NORTH-WEST UNIVERSITY
YUNIBESITI YA BOKONE-BOPHIRIMA
NOORDWES-UNIVERSITEIT

Exposure of workers to ammonia and oxides of nitrogen from blasting fumes in an underground mining setup

Daniel Christiaan Cronje B.Sc. (Hons.)

Mini-dissertation submitted in partial fulfilment of the requirements for the degree *Magister Scientiae* in Occupational Hygiene at the Potchefstroom campus of the North-West University.

Supervisor:	Mr. M. N. van Aarde
Co-supervisor:	Ms. A. Franken

November 2010

Acknowledgements

I dedicate this Mini-dissertation to the following people. Without them, this would never have been possible for me:

- My Heavenly father for his continuous blessings with this project, I could never have done this without him.

- I would like to thank Mr. M. N. van Aarde, my supervisor and Ms. A. Franken, my co-supervisor for their direction, assistance, and guidance. In particular, Ms. A. Franken's recommendations and suggestions have been invaluable for this project.

- I also wish to thank my family and friends for every positive word of advice and encouragement.

- Thanks are also due to Dr. C. J. Badenhorst and Mr. J. J. van Staden for providing me with the necessary resources to complete my project. Special thanks should be given to Ms. B. Winter, for getting me to the right people at the right time and helping me to get the full experience of working in an underground mine.

- My gratitude to the senior management of the mine under study, who supported this study, including Themba, Freddie and Gavin for their assistance in the collection of data.

- Mr. W. Wepener for the analysis of the samples and Prof. J. du Plessis for the statistical analysis and Ms. H. Pienaar for language editing.

- Finally, words alone cannot express the thanks I owe to the underground mine workers who participated in the study, because without them there would have been no study at all.

TABLE OF CONTENTS

Author's contribution

The following table depicts the contribution of each of the researchers involved in this study.

Name	Contribution
Mr. D. C. Cronje B.Sc. (Hons.)	Responsible for: Literature searches, research proposal, personal sampling, statistical analysis of data. Interpretation of results. Planning, design and writing of the article.
Mr. M. N. van Aarde M.Sc. (Occupational Hygienist, physiologist)	Supervisor Supervised with the designing and planning of the Mini-dissertation, approval of protocol, reviewing the Mini-dissertation and interpretation of results.
Ms. A. Franken M.Sc. (Occupational Hygiene Technologist, physiologist)	Co-supervisor Co-supervised the initial planning and design of research proposal and Mini-dissertation. Reviewing of the documentation of the study.

The following is a statement of the above named researchers confirming their individual roles in the study:

I declare that I have approved the article and that my role in the study as indicated above is representative of my actual contribution and that I hereby give my consent that it may be published as part of the M.Sc. Mini-dissertation of Mr. D. C. Cronje.

Mr. M. N. van Aarde

Ms. A. Franken

List of abbreviations

ACGIH	American Conference of Governmental Industrial Hygienists
AIHA	American Industrial Hygiene Association
ANFO	Ammonium Nitrate Fuel Oil
BIC	Bushveld Indigenous Complex
CL	Control Limit
C_nH_{2n+2}	Fuel oil
CO_2	Carbon dioxide
COPD	Chronic obstructive pulmonary disease
DME	Department of Minerals and Energy
DOT	Department of Transportation
FEV1	Forced expiratory volume in one second
H_2O	Water
HONO	Nitrous acid
IDLH	Immediately Dangerous to Life or Health
mg/m^3	Milligram per cubic meter
MSDS	Material Safety Data Sheet
N_2	Nitrogen
NH_3	Ammonia
NH_4NO_3	Ammonium nitrate
NIOSH	National Institute for Occupational Safety and Health
NO	Nitric oxide
NO_2	Nitrogen dioxide
NO_x	Oxides of nitrogen
O_3	Ozone
OEL – CL	Occupational Exposure Limit – Control Limit
OEL-TWA	Occupational Exposure Limit - Time Weighted Average
OSHA	Occupational Safety and Health Administration
PEL	Permissible Exposure Limits
PGM	Platinum Group Metals
PPE	Personal protective equipment
ppm	parts per million
ppb	parts per billion
REL	Recommended Exposure Limits
RL	Recommended Limit
SAIOH	Southern African Institute of Occupational Hygiene
SD	Standard deviation

SO_2	Sulphur dioxide
STEL	Short Term Exposure Limit
TBG	Tydbeswaarde Gemiddelde
TEA	Triethanolamine-treated
TLV	Threshold Limit Value
TWA	Time Weighted Average

Preface

The researcher would like to make the following statement. The measurements for the present study were taken during the charge up process when explosives are being loaded into the boreholes. Although blasting did take place 12 hours previously, the area was first ventilated for a specified period of time as stipulated by legislation and then cleaned up by night shift mine workers. Samples were then taken from underground mine workers who were responsible for loading the boreholes with explosives. Although there is a reference to blasting fumes in the title, it is actually a reference to the whole blasting process including the charge up process. The term ammonia vapours will be used to describe the vapours released from the ANFO during the charge up process, while the term blasting fumes will be used to describe the detonation products produced after blasting took place. These results only indicate the exposure of a group of underground mine workers to explosives during the charge up process. Legislation dictates that no person may enter an area for a certain period where blasting took place. Due to work related limitations it was decided to determine the exposure of underground mine workers during the handling, transportation and charge up of explosives. Recommendations regarding this limitation will be discussed in Chapter 4 and Chapter 5.

This Mini-dissertation is presented for the partial completion of the M.Sc. degree in Occupational Hygiene at the Potchefstroom campus of the North-West University. This Mini-dissertation will be presented in article format for submission for publication to the accredited journal, Occupational Health Southern Africa. References are inserted as superscript numbers in text and reference as set out in Vancouver style.

This Mini-dissertation has five chapters, each of which focuses on different aspects of the exposure of workers to oxides of nitrogen (NO_x) and ammonia (NH_3) from blasting fumes in an underground mining setup. Chapter 1 gives a general introduction of the project. Chapter 2 gives a detailed literature background. Chapter 3 is a manuscript in the form of a research article. In Chapter 4 a proposed method for measuring blasting fumes are represented. Further discussions and recommendations are presented in the final chapter, Chapter 5.

The primary emphasis of this Mini-dissertation will be on the exposure of workers in an underground mining setup to NO_x and NH_3 from blasting fumes and ANFO. The Mine Health and Safety Regulations of the Mine Health and Safety Act (Act No. 29 of 1996) will also be examined and the exposure level of each mine worker will be compared to the Occupational Exposure Limits (OELs) published in regulation 22.9(2)(a) - occupational exposure limits for airborne pollutants.

Abstract

English Title: Exposure of workers to ammonia and oxides of nitrogen from blasting fumes in an underground mining setup

There is limited information available on the exposure of workers to NO_x and NH_3 from blasting fumes in the underground mining setup. This study is therefore motivated to improve the working conditions of underground mine workers handling these explosives, thus minimizing their potential exposure to NO_x and NH_3. Only a few epidemiological studies are available addressing the cumulative exposure of underground mine workers to blasting fumes, as well as the incidents of so-called gassing cases, although such cases do occur on a regular basis in an underground mining setup. Underground mine workers undertaking handling, transportation and charge up of explosives are potentially exposed to blasting fumes on a daily basis and cumulative exposure is therefore a major risk factor and could lead to serious health effects.

The Mine Health and Safety Regulations of the Mine Health and Safety Act (Act No. 29 of 1996) has recommended limits for the components of blasting fumes, but there is an absence of a limit specifically set for blasting fumes as a single gas exposure. In blasting fumes there are mixtures of gases that can cause respiratory and systemic health effects at much lower levels. To determine the exposure of underground mine workers to NO_x and NH_3 from blasting fumes and ANFO, samples were taken for a period of three hours and then time weighted to an 8-hour time weighted average (TWA) and compared to existing standards.

Active sampling and passive diffusive sampling were conducted to determine the difference of occupational exposure levels to NO_x and NH_3 among underground mine workers and surface workers. Samples were taken 12 hours after the previous blast due to work related limitations making it impossible to sample night shift workers.

Active sampling for a duration of 180 minutes, time weighted to an 8-hour exposure, indicated that occupational exposure to blasting fumes of underground mine workers responsible for charge up did not exceed the OELs of the Regulations of the Mine Health and Safety Act (Act No. 29 of 1996). Passive diffusive sampling for a duration of 180 minutes, time weighted to an 8-hour exposure, indicated that occupational exposure to blasting fumes of three underground mine workers responsible for charge did exceed the OELs of the Regulations of the Mine Health and Safety Act (Act No. 29 of 1996).. There was a significant positive correlation between personal exposures to NH_3 between the two measurement methods. There was a positive, insignificant correlation, as well as a strong agreement between personal exposures to nitrogen dioxide (NO_2). This correlation proved that any of these two approved conventional

measurement methodologies could be used to determine the exposure of underground mine workers to NH_3 or NO_2.

Limitations of the study as well as recommendations for future studies are also presented in Chapter 5.

This study however does not exclude the effect of cumulative exposure to blasting fumes over an extended period of time. Short term exposure is also a major concern when working with toxic fumes and should be determined in future studies.

Opsomming

Afrikaanse titel: Blootstelling van werkers aan ammoniak en oksiede van stikstof vanaf plofstofdampe in 'n ondergrondse mynopset.

Daar is beperkte inligting oor die blootstelling van werkers aan oksiede van stikstof (NO_x) en ammoniak (NH_3) vanaf plofstofdampe in die ondergrondse mynopset. Hierdie studie is om hierdie rede gemotiveer om die werkstoestande van ondergrondse mynwerkers wat verantwoordelik is vir die hantering van plofstowwe te verbeter en om hul potensiële blootstelling aan NO_x en NH_3 te verminder. Daar is egter min epidemiologiese studies beskikbaar wat die kumulatiwe blootstelling van ondergrondse mynwerkers aan plofstofdampe aanspreek, sowel as die insidente van sogenaamde vergassingsgevalle, alhoewel sodanige gevalle wel voorkom in 'n gewone ondergrondse mynopset. Ondergrondse mynwerkers wat verantwoordelik is vir die hantering, transportasie en laai van plofstof in boorgate word potensieel blootgestel aan plofstofdampe op 'n daagliks basis en kumulatiewe blootstelling is om hierdie rede 'n hoof risiko faktor en kan lei tot ernstige nadelige gesondheidseffekte.

Die Regulasies van die Wet op Gesondheid en Veiligheid in Myne (Wet No. 29 van 1996) het aanbevole drempels vir die komponente van plofstofdampe, maar daar is 'n afwesigheid van spesifieke beroepsblootstellingsdrempels vir plofstofdampe as 'n enkele gas blootstelling. Plofstofdampe bestaan uit ’n mengsel van gasse wat kan lei tot respiratoriese en sistemiese gesondheidseffekte by veel laer vlakke. Om die blootstelling van ondergrondse mynwerkers aan NO_x en NH_3 van plofstofdampe te bepaal, was monsters vir 'n periode van drie ure geneem en dan tydbeswaar tot 'n 8-uur tydbeswaarde gemiddelde (TBG) en vergelyk met bestaande standaarde.

Aktiewe monsterneming en passiewe diffusie monsterneming was uitgevoer om die verskil in beroepsblootstellingsvlakke aan NO_x en NH_3 tussen ondergrondse mynwerkers en bogrondse werkers te bepaal. Monsters was 12 uur na die vorige skietlading geneem, omdat werksverwante beperkinge dit onuitvoerbaar gemaak het om aandskof werkers te moniteer.

Aktiewe monsterneming vir’n tydperk van 180 minute, tydbesaar na ‘n 8-uur blootstelling, het aangedui dat beroepsblootstelling aan plofstofdampe van ondergrondse mynwerkers wat verantwoordelik is vir die laai van plofstof in boorgate, nie die beroepsblootstellingsdrempels van die Regulasies van die Wet op Gesondheid en Veiligheid in Myne (Wet No. 29 van 1996) oorskry het nie. Passiewe monsterneming vir ’n tydperk van 180 minute, tydbesaar na ‘n 8-uur blootstelling, het aangedui dat beroepsblootstelling aan plofstofdampe van drie ondergrondse mynwerkers wat verantwoordelik is vir die laai van plofstof in boorgate die beroepsblootstellingsdrempels van die Regulasies van die Wet op Gesondheid en Veiligheid in

Myne (Wet No. 29 van 1996) oorskry het. Daar was 'n beduidende positiewe korrelasie tussen persoonlike blootstelling aan NH_3 tussen die twee meet metodes. Daar was 'n positiewe, nie beduidend korrelasie, asook ‘n sterk ooreenkoms tussen persoonlike blootstelling aan NO_2. Hierdie korrelasie bewys dat enige van hierdie twee goedgekeurde konvensionele meetmetodes gebruik kan word om die blootstelling van ondergrondse mynwerkers aan NH_3 of NO_2 te bepaal.

Die beperkinge van die studie, asook aanbevelings vir toekomstige studies word ook in Hoofstuk 5 bespreek.

