

Sulphur loading of respirable and inhalable dust at a platinum smelter

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Preface

For the aim of this mini-dissertation it was decided to use article format. For uniformity the whole dissertation is according to the guidelines of the chosen journal for potential publication which is the Annals of Occupational Hygiene. The journal requires that the references in the text should be in the form Jones (1995), or Jones and Brown (1995), or Jones *et al.* (1995) if there are more than two authors. References should be listed in alphabetical order by name of first author, using the Vancouver Style of abbreviation and punctuation. Annals of Occupational hygiene limits the word count of the article to 5 000 words, excluding tables and the abstract. This word count is exceeded by 223 words as a result of an in depth discussion.

Chapter 1 contributes a brief introduction to adverse health implications associated with sulphates adhered to particulate dust, as well as the gross mechanism for sulphur loading onto particulate dust. Furthermore, it includes the problem statement, research question, and hypothesis. Chapter 2 consists of an in-depth discussion of smelting by means of electric furnaces, the oxidation of sulphur dioxide to sulphate salts, health effects ascribed to sulphur dioxide – and sulphates adhered to particulate dust exposure, and basic information on the equipment used. Chapter 3: Sulphur loading of respirable and inhalable dust at a platinum smelter, is written in article format. All tables and figures are included here, along with text, to present the findings of this study in a readable and understandable format. The article will be submitted to the Annals of Occupational Hygiene for peer reviewing and publication. Chapter 4 includes a final summary and conclusion, as well as recommendations for future studies. Chapter 5 consists of the appendices.

In order to prevent confusion, the following explains the context of the definitions:

Foam dust: Respirable dust subtracted from inhalable dust. This dust fraction represents dust particles between 10 and 100 μm .

Furnace: An enclosed chamber in which heat is produced by electrodes to smelt concentrate.

Inhalable dust: Dust particles with an aerodynamic diameter up to 100 μm , with a 50 % cut-point of 100 μm .

Respirable dust: Dust particles with an aerodynamic diameter up to 10 μm , with a 50 % cut-point of 4 μm .

Smelter: A structure that contains three furnaces, furnace 1 and 2, and a slag cleaning furnace (SCF).

Sulphur loading: The oxidation of sulphur dioxide, which results in the formation of particulate sulphur species on dust.

Author's Contribution

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

Name	Contribution
Mr JD Swanepoel	<ul style="list-style-type: none">• Designing and planning of the study;• Literature searches, interpretation of data and writing of article;• Execution of all monitoring processes.
Ms A Franken	<ul style="list-style-type: none">• Supervisor;• Assisted with approval of protocol, interpretation of results and documentation of the study;• Giving guidance with scientific aspects of the study.
Mr PJ Laubscher	<ul style="list-style-type: none">• Co-Supervisor;• Assisted with designing and planning of the study, approval of protocol, interpretation of results and documentation of the study;

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

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

Ms A Franken
(Supervisor)

Mr PJ Laubscher
(Co-Supervisor)

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- Mr PJ Laubscher
- Prof. FC Eloff

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Abstract

The contribution that sulphur, in the form of sulphates, has on ill health is still a focal point of many a study, especially in environmental studies depicting the effects that particulate air pollution has on health. Although the implication of sulphur on particulate matter is not yet well defined, numerous studies do state that the presence of sulphur on particulate matter contributes to poor health. Sulphur adhered to dust has been associated with cardiovascular mortality and the ability to bring about pathological lung changes, which correlate with changes seen in asthma. There are currently no information regarding the possibility of sulphur loading on particulate dust in a platinum smelter, and consequently, the associated health risk is undefined.

Aim: This study aimed to quantify the sulphur content of inhalable and respirable dust in a platinum smelter, as well as to explore the possibility of a correlation between sulphur dioxide exposure and the sulphur content of dust. **Method:** Three potential high risk activities around the furnaces were identified, and personal sampling was conducted on workers concerned with these tasks. Multi-dust sampling was conducted using an IOM sampler (SKC®) fitted with both a MCE filter and a foam insert. Simultaneously, personal sulphur dioxide exposure was monitored using a Dräger Pac® 7000. The gross airflow direction and velocity was recorded in the proximity of the furnaces, together with relative humidity and dry bulb temperature. Area samples were also obtained with the goal of being subjected to electron microscopy and to determine the pH of the dust. Data was Box-Cox transformed to normalise the distribution, and the transformed data was used for further statistical calculations. **Results:** Environmental factors were similar on the different floors of the smelter. Sulphur was present on both the respirable and inhalable dust fractions, and the highest sulphur percentage was recorded on the tapping floor. The sulphur content of respirable dust was significantly higher ($p = 0.03$) than the sulphur content of the IOM foam dust (inhalable and thoracic portion combined). A medium correlation with statistical significance was obtained between respirable sulphur and the SO_2 concentration of the ceramic workers ($r = 0.27$; $p < 0.05$), as well as the foam sulphur and the SO_2 concentrations of the paste loaders ($r = 0.32$; $p < 0.05$). No significant correlation could be found between SO_2 concentrations and sulphur content of particles when all the samples were considered. **Conclusion:** Environmental differences recorded on the different floors did not significantly influence sulphur loading. Sulphur contained in smaller particles (respirable dust) is significantly higher than that of the larger particles sampled possible because of an increase in oxidation of SO_2 due to an increase in surface area available for sulphur loading in the smaller aerodynamic fraction. The sulphur could however also be attributed to the escape of sulphur containing iron pyrite via the electrodes.

Key Words: Sulphur content, platinum smelting, sulphur dioxide oxidation, sulphur loading, respirable and inhalable dust.

Opsomming

Titel: *Swawelbelading van inasembare en respireerbare stof by 'n platinum smelter.*

Die bydra van swawel, in sulfaat vorm, tot swak gesondheid is nog steeds 'n fokuspunt van baie studies, veral in omgewingstudies wat die uitwerking van partikulêre lugbesoedeling op die gesondheid probeer vasstel. Hoewel die implikasie van swawel op stofdeeltjies nog nie volkome gedefinieer is, is daar talle studies wat toon dat die teenwoordigheid van swawel bydra tot swak gesondheid. Swawel gebonde aan stofdeeltjies word geassosieer met kardiovaskulêre mortaliteit en die vermoë om patologiese long veranderinge, wat ooreenstem met die veranderinge in asma, mee te bring. Daar is tans geen inligting beskikbaar oor die moontlikheid van swawelbelading op stofdeeltjies by 'n platinum-smelter nie. Gevolglik is die gepaardgaande gesondheidsrisiko ook ongedefinieerd.

Doel: Hierdie studie het gepoog om die swawel inhoud van inasembare en respireerbare stof in 'n platinum-smelter te kwantifiseer, sowel as die moontlikheid van 'n korrelasie tussen die swaweldioksied blootstelling en die swawel inhoud van stofdeeltjies te verken. **Metode:** Drie potensiële hoë risiko aktiwiteite om die oonde was geïdentifiseer, en persoonlike monsterneming was uitgevoer op werkers bemoei met hierdie take. Meervoudige stof monsternemings is gedoen met behulp van 'n IOM monsternemer wat toegerus was met beide 'n multi-sellulose ester filter en 'n spons insetsel. Terselfdertyd is persoonlike swaweldioksied blootstelling gemonitor met behulp van 'n Dräger Pac @ 7000. Die algemene lugvloerigting en snelheid was genoteer saam met relatiewe humiditeit en droëbal temperatuur om die oonde. Area monsters is ook geneem met die doel om dit te stuur vir elektronmikroskopie en om die pH van die stof te bepaal. Die data was Box-Cox getransformeer omdat dit nie normaal versprei was nie. Die getransformeerde data was gebruik vir verdere statistiese berekening. **Resultate:** Die omgewingstoestande was ooreenstemmend gewees op die verskillende vloere van die smelter. Swawel was teenwoordig op beide die respireerbare en inasembare stof, en die hoogste swawel persentasie was aangetref op die tapvloer. Die swawel inhoud van die inasembare stof was statisties beduidende hoër ($p = 0.03$) as die swawel inhoud van die IOM spons stof (inasembare en torakale fraksies gekombineerd). 'n Medium korrelasie wat statisties betekenisvol is, is verkry tussen respireerbare swawel en die SO_2 konsentrasie van die keramiek werkers ($r = 0,27$, $p < 0,05$), sowel as die spons swawel en die SO_2 konsentrasies van die pasta laaiers ($r = 0,32$, $p < 0,05$). Geen betekenisvolle korrelasie kon gevind word tussen SO_2 konsentrasies en die swawel inhoud van deeltjies wanneer al die monsters oorweeg is nie. **Gevolgtrekking:** Omgewingsverskille wat aangeteken is op die verskillende vloere het nie 'n beduidende invloed op swawelbelading gehad nie. Swawel vervat in kleiner deeltjies (respireerbare stof) is aansienlik hoër as dié van die groter deeltjies, waarskynlik as gevolg van 'n toename in oksidasie van SO_2 omdat daar 'n toename in oppervlakte vir swawel belading op die kleiner aërodinamiese fraksie beskikbaar is. Dit kan egter ook toegeskryf word aan die ontsnapping van swaelbevattende ysterperiet vanaf die elektrodes.

Sleutelwoorde: Swawelinhoud, platinum smelter, oksidasie van swawel dioksied, swawel belading, respireerbare en inasembare stof

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List of Symbols and Abbreviations

Symbols

%	Percentage
(g)	Gas phase of matter
(l)	Liquid phase of matter
(s)	Solid phase of matter
~	Approximates
°C	Degrees Celsius
<	Smaller than
>	Larger than
±	Plus-minus
µg/g	Microgram per gram
µm	Micrometre
·X	Electron radical, X is used as a surrogate for an element
Co	Cobalt
Cu	Copper
CuO	Copper oxide
Fe	Iron
Fe(III)	Iron in the 3 ⁺ oxidative state
Fe ₂ O ₃	Iron (III) oxide
FeO	Iron oxide
FeS	Iron sulphide
HSO ₃ ²⁻	Hydrogen sulphite
L.min ⁻¹	Litre per minute
m.s ⁻¹	Metre per second
mg	Milligram
mg.m ⁻³	Milligram per cubic meter
mm	Millimeter
Mn(II)	Manganese in the 2 ⁺ oxidative state
Mn(III)	Manganese in the 3 ⁺ oxidative state

MnO ₂	Manganese oxide
MS	Metal sulphides
O ₂	Oxygen
OH	Hydroxyl
PbO	Lead oxide
pH	Hydrogen ion concentration
ppm	Parts per million
ppb	Parts per billion
Pt ₃ Fe	Isoferroplatinum
PtAs ₂	Sperrylite
PtS	Cooperite
S	Sulphur
S(IV)	Sulphur in the 4 ⁺ oxidative state
S(VI)	Sulphur in the 6 ⁺ oxidative state
S ²⁻	Sulphide
S ₂ O ₅ ²⁻	Metabisulfite
SiO ₂	Silica oxide
SO ₂	Sulphur dioxide
SO ₂ .H ₂ O	Hydrated sulphur dioxide
SO ₃	Sulphur trioxide
SO ₃ ²⁻	Sulphite
SO ₄ ²⁻	Sulphate
SO _x	Sulphur oxide
V ₂ O ₅	Vanadium pentoxide
XSO ₄	Sulphate salts

Abbreviations

ACGIH	American Conference of Governmental Industrial Hygienists
ASD	Asian sand dust
CEN	Committee of European Norms
CP	Converting process
e.g.	As an example
EF	Electric furnace
EUR	European Commission
HSDB	Hazardous Substances Data Bank
HSE	Health and Safety Executive
i.e.	That is
IARC	International Agency for Research on Cancer
IOM	Institute of Occupational Medicine
ISO	International Organization for Standardization
MDHS	Methods for the Determination of Hazardous Substances
MHS	Mine Health and Safety
NIOSH	National Institute for Occupational Safety and Health
OEL	Occupational exposure limit
OESSM	Occupational Exposure Sampling Strategies Manual
PGM	Platinum group metals
PM	Particulate matter
PM _{2.5}	The particulate diameter which is captured with 50 % efficiency
PNOC	Particles not otherwise classified
SCF	Slag cleaning furnace
STEL	Short term exposure limit
USEPA	United States Environmental Protection Agency
WHO	World health organisation

CHAPTER 1

INTRODUCTION

1.1 Overview

It is evident that sulphur dioxide (SO₂) and dust are present in a smelter. Personal exposures to SO₂ and nuisance dust are routinely monitored by occupational hygienists that are employed at the smelter however, the sulphur content of the dust is yet to be determined. The most apparent personal protection in regards to aerosol exposure is the use of a respirator fitted with a filter for particulate matter and additional filter for SO₂. The use of a respirator is not mandatory on all floors of the smelter - the exception being the top floors. It is however mandatory for individuals to have a respirator with them at all times, exercising one's own discretion in deciding when to use it. Health effects ascribed to exposure to sulphates (SO₄²⁻) adhered to particulate matter is a subject still receiving much attention - especially by environmental studies exploring the effects of air pollution on selected populations. Exposure to particulate sulphate has been linked to respiratory and cardiopulmonary pathology and mortality (Ichinose *et al.*, 2008; Kan *et al.*, 2010; Ostro *et al.*, 2010).

Oxidation of SO₂ to sulphate on dust will result in sulphur loading. This oxidation can occur via reaction mechanisms such as gas-phase oxidation, photochemical oxidation, aqueous-phase oxidation (homogeneous oxidation) and heterogeneous oxidation (Held *et al.*, 1996). The role of relative humidity in the oxidation of SO₂ on the surfaces of solid particles is emphasized by Sakurai *et al.* (1998), homogenous oxidation occurs when the relative humidity is greater than 30 %, and heterogeneous oxidation when the relative humidity is less than 0.5 %. Other determinants in formation of sulphates are the chemical composition of the solid particle, the specific surface area, and temperature.

The primary question to be asked: is there sulphur present in or on the dust, which could therefore be inhaled? Furthermore, what contribution does sulphur make to the total mass of the exposed particulate matter. Sulphur loading onto dust particles presents an additional source of exposure to sulphurous compounds. Thus, instead of exposure to sulphur mainly via gaseous SO₂, secondary exposure could also occur via sulphurous salts adhered to dust particles. There are currently no studies depicting the association between sulphur dioxide exposure and sulphur loading on particulate matter in a platinum smelter.

The research objectives are:

- 1) to quantify the sulphur content on respirable and inhalable dust (sulphur loading);
- 2) to determine if there is a correlation between SO₂ exposure and sulphur loading;
- 3) to determine if there is a difference in sulphur loading between respirable and foam dust.

Personal sampling was conducted at a platinum smelter. Only workers present in the furnace were sampled. Their exposure to SO₂ and particulate matter (inhalable and respirable dust) were simultaneously sampled. Three working activities were identified as high risk actions: tapping, paste loading and contractors on the ceramic floor. Sampling was conducted on workers concerned with these tasks. In addition to personal sampling, area samples for airborne particulate matter was also collected, the function of which was to determine the pH of the dust and to submit samples for electron microscopy.

The prevailing direction- and speed of air flow was recorded on fixed positions within the smelter, as well as the relative humidity.

1.2 Problem Statement

There is no occupational exposure limit ascribed to sulphur as a constituent of particulate matter. The contribution that sulphur makes to the total mass of particulate matter in the smelter is unknown, and consequently, so is the correlation between (sulphur dioxide) SO₂ and sulphur loading on dust. Accordingly, the potential detrimental effect attributed to sulphate exposure is yet to be determined.

1.3 Research Question

Does sulphur loading occur on inhalable and respirable dust particles in a platinum smelter, and if indeed so, to what magnitude does it occur?

1.4 Hypothesis

SO₂ gas present in the furnaces is possible the main source of sulphur, and SO₂ can adhere to particles in the form of sulphates, therefore:

- 1) there will be a positive correlation between the recorded SO₂ levels and the sulphur content of dust particles.

Considering the nature of warm particles to rise, and the high temperature of the furnaces, the upper levels of the smelter has a higher concentration of both SO₂ and dust than the lower levels. Furthermore, it is the only designated respirator zone, therefore:

- 2) the upper levels of the furnace will have higher exposure to particulate sulphur than the lower levels.

