrophil concentrations in the lungs upon inhalation of amorphous silica (Cho *et al.*, 2007). Amorphous silica has a large surface area and has greater solubility in the lungs, and is rapidly cleared out of the lungs to other organs (NIOSH, 2003b; O'Reilly *et al.*, 2005; Cho *et al.*, 2007). Both crystalline and amorphous silica have the potential to induce pulmonary inflammation, but only the inhalation of crystalline silica leads to the development of pulmonary fibrosis (O'Reilly *et al.*, 2005).

2.5 Toxicology

2.5.1 Route of exposure

The primary route of exposure to silica is through inhalation of airborne crystalline silica-containing dust (Dutta and Moudgil, 2007).

2.5.2 Important factors that contribute to biological toxicity of crystalline silica

Important factors that contribute to the biological toxicity of crystalline silica include chemical components and composition, size and structure, surface reactivity and age, as well as the mechanism of crystalline silica pathogenicity. These are discussed below.

2.5.2.1 Chemical components and composition

The matrix containing the silica particle plays a role in the toxicity of the particle (Makinson, 2008). Trace amounts of elements like aluminium, potassium and magnesium are closely associated with silica's structure and influence biological activity (Dutta and Moudgil, 2007). Iron can be present in crystalline silica and can act as a catalyst, resulting in the formation of reactive oxygen species (ROS) (Guthrie and Driscoll, 2010). Aluminium is closely associated with quartz, especially in rock formations, and its presence has a protective function in the lungs (AIOH, 2009). Aluminium compounds can be applied as a coating to modify the particle surface which, in turn, will reduce surface toxicity (Guthrie and Driscoll, 2010).

2.5.2.2 Size and structure

Particle size (aerodynamic diameter) determines the portion of the airway in which particles are deposited. Respirable particle fractions with smaller than 10 μm aerodynamic diameter will cause more damage to the lungs than larger fractions.

Particles smaller than 1 μm are capable of penetrating to the alveoli, resulting in the development of silica disease. The different crystalline polymorphs have different levels of toxicity, and they also differ in terms of strength and ionisation state. Also, structural differences can be observed in polymorphs. This can be seen by the arrangement of silanol groups; evidence to this end is found in studies conducted on stishovite, which exhibits an octahedral structure in comparison with the tetrahedral structure of the other crystalline silica polymorphs. These structural differences contribute to toxicity. The hierarchical order of toxicity of different polymorphs is as follows: quartz, tridymite, cristobalite, opal, moganite, keatite, coesite and stishovite (Guthrie and Driscoll, 2010).

2.5.2.3 Surface reactivity and age

The surface of the crystalline silica particle interacts with biological fluids, molecules and body cells. These properties of the particle surface determine its toxicity (Makinson, 2008; Guthrie and Driscoll, 2010).

Crystalline silica particles are cleaved into smaller particles through cutting, grinding, crushing or milling. These processes result in the formation of reactive free radical species on the newly generated particle surface. This occurs in occupations such as sandblasting, rock drilling, tunnelling and silica milling. On newly generated particle surfaces, there are an increased number of silicon and siloxyl radicals. Freshly fractured crystalline silica quartz contributes to greater pulmonary inflammation in the lungs (Meldrum and Howden, 2002; Porter *et al.*, 2002; Makinson, 2008). Most of these freshly fractured surfaces become protonated in air over a specific period of time and then become “aged”. These free radicals can react with aqueous environments to form hydroxyl radicals through the production of hydrogen peroxide (H_2O_2); this process occurs more rapidly. According to Guthrie and Driscoll (2010), the proton-donating silanols on the surface of crystalline silica are responsible for the attachment of silica to the cell membrane, whereas the negatively charged ionised groups contribute to the lytic activity of silica. The acidity of the hydrogen bonds is variable for each silica polymorph. Research suggests that freshly cut surfaces of crystalline silica are more harmful than old (“aged”) surfaces due to the generation of free radicals. The use of wetting processes and metals could influence the reactivity of freshly cut surfaces by altering the formation of free radicals; this is dependent on the time interval

between dust generation and inhalation, as well as the effectiveness of the wetting process (Meldrum and Howden, 2002).

2.5.2.4 Mechanism of crystalline silica pathogenicity

The development of crystalline silica-related disease is related to the crystalline silica concentration in the alveolar region and its effect on the alveolar macrophages (Brown, 2009). Once crystalline silica particles enter the lungs (alveolar region), the immune system is activated and alveolar macrophages are assembled to eliminate the particles. This leads to the production of reactive oxygen species (ROS), inflammatory cytokines and growth factors (Makinson, 2008). The increased burden of ROS leads to elevated levels of oxygen consumption, resulting in oxidative damage to the lung cells (Mbatha, 2009).

With high concentrations of crystalline silica present, the clearance by alveolar macrophages becomes impaired. The presence of high concentrations of crystalline silica will result in the destruction of alveolar macrophages (Gilberti *et al.*, 2008), giving rise to the release of additional ROS, cytokines, the activation of transcription factors, chemokines and the activation of polymorphonuclear leukocytes (PMN). These effects contribute to the inflammation process which can become uncontrolled and excessive, resulting in cell and tissue damage. Severe inflammation that occurs due to crystalline silica exposure appears to be an initiating step in the development of silicosis (Makinson, 2008; Mbatha, 2009).

Crystalline silica can also induce silicosis through direct cytotoxicity. This involves the generated ROS on the surface of silica particles. ROS can cause the destruction of lung membranes and cell damage through lipid peroxidation. The increased production of ROS leads to oxidative stress and inflammation in the lungs, resulting in scarring and fibrosis (Makinson, 2008).

2.6 Crystalline silica exposure and disease development

Crystalline silica-associated diseases remain an important public health concern (Rees and Murray, 2007). Crystalline silica exposure can cause multiple diseases and also has lethal consequences. Data from exposures in mines and industrial processes demonstrate adverse respiratory health effects of exposure to crystalline silica. Workers in gold mining countries, such as South-Africa, are particularly affected by

crystalline silica-associated diseases due to underground mining activities (Gibbs and Du Toit, 2002).

Symptoms like coughing, shortness of breath and pulmonary lipoproteinosis (acute silicosis) are closely associated with high concentrations of respirable crystalline silica exposure (Collins *et al.*, 2005). In humans, the most common disease associated with the inhalation of crystalline silica is silicosis, a disease characterised by a severe decline in the respiratory function and premature death (NIOSH, 2002; Porter *et al.*, 2002).

The non-respiratory health effects of crystalline silica exposure include rheumatoid arthritis, scleroderma, Sjogem's syndrome, stomach cancer and chronic renal disease (Akbar-Khanzadeh and Brillhart, 2002; Brown, 2009). Respiratory diseases include pulmonary tuberculosis, interstitial fibrosis, industrial bronchitis, small airway disease, emphysema and lung cancer (Ding *et al.*, 2002; Ghiazza *et al.*, 2011). Workers that have been exposed to crystalline silica have an increased risk of developing tuberculosis during exposure and this risk increases with prolonged exposure.

Crystalline silica particles are responsible for altering the metabolism of macrophages and this, in turn, reduces their antibacterial effectiveness. This can be seen in both silicotic and non-silicotic individuals (Ding *et al.*, 2002; Mason and Thompson, 2010). The incident rate of tuberculosis among South African gold miners is very high at 3 000 per 100 000 workers when compared to rates among coal and platinum miners in South Africa. Tuberculosis, as well as HIV/AIDS, has high prevalence among workers in gold mines in South Africa. Exposure to crystalline silica exacerbates the effects of diseases like tuberculosis and HIV/AIDS (Ding *et al.*, 2002).

Tuberculosis-associated mortality has increased over the last decades and it is one of the leading causes of death among mineworkers situated in South Africa. HIV/AIDS also reduces the functioning of the immune system. Workers exposed to crystalline silica who also have the HIV/AIDS virus have an even greater risk of developing tuberculosis, due to a poor immune system. A study conducted by TeWaternaude *et al.*, (2006) found a 35% prevalence of tuberculosis among 520 gold miners in South Africa aged 37 years, although their quartz exposure was below the occupational exposure limit of 0.1 mg/m^3 . Studies like these also highlight the necessity of effective occupational hygiene and medical surveillance practices in mines. Early detection and

treatment of active tuberculosis are vital in controlling the spread of the disease among co-workers and communities (Martinez *et al.*, 2010).

2.7 Crystalline silica and lung cancer

In 1987, the IARC (International Agency for Research on Cancer) classified crystalline silica in group 2A, meaning it is probably carcinogenic to humans. This changed in 1997 when the IARC revised its classification of crystalline silica to Group 1; carcinogenic to humans (IARC, 1997; Mason and Thompson, 2010).

Several studies indicated a relationship between the degree of silicosis disability and the risk of developing lung cancer (IARC, 1997; OSHA, 2009). There is indeed a definite relationship between cumulative crystalline silica dust exposure and an increase in mortality due to lung cancer. In addition to this classification, it was apparent that the carcinogenicity in humans was not identified in all industrial circumstances. This might be due to inherent characteristics of crystalline silica, external factors affecting its biological activity and also the distribution of its polymorphs (Brown, 2009). The conclusion by the IARC remains controversial. The carcinogenic role of crystalline silica was discussed in a nested case control study conducted among tin and ore miners. Lung cancer risk was observed to increase with cumulative exposure to crystalline silica-mixed dust in four tin mines. Among the ore miners who were potentially exposed to crystalline silica dust, a similar relationship between crystalline silica and lung cancer was not observed. Studies conducted by the IARC suggested an increase in cancer development with the presence of silicosis and the duration of follow-up period from the first diagnosis of silicosis (Chen *et al.*, 2006).

Another factor that plays a role in cancer incidence is smoking. According to Kurrihara and Wada (2004), the risk of lung cancer in smokers with silicosis was estimated at 4.47 % and at 2.24 % in non-smokers. It is clear that the risk of developing lung cancer among smokers (as compared to non-smokers) in silicotic patients was found to be higher. Preventing silicosis and encouraging smoking cessation may be the most effective measures to reduce lung cancer incidence in silica-exposed workers (Chen *et al.*, 2006).

2.8 History of silicosis

Silicosis is a historic disease that dates back to the ancient Greeks (OSHA, 2009; Mason and Thompson, 2010). It is also a naturally occurring disease and its development is directly associated with workplace exposure to respirable crystalline silica dust.

Silicosis was initially referred to as “pneumoconiosis”, which means dust in the lungs, but this term was replaced with silicosis in 1870 by Visconti (Dutta and Moudgil, 2007). In the 1950s, silicosis was perceived to be prevalent in developed countries, but this perception has proved to be incorrect. Actually, the disease is a major hazard in developing countries due to poor medical surveillance and insufficient control measures. According to Rees and Murray (2007), developing (and low-income) countries have a poor capacity to control dust and to enforce legislation and standards. These aspects give rise to the prevalence of traumatic injuries and the occurrence of infectious disease in developing countries.

In the United States alone, 2.2 million workers are exposed to crystalline silica. Every year more than 250 workers in the United States die from silicosis and hundreds become disabled (NIOSH, 2002). It has been estimated that approximately 5% (100 000) of the 2 million crystalline silica exposed workers are exposed to silica levels above the current permissible exposure limit (PEL) of 0.1 mg/m^3 (Sherson, 2002). In the early twentieth century, silicosis was closely associated with the mining industry – but now the disease is prevalent among hard-rock miners, sandblasters, potters, foundry and steel workers. According to NIOSH (2002), approximately one per cent of exposed workers will develop silicosis after a 40-year working life. A study by Greaves (2000) concluded that the risk of developing silicosis following a lifetime of exposure at a lower exposure limit of 0.05 mg/m^3 is still likely to be 20-40%.

In South Africa, crystalline silica exposure is associated with gold mining and has been observed for over a century (Churchyard *et al.*, 2004). The high prevalence (almost 20%) of silicosis among older in-service mineworkers confirms the existence of a significant epidemic of silicosis in the South African gold mining industry (Rees and Murray, 2007).

2.9 Factors that influence the development of silicosis

Silicosis can be differentiated in three forms; the specific form that develops largely depends on the intensity of exposure to crystalline silica, as well as cumulative exposure. Silicosis can develop from long exposures at low concentrations, or from shorter exposures at high concentrations or from very short exposures to very high concentrations (NIOSH, 2002). Host factors also influence individual susceptibility and smaller particles increase the fibrogenicity of the dust (Rees and Murray, 2007). Other factors that play a role in silicosis development are (1) the particle size of crystalline silica; (2) the natural form (crystalline or non-crystalline); (3) the duration of dust exposures; and (4) the time period from first exposure to diagnosis (NIOSH, 2002).

2.9.1 The pathological features of silicosis

An exposed worker can develop five types of silicosis, namely: alveolar lipoproteinosis (acute silicosis), accelerated silicosis, chronic silicosis, simple silicosis and complicated silicosis.

2.9.1.1 Alveolar lipoproteinosis (Acute silicosis)

This form of silicosis develops after intense, short exposures to crystalline silica, and is the most aggressive form of silicosis. Acute silicosis develops within months (six months to five years of exposure) and has a high mortality rate (Ding *et al.*, 2002; Rees and Murray, 2007). It is characterised by the filling of the alveoli by eosinophilic-granular, lipid-rich pulmonary edema and interstitial inflammation. Lamellar bodies in neutrophils and alveolar macrophages can be observed. A rapid increase in the rate of synthesis and deposition of lung collagen can be observed, which is unique to silica-induced lung disease and differs from normal collagen (OSHA, 2009). Symptoms include coughing, weight loss and fatigue.

Accelerated loss of pulmonary function occurs, resulting in death within a few months (Ding *et al.*, 2002). Acute silicosis is observed in occupations such as sandblasting, surface drilling, silica flour milling and pottery manufacturing where silica particles are mechanically fractured (Ding *et al.*, 2002; OSHA, 2009). Acute silicosis is not as common as the other forms of silicosis.

2.9.1.2 Accelerated silicosis

This type of silicosis develops five to fifteen years after intense exposure to crystalline silica (NIOSH, 2002; OSHA, 2009). This form of the disease has a shorter latency period than chronic silicosis and is less common than acute silicosis. Inflammation with rapid development of silicotic lesions can be observed in exposed workers (Dutta and Moudgil, 2007;). An increase in the number of alveolar macrophages can be observed and nodules are generally small and found in the mid-zones of the lungs. Accelerated silicosis has been associated with occupations where silica is mechanically crushed and fractured, such as abrasive blasting.

2.9.1.3 Chronic silicosis

This is the most prevalent and common form of silicosis. It occurs after a long period of exposure to low concentrations of crystalline silica dust. Chronic silicosis is prevalent after ten to twenty years of exposure to silica dust (OSHA, 2009).

The disease is characterised by distinct silicotic nodules, which are hyalinised in the lymph nodes. The nodules can be found in the upper lobes of the lungs and measure approximately 3 mm in diameter. As the disease progresses, nodules can be found in the pleura and in the mid basal zones. These nodules grow bigger in diameter, up to 3-10 mm. A number of dust-laden macrophages and cellular infiltrates are present in the periphery, while the intervening lung parenchyma still remains normal. The nodules are filled with hyalinised collagen fibers with calcification and small amounts of dusts (Ding *et al.*, 2002). Two types of chronic silicosis exist, namely simple and complicated silicosis.