Hierdie studie sluit nie die effek van kumulatiewe blootstelling aan plofstofdampe oor 'n uitgebreide periode uit nie. Korttermynblootstelling is 'n hoof bekommernis wanneer daar met toksiese dampe gewerk word en behoort in toekomstige studies bepaal te word.

CHAPTER 1

GENERAL INTRODUCTION

GENERAL INTRODUCTION

1. Introduction

Blasting operations in an underground mine produce both toxic and non-toxic gaseous products; the toxic products being mainly NO_x and NH_3.[1,2] The ideal gaseous detonation products of explosives should consist of water (H_2O), carbon dioxide (CO_2) and nitrogen (N_2), but this is not possible due to the fact that detonation of explosives in a blasting operation also produces nitrogen dioxide (NO_2), nitric oxide (NO), ammonia (NH_3) and carbon monoxide(CO) that is toxic to the human body.[1,3] The exposure of workers to CO produced as a by-product during blasting operations were not monitored in the present study due to limited availability and practicality of sampling equipment as discussed in Chapter 4 and Chapter 5. There are limited occupational exposure data available on the incidents of so-called “gassing cases”, i.e. excessive exposure to gasses associated with the use of explosives in an underground mining setup, although such cases do occur on a regular basis in an underground mining setup.

Underground mine workers handling explosives are potentially exposed to blasting fumes on a daily basis and cumulative exposure is therefore a major risk factor for impairing their lung function.[4] Exposure to blasting fumes may also cause nasal mucosal swelling and increased levels of exhaled NO, indicating signs of upper and lower airway inflammation.[5]

The Mine Health and Safety Act (Act No. 29 of 1996) states that the employer of every active mine must provide, as far as reasonably practical, conditions for safe operation and a healthy working environment in such a way that employees can perform their work without endangering the health and safety of themselves or any other person. Occupational hygiene measurements must also be conducted by the employer to ensure that these requirements are met.[6] Both NO, NO_2 and NH_3 can cause damage to an exposed organism.[10] The OEL-TWA according to the Mine Health and Safety Regulations of the Mine Health and Safety Act (Act No. 29 of 1996) for NH_3, NO, NO_2 and CO is as follows: 25 ppm for NH_3, 25 ppm for NO, 3 ppm for NO_2 and 50 ppm for CO.[6] According to National Institute for Occupational Safety and Health (NIOSH), the recommended exposure limits (REL) for a 10-hour work day for NO, NO_2 and NH_3 are 25 parts per million (ppm), 2 ppm and 25 ppm respectively.[7] The concentrations Immediately Dangerous to Life or Health (IDLH) are 20 ppm for NO_2, 100 ppm for NO and 500 ppm for NH_3 respectively.[7]

If possible, the production of blasting fumes should always be eliminated as far as possible or otherwise controlled by means of physical and chemical processes. The orange or red coloration or cloud of the blasting fumes is caused by the presence and in effect the excessive production of NO_2. To minimize the production of NO_x form blasting fumes and NH_3 from ANFO vapours, the boreholes must be properly loaded with the appropriate amount, composition and proportion of ammonium nitrate fuel oil (ANFO). There is limited evidence on the precise concentrations of NO_x or NH_3 in a blasting fume cloud and therefore people should not be in contact with the orange cloud that is produced right after the detonation process takes place.[1,3]

The occupational health and safety team and management of the mine under study are aware of the hazards of these gases and have tried to ensure adequate ventilation to quickly dilute NO_x below the time weighted average-occupational exposure limits (TWA-OEL). In an effort to protect the workers, extensive research has been done on the toxic fumes generated by the detonation of high explosives. The NIOSH constructed a facility at the Pittsburgh research centre's experimental mine for detonating large, confined charges in a controlled volume. These exploratory laboratorial studies were done to identify factors that may contribute to NO_x production. NIOSH concluded that NO_x production were dependant on confinement, boosters, charge diameter and charge length.[8] A technique for measuring toxic gases produced by blasting agents were developed by NIOSH and is the first of its kind and may be developed as a standard test to measure fumes produced by blasting agents or may even be used to provide data with which to develop a computer model that will reliably predict the expected fume production based on chemical composition.[9]

There is limited information about the exposure of workers to NO_x and NH_3 from blasting fumes in an underground mining setup and this study is therefore motivated to determine the exposure of underground mine workers to NO_x and NH_3 from blasting fumes and ANFO vapours respectively.

2. General and specific objectives

The research objectives can be divided into a general and specific objective.

General objective

The general objective is to determine the exposure of mine workers to NO_x and NH_3 as by-products during blasting in an underground mine over an 8-hour working shift.

Specific objective

- To assess the occupational exposure by means of a single exposure measurement over an 8-hour working shift of underground mine workers' exposure to NO_x and NH_3 generated as by-products during blasting.
- To determine the difference in occupational exposure levels to NO_x and NH_3 between two different groups of mine workers working underground and on the surface respectively.
- To determine the difference between parallel measurements by means of two approved conventional measurement methodologies.

3. Hypothesis

Underground mine workers will be exposed to NO_x and NH_3 concentrations exceeding OELs during an 8-hour work shift.

4. References

1. Mainiero RJ, Harris ML, Rowland JH. Dangers of toxic fumes during blasting. National Institute for Occupational Safety and Health (NIOSH) [Online]. 2006 [cited 2009 Apr 15]; Available from: URL:http://www.cdc.gov/niosh/mining/pubs/pdfs/dotff.pdf

2 Harris ML, Mainiero RJ. Monitoring and removal of CO in blasting operations. Saf Sci 2008;(46): 1393–1405.

3 Eltschlager KK, Shuss W, Kovalchuk TE. Carbon Monoxide Poisoning at a Surface Coal Mine - A Case Study. National Institute for Occupational Safety and Health (NIOSH) [Online]. 2006 [cited 2009 Apr 13]; Available from: URL:http://www.arblast.osmre.gov/downloads/OSM%20Reports/ISEE%202001-CO3.pdf

4 Bakke B, Ulvestad B, Stewart P, Eduard W. Cumulative exposure to dust and gases as determinants of lung function decline in tunnel construction workers. Occup Environ Med 2004;(61):262-69.

5 Ulvestad B, Lund MB, Bakke B, Djupeslandz PG, Kongerud J, Boe J. Gas and dust exposure in underground construction is associated with signs of airway inflammation. Eur Respir J 2001;(17): 416–21.

6 Department of Minerals and Energy. South Africa. Mine Health and Safety Regulations (GN R904, 2 Jul 2002 as last amended by GN R94, 1 Feb 2008). Accessed on 26 Apr 2010. Pretoria: Government Printer.

7 National Institute for Occupational Safety and Health. NIOSH Pocket Guide to Chemical Hazards. Cincinnati: Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health. DHHS (NIOSH) Publication 2005-149.

8 Mainero J. A technique for measuring toxic gases produced by blasting agents. National Institute for Occupational Safety and Health (NIOSH) [Online]. 2006 [cited 2009 Apr 19]; Available from: URL:http://www.cdc.gov/niosh/mining/pubs/pdfs/tfmt.pdf

9 Sapko M, Rowland J, Mainero RJ, Zlochower I. Chemical and physical factors that influence NO_x production during blasting – exploratory study. National Institute for Occupational Safety and Health (NIOSH) [Online]. 2006 [cited 2009 May 25]; Available from: URL:http://www.cdc.gov/niosh/mining/pubs/pdfs/capft.pdf

10 Pritchard JD. Ammonia – Toxicological overview. Health protection agency. [Online]. 2007 [cited 2010 Feb 10]; Available from: URL:www.hpa.org.uk/web/HPAwebFile/HPAweb_C/1194947398510

CHAPTER 2

LITERATURE REVIEW

LITERATURE REVIEW

This chapter reviews existing material relevant to this study. It discusses the mining profession in general, as well as the negative health effects it has on the human body. The main focus area of this study was the use of explosives, focusing on the handling, transportation and storage of explosives. Underground blasting in a mining setup will also be reviewed. Exposure of mine workers to blasting fumes, in particular NH_3 and NO_x, is therefore discussed, along with information on how to control the exposure of mine workers to these blasting fumes. There will be an in depth review of the legislation regarding the Occupational Exposure Limits (OELs) of NH_3 and NO_x respectively.

It was decided to determine the exposure of underground mine workers during the handling, transportation and charge up of explosives and not night shift mine workers cleaning up the working area, due to work related limitations.

1. The mining profession

Although agriculture was the first endeavours of mankind, mining may well have been one of the next endeavours, due to the fact that mining of stone and metal has been done since prehistoric times, with the oldest known mine on archaeological record being the "Lion Cave" in Swaziland. Radio carbon dating proved the mine to be about 43,000 years old. The first mineral to be mined by Paleolithic humans was hematite, which contained iron and was used to produce the red pigment ochre.[1]

Although Platinum was first identified in Spanish South America in the mid 15th century, the Spanish government prohibited its export to other countries and the first actual reference to platinum can be found in a narrative.[2] This document was published in 1748 by Don Antonio de Ulloa y Gracia de la Torre on his journey to Peru. In his work he mentions the occurrence of the metal, together with gold, in Columbia. This metal was first referred to as Platino del Pinto. Plata being the Spanish diminutive for silver and Pinto the name of the river where it was first found. Grains of the metal however had reached Sir William Watson, an English physicist, as early as 1741 and it was he who first described it in 1750 as a new semi metal or metalloid.[3] From about the mid 18th century, the metal became more common in Europe and major deposits were also found in the Ural Mountains of Russia in 1823.[2] Although the metal was first described as being waste, its remarkable properties began to attract the attention of scientists. This led to a series of investigations on crude platinum and it was then later discovered that the metal was not entirely composed of platinum, but rather a complex mixture of several types of metals namely platinum, palladium, iridium, rhodium, ruthenium and osmium. These where then known as the platinum group metals. [3,4]

Platinum is a hard greyish-white metal which is exceedingly malleable and ductile and is practically infusible and unoxidisable and unattacked by any acid except aqua regia.[3] Platinum is also a good conductor of electricity and heat, but has the lowest coefficient of expansion of any metal.[2] Platinum was also found to share the infusibility of porcelain with the chemical inertness of gold.[2] It also has the capability of absorbing large quantities of hydrogen and other gases and it is for this reasons that it is use as a catalyst. Platinum was then used mainly in the construction of stills (apparatus used to distill liquid mixtures) for the concentration of sulphuric acid.[2] Today, however, platinum is used in a wide variety of industries, but the most important being jewellery, laboratory equipment, electrical contacts and electrodes, platinum resistance thermometers, dentistry equipment, diamond setting and engagement rings.[2,3] Platinum is also used in automobiles as a catalytic converter, which allows the complete combustion of low concentrations of unburned hydrocarbon from the exhaust into carbon dioxide and water vapour.[54,55]

In 1923 geologist, Hans Merensky, heard that platinum was discovered by Adolph Erasmus in the Waterberg, Transvaal and he started his search for the mother lode (principal vein or zone of veins of platinum or silver ore) which was the source of the alluvial platinum ore. Merensky soon found a platinum reef extending for some 300 km and by far the largest reserve of platinum ore in the world.[2] South Africa only began mining for platinum in 1926, when 4 951 fine platinum ounces were produced by South Africa, while the world production was 167 500 ounces that year, followed by 10 431 fine platinum ounces produced in 1927 and 17 828 fine platinum ounces produced in 1928.[2,3] The price was £25 an ounce back then.[2] The Swartklip facies (body of rock with specified characteristics) was developed on two farms 26 km north from Pilansberg. Three incline shafts known as No 4, 7 and 9 were used to open up the Bushveld Indigenous Complex (BIC) with depths of 119, 95 and 152 metres respectively.[3]

Mining techniques can be divided into two common excavation types: surface mining and sub-surface (underground) mining. Sub-surface or underground mining however, requires the use of explosives for blasting or shot firing. Blasting or shot firing are the processes of fragmentation or loosening of solid materials such as rock, earth or masonry by means of an explosive charge. The normal sequence consists of drilling a hole, inserting a charge, stemming (covering the charge with a dense material to prevent dissipation of the explosive force) and firing by means of a detonator or fuse.[6]

Surface mining is much more common and produces 85% of minerals, excluding petroleum and natural gas, in the United States. Surface mining alone also produces 98% of metallic ores in the United States.[5] In South Africa about 55 different minerals were produced from 1113 mines and quarries in 2005. Of these 1113 mines and quarries, 45 produced gold, 26 produced platinum-group minerals, 64 produced coal and 202 produced diamonds, all as primary commodities. This was an increase of 120 mines from the previous year.[36,52]

South Africa is the largest platinum producer in the world and produces 79% of all the platinum in the world today and currently holds 55% of all the global reserves.[4,38] The list of minerals South Africa also produces, includes 80% manganese, 73% chrome, 45% vanadium and 41% gold.[38] South Africa alone produced 85 000 kg of platinum in 2006.[37] In 2006 precious metals production contributed to 65% of the country's mineral export earnings and 21% of total exports of goods. The mining industry is also South Africa's biggest employer, with around 460 000 workers employed by mines.[38] The price of platinum fluctuated quite dramatically in 2008, reaching a high of $2300 in March 2008 and a low of $782 in October 2008.[4,52]