Finer particles have a larger surface area to mass ratio than larger particles, therefore:

- 3) sulphur loading on respirable dust will be greater than on inhalable dust.

1.5 References

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CHAPTER 2

LITERATURE STUDY

Introduction

South Africa has more than three quarters of the world's platinum reserves, and is the world's largest producer of platinum group metals (PGM) (Jones, 2005). The mining industry contributed to the creation of approximately 1 million jobs in 2009, and was responsible for 7.8 % of the total private sector non-agricultural employment (Chamber of Mines South Africa, 2011). When one considers these statistics, it is easy to grasp the importance of occupational hygiene - a genre that aims to anticipate, identify, evaluate, and eliminate occupational risks and hazards. This is done to protect the work force, and create an optimal working environment with no unknown hazards - in a country where mining plays a key role in sustaining the economy, and employs such a vast work force.

The health effects due to exposure to sulphur dioxide (SO₂) has been the research aim for many a study, and can be dated back to the late 1930's. The health effects that are elicited by sulphates (SO₄²⁻) have also been a subject that has been investigated for more than two decades. SO₂, and consequently sulphur (S) adhered to particulate matter (PM), has enjoyed increasing attention by researchers, and it is considered by the United States Environmental Protection Agency as an air pollutant (Douglas *et al.*, 2011). Although some research is available on the mechanism underlying sulphur loading in ambient concentrations of SO₂, sulphur loading in an occupational setting is yet to be investigated.

The processing of precious metals includes the use of smelting. This technique converts the solid ore into a liquid medium in order to distinguish between the sought minerals and slag. This result in the release of numerous gasses, of which SO₂ in particular proves to be problematic, and the employment of engineering control aims to keep ambient SO₂ as low as possible.

This chapter will provide information about the smelting process by means of electric furnaces, explain a possible mechanism of sulphur loading, give a brief discussion regarding the health effects associated with SO₂ and sulphate exposure, as well as the methodology involved in aerodynamic fraction sampling.

2.1 Smelting Process: Pyrometallurgy

Smelting forms part of the train of events in the production of metals, during which ore is smelted or fused in order to separate the metallic components (Burgess *et al.*, 2001). The objective is to process wet concentrate in order to produce sulphur-deficient, nickel-copper matte enriched in PGM, gold, and base metals (Jacobs, 2006; Crundwell *et al.*, 2011). Additional steps in the reduction of metals include: roasting, calcining (heating of a substance so that it oxidizes or reduces), sintering (causes ores or powdery metals to become a coherent mass by heating without melting), converting, and refining, which are considered part of the overall smelting process (Burgess *et al.*, 2001). The converter matte is further processed by separating the PGM from the base metals in a base metal refinery and purifying the individual PGM in a precious metal refinery (Crundwell *et al.*, 2011).

There are two smelting techniques: Pyrometallurgy and hydrometallurgy, and it may be combined in smelting operations. For this study, only pyrometallurgy is of relevance, and will be thoroughly discussed. Pyrometallurgy involves heating of the ore to temperatures sufficient to reduce metal oxides to their metallic form, whereas in hydrometallurgy, metal ores are processed through chemical treatments (Burgess *et al.*, 2001).

Crundwell *et al.* (2011) describes the main steps of smelting and converting as:

- a) drying of the concentrate;
- b) smelting of the concentrate to a furnace matte rich in platinum group elements;
- c) and production of a final converter matte by converting the furnace matte.

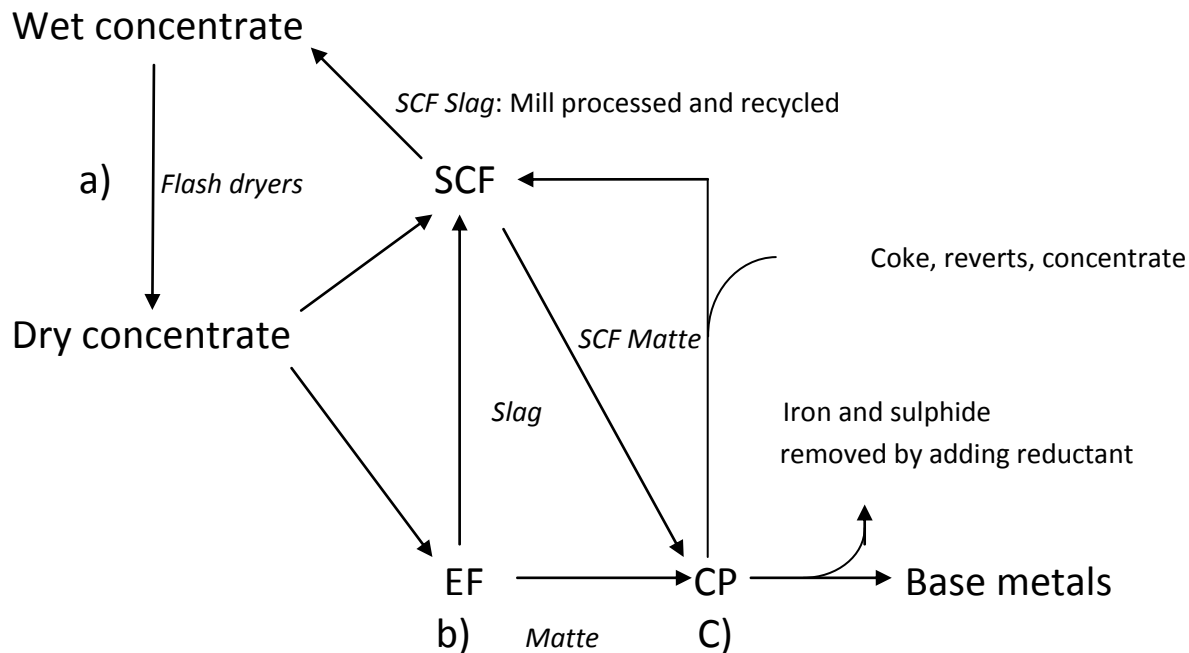


Figure 1: Schematic illustration of the smelting process. EF: electric furnace; SCF: slag cleaning furnace; CP: converting process.

Wet concentrate is dried prior to melting in electrical furnaces (Jacobs, 2006). This reduces the energy requirement for smelting, and also aids the removal of impurities such as sulphur by conversion to oxides (Jones, 2005; Jacobs, 2006). The dry concentrate is then heated to high temperatures, usually in an electrical or reverberatory furnace. This converts metal oxides to –sulphides (S^{2-}) and further removes impurities (Burgess *et al.*, 2001). In the furnace, two immiscible liquid phases form during primary smelting of dry concentrate, which are matte and slag (Jacobs, 2006; Crundwell *et al.*, 2011). Matte, containing a considerable higher concentration of the sought material i.e. most of the base metal sulphides and PGM, naturally settles to the bottom of the furnace as it is denser than the slag. The less-dense slag layer containing most of the oxides and little PGM float to the top of the furnace (Burgess *et al.*, 2001; Jacobs, 2006; Crundwell *et al.*, 2011). South African concentrates usually contain enough silica to ensure that the two phases are immiscible (Crundwell *et al.*, 2011). In preparation to generate substrate for the refining of the sought metals, conversion of the granulated furnace matte has to take place. This entails oxidising the iron (Fe) and sulphur in the matte, using air or an air mixture, in a conversion process (Jacobs, 2006; Crundwell *et al.*, 2011). Thus, excess iron and sulphides are removed from the granulated matte at a conversion plant and the product becomes suitable feed for the refining of the metals.

2.1.1 Primary Smelting

Smelting of PGM in South Africa are primarily conducted in electrical furnaces (Jones, 2005). Rectangular furnaces, with six-in-line carbon electrodes are most widely used, although there are also some circular three-electrode furnaces in operation (Jones, 2005 Crundwell *et al.*, 2011). Jacobs (2006) describes an existing furnace, used for platinum smelting, that accommodates six continuous 1 250 mm diameter Söderberg electrodes. The shell consists of refractory bricks that are held together by a precision-designed tension system. The slag-contact zone is constructed of water cooled copper plates, and the matte contact zone consists of chrome-magnesia bricks. The upper wall and roof consists of super-duty alumina-silicate bricks. The furnaces are fed blended dry concentrate via air slides to either side of the electrodes. Furthermore, slag from the converter process, reverts, and other material can be batch fed to the furnace via charge ports in the sides of the furnace's roof. Melting is continuous, and the furnace normally operates with a layer of non-molten concentrate on top of the slag layer (Jones, 2005; Jacobs, 2006; Crundwell *et al.*, 2011). This limits the amount of radiation from the surface of the bath, to the walls and roof of the furnace (Jones, 2005). Energy generated in the furnace melts the concentrate when electrical current passes through the electrodes and the resistive slag layer (Jacobs, 2006). Resistance of the slag to current flow heats the slag, which in turn, heats and melts the concentrate (Crundwell *et al.*, 2011). The temperature differential between the matte and slag is regulated by the electrode position, slag depth, and applied voltage (Jacobs, 2006). Lime blended with the concentrate acts as a flux, aiding formation of a fluid slag at normal operating temperatures (Jacobs, 2006).

A furnace produces much more slag than matte, with a typical production ratio of matte to slag of 1:5 (Crundwell *et al.*, 2011). Consequently, furnace matte is tapped intermittently into refractory-lined ladles that are transported to the granulation station, where fine particles form that are suitable for dry feeding into a converting process (Jacobs, 2006; Crundwell *et al.*, 2011). Matte is tapped as needed to maintain a specific level in the furnace. Slag is tapped almost continuously via water cooled copper tapholes (Jacobs, 2006; Crundwell *et al.*, 2011). Slag is granulated and fed to the slag milling plant for recovery of PGM, nickel (Ni), copper (Cu), and cobalt (Co) (Jacobs, 2006).

2.1.2 Slag Cleaning

A slag-cleaning furnace (SCF), which is also an electrical furnace, treats granulated converter slag from the converter process for the recovery of the base and precious metals. SCF matte is recycled to a converting process, while the SCF slag is processed by a slag mill to produce a concentrate recycle (Hundermark, 2011). The SCF requires a higher current than the primary furnace due to the high conductivity of the slag. The composition of a SCF may differ from the primary furnace. An example of a SCF, as described by Jacobs (2006), consists of three Söderberg electrodes, each 1 400 mm in diameter. The hearth and matte areas are bricked with chrome-magnesia refractory bricks and the roof is constructed of super-duty alumino-silicate bricks. Excess energy, due to the high slag temperatures, is removed by water-cooled copper sidewalls (Jacobs, 2006).

The SCF is fed via conveyer to feed bins above the furnace roof. The feed is a combination of converting process slag, concentrate, reverts (concrete used for canalising molten matte and slag while tapping, that after use contains PGM), silica, and coke (carbon based reduction agent) - the feed ratios are pre-determined and calculated to maximize metal recoveries. The substrate of the SCF is highly oxidized, and reductant addition is needed to reduce the metal oxides to metal. Additionally, a sulphur source is needed to form metal sulphides in order to collect the metal in a matte phase. This is achieved by the addition of either concentrate, or furnace matte. The slag properties can be modified by adding silica. This significantly reduces the electrical conductivity of the slag so that the acceptable electrode immersion can be achieved. SCF matte is tapped as required and sent to granulation to be processed by a converting process, and slag is granulated and processed further in a slag mill (Jacobs, 2006).

In order for the sulphides to effectively collect the PGM, the feed to the smelting furnace must contain sufficient sulphur. The mineral assemblies containing the PGM are small, sometimes less than 10 μm in size. Droplets of this size would take a long time to settle through the slag in the matte (Nelson *et al.*, 2005). In practise, they coalesce with the sulphides droplets as it both descends towards the matte layer. Too low sulphur may be amended by blending concentrate with high sulphur content (Crundwell *et al.*, 2011). All of the PGM have a much greater affinity for the sulphide matte phase rather than the oxide slag phase in the furnace. The assertion is emphasized by the observation that the PGM occur in nature as sulphides (such as cooperite, PtS), alloys (such as isoferroplatinum, Pt₃Fe) and arsenides (such as sperrylite, PtAs₂). Oxide minerals of the PGM are easily found in nature (Crundwell *et al.*, 2011).

2.1.3 Sulphur Dioxide as Waste Gas

SO₂ is a common waste gas from the smelting process (Burgess *et al.*, 2001; Jacobs, 2006). Gasses from a smelter containing dust and SO₂, hereafter referred at as off-gas, can be recycled and used in the production of H₂SO₄. Off-gas from the furnaces and converter are treated through the tower- and contact acid plants for production H₂SO₄, which is sold to the fertiliser industry (Jacobs, 2006). Hundermark (2011) states that off-gas from various furnaces are recycled differently. This includes the use of dry electrostatic precipitators, high temperature baghouses, ceramic filters, and wet venturi scrubbers. Sixty percent of sulphur that enters the smelter leaves in the converter gases, 20 % in the furnace gases, 15 % in the converter matte, and 5 % in the furnace slag (Jones, 2005). It is these gases that are collected, treated and used in the production of H₂SO₄.

As previously stated, many metals are in complex with sulphides, and SO₂ is produced when sulphides oxidise during heating. Other sulphur species may also be produced when SO₂ is oxidized, especially sulphates. Sulphates may bind with metal-containing aerosols, forming stable transition metal complexes (Burgess *et al.*, 2001).

In conclusion, smelting removes most gangue minerals (oxide and silicate) as molten slag, while concentrating the sought minerals into a matte phase. Furnace matte is granulated and becomes the substrate for a converting process, where excess iron and sulphides are removed by oxidation with air or oxygen (O₂). Converter matte is further processed and refined. Converter- and furnace slag that still contain some of the base metals and PGM are recycled in a SCF. SO₂ is produced during smelting, and may become the precursor compound for the formation of other sulphurous chemical species.

2.2 Formation of Sulphurous Chemical Species

The sulphur present in the smelter originates from the concentrate containing base-metal sulphides that is fed to the furnaces. For sulphur to adhere to dust, it must firstly leave the molten matter and become airborne, and then undergo further chemical transformation. This section will explain the formation of SO₂, that serve as the precursor for the formation of other sulphurous chemical species, and the formation of sulphates that can readily adhere to dust, and therefore, contribute to sulphur loading.

Table 1: Physical and chemical properties of SO₂.

Characteristic	Value
Molecular weight	64.064
Vapour Density	2.264 at 0 °C (Air = 1)
Melting point	-75.5 °C
Boiling point	-10.05 °C
TWA-OEL	2 ppm
STEL	5 ppm
Solubility in water	1.07x10 ⁵ mg.L ⁻¹ at 21 °C
CAS number	7446-09-5
Conversion factor in air, 1 Atm	1 ppm = 2.6 mg.m ⁻³

TWA-OEL: Time Weighted Average – Occupational Exposure Limit; STEL: Short Term Exposure Limit; Atm: Atmosphere; CAS: Chemical Abstracts Service (MHS Act 29, 1996; HSDB, 2012).

2.2.1 Formation and Oxidation of S(IV)

The notation S(IV) and S(VI) respectively refers to sulphur in the 4⁺ (e.g. SO₂) and 6⁺ (e.g. SO₄²⁻) oxidative state (Seinfeld, 1986). SO₂ is formed when sulphur is oxidised by O₂, and during the oxidation of metal sulphides. Combustion of sulphur-containing material will lead to the oxidation of sulphur with O₂ (Dunn, 1997). In the smelter, more specifically the furnace, metal-sulphide compounds serve as the sulphur source and during smelting, oxidation of sulphur by O₂ leads to the formation of SO₂. The balanced reaction: $S + O_2 \rightarrow SO_2$.

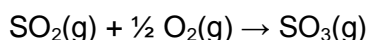
Gaseous sulphur present in the smelter may react with metal containing dust particles, e.g. FeO that forms FeS (Corbari *et al.*, 2008). The balanced equation for oxidation of metal sulphides: $MS(s) + 1.5 O_2(g) \rightarrow MO(s) + SO_2(g)$ (Dunn, 1997).

Ambient SO₂ can serve as a reservoir/precursor in the formation for other sulphurous chemical species such as sulphur trioxide (SO₃), sulphate salts (XSO₄), and sulphides species (Seinfeld, 1986; Burgess *et al.*, 2001). The oxidation of SO₂ to XSO₄ can occur:

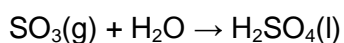
- A. in the gas phase.
- B. via photochemical reactions.
- C. in the fluid phase.
- D. by means of heterogeneous reactions (Breytenbach, 1995).