2.9.1.4 Simple silicosis

Silicotic lesions are less than 1 cm in diameter (3-6 mm) and can be found in the upper and middle lung areas. No respiratory symptoms or lung function abnormalities are observed in this instance, but lung volumes may be slightly reduced (Ding *et al.*, 2002).

2.9.1.5 Complicated silicosis

In the case of complicated silicosis, the silicotic lesions are greater than 1 cm in diameter and are characterised by necrosis, a decrease in lung function and mycobacterial infections are also common. Progressive massive fibrosis or

conglomerate silicosis is characterised by the destruction of surrounding pulmonary architecture. Airway obstruction may occur in the upper lobes, while emphysematous changes are observed in lower lobes of the lung (OSHA, 2009).

2.9.2 Symptoms of silicosis

Symptoms of silicosis may only become visible after many years. This complicates the diagnosis of the disease. Shortness of breath, coughing, respiratory failure, low lung volumes and abnormal pulmonary functions can be observed as the disease progresses in exposed individuals (OSHA, 2009). Silicosis can progress even after the exposed individual has been removed from the source of exposure, and abnormalities may only be visible after fifteen to twenty years after exposure has occurred (NIOSH, 2002; Rees and Murray, 2007; OSHA, 2009).

2.9.3 Silicosis and its diagnosis

Silicosis is difficult to detect in the early stages of the disease, because of its asymptomatic nature. The disease can be diagnosed by means of a chest X-ray, a lung function test, sputum analyses and lung biopsies. To make a full diagnosis, historic exposure information needs to be gathered. This can also be difficult to ascertain if exposure occurred long ago, or if it has been forgotten in light of movement across occupations (RSA DOL, 2006; Rees and Murray, 2007). Lung biopsies are rarely required, but can be used as a diagnostic tool to distinguish between tuberculosis, lung cancer and pulmonary fibrosis (PMF). Crystalline silica exposure evaluation can also be used to assess current risk and is an important indicator in the diagnostic process. The International Labour Organization (ILO) has standardised the radiographic classification of pneumoconiosis by providing a set of standardised radiographs and guidelines for use in this regard. In the most common form of silicosis, namely chronic silicosis, chest X-rays are characterised by rounded opacities distributed in the upper zones of the chest X-ray. In simple silicosis, the rounded opacities can be classified as category 1, 2 or 3, according to their profusion. Complicated silicosis is classified as category 2/3 simple silicosis (Rees and Murray, 2007).

2.10 Prevention and treatment of silicosis

Silicosis is a preventable occupational disease that has no cure. A comprehensive approach is needed to prevent silica-associated diseases. An important preventative

measure is the control of dust concentrations in the workplace. This is an essential form of prevention and should be the governing goal of national and workplace occupational health programmes (Rees and Murray, 2007). According to Rees and Murray (2007), relatively short excursions over the control limit of silicosis have been found to increase the risk of silicosis dramatically. It is important to take note of the fact that the accelerated progression of pulmonary fibrosis (PMF) has been associated with higher cumulative exposures and dust burdens in the lungs. Preventative measures include the enforcement of strict regulations, safety standards, engineering, administrative control, personal protective equipment (PPE), evaluation and improved hazard identification, medical surveillance, training, health education and the monitoring of workers through occupational hygiene programmes (RSA DOL, 2006; OSHA, 2009; Thompson and Kelley, 2010).

Sweden and other high-income (developed) countries have shown progress in efforts to prevent crystalline silica-associated disease. This can be accomplished by well-organised silicosis prevention programmes. Although the main focus should be on primary prevention, crystalline silica-associated diseases with long latency will continue to occur in future based on contemporary exposure. The reduction of very low concentrations of crystalline silica is time-consuming but this is an important component of efforts to prevent the disease. The only truly effective prevention strategy is to avoid the inhalation of crystalline silica-containing dust altogether. Another important factor is the removal of exposed workers from the source of exposure. This in itself will not guarantee that crystalline silica-related diseases will not develop after exposure has ceased. Exposed individuals should be encouraged to give up smoking. Supportive medical treatment for workers with respiratory conditions and their consequences is also vital. Also of importance are the prevention and management of tuberculosis. Treatment for tuberculosis-infected people with silicosis (especially those infected with HIV) is recommended. A study of HIV-infected gold miners with a high prevalence of silicosis reported a reduction of incidence of 38% after routine preventative therapy (Rees and Murray, 2007).

2.11 Occupational exposure to silica

2.11.1 Industries where silica exposure occurs

Crystalline silica is used in a variety of industries (NIOSH, 2002). Due to its frequency of use, silica exposure takes place over a broad range of industries (AIOH, 2009).

These industries include mining, construction, agriculture, manufacturing, foundries, ceramics, exploration, quarrying, sandblasting and electronics (Yassin *et al.*, 2005; Scarselli *et al.*, 2008; AIOH, 2009). High-risk exposure can take place where crystalline silica-containing material is drilled, blasted, crushed or where it is released through distribution processes. The released respirable silica particles can induce lung impairment after inhalation (AIOH, 2009).

Table 2 lists the main industries around the world in which silica exposure has been reported (NIOSH, 2002).

Table 2.2: Main industries and activities around the world in which silica exposure has been reported.

Industry or activity	Operations and tasks	Source materials
Agriculture	Ploughing, harvesting, using machinery, burning agricultural waste, processing agricultural products	Soil
Mining and related milling operations	Most occupations (underground, surface, mill) and mines (metal and non-metal, coal), rock drilling, dredging	Ores, associated rock
Quarrying and related milling operations	Quarrying and related milling operations Crushing stone, sand and gravel processing, stone monument cutting and abrasive blasting, slate work (e.g. pencil manufacturing), diatomite calcinations	Sandstone, granite, flint, sand, gravel, slate, diatomaceous earth
Construction	Abrasive blasting of structures and buildings, highway and tunnel construction, excavation, earth-moving and digging, masonry, concrete work, demolition, dry-sweeping and brushing, pressurised air blowing, jack-hammering, laying railroad tracks, removing rust or paint, sanding and scaling, replacement of asphalt roofing, hauling, pouring, mixing, or dumping silica-containing materials	Sand, concrete, rock, soil, mortar, plaster, shingles
Glass, including fibreglass	Raw material processing, refractory installation and repair	Sand, crushed quartz, refractory materials
Cement	Raw material processing	Clay, sand, limestone, diatomaceous earth
Abrasives	Silicon carbide production, abrasive products fabrication	Sand, tripoli, sandstone
Ceramics, including bricks, tiles, sanitary ware, porcelain, pottery, refractories, vitreous enamels	Mixing, moulding, glaze or enamel spraying, finishing, sculpting, firing	Clay, shale, flint, sand, quartzite, diatomaceous earth
Iron and steel mills	Refractory preparation and furnace repair	Refractory material

Industry or activity	Operations and tasks	Source materials
Silicon and ferro-silicon foundries (ferrous and nonferrous)	Raw materials handling, casting, moulding and shaking out, abrasive blasting, fettling, furnace installation and repair	Sand, refractory material
Metal products, including structural metal, machinery, transportation of equipment and abrasive sand blasting	Abrasive blasting	Sand
Shipbuilding and repair Abrasive blasting	Abrasive blasting	Sand
Rubber and plastics Raw materials handling	Raw materials handling	Fillers (tripoli, diatomaceous earth, silica flour)
Paint	Raw materials handling, site preparation	Fillers (tripoli, diatomaceous earth, silica flour)
Soaps and cosmetics	Manufacturing or occupational use of abrasive soaps and scouring powders	Silica flour
Roofing, asphalt felt Sand and aggregate, diatomaceous earth	Filling and granule application	Sand and aggregate, diatomaceous earth
Agricultural chemicals	Raw material crushing, handling, bagging, or dumping products or raw materials	Phosphate ores and rock
Jewellery	Cutting, grinding, polishing, buffing, etching, engraving, casting, chipping, sharpening, sculpting	Semiprecious gems or stones, abrasives, glass
Arts, crafts, sculpture	Pottery firing, ceramics, clay mixing, kiln repairs, abrasive blasting, sand blasting, engraving, cutting, grinding, polishing, buffing, etching, engraving, casting, chipping, sharpening, sculpting	Clays, glazes, bricks, stones, rocks, minerals, sand, silica flour
Dental material	Sand-blasting, polishing	Sand, abrasives
Boiler scaling	Coal-fired boilers	Ash and concretions
Automobile repair	Abrasive blasting, sanding, removing paint and rust	Sand, metals, priming putty

Source: NIOSH. 2002 NIOSH HAZARD: Health Effects of Occupational Exposure to Respirable Crystalline Silica Available from: URL: (<http://www.cdc.gov/niosh/docs/2002-129/pdfs/2002-129.pdf>).

2.11.2 Silica exposure in mining

Silica exposure still takes place on a global scale. Despite strict rules, regulations and exposure limits, silica exposure remains a subject of global concern. This is seen by the high prevalence of silicosis cases that are being reported annually (Rees *et al.*, 2009). Silica dust is present in mines and quarries where quartz concentrations are high. Silicosis has long been associated with underground mining, which is most

frequently the case in deep level underground mines in South Africa (Nelson *et al.*, 2010). Churchyard *et al.* (2004) reported a prevalence of 18.3% to 19.9% in black miners older than 37 years. This is due to silica quarts which is freshly fractured by drilling, blasting and mining of rock. These activities lead to the creation of smaller particle fractions that can be inhaled. This contributes to the fibrogenicity of silica (Rees *et al.*, 2009). Another factor that contributes to prolonged exposure in the mining industry would be the total number of years spent in mines (Nelson *et al.*, 2010). The years spent in mining have increased from 6 to 16 years, with corresponding increases in silicosis rates from 3% to 34 % (Rees *et al.*, 2009). As miners age and as the years that they work add up, the burden of silicosis and associated diseases will continue to rise. The high proportion of South African gold miners with silicosis will give rise to higher morbidity and mortality rates in current and ex-miners. South Africa is committed to global efforts to eliminate silicosis. This can only be achieved by recording valid, reliable dust measurements linked to ongoing medical surveillance, co-operation with government, industries and unions (Nelson *et al.*, 2010).

2.11.3 Silica exposure in a heavy mineral processing mine

Crystalline silica, commonly known as quartz, occurs in numerous rock types and is a common mineral in most beach sands. Heavy minerals are extracted from beach sand by dredge mining to obtain titanium which is found in minerals such as rutile and ilmenite. Titanium is needed for the production of titanium dioxide, which is a very important commercial product. Rutile deposits are mostly found in beach sand where these are mined, concentrated and separated to obtain ilmenite that acts as a raw material for the production of titanium dioxide (Zhang *et al.*, 2011). Titanium dioxide, which is obtained by industrial processing methods such as roasting and smelting, can be treated further to produce different grades of titanium dioxide.

The mining process extracts heavy mineral sands from sand dunes by dredging in order to produce a heavy mineral concentrate (HMC), which is further processed in the final smelting and processing plants (Williams and Steenkamp, 2006). The final product and processing phases consist of individual plants needed to purify the heavy mineral concentrate delivered from the mining ponds.

At a heavy mineral surface mine, individual plants that are involved and which lead to the production of titanium dioxide include:

- **Mining Ponds A, C, D and E (MPA, MPC, MPD, and MPE)** – Responsible for extracting heavy mineral sands from sand dunes by means of dredging to produce a heavy mineral concentrate (HMC)
- **The mineral separation plant** - Responsible for the separation of three important minerals from the heavy mineral concentrate. Rutile and zircon are stored in bags or rail cars. The third mineral (ilmenite) is stockpiled before being transferred to the roaster plant.
- **Roaster plant** - Ilmenite from the stockpiles is heated to high temperatures to obtain pure ilmenite from the tailings. After the roasting process, the roasted ilmenite is cooled and transferred in the form of iron ore via a conveyor to storage silos.
- **Smelter plant** - Roasted ilmenite and dry char are transferred from silos via the conveyors to the furnace for smelting. The smelter consists of electric arc furnaces which are used to produce titania slag (titanium dioxide) which is transported to the slag cooling bay.
- **Slag plant** – In the slag cooling area, water sprays are used to further cool the slag. The cooled slag is crushed, milled in the slag plant and stored in various storage silos.
- **Alton bagging plant** - The two minerals zircon and rutile are bagged and distributed to buyer.

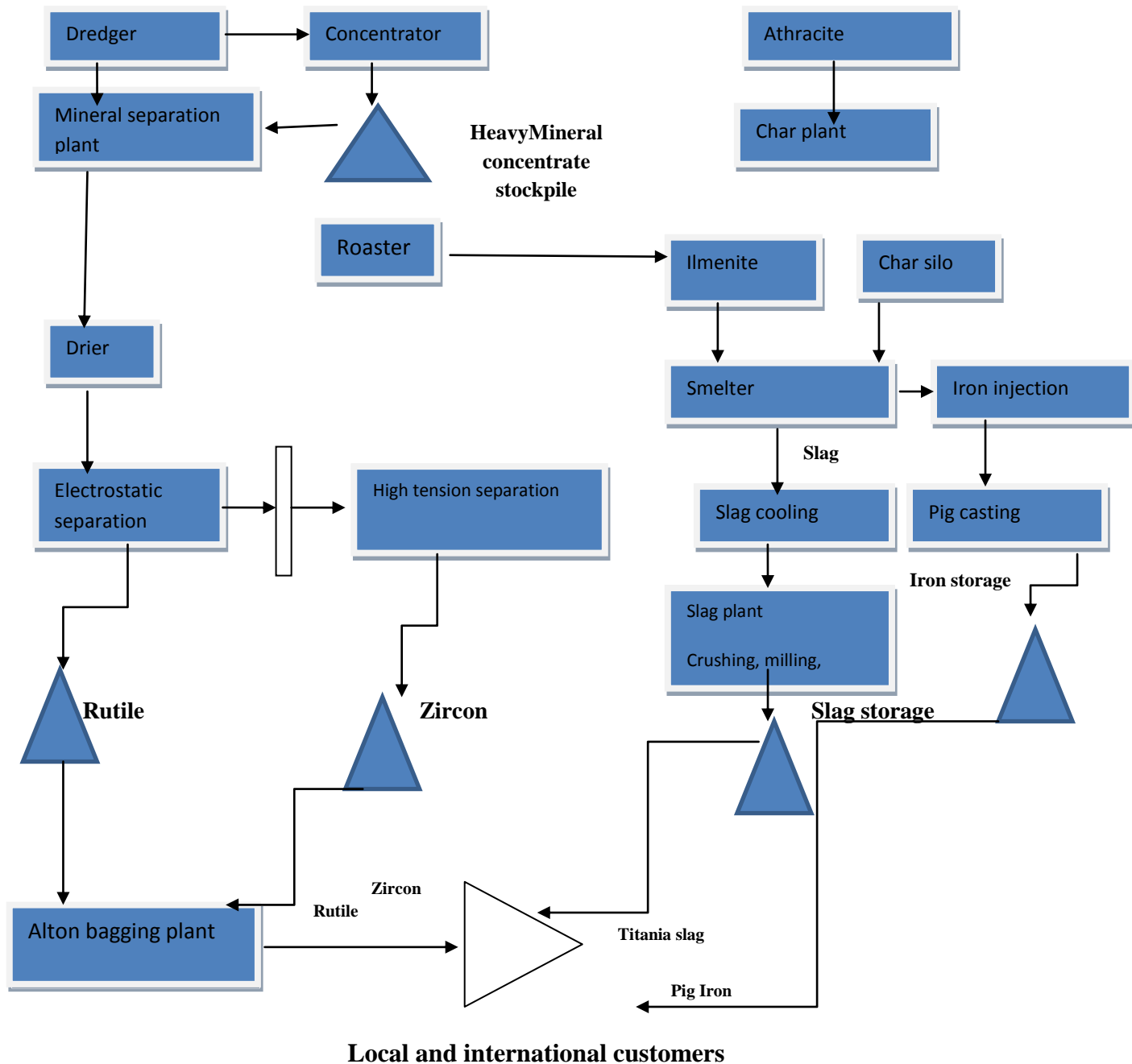


Figure 2.4: Process overview of a heavy mineral processing mine

2.12 Occupational exposure limits

The Hazardous Chemical Substances Regulations (1995) of the South African Occupational Health and Safety Act, (Act no. 85 of 1993, have set an occupational exposure limit: a control limit of 0.1 mg/m^3 for silica crystalline respirable dust, and an occupational exposure-recommended limit of 3 mg/m^3 for amorphous respirable dust (HCS Regulations, 1995).