The Platinum Group Metals (PGM) sector dominated total and export sales revenues in 2004. Total export sales contributed to $5 165 million or 26.6%, while export sales contributed to $4 577 million or 33.0% of the mining industry. The total PGM's sales revenue increased by 35.6% from $3 810 million, while the export sales revenue increased by 35.5% from $3 378 million compared to 2003. PGMs occupied the third position in domestic sales, contributing a $587 million or 10.7% to the revenue, compared with $433 million in 2003.[51]

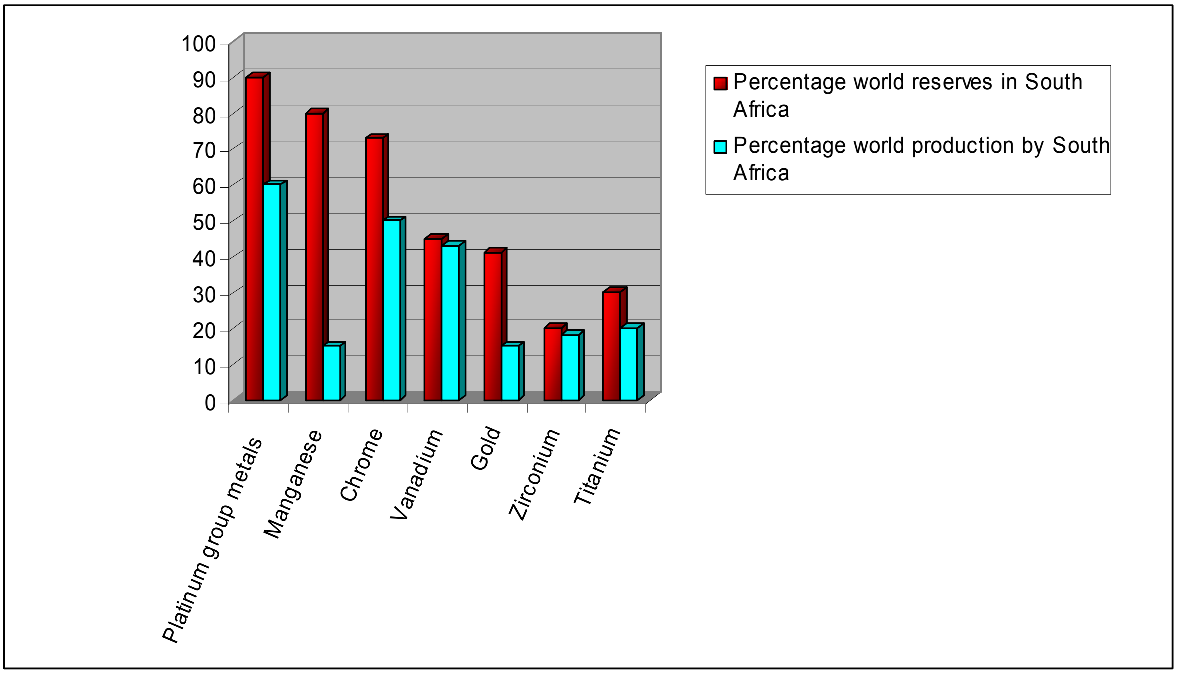

Figure 1: South Africa's share of world reserves and world production of metals (Adapted from DME)

2. Negative health effects of the mining profession

Within the mining profession the wellbeing of mine workers are very important because mine workers play a critical role in the production phase of platinum in a mine. Although the mining profession provides a very important service to the public, it is known that its processes can have a negative effect on the health of the general population with research concluding that subjects living near a mining area had extremely high levels of cobalt and other toxic metals like arsenic, cadmium, copper, lead and uranium in their urine samples.[7] Numerous studies have been done over the years to determine the effects of these processes on the human body, with one study concluding that mine workers were at an increased risk of chronic obstructive pulmonary diseases (COPD). Respiratory symptoms included accelerated decline in forced expiratory volume in one second (FEV_1), a higher prevalence of cough during the day, shortness of breath with exercise, chest tightness and wheezing. These symptoms were all experienced while being exposed to dust and gases from diesel exhaust, blasting, drilling and rock transport.[8] Mining processes can also induce higher chronic heart, respiratory and kidney disease mortality in mining areas due to environmental exposure to particulate matter or toxic agents present in mining processes.[9] The inhalation of chemical agents like platinum salts may also lead to asthma.[10] Gas and dust exposure in underground construction may induce airway inflammation. Workers who didn't smoke and with no previous work experience in tunnels showed signs of upper and lower airway inflammation after one year of exposure to dust and gases in tunnel work.[11]

The association between air pollution in industrialized areas and health status has been well established in epidemiologic studies. Recent studies showed that respiratory tract symptoms were related to photochemical oxidants like nitrogen dioxide (NO_2) and sulphur dioxide (SO_2). The prevalence of respiratory tract symptoms was about 17% higher in areas where the highest contamination took place. In Ontario, air pollutants like SO_2 and ozone (O_3) produced during mining processes during the summer had a strong relation to hospital admissions for acute respiratory tract symptoms. In the assessment of air pollution at home, young children in households with gas stoves, where NO_2, reached peak values of > 1100 μg/m3, had a higher incidence of respiratory disease and decreased pulmonary function than children from households with electric stoves.[12]

In the year 2002, the U.S. Poison Control Centers reported almost 6 000 cases of toxic NH_3 exposures. Ninety-three percent of these exposures were unintentional, while 11% resulted in moderate-to-severe outcomes. Seventy percent of these exposures occurred in adults and 20% occurred in children younger than six years.[46] In the year 2007, the Annual Report of the American Association of Poison Control Centers' National Poison Data System reported 2984 single exposures of ammonia. Ninety-four percent of these were unintentional, while 2 deaths due to NH_3 exposure where reported in that year. 1406 exposures occurred in those older than 19 years, 339 exposures occurred in those aged 6 to 19 years and 751 exposures occurred in those younger than 6 years. [29]

3. History of explosives and blasting

Although the mankind has been in the profession of mining for a long time, it was not until 50 B.C. before they extended their knowledge and capabilities into using explosives for mining purposes. The first known explosives to be used were an early form of a seismoscope used in China, but it was not until 668 A.D. that early weapons contained explosives such as Greek fire. Then came the significant era of black powder that changed the explosive industry forever. The first ever recorded use of black powder for rock blasting came in 1627 in Hungary. However, this black powder was sensitive to water and produced a lot of dark smoke. Black powder was then replaced by nitroglycerine, nitrocellulose, smokeless powder, dynamite and then gelignite. The first time ammonium nitrate fuel oil (ANFO) was used for explosives came in 1956 when the U.S. Steel Corporation's Oliver Mining Division utilized its potential.[13]

Today however blasters use more than 6 billion pounds of explosives and 75 million detonators per year in the U.S and Canada alone, with coal mining accounting for more than two-thirds of these consumed explosives. Eighty percent of these explosives are ANFO. New technologies and explosive materials are being utilized to improve the quality of life of everyone.[13]

For example, computers are used to:

- drill, log and monitor blast holes;
- automate bulk trucks with blending and delivery;
- determine face conditions and face heights;
- design blast patterns and analyze production efficiency.[13]

4. Storage, handling and transportation of explosives

The International Mine Action Standards clearly states that the following requirements should be met. The area where explosives are stored should be well ventilated and kept dry.[6,14] Explosives should also be kept as cool as possible and free from excessive or frequent changes in temperature.[40] It should also be protected from direct sunlight and kept free from excessive and constant vibration.[35,40] This storage place should be segregated, approved and labelled.[40] For the construction of permanent or portable magazines, the following general requirements should be met. The magazine should be bullet resistant, fire-resistant, theft resistant, weather resistant and well ventilated. The fitting of the doors should be done to ensure that the door open outwards and that the doors fit tightly. When the door is locked the hinges and lockingware should be secured by welding, riveting or bolting the door.[14] The explosives should not be stored closer than 100 m from any shaft or 20 m from any electrical or mechanical devices, while separate compartments should be built for detonators and incendiary devices.[6,40] All the activities in the stores should be carried out by authorised workers and entry to the store should be restricted to the storekeeper and supervisors only.[6]

The handling of explosives should include the following requirements. Only suitable, qualified personnel or personnel supervised by a qualified supervisor should use or handle explosives. The manufacturers' instructions and specifications should be followed at all times when handling explosives. The access to explosives should be tightly controlled by any means necessary.[14] Care should be taken that the blasting point is free of detonating gas, inflammable objects, sparking or damaged wiring systems, stray currents and static electricity.[6] Always wear personal protective equipment and avoid skin and eye contact. It is very important to ensure that there is adequate ventilation to protect the mine workers against the inhalation of vapours or spray mist. Keep away from flames and sparks and try to minimize handling and mechanical stressing of product.[40] The Explosives Regulations No. 109 of the Occupational Health and Safety Act (Act No. 85 of 1993) states that an employer should ensure that all explosives or ingredients thereof are at all times free of foreign material. All reasonable precautions should also be taken to prevent the spillage of explosives and prescribe a cleaning procedure in the case of accidental spillage of explosives. All waste, paper, timber, rags, cotton, and similar materials that have been in contact with explosives should be disposed of in a manner prescribed by an explosives manager. Any explosive or partly mixed explosive should be conveyed as soon as possible and taking such precautions to effectively guard it against any accidental ignition or explosion. All material, equipment, tools or similar articles should be decontaminated after use and no person shall use explosives in workplaces other than in the approved explosives workplaces. No person should leave explosives unattended or allow unauthorized access to such explosives. No person should bury, dump, hide or abandon any explosives.[35]

The transportation of explosives should include the following requirements. Always try to avoid accidents as far as reasonably practical. The manufacturers' instructions and specifications must be followed at all times when transporting explosives. The security of explosives should be tightly controlled by any means necessary. The transporting of passengers is strongly discouraged and should be eliminated as far as possible. The following special equipment should also be kept on the vehicle: two fire extinguishers with a volume of nine litres and a container for storing smoking material.[14] Do not use transport vehicles which do not sufficiently protect the explosives against shocks, friction, collision, direct sunlight or sparking. Always clear the roads ahead when transporting explosives. Never allow untrained or undisciplined workers to load, transport or unload explosives. Detonators should be separated from the other explosives by transporting them in separate containers.[6] The Explosives Regulations No. 109 of the Occupational Health and Safety (Act No. 85 of 1993) states that only containers provided for the conveyance of explosives are used for transporting explosives or partly mixed explosives and those containers should be kept clean, free from grit and in a good state of repair. Vehicles containing explosives should not be left unattended.[35]

5. Underground blasting in a mining environment

Blasting is basically either primary or secondary. Primary blasting is used in boreholes or blasting of bulk charges in underground chambers also known as coyote blasting. Secondary blasting can also be used in boreholes if necessary, but is mainly used in surface charge also known as plaster shooting.[6] The primary explosive used for underground blasting in the mine under study is ANFO. Under most conditions ANFO is considered an insensitive high explosive. It decomposes with a high velocity through detonation rather than deflagration and is a tertiary explosive consisting of distinct oxidizer and fuel phases, but requires confinement for efficient detonation. Advantages of insensitive dry blasting such as ANFO include their safety, ease of loading, and their low price. In the free-flowing form, they have a great advantage over cartridge explosives because they fill the boreholes completely. ANFO however, is water soluble making it impossible to fill wet boreholes.[41] This product is manufactured by a local company and transported to the mine. ANFO is a solid, white to grey material with a characteristically oily odour. It has a pH between 4.5 to 6.0 and a melting point of 273 °C. It's also highly soluble in water with a density between 0.60 to 0.85 g/cm^3. The composition of ingredients is 93% ammonium nitrate (NH_4NO_3) and 7% fuel oil (C_nH_{2n+2}). The fuel oil can either be diesel gas oil or Kerosine (petroleum).[40] The chemical reaction that takes place during blasting is as follows:

$$C_nH_{2n+2} + (3_{n+1})NH_4NO_3 \longrightarrow nCO_2 + (7_{n+1})H_20 + 3nN_2$$

The fuel oil is not precisely CH_2, but is sufficiently accurate to characterize the reaction. The right side of the equation contains only the desirable gases of detonation, although some CO and NO_2 are always formed. As in other combustion reactions, a deficiency of oxygen favours the formation of carbon monoxide and unburned organic compounds and produces little, if any, nitrogen oxides. An excess of oxygen causes more nitrogen oxides and less carbon monoxide and other unburned organics. For ANFO mixtures, a fuel oil content of more than 5.5 percent creates a deficiency of oxygen.[41]

The following figure demonstrates a typical development area being developed by an underground developing team. There are two rock faces being mined in this area: the one being in the Holegen and the other one being in the cross cut. Supporting beams are also installed for safety precautions and to direct the flow of air. The ventilation direction is also indicated on the figure to supply fresh air to workers and dilute any existing fumes that may exist.