A) Oxidation of SO₂ in the Gas Phase to Form SO₃, S(VI)

When considering thermodynamic principles, SO₃ can form via the reaction between SO₂ and O₂, although the rate of this reaction is so slow in the absence of catalysers, that it can be ignored as a source of atmospheric SO₃ (Seinfeld, 1986).



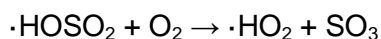
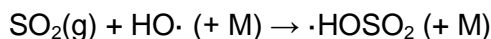
When SO₃ does form, it immediately reacts with water vapour to form H₂SO₄.



SO₃ is stable at room temperature or high pressure. Oxidation of SO₃ can occur at room temperature in the presence of water, and it can dissociate at temperatures higher than 1200 °C (Schmidt and Siebert, 1986). Platinum- or vanadium pentoxide – catalysers are used in a contact process to produce industrial H₂SO₄ (Faith *et al.*, 1966). Furnace and converter off-gas are treated in this manner to produce H₂SO₄.

B) Photochemical Dissociation of SO₂

Although photochemical dissociation of SO₂ can also occur, it is not an important oxidation path of SO₂. SO₂ absorbs ultra violet light to form SO₂ radicals ($\cdot\text{SO}_2$), and this molecule is stable and does not readily dissociate (Calvert *et al.*, 1978). Only a few radical entities appear to play a remarkable role in the oxidation of SO₂. Herewith, the dominant oxidation path of SO₂ seems to be the reaction with hydroxyl radicals ($\cdot\text{HO}$) (Seinfeld, 1986).



The reaction above is immediately succeeded by the formation of H₂SO₄ via the reaction between SO₃ and water.

Metal ions are needed for the oxidation of SO₂ by O₂ to take place in an aqueous medium - no reaction is observable in de-ionised water. Trace amount of metal ions or organic debris are needed for ion exchange. The oxidation of S(IV) in airborne water are catalysed by trace amounts of metals and impurities present even in the best quality water (Warneck, 1991).

C) Homogeneous Catalysed Oxidation Process in the Fluid Phase

Homogeneous oxidation of S(IV) can occur on moist surfaces of solid particles, and therefore contribute to sulphur loading (Sakurai *et al.*, 1998). Water vapour, as indicated by relative humidity, can adsorb onto dust particles, and provide a aqueous medium for homogeneous oxidation of S(IV). Three acid-basic entities can form when SO₂ dissolves in water namely: hydrated sulphur dioxide (SO₂.H₂O), hydrogen sulphite ion (HSO₃²⁻), and sulphite ion (SO₃²⁻) (Seinfeld, 1986). Metabisulfite ions (S₂O₅²⁻) can also form, but is negligible at low concentrations of S(IV) (Seinfeld, 1986). These three entities are all in the 4⁺ oxidative state, and are collectively referred to as S(IV). Multiple investigations indicated that dissolved O₂ does not oxidize S(IV)-compounds in the absence of catalysers (Calvert *et al.*, 1985; Hobson *et al.*, 1986). In order for metal ions to catalyse the oxidation of S(IV), the metal ion must be able to extract an electron from the S(IV) entity. Further, there must be an energy appropriate reaction path, which the reduced metal ions can follow to return to the high valence conditions (Huss *et al.*, 1982).

Metal ions catalyse the oxidation of S(IV). The velocity of this catalytic oxidation is pH dependant, and maximum velocities can be observed within narrow pH parameters, and where the pH of the solution is too great, the catalytic effect is lost.

For example, Fe(III) ions catalyses with maximum velocity constant in the pH range of 3.5 - 4. There is no observable catalytic effect noticeable at pH > 6. The reaction is a first order in terms of the S(IV) concentration at pH 4 and 20 °C (Huss *et al.*, 1982; Kraft and Van Eldik, 1989). The production of sulphate significantly augments with an increase in total Fe(III) concentration. It slightly decreases when total S(IV) concentration is increased, and stays steady when the pH of the reaction mixture changes from (1.2 – 3.0) (Grgic *et al.*, 1991).

Synergistic effects can also occur. During interaction between Fe, manganese (Mn), and Co ions, a synergistic effect can be observed. It is proposed that these metal ions oxidize Mn(II) to Mn(III) ions, and thereafter, Mn(III) is responsible for the auto oxidation of S(IV). The synergistic effect occurs at any concentrations of Mn(II) and Fe(III). The synergistic effect is higher for high Mn(II)/Fe(III) concentrations, than for high Fe(III)/Mn(II) ratio (Martin and Good, 1991).

This demonstrates that the presence of catalyst in an aqueous medium alone is not enough to support the formation of SO₄²⁻, but the catalytic effect is also subjected to the pH of the solution and the concentration of the catalysts.

D) Heterogeneous Catalysed Oxidation Process

Heterogeneous catalysed oxidation on the surfaces' of solid particles occur when moisture is absent from the surface, and consequently, relative humidity is low (lower than 0.5 %) (Sakurai *et al.*, 1998). Five general different reaction steps can be distinguished, which catalyses the oxidation of SO₂ in atmospheric processes:

- i) Diffusion of the reagents to the surface.
- ii) Adsorption of the reagents to the surface.
- iii) Reaction on the surface.
- iv) Desorption of the product from the surface.
- v) Diffusion of the product away from the surface.

Step (i) and (v) are rarely the rate determining steps (Seinfeld, 1986). The atmospheric oxidation of SO₂ on solids' surfaces is the exception to the rule, because the sulphate that forms is also solids. An

accurate determination of the pH of a heterogeneous (gas/fluid or fluid/solid) reaction surface is very difficult because it is difficult to accurately determine the different ion concentrations on the surface (Burger, 1993).

Similar to homogeneous catalysed oxidation, optimal oxidation for heterogeneous oxidation of S(IV) favours certain pH parameters. For silica oxide (SiO₂) to catalyse the oxidation, adsorption of both S(IV) and oxygen to the SiO₂ surface are prerequisites. S(IV) is predominantly present as SO₃²⁻ in the pH ~ 4 range, and only a fraction is present in the SO₂.H₂O and HSO₃²⁻ form (Prasad and Rani, 1992). This reaction is a surface catalysed process.

Activated carbon produces a sulphate concentration proportional to the mass of the carbon (Scmakov *et al.*, 1989). The forming of sulphate is further subjected to the SO₂ concentration, relative humidity and exposure time (Mamane and Gotlied, 1989). In an acidic medium (pH < 4), the reaction velocity is augmented with an increase in pH (Shmakov *et al.*, 1989).

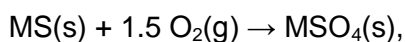
Where metal oxides is relevant, MnO₂ is the most active heterogeneous oxidation catalyser of S(IV) at room temperature. Other metal oxides also capable of catalytic activity are: PbO, CuO and Fe₂O₃ (Vadjic *et al.*, 1986). During atmospheric conditions, iron oxide is by far the most likely S(IV) oxidation catalyser in the atmosphere (Seinfeld, 1986). Fe₂O₃ is a good catalyser for the reaction between SO₂ and O₂ to produce SO₃ at high temperatures (640 – 670 °C). This catalytic effect is absent in darkness (Burger, 1993).

The heterogeneous oxidation process of SO₂ on the surface of a non-hygroscopic metal oxide is not a true catalysed reaction. The products of these reactions occupy the active site on the metal oxide surface, and are shielded from further activity. The oxidation process of SO₂ on the surface of Fe(III)O particles forms a limited amount of H₂SO₄, and the amount is directly proportional to the number of available absorption points. This process can be described as “capacity-limited heterogeneous oxidation” (Chun and Quon, 1973).

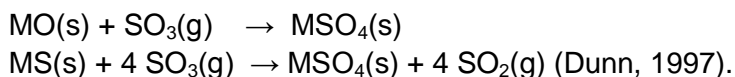
2.2.1.1 Sulphide Oxidation

The previous section explained the formation of sulphates via the oxidation of S(IV), and to a lesser extent, the oxidation of gaseous SO₂. An alternative process for the formation of sulphate, is the oxidation of sulphides, opposed to oxidation of S(IV).

Sulphate can be produced by two possible reactions: the direct oxidation of sulphide:



or sulphation of an oxide with SO₃:



A fraction of the sulphur gaseous species released from the smelter may react with dust particles generated in the process, forming stable transition metal compounds (Burgess *et al.*, 2001; Corbari *et al.*, 2008). The rate of formation is dependent on the acidity of the mixture. These newly formed sulphur species may be important respiratory irritants. Iron and copper combined with SO₂ have been measured in smelter plumes from copper and lead smelters, and these complexes may be more toxic than SO₂ alone (Burgess *et al.*, 2001). This will be discussed consequently.

2.2.2 Factors Influencing Oxidation

The reactivity of the catalysed oxidation process of S(IV) is influenced by external factors. This includes buffer entities, ion strength, pH, temperature, and particle size.

pH

As previously mentioned, catalyst favour certain pH ranges for optimum catalytic effect. The Fe(II) ion catalysed oxidation of S(IV) with hydrogen peroxide increases with an increase in pH. The strong pH dependency of this process can be explained by the fact that Fe(III) are active catalytic entities (Huss *et al.*, 1982). During the reaction between Fe(II) and H₂O₂, Fe(III) and ·HO are formed (the Fenton reaction), and this accelerates the oxidation process (Graedel *et al.*, 1985).

The Mn(II)- and Fe(II)ion catalysed oxidation reaction of S(IV) is retarded by acids as well as salts. The Mn(II) catalysed reaction is independent of the reaction pH up to pH of 4. The reaction rate is augmented greatly for values greater than 4 (Huss *et al.*, 1982). S(IV)'s solubility decreases with an increase in acid strength. This may explain why the oxidation rate decreases at lower pH values (Huss *et al.*, 1982).

The ratio of S(IV) entities varies at specific pH values, e.g. at pH 4, SO₃²⁻ is the predominant compound, and only a fraction is present in the SO₂·H₂O and HSO₃²⁻ form (Huss *et al.*, 1982).

Temperature

The oxidation rate of manganese catalysed oxidation of S(IV) with O₂ decreases five to ten times with a temperature reduction of 25 °C to 8 °C (Barrie and Georgii, 1976).

Particle Size

Particle size plays an important role where surface processes are relevant. Particle size influence the available adsorption points, the residency of particles in air suspension, and the induction period (Rani *et al.*, 1992). Smaller particles have higher solubility because they have a high surface-to-volume-ratio (Fahlman, 2011).

2.3 Health Effects

Adverse health effects due to SO₂ exposure have enjoyed much attention in the last century and have yielded some contradicting results. The effects of sulphate containing aerosols can be traced back to the early 1940's, as it also forms part of air pollution, and contributes to ill health due to sulphate adhered to fine PM. The part that sulphate play in adversely affecting health, are investigated experimentally and cohort studies are still conducted to determine the association between fine PM exposure and the role the chemical constitution of these particles play.

Aside from the intrinsic detrimental health effects that SO₂ exposure holds, ambient SO₂ can also be a precursor for the formation of other sulphurous chemical species such as: H₂SO₄, SO₃ which is readily converted to H₂SO₄, and sulphate, which also has their own detrimental effects ascribed to it. Only SO₂ and particulate sulphate will be discussed: SO₂ as it is the most abundant known source of airborne sulphurous species that is routinely monitored, and particulate sulphate, as it is the aim of this study.

2.3.1 Health Effects Due to SO₂ Exposure

Respiratory Toxicology

The main concern regarding acute SO₂ exposure is that it elicits asthma and asthma like symptoms in exposed persons, even in non-asthmatics (Kilic, 2003; Meng *et al.*, 2003; Sunyer *et al.*, 2003). These effects are subscribed to SO₂'s ability to induce bronchoconstriction - and consequently increase airway resistance in exposed subjects. Nadel *et al.* (1965) hypothesised a possible mechanism by which inhalation of SO₂ decreases airway conductance in exposed subjects. Although the exact mechanism of bronchoconstriction induced by SO₂ is not completely understood, limited evidence suggests the involvement of both parasympathetic pathways and inflammatory processes (Douglas *et al.*, 2011). Bronchoconstriction occurs via stimulation of parasympathetic pathways that in turn induces constriction of smooth muscle. SO₂ stimulates fibres in the trachea and bronchi, believed to arise from chemo-receptors. This in turn stimulates the vagus nerve, which constitutes the efferent limb of bronchoconstriction caused by inhalation of SO₂ (Nadel *et al.*, 1965).

SO₂ is well absorbed in the upper respiratory system, and human studies indicate absorption of 40 – 90 % in this region (WHO, 1979). The mode of breathing, nasally versus oronasally (mouth), and ventilation rate is the two determinants affecting absorption. During nasal breathing at rest, more than 90 % of inhaled SO₂ is absorbed in the nasal passages (Speizer and Frank, 1966). When breathing is switched from nasal to oronasal with accompanying increase in ventilation, like during laborious work or exercise, SO₂ has deeper penetration into the lungs (Frank *et al.*, 1969; Costa and Amdur, 1996). Inhaled SO₂ is absorbed into the bloodstream and widely distributed throughout the body. It is rapidly detoxified by the liver via the sulphite oxidase enzyme system, and the metabolites (SO₄²⁻) are excreted via the urinary tract (HSDB, 2012). Residual SO₂ can persist in the respiratory system for a week or more after exposure, possibly as a result of S binding to protein (Yokoyama *et al.*, 1971).

Contradictory results regarding the toxicological effect of absorbed SO₂ have emerged. Numerous studies by Meng *et al.* (2002a; 2002b; 2002c; 2002d) proposed that exposure to inhaled SO₂ may have genotoxic potential based on animal studies. Ziemann *et al.* (2010) confirmed the readily systemic availability of inhaled SO₂, and the reactivity towards blood erythrocytes, but did not observe the genotoxic effect in the bone marrow of mice as documented by Meng *et al.* (2002a; 2002b).

There are also some controversy associated with SO₂ exposure, especially with chronic exposure and permanent pathological changes. Piirila *et al.* (1996) states that exposure to high concentrations of SO₂ leads to bronchial hyper-reactivity. The authors reported this hyper-reactivity 13 years after an accidental exposure to SO₂ in a pyrite mine, and refers to it as reactive airway dysfunction syndrome – an inflammatory bronchial obstruction combined with bronchial hyperactivity caused by a single exposure to

high concentrations of an irritant (Piirila *et al.*, 1996). Ermis *et al.* (2010) studied apricot workers that are seasonally exposed to high concentrations (106.6 – 721.0 ppm) of SO₂, and a control group, and found no statistical significant changes in pulmonary function ascribable to SO₂ exposure. The author concluded that the asthma-like symptoms caused by intermitted occupational exposure to high concentrations of SO₂ was acute and reversible, and without bronchial reactivity (Ermis *et al.*, 2010).

It is also worth mentioning that in general, asthmatics are also more susceptible to the bronchoconstriction effect of SO₂ than non-asthmatics, and the constricting effects can be elicited at lower concentrations than for non-asthmatics (Johns *et al.*, 2010).

As previously mentioned, the main focus of SO₂ effect is the elicitation of asthma and asthma like symptoms, although exposure has also been linked to other respiratory diseases. Chronic bronchitis, and chronic inflammation without the presence of bacterial infection has been observed in animal studies (Chakrin and Saunders, 1974; Shore *et al.*, 1987). Pulmonary oedema, dyspnoea, cyanosis and even lung cancer is also associated with occupational exposure to SO₂ (Charan *et al.*, 1979; Woodford *et al.*, 1979; Piirilä *et al.*, 1996; Lee *et al.*, 2002).

Non Respiratory Effects Elicited by SO₂ Exposure.