The occupational hygiene regulations set out under the Mine Health and Safety Act, 29 of 1996, provide an occupational exposure limit of 0.1 mg/m^3 for respirable silica quartz, cristobalite and tridymite. The occupational exposure limit for respirable amorphous silica dust has been set at 3 mg/m^3 (MHSA, section 22.23, 1996). An occupational exposure limit (OEL) is defined as a time-weighted average concentration for an 8-hour working day and a 40-hour working week to which nearly all workers may be repeatedly exposed without adverse health effects. The Occupational Health and Safety Administration (OSHA) of the United States of America has set a permissible exposure limit of 0.1 mg/m^3 for respirable crystalline silica for an 8-hour time-weighted average compared to the National Institute of Safety and Health's (NIOSH) recommended exposure limit of 0.05 mg/m^3 for a 10-hour time-weighted average (OSHA, 2009; Thompson and Kelly, 2010).

A study conducted by Churchyard *et al.* (2004) on South African gold miners indicated a silicosis prevalence of 18.3-19.9% in gold miners who were exposed to crystalline silica (quartz) dust. This research indicates that the occupational exposure limit of 0.1 mg/m^3 is not sufficiently protective against silicosis. Recent epidemiological studies demonstrate that workers have a significant risk of developing chronic silicosis when they are exposed to respirable crystalline silica over a working lifetime at the current OEL of 0.05 mg/m^3 recommended by NIOSH (2002). Reports done for the ACGIH show that a lifetime exposure to silica at an OEL of 0.06 mg/m^3 has a significant increase in developing silicosis, which suggests that an OEL of 0.05 mg/m^3 is not sufficiently protective (ACGIH, 2012). This could pose a problem in the South-African mining industry as the OEL value for crystalline silica is set at 0.1 mg/m^3 (MHSA Regulations, section 22.23, 1996). The ACGIH is already recommending an OEL of 0.025 mg/m^3 (ACGIH, 2012). However, NIOSH still continues to recommend an exposure limit of 0.05 mg/m^3 as a time-weighted average (TWA) for up to a 10-hour workday during a 40-hour work week until improved sampling and analytical methods are developed for respirable crystalline silica (NIOSH, 2002).

2.12.1 General monitoring of airborne particulates

Direct-reading portable dust instruments and personal aerosol samplers are used to measure respirable dust. Direct-reading instruments provide rapid measurements of dust concentrations and operate as assessment tools for control and identification of dust-producing operations. Direct-reading instruments can be used to take multiple

measurements over a period of time; peak exposures and peak exposure patterns can also be observed (Thorpe and Walsch, 2002). A wide range of direct reading devices are available and these allow one to take immediate action with regard to major dust-producing sources. An example is the pDR-1000An, a light-scattering photometer from the Thermo Electron Corporation. This instrument operates on the principle of ambient air movement rather than a pump to introduce airborne particles to a sensor chamber (Thorpe, 2006). Direct-reading devices are not recommended for compliance sampling, but they can be used as diagnostic tools by regulatory agencies (US DOL, 2008).

2.12.2 Personal airborne particulate exposure sampling of silica

Two standard sampling methods are used for crystalline silica sampling and analyses. Both methods make use of either 10 mm Nylon or Higgins Dewell cyclones that operate at a flow rate of either 1.7 or 2.2 litres/min (ℓ/min) respectively (NIOSH, 2003e). These cyclones have been evaluated for their compliance with the ISO/CEN/ACGIH respirable aerosol sampling convention (NIOSH, 2003b). The specific flow rate ensures that the cyclone properly separates the respirable from the non-respirable fractions. The dust mass on the filters is divided by the volume of air sampled. The concentration obtained will be expressed in mg/m^3 . In order to determine the crystalline silica content of the collected dust, analyses are conventionally performed by means of infra-red spectrometry or X-ray powder diffraction (NIOSH, 2003e). All sampling need to be conducted over a period that is representative of the actual daily exposure durations, i.e. exposure sampling must cover at least 80% of the actual exposure period. Dust on the filters can be analysed by a laboratory utilising different methods, such as scanning electron microscopy (SEM), X-ray diffraction (XRD) and infra-red spectrophotometry (IR) (Verma *et al.*, 2002; NIOSH, 2003d; Lee *et al.*, 2010).

2.12.3 Bulk sampling

Bulk samples are an important method used in the identification of unknown exposures and the identification of sources of exposure to airborne silica. A bulk sample is defined as a large sample taken from a sample of material. Bulk air and bulk mass samples (liquid and solid) are two major types of bulk samples. Bulk samples can be collected with a scoop or any other large container in areas where workers perform their tasks. In the case of dust sampling, bulk samples should be representative of the

airborne dust to which the workers are exposed. The dust needs to be representative of the workers' job site or area of activity (NIOSH, 2003b). It is important that bulk samples should be small in size with a view to optimize the laboratory's time.

2.12.4 Quality assurance programme for crystalline silica for sampling

The establishment of a quality assurance programme for crystalline silica is essential towards ensuring strict adherence to standardised procedures (NIOSH, 2003a). The main focus of such a programme is to follow the analytical methods exactly as these are set out in the written document. Deviations from the original method should be avoided. It is important to record any modifications made in the methods of daily laboratory practices. These modifications should be accompanied by validation data demonstrating the equivalence of the modified method. Other factors such as sample preparation, calibration and proficiency testing need to be monitored with a view to ensure measurement accuracy and precision.

Laboratory results can also be checked by an external agency. This can be performed by an external quality assurance (EQA) programme, or by a proficiency scheme. Data from the proficiency testing programme such as the Health and Safety Executive's workplace analysis Scheme for Proficiency (WASP) Programme (U.K.) can be used by a laboratory to demonstrate reproducible results when compared to other laboratories participating in the programme.

2.12.5 Environmental exposure to silica at the mines

Environmental exposure can take place near peak sites, for example mining operations, industrial sites (foundries) and quarries (Humphrey, 2006). A peak site is defined as an area which is likely to release respirable silica particles. Communities living in the immediate vicinities of these operations can be potentially exposed to elevated concentrations of respirable crystalline silica (NIOSH, 2002; OEHHA, 2005).

2.13 Control measures to lower silica exposure

Crystalline silica dust exposure can be controlled by the same techniques that are used for controlling airborne dust exposure (Mason and Thompson, 2010). Elimination and substitution are the most effective controls used to remove a hazard, but are also the most difficult to implement. In the case of the current study, these control measures cannot be implemented because crystalline silica forms part of beach sand.

Engineering controls are used to remove a hazard or to place a barrier between the worker and the hazard, for example by means of local exhaust ventilation. Administrative controls and personal protective equipment are also used in existing processes when hazards are not properly controlled. Administrative controls may include job rotation of workers away from the dusty area.

Engineering controls are regarded as one of the most effective methods that can be used to control crystalline silica exposure. According to Lahari *et al.* (2005), the application of engineering control programmes is cost-effective in both low and high-income countries, but the cost of engineering equipment varies from country to country. The best control method is the prevention of crystalline silica exposure that can lead to inhalation (RSA DOL, 2006).

The use of personal protective equipment (PPE) is regarded as the last control that must be applied when all other means of control do not lower the exposure. However, the selection of respiratory protective equipment should not be heavily relied on as a main source of protection (Mason and Thompson, 2010; Thompson and Kelley, 2010).

Another key control measure is the establishment of a national silicosis elimination programme. A number of countries, including South Africa, have adapted this programme. Programmes like these cover aspects like awareness, training and education, targeting of priority industries for dust control, improved case finding and compensation (Rees and Murray, 2007). South Africa has committed itself to the goal of no new occupational related silicosis cases by 2030 (RSA DOL, 2006).

Every crystalline silica-exposed worker should undergo regular medical examinations. These include an annual large chest plate X-ray and lung function tests. Promoting a healthy lifestyle among exposed employees is also important in health promotion (Thompson and Kelley, 2010). Educating workers about the dangers of crystalline silica exposure is key in preventing fatal consequences. Several sources are available from government agencies such as NIOH and local Department of Labour (DOL) offices.

2.14 References

- ACGIH (AMERICAN CONFERENCE OF GOVERNMENTAL INDUSTRIAL HYGIENIST). (2012) Threshold Limit Values for Chemical Substances and Physical Agents & Biological Exposure Indices. Cincinnati (OH): 238 p.
- AIOH (AUSTRALIAN INSTITUTE OF OCCUPATIONAL HYGIENIST). (2009) Respirable crystalline silica and occupational health issues. Available from: URL: http://www.aioh.org.au/downloads/documents/PositionPapers/AIOH_RCSPositionPaper.pdf. Accessed 21 Sep 2011.
- Akbar-Khanzadeh F, Brillhart RL. (2002) Respirable crystalline silica dust exposure during concrete finishing (grinding) using hand-held grinders in the construction industry. *Ann Occup Hyg*; 46: 341-6.
- Brown T. (2009) Silica exposure, smoking, silicosis and lung cancer-complex interactions. *Occup Med*; 59: 89-95.
- CCOHS (CANADIAN CENTRE FOR OCCUPATIONAL HEALTH AND SAFETY). (2011) How do particulates enter the respiratory system. Available from: URL: http://www.ccohs.ca/oshanswers/chemicals/how_do.html. Accessed 26 Aug 2011.
- Chen W, Yang J, Chen J *et al.* (2006) Exposure to silica mixed dust and cohort mortality study in tin mines: Exposure-response analysis and risk assessment of lung cancer. *Am J Ind Med*; 49: 67-76.
- Cho WS, Choi M, Han BS *et al.* (2007) Inflammatory mediators induced by intratracheal instillation of ultrafine amorphous silica particles. *Toxicol Lett*; 175: 24-33.
- Churchyard GJ, Ehrlich R, TeWaternaude JM *et al.* (2004) Silicosis prevalence and exposure-response relations in South-African goldminers. *Occup Environ Med*; 61: 811-6.
- Collins JF, Salmon AG, Brown JP *et al.* (2005) Development of a chronic inhalation reference level for respirable crystalline silica. *Regul Toxicol Pharmacol*; 43: 292-300.

- Ding M, Chen F, Shi X *et al.* (2002) Disease caused by silica: Mechanisms of injury and disease development. *Int Immunopharmacol*; 2: 173-182.
- Dutch S. (2009) Silica polymorphs. Available from: URL: <http://www.uwgb.edu/dutchs/Petrology/Silica%20Poly.HTM>. Accessed 4 October 2011.
- Dutta D, Moudgil BM. (2007) Crystalline silica particles mediated lung injury. Available from: URL: http://www.kona.or.jp/searh/25_076.pdf. Accessed 25 Aug 2011.
- Ghiazza M, Scherbart AM, Fenoglio I *et al.* (2011) Surface iron inhibits quartz-induced cytotoxic and inflammatory responses in alveolar macrophages. *Chem Res Toxicol*; 24: 99-100.
- Gibbs GW, Du Toit RSJ. (2002) Quartz exposure of South-African gold miners. *Ann Occup Hyg*; 46: 597-607.
- Gilberti RM, Gaurav N, Joshi D *et al.* (2008) The phagocytosis of crystalline silica particles by macrophages. *Am J Resp Cell Mol Bio*; 39: 619-627.
- Greaves IA. (2000) Not-so simple silicosis: a case for public health action. *Am J Ind Med*; 37: 245-251.
- Guthrie KE, Driscoll GD. (2010) Crystalline silica and silicosis. *Comp Toxicol*; 8: 331-5.
- HCS Regulations (HAZARDOUS CHEMICAL SUBSTANCES REGULATIONS). (1995) Occupational Health and Safety Act 85 of 1993. Available from: URL: <http://www.info.gov.za/acts/1996/a29-26.pdf>. Accessed 28 Nov 2012.
- Humphrey E. (2006) Somersby Action Committee, submissions to Senate Inquiry Workplace exposure to toxic dust. Commonwealth of Australia 2006. Available from: URL: http://www.maqohsc.sa.gov.au/_upload_docs/20080129034136.exposure_toxic_dust.pdf. Accessed 5 Oct 2011.
- IARC (INTERNATIONAL AGENCY FOR RESEARCH ON CANCER). (1997) Monographs on cancer on the evaluation of carcinogenic risks to humans. Silica, some silicates coal dust and para-aramid fibrils. Available from: URL:

- <http://monographs.iarc.fr/ENG/Monographs/vol68/volume68.pdf>. Accessed 25 Aug 2011.
- Keawamatawong T, Kawamura N, Okajima M *et al.* (2005) Acute pulmonary toxicity caused by exposure to colloidal silica: particle size dependant pathological changes in mice. *Toxicol Pathol*; 33: 745-751.
- Kurrihara N, Wada O. (2004) Silicosis and smoking strongly increase lung cancer risk in silica-exposed workers. *Ind Health*; 42: 303-14.
- Lahari S, Levenstein C, Nelson DI *et al.* (2005) The cost effectiveness of occupational health interventions: Prevention of silicosis. *Am J Ind Med*; 48: 503-14.
- Lange JB. (2008) Effects of wood dust: Inflammation, genotoxicity and cancer. Copenhagen: UCPH (Thesis-PhD).
- Lee T, Kim SW, Chisholm WP *et al.* (2010) Performance of high flow rate samplers for respirable particle collection. *Ann Occup Hyg*; 6: 697-709.
- Makinson KS. (2008) Validation of biomarkers for improved assessment of exposure and early effect from exposure to crystalline silica. Johannesburg: University of the Witwatersrand (Thesis – MSc).
- Martinez C, Prieto A, Gara L *et al.* (2010) Silicosis: A disease with an active present. *Arch Bronconeumol*; 46: 97-100.
- Mason E, Thompson SK. (2010) A brief overview of crystalline silica. *J Chem Health Saf*; 7: 6-8.
- Mbatha N. (2009) Crystalline silica-induced inflammation. Johannesburg: University of Johannesburg (Dissertation - MTech).
- Meldrum M, Howden P. (2002) Crystalline silica: Variability in fibrogenic potency. *Ann Occup Hyg*; 46: 27-30.
- MHSA (MINE HEALTH AND SAFETY ACT). (1996) Act 29 of 1996. Available from: URL: <http://www.info.gov.za/acts/1996/a29-96.pdf>. Accessed 12 Nov 2011.