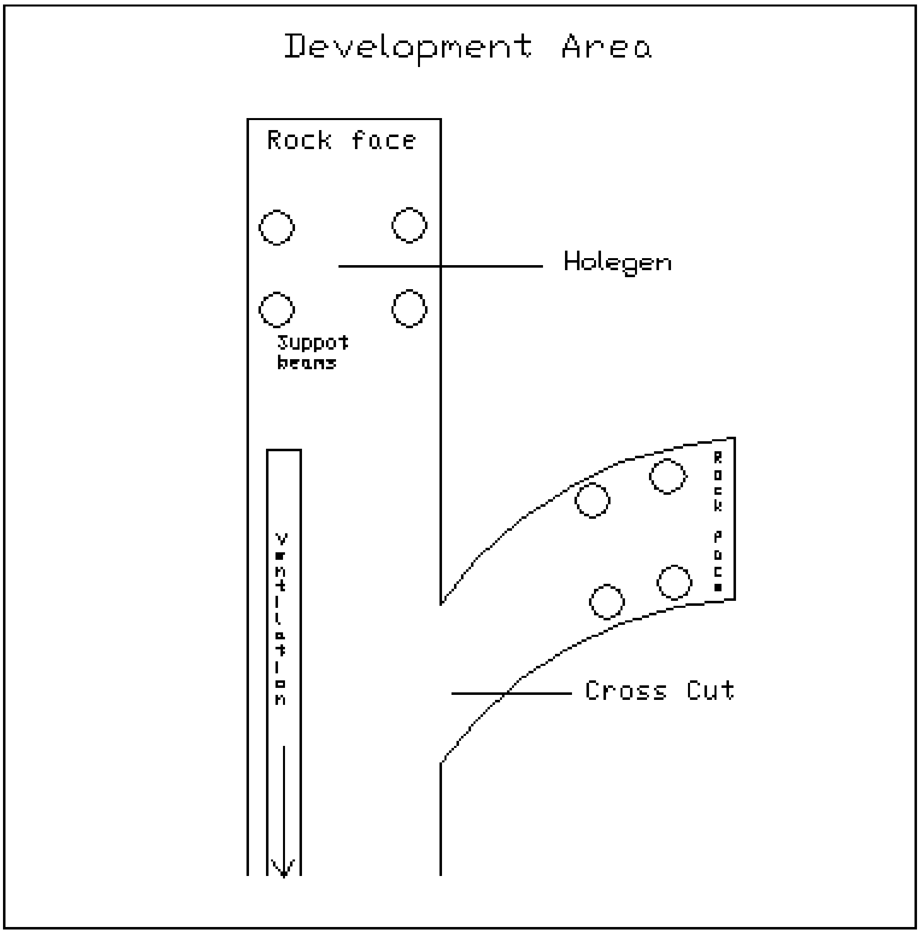

Figure 2: An example of an underground mining setup of a development area being developed by underground mine workers.

Observations made by the researcher and information provided by the mine indicates that there are mainly two phases in which the blasting takes place. The first phase implements the calculating and drilling of the boreholes in the rock face. Depending on the diameters and composition of the rock face, as well as the formulation, confinement, age and contamination of the explosive, it is calculated how many boreholes must be drilled to get the maximal distance with each blast, ensuring that the debris is broken into small enough pieces to be transported to the surface. This is a very important phase in which it is necessary to determine the minimal explosives which are going to be used for the maximum effect it has to produce. After the rock face has been clearly marked where the boreholes should be drilled, the machine operator starts drilling each of the required holes in the rock face. Depending on the number of holes which is needed to be drilled, this can take anything from 60 minutes to 360 minutes. The holes are then dried out with compressed air to ensure that no contamination of the ANFO with water will take place. The second phase represents the physical charge up where the boreholes are being loaded with ANFO. One mineworker is required to insert the detonator and to load each hole with ANFO. The detonators are placed at the end of each borehole and then charged up with ANFO using compressed air. Another mineworker is required to operate the machine supplying the compressed air. After the charge up is completed, the area where blasting is going to take place is evacuated. This is also the end of the shift for underground mine workers working day shift and they are transported to the surface. The detonation of the blast is done by means of a centralized blasting form surface, which requires the entire shaft to be evacuated and only then is each blast detonated one by one. The whole shaft is then closed for a minimum of three hours to effectively dilute the fumes produced by explosives and no one is permitted to enter the shaft for this period of time. After three hours, the shaft is then opened again for the mine workers working night shift to enter the different areas where blasting took place. The area is then firstly secured and the necessary safety measures such as installing supporting beams, determining the air quality and removing any waste material is then conducted. Three underground mine workers are then required to load the debris containing the precious metals into a locomotive. If debris is too big to be loaded into the locomotive, it is drilled into smaller pieces and then loaded into the locomotive and transported to the surface using conveyor belts and cages. This is repeated until the area is cleared of all debris. The underground mine workers are then transported to the surface, thus ending their night shift. Depending on the availability of explosives and the time it takes to drill the boreholes in the rock face, the whole process is then repeated on a day to day basis to maximize the production process. Exposure to blasting fumes can occur at any time during these two phases, but especially during the charge up period when ANFO is dispersed into the ambient air because of the use of compressed air to compact the ANFO into the boreholes. Overloading of boreholes should also be avoided as far as possible to eliminate any accidental exposure.

Figure 3 represents an example of a rock face drilled with 27 boreholes. The diameters of the rock face are 1.5 meters by 1.5 meters. The four red dots represent the four corners of the rock face. These four corners will act as corner stones to prevent the rock face from exploding inwards or outwards and to keep the face square at all times. The nine blue dots in the middle of the rock face represent the "brain" of the blast where all the detonators from each borehole will connect. This will ensure that the rock face explode inwards, thus maximizing the impact of the blast and ensuring that the debris is broken into small enough pieces. It is important to determine the exact number of boreholes needed to ensure that the least amount of ANFO is used, but the maximum impact is still produced. Boreholes may range from 2.5 to 38 cm in diameter and up to 10 m in depth.[6]

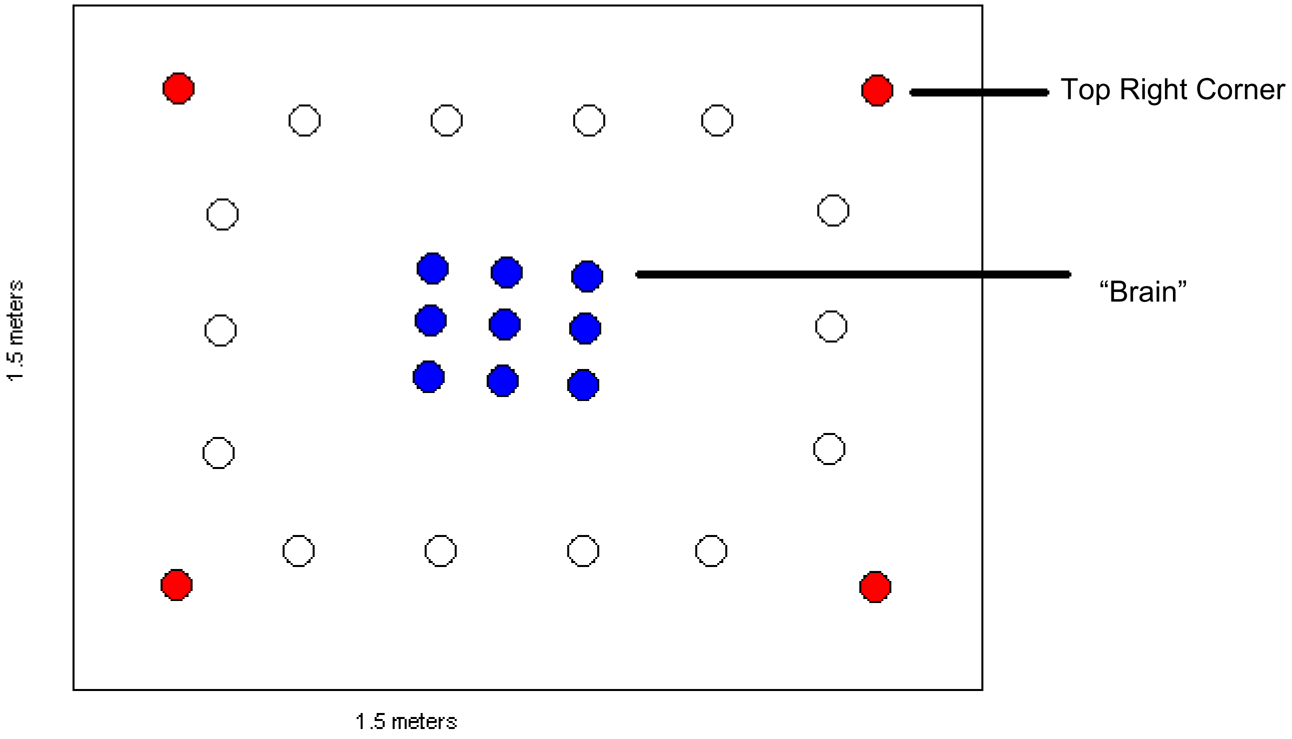

Figure 3: Rock face of 1.5 meters by 1.5 meters, displaying an example of 27 boreholes before charging up with ANFO

Blasting usually takes place in two different areas of the mine, the first being the development area and the second being the stoping area. Blasting takes place on a daily basis, but it depends on a lot of factors including the measurements of the rock face, amount of machine drill operators, availability of explosives and safety factors. There are currently 114 workers on the shaft responsible for the charge up of the explosives, thus providing each rock face with two workers responsible for the charge up. After detonation takes place, it is mandatory that no worker may enter the area where blasting took place for at least three hours. It must also be ensured that the ventilation system is working properly during these three hours to dilute any gases produced during the detonation process.

Two separate incidents of so-called "gassing cases" occurred in 2009. On 22 November 2009, 104 mine workers died after an explosion at the Xinxing Coal Mine in Hegang City, north-east of China, in the Heilongjiang Province. A total of 528 miners were working underground when the blast happened around 2:30 a.m. on a Saturday morning. Sixteen people were trapped underground after the explosion took place. This was China's worst mining disaster in almost two years, despite efforts to improve safety standards. There were speculations that there might be a possible abuse of power, government inaction or misconduct, as well as under-the-table deals at the mine that may have compromised safety standards. The explosion resulted from a massive gas build up and revealed gaps in work safety and inadequacies in gas prevention and control measures.[42] On 22 February

2009, 72 people were also killed by an explosion at a mine in Gujiao, Shanxi province. In this incident, none of the mine's alarms sounded and even as gas indicators measured dangerous levels, nobody at the control room took action.[42] On 22 August 2007 two collieries (coal mining plants) were flooded after a mine blast in Xintai, Shandong province, killing 181 miners. In the year 2008, 3 200 people were killed in the mining industry in China alone.[43]

A case study in April 2000 reported that blasting fumes migrated about 400 feet away from the blasting area and into a nearby house and poisoned two adults and their newborn infant. They received medical treatment at a nearby hospital where it was determined that their Carboxyhemoglobin levels, which inhibits oxygen uptake, were 28% for the father, 17% for the mother and 31% for the infant. All other sources of carbon monoxide were ruled out. The following conditions led to the migration of blasting fumes into the house: the geological structure was fractured and served as a conduit for the blasting fumes to enter the house and the well was also connected to the drains in the basement floor.[32]

There is limited information about the exposure of workers to NO_x and NH_3 from blasting fumes in underground mining setups and this study is therefore motivated to improve the working conditions of underground mine workers handling these explosives, thus minimizing their potential exposure to NO_x and NH_3. Incidents like these could then be better controlled or even eliminated if sufficient evidence is provided through continuous and precise research into the world of blasting and its associated gasses. The purpose of this study will be to determine the exposure of mine workers to NO_x and NH_3 from handling explosives in an underground mine over an 8-hour working shift and comparing it to existing OELs, as stated in the objectives. The object of this study was not to determine the exposure of night shift workers during the clean up the area where blasting took place, but rather determining the exposure of underground mine workers responsible for the charge up process.