SO₂ may also have detrimental effects to physiological systems other than the respiratory system and has been implemented in causing oxidative stress. Meng *et al.*, (2003) found that exposure leads to a statistical significant increase in lipid peroxidation process in the heart and lungs of mice, which is accompanied by changes of antioxidant status in these organs. The author continues and states that SO₂ is not only toxic to the respiratory system, but also to the entire cardiopulmonary system. Furthermore, SO₂ is an *in vivo* glutathione depleting agent, which might also be a contributing factor to its ability to induce oxidative damage (Langley-Evans *et al.*, 1996). Yargicoglu *et al.* (2007) observed increased lipid peroxidation and alterations in antioxidant enzyme activities, especially inhibition of glutathione peroxidation after exposure in animal studies. Similarly, Gokirmak *et al.*, (2003) states that occupational exposure to high concentrations of SO₂ enhances respiratory oxidative stress and lipid peroxidation in humans. The International Agency for Research on Cancer classified occupational exposure to SO₂ in class 3: not carcinogenic to humans, based on inadequate conclusive data (IARC, 1997).

H₂SO₄ can form via the reaction between atmospheric OH· in water vapour and atmospheric SO₂ (Salonen *et al.*, 2008). It can also form when SO₂ makes contact with mucous membranes (Komarnisky *et al.*, 2003). The latter is responsible for the severe irritant effect it has on eyes, mucous membranes and skin (Komarnisky *et al.*, 2003). H₂SO₄ can also form when SO₂ comes in contact with sweat, and this can cause skin irritations. The irritant effect of H₂SO₄ can be subscribed to its corrosive properties, and exposure leads to coagulation necrosis (Noah *et al.*, 2003).

Furthermore, H₂SO₄ depresses pulmonary particle clearance (Amdur, 1989). The International Agency for Research on Cancer classified long-term occupational exposure to sulphuric acid mists in class 1: carcinogenic to humans (IARC, 1997).

Pope *et al.* (2002) found a positive association between combustion related (of which SO₂ gas forms part of) fine particulate air pollution exposure (PM_{2.5}) and lung cancer- and cardiopulmonary mortality during a cohort study. Exposure to SO₂ was significantly associated with elevated mortality from respiratory- and cardiopulmonary pathology and lung cancer incidence and -mortality (Kan *et al.*, 2010; Pope *et al.*, 2002).

2.3.2 Health Effects of Sulphate Adhered to PM

The conversion of SO₂ gas to sulphate salts onto aerosols, implies an additional source of exposure to these airborne sulphates, and it also has its' own health implications for exposed people.

Wolff (1986) investigated, amongst other aerosol pollutants, the effects that sulphate have on mucociliary clearance and states that alterations in mucociliary clearance due to exposure to irritant pollutants is an indication of adverse health effects. The author found that exposure to sulphur oxides (SO_x) and sulphate do bring about changes in mucociliary clearance (Wolf, 1986).

More recent studies use lung permeability as a parameter for detrimental effects to the lungs. The rationality is that the decay in lung homeostasis results in greater movement of soluble components of PM to systemic circulation (Tankersley *et al.*, 2003).

Hiyoshi *et al.* (2005) studied the effect of Asian sand dust (ASD), and ASD treated with sulphate on mice lungs, and found that ASD and the treated ASD induced bronchitis and alveolitis in mice lungs. ASD naturally contains 900µg/g sulphate. One gram of dust particles was exposed to 100 ppb SO₂ for 2 days in a 1 L glass bottle to produce sulphate bonding on the dust particles. The study found that the sulphate produced by SO₂ did not have an aggravating effect on allergic diseases. Ichinose *et al.* (2008) used thermo-treatment on ASD particles to remove toxic microbiological materials and chemical species like sulphate, and found that the heat treated dust only led to slight pathological changes, less than the crude ASD. Therefore, ASD with sulphate (crude ASD) lead to more pathological changes in lung tissue such as inflammatory response when compared to ASD without sulphate. Infiltration of eosinophils and lymphocytes occurred, together with proliferation of goblet- and epithelial cells. These changes correlate with changes seen in human asthma (Ichinose *et al.*, 2008).

Environmental studies that focus on the association between PM exposure and cardiovascular effects, observed an association between cardiovascular mortality and sulphate exposure (Brook *et al.*, 2010; Ostro *et al.*, 2011). Although there are still some precautions surrounding the full extent of the toxicological effect exerted by sulphate, the direct role of particulate sulphate in causing cardiovascular events cannot be excluded entirely (Schlesinger, 2007; Franklin *et al.*, 2008). Franklin *et al.* (2008), discovered that cardiovascular risk was increased when PM mass contained a higher proportion of sulphate, as well as some metals (aluminum, arsenic, silicon, and nickel). A similar observation was made by Fernandez *et al.* (2004), who found that exposure to particles containing zinc and sulphur had a greater increase in lung permeability in mice lungs, than exposure to the individual compounds. Thus, when evaluating the health implication of exposure to PM, other variables must also be kept in mind e.g. the chemical composition; trace element content; strong acid content; sulphate content; and particle size distribution of particulate matter, as these variables may be contributing factors in its toxicity (Harrison & Yin, 2000; Stanek *et al.*, 2011).

A review study by Reiss *et al.* (2007) cautions the interpretation of data gathered from environmental studies depicting health effects due to exposure to both PM and sulphate. Health effects ascribed to the sulphate component of PM, may be due to non-sulphate constituents and the authors critiques the interpretation of such data. The absence of a well-established biological mechanism to explain the association between PM and health effects further burdens the interpretation of results.

2.3.3 Possible Additive- or Synergistic Effect

If one considers the afore mentioned information regarding the health effects due to exposure to sulphurous species, it is not an unreasonable deduction to ponder the possibility of an additive-, or synergistic effect that simultaneous exposure may have on human health. The health implications that are associated with exposure to SO₂ and sulphate have overlapping effects. There have been reports on both SO₂ and sulphate which induce pulmonary inflammation (Ichinose *et al.*, 2008; Sun *et al.*, 2010). Meng *et al.* (2003) states that the deleterious effect of SO₂ is not only isolated to the respiratory system, but also has adverse effects in the cardiopulmonary system. Furthermore, Kan *et al.* (2010) and Pope *et al.* (2002) found a positive association between cardiopulmonary mortality and ambient SO₂ exposure. Pope *et al.* (2002) and Ostro *et al.* (2010) reported an association between cardiopulmonary mortality and exposure to sulphate - associated with fine particulate matter.

An increase in lung permeability due to sulphate exposure, would not only implicate an even greater absorption of SO₂ in the lungs, but could also facilitate the absorption of other chemicals, or microbes, into the circulatory system (Prasad *et al.*, 1988). This may be further aggravated by depression of mucocilliary clearance, caused by the formation of H₂SO₄ in the respiratory tract, which could lead to longer residency time of inhaled matter in the lungs, further increasing the absorption of inhaled particles (Amdur, 1989).

Evaluation of the health effects caused by SO₂ together with PM containing sulphate are commonly done in environmental studies, in an attempt to determine the effect of ambient exposure to these substances. No studies are available that explain or states any additive or synergistic effect due to exposure to these substances.

2.4 Sampling

2.4.1 Aerodynamic Fractions

Aerodynamic diameter refers to the diameter of a sphere of unit density, which behaves aerodynamically like the particle of the test substance. It is used to compare the aerodynamic behaviour of particles of different sizes, shapes and densities, and play an important, if not deterministic role, in lung deposition of a particle (EUR, 2002; MHDS 14/3, 2000).

Aerodynamic fractions are defined as:

- Inhalable fraction (particles with a size of up to 100 μm , with a 50 % cut-point of 100 μm , i.e., the particulate diameter which is captured with 50 % efficiency): the fraction of airborne material that can be inhaled by the nose or mouth, and is available for deposition in the respiratory tract. The dust that deposits in these areas can accumulate in the sputum or mucus, and can be coughed out or swallowed, making it possible for absorption in the digestive system (Belle and Stanton, 2007). The inhalable occupational exposure limit (OEL) for particles not otherwise classified (PNOC) is 10 $\text{mg}\cdot\text{m}^{-3}$ (MHS Act 29, 1996).
- Thoracic fraction (particles smaller than 30 μm , with a 50 % cut-point of 10 μm), the fraction of airborne material particles that passes the larynx and may be deposited in the lung airways or the gas exchange regions of the lungs – the alveoli. There are currently no thoracic OEL listed by the department of minerals and energy (Belle and Stanton, 2007).
- Respirable fraction (particles up to 10 μm , with a 50 % cut-point of 4 μm), the fraction of particles that penetrate the gas exchange region of the lung. Various forms of crystalline silica (such as quartz, cristobalite and tridymite) and coal dust are examples of this fraction (Belle and Stanton, 2007). The OEL for respirable PNOC dust is 3 $\text{mg}\cdot\text{m}^{-3}$ (MHS Act 29, 1996).

It is also worth mentioning that recent environmental studies almost exclusively focus on PM with aerodynamic fractions of 2.5 μm and 10 μm (respirable fraction).

2.4.2 Environmental Factors

Studies have been conducted to determine external factors that influence the deposition of SO_2 onto particulate matter. Sakurai *et al.* (1998) used synthetic zeolite (a model material soil particles) as a surrogate. The authors found that the amount of sulphate formation that occurred due to SO_2 oxidation is affected by the chemical composition, specific surface area, relative humidity and temperature. Sulphate formation is augmented when specific surface area, relative humidity in the air and temperature are high. The authors further state oxidation of SO_2 is heterogeneous when the relative humidity is less than 0.5 %, and homogeneous oxidation (solution oxidation) reaction as relative humidity rises over 15 % (Sakurai *et al.*, 1998). Sorimachi and Sakamoto (2007) affirm the dependency of SO_2 deposition on solid particles and relative humidity.

2.5 Sampling Equipment

2.5.1 The IOM sampler

The IOM sampler can be used to determine inhalable and respirable exposure in a single sample and meets the international standards of:

- ACGIH sampling criteria for inhalable particulate
- ISO/CEN health-related fraction of bioaerosols
- Preferred sampler for HSE Method MDHS 14/3
- Australian standard for inhalable particulate

(SKC Inc, 2012)

When comparing the sampling efficiency with other commercially available inhalable personal samplers under the same test conditions, the IOM sampler's performance emerged as the best reference instrument for collecting inhalable airborne particles (Zhou & Cheng, 2010). Linnainmaa *et al.* (2008) confirmed the IOM sampler's usability in calm working environments. Because both the cassette and filter are weighed after sampling, underestimation of dust concentrations due to particle deposition on the internal walls does not occur (Linnainmaa *et al.*, 2008).

Linnainmaa *et al.* (2008) and Zhou & Cheng, (2010) also found that there are certain limitations to the IOM sampler. In general, the sampling efficiency decreases as the wind speed increases. The IOM sampler could possibly collect insufficient material for chemical analysis when it operates at the designed flow rate, of 2 L.min⁻¹, with a low concentration of aerosol. The sampler's inlet orientation to wind also has an effect on the sampling efficiency. Sampling efficiency is higher, especially for large particles, when the inlet faced directly into the wind (Zhou & Cheng, 2010). The efficiency of the IOM sampler at wind speeds ranging from 0.4 – 1.6 m.s⁻¹ closely resembled the inhalable particulate curve (Zhou & Cheng, 2010). According to the MHDS 14/3 (2000), bias of less than ± 5 % is typical for the IOM sampler.

Linnainmaa *et al.* (2008) recommends that when both inhalable and the respirable fractions are measured, two different IOM samplers; one with and another without the foam insert; should be used. The author states that during field studies, the foam sampler yielded higher inhalable dust concentrations, than the IOM sampler without the foam insert – probably due to moisture absorption of the foam. Samples exceeding 4 mg should be avoided with the IOM sampler for respirable dust, because of increase in the filtering efficiency of the foam at high dust loads. They recommended the foam insert only for respirable dust due to its moisture absorption. Linnainmaa *et al.* (2008) concludes that there is no sampling device that would permit both inhalable and respirable dust reliably at the same time.

The IOM sampler will be used regardless of the know limitations as stated by Linnainmaa *et al.* (2008), as it is cost effective, and more convenient for the worker being sampled. Alternatives that were explored included using two pumps, each with its' own sampling train, but this will be to cumbersome for the wearers in their demanding work environment. One pump in conjunction with a low flow adjustable splitter tube was also considered, but dismissed because the demand of 2 sampling trains, each requiring airflow of 2 L.min⁻¹, on a single pump would exceed the available pump's capacity. The use of area samples was dismissed because the workers do not operate in a single location for a whole shift, and thus, area samples would not be representative of a worker's personal exposure during a work cycle. For example, paste loaders leave the furnace area once a task is completed and wait for their next assignment. Similarly, tappers are only present on the tapping floor whilst tapping is in progress, and

may be found in the control room once this activity has been concluded. Even though the aim of this study is not test adherence to legal standards regarding personal exposure limits, the use of personal sampling does give extended insight to what can be expected for personal exposure in a normal working cycle.

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CHAPTER 3

ARTICLE

This article will be submitted to the Annals of Occupational Hygiene. The author's instructions are as follows:

- *Structure.* Papers should generally conform to the pattern: Introduction, Methods, Results, Discussion and Conclusions - consult a recent issue for style of headings. A paper must be prefaced by an abstract of the argument and findings, which may be arranged under the headings: Objectives, Methods, Results, and Conclusions. Keywords should be given after the list of authors.
- *Units and symbols.* SI units should be used, though their equivalent in other systems may be given as well.
- *Figures.* Good quality low resolution electronic copies of figures, which include photographs, diagrams and charts, should be sent with the first submission. It is helpful to reviewers to incorporate them in the word-processor text or at the end. The revised version, after refereeing, should be accompanied by high-resolution electronic copies in a form and of a quality suitable for reproduction. They should be about the size they are to be reproduced in, with font size at least 6 point, using the standard Adobe set of fonts.
- *Tables.* Tables should be numbered consecutively and given a suitable caption, and each table typed on a separate page. Footnotes to tables should be typed below the table and should be referred to by superscript lowercase letters.
- *References.* References should only be included if essential to the development of an argument or hypothesis, or which describe methods for which the original account is too long to be reproduced. Only publications which can be obtained by the reader should be referenced. References in the text should be in the form Jones (1995), or Jones and Brown (1995), or Jones *et al.* (1995) if there are more than two authors. For example: Jones and Brown (1995) observed total breakdown of control... or Total breakdown of control has sometimes been observed (Jones and Brown, 1995).

- At the end of the paper, references should be listed in alphabetical order by name of first author, using the Vancouver Style of abbreviation and punctuation. Examples are given below. ISBNs should be given for books and other publications where appropriate. Material unobtainable by readers should not be cited. Personal Communications, if essential, should be cited in the text in the form (Professor S.M. Rappaport, University of California). References will not be checked editorially, and their accuracy is the responsibility of authors.

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Sulphur Loading of Respirable and Inhalable Dust at a Platinum Smelter

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Word Count: 5223

Abstract:

Sulphur plays a crucial role in the smelting of platinum, as it collects the sought precious metals in a matte phase. During this smelting process, sulphur is released into the ambient air of the smelter as sulphur dioxide. The oxidation of sulphur dioxide onto dust can be an additional source of sulphur exposure. Exposure to particulate sulphate has been associated with cardiopulmonary mortality.

Aim: The aim of this study was to quantify the sulphur content of inhalable and respirable dust in a platinum smelter. **Method:** Simultaneous personal sampling of SO₂ and dust were conducted using a Dräger Pac and IOM sampler respectively. Samples were divided into 3 groups, representing 3 different floors of the smelter. Relative humidity, temperature and air velocity were also recorded. Data was Box-Cox transformed to normalise the distribution, and the transformed data was used for further statistical calculations. **Results:** Environmental factors were stable on the different floors of the furnace. Sulphur was present on both the respirable and inhalable dust fractions, and the highest sulphur percentage was recorded on the tapping floor. The sulphur content of respirable dust was significantly higher ($p = 0.03$) than the sulphur content of the IOM foam dust (inhalable and thoracic portion combined). A statistical significant correlation was obtained between respirable sulphur and the SO₂ concentration of the ceramic workers ($r = 0.27$; $p < 0.05$), as well as the foam sulphur and the SO₂ concentrations of eh paste loaders ($r = 0.32$; $p < 0.05$). No significant correlation could be found between SO₂ concentrations and sulphur content of particles when all the samples were considered. **Conclusion:** Environmental differences recorded on the different floors did not significantly influence sulphur loading. Sulphur contained in smaller particles (respirable dust) is significantly higher than that of the larger particles sampled probably because of an increase oxidation of SO₂ due to an increase in surface area available for sulphur loading in the smaller aerodynamic fraction. It could however also be attributed to the escape of sulphur containing iron pyrite via the electrodes.