- Nelson G, Girdler-Brown B, Ndlovu N *et al.* (2010) Three decades of silicosis: Disease trends at autopsy in South-African gold miners. *Environ Health Perspect*; 118: 421-426.
- NIOSH (NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH). (2002) Health effects of occupational exposure to respirable crystalline silica. Available from: URL: <http://www.cdc.gov/niosh/docs/2002-129/pdfs/2002-129.pdf>. Accessed 26 Aug 2011.
- NIOSH (NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH). (2003a) General considerations for sampling airborne contaminants. Available from: URL: <http://www.cdc.gov/niosh/docs/2003-154/pdfs/chapter-d.pdf>. Accessed 25 Aug 2011.
- NIOSH (NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH) (2003b) Manual of analytical methods. Determination of airborne crystalline silica. Available from: URL: <http://www.cdc.gov/niosh/docs/2003-154/pdfs/chapter-r.pdf>. Accessed 25 Aug 2011.
- NIOSH (NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH). (2003c) Silica amorphous. Available from: URL: <http://www.cdc.gov/niosh/docs/2003-154/pdfs/7501.pdf>. Accessed 21 Aug 2011.
- NIOSH (NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH). (2003d) Silica, crystalline, by XRD (filter redeposition). Available from: URL: <http://www.cdc.gov/niosh/docs/2003-154/pdfs/7500.pdf>. Accessed 21 Aug 2011.
- NIOSH (NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH). (2003e) Silica, crystalline by IR. Available from: URL: <http://www.cdc.gov/niosh/docs/2003-154/pdfs/7602.pdf>. Accessed 21 Aug 2011.
- OEHHA (OFFICE ON ENVIRONMENTAL HEALTH HAZARDS ASSESSMENT). (2005) Adoption of chronic reference exposure level for silica, crystalline respirable. Available from: URL: <http://www.oehha.ca.gov/air/chronic/silica>. Accessed 12 Oct 2011.

- O'Reilly KMA, Phipps RP, Thatcher, TH *et al.* (2005) Crystalline and amorphous silica differentially regulate the cyclooxygenase-prostaglandin pathway in pulmonary fibroblasts: Implications for pulmonary fibrosis. *Am J Physiol Lung Cell Mol Physiol*; 288: 10-6.
- OSHA (OCCUPATIONAL SAFETY AND HEALTH ADMINISTRATION). (2009) Health considerations for workplace exposure to silica. Available from: URL: <http://www.dli.mn.gov/osh/PDF/silica.pdf>. Accessed 26 Aug 2011.
- Porter DW, Barger M, Robinson, VA *et al.* (2002) Comparison of low doses of aged and fresh fractured silica on pulmonary inflammation and damage in the rat. *Toxicology*; 75: 63-71.
- Rees D, Murray J. (2007) Silica, silicosis and tuberculosis. *Int J Tuberc Lung Dis*; 11: 474-84.
- Rees D, Murray J, Nelson G *et al.* (2009) Oscillating migration and the epidemics of silicosis, tuberculosis, and HIV infection in South African gold miners. *Am J Ind Med*; 53: 398-404.
- RSA DOL (REPUBLIC OF SOUTH-AFRICA DEPARTMENT OF LABOUR). (2006) Silica exposure and its effect on the physiology of workers. Available from: URL: <http://www.labour.gov.za/documents/useful-documents/occupational-health-and-safety/silica-exposure-and-its-effect-on-the-physiology-of-workers>. Accessed 25 August 2011.
- Samal S, Mohapatra BK, Mukherjee PS. (2010) The effect of heat treatment on titania slag. *J Min Mat Char Eng*; 9: 795-809.
- Scarselli A, Binazzi A, Marinaccio A. (2008) Occupational exposure to crystalline silica: Estimating the number of workers potentially at high risk in Italy. *Am J Ind Med*; 51: 941-9.
- Sherson, D. (2002) Silicosis in the twenty first century. *Occup Environ Med*; 59: 721-2.
- TCEQ (TEXAS COMMISSION ON ENVIRONMENTAL QUALITY). (2009) Silica, crystalline forms. Development support document. Available from: URL:

- http://www.tceq.com/assets/public/implementation/tox/dsd/final/october09/silica_crystalline_forms.pdf. Accessed 25 Aug 2011.
- TeWaternaude JM, Ehrlich RT, Churchyard GJ *et al.* (2006) Tuberculosis and silica exposure in South African gold miners. *Occup Environ Med*; 63: 187-92.
- Thompson CR, Kelley TR. (2010) A brief review of silicosis in the United States. *Environ Health Insights*; 4: 21-6.
- Thorpe A. (2006) Assessment of personal direct-reading dust monitors for the measurement of airborne inhalable dust. *Ann Occup Hyg*; 51: 97-112.
- Thorpe A, Walsch PT. (2002) Performance testing of three portable, direct-reading dust monitors. *Ann Occup Hyg*; 46: 197-207.
- US DOL (UNITES STATES DEPARTMENT OF LABOUR). (2008) A practical guide to an occupational health program for respirable crystalline silica. Available from: URL: <http://www.msha.gov/alliances/formed/IG103.pdf>. Accessed 20 Sep 2011.
- Verma DK, Johnson DM, Tombe KD. (2002) A method for determining crystalline silica in bulk samples by fourier transform infrared spectrophotometry. *Ann Occup Hyg*; 7: 609-61.
- Williams GE, Steenkamp JD. (2006) Heavy mineral processing at Richards Bay Minerals. *Southern African Pyrometallurgy*; 5: 181-8.
- Yassin A, Yebesi F, Tingle R. (2005) Occupational exposure to crystalline silica dust in the United States, 1988-2003. *Environ Health Perspect*; 113: 255-60.
- Zang W, Zhu Z, Cheng CY. (2011) A literature review of titanium metallurgical process. *Hydrometallurgy*; 108: 177-88.

CHAPTER 3

ARTICLE

Guidelines for Authors

Annals of Occupational Hygiene

The Annals of Occupational Hygiene publishes material that significantly extends knowledge on aspects of occupational health and hygiene. All submissions which include scientific data or opinions are sent to two referees. The editors will make a decision within two months of receiving the paper. After two months, a decision will be sent to the author. The editor's decision in this aspect is final. Original work should be submitted and should not be published elsewhere.

The corresponding author should be identified and all sources of financial support for work must be stated. The manuscript must be in English with the use of either British or American styles and spelling.

The length of the paper depends on the subject and it must be consistent with clarity. If the length of the paper exceeds 5 000 words, a statement must be included that justifies the extra length.

The paper should consist of an Introduction, Method, Results, Discussion and Conclusion. An abstract of the arguments and findings should be included and may be arranged under Objectives, Methods, Results and Conclusions.

Figures should be good quality with low resolution and should be on separate pages at the end of the text. Tables should be numbered consecutively, given a suitable caption and on separate pages. Footnotes of tables should be typed in superscript below the table.

References at the end of the paper should be listed in alphabetical order, using the Vancouver style of abbreviations and punctuation.

Morse SS. (1995) Factors in the emergence of infectious disease. *Emerg Infect Dis* [serial online] 1995 Jan-Mar; 1 (1). Available from: URL: <http://www.cdc.gov/nicidod/EID/eid.htm>

Simson, AT, Groves, JA, Unwin J, Piney, M. (2000) Mineral oil metal working fluids (MwFs) - Development of practical criteria for mist sampling. *Ann Occup Hyg*; 44 165-72

Note: The journal requires that tables and figures should be on separate pages at the end of the text. However, with a view to improve readability, the tables and figures in the following article were placed in the text.

For examination purposes the article contains more than 5 000 words. In the final publication of this article, the number of words will be reduced to less than 5 000.

Exposure to silica during the production of titanium dioxide from beach sand

¹Maryda Draai, ¹Fritz Eloff, ²Jaco van Rensburg

**Affiliation: ¹ School of Physiology, Nutrition and Consumer Sciences,
North-West University, Potchefstroom Campus, Private Bag X6001,
Potchefstroom 2520, South Africa
² Gijima Occupational Hygiene and Environmental Services,
Private Bag X1807, Middelburg, South Africa**

Corresponding Author

Miss M. Draai

School of Physiology, Nutrition and Consumer Sciences

North-West University, Potchefstroom Campus

Private Bag X6001

Potchefstroom 2520

South Africa

Tel/Fax. 018 299 2442

Word Count: 6235

Abstract

Objectives: To characterise silica structure and evaluate the risk of developing silicosis amongst exposed workers at different production phases of titanium dioxide from beach sand.

Methods: At each sand mining and titanium dioxide production phase, personal respirable airborne particulate exposure was measured using personal air sampling pumps, cyclones and filter cassette assemblies. Respirable airborne particulates were analysed for their silica content by an accredited laboratory, from which personal respirable silica exposure levels were calculated. Bulk samples of the sources of airborne dust were obtained from the mining and individual production phases and were analysed by an accredited laboratory. The differences in silica crystal structure and exposure levels obtained from each mining and production phase were characterised by means of X-ray diffraction.

Results: Silica quartz was detected in personal respirable exposure and bulk samples obtained from the mining and production plants. Amorphous silica was only detected in three personal exposure samples at the Slag plant and in the bulk sample obtained from the Roaster plant. All the silica quartz and amorphous silica concentrations in personal exposure samples were well below their respective exposure limits of 0.1 mg/m^3 (quartz) and 3 mg/m^3 (amorphous). No significant differences were found between the silica quartz concentrations in personal respirable exposure samples obtained from the mining ponds and the production plants, although a practical significance was found between some mining and production area personal exposure samples. The silica quartz content in personal respirable exposure and bulk samples increased from the mining ponds to production plants.

Conclusion: All the silica quartz and amorphous silica concentrations in personal exposure samples were below their respective exposure limits. The non-significant differences between exposure concentrations and a practical significance suggest the use of a larger sample group in future. Other studies done in non-mining industries showed that some workers were over exposed to respirable silica dust. Compared to these findings the results of the present study showed the opposite, with respirable silica dust levels being below the South African action level and OEL. Further research, involving more samples, over a longer period of time, would probably be able to show a clear trend as to how quartz structures and exposure profiles change from the

mining to the various production processes. Over-exposure to silica quartz anywhere at the mine and production processes is considered unlikely, with the risk of developing silicosis being low.

Keywords: silica, respirable dust, beach sand, silicosis, titanium dioxide

1. Introduction

Silica, a common silicon oxide (SiO_2) occurs naturally and is a colourless, odourless non-combustible solid (Yassin *et al.*, 2005). Silica can be either crystalline or non-crystalline (amorphous). Crystalline forms include alpha and beta quartz, cristobalite and tridymite (OSHA, 2009; Mason and Thompson, 2010). Alpha quartz is the most frequently found crystalline polymorph and is also the most thermodynamically stable under ambient conditions. Beach sand and volcanic glass consist almost purely of silica, whereas topsoil, sands, sedimentary rocks and stones contain varying amounts of quartz. Alpha quartz is most frequently associated with occupational exposure problems since it is released during mining, blasting, foundry and construction activities (NIOSH, 2003).

Silica, both in its amorphous and crystalline states, can transform at extreme heat or very slow-cooling conditions (NIOSH, 2003). Amorphous silica can transform into crystalline silica at temperatures higher than 1 000 °C (OSHA, 2009).

Titanium dioxide is commonly found in nature in ilmenite ores in association with various amounts of oxide impurities of elements such as iron, silicon, magnesium and others. Ilmenite can be commercially upgraded into titania slag. Titania slag is an odourless black solid produced by electric arc smelting at 1 700 °C, which is above the melting point of silica. Titania slag is composed of an abundance of the crystal phase known as pseudobrookite-karooite (>97%); it also comprises a glassy amorphous silica phase (<3%). Titania slag is rapidly cooled by air after smelting and then water-cooled by means of a water spray system. By means of these heating and rapid cooling processes, the silica structure changes from crystalline solid (quartz), to liquid, to amorphous solid (Samal *et al.*, 2010).

Silica quartz can also be transformed during industrial processes, and these can alter the crystalline formation, especially when heated (OSHA, 2009; Samal *et al.*, 2010). Alpha and beta quartz are sub-polymorphs of quartz, and alpha quartz is the most

common formation of the two. Upon heating, alpha quartz can be transformed into beta quartz at temperatures above 570 °C, and reverts back to the original alpha quartz structure when cooled. When the heating process exceeds 578 °C but remains below 1470 °C, tridymite will be formed. At temperatures above 1470 °C cristobalite will be formed. Neither tridymite or cristobalite can convert back to alpha quartz (RSA DOL, 2006; Guthrie and Driscoll, 2010). Cristobalite and tridymite exposures seldom occur and can only be encountered when silica-containing materials are exposed to extreme temperatures (Guthrie and Driscoll, 2010).

The inhalation of excessive crystalline silica (quartz) is associated with the development of silicosis, a pulmonary disease which is characterised by a decline in respiratory function and premature death (Porter *et al.*, 2002; Schatzel, 2009). Silicosis occurs in three pathological forms. These include acute, accelerated and chronic silicosis (Makinson, 2008). Symptoms of silicosis may only become visible after many years. This makes the diagnosis of the disease very difficult.

Symptoms such as coughing, shortness of breath and acute silicosis are closely associated with high concentrations of crystalline (quartz) exposure (Collins *et al.*, 2005). Crystalline silica exposure has also been implicated in the development of autoimmune diseases such as rheumatoid arthritis, scleroderma, systemic lupus and chronic renal disease (Akbar-Khanzadeh and Brillhart, 2002; Brown, 2009). Occupational exposure to crystalline silica has been associated with lung cancer risk in humans, and this led to the classification of crystalline silica as a Group 1 carcinogen by the International Agency for Research on Cancer (IARC) in 1997 (IARC, 1997).

Factors such as the origin, the chemical components associated with the particle and the composition of the particle play a role in the biological toxicity of crystalline silica. Elements like aluminium and iron are closely associated with crystalline silica. Aluminium can have a protective effect, while the presence of iron can lead to the formation of reactive oxygen species (AIOH, 2009; Guthrie and Driscoll, 2010).

Respirable particle fractions smaller than 10 µm are more toxic to the lungs than larger fractions. These particles and those up to 10 µm in aerodynamic diameter can penetrate to the alveoli, resulting in the development of silica disease. Structural differences in polymorphs can also contribute towards toxicity (Guthrie and Driscoll, 2010). The surface of the crystalline silica particle interacts with the lung fluids, molecules and cells; therefore, the properties of the particle surface determine its

toxicity. Processes like cutting, grinding, crushing or milling cleave silica particles into smaller particles. This, in turn, leads to the formation of reactive free radical species like silicon and siloxyl radicals at the newly generated particle surface (Porter *et al.*, 2002; Meldrum and Howden, 2002). Research suggests that freshly cut surfaces of crystalline silica are more harmful than old or “aged” surfaces (Meldrum and Howden, 2002; NIOSH, 2002).