6. Blasting fumes

The orange or red coloration or cloud of the blasting fumes is caused by the presence and in effect the excessive production of NO_2 which is a direct product of the detonation process and is also produced in the after burning reactions and by the secondary oxidation of NO to NO_2. NO_x is very toxic and is a concern in surface blasting because it is much more toxic than CO.[31,32] Although this study focused on the production of NO_x from blasting fumes, research concluded that diesel engines were the main source of NO, while the main source of NO_2 was due to explosives.[53]

6.1. NO_x

6.1.1. Chemical and physical properties of NO and NO_2

Table 1: Chemical and physical properties of NO [15]

CAS Number	10102-43-9
Molecular weight	30.01
Density	1.04
DOT label	Poisonous gas UN 1660

NO is an odd-electron molecule (paramagnetic) and has 11 valence electrons with one unpaired electron, thus making it a free radical. This compound has been found to play an important role in a number of biochemical processes. This compound is formed when atmospheric nitrogen and oxygen combine when they are heated in internal combustion processes. In the presence of oxygen, NO rapidly forms NO_2. NO is also found in urban polluted air.[18] NO has a sharp, but sweet odour when in gaseous state, while having a deep blue colour when in liquid form.[15] According to the NIOSH pocket guide to chemical hazards, NO is a colourless, non flammable gas and also a poisonous, oxidizing gas with an irritating odour.[16,17,50] NO will enhance and accelerate the burning of combustible materials and is extremely toxic if inhaled and symptoms of inhalation will only prevail after 72 hours of exposure.[16,17] If NO combines with oxygen, it forms brown fumes of nitrogen dioxide and is extremely reactive and a strong oxidizing agent.[17]

The following depicts a balanced chemical reaction between nitric oxide and oxygen:

$$2NO\ (g) + O_2 \longrightarrow 2NO_2\ (g)$$

Table 2: Chemical and physical properties of NO_2 [15]

CAS Number	10102-44-0
Molecular weight	46.01
Density	1.58
DOT label	Poisonous gas and oxidizer UN 1067

NO_2 is a brown paramagnetic gas when exposed to direct sunlight and is one of the main delinquents in air pollution. NO_2 is also an odd-electron molecule and has 21 valence electrons, but the odd electron largely resides on the N atom.[18] NO_2 is a yellowish-brown liquid or reddish brown gas with an acrid, pungent acid odour.[15,16,50] NO_2 is non-combustible, but will accelerate the burning of combustible materials.[16] It also reacts with water to form nitric acid and nitric oxide.[15]

6.1.2. Uses and Exposure risk of NO and NO_2

NO is used as an intermediate in the manufacturing of nitric acid, the preparation of metal nitrosyls, bleaching of rayon, textile industry and in incandescent lamps. People working in these industries have a higher exposure risk to NO. NO is produced by heating air at high temperatures.[15,50]

NO_2 occurs in the exhausts of internal combustion engines and in cigarette smoke. It is also used in the production of sulphuric acid, rocket fuel and bleaching flour.[15]

Incomplete combustion of the oxides of nitrogen will lead to the release of hydrocarbons which will lead to the formation of dry gases or washed out of the atmosphere to produce acid precipitation in rain and snow.[21]

People working in the following occupations will have a higher exposure risk:

- Fire fighting, arc welding and work at missile sites
- Manufacturing of explosives, jet fuels, dyes, lacquers and celluloid
- Ice rink resurfacing
- Grain silos, which release nitrogen dioxide within the first few weeks after filling
- Farm workers are at risk for silo-fillers' disease [22]

Environmental sources include decaying organic matter, volcanic emissions, atmospheric lightning, fires, and burning of fossil fuels. [22]

6.1.3. Health effects

NO is naturally formed in the body from the amino acid L-arginine and performs a second messenger function in nerve tissues, blood vessels and the immune system. Parasympathetic stimulation of arteries involves neurons that release NO that causes smooth muscles in the arterial wall to relax, resulting in increased blood flow to organs, especially in the pulmonary circulation.[19] NO is especially secreted by nerve terminals in areas of the brain responsible for long-term behaviour and memory.[20]

There is variability in the biological response to NO_x. Healthy individuals tend to be less responsive to the effects of NO_x than individuals with lung diseases. To date, asthmatics are the most responsive group to NO_x. Individuals with COPD may also be more responsive to NO_x than healthy individuals, because they have limited capacity to respond to NO_x and thus quantitative differences between COPD patients and others are difficult to assess. Inhaled NO concentrations above 6000 $\mu g/m^3$ (5 ppm) can cause vasodilatation in the pulmonary circulation without affecting the systemic circulation.[58]

NO is produced from the detonation process during blasting and can combine with the H_2O in the lungs to form nitrous acid (HONO).[25,50] Nitrous acid can also be formed as a primary product of gas combustion. This acid molecule may be harmful to the human body by means of three mechanisms. Firstly because it is an acid it may cause damage to mucous membranes of the lungs, secondly it may combine with amines *in vivo* to produce carcinogenic nitrosamines and thirdly it may form highly oxidative free hydroxyl radicals from photolysis in the air, which may in turn cause chronic bronchitis or asthma.[25] NO have recently been shown to be a neurotransmitter to be released at the synapse of neurons. Disruption in the homeostasis of NO in the neurons will lead to inexplicable inhibitory or excitatory effects.[19] NO is a strong irritant to the eyes, nose and throat and inhalation causes methemoglobinemia, thus replicating the action of carbon monoxide. NO binds with haemoglobin in blood to form methemoglobin, affecting the transportation of oxygen to body tissues and organs.[15]

$$\text{Hb} + \text{NO} \longrightarrow \text{NOHb}$$ [15]

NO_2 is a highly toxic gas. It is an irritant to the eyes, nose, throat and respiratory system. The toxic symptoms are coughing, frothy sputum, chest pain, dyspnea, congestion and inflammation of the lungs. Even short exposure can cause haemorrhaging and lung injury. Death may result within a few days after exposure. Symptoms of toxic exposure to NO_2 may be noted in humans exposed to 10 ppm for 10 minutes. One or two minutes of exposure to 200 ppm, as in a building fire, can be lethal to humans, because it may result in pulmonary edema and lung injury.[15,39] Continued exposure to high NO_2 levels can contribute to the development of acute or chronic bronchitis. Low level NO_2 exposure may cause increased bronchial reactivity in some asthmatics and increase the risk of respiratory infections, especially in young children.[39]

Cumulative exposure to NO_2 for 5 to 8-hours on average daily, over a period of six years appeared to decrease lung function in tunnel construction workers and is therefore a major risk factor. Research concluded that other agents may also have contributed to the observed effect, but information on these other agents were not available for that specific data set.[23] Bakke, Ulvestad, Stewart, Lund and Eduard focused on the influence of NO_2 on lung function and found that workers who where exposed to 1.5 ppm NO_2 for 3 hours shared negative effects of lung functions.[24] Exposure may also cause nasal mucosal swelling and increased levels of exhaled NO, indicating signs of upper and lower airway inflammation.[11]

Ciliated epithelial cells are extremely sensitive to injury by toxic inhalants such as NO_2. Damage to these cells may be manifested as ciliostasis, detachment or reabsorption of cilia or cell death. The end result is impairment of mucociliary clearance, but luckily this impairment can be reversed. Increased susceptibility to respiratory infections also occurs if alveolar macrophage functions are compromised by oxidant injury caused by NO_2. However, experimental production of emphysema by exposing animals to NO_2 has not been consistently successful.[12]

Haschek and Rousseaux concluded that after NO_2 inhalation there is increased susceptibility to airway infection. In an experimental study done by them they injected a squirrel monkey with *Klebsiella pneumoniae* and influenza virus and results showed that the squirrel monkey had increased susceptibility to airway inflammation. The same results were obtained by injecting a rat with *Listeria monocytogenes*. In such experiments, the concentration of NO_2 had a greater impact than the duration of exposure.[12]

6.2. NH_3

6.2.1. Chemical and physical properties of NH_3

Table 3: Chemical and physical properties of NH_3 [15,49]

CAS Number	7664-41-7
Molecular weight	17.04
Density	0.58

NH_3 is a colourless gas with a pungent, suffocating odour and easily liquefies under pressure and should be treated as a flammable gas.[15,16,46,48,56,57] NH_3 is highly soluble in water, alcohol and ether and reacts violently with halogens.[15,48,56]

6.2.2. Uses and Exposure Risk

NH_3 is used in the manufacturing if nitric acid, hydrazine hydrates and acrylonitrile. NH_3 is also used in fertilizers, explosives and synthetic fibres and everyday household refrigerators.[15,46,56] Approximately 20 million tons of NH_3 are produced annually and 80% of this is used as fertilizer.[46]

People working with the following substances will have a higher exposure risk

- Anhydrous ammonia is used in the production of fertilizers, dyes, plastics, synthetic fibres, and other chemicals and pharmaceuticals; commercial refrigerant gas; nitrogen fertilizer; and explosives.[22,46,56]
- Aqueous ammonia is an ingredient in many household (usually at a concentration of 5% to 10%) and commercial (usually at concentrations above 25%) cleaning agents.[22]

6.2.3. Health effects

Hamid and El-gazzar concluded that exposure to NH_3 caused inhibition in the activity of catalase enzymes. This inhibition could lead to deleterious effects on electrical stability, permeability and fluidity of membranes, thus causing the brain and liver to be more susceptible to hepatotoxic and neurotoxic alterations. Monoamine oxidase was significantly inhibited, while liver activities were significantly increased.[26] These results differ from a study which found that there were no differences in respiratory or cutaneous symptoms, sense of smell, baseline lung function or change in lung function between two different exposure groups.[27] Yadaf and Kaushik focused on the genotoxic potential of NH_3 and results showed an increased frequency of chromosome aberrations and sister chromatid exchanges. Smoking or drinking combined with NH_3 exposure also showed higher values of mitotic index, satellite associations and micronuclei.[28] Injury from NH_3 is most commonly caused by inhalation, but it may also follow after ingestion or direct contact with the eyes, respiratory tract or skin.[15,29,56] The most common mechanism by which NH_3 gas causes damage occurs when anhydrous NH_3, which represents the absence of water in NH_3, reacts with tissue water to form a strong alkaline solution, ammonium hydroxide. This alkaline solution causes severe alkaline chemical burns to the skin, eyes and respiratory system, while the gastrointestinal tract may also be affected if ingested. Tissue damage from ammonium hydroxide is caused by liquefaction necrosis when the tissue breakdown liberates water, thus perpetuating the conversion of NH_3 to ammonium hydroxide which is highly corrosive.[15,29] Destruction of cilia and infection of the mucosal barriers also occur in the respiratory system.[29] NH_3 is extremely toxic, even in low concentrations and must be eliminated as soon as possible.[19] If diluted in water, it can be eliminated from the body rapidly and safely because of its soluble properties.[21] Toxic effects include lacrymation, respiratory distress, chest pain and pulmonary edema. A concentration of 100 ppm may be detected by odour, irritation of the eyes and nose and is perceptible at 200 ppm and a few minutes of exposure to 300 ppm can be intolerable, causing serious blistering of the skin, lung edema and asphyxia.[15] Brautbar et al depicted that exposure to NH_3 is also associated with a range of upper respiratory symptoms, including severe cases of chemical pneumonitis and intense pulmonary inflammation. Although interstitial lung disease is an uncommon effect of NH_3, they suggested that repetitive, long-term, cumulative occupational exposure to NH_3 may be associated with interstitial lung fibrosis.[56]

Haschek and Rousseaux proposed the sites of damage and results in the central nervous system for NH_3 being astrocytic swelling (Alzheimer Type II astrocytes) and hepatoencephalopathy. They also projected excess astrocytic conversion of NH_3 to glutamine as the primary mechanism of action, but the sensitivity to species was non-specific.[12]

Holness, Purdham and Nethercott have done a study on the acute and chronic respiratory effects of occupational exposure to ammonia by comparing 58 workers who were exposed to airborne ammonia levels of 9.2 ppm with 31 control workers who were exposed to airborne ammonia levels of 0.3 ppm. However, they concluded that there were no significant differences between the two groups when it came to comparing respiratory or cutaneous symptoms, sense of smell, baseline lung function or change in lung function over a work shift at the beginning and end of a work week. There were no relationships between level or length of ammonia exposure and lung function.[45]

Table 4: Summary of toxic effects following acute exposure to NH_3 [46,47, 48,49,57]

Exposure level (ppm)	**Effects on the human Body**	**Permissible Exposure**
25-50	Detectable odour by most people	Unlikely to experience adverse effects
50-100	Mild irritation of eyes, nose, and throat	May develop tolerance in 1-2 weeks with no adverse effects thereafter
250	Tolerated by most humans	30 to 60 minutes
700	Immediate eye and throat injury	60 minutes maximum exposure
1 700	Laryngospasm and pulmonary edema	No exposure permissible
2 500	Fatality	No exposure permissible
5 000	Rapidly fatal exposure	No exposure permissible

7. Legislation

7.1. Mine Health and Safety Act

7.1.1. Employer to ensure safety

The Mine Health and Safety Act and Regulations (Act No. 29 of 1996) states that the employer of every mine that is being worked at must provide, as far as reasonably practical, conditions for safe operation and a healthy working environment in such a way that employees can perform their work without endangering the health and safety of themselves or any other person. A 15-minute TWA exposure should not be exceeded at any time during a workday even if the 8-hour TWA is within the OEL-TWA. Exposures above the OEL-TWA up to the STEL should not be longer than 15 minutes and should not occur more than four times per day. There should also be at least 60 minutes between successive exposures. The employer should ensure that the mine is commissioned, operated, maintained and decommissioned for employees to achieve this goal. Employees must be properly trained to deal with every risk regarding the health and safety measures necessary to eliminate, control and minimize those risks as well as procedures to follow to perform their work and any relevant emergency procedures. A manager should be appointed to be responsible for day to day management and operation of the mine. An employer must prepare and implement a code of practice on any matter affecting the health and safety of employees· The employer should conduct occupational hygiene measurements if, after assessing risks, it is necessary to or required to do so by regulation to measure levels of exposure to hazards at the mine. Every person who manufactures, imports or supplies any hazardous substance for use at a mine must ensure, as far as reasonably practicable, that the substance is safe and without risks to the health and safety when used, handled, processed, stored or transported at a mine. Manufacturers and suppliers should also provide adequate information about the use of the substance, risks to health and safety associated with the use of the substance and any other restrictions or control measurements necessary on the use of the specific substance. It is also mandatory for the manufacturer and suppliers to include information about the transport and storage of the substance, including exposure limits and safety precautions to ensure product is without risk. Procedures to be followed in the case of an accident involving excessive exposure to the substance, the disposal of used containers in which the substance was stored and any waste involving the substance should also be provided by the manufacturer or supplier. Information provided should also comply with the provisions of the Hazardous Substances Act 1973 (Act No. 15 of 1973).[30]