Keywords:

Sulphur content, platinum smelting, sulphur dioxide oxidation, sulphur loading, respirable and inhalable dust.

Introduction

The refining process of platinum comprises of a series of processes, of which the conglomerate goal is to concentrate the sought out materials i.e. platinum group metals (PGM) (Jones, 2005; Jacobs, 2006; Crundwell *et al.*, 2011). Smelting forms part of the refining process and the goal is to produce sulphur-deficient nickel-copper matte rich in PGM.

Pyro-melting entails heating of dry concentrate in a furnace, in order to form two immiscible liquid layers – matte and slag (Jacobs, 2006; Crundwell *et al.*, 2011). Matte contains most of the base metal sulphides and PGM, and naturally settles to the bottom of the furnace. The less dense slag, forms a layer on top of the matte, and contains mostly oxides and some of the PGM (Burgess *et al.*, 2001; Jacobs, 2006; Crundwell *et al.*, 2011).

Sulphur originates from sulphides in the concentrate, and serves a purpose in that the sulphides collect the precious metals in the matte phase (Jones, 2009). During tapping of matte and slag, sulphur dioxide (SO₂) is released into the ambient atmosphere of the smelter (Burgess *et al.*, 2001; Jacobs, 2006). Sulphur can be added, if needed, by blending concentrate with high sulphur content (Crundwell *et al.*, 2011). SO₂ forms when the sulphides in the molten matte and slag react with oxygen in the ambient atmosphere. Emission of SO₂ from furnaces is hard to avoid when using a sulphur-based matte-smelting process (Jones, 2009). Consequently, SO₂ in the smelter is a known problem to the mining industry and is routinely monitored. There is however, limited insight on the presence of sulphur on dust.

Dust present in the furnace originates from leakages in the electrode pipes. Holes in these pipes allow dust to be introduced into air suspension. The occurrence of blowbacks, which are explosions inside the furnace, further contributes to large amounts of dust to enter air suspension (Personal communication, Occupational Technologist Platinum smelter).

The oxidation of SO₂ on dust leads to the synthesis of sulphate salts. This oxidation can occur via numerous reactions such as oxidation in the gas phase, photochemical oxidation, oxidation in the fluid phase (homogeneous oxidation), and by means of heterogeneous oxidation. Homogeneous and heterogeneous oxidation are especially of importance in sulphate formation on dust (Halstead *et al.*, 1990; Sakurai *et al.*, 1998). The term sulphur loading will be used to refer to the mechanism during which sulphur adheres to dust.

Homogeneous oxidation of SO₂ occurs in an aqueous medium and entails the dissolving of SO₂ in water. When this occurs, the sulphur containing entities that form are all in the 4⁺ oxidative state, and are collectively referred to as S(IV) (Seinfeld, 1986). Metal ions serve as the catalyst for the oxidation of S(IV) in an aqueous medium. The velocity of this catalytic oxidation is pH dependant, and maximum velocities can be observed within narrow pH parameters. Where the pH of the solution is too alkaline, the catalytic effect is lost (Huss *et al.*, 1982; Kraft and Van Eldik, 1989). Fe(III) is known to catalyse this oxidation, and the production of sulphates are significantly augmented with an increase in total Fe(III) concentration (Grgic *et al.*, 1991). Burger (1993) reports that Fe₂O₃ can catalyse the oxidation of SO₂ by oxygen, if the reaction is heated. Using Fe₂O₃ as a catalyst, only 15 % of the SO₂ was not converted to sulphate at 100 °C. The amount of SO₂ not oxidised diminished close to 0 % when the reaction temperature increased to 350 °C (Burger, 1993).

Heterogeneous oxidation (interaction between a gas and solid) does not necessarily occur in an aqueous medium, although water may be present. Halstead *et al.* (1990) prefers the term non-aqueous heterogeneous oxidation. pH influences heterogeneous oxidation of SO₂, although it is difficult to accurately determine the surface pH of such a reaction, because it is difficult to determine the different ion concentrations on the surface (Burger, 1993). Metal oxides known to catalyse heterogeneous

oxidation of SO₂ include silicone oxide (SiO₂), copper oxide (CuO), and iron(III)oxide (Fe₂O₃) (Vadjic *et al.*, 1986; Prasad and Rani, 1992).

The aim of this study is to determine whether sulphur loading occurs on dust, in a Platinum smelter. Sulphur loading onto respirable and inhalable dust implies an additional source of inspirable sulphur exposure, in addition to SO₂. Adverse health effects associated with exposure to particulate sulphate is not yet well-defined and the absence of a well-established biological mechanism burdens the interpretation of data gathered from environmental studies concerned with portraying the association between particulate matter exposure and health effects (Reiss *et al.*, 2007). Even though there are uncertainty surrounding the full extent of the toxicological effect exerted by sulphate, the direct role of particulate sulphate in causing cardiovascular events cannot be excluded (Schlesinger, 2007; Franklin *et al.*, 2008). Exposure to particulate matter containing sulphate has been associated with cardiopulmonary mortality (Pope *et al.*, 2002; Ostro *et al.*, 2010). Franklin *et al.* (2008), discovered that cardiovascular risk was increased when particulate matter mass contained a higher proportion of sulphate, as well as some metals.

Methodology

Work place description

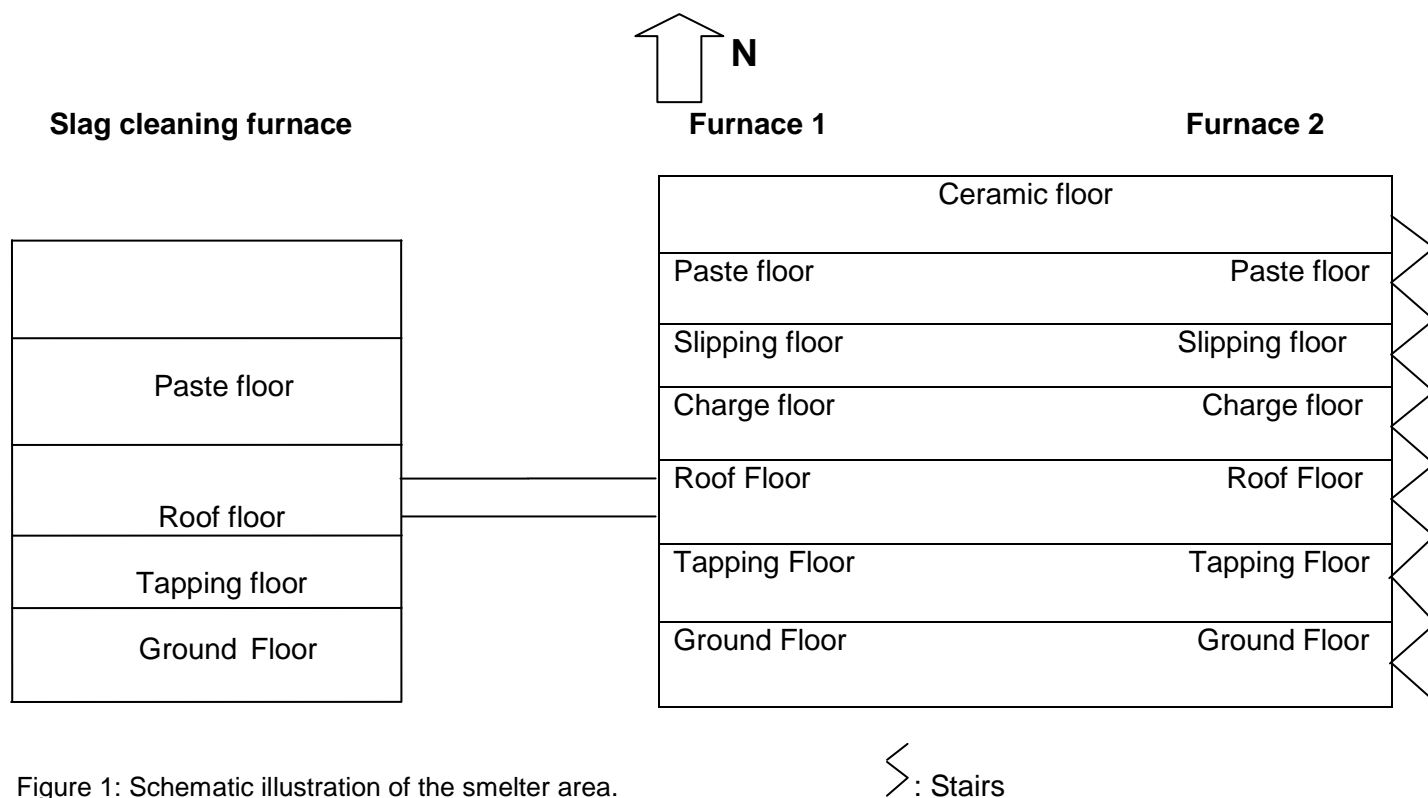


Figure 1: Schematic illustration of the smelter area.

The smelter contains 3 electrical furnaces, furnace 1 and 2 and a slag cleaning furnace (SCF). Furnace 1 and 2 are identical, with no physical border or passages that separate these structures and moreover, movement between furnace 1 and 2 is unrestricted on the paste floor. Furnace 1 is also connected to SCF, but movement is restricted and passages have to be used in order to move between the furnaces. Movement from furnace 1 to SCF is not possible on all the floors.

The tapping floor is open on the northern and southern side, while the paste floors are closed off on its southern side. The ceramic floor is unshielded on the eastern and western sides.

MHDS 14/3: General Methods for Sampling and Gravimetric Analysis of Respirable and Inhalable Dust (2000)

IOM samplers (SKC®) equipped with multi cellulose ester filter (25mm, 0.8µm pore size) and foam insert were used to conduct dust sampling. A sampling train consisted of the cassette enclosed in the IOM sampler, flexible tubing and the GilAir-3® sampling pump. Personal sampling was conducted at a 2 L.min⁻¹ flow rate for an 8 hour period. Calibration of pumps was conducted, before and after the sampling period. Samples were stored at room temperature in a shock resistant carry case.

The IOM sampler, in conjunction with the foam insert, can be used to simultaneously sample for respirable and inhalable dust. Foam inserts are accompanied by a certificate of conformity, which indicate that the foam inserts complied with the bias performance criteria of BS EN 13205 (SKC Inc, 2012). Larger dust particles are entrapped in the foam insert, and the smaller particles, the respirable dust fraction, accumulates on the filter behind the foam insert. To determine inhalable dust, the dust on the filter must be summated with the dust on the foam.

Because inhalable dust is the sum of the respirable- and foam fraction, inhalable dust was not used to determine statistical significant differences in sulphur content. Rather, the respirable fraction, representing dust with a size up to 10 µm, and the foam fraction, representing larger dust particles, between 10 and 100 µm, was used to compare the sulphur content of larger and smaller dust fractions. From here forth, foam dust will be used to indicate the fraction of dust on the foam.

SO₂ Measurement

The Dräger Pac® 7000 was used to determine personal exposure to SO₂. This is a direct reading device, and at the end of a shift, data was transferred using software provided by the manufacturer to electronically determine the time weighted average for SO₂. The device records concentrations in parts per million (ppm). Ppm was converted to mg.m⁻³ in order to make SO₂ data comparable with dust data. The following formula was used: ppm = (X mg/m³)(24.45)/(molecular weight).

A single worker was simultaneously equipped with an IOM sampler and a Dräger Pac® 7000.

Sulphur Content Analysis

There is currently no standardised method for the determination of sulphur content in particulate matter. The LECO® model CS-200 was used to determine the sulphur content of the dust (LECO corporation, 2007). This method heats samples in an induction furnace, to high enough temperatures in order to let metals and their alloys burn in oxygen. The sulphur present converts to SO₂, which is measured by infrared detectors (LECO corporation, 2007). Gazulla *et al.* (2011) reports that the use of the LECO® method to determine sulphur on particulate matter presented representative values, which the author describes as “certificate or recommended values”.

pH Analysis

The pH measurements were done in accordance with the Environmental Protection Agency, Method 9045 C, which depicts the measurement of pH of soil and waste samples (USEPA, 1995).

Workers Measured

Three potential high risk activities were identified, based on historic data, a walkthrough survey, consultation with onsite Occupational Hygienist, and the orientation of the working activities to the hazards. The first activity that had been identified was on the tapping floor. Workers concerned with this activity, from here on referred to as tappers, are closest to the SO₂ source. Although historically they do

not show concerning dust exposure, data gathered from these workers will aid in determining the correlation between SO₂ and sulphur loading. Sixteen tappers were sampled.

The second group was the paste loaders, working exclusively on the paste floors. Historically, these workers had high exposure to both SO₂ and dust and sixteen workers were sampled.

The final group of workers was on the ceramic floor. This floor is situated above the paste floor, and also reported high exposure to both SO₂ and dust in the past. Ten workers were sampled.

A total of forty-two workers were sampled within the 3 groups. This number is not a representation of the total work force present in the smelter, but does adhere to OESSM (occupational exposure sampling strategies manual) standard for selecting potential high risk workers (NIOSH, 1977). It is also important to note that the aim of this study was not to determine exposure compliance with standard regulations, but solely to determine the sulphur content of particulate matter, and the association between SO₂ exposure and the sulphur content.

In addition, 12 area dust samples were collected. Six samples were used to determine the pH of the dust and the remaining six were analysed by an environmental scanning electron microscope.

Humidity and the prevailing directing of airflow were recorded simultaneously by means of a Kestrel® 4000. The gross direction of air flow was determined by expelling smoke from Dräger® smoke tubes. The device was held an arm's length away, with the sensing fan blades perpendicular to the air flow. The device's data logging feature was used to make recordings. Fixed locations were measured twice daily. Environmental factors were only recorded on floors where sampling had been conducted.

Statistical Analysis

Statistica 10 (StarSoft, Inc., 2011) was utilized in order to perform statistical analyses. In order to perform statistical analysis, data was Box-Cox transformed since it was not normally distributed. Partial correlations, corrected for total dust, were performed to obtain the correlation between SO₂ and the sulphur content. A p-value ≤ 0.05 was regarded as statistical significant. One-way analyses of covariance (ANCOVA), corrected for total dust, were used to compare the sulphur content of the respirable- and foam dust of the 3 groups. Wilcoxon matched pair tests were performed to investigate the difference between the sulphur content of the respirable dust fraction, and the foam dust fraction.

Results

Table 1 depicts descriptive statistical values for air velocity, relative humidity, and temperature as recorded on the different floors. Relative humidity and temperature appears stable across the 3 different floors. The highest mean relative humidity was recorded on the tapping floor (42.9 %), while the lowest mean value was recorded on the ceramic floor (38.6 %). The highest mean temperature was recorded on the ceramic floor (33.8 °C), and the lowest on the tapping floor (32.5 °C). Dust samples taken on the ceramic floor were the most acidic (pH = 4.5). The paste floor had the highest mean air velocity (0.8 m.s⁻¹).

Table 1: Descriptive statistical results of the environmental factors measured at each floor.

Floor	pH of dust samples	Environmental variable	Mean ± Std. Dev.	Min	Max
Ceramics	4.5	Air velocity (m.s ⁻¹)	0.1 ± 0.2	0.0	0.4
		Relative humidity (%)	38.6 ± 4.0	35.4	44.3
		Temperature (°C)	33.8 ± 0.4	33.4	34.1
Paste floor	6.2	Air velocity (m.s ⁻¹)	0.8 ± 0.7	0.0	2.0
		Relative humidity (%)	41.3 ± 3.1	36.8	47.5
		Temperature (°C)	32.8 ± 0.9	31.5	34.2
Tapping floor	6.5	Air velocity (m.s ⁻¹)	0.2 ± 0.2	0.0	0.6
		Relative humidity (%)	42.9 ± 4.4	31.4	48.6
		Temperature (°C)	32.5 ± 1.6	30.1	35.3

Table 2 shows the respirable- and inhalable dust concentration of the different groups, including the sulphur constituent of the dust. Sulphur was recorded on the dust sampled at all three the groups. The highest mean dust- and sulphur exposure, for both the respirable– and inhalable dust fractions, were recorded at the ceramic group. The mean respirable dust exposure was $8.24 \pm 11.83 \text{ mg.m}^{-3}$, and the corresponding sulphur exposure $0.18 \pm 0.25 \text{ mg.m}^{-3}$. The mean inhalable dust exposure was $46.66 \pm 46.08 \text{ mg.m}^{-3}$, and the corresponding sulphur exposure was $0.96 \pm 0.94 \text{ mg.m}^{-3}$. On the contrary, the tappers reported the lowest exposure to both dust and sulphur exposure, for the two fractions.