Amorphous silica is considered to be less hazardous than crystalline silica. This perception is based on its solubility in the lungs and rapid clearance to other organs. Amorphous silica and crystalline silica can both cause pulmonary inflammation, while only crystalline silica is implicated in the development of pulmonary fibrosis (O’ Reilly *et al.*, 2005; Cho *et al.*, 2007).

Countless research experiments have been conducted regarding crystalline silica exposure around the world because of its crippling effects. However, the exposure of workers to silica due to industrial processes in mineral mining has not been researched to a great degree of detail. In South Africa, crystalline silica exposure is closely associated with gold mining (Gibbs and Du Toit, 2002; RSA DOL, 2006).

The aim of this study is to investigate the different forms of crystalline silica and amorphous silica at the different phases of titanium dioxide production by means of personal respirable airborne particulate monitoring, and to quantify the crystalline silica content of the personal airborne and bulk samples by means of X-ray diffraction and evaluate the risk of developing silicosis.

2. Materials and methods

2.1 Study design

2.1.1 Workers

Workers at a heavy mineral processing mine located in KwaZulu–Natal, South Africa, who had been potentially exposed to silica dust, were selected to participate in this study. Five plant operators from each production phase of titanium dioxide production participated in this study. The selected five plant operators represented workers with potentially the highest exposure. Forty five plant operators in total participated. The test subjects performed different tasks applicable to every mining and production area. The selected workers included both male and female employees.

Sample strategies

Description of the work areas of potentially exposed workers

The mining process entails extracting heavy mineral sands from sand dunes by means of dredging in order to produce a heavy mineral concentrate (HMC) which is further processed by the final product processing plants. The final product processing phases consist of plants in which the heavy mineral concentrate delivered from the mining ponds is purified.

Individual plants involved, which lead to the production of titanium dioxide include:

- **Mining Ponds A, C, D and E (MPA, MPC, MPD, and MPE)** – Responsible for extracting heavy mineral sands from sand dunes by means of dredging to produce a heavy mineral concentrate (HMC)
- **The mineral separation plant (MSP)** - Responsible for the separation of three important minerals from the heavy mineral concentrate. Rutile and zircon are stored in bags or rail cars. The third mineral (ilmenite) is stockpiled before being transferred to the roaster plant.
- **Roaster plant** - Ilmenite from the stockpiles is heated to high temperatures to obtain pure ilmenite from the tailings. After the roasting process, the roasted ilmenite is cooled and transferred in the form of iron ore via a conveyor to storage silos. All through this chapter Roaster plant will be referred to as Roaster.
- **Smelter plant** - Roasted ilmenite and dry char are separately transferred from silos via the conveyors to the furnace for smelting. The smelter consists of electric arc furnaces which are used to produce titania slag (titanium dioxide) which is transported to the slag cooling bay. All through this chapter Smelter plant will be referred to as Smelter.
- **Slag plant** – In the slag cooling area, water sprays are used to further cool the slag. The cooled slag is crushed, milled in the slag plant and stored in various storage silos.
- **Alton bagging plant** – The two minerals, zircon and rutile are bagged and distributed to buyers. All through this chapter Alton bagging plant will be referred to as Alton.

Two production streams exist, and include the following areas:

Production stream 1 - Includes mining ponds A, C, D, E, MSP and Alton. Sand dunes are mined at the ponds to produce a heavy mineral concentrate (HMC) which is transferred to the Mineral Separation plant (MSP) to separate rutile, zircon and ilmenite from the heavy mineral concentrate. From here rutile and zircon are transferred to Alton to be bagged and shipped to buyers.

Production stream 2 - Also includes mining ponds A, C, D, E, MSP but also includes the Roaster, Smelter and Slag plant. Ilmenite separated from the heavy mineral concentrate is transferred to the Roaster and Roaster feed and char are conveyed to the Smelter to produce titanium dioxide (titanium slag) which is cooled in the slag cooling bay and later crushed and ground to produce different grades of slag. In Figure 3.1 the percentage silica quartz in respirable dust exposure samples from the mining and different production areas is indicated.

2.1.2 Personal respirable airborne particulate sampling and analysis for silica

The NIOSH 0600 method was used to determine the respirable particles present in the breathing zones of workers during an eight-hour shift. Personal air samples were collected using Casella Apex pumps connected to Higgins Dewell cyclones. Each sampling train consisted of

- a 37 mm, 0.8 μm mixed cellulose ester filter; and
- a cellulose support pad contained in a filter cassette attached to a cyclone used to capture respirable dust.

The sampling train was assembled before each monitoring day with the pump calibrated with a Gillian flow meter at a flow rate of 2.2 ℓ/min before and after sampling.

Personal respirable dust exposure samples were sealed in filter cassettes and stored at room temperature of 25 °C after each monitoring.

2.1.3 Bulk samples

Representative bulk samples from the sources of airborne dust were obtained from each monitoring area. Twenty bulk samples were collected in total. The settled dust from overhead structures was collected in plastic containers and stored at room temperature of 25 °C. Three bulk samples were obtained from the Slag plant namely Slag-chloride, Slag-sulphate and Slag-dust.

Both the personal respirable exposure samples and the bulk samples were sent to a SANAS accredited laboratory for analysis by X-Ray diffraction. Due to the fact that NIOSH method 7500 had to be used to analyse the samples for crystalline and amorphous silica, the analysis was outsourced to another laboratory, accredited for this analysis method.

2.1.4 Statistical analysis

The statistical analysis of the results was carried out using PASW Statistics 18 (SPSS Inc). Basic descriptive statistics, including the calculation of the mean and standard deviation, were performed. The Kolomogorov-Smirnov and Shapiro-Wilk tests were performed to test for normality. A comparative analysis between the silica exposure concentrations (amorphous and quartz) at the mining and production areas was performed, using the ANOVA analytical test. The effect sizes between the silica concentrations (amorphous and quartz), measured at the mining and production areas, were calculated to determine the practical significance between the results from the production areas. The non-parametric version of an ANOVA , the Kruskal-Wallis test, was also performed to ensure accurate representation personal exposure samples.

The original data is attached as Addendum 1. The analytical detection limit for silica (amorphous and quartz) was 0.005 mg. All values below the detection limit were adjusted by the following formula: $0.005 \text{ mg}/\sqrt{2}$. This decision was guided by relative uncertainty regarding how far the silica contents of the samples were below the detection limit. The values could not be recorded as zero or 0.005 mg.

3. Results

The personal exposure to silica of employees at a heavy mineral surface mine was determined by personal respirable airborne dust exposure sampling. In total, 45 personal respirable airborne dust exposure samples were collected from employees and 20 representative bulk samples from the sources of airborne dust were obtained from monitoring areas to ensure accurate representation of employees. Five personal respirable exposure samplers were collected from each area. The samples were analysed for their silica content (both amorphous and crystalline). The 45 employees included both male and female workers.

Table 3.1 reflects the mean values and the standard deviations for the personal exposure levels measured at the mining and production areas. Table 3.2 indicates the results for bulk samples collected within the mining and production areas, expressed as a percentage for silica quartz and amorphous silica. The mean (\pm SD) exposure to silica quartz in the Slag plant was $0.0024 \pm 0.026 \text{ mg/m}^3$, indicating a large variance in the samples. The mean (\pm SD) exposure to amorphous silica in the Slag plant was $0.329 \pm 0.421 \text{ mg/m}^3$, also indicating a large variance in the samples. The Slag plant results show both silica quartz and amorphous silica exposures. The highest silica quartz exposure was detected at the Slag plant, and Mining Pond C had the lowest exposure.

Table 3.1: The mean silica quartz and amorphous exposure concentrations (mg/m^3) and standard deviation for the mining (MPA, MPC, MPD, MPE) and production areas.

Area	N	Mean silica quartz (mg/m^3) and SD	Mean amorphous (mg/m^3) and SD
MSP	5	0.012 ± 0.006	0.004 ± 0.000
Roaster	5	0.012 ± 0.003	0.004 ± 0.000
Smelter	5	0.010 ± 0.003	0.004 ± 0.000
Slag plant	5	0.024 ± 0.026	0.392 ± 0.421
Alton	5	0.007 ± 0.001	0.004 ± 0.0005
MPA	5	0.007 ± 0.001	0.004 ± 0.0004
MPC	5	0.006 ± 0.007	0.004 ± 0.0004
MPD	5	0.008 ± 0.004	0.005 ± 0.000
MPE	5	0.010 ± 0.002	0.004 ± 0.0004

Legend: N-number of samples; Mean - concentrations; SD - standard deviation; MSP - Mineral Separation Plant; MPA - Mining Pond Alpha; MPC - Mining Pond Charlie; MPD - Mining Pond Delta; MPE- Mining Pond Echo

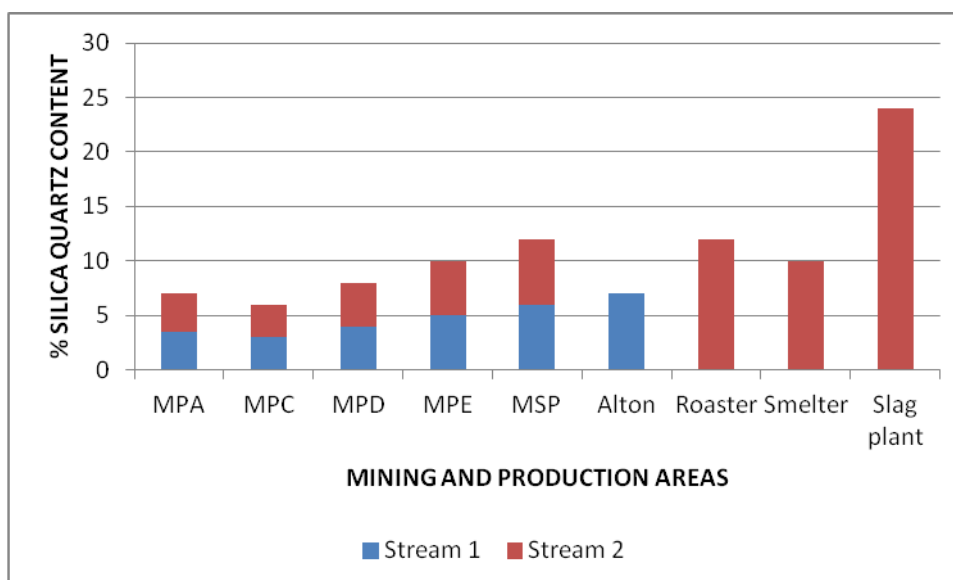


Figure 3.1: The mean % silica quartz content in respirable dust exposure samples for production streams 1 and 2

Two colours are used in the figures to distinguish between the two streams.

The amorphous silica concentration in the Slag plant was significantly higher than all the other productions areas, Figure 3.2).

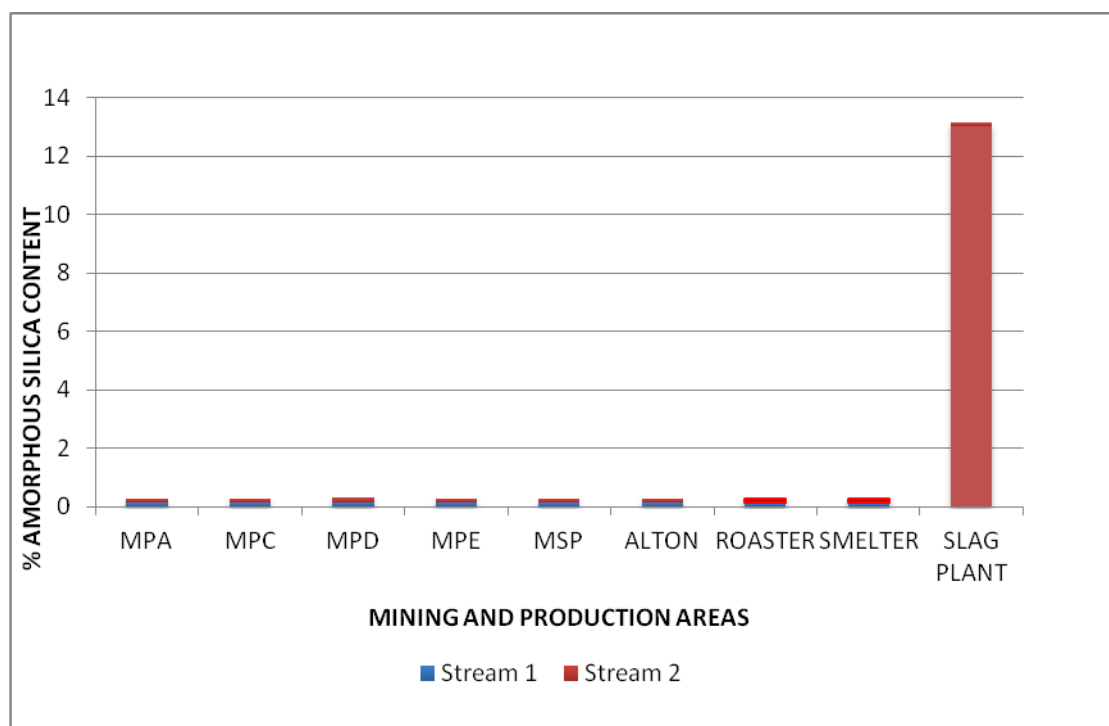


Figure 3.2: The mean % amorphous silica content in respirable dust exposure samples for production streams 1 and 2

Figure 3.3 shows the mean silica quartz exposures for all mining and production areas were below the action level (0.05 mg/m^3) and the occupational exposure limit (0.1 mg/m^3).