7.1.2. Occupational exposure limits

Occupational exposure limit (OEL) means the time weighted average (TWA) concentration for an 8-hour workday and a 40 hour work week to which nearly all workers may be repeatedly exposed to without adverse health effects. The OEL can further be divided into two categories. OEL-Ceiling (OEL-C) limit which is the instantaneous value which must never be exceeded during any part of the working exposure and the OEL-Short term exposure limit (OEL-STEL) means a 15 minute TWA exposure which should not be exceeded at any time during a workday, even if the 8-hour TWA is within the OEL-TWA.[30]

The OEL-TWA for NH_3, NO and NO_2 according to the Mine Health and Safety Regulations of the Mine Health and Safety Act (Act No. 29 of 1996) is as follows: 25 ppm for NH_3, 25 ppm for NO and 3 ppm for NO_2.[30] Although the mine is obliged to use the previously mentioned Act, the Regulations for Hazardous Chemical Substances Act (Act No. 85 of 1993) may also be used as a legislative measure to determine the OEL-TWA. The OEL-TWA for NH_3, NO and NO_2 according to the Regulations for Hazardous Chemical Substances (1995)[59] under the Occupational Health and Safety Act (Act No. 85 of 1993) is the same as the Mine Health and Safety Regulations of the Mine Health and Safety Act (Act No. 29 of 1996).[30]

There are four sources regarding the international recommendations for the OEL. The first two organizations are private professional organizations namely the American Industrial Hygiene Association (AIHA) and the American Conference of Governmental Industrial Hygienists (ACGIH). The third is a governmental educational and research organization namely the NIOSH and lastly the Occupational Safety and Health Administration of America (OSHA) which is the only regulatory and enforcement agency.

NO, NO_2 and NH_3 are toxic gases, as indicated by the NIOSH recommended exposure limits (REL) for a 10-hour workday of 25 ppm, 2 ppm and 25 ppm respectively.[16] The concentrations Immediately Dangerous to Life or Health (IDLH) are 20 ppm for NO_2, 100 ppm for NO and 300 ppm for NH_3 respectively.[16]

7.2. Occupational Health and Safety Act - Explosives Regulations No. 109

This regulation applies to any employer, self-employed person or user who operates an explosives workplace for the purpose of manufacturing, testing, storing or using of explosives. An employer shall ensure that entry and exit from danger areas is only permitted at a specific point of entry, even for vehicles and visitors to danger areas. No persons shall enter or exit the danger area through an unauthorized point of entry with tobacco, matches, cigarettes lighters, intoxicating liquor, narcotics, food, medicine, drinkable fluids, a radio transmitter or cellular telephone. Hazard warning signs should be clearly displayed at the entrances to any danger area, magazines or workplace. An employer shall ensure that all fire-fighting appliances and emergency equipment provided in the danger building or room are placed and kept where they are readily visible, accessible and available for use when required. An employer shall ensure that no danger building is used unless the ambient temperature and relative humidity inside the building are within limits described by the explosives manager. An employer shall ensure that an explosives workplace is established, erected, operated and maintained in such a manner that prevents the exposure of persons to hazardous or potentially hazardous conditions or circumstances and may only be used for this purpose. In the event of any abnormal conditions or an unusual occurrence, the operations should be stopped immediately. An employer should appoint a competent and certified person in a full-time capacity to be explosives manager in respect of every workplace where explosives are being used, tested, stored or manufactured. The explosives manager should also ensure that all persons under his control are informed of the hazards related to their tasks and are thoroughly trained in safe work procedures. The explosives manager should also provide the necessary protective clothing and equipment and ensure that the processes and equipment are safe and appropriate to use.[35]

Table 5: Recommended exposure levels for blasting fumes[60]

	Mine Health and Safety Regulations	**AIHA**	**ACGIH**	**NIOSH**	**OSHA**
	(Act No. 29 of 1996),				
	8-hour-TWA	**8-hour-WEELs**	**8-hour-TLV**	**10-hour-REL**	**8-hour-PEL**
	OEL-RL				
Blasting fumes	mg/m^3	mg/m^3	mg/m^3	mg/m^3	mg/m^3
NH_3	17	17	17	17	35
NO	30	-	31	31	31
NO_2	5	2	6	4	9

TWA-OEL-RL, Time weighted average occupational exposure limits – recommended limit

WEEL, Workplace Environment Exposure Level Guidelines

TLV, Threshold Limit Values

TWA, Time Weighted Average Exposure Limits

PEL, Permissible Exposure Limits

8. Control

The production of blasting fumes should always be eliminated as far as possible or otherwise controlled by means of physical and chemical processes.[31] To minimize the production of NO_x and NH_3, the boreholes must be properly loaded with the appropriate amount, composition and proportion of ANFO. There is limited evidence on the precise concentrations of NO_x or NH_3 in a blasting product cloud and therefore people should not be in contact with the orange cloud that is produced right after the detonation process took place.[31,32]

Engineering control measures that can be implemented include the use of explosion-proof electrical equipment used for ventilating, lighting and handling of material. In the case of already installed equipment, it should be replaced as soon as possible. Exposure could also be minimized by reducing the handling and mechanical stressing of the product.[40]

Personal protective equipment (PPE) as control measures that can be implemented includes the use of suitable respiratory protection. Hand protection includes gloves made from natural rubber or latex, polychloroprene, polyvinylchloride or butylrubber and should be suitable for permanent contact. Breakthrough time should not be less than eight hours and using leather as gloves should be avoided.

Eye protection that can be used includes safety goggles. Skin and body should be protected by lightweight protective clothing. Personal hygiene control measures include washing hands before breaks and immediately after handling the ANFO.[40,48]

Typical underground control procedures employed by engineers include reducing or preventing the amount of blasting fumes liberated by the blasting process. This can be obtained through the proper selection of explosives and blasting techniques, blasting off-shift or at restricted times, removing the fumes through local exhaust systems or auxiliary ventilation (dilution ventilation). Localizing or isolating the effects of blasting where workplaces are isolated or sectionalized in the ventilation system can also be implemented. Some of the components of the blasting fumes could also be absorbed using air-water sprays. The most effective universally applied control measure against blasting fumes is dilution, but it is necessary to determine the precise dilution necessary to reach safe concentrations for each blasting fume. It is also important to determine the concentration of toxic fumes produced by the explosives.

One method of doing so is to determine the type and volume of gases produced from blasting fumes by means of thermo-hydrodynamic calculations, but commercial explosives exhibit non-ideal behaviour which is enhanced by the relatively small diameters of application in underground mines. The confinement of the surrounding rock further complicates the situation, because it affects the performance and fume generation. The following factors should be considered when selecting a proper control technique for blasting fume generation: confinement, shock desensitization and incomplete detonations.[44] De Souza and Katsabanis developed a mathematical model which is capable of determining dilution ventilation requirements, as well as dilution times to reduce the fume concentrations in a blasting zone to acceptable levels. This model will also be incorporated into a network system to simulate the effects of blasting in typical mine ventilation systems.[44] De Souza and Katsabanis recommended the following solutions for the control of blasting fumes: implementation of control procedures to prevent and reduce the amount of fumes liberated from blasting, the use of explosives that produce less fumes, proper blasting techniques, dilution ventilation and filtration. These methods can be combined effectively for the best results to control fume production and save on costs.[44]

The occupational health and safety team and management of the mine under study, have long been aware of the hazards of these gases and must ensure adequate ventilation to quickly dilute NO_x and NH_3 below the TWA-OELs. In an effort to protect the workers, extensive research has been done on the toxic fumes generated by the detonation of high explosives. NIOSH constructed a facility at the Pittsburg research centre's experimental mine for detonating large, confined charges in a controlled volume. These exploratory laboratory studies were done to identify factors that may contribute to NO_x production. NIOSH concluded that NO_x production was dependant on confinement, boosters, charge diameter and charge length.[33] This technique is the first of its kind and may be developed as a standard test to measure fumes produced by blasting agents or may be used to provide data with which to develop a computer model that will reliably predict the expected fume production based on chemical composition.[34]

9. References

1 Swaziland National Trust Commission - Cultural Resources - Malolotja Archaeology, Lion Cavern. [Online]. 2009 [cited 2010 Jan 20]; Available from: URL:http://www.sntc.org.sz/cultural/malarch.asp

2 Sander I. Development, diamonds, gold and platinum: The story of the Johannesburg Consolidated Investment Company. Cape Town: Struik Publishers; 2000. p. 295-315.

3 Wagner PA. Platinum deposits and mines of South Africa. Edinburgh: Oliver and Boyd; 1929. p. 1-6,128-144.

4 Mbendi information services. An Mbendi profile South Africa – Mining platinum group element mining overview. [Online]. 2008 [cited 2010 Jan 23]; Available from: URL:http://www.mbendi.com/indy/ming/plat/af/sa/p0005.htm

5 Introduction to mining. [Online]. 2002 [cited 2010 Jan 19]; Available from: URL:http://media.wiley.com/product_data/excerpt/11/04713485/0471348511.pdf

6 Parmeggiani L. Encyclopedia of occupational health and safety. Geneva: International labour Office; 1983. Vol 1 p. 295-297.

7 Banza LN, Nawrot TS, Haufroid V, Decree S, De Putter T, Smolders E et al. High human exposure to cobalt and other metals in Katanga, a mining area of the Democratic Republic of Congo. Environ Res. 2009 Apr 27;109:745-52.

8 Ulvestad B, Bakke B, Melbostad E, Fuglerud P, Kongerud J, Lund, MB. Tunnel workers are at increased risk of obstructive pulmonary disease. Thorax. 2000 Jan 7;55:277-82.

9 Hendryx M. Mortality from heart, respiratory, and kidney disease in coal mining areas of Appalachia. Int Arch Occup Environ Health. 2009 Apr 28;82:243–49.

10 Pepys J, Pickering AC, Hughes G. Asthma due to inhaled chemical agents-complex salts of platinum. Clin Allergy. 1972;2:391-396.

11 Ulvestad B, Lund MB, Bakke B, Djupeslandz PG, Kongerud J, Boe J. Gas and dust exposure in underground construction is associated with signs of airway inflammation. Eur Respir J. 2001 Sept 14;17:416–21.

12 Haschek WM, Rousseaux CG. Fundamentals of toxicologic pathology. San Diego: Academic press; 1998. p. 95,98,120,258,367.

13 Society of Explosive Engineers. The world of explosives – history of explosives and blasting. [Online]. 2006 [cited 2010 Jan 10]; Available from: URL:http://www.explosives.org/HistoryofExplosives.htm

14 International Mine Action Standards. Safety and occupational health - Storage, transportation and handling of explosives. [Online]. 2003 Jan 1 [cited 2009 Oct 10]; Available from: URL:http://www.mineactionstandards.org/IMAS_archive/Amended/Amended3/IMAS%2010.50%20S&OH%20Storage,%20transportation%20and%20handling%20of%20explosives%20_Edition%202_.pdf

15 Patniak P. A comprehensive guide to the hazardous properties of chemical substances. 2nd ed. New York: Wiley; 1999. p. 371-373.

16 National Institute for Occupational Safety and Health. NIOSH Pocket Guide to Chemical Hazards. Cincinnati: Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health. DHHS (NIOSH) Publication 2005-149.

17 Heidem SA. Material Safety Data Sheet – Nitric oxide. [Online]. 2000 [cited 2009 Sept 16]; Available from: URL:http://www.airproducts.com

18 Kotz JC, Treichel PM. Chemistry and chemical reactivity. 5th ed. Australia: Thompson Learning; 2003. p. 907-909.

19 Martini FH, Bartholomew EF. Essentials of anatomy and physiology. 3rd ed. San Francisco: Pearson education as Benjamin Cummings; 2003. p. 237,530-31,555,589.

20 Guyton AC, Hall, JE. Textbook of medical physiology. 11th ed. China: Elsevier Saunders; 2006. p. 564.

21 Taylor DJ, Green NPO, Stout GW. Biological science. 3rd ed. Cambridge: Cambridge university press; 1997. p. 328,674.

22 Dart RC, Hurlbut KM, Kuffner EK, Yip L. The 5 minute toxicology consult. Philadelphia: Lippincott Williams+Wilkins; 2000. p. 182,542.

23 Bakke B, Ulvestad, B, Steward P, Eduard W. Cumulative exposure to dust and gases as determinants of lung function decline construction workers. Occup Environ Med. 2003 Jul 21; 61:262-69.

24 Bakke B, Ulvestad B, Stewart P, Lund MB, Eduard W. Effects of blasting fumes on exposure and short-term lung function changes in tunnel construction workers. Scand J Work Environ Health 2001;27(4):250—57.

25 Jarvis DL, Leaderer BP, Chinn S, Burney PG. Indoor nitrous acid and respiratory symptoms and lung function in adults. Thorax. 2005;60:474-79.