Table 2: Descriptive statistics of respirable and inhalable dust with the corresponding sulphur content for the tapping, paste loaders, and ceramic groups.

	Variable	n	Mean \pm Std. Dev (mg.m^{-3})	Minimum (mg.m^{-3})	Maximum (mg.m^{-3})
All samples	Respirable dust	42	3.12 ± 6.77	0.07	36.75
	Respirable dust's sulphur content	42	0.07 ± 0.15	0.01	0.74
	Inhalable dust	42	19.70 ± 29.14	0.78	126.78
	Inhalable dust's sulphur content	42	0.40 ± 0.59	0.005	2.74
	SO ₂	42	10.67 ± 13.74	0.29	59.58
Ceramics	Respirable dust	11	8.42 ± 11.83	0.07	36.75
	Respirable dust's sulphur content	11	0.18 ± 0.25	0.01	0.74
	Inhalable dust	11	46.66 ± 46.08	4.13	126.78
	Inhalable dust's sulphur content	11	0.96 ± 0.94	0.04	2.74
	SO ₂	11	20.01 ± 18.64	1.18	59.58
Paste Loaders	Respirable dust	16	1.96 ± 1.67	0.43	6.88
	Respirable dust's sulphur content	16	0.05 ± 0.06	0.01	0.23
	Inhalable dust	16	14.79 ± 10.58	2.33	36.33
	Inhalable dust's sulphur content	16	0.28 ± 0.19	0.02	0.63
	SO ₂	16	11.35 ± 12.52	1.15	49.02
Tappers	Respirable dust	15	0.47 ± 0.24	0.08	0.93
	Respirable dust's sulphur content	15	0.02 ± 0.01	0.01	0.03
	Inhalable dust	15	5.18 ± 5.15	0.78	21.38
	Inhalable dust's sulphur content	15	0.12 ± 0.12	0.01	0.49
	SO ₂	15	3.11 ± 2.57	0.29	9.54

Figure 2 illustrates the mean concentration of respirable dust, foam dust and the inhalable dust of the three different groups and for all the samples. Foam dust is the respirable dust subtracted from the inhalable dust. The figure also indicates the sulphur percentage that sulphur contributed to the respective fractions' concentration.

The sulphur percentage on the respirable dust is greater than the sulphur percentage on the inhalable dust. This is true for each of the groups as well as for all the samples. For all the samples, the mean percentage of sulphur present on inhalable dust was 2.20 % \pm 0.88 %, and for the respirable dust 3.14 % \pm 2.38 %. The tappers yielded the maximum percentage of sulphur for inhalable dust (4.84 %), as well as for respirable dust (12.44 %). The ceramic group yielded the highest exposure for respirable- and inhalable dust, with the lowest percentage sulphur. On the contrary, the tappers yielded the lowest dust exposure for the different fractions, with the highest sulphur percentage for each fraction. Overall, respirable dust yielded the largest sulphur percentage for all the groups.

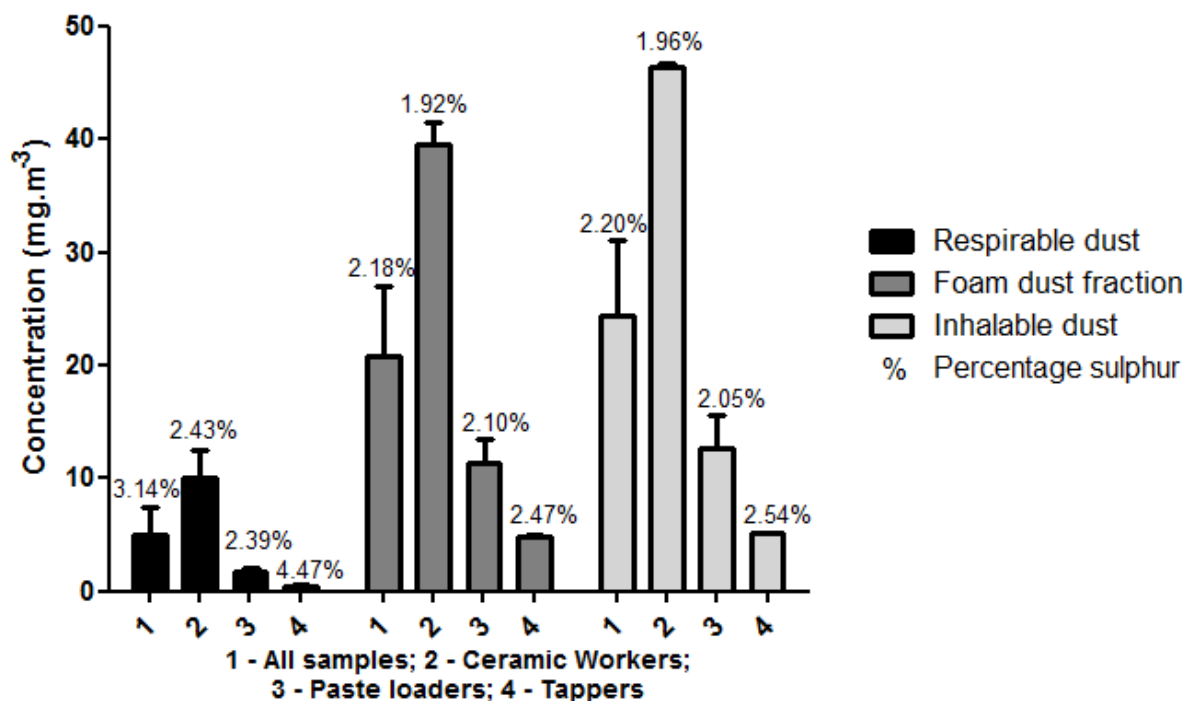


Figure 2: Comparison of respirable-, foam-, and inhalable dusts' sulphur percentage of the three different groups and all the samples.

Figure 3 illustrates the linear regression of transformed inhalable sulphur against transformed inhalable dust. Statistical significant correlations were obtained between: inhalable dust and –sulphur ($r = 0.94$; $p < 0.05$) illustrated in figure 3, respirable dust and -sulphur ($r = 0.82$; $p < 0.05$), and between foam dust and –sulphur ($r = 0.93$; $p < 0.05$). These strong correlations indicate that higher dust exposure will lead to higher sulphur exposure. Correlation values are used to indicate practical significant linear relationships between the two variables.

Here $r = 0.1$ indicates a small effects – no practically significant correlation;

$r = 0.3$ a medium effect – practically visible correlation and;

$r = 0.5$ a large effect – practically significant correlation (Field A, 2009).

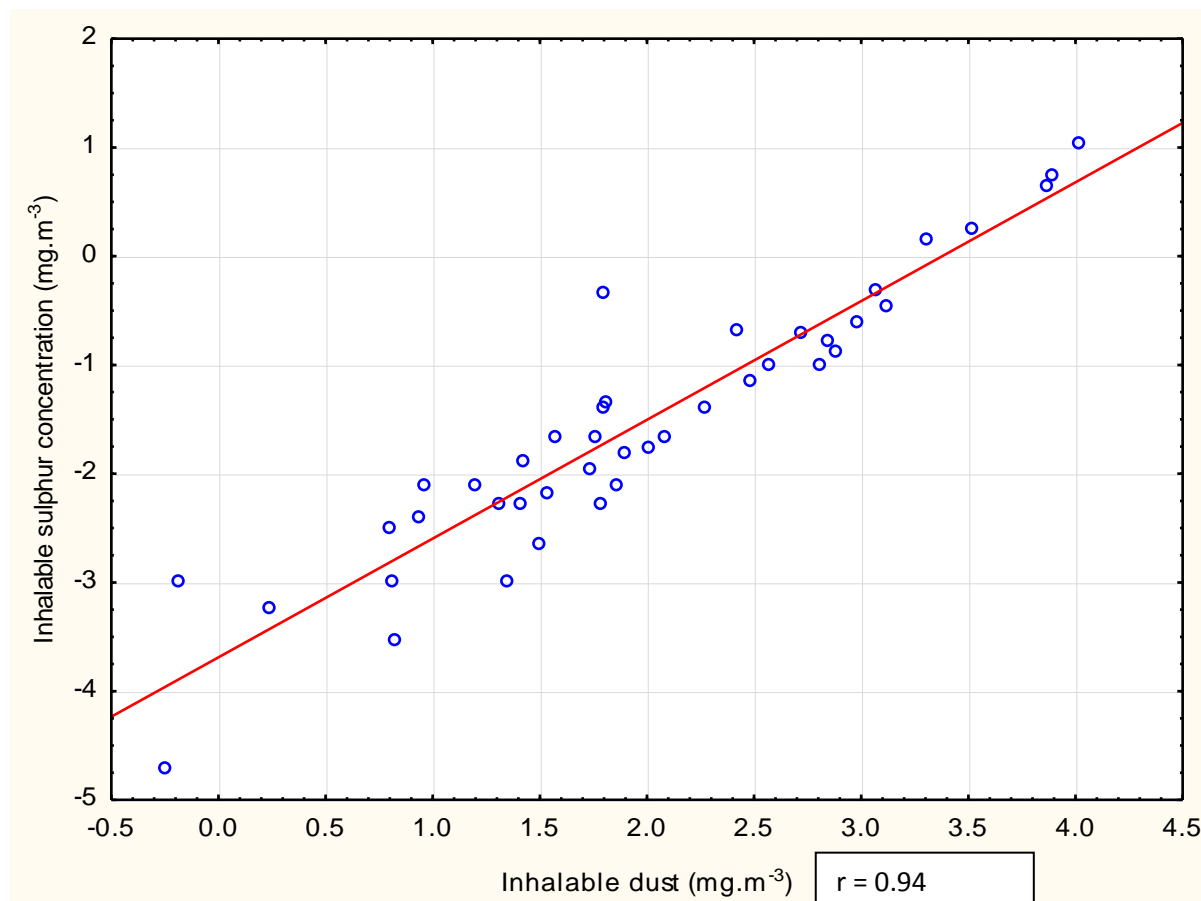


Figure 3: Linear regression between inhalable dust and inhalable sulphur.

Table 3 reports p-values as determined by one-way ANCOVA, to determine statistical significant differences between the sulphur mean percentages of respirable-, foam-, and inhalable dust fractions between the three groups, correcting for total dust. This was followed by multiple comparisons between pairs of groups, and p-values ≤ 0.05 were regarded as statistical significant (expressed in bold). A statistical significant difference between the tappers and paste loaders were obtained for the respirable sulphur percentage ($p = 0.04$).

Table 3: Statistical results of multiple comparisons of group means, for the sulphur percentage of respirable-, foam- and inhalable dust (p-values).

	Group	Tappers	Paste loaders	Ceramics
Respirable sulphur	Ceramics	0.09	1.00	-
	Paste loaders	0.04	-	1.00
	Tappers	-	0.04	0.09
Foam sulphur	Ceramics	0.34	0.88	-
	Paste loaders	0.51	-	0.88
	Tappers	-	0.51	0.34
Inhalable sulphur	Ceramics	0.27	0.97	-
	Paste loaders	0.28	-	0.97
	Tappers	-	0.28	0.27

Figure 4 illustrates the sulphur content of the different dust fractions, expressed as the percentage that sulphur contributed to the respective concentration. Respirable dust contains the largest sulphur percentage for all 3 groups and all the samples. Thus, the sulphur constitute of the smaller particles (respirable dust) is greater than the sulphur constitute of the larger particles (foam dust). A statistical significant difference between the respirable- and inhalable dust is indicated for the entire sampling group ($p = 0.04$) and for the tappers ($p = 0.03$).

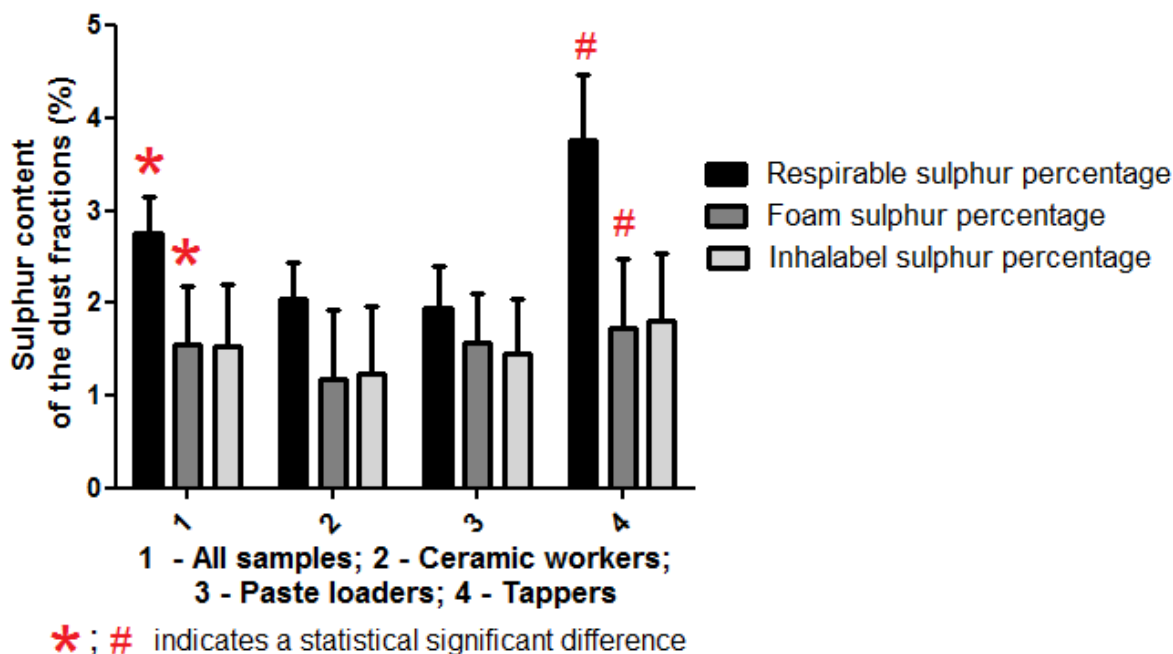


Figure 4: The sulphur content in each dust fraction, expressed as a percentage.

Table 4 indicates statistical significant difference, as determined by Wilcoxon matched pair tests, between the percentage respirable sulphur and the percentage foam sulphur. p -values ≤ 0.05 were regarded as statistical significant and are indicated in bold. A statistical significant difference was reported for the tappers group and the entire sampling group.

Table 4: Statistical significant difference between the percentage respirable sulphur and percentage foam sulphur.

Group	n	p - value
All samples	42	0.03
Ceramics	11	0.72
Paste Loaders	16	0.41
Tappers	15	0.04

Table 5 displays partial correlations between SO₂ and the sulphur fractions. The results illustrate the comparison between the different groups and all the samples. Included are the Box-Cox transformed means and standard deviation. The correlation (r) value is of importance. A meaningful correlation of 0.32 (medium effect) can be observed between the foam sulphur and SO₂ for the paste loaders. For the ceramic group, the correlation between respirable sulphur and SO₂ were r = 0.27 (medium effect). Statistical significant r- values (p-values ≤ 0.05) are indicated in bold.

Table 5: Partial correlations, corrected for total dust, between SO₂ and the sulphur on the respirable- and inhalable fraction, as well as the foam fraction, of Box-Cox transformed data.