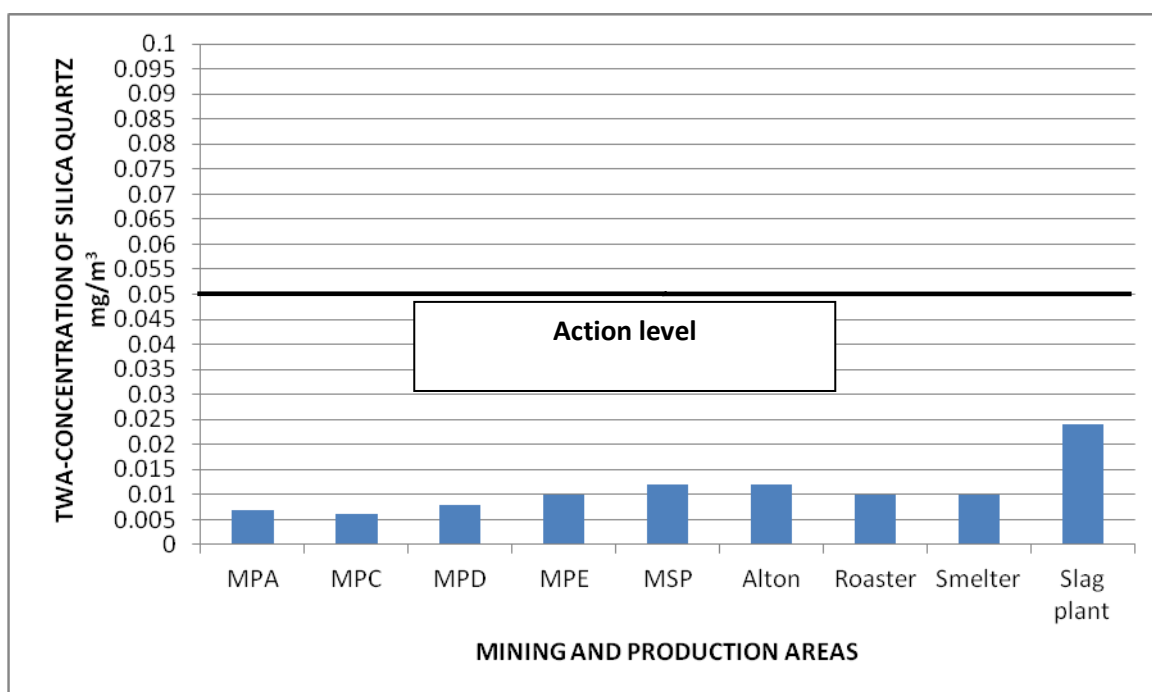


Figure 3.3: The mean TWA-concentration of silica quartz in the different mining and production areas

The mean amorphous silica exposures for all mining and production areas were below the action level (1.5 mg/m^3) and the occupational exposure limit (3 mg/m^3) with Slag plant having the highest exposure (Figure 3.4).

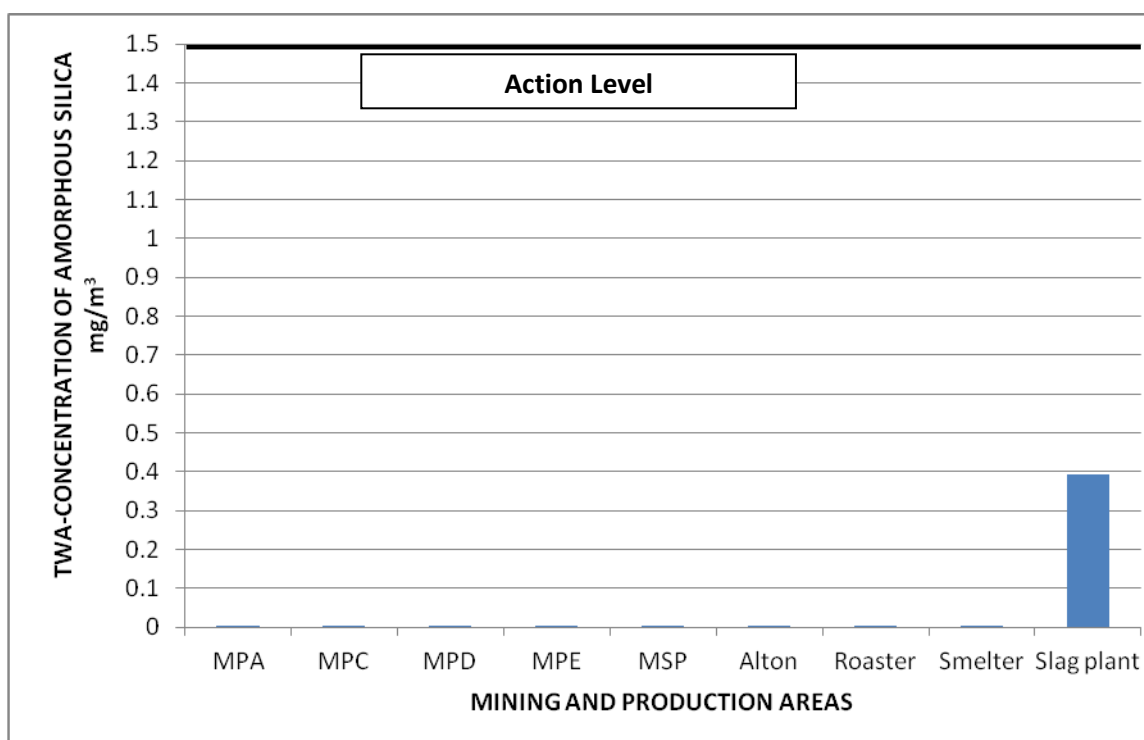


Figure 3.4: The mean TWA-concentration of amorphous silica in the different mining and production areas

In Table 3.2 the results for bulk samples collected in the production areas expressed as a percentage for silica quartz or amorphous silica. Amorphous silica in bulk samples was detected only in the Roaster.

Table 3.2: The percentage of silica quartz or amorphous silica content of total bulk samples obtained from the mining and production areas.

Area-bulk sample	% Silica (quartz or amorphous)
MPA-Stockpile	0.012
MPA-Dunes	0.064
MPC-Stockpile	0.031
MPC-Dunes	0.059
MPD-Stockpile	0.008
MPD-Dunes	0.047
MPE- Stockpile	0.028
MPE-Dunes	0.110
MSP-Dry Mill 1 (DM1) Rutile	0.154
MSP-Dry Mill 1 (DM1) Zircon	0.206
MSP-Dry Mill 2 (DM2) Rutile	0.136
MSP-Dry Mill 2 (DM2) Zircon	0.253
MSP-Zircon Treatment Plant (ZTP)	0.195
Roaster	0.261 Amorphous
Smelter	0.180
Slag-Chloride	0.575
Slag-Sulphate	0.644
Slag-Dust	1.316
Alton-Rutile	0.217
Alton- Zircon	0.263

Legend: MSP - Mineral Separation Plant; MPA - Mining Pond Alpha; MPC - Mining Pond Charlie; MPD - Mining Pond Delta; MPE - Mining Pond Echo

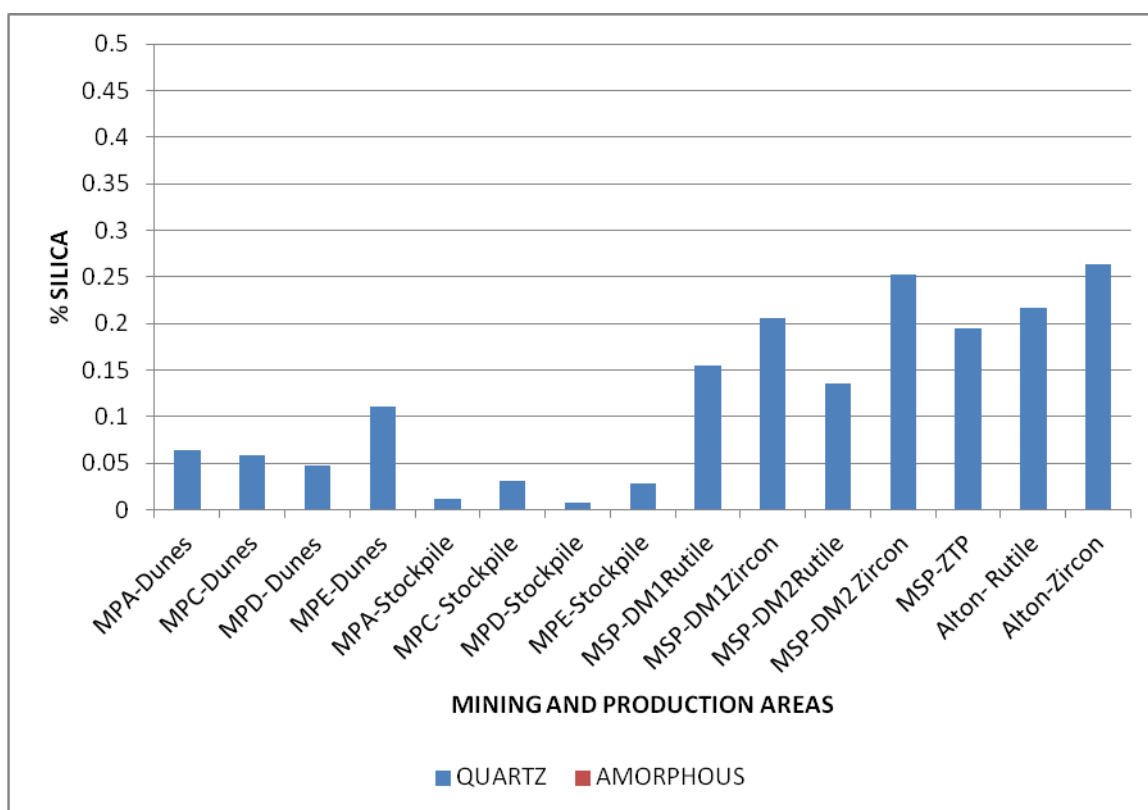


Figure 3.5: The % silica quartz or amorphous silica in bulk samples obtained from the different mining and production areas – Stream 1

The Slag plant significantly showed the highest quartz content in bulk samples, with all the mining and production areas showing low crystalline silica quartz (Figure 3.5 and 3.6).

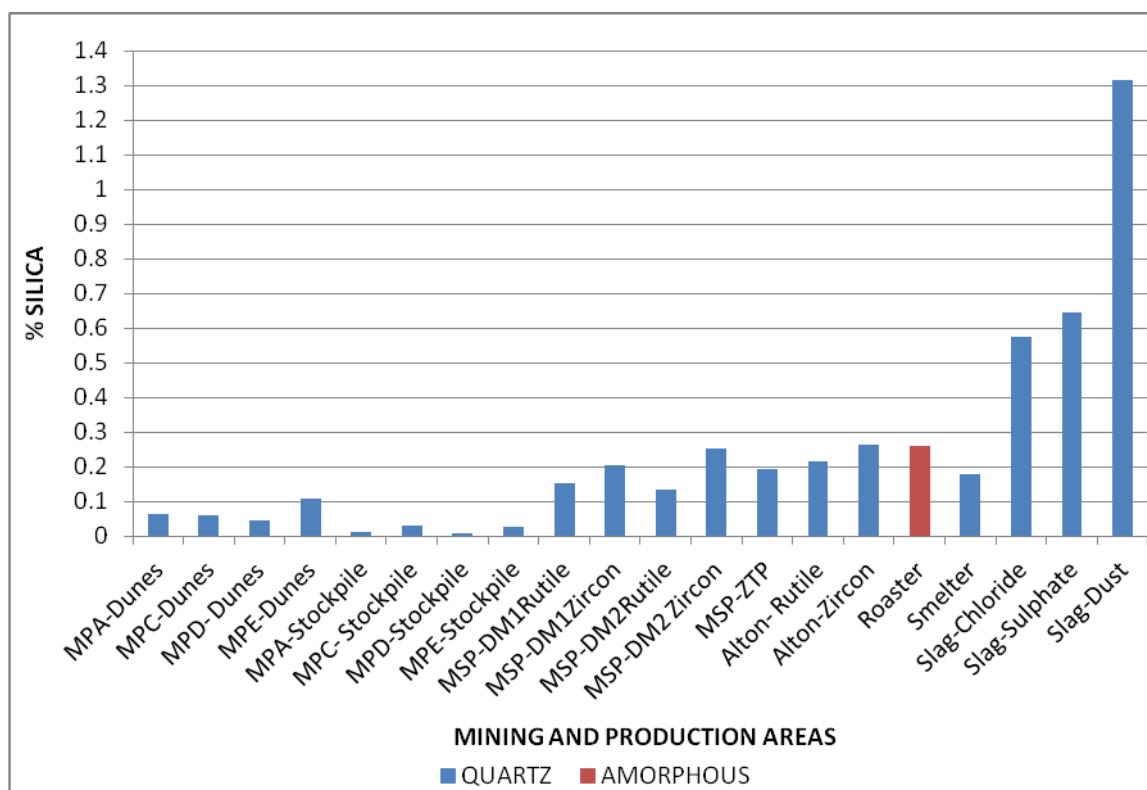


Figure 3.6: The % silica quartz or amorphous silica in bulk samples obtained from the different mining and production areas - Stream 2

Two tests (Kolmogorov-Smirnov and Shapiro-Wilk) were performed to test for normality. Both these tests revealed that the exposure concentration data (quartz and amorphous silica) was not normally distributed, with p-values < 0.05. “The Central Limit Theorem (CLT) states that the behaviour of the average (or, equivalently, the sum) of a large number of the independent and identically distributed random variables will resemble the behaviour of a standard random variable”. Furthermore, “A popular rule of thumb is that the normal approximation can be used if $n \geq 30$ ” (Trosset, 2006). Data obtained from convenience sampling is then analyzed as if it were obtained by means of random sampling (Ellis and Steyn, 2003).

With a view to investigate the extent of the non-normality of data a histogram and Q-Q plots were generated. Both the diagrams confirmed that the data deviated somewhat from normality, as the histogram was not bell-shaped and the Q-Q plots data points were not linear. Diagrams are not shown.

An Effect size (also known as the strength of association) is a set of statistics that indicates the relative magnitude of the differences between means or the amount of total variance in the dependent variable that is predictable from knowledge of the levels

of the independent variance (Pallant, 2007). The effect sizes between the nine mining and production areas were calculated in order to determine practical significance.

Effect sizes are used in cases where data obtained from small populations has no relevant statistical inference and p-values. Practical significance, as measured by a d-value which is calculated as the absolute difference between the means of the two groups divided by the maximum standard deviation, can be understood as a sufficiently large difference to have an effect in practice. Comparisons with $d > 0.8$ are considered to be of large effect and practically significant, $d > 0.5$ is a medium effect and $d > 0.2$ refers to a small effect and is not practically significant (Ellis and Steyn, 2003). Table 3.3 shows the practical significance of compared production areas.

Table 3.3: Effect sizes for silica quartz and amorphous silica for mining ponds (MPA, MPC, MPD, MPE) and production areas.

Area	Compared to area	Effect size (d)
Silica quartz		
MSP	MPC	0.819
Roaster	Smelter	0.832
Roaster	Alton	1.659
Roaster	MPA	1.929
Roaster	MPC	2.017
Roaster	MPD	1.052
Roaster	MPE	0.830
Smelter	MPA	0.973
Smelter	MPC	1.055
Alton	MPE	1.045
MPA	MPE	1.386
MPC	MPE	1.497

Area	Compared to area	Effect size (d)
Silica amorphous		
MSP	Slag Plant	0.921
MSP	MPA	1.788
MSP	MPC	1.788
MSP	MPE	1.788
Roaster	Slag plant	0.921
Roaster	MPA	1.788
Roaster	MPC	1.788
Roaster	MPD	1.788
Roaster	MPE	1.788
Smelter	Slag plant	0.921
Smelter	Alton	1.788
Smelter	MPE	1.788
Slag plant	Alton	0.920
Slag plant	MPA	0.919
Slag plant	MPD	0.919
Slag plant	MPE	0.919
Alton	MPD	1.095

Legend: MSP - Mineral Separation Plant; MPA - Mining Pond Alpha; MPC - Mining Pond Charlie; MPD - Mining Pond Delta; MPE - Mining Pond Echo

If one were to suppose that one would be confronted with a “non-significant” p and a “large” effect size, the question may well be posed as to what this, in fact, means. If one simply concluded on the basis of the significance level that “nothing happened”, one might be making a serious mistake: “A small sample size may have led to failure to detect the true effect, in which case, we should continue this line of investigation with a larger sample size” (Pallant, 2007).