26 Hamid HA, El-Gazzar RM. Effect of occupational exposure to ammonia on enzymatic activities of catalase and mono amine oxidase. Egypt Public Health Assoc. 1996;71(5-6):465-75.

27 Holness DL, Lynde CB, Obadia M, Liss GM, Ribeiro M, Tarlo SM. Cutaneous and respiratory symptoms among professional cleaners. Occup Med. 2009 Jun;59(4):249-54.

28 Yadav JS Kaushik VK. Genotoxic effect of ammonia exposure on workers in a fertilizer factory. Indian J Exp Biol. 1997 May;35:487-92.

29 Issley S, Lang E. Toxicity, Ammonia. [Online]. 2009 [cited 2009 Oct 13]; Available from: URL:http://emedicine.medscape.com/article/820298-overview

30 Department of Minerals and Energy. South Africa. Mine Health and Safety Regulations (GN R904, 2 Jul 2002 as last amended by GN R94, 1 Feb 2008). Accessed on 26 Apr 2010. Pretoria: Government Printer.

31 Mainiero RJ, Harris ML and Rowland JH. Dangers of toxic fumes during blasting. National Institute for Occupational Safety and Health (NIOSH) [Online]. 2006 [cited 2009 Apr 15];
Available from: URL:http://www.cdc.gov/niosh/mining/pubs/pdfs/dotff.pdf

32 Eltschlager KK, Shuss W and Kovalchuk TE. Carbon Monoxide Poisoning at a Surface Coal Mine - A Case Study. National Institute for Occupational Safety and Health (NIOSH) [Online]. 2006 [cited 2009 Apr 13]; Available from: URL:http://www.arblast.osmre.gov/downloads/OSM%20Reports/ISEE%202001-CO3.pdf

33 Mainero J. A technique for measuring toxic gases produced by blasting agents. National Institute for Occupational Safety and Health (NIOSH) [Online]. 2006 [cited 2009 May 16];
Available from: URL:http://www.cdc.gov/niosh/mining/pubs/pdfs/tfmt.pdf

34 Sapko M, Rowland J, Mainero RJ and Zlochower I. Chemical and physical factors that influence NO_x production during blasting – exploratory study. National Institute for Occupational Safety and Health (NIOSH) [Online] 2006 [cited 2009 Jun 10]; Available from: URL:http://www.cdc.gov/niosh/mining/pubs/pdfs/capft.pdf

35 Department of Labour. South Africa. Occupational Health and Safety Act and its regulations. 23 Jun 1993. Accessed on 25 Apr 2010. Pretoria: Government Printer.

36 Department: Minerals and Energy South Africa. Overview of the minerals industry. [Online]. 2009 [cited 2010 Jan 26]; Available from: URL:http://www.dme.gov.za/minerals/mineral_info.stm

37 Index Mundi. Minerals produced in South Africa. [Online]. 2009 [cited 2010 Jan 27]; Available from: URL:http://www.indexmundi.com/minerals/?country=za&graph=production

38 South Africa info. Mining and minerals in South Africa. [Online]. 2009 [cited 2010 Jan 26]; Available from: URL:http://www.southafrica.info/business/economy/sectors/mining.htm

39 United States Environmental Protection Agency. Nitrogen dioxide – An Introduction to indoor air Quality. [Online]. 2009 [cited 2010 Jan 27]; Available from: URL:http://www.epa.gov/iaq/no2.html

40 Shamase B. Material Safety Data Sheet – Expanfo 300 [MSDS]. South Africa; 2009. Print Date: 09/07/2009. Revision Date: 09/07/2009. Version 1.00.

41 Pike J. Global Security. Explosives - ANFO (Ammonium Nitrate - Fuel Oil). [Online]. 2009 [cited 2010 Jan 28]; Available from: URL:http://www.globalsecurity.org/military/systems/munitions/explosives-anfo.htm

42 Death toll rises to 104 in coal mine blast. China Daily 2009 Nov 23; [Online]. 2009 [cited 2010 Jan 29]; Available from: URL:http://www.chinadaily.com.cn/china/2009-11/23/content_9020827.htm

43 Yinan H.. Hope fades for trapped miners in Xintai. China Daily 2007 Aug 22; [Online]. 2009 [cited 2010 Jan 29]; Available from: URL:http://www.chinadaily.com.cn/china/2007-08/22/content_6035739.htm

44 De Souza E, Katsabanis, PD, Roberts W, Heidrich H. Proceedings of the 6th US mine ventilation symposium. 6th. Ed. Utah (Salt Lake City): Littleton Colo; 1993.

45 Holness DL, Purdham JT, Nethercott JR. Acute and chronic respiratory effects of occupational exposure to ammonia. Am Ind Hyg Assoc J. 1989 Dec;50(12):646-50.

46 Welch A. Exposing the dangers of anhydrous ammonia. The nurse practitioner. 2006 Nov;31(11):40-45.

47 Pritchard JD. Ammonia – Toxicological overview. Health protection agency. [Online]. 2007 [cited 2010 Feb 10]; Available from: URL:www.hpa.org.uk/web/HPAwebFile/HPAweb_C/1194947398510

48 Salocks C, Kaley KB. Technical Support Document: Toxicology - Clandestine Drug Labs: Methamphetamine. Office of Environmental Health Hazard Assessment. [Online]. 2003 [cited 2010 Feb 8]; Available from: URL:http://oehha.ca.gov/public_info/pdf/TSD%20Methamphetamine%20Meth%20Labs%2010%278%2703.pdf

49 Pritchard JD. Ammonia – Incident management. Health protection agency. [Online]. 2007 [cited 2010 Feb 10]; Available from: URL:www.hpa.org.uk/web/HPAwebFile/HPAweb_C/1194947405180

50 World Bank Group. Pollutant prevention and abatement handbook – Nitrogen oxides. [Online]. 1998 [cited 2010 Feb 15]; Available from: URL:http://www.ifc.org/ifcext/enviro.nsf/AttachmentsByTitle/p_ppah_pguiNitrogenOxides/$FILE/HandbookNitrogenOxides.pdf

51 Roberts M. Department of Minerals and Energy – Directorate mineral economics. South Africa's mineral production and sales – 1985 to 2004. [Report]. South Africa: Department of Minerals and Energy; 2005 Sept.

52 Masetlana TR, Dlambulo N, Themba LA, Mwape P, Mabuza M, Bonga M. Department of Minerals and Energy – Directorate mineral economics. South Africa's mineral industry – 2007/2008. [Report]. South Africa: Department of minerals and energy; 2008 Dec.

53 Dahmann D, Morfeld P, Monz C, Noll B, Gast F. Exposure assessment for nitrogen oxides and carbon monoxide in German hard coal mining. Int Arch Occup Environ Health. 2009 Apr 8;82:1267–1279.

54 George MW. U.S. Geological Survey, Mineral Commodity Summaries - Platinum–Group Metals. [Online]. 2007 Jan. [cited 2010 Feb 19]; Available from: URL:http://minerals.usgs.gov/minerals/pubs/commodity/platinum/platimcs07.pdf

55 George MW. U.S. Geological Survey, Mineral Commodity Summaries - Mineral Resources Program. [Online]. 2008 Jan. [cited 2010 Feb 19]; Available from: URL:http://minerals.usgs.gov/minerals/pubs/commodity/platinum/mcs-2008-plati.pdf

56 Brautbar N, Wu M, Richter E. Chronic Ammonia Inhalation and Interstitial Pulmonary Fibrosis: A Case Report and Review of the Literature. Arch of Environ Health. 2003 September;58:592-96.

57 Bai Z, Dong Y, Wang Z, Zhu T. Emission of ammonia from indoor concrete wall and assessment of human exposure. Environ Int. 2006; 32:303–11.

58 Graham JA, Grant LD, Folinsbee LJ, Kotchmar DJ, Garner JHB. World Health Organization / International Programme on Chemical Safety. Environmental Health Criteria 188. Nitrogen oxides. [pamphlet] 1997.

59 Department of Labour. South Africa. Regulations for Hazardous Chemical Substances (GN R1179, 25 Aug 1995 as amended by GN R930, 25 Jun 2003 and GN R683, 27 Jun 2008. Accessed on 25 Apr 2010. Pretoria: Government Printer.

60 National Institute for Occupational Safety and Health. NIOSH Pocket Guide to Chemical Hazards. Cincinnati: Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health. DHHS (NIOSH) Publication 2005-149.

CHAPTER 3

ARTICLE

ARTICLE

This article is to be submitted for publication in **Occupational Health Southern Africa**, which is on the list of approved South African Journals. Occupational Health Southern Africa is the official journal of the South African Society of Occupational Health Nursing Practitioners (SASOHN), the South African Society of Occupational Medicine (SASOM), the Southern African Institute for Occupational Hygiene (SAIOH) and the Mine Medical Professionals' Association (MMPA).

GUIDELINES FOR AUTHORS

Guidelines for articles categories:

- Original and review

  The article should follow the following format of: Introduction, Methodology, Results, Discussion, Conclusions, Recommendations and References. Whilst the length should be between 2000 and 2500 words, the inclusion of this article will exceed the word allocation set out in the guidelines. The article must include a short abstract of less than 150 words.

References

References should be inserted in the text as superscript numbers and listed at the end of the article in numerical order. References should be set out in Vancouver style and only approved abbreviations of journal titles should be used.

Manuscript

The manuscript should be typed in 1.5 spacing, using only one side of the paper. Pages should be numbered consecutively and leave wide margins. Scientific measurements should be expressed in S.I. units. Abbreviations and acronyms should only be used if absolutely necessary and must be defined on first use. Illustrations, tables and graphs should be clearly identified and should be submitted separate to text in electronic format. They should be clearly identified and not embedded in MS Word documents. Tables should use Arabic numerals, 1, 2, 3, etc. and illustrations Figure 1, 2, 3, etc.

Author's details

A separate title page should contain the title, the author(s)' full names and contact details relevant to correspondence and the author(s)' place of work and job designation. A word count should be included on this page.

Exposure of workers to ammonia and oxides of nitrogen from blasting fumes in an underground mining setup

Daniel Christiaan Cronje, Michiel Nicolaas van Aarde, Anja Franken

School of Physiology, Nutrition and Consumer Sciences,
North-West University, Potchefstroom Campus,
South Africa

Corresponding Author:
Mr. D.C. Cronje
School of Physiology, Nutrition and Consumer Sciences
North-West University, Potchefstroom Campus
Private Bag X6001
Potchefstroom
South Africa
2520
Tel: +27 18 294 8159
Fax: +27 18 294 8159
E-mail: 20095112@nwu.ac.za

Word Count: 3520

ABSTRACT

The prevalence of mine workers being exposed to ammonia (NH_3) and oxides of nitrogen (NO_x) from blasting fumes in an underground mining setup was investigated. The general objective was to determine the exposure of underground mine workers to NH_3 and $NO_{x,}$ 12 hours after the previous blast, as well as the variance between parallel measurement methods. A study group of 20 underground mine workers and a control group of 10 surface workers were examined. Measurements were determined by active air sampling and passive diffusive sampling at the same time. Active sampling for a duration of 180 minutes, time weighted to an 8-hour exposure, indicated that occupational exposure to blasting fumes of underground mine workers responsible for charge up did not exceed the OELs. Passive diffusive sampling for a duration of 180 minutes, time weighted to an 8-hour exposure, indicated that occupational exposure to blasting fumes of three underground mine workers responsible for charge did exceed the OELs. Underground mine workers and surface workers had similar exposure to nitric oxide (NO) and nitrogen dioxide (NO_2) over an 8-hour work shift, starting 12 hours after the previous blast. There was a significant, positive correlation ($r = 0.827$) between personal exposure to NH_3 between the two measurement methods. The correlation between personal exposures to NO_2 was positive ($r = 0.624$), but insignificant and had a strong agreement between the two measurement methods.

INTRODUCTION

Underground blasting operations in a mine produce both toxic and non-toxic gaseous products; the toxic products being mainly the oxides of nitrogen (NO_x), ammonia (NH_3) and carbon monoxide (CO).[1,2] The exposure of workers to CO produced as a by-product during blasting operations were not monitored in the present study due to limited availability and practicality of sampling equipment. There are limited occupational exposure data available on the excessive exposure to gasses associated with the use of explosives or so-called “gassing cases” in an underground mining setup. Occupational hygiene measurements must therefore be conducted by the employer to ensure that requirements are met and also to improve the working conditions of underground mine workers handling these explosives, thus minimizing their potential exposure to NO_x and NH_3.[3]

Underground mine workers handling explosives are potentially exposed to blasting fumes on a daily basis and cumulative exposure is therefore a major risk factor for decreasing their lung function.[4] Exposure to blasting fumes may also cause nasal mucosal swelling and increased levels of exhaled NO, indicating signs of upper and lower airway inflammation.[5] Accelerated decline in forced expiratory volume in one second (FEV_1), a higher prevalence of cough during the day, shortness of breath with exercise, chest tightness and wheezing is also associated with exposure to blasting fumes.[6]

The primary explosive used for underground blasting in the mine under study is Ammonium Nitrate Fuel Oil (ANFO) and the chemical reaction that takes place during blasting is as follows:[7]

$$C_nH_{2n+2} + (3_{n+1})NH_4NO_3 \longrightarrow nCO_2 + (7_{n+1})H_2O + 3nN_2$$

The orange or red colouration or cloud of the blasting fumes is caused by the presence and in effect the excessive production of NO_2 and is also produced in the after burning reactions and by the secondary oxidation of NO to NO_2.[8,9] NO can combine with the water (H_2O) in the lungs to form nitrous acid[10] or bind with haemoglobin in the blood to form methemoglobin, affecting the transportation of oxygen to body tissues and organs.[11] Handling of NH_3 could possibly have a detrimental effect on electrical stability, permeability and fluidity of membranes, thus causing the brain and liver to be more susceptible to hepatotoxic and neurotoxic alterations.[12]

The aims of the study were to determine the exposure of mine workers to NO_x and NH_3 from blasting fumes 12 hours after the previous blast, while determining the variance between parallel measurements by means of approved conventional measurement methodologies at the same time.