Group	Variable	Means	Std. Dev.	r
All samples	SO ₂	1.71	1.25	-
	Respirable Sulphur	-5.99	2.79	0.14
	Foam Sulphur	-1.78	1.20	-0.002
	Inhalable Sulphur	-1.54	1.21	-0.04
Ceramics	SO ₂	2.50	1.26	-
	Respirable Sulphur	-4.75	3.66	0.27
	Foam Sulphur	-1.00	1.46	-0.47
	Inhalable Sulphur	-0.74	1.46	-0.39
Paste Loaders	SO ₂	2.03	0.95	-
	Respirable Sulphur	-5.69	2.48	0.19
	Foam Sulphur	-1.55	0.63	0.32
	Inhalable Sulphur	-1.34	0.83	-0.02
Tappers	SO ₂	0.77	0.970	-
	Respirable Sulphur	-7.23	1.87	< 0.01
	Foam Sulphur	-2.58	1.01	0.14
	Inhalable Sulphur	-2.34	0.91	0.15

Figure 5 depicts a typical data recording as measured by the Dräger Pac, a direct reading instrument for measuring SO₂ concentration. Note that the device measures concentration in parts per million (ppm). Ppm was converted to milligram per cubic metre (mg.m⁻³), as described in the methodology, to ensure comparable data between dust- and SO₂ exposure. This figure illustrates fluctuations of SO₂ that typically occurs in the furnace. Transient increases can be observed, with a maximum of 25.5 ppm (66.3 mg.m⁻³). The TWA for this recording is 1.89 ppm (4.9 mg.m⁻³), while the average is 2.51 ppm (6.5 mg.m⁻³).

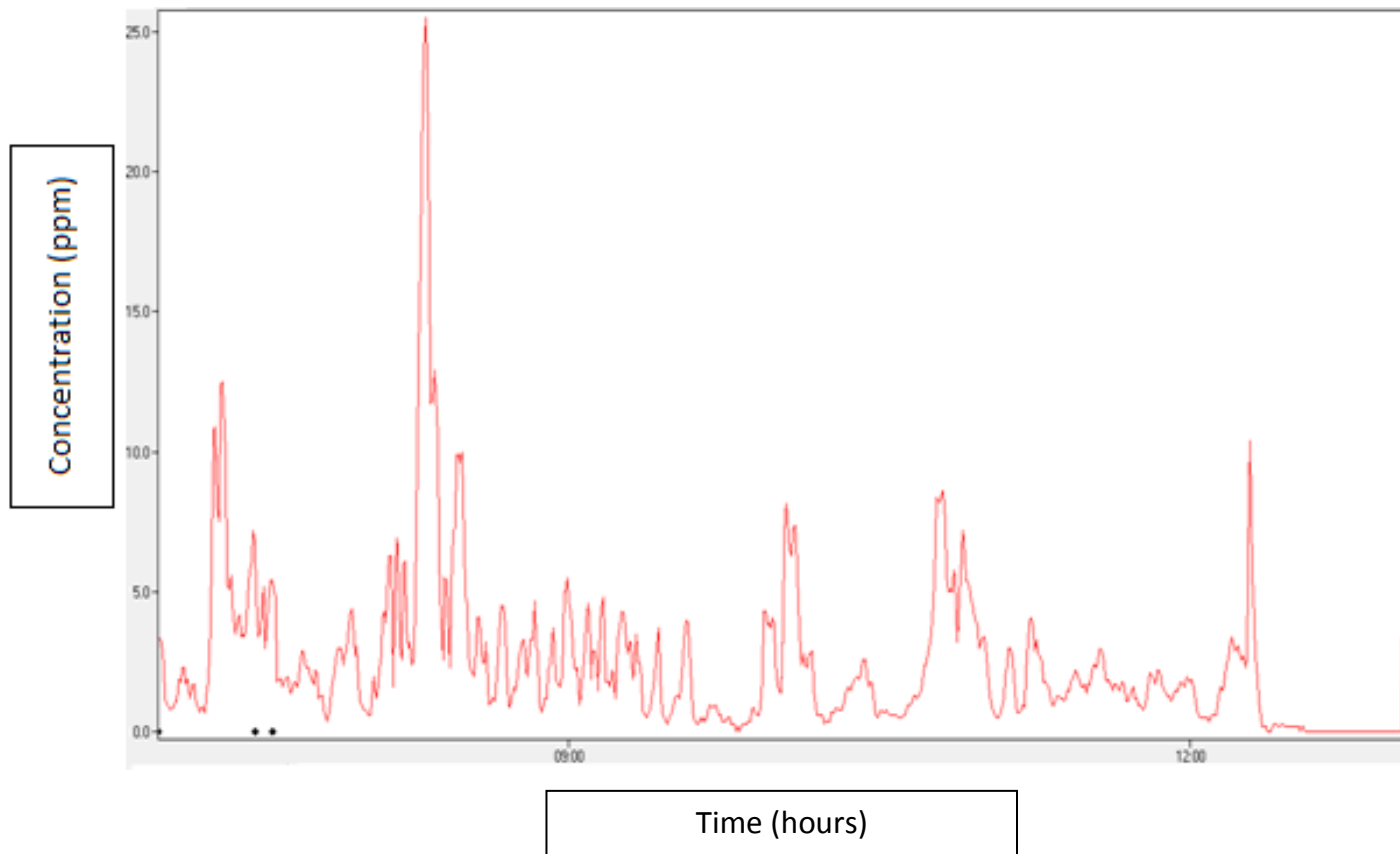


Figure 5: Typical SO₂ fluctuations in the furnace as measured by the Dräger Pac.

Table 6 illustrates that oxygen and carbon are the main contributors to the mass of the dust, 43.91 % and 32.73 % respectively. The contribution to weight, by metal known to catalyse the oxidation of SO₂, is silicone, 8.47 %, iron, 4.40 %, copper, 0.59 %. The weight percentage of sulphur is 1.00 %.

Table 6: Elemental composition and the contribution of each element to the weight of dust present in the smelter, as determined by microanalysis using an environmental scanning electron microscope.

Element	Percentage weight contribution (%)
Oxygen	43.91
Carbon	32.73
Silicone	8.47
Magnesium	5.29
Iron	4.40
Aluminium	1.26
Calcium	1.00
Sulphur	1.00
Copper	0.59
Chromium	0.51
Chlorine	0.45
Nickel	0.39

Discussion

The presence of sulphur on the dust fractions, and the influence of environmental factors on sulphur loading

From the data gathered, it is evident that sulphur is present on both respirable- and inhalable dust which implies an additional source of sulphur exposure via inspiration, additional to the known SO₂. Even though there currently is no occupation exposure limit (OEL) governing the fraction that sulphur may occupy in dust, there are OELs for sulphur containing chemical species such as H₂SO₄ (1 mg.m⁻³) and SO₂ (2 ppm or 5 mg.m⁻³) (MHS Act 29, 1996). Dusts' aerodynamic diameter plays a deterministic role in the deposition of the particles in the lungs. Inhalable dust can be inhaled by the nose or mouth, and is available for deposition in the respiratory tract. Accumulation of inhalable dust can occur in the sputum or mucus which can be coughed out or swallowed (Belle and Stanton, 2007). Swallowing permits the absorption of soluble chemical species adhered to dust in digestive system. Respirable dust can penetrate the lung alveoli (Belle and Stanton, 2007). Thus, the deposition of sulphur species in the body is determined by the aerodynamic diameter it adheres to.

The sulphur species present on the inspired dust will determine the health effect elicited. Exposure to sulphate containing aerosols have been implicated in increasing lung permeability, which entails augmented absorption of other chemical species or microbes that may be present on dust, and it has been associated with cardiopulmonary mortality (Prasad *et al.*, 1988; Brook *et al.*, 2010; Ostro *et al.*, 2011). Iron pyrite (FeS₂) can synthesise hydrogen peroxide and hydroxyl radicals in the presence of oxygenated solutions (Borda *et al.*, 2003; Schoonen *et al.*, 2010). Therefore, inhalation of dust in an environment containing iron pyrite potentiates the risk for mineral induced reactive oxygen species in exposed personnel (Fisher *et al.*, 2012).

Because of the small variance in the recorded environmental factors (table 1), it can be concluded that it did not play a major role in contributing to sulphur loading between the different floors. This is emphasised by the maximum and minimum mean temperature which only differs with 1.3 °C, and the

maximum and minimum mean relative humidity that differs with 4.3 %. Natural air flow in the smelter is restricted because of the structure's closed off eastern and western sides. This results in only northern and southern external winds affecting air velocities on the tapping floors, and to a lesser extent on the paste floor. The opposite occurs on the ceramic floor: external air flow is canalised from east to west as a result of open ends on these sides.

Difference in the sulphur component of the tappers, paste loaders and the ceramic workers

From table 2 and figure 2, it is apparent that the highest concentration of dust exposure was recorded on the ceramic floor, while the tappers yielded the lowest exposure to dust. The highest mean sulphur concentration was also recorded at the ceramic group, and the lowest mean sulphur concentration at the tappers. A statistical significant difference was reported for the respirable sulphur between the paste loaders and the tappers ($p = 0.04$; table 3). Overall, the tappers yielded the highest sulphur percentage for all the aerodynamic fractions, illustrated in figure 4. Due to a lack of knowledge regarding the chemical species present on the dust, it can only be speculated why greater sulphur loading occurred on the dust that the tappers were exposed to.

The paste- and ceramic floors are designated respirator areas. The high concentration of dust and SO_2 on the upper levels of the smelter, which include the paste- and the ceramic floor, can be explained by the stack effect. The stack effect is the result of the temperature differences on the different floors (table 1) that creates a temperature gradient (Walker, 2010). The consequence of the temperature gradient is the ascension of heated air, during which aerosols are vectored to upper levels, resulting in higher concentrations of dust and SO_2 on the paste- and ceramic's floor, when compared to the tapping floor.

Figure 2 illustrates the sulphur content of the three groups as a percentage of the dust concentration. This figure indicates that the dust sampled at the tappers had a greater sulphur component, expressed as a percentage, compared to the other two groups, even though it had the lowest concentration of sulphur contained in each dust fraction. In contrast, the ceramic group reported the highest concentration of dust and sulphur exposure, while the sulphur percentage was the lowest. Thus, sulphur contributed more to the dust concentration of the tappers, than the ceramic group. It is therefore reasonable to conclude that the ceramic group had a greater exposure to particulate sulphur, primarily because they had the greatest exposure to dust. Thus, higher dust concentration will lead to greater sulphur concentrations. This conclusion is further supported by figure 3 which illustrates a very strong correlation ($r = 0.94$) between inhalable dust and inhalable sulphur. This however, still does not give insight to the sulphur content of the dust, and consequently, the partial correlations were corrected for total dust, to mitigate this effect. Potential explanations for the sulphur content will follow subsequently.

Difference between the sulphur constitute on respirable and inhalable dust

All three groups reported that the sulphur component was greater for the respirable dust, than the foam dust, as indicated by table- and figure 4. The difference between these fractions were statistically significant for the tappers group ($p = 0.04$) and when considering all the samples ($p = 0.03$).

The surface area to volume ration plays an integral role in the interaction between gas phase and surface reactions (Teubner *et al.*, 1999). Furthermore, smaller particles are generally more toxic than larger particles of the same insoluble material, because more molecules are available for chemical interactions on its surface (Fahlman, 2011). Respirable dust, by definition, has a smaller aerodynamic diameter than foam dust (Belle and Stanton, 2007). Consequently, respirable dust of the same concentration as foam dust, has a larger surface area that is available for attachment of chemicals such as sulphur (Belle and Stanton, 2007; Fahlman, 2011). Therefore, it can be expected that the sulphur content of the smaller particles will be larger than that of the larger particles, and that the associated health risk is higher.

A fingerprint survey by Anglo Platinum (as cited by Steyn, 2005) at a platinum smelter, indicated that dust comprised amongst other constituents, of ~ 6 % iron, ~ 1 % copper and ~ 2 % sulphur. Table 6 indicates that dust sampled in the smelter does not contain PGM and therefore, the dust that escapes from the electrodes is not concentrate. This does not exclude the possibility of sulphur already being present on dust prior to being air suspended in the ambient atmosphere of the smelter, which will be explained subsequently. Results from the microanalysis (table 6) affirmed the presence of iron (4.40 %), copper (0.59 %) and additionally, silicone (8.47 %). Oxygen occupied 43.91 % of the total mass and 1 % sulphur was present on the dust. Considering the high prevalence of oxygen on the dust, it is reasonable to postulate that the metals are present as oxides. Fe_2O_3 , SiO_2 , and CuO are able to catalyse the oxidation of SO_2 (Vadjic *et al.*, 1986; Prasad and Rani, 1992). Therefore, if any of these metal oxides are present on the dust, catalytic oxidation of SO_2 on dust is possible under ideal circumstances.

A heat increase to 350 °C is sufficient to augment the oxidation of SO_2 to sulphate up to 100 %, when using Fe_2O_3 as a catalyst (Burger, 1993). When considering the conventional slag temperature is between 1500 and 1550 °C, it is therefore reasonable to postulate that a heat gradient can exist within the furnace that favours the synthesis of sulphate on dust that contains iron (Jacobs, 2006; Hundermark, 2011).

Regarding the pH values of the dust reported for the different floors (table 1), being 6.5, 6.2, and 4.5, it is unlikely that the homogeneous oxidation of SO_2 took place in an aqueous medium, while synthesis of sulphates were catalysed by iron(III). Iron(III)hydroxide bonds precipitates out of solution at pH > 4.0 (Burger, 1993). Even though Fe(III) cannot catalyze the oxidation in such alkaline conditions, colloidal Fe_2O_3 is capable of acting as a catalyst in an alkaline medium. Colloidal Fe_2O_3 can induce photocatalytic oxidation of S(IV) within the parameters of pH 1 – 7 (Faust, 1989). SiO_2 and CuO are also known catalyst for the oxidation of SO_2 (Vadjic *et al.*, 1986; Prasad and Rani, 1992). Therefore, if either Fe_2O_3 , SiO_2 , or CuO is present on dust, it is possible for sulphur loading to occur via heterogeneous oxidation of SO_2 .

Correlation between SO_2 exposure and particulate sulphur

Two correlations of medium effect were obtained between SO_2 exposure and particulate sulphur, as indicated in table 5. The sulphur recorded on the foam of the paste loaders ($r = 0.32$), and the respirable dust of the ceramic workers ($r = 0.27$) yielded significant correlations with SO_2 exposure. The use of $p \leq 0.05$ to indicated statistical significant values entails that there is 5 % probability to obtain a statistical significant value. Thus 1 in 20 values will be statistically significant. Considering this 5 % probability to obtain a statistical significant value, the occurrence of the paste loaders' foam sulphur and the ceramic workers' respirable sulphur may be explained.

A possible explanation for the lack of correlations may be that the data used for statistical analyses are the recorded mean values for each case, over a time period. The usage of mean values intrinsically makes the assumption that the mean concentration reflects similar exposure during the whole shift, but during a typical routine shift, the SO_2 concentration in the working areas may transiently increase numerous times. Figure 5 illustrates a typical recording made using the Dräger Pac. It is possible that the mean concentration does not reflect transient peak exposure(s). Correlations may lack when using such data to determine correlations, because the mean SO_2 concentration does not accurately reflect transient increases. Intermittent release of SO_2 in the furnace further burdens accurate correlations between SO_2 exposure and particulate sulphur as this entails that continuous interactions between the two pollutants do not occur because they are not simultaneously present. Interaction between the catalyst containing dust and SO_2 is essential for the oxidation of SO_2 (Vadjic *et al.*, 1986; Prasad and Rani, 1992). Thus, if interaction between the two pollutants is absent, sulphur loading cannot occur.

The mechanism for SO₂ to permanently adhere to particulate dust may be time taxing. Thus, SO₂ needs a longer time to adhere to dust. Faust (1989) reports that at lower light intensities, the oxidation of S(IV) increases with time when the reaction is photocatalysed. Sakurai *et al.* (1998) made a similar report, and states that the amount of SO₂ absorbed to distilled water increased with time. The reaction rate of heterogeneous reaction is dependent on the surface area, absorption and desorption of the gas, and the reaction on the surface (Ruggeri, 2011).

A conclusion that may be derived is that the monitored SO₂ does not immediately affect the sulphur component of the dust that was sampled simultaneously. Furthermore, it is possible that particulate dust has a limited capacity to accommodate sulphur loading. Thus, once all the available active sites have been occupied, the ambient SO₂ concentrations will be of insignificant importance.