In this study, there were a number of concerns regarding the homogeneity of variance between amorphous or quartz concentrations of the production and mining areas. Therefore, the non-parametric version of the ANOVA test, the Kruskal-Wallis test, was also performed with a view to ensure accurate representation. Both types of tests were performed since parametric test are more powerful, while non-parametric tests are less

sensitive to violations of assumptions and make no assumptions regarding the distribution of the data.

For silica quartz at the mining and production areas, the Kruskal-Wallis revealed no statistically significant differences between the concentrations (silica quartz) of nine mining and production areas ($p = 0.108$). The Games-Howell Post-hoc test was used to determine which mining and production areas differ from each other; no significant differences were found between the mining and production areas. The Tukey-B Post-hoc test confirmed this finding.

The Brown-Forsythe and Games-Howell Post-hoc tests for amorphous silica could not be performed due to observations being similar in some areas, because minimum observation levels were used and the variance for those areas was zero. The Tukey B Post-hoc test indicated that the Slag plant differs significantly from the other mining and production areas. Indeed, the non-parametric Kruskal-Wallis test concluded that the slag plant differs significantly from these areas: MSP ($p = 0.0247$), Roaster ($p = 0.0247$) and Smelter ($p = 0.0247$).

In terms of silica quartz, the mining areas (MPA, MPC, MPD, MPE) were considered as one combined area ($n = 20$). This was done to increase the possibility to obtain better and meaningful statistical differences. Both the ANOVA ($p = 0.38$) and Kruskal-Wallis ($p = 0.14$) revealed no statistically significant differences between the concentrations (quartz) of the “6” production areas. The six areas include the mining area (combined area), MSP, Roaster, Smelter, Alton and Slag plant.

Results obtained from the Brown-Forsythe test also revealed that there were no statistically significant differences in the mean silica quartz concentration levels of the six areas ($p = 0.316$) which includes the mining area (combined area), MSP, Roaster, Smelter, Alton and Slag plant. The Games-Howell Post-hoc test was used to determine which groups differ from another; again, no significant differences were found between groups. The Tukey-B Post-hoc test confirmed this finding. For amorphous silica, if the mining areas (MPA, MPC, MPD, MPE) were considered as 1 combined area ($n = 20$), the ANOVA test ($p = < 0.05$) showed a significant difference between the mean levels of the six areas, but the assumptions of this test had been violated because data was not normally distributed and equal variance was not found between data. The six areas include the mining area (combined area), MSP, Roaster, Smelter, Alton and Slag plant.

The Brown-Forsythe and Games-Howell Post-hoc tests could not be performed because observations in some areas were similar. This was due to the use of minimum observation levels and the variance for those areas being zero. The Tukey B Post-hoc test indicated that the Slag plant differed significantly from the other production areas. Also, the Kruskal-Wallis test revealed that the Slag plant differed significantly from MSP ($p = 0.0102$), Roaster ($p = 0.0102$) and Smelter ($p = 0.0102$). Table 4 reflects the mean values and the standard deviations for the personal exposure levels measured for the six (mining and production) areas where the mining areas (MPA, MPC, MPD, MPE) were considered as one combined area.

Table 3.4: Mean and standard deviations of silica quartz and amorphous silica exposure concentrations (mg/m^3) for the six mining (combined area) and production areas.

Area	N	Mean silica quartz (mg/m^3)	Mean amorphous silica (mg/m^3)
Mining	20	0.008 ± 0.002	0.004 ± 0.000
MSP	5	0.012 ± 0.006	0.004 ± 0.000
Roaster	5	0.012 ± 0.003	0.004 ± 0.000
Smelter	5	0.010 ± 0.003	0.004 ± 0.000
Slag	5	0.024 ± 0.026	0.329 ± 0.421
Alton	5	0.007 ± 0.001	0.004 ± 0.005

N - Number of samples; Mean - concentrations; SD - standard deviation; MSP - Mineral Separation Plant.

The effect sizes between the six areas were calculated to determine practical significance. Table 3.5 shows the practical significance between compared areas.

Table 3.5: Effect sizes for silica quartz and amorphous silica for the six mining (combined) areas and production areas.

Area	Compared area	Effect size (d)
Silica quartz		
Roaster	Smelter	0.832
Roaster	Alton	1.659
Amorphous silica		
Mining	MSP	2.320
Mining	Roaster	2.320
Mining	Smelter	2.320
Mining	Slag	0.919
Mining	Alton	0.821
MSP	Slag plant	0.921
Roaster	Slag plant	0.921
Smelter	Slag plant	0.921
Slag Plant	Alton	0.920

4. Discussion

During this study, the personal respirable airborne silica particulate exposure of workers was measured over the full eight-hour shift and representative bulk samples were obtained from the sources of airborne dust from each monitoring area. All the personal airborne silica particulate measurements obtained from workers that contained silica quartz showed exposures below the action level (50% of the OEL) and the OEL for silica quartz.

The Slag plant showed the highest silica quartz content (24%) in personal respirable exposure and bulk samples (Slag chloride 0.575%, Slag sulphate 0.644% and Slag dust 1.316%). This can be ascribed to the high dust levels being generated by mechanical processes such as crushing and milling of the slag. Settled dust also becomes a secondary inhalation source when mechanically disturbed. This area can be seen as a potential risk area, for silica quartz exposure. In this view the silica quartz exposure was below the action level (50% of the OEL) and the OEL (0.1 mg/m^3) for silica

quartz. The high temperatures at the Smelter can contribute to quartz formation, which can still be present in the slag blocks when cooled (Samal *et al.*, 2010).

The lowest silica quartz content was found in personal respirable samples from Mining pond C (6%). The mining process is a wet process (dredging) and low levels of dust are generated and silica quartz exposure should not be an occupational risk during the mining phase of the operation.

Amorphous silica was detected in three personal respirable exposure samples (13%), which was below the action level and the OEL (3 mg/m³) for amorphous silica.

Bulk samples from MPE showed the highest silica quartz content when compared to the other mining ponds. Bulk samples from MPE dunes (0.064%) showed higher quartz silica content than bulk samples obtained from the MPE stockpile area (0.028%), after the mining and concentrating processes had been conducted. These results were expected because the beach sand from the dunes forms slurry, which is pumped onto a floating concentrator. Here the titanium minerals are separated from the sand according to their mineral densities. Due to silica quartz particulates being lighter than the titanium minerals, they are discarded with the tailings and are not concentrated with the titanium heavy mineral concentrate. This result was noted for all the bulk samples obtained from the mining ponds.

With the progression along the production stream of titanium dioxide it was apparent that in production stream 1 the mean silica quartz content (12%) was higher than the silica quartz content of personal respirable exposure samples and bulk samples obtained from the mining ponds. This is due to the fact that heavy mineral concentrate from the Mining ponds are re-slurried in the feed preparation circuit, where the slurry is passed over stages of low- and high-intensity magnets to remove the ilmenite needed as feedstock for the Smelter. Upon the removal of ilmenite from the heavy mineral concentrate, the silica quartz content increases when concentrated with rutile and zircon. The non-magnetic materials zircon and rutile are concentrated for further processing in the dry mills. From the feed preparation process, zircon and rutile are further upgraded in a number of stages of high-tension electrostatic separation, magnetic separation, gravity separation and screening at the dry mills. Depending on the stage of separation, the silica quartz concentration is either increased or decreased when rutile and zircon are separated by the differences in their conductivities.

The silica quartz content in the personal respirable exposure samples obtained from the Alton bagging plant were lower. This result was expected to be the same as at Mineral Separation plant (MSP), as rutile and zircon are directly transported to the Alton bagging plant after the separation process. The bulk samples showed a similar silica quartz content as found in bulk samples from the Mineral Separation plant (MSP). This was expected as rutile and zircon from the Mineral Separation plant (MSP) are bagged directly as raw materials at this plant. The bagging operation generates low levels of airborne dust as the process is mostly enclosed and automated.

In production stream 2 the amount of silica quartz present in personal respirable exposure samples from the Roaster plant (12%) was found to be similar to the silica quartz content present in personal exposure samples at the Mineral Separation plant (MSP). The silica quartz present in personal exposure samples at the Roaster plant was higher than the silica quartz content found in personal exposure samples at the Mining ponds. This can be ascribed to the Roaster plant having higher concentrations of airborne dust than the Mining ponds, as ilmenite from the Mineral Separation plant is directly transferred from the roaster feed stockpile to the Roaster plant. The bulk sample obtained from the Roaster plant showed amorphous silica content of 0.261%. The reason for the presence of amorphous silica in this bulk sample is uncertain. The silica quartz content in personal exposure samples from the Smelter plant (10%) was lower, compared to the quartz content detected in personal respirable exposure samples obtained in the Roaster plant. This is most likely due to the high temperatures in the smelting process. The silica quartz content in the bulk sample obtained from the Smelter (0.180%) decreased from the quartz obtained in bulk samples from the Mining ponds and the Mineral Separation plant (MSP). This is due to the smelting process where temperatures are increased to 1 700 °C, above silica's melting point of 1 600 °C and a change in silica structure occurs. The presence of silica quartz in the bulk samples can also be due to dust emissions from char dust which is fed by conveyors to the furnaces.

No statistical difference was found between concentrations of silica quartz and amorphous silica in personal exposure samples obtained in the mining and production areas. Even when the areas were combined (Mining ponds A, C, D, and E) no statistical difference was found between personal exposure samples obtained in the mining and production areas.

Effect sizes are very helpful in the cases where data obtained from small populations has no relevant statistical inference and p-values, it can indicate whether a practical significant difference can be found between areas.

It can be seen from the results that the Slag plant is the high risk area, with the highest exposure to silica quartz. It had the highest % silica quartz in both respirable dust and the bulk samples.

With the use of effects sizes it was apparent that the Slag plant showed a practically significant difference in comparison with the other areas. This was also confirmed by the Tukey B post-hoc test.

The personal silica quartz exposure for one of the Slag plant operators of 0.056 mg/m^3 was below the South-African exposure limit for silica quartz, but above the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV) of 0.025 mg/m^3 (ACGIH, 2012). The average silica quartz exposure measured in the Slag plant of 0.024 mg/m^3 was also near the ACGIH TLV.

Although silica quartz exposure is low in all areas, there are signs that there may be a risk in the Slag plant.

Swanepoel and Rees (2011) studied the exposure of farm workers to silica quartz on three farms in the agriculture sector of South Africa. They found that exposure levels varied with different soil types with some exposures on sandy soil and sandy loam farms exceeding the South African OEL of 0.1 mg/m^3 . On a clay soil farm no exposures above 0.1 mg/m^3 was measured. The measurements on the sandy, sandy loam and clay soil farms were, respectively 57%, 59% and 81% above the ACGIH TLV of 0.025 mg/m^3 .

Another study done by Khoza *et al.* (2012) to determine worker's exposure to silica in non-mining industries showed that of all the measurements taken, the South African OEL for respirable quartz was exceeded in foundries, sandstone factories, ceramics/pottery and refractories by 64%, 56%, 53% and 35%, respectively.

The two studies clearly show that in non-mining industries some workers are overexposed to respirable silica dust. Compared to these findings the results of the present study showed the opposite, with respirable silica dust levels being below the South African action level and OEL. The workers monitored throughout all the mining

and production areas are better off and the risk developing silicosis is low during the production of titanium dioxide from beach sand.

It can be concluded from these positive results that silica quartz is present throughout the mining and production areas, but not in concentrations that are near the stipulated South-African OEL.

5. Conclusion

The personal exposure samples indicated a higher silica quartz content at the Mineral Separation plant than at the Mining ponds. However, the silica quartz content in personal exposure samples at the Alton bagging plant was lower than that of the Mineral Separation plant (MSP). The personal exposure samples also indicated a higher silica quartz content at the Mineral Separation plant (MSP), Roaster, Smelter and the Slag plant than that at the Mining ponds.

As observed from the results, the silica quartz content of bulk samples was higher at the Mineral Separation plant (MSP) than at the Mining ponds. The Alton bagging plant, however, showed a similar quartz content in bulk samples to that of the Mineral Separation plant (MSP). The quartz content of bulk samples was also higher at the Mineral Separation plant (MSP), Smelter and the Slag plant than that of the Mining ponds. The bulk samples were representative of the dust in a specific area, the silica quartz levels were found to be very low in bulk samples and this was also notable in the respirable personal exposure samples.

Although no statistically significant difference was found with conventional statistical analysis between silica quartz concentrations in the mining and production areas, a practical significance was found between certain areas, as determined by the calculation of effect sizes. Non-parametric test were conducted but the assumptions of this test had been violated because data was not normally distributed and equal variance was not found to exist between data sets. In most of the areas, no amorphous silica above the detection limit was detected. The detection of both amorphous and silica quartz indicates that silica, when exposed to different industrial settings, such as heating and cooling, as well as separation processes, can result in changes in terms of structure and concentration. The silica quartz concentration when present in the ore from the Mining ponds can either be increased or decreased when rutile and zircon is separated from heavy mineral concentrate from the mining stockpiles or when it is

present in the ilmenite feedstock which is transferred to the Roaster plant. The high temperatures (1700°C) used in the smelting process are above the melting point of silica ($1\,600^{\circ}\text{C}$); this contributes to changes in the structure of silica.

The practically significant differences that were found between certain areas as determined by the calculation of effect sizes could indicate that an increase in the number of measurements and workers monitored could result in statistical significance between areas.

Further studies, involving more samples, over a longer period of time, would probably be able to show a clear trend on how the quartz structure and exposure profiles change from mining and along the production processes.

Provided that respirable dust exposure levels can be maintained at very low levels, as encountered during this study, overexposure to silica quartz anywhere at the mine (including production processes) is considered unlikely, with a low risk of developing silicosis.