It is also possible to explain the lack of correlation between particulate sulphur and SO₂ if sulphur loading does not occur in the ambient air of the smelter, but rather within the furnace itself. This would imply that the sulphur present on the dust does not originate from the ambient SO₂, rather sulphur is already present on the dust prior to being introduced to the atmosphere of the smelter. Consequently, ambient SO₂ concentrations will have little or no significant effect on the amount of sulphur recorded on dust fractions. The chemical constitute of the dust plays an important role in determining the mechanism of sulphur loading. As stated earlier, dust in the smelter contains both iron and sulphur. For iron to act as a catalyst for the oxidation of SO₂, it must either be in ion form or Fe₂O₃ (Faust, 1989; Burger, 1993). If present as FeS₂ (iron pyrite), the iron cannot catalyse the oxidation of SO₂, but will still contribute to the recorded sulphur content of the dust.

Conclusion

The sulphur content on dust present in the furnace of a platinum smelter has been quantified. Because there are currently no OEL governing the fraction that sulphur may occupy in dust, and consequently there is no value to compare these exposures to, the magnitudes of the associated health risk to exposed workers are still undefined in the smelter. The associated health risk is determined by the sulphur species present, as well as onto which aerodynamic fraction sulphur adheres. Respirable dust contained the largest sulphur component, and can be considered a greater risk than the foam dust, concerning the sulphur component, regardless of the origin of the particulate sulphur. Furthermore, dust with a smaller aerodynamic diameter (respirable dust) contained more sulphur than dust with a larger aerodynamic diameter (foam dust).

It is possible for sulphur loading to occur via the oxidation of SO₂ on respirable- and inhalable dust when considering the high temperatures in the furnace, the presence of iron, silicone and copper on dust, and the high relative humidity. Thus, conditions within the furnace may exist which favours the synthesis of sulphates on dust via the oxidation of SO₂. The most probable explanation is that sulphur loading occurs within the furnace, before the dust escapes through the electrodes. It is also possible that sulphur is intrinsic to the dust as it escapes via the electrodes, in the form of metal sulphide for example FeS₂. More insight is needed about the chemical species on the dust, as well as the sulphur species present, to conclude with certainty whether sulphur loading did occur, or whether the sulphur is intrinsic to the dust.

Even though the dust on the tapping floor contained a larger percentage of sulphur, workers operating on the upper levels of the furnace have a greater risk to be exposed to a larger quantity of particulate sulphur because of the stack effect.

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CHAPTER 4

CONCLUDING CHAPTER

4.1 Further Discussion and Final Conclusion

It is possible for sulphur loading to occur on dust particles in a platinum smelter, and consequently, exposure to particulate sulphur is possible. High concentrations of sulphur can occur on dust as a result of sulphur loading under ideal circumstance. Because sulphur species have to adhere to dust, occupational exposure to particulate sulphur is mainly determined by the amount of dust workers are exposed to. This is affirmed by the strong correlations between dust and sulphur exposure for all the aerodynamic fractions. There were no meaningful correlations between personal SO₂ exposure and the sulphur content on the different dust fractions. The absence of a correlation between SO₂ and particulate sulphur exposure suggests that the oxidation of SO₂ does not occur in the smelter's ambient air, but rather in the furnace before the dust escapes via the electrodes. Furthermore, it is also possible that the particulate sulphur originates from metal sulphides opposed to the oxidation of SO₂. Sulphur loading occurs to a greater magnitude on respirable dust than foam dust. This phenomena can be ascribed to the increased surface area of smaller particles (respirable dust) when compared to the same mass of larger particles (foam dust) (Teubner *et al.*, 1999; Belle and Stanton, 2007). Increased surface area results in more molecules available for chemical reaction on the dusts' surface (Falman, 2011).

4.1.1 Addressing of Hypothesis

As previously stated, there were no meaningful correlations obtained between SO₂ and particulate sulphur exposure. Consequently, hypothesis 1, that there will be a positive correlation between the recorded SO₂ exposure and the sulphur content of the dust is rejected.

Because of the strong positive correlation between particulate sulphur exposure and dust exposure, hypothesis 2 is accepted: there is more exposure to particulate sulphur on the upper levels of the smelter.

Hypothesis 3, postulating that respirable dust will have greater sulphur loading than inhalable dust is accepted. The sulphur content on respirable dust was significantly more than the sulphur content on the foam dust, therefore, sulphur loading was greater on respirable dust than the foam dust.

4.1.2 Health Effects

Although this study succeeded in quantifying the sulphur content of respirable- and inhalable dust in a platinum smelter, it is inconclusive in identifying the primary contributor to particulate sulphur. Because the form of sulphur on the dust is unknown, the risk associated with exposure to sulphur containing dust is undefined. The contribution to particulate sulphur on dust, by means of SO₂ oxidation and sulphur containing molecules (e.g. FeS₂), will determine the associated health risks. Exposure to particulate sulphate has been associated with cardiopulmonary and –vascular diseases, while exposure to sulphide containing particles, e.g. FeS₂ has been implicated in promoting reactive oxygen species formation (Brook *et al.*, 2010; Ostro *et al.*, 2011; Fisher *et al.*, 2012). Thus, to comprehend the full extent of occupational exposure to sulphur containing dust in the smelter, the main contributor to particulate sulphur must be identified.

The interpretation of the associated health risk is further burdened because there is currently no OEL specifically governing the sulphur component of dust. There is an OEL for iron salts (1 mg.m⁻³), which will consequently include FeS₂, but is not specific to the sulphide component (MHS Act 29, 1996). The most relevant OEL addressing respirable particulate sulphates governs barium sulphate exposure (2 mg.m⁻³) (MHS Act 29, 1996).

SO₂ can be the precursor for the formation of H₂SO₄ when SO₂ comes into contact with mucous membranes or perspiration (Komarnisky *et al.*, 2003). The OEL ascribed to H₂SO₄ exposure is 1 mg.m⁻³ (MHS Act 29, 1996). Aside from the severe irritant effect H₂SO₄ has on exposed areas, it also depresses

pulmonary particle clearance (Amdur, 1989; Komarnisky *et al.*, 2003). The depression of pulmonary clearance may exacerbate the detrimental effects caused by the inhaled sulphurous species as it would increase the residency on the inhaled particles in the lungs.

Images of dust taken by means of electron microscopy

Figure 1 illustrates electron microscopy photos of dust samples taken in the smelter. Although these images do not give insight in the chemical composition of the dust, they do give insight to the dust's morphology. From these images it is clear that the dust particles have a large surface area available for other particles to adhere to. These images clearly depict that the dust is a conglomerate of solid particles, with smaller solid fragments present on the dust. Dislodging of these smaller fragments, especially after inhalation, could have further deleterious health effects.

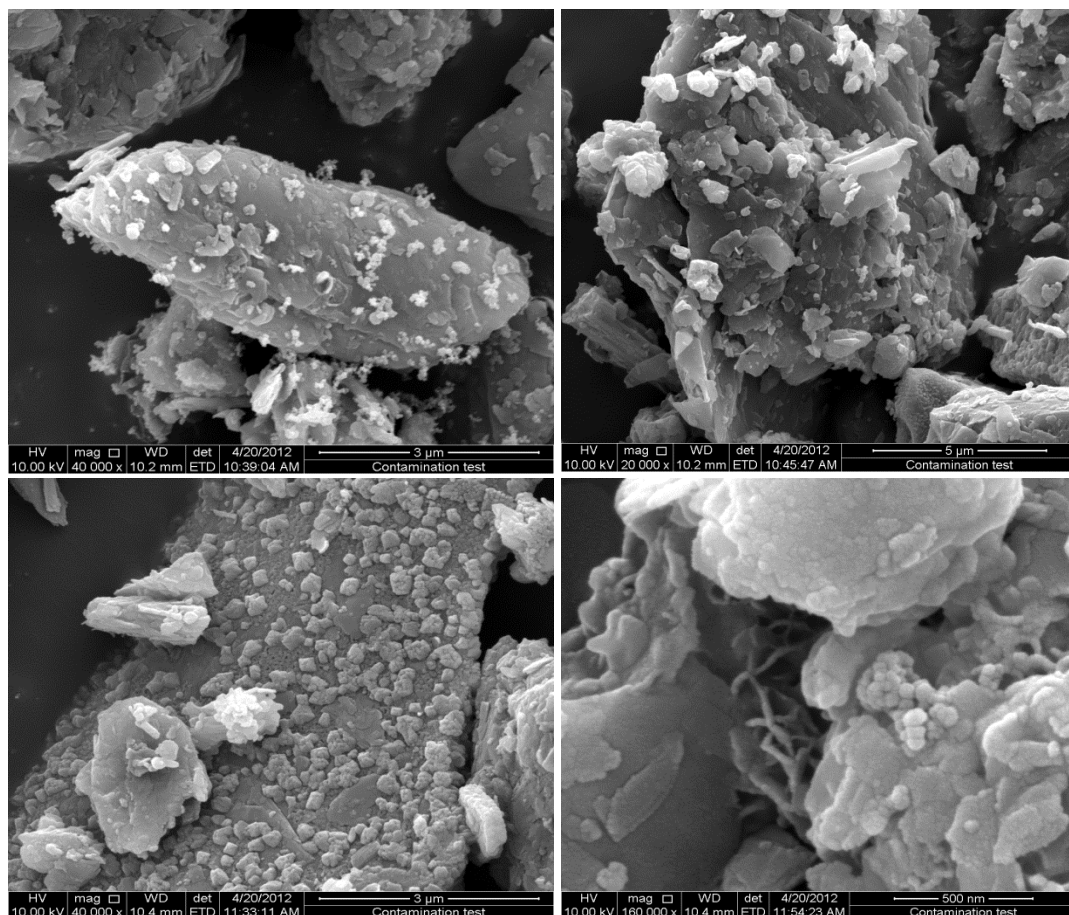


Figure 1: Photos taken of dust samples by means of electron microscopy.

4.1.3 Stack Effect

Measurements of air velocities recorded vertically over the stairs on the paste floor indicated that at times, air was transported to the upper levels of the smelter at an average velocity of $1.8 \text{ m}\cdot\text{s}^{-1}$. This is relatively high considering the average horizontal air flow on this floor was $0.8 \text{ m}\cdot\text{s}^{-1}$. It is this ascending air that transports pollutants to the upper floors of the smelter, resulting in high ambient concentrations and consequently high exposures on upper floors. Increased ventilation, either natural or mechanical, can combat these high ambient concentrations. Regarding natural ventilation, the prevailing direction of external air flow and the air velocity will greatly affect the effectiveness of these measures. The prevailing diurnal airflow in the area where the smelter is localised is north-western. The paste and tapping floors canalise northern or southern winds due to openings on these sides. In contrast, the ceramic floor is open on the eastern and western side, and is affected by external winds moving in this direction. Thus, when external airflow is north-western, it is possible for natural ventilation to occur on

both the paste floor and the ceramic floor, which are the high risk areas. However, if this oblique angle of external airflow is absent, natural ventilation cannot occur on both the high risk floors. Natural ventilation is not consistent and the implementation of mechanical ventilation by means of fans can supplement natural ventilation.

4.1.4 Challenges in This Study

Data gathering was burdened by numerous spoiled samples, mainly due to the prevalence of loss of the foam insert of the IOM sampler. It is difficult to identify the cause of this problem as it has not been reported previously. It is possible that the foam inserts were lost due to tampering, or due to accidental removal. For example, tappers have to wear a tapping suit to protect them against thermal stress. It is possible that foam inserts were lost during donning and doffing of these garments, or under similar mechanical friction, resulting in the foam insert being pulled from the IOM sampler. Considering that the foam insert is under negative pressure and there is no literature that reports similar problems when using the IOM sampler, it is unlikely that the foam insert were lost due to gravimetric pull. Regarding the high prevalence of lost foam inserts, it is not recommend using the IOM sampler with a foam insert to sample dual dust fractions in environments where workers have to wear full body protection garments.

Because simultaneous monitoring was conducted to investigate the correlation between particulate sulphur and SO₂ exposure, an error on either one of the sampling techniques resulted in spoiled samples for both the dust and SO₂ sampling. Loss of the foam inserts rendered numerous samples useless. Tampering with the Dräger Pac, by switching it off, also resulted in spoiled samples. All spoiled samples had to be recaptured.

Personal sampling was conducted on three different groups of workers, each representing a related floor, which burdens establishing the effect that environmental factors have on sulphur loading. The use of area sampling may yield more insightful data than the personal sampling, as this eliminates the influence that workers' routines may have on data. Also, environmental factors become more relevant, because the sampling media is only exposed to recorded environmental values. For example, during a routine shift, a paste loader may leave the paste floor for a time period to attend other matters. During this time, the worker's exposure to the two pollutants and the environmental factors may differ from the exposure on the paste floor. Although personal sampling does reflect the workers' exposure, it does not accurately reflect concentrations present on the paste floors, and makes it difficult to accurately compare sulphur loading on the different floors.

A lack of knowledge of the form of sulphur present on the dust left a void in the associated health risk, as well as the mechanism of sulphur loading.

4.1.5 Future Investigations

Future investigations of sulphur loading on dust particles in a smelter may be improved by approaching the following aspects differently:

It is recommended to use a larger subject group. The small number of samples that were taken per group limited the results as well as the statistical analysis.

To further investigate the sulphur loading in a smelter, it must be established where sulphur loading occurs: does it occur in the ambient air of the smelter, or does it occur within the furnace prior to being introduced into air suspension? Taking dust samples close to where dust leaks from the electrodes can aid in determining whether sulphur loading occurs within the furnace or within the atmosphere of the smelter. It has been established that the dust escaping from the electrodes is not concentrated fed to the furnace, as the dust does not contain PGM. Therefore, if dust already contains particulate sulphur as it escapes the electrodes, a strong probability exists that the oxidation of SO₂ occurs within the furnace,

before being subjected to the ambient air of the smelter, or the sulphur is present as metal sulphide e.g. FeS_2 . Such a finding will explain the lack of a correlation between SO_2 and particulate sulphur exposure.

Finally, knowledge of the chemical composition of the dust will elucidate the mechanism of sulphur loading and the associated health risk. It is important to determine in which form the iron, silicon and copper are present on the dust. CuO , SiO_2 and Fe_2O_3 can act as a catalyst for the oxidation of SO_2 , which synthesises sulphate species (Vadjic *et al.*, 1986; Prasad and Rani, 1992; Burger, 1993). If the metals are present are bound to sulphides (e.g. FeS_2), they cannot catalyse the oxidation of SO_2 .

4.2 Occupational Hygiene Recommendation

4.2.1 Engineering control

The implementation of extraction ducts is recommended to remove air suspended dust particles and SO_2 .

Installation of extraction fans close to the origin of the pollutants will reduce the high concentrations in the ambient air. In addition, the installation of a cyclone will enable the separation of the gaseous SO_2 and dust particles. SO_2 can be discharged in the existing SO_2 ducts that are used in the production of H_2SO_4 , while the dust is recycled. Because the dust contains sulphur, it can be recycled as a sulphur source to the SCF.

Increased ventilation by means of fans can also aid in reducing the high concentrations of aerosol pollutants on the different floors. This will however reduce the recycling of SO_2 and dust as well as pollute the area outside the furnace. Therefore, this will merely transpose the problem rather than solve it.

4.2.2 Administrative control

Because the tapping of matte and slag results in the release of high concentrations of SO_2 , which is transported to the upper floors, it is recommend to halt work on the upper floors of the smelter while tapping is in progress if reasonably practical.

4.2.3 Respiratory protection (PPE)

The use of respirators equipped with ABE 1 canisters to remove SO_2 from inspired air, in conjunction with a particulate filter, as currently implemented by the smelter, can be effective in protecting workers against exposure to SO_2 and particulate matter. The 3M® P2 filter currently used to protect against dust exposure adheres to the requirements of NIOSH N95 specifications (NIOSH, 2011). The NIOSH N95 standards states that filters must be 95 % efficient when tested against $\sim 0.3 \mu\text{m}$ sodium chloride aerosol at a flow rate of $85 \text{ L}\cdot\text{min}^{-1}$ (NIOSH, 2011). Therefore, this will protect against respirable and inhalable dust, while the ABE 1 canister protects against SO_2 exposure.

4.2 References

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