6. References

- ACGIH (AMERICAN CONFERENCE OF GOVERNMENTAL INDUSTRIAL HYGIENISTS). (2012) Threshold Limit Values for Chemical Substances and Physical Agents & Biological Exposure Indices. Cincinnati (OH): 238 p.
- AIOH (AUSTRALIAN INSTITUTE OF OCCUPATIONAL HYGIENIST). (2009) Respirable crystalline silica and occupational health issues. Available from: URL: http://www.aioh.org.au/downloads/documents/PositionPapers/AIOH_RCSPositionPaper.pdf. Accessed 21 Sep 2011.
- Akbar-Khanzadeh F, Brillhart RL. (2002) Respirable crystalline silica dust exposure during concrete finishing (grinding) using hand-held grinders in the construction industry. *Ann Occup Hyg*; 46: 341-6.
- Brown T. (2009) Silica exposure, smoking, silicosis and lung cancer-complex interactions. *Occup Med*; 59: 89-95.
- Cho WS, Choi M, Han BS *et al.* (2007) Inflammatory mediators induced by intratracheal instillation of ultrafine amorphous silica particles. *Toxicol Lett*; 175: 24-33.
- Collins JF, Salmon AG, Brown JP *et al.* (2005) Development of a chronic inhalation reference level for respirable crystalline silica. *Regul Toxicol Pharmacol*; 43: 292-300.
- Ellis SM, Steyn HS. (2003) Practical significance (effect sizes) versus or in combination with statistical significance (p-values). *Management Dynamics*; 4: 51-3.
- Gibbs GW, Du Toit RSJ. (2002) Quartz exposure of South-African gold miners. *Ann Occup Hyg*; 46: 597-607.
- Guthrie KE, Driscoll GD. (2010) Crystalline silica and silicosis. *Comp Toxicol*; 8: 331-5.
- IARC (INTERNATIONAL AGENCY FOR RESEARCH ON CANCER). (1997) Monographs on cancer on the evaluation of carcinogenic risks to humans. Silica, some silicates coal dust and para-aramid fibrils. Available from: URL:

- <http://monographs.iarc.fr/ENG/Monographs/vol68/volume68.pdf>. Accessed 25 Aug 2011.
- Khoza NN, Grove T, Schutte PC. (2012) Worker exposure to silica dust in South African non-mining industries in Gauteng: An exploratory study. *Occup Health Southern Africa*; 18(3): 18-26.
- Makinson KS. (2008) Validation of biomarkers for improved assessment of exposure and early effect from exposure to crystalline silica. Johannesburg: University of the Witwatersrand (Thesis – MSc).
- Mason E, Thompson SK. (2010) A brief overview of crystalline silica. *J Chem Health Saf*; 7: 6-8.
- Meldrum M, Howden P. (2002) Crystalline silica: Variability in fibrogenic potency. *Ann Occup Hyg*; 46: 27-30.
- NIOSH (NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH). (2002) Health effects of occupational exposure to respirable crystalline silica. Available from: URL: <http://www.cdc.gov/niosh/docs/2002-129/pdfs/2002-129.pdf>. Accessed 26 Aug 2011.
- NIOSH (NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH). (2003) General considerations for sampling airborne contaminants. Available from: URL: <http://www.cdc.gov/niosh/docs/2003-154/pdfs/chapter-d.pdf>. Accessed 25 Aug 2011.
- O'Reilly KMA, Phipps RP, Thatcher TH *et al.* (2005) Crystalline and amorphous silica differentially regulate the cyclooxygenase-prostaglandin pathway in pulmonary fibroblasts: Implications for pulmonary fibrosis. *Am J Physiol Lung Cell Mol Physiol*; 288: 10-6.
- OSHA (OCCUPATIONAL SAFETY AND HEALTH ADMINISTRATION). (2009) Health considerations for workplace exposure to silica. Available from: URL: <http://www.dli.mn.gov/osha/PDF/silica.pdf>. Accessed 26 Aug 2011

- Pallant J. (2007) SPSS survival manual: A step by step guide to data analysis using SPSS for Windows. Maidenhead, England: McGraw-Hill. ISBN: 0 335 22366 4.
- Porter DW, Barger M, Robinson VA *et al.* (2002) Comparison of low doses of aged and fresh fractured silica on pulmonary inflammation and damage in the rat. *Toxicol*; 75: 63-71.
- RSA DOL (REPUBLIC OF SOUTH-AFRICA DEPARTMENT OF LABOUR). (2006) Silica exposure and its effect on the physiology of workers. Available from: URL: <http://www.labour.gov.za/documents/useful-documents/occupational-health-and-safety/silica-exposure-and-its-effect-on-the-physiology-of-workers>. Accessed 25 August 2011.
- Samal S, Mohapatra BK, Mukherjee PS. (2010) The effect of heat treatment on Titania slag. *J Min Mat Char Eng*; 9: 795-809.
- Swanepoel AJ, Rees E. (2011) Silica exposure in South-African farming. *Occup Health Southern Africa*; 17(6): 14-11.
- Trosset MW. (2006) An introduction to statistical interferences and it's complications. Available from: URL: http://www.astrohandbook.com/ch17/statistical_inference.pdf accessed 28 Aug 2011
- Yassin A, Yebesi F, Tingle R. (2005) Occupational exposure to crystalline silica dust in the United States, 1988-2003. *Environ Health Perspect*; 113: 255-60.

CHAPTER 4

CONCLUSIONS, LIMITATIONS AND RECOMMENDATIONS

4.1 Conclusions

The levels of exposure to respirable particulates of workers at a heavy mineral processing mine were determined by means of personal airborne particulate sampling and the collection of representative bulk samples from the sources of airborne dust.

Silica quartz was detected in all respirable exposure samples but amorphous silica which was detected in three respirable exposure samples at the Slag plant. Silica quartz was detected in all bulk samples, with amorphous silica being present only at the Roaster plant. None of the workers were exposed to respirable silica quartz and respirable amorphous silica concentrations higher than their respective OELs or action levels. The OEL for silica quartz and amorphous silica is stipulated in the South African Mine Health and Safety Act (MHSA), in Regulations. section 22.23 (MHSA, 1996).

Compared with the more stringent ACGIH TLV of 0.025 mg/m^3 for silica quartz, workers in the Slag plant could be at risk (ACGIH, 2012). This implies that exposure in the Slag plant should be monitored on a regular basis.

The personal exposure samples also indicated higher respirable silica quartz content in terms of mass at the Mineral Separation Plant (MSP), Roaster, Smelter and the Slag plant than at the Mining ponds. A decrease in silica quartz content was expected, due to most of the silica quartz being discarded by separation processes at the Mineral Separation Plant (MSP) and being converted to amorphous silica during smelting and slag production. The results indicate that the MSP does not decrease the silica quartz content of the product.

A statistically significant difference was not found between the silica quartz concentrations of the mining and production areas. This is due to the respirable dust concentrations being very low throughout the mining and production processes. The non-significant difference and a large practical significance imply that a larger sample group would be required in future research in order to provide a more accurate account of exposures experienced.

All the aims of this study were reached and the results were positive with exposures being below the South-African OEL and action level.

The hypothesis of this study suggested that the changes in the structure of silica in the airborne dust inhaled during the course of titanium dioxide production from beach sand does not pose a risk of developing silicosis.

During this study no significant change in the structure of silica was observed and exposures measured were below the action levels and South-African OELs. The hypothesis can therefore be accepted and there is a low risk for the development of silicosis.

4.2 Limitations of this study

Only the plant operators were included in this study. Therefore, in future studies, a larger group should be composed which also includes the general and maintenance workers. More samples should be collected, over longer periods of time.

4.3 Recommendations

- In the case of silica quartz exposure, the respirable fraction is a cause of concern due to its negative health effects; therefore the respirable dust fraction should be collected. Regular respirable particulate exposure monitoring should be conducted to detect any changes in the level of exposure, as total inhalable dust sampling was for the most part conducted in the past.
- Since the Slag plant was identified as the area with the highest risk of silica quartz exposure, it is recommended that the area be monitored on a regular basis.
- Samples from the dunes should annually be tested for silica quartz content before the mining process.
- Workers need to be trained and educated in the health effects associated with silica quartz dust, and
- Although silica quartz exposure is low, PPE is worn by workers and it is recommended that PPE, e.g. dust masks designated as a N95 respirator, can be used to ensure protection against nuisance dust. Because no safe level of exposure to silica quartz is known, it is imperative that PPE is used by workers.

ADDENDUMS

Addendum 1: The occupational exposure (concentration) to airborne silica quartz and airborne amorphous silica.

Employee title	Concentration of silica quartz (mg/m ³)	Concentration of amorphous silica (mg/m ³)
MPA Plant		
MPA plant operator	0.007	0.004
MPA plant operator	0.006	0.005
MPA plant operator	0.009	0.005
MPA plant operator	0.008	0.005
MPA plant operator	0.006	0.005
MPC Plant		
MPC plant operator	0.008	0.004
MPC plant operator	0.006	0.005
MPC plant operator	0.007	0.005
MPC plant operator	0.007	0.005
MPC plant operator	0.007	0.005
MSP Plant		
MSP plant Operator	0.006	0.004
MSP plant Operator	0.015	0.004
MSP plant Operator	0.022	0.004
MSP plant Operator	0.006	0.004
MSP plant Operator	0.012	0.004
MPD Plant		
MPD plant operator	0.006	0.005
MPD plant operator	0.006	0.005
MPD plant operator	0.006	0.005
MPD plant operator	0.016	0.005
MPD plant operator	0.008	0.005
MPE Plant		
MPE plant Operator	0.009	0.005
MPE plant Operator	0.010	0.005
MPE plant Operator	0.009	0.004
MPE plant Operator	0.015	0.005
MPE plant Operator	0.009	0.005

Roaster Plant		
Roaster plant Operator	0.009	0.004
Roaster plant Operator	0.012	0.004
Roaster plant Operator	0.014	0.004
Roaster plant Operator	0.015	0.004
Roaster plant Operator	0.017	0.004
Smelter		
Smelter plant Operator	0.016	0.004
Smelter plant Operator	0.007	0.004
Smelter plant Operator	0.010	0.004
Smelter plant Operator	0.009	0.004
Smelter plant Operator	0.008	0.004
Slag Plant		
Slag plant Operator	0.005	1.021
Slag plant Operator	0.004	0.413
Slag plant Operator	0.005	0.520
Slag plant Operator	0.051	0.005
Slag plant Operator	0.056	0.005
Alton Plant		
Alton plant Operator	0.008	0.005
Alton plant Operator	0.007	0.004
Alton plant Operator	0.010	0.005
Alton plant Operator	0.008	0.004
Alton plant Operator	0.007	0.004

Legend: MSP - Mineral Separation Plant; MPA - Mining Pond Alpha; MPC - Mining Pond Charlie; MPD - Mining Pond Delta; MPE - Mining Pond Echo; OEL respirable silica quartz: 0.1 mg/m³, OEL respirable amorphous silica: 3 mg/m³.

**TEST REPORT**

DATE OF REPORT : 7 December 2011

REFERENCE NO : CLS113143

CLIENT ORDER NO :

CONTACT PERSON : Adri Cowley

CLIENT : Richards Bay Minerals

CLIENT ADDRESS : P.O. Box 401

RICHARDSBAY

3900

CLIENT CONTACT PERSON : Maryda Draai

CLIENT TELEPHONE NO : (035) 901 4865

CLIENT FAX NO : (035) 901 3480

CLIENT e-MAIL ADDRESS : Vanitha.Govender@rbm.co.za

ANALYSIS REQUIRED : Analysis for Alpha Quartz*

TEST METHOD USED : NIOSH 7500*

Table 1 – Analysis for Alpha Quartz.

<i>TEST ITEM DESCRIPTION</i>	<i>TEST ITEM CONDITION</i>	<i>DATE RECEIVED</i>	<i>DATE OF ANALYSIS</i>
<i>Filters</i> <i>Bulk Samples</i>	<i>Sealed in 37 mm plastic filter cassettes.</i> <i>Bulk samples sealed in bottles.</i> <i>Received at ambient temperature.</i>	<i>2/11/2011</i>	<i>7/11/2011</i>

RESULTS: (mg)

<i>Sample Number</i>	<i>Alpha Quartz (mg)</i>
340	0.007
341	0.006
342	0.007
343	0.009
344	0.006
321	0.011
327	0.006
325	0.021
322	0.014
337	0.006
329	0.016
330	0.014
335	0.013
336	0.011
313	0.008
334	0.008
333	0.009
332	0.010
324	0.007
339	0.015
316	0.045
306	0.050

RESULTS: (%)

<i>Sample Number</i>	<i>Alpha Quartz (%)</i>
<i>ALTON-RUTILE</i>	0.217
<i>ALTON-ZIRCON</i>	0.263
<i>MSP-DRY MILL RUTILE</i>	0.154
<i>MSP-DRY MILL ZIRCON</i>	0.206

Physical: 732 Makou Street, Monument Park, Pretoria. Postal: P.O. Box 25825, Monument Park, 0105
 Telephone/Facsimile: +27(0) 12 347 4979, E-Mail: info@chemtechlab.co.za, Web: www.chemtechlab.co.za

Page 2 of 4

Report No. CLS113143

CHEMTECH

<i>Sample Number</i>	<i>Alpha Quartz (%)</i>
<i>MSP-ZTP</i>	<i>0.195</i>
<i>SMELTER</i>	<i>0.180</i>
<i>SLAG-CHLORIDE</i>	<i>0.575</i>
<i>SLAG-SULPHATE</i>	<i>0.644</i>
<i>SLAG-DUST</i>	<i>1.316</i>
<i>MSP-DRY MILL RUTILE</i>	<i>0.136</i>
<i>MSP-DRY MILL ZIRCON</i>	<i>0.253</i>

<i>Specific Test Conditions</i>	<i>Samples stored at room temperature prior to analysis.</i>
<i>Deviations</i>	<i>None.</i>
<i>Comments</i>	<i>A sub-contracting laboratory was used to perform the above analysis.</i>

Table 2 – Analysis for Amorphous Quartz.

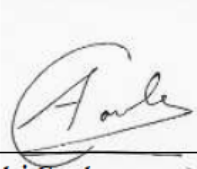
<i>TEST ITEM DESCRIPTION</i>	<i>TEST ITEM CONDITION</i>	<i>DATE RECEIVED</i>	<i>DATE OF ANALYSIS</i>
<i>Filters</i>	<i>Sealed in 37 mm plastic filter cassettes.</i>	<i>2/11/2011</i>	<i>7/11/2011</i>
<i>Bulk Samples</i>	<i>Bulk samples sealed in bottles. Received at ambient temperature.</i>		

RESULTS:

<i>Sample Number</i>	<i>Amorphous Quartz (mg)</i>	<i>Amorphous Quartz (%)</i>
<i>319</i>	<i>0.885</i>	<i>-</i>
<i>314</i>	<i>0.370</i>	<i>-</i>
<i>315</i>	<i>0.462</i>	<i>-</i>
<i>Roaster</i>	<i>-</i>	<i>0.261</i>

<i>Specific Test Conditions</i>	<i>Samples stored at room temperature prior to analysis.</i>
<i>Deviations</i>	<i>None.</i>
<i>Comments</i>	<i>A sub-contracting laboratory was used to perform the above analysis.</i>

WORK APPROVED BY:


Adri Cowley
(Laboratory Manager)
(Technical Signatory)

7/12/2011

Date

RESULTS: (mg)

<i>Sample Number</i>	<i>Alpha Quartz (mg)</i>
310	0.008
312	0.007
349	0.005
354	0.006
351	0.005
357	0.006
352	0.006
304	0.005
309	0.006
308	0.007
359	0.005
356	0.005
353	0.005
345	0.007
347	0.014
302	0.013
305	0.008
355	0.008
348	0.009
301	0.008

RESULTS: (%)

<i>Sample Number</i>	<i>Alpha Quartz (%)</i>
MPA-STOCKPILE	0.012
MPC-STOCKPILE	0.031
MPD-STOCKPILE	0.008
MPE-STOCKPILE	0.028
MPA-DUNES	0.064
MPC-DUNES	0.059

Physical: 732 Makou Street, Monument Park, Pretoria. Postal: P.O. Box 25825, Monument Park, 0105

Telephone/Facsimile: +27(0) 12 347 4979, E-Mail: info@chemtechlab.co.za, Web: www.chemtechlab.co.za

Page 2 of 3

Report No. CLS113548

<i>Sample Number</i>	<i>Alpha Quartz (%)</i>
MPD-DUNES	0.047
MPE-DUNES	0.110