METHODOLOGY

Representative measurement sites and workplaces were selected in order to provide significant data for epidemiological purposes.

Research setting

The research was conducted at a Platinum mine in the Bushveld indigenous complex. The mine under study operates two vertical shafts, shaft A and shaft B. The research was conducted on different levels of shaft A to accomplish a representative of that specific shaft.

Research design

A quantitative design was used to determine the occupational exposure of mine workers to NO_x and NH_3 from blasting fumes and ANFO fumes respectively, starting 12 hours after the previous blast. Personal exposure was determined over a period of 180 minutes and then time weighted to an 8-hour value in order to compare the results with Occupational Exposure Limits (OELs) with the assumption that the workers' exposure during the remainder of the work shift was limited. The difference between parallel measurements by means of approved conventional measurement methodologies was also determined.

Sampling strategy

It was decided to use mine workers from four different levels on shaft A. Each level was then divided into two regions namely North and South. The total production area consisted of 114 mine workers. This group was then divided into two groups being Cheesa Stoping which was 90 workers and Cheesa Developing which was 24 workers. Cheesa workers were responsible for loading the boreholes with explosives. Underground mine workers and control subjects were then identified and divided into three groups. Group A was 10 cheesas working in the stope (CS A). Group B was 10 cheesas working on development (CD B) and group C was 10 office workers working on the surface of the mine (CG C), but who were not exposed to explosives. Due to time constraints to complete the sampling and work-related limitations limiting the amount of sampling media, the number of subjects was limited to 10 per group. A number of 10 subjects per group were seen as a limitation in the present study, due to the probability of including the highest risk worker in these 10 subjects. This limitation will be discussed in Chapter 5.

After having the aims and objectives of the study explained to each worker, informed consent was obtained from everyone.

Personal active air sampling assessment

Personal air sampling was conducted in accordance with National Institute for Occupational Safety and Health (NIOSH) 6014 and NIOSH 6015 methods.[16,17] Personal exposure was determined by sampling ten workers in each of the three different groups (n=30) for a period of 180 minutes, but this was dependant on the time it took to charge up the boreholes with explosives, also known as charging up.

Ammonia

NIOSH 6015 sampling method was used to determine to exposure of each worker to ammonia. Each worker was fitted with a battery operated personal air sampling pump (Gilair) which was calibrated to the specified airflow of 0.150 l/min. The sampling pump was then fitted to the belt of each worker and the sorbent tube was placed in the breathing zone on the left side of the mine workers collar. One sorbent tube containing silica gel treated with sulphuric acid was used at a time and fitted before charge up took place. After the mine workers finished with the charge up, the sampling train was then removed, sealed and transported to the surface. Post flow calibration was done and the sorbent tubes were then stored at 5 ºC. The sorbent tubes were then sent to an accredited laboratory for analysis. Two field blank samples were used and analyzed for NH_3.

Sensidyne's Gilian Gilibrator-2 with a Gilian low flow cell (1 to 250 cc/min) was used to calibrate the personal air sampling pump to 0.150 l/min. Calibration was done with the representative sampler in line by breaking off the ends of the sorbent tube immediately before sampling and attaching it to the sampling pump via flexible tubing. The flow rate was measured three times and an average of the three was used to acquire the specified airflow of 0.150 l/min.

Oxides of nitrogen

NIOSH 6014 sampling method was used to determine to exposure of each worker to oxide of nitrogen. Each worker was fitted with a battery operated personal air sampling pump (Gilair) which was calibrated to the specified airflow of 0.025 l/min. The sampling pump and the sorbent tubes were placed as mentioned above. Three sorbent tubes in series were used each time; nitrogen dioxide (NO_2) was collected in the first tube treated with triethanolamine and was thereby separated from nitric oxide (NO) by a second tube treated with an oxidizer and collected on the third tube which is also treated with triethanolamine. The sampling train was fitted and removed and all procedures were done as mentioned above. Two field blank samples were used and analyzed for both NO and NO_2.

Calibration of the sampling pump to the specified airflow of 0.025 l/min was done as mentioned above.

Passive diffusive air sampling assessment

Passive diffusive air sampling was conducted using a diffusive sampler developed by Radiello. Personal exposure was determined by sampling twelve underground mine workers (n=12).

The adsorbing cartridge for NH_3 is made of microporous polyethylene impregnated with phosphoric acid. NH_3 is chemically adsorbed as ammonium ions and then quantified by visible spectrometry as indophenols. The adsorbing cartridge for NO_2 is made of mycroporous polyethylene coated with triethanolamine (TEA). NO_2 is chemically adsorbed onto the TEA as nitrite and then quantified by visible spectrophotometry. The cartridge was placed into a diffusive body and attached to the supporting plate and labelled with a self adhesive sticker all developed by Radiello. The diffusive sampler was then fitted in the breathing zone on the right side of the mine workers' collar. One diffusive sampler was used at a time and fitted before charge up took place. After the mine workers finished with the charge up, the diffusive sampler was removed and placed into a tube and sealed. The label was then removed and attached to the corresponding tube. The diffusive samplers were then sent to an accredited laboratory for analysis.

No calibration was required for passive diffusive air sampling assessments using the Radiello sampling equipment.

Statistical analysis

Data were analyzed by using statistical software which included Microsoft Excel and Statistica Nine. The data was non-parametric and a Kruskal-Wallis test was therefore performed in order to determine if there was any statistical significant difference between the three different groups regarding their occupational exposure. All differences were evaluated at a significance level of 0.05. Statistical analysis also included basic statistics such as mean, correlation, standard deviation and variation. Limits of agreement between active and passive sampling were also determined.

RESULTS

Personal sampling of three blasting fumes was conducted in different areas of vertical shaft A of a local platinum mine. A total of 30 samples were collected for NH_3, NO and NO_2 by means of active sampling. A total of 12 samples were collected at the same time for NH_3 and NO_2 from passive diffusive sampling.

Personal active air sampling

Table 1: Time weighted average (TWA) exposure of Cheesa Stoping (CS A), Cheesa Development (CD B) and Surface workers (CG C) to NH_3 and NO_x generated as by-products during blasting, measured by means of active sampling as a single exposure measurement, (n=30).

		Ammonia (NH_3)	**Nitric Oxide (NO)**	**Nitrogen Dioxide (NO_2)**
	OEL-TWA (mg/m^3)	**17**	**30**	**5**
	Sample number (n=30)	**TWA (mg/m^3)**	**TWA (mg/m^3)**	**TWA (mg/m^3)**
Cheesa Stoping (CS A)	1	0.381	0.039	0.060
	2	2.382	0.042	0.065
	3	7.339	0.071	0.066
	4	0.709	0.040	0.061
	5	1.084	0.043	0.067
	6	0.491	0.042	0.065
	7	0.873	0.041	0.063
	8	4.095	0.043	0.041
	9	1.046	0.043	0.066
	10	5.395	0.040	0.061
Mean (mg/m^3) (n=10)		**2.379**	**0.044**	**0.061**
Cheesa Development (CD B)	1	0.833	0.041	0.063
	2	0.028	0.042	0.065
	3	0.027	0.041	0.063
	4	0.600	0.040	0.062
	5	0.658	0.040	0.062
	6	0.028	0.043	0.066
	7	0.487	0.043	0.065
	8	1.492	0.038	0.058
	9	2.283	0.041	0.063
	10	2.633	0.042	0.064
Mean (mg/m^3) (n=10)		**0.907**	**0.041**	**0.063**
Surface Workers (CG C)	1	0.024	0.034	0.053
	2	0.025	0.038	0.059
	3	0.027	0.043	0.065
	4	0.025	0.037	0.057
	5	0.028	0.037	0.057
	6	0.028	0.042	0.064
	7	0.027	0.044	0.067
	8	0.028	0.042	0.064
	9	0.029	0.043	0.066
	10	0.027	0.043	0.067
Mean (mg/m^3) (n=10)		**0.027**	**0.040**	**0.062**

The TWA personal exposure to NH_3 and NO_x of Cheesa Stoping (CS A), Cheesa Development (CD B) and Surface workers (CG C) is shown in Table 1. Cheesa Stoping (CS A) had a mean TWA exposure of 2.379 mg/m^3 (± 2.419) for NH_3, 0.044 mg/m^3 (± 0.009) for NO and 0.061 mg/m^3 (± 0.007) for NO_2 respectively. Cheesa Development (CS B) had a mean TWA exposure of 0.907 mg/m^3 (± 0.936) for NH_3, 0.041 mg/m^3 (± 0.001) for NO and 0.063 mg/m^3 (± 0.002) for NO_2 respectively. Surface Workers (CG C) had a mean TWA exposure of 0.027 mg/m^3 (± 0.001) for NH_3, 0.040 mg/m^3 (± 0.003) for NO and 0.062 mg/m^3 (± 0.005) for NO_2 respectively.

Table 1 indicate that the TWA personal exposure to NH_3, NO and NO_2 of Cheesa Stoping (CS A), Cheesa Development (CD B) and Surface workers (CG C) were lower than the OELs of the Mine Health and Safety Regulations of the Mine Health and Safety Act (Act No. 29 of 1996). None of the mine workers' exposure among the three groups exceeded the OEL-TWA or the action level for these three blasting fumes. The Kruskal-Wallis test indicated that there was a significant difference ($p = 0.001$) between the three different groups regarding their exposure to NH_3, but the Kruskal-Wallis test indicated no statistical difference ($p = 0.164$, $p = 0.372$) between the exposure to NO or NO_2 respectively among the three different groups.

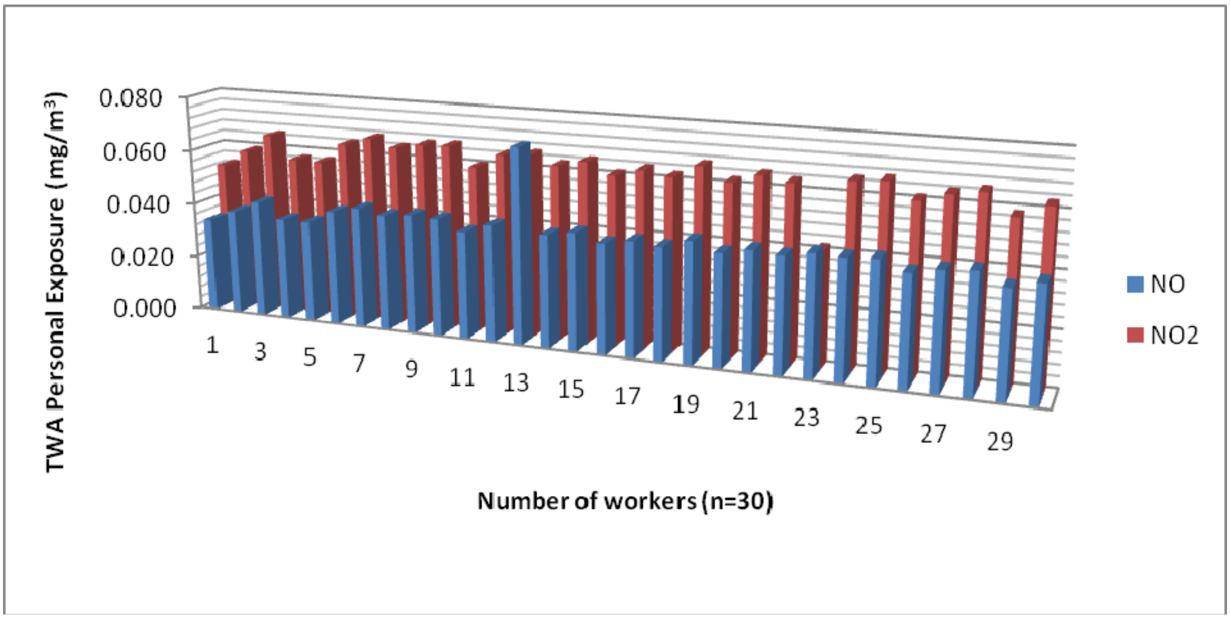

Figure 1: TWA personal exposure of Cheesa Stoping (CS A), Cheesa Development (CD B) and Surface workers (CG C) to NO and NO_2 generated as by-products during blasting measured by means of active sampling as a single exposure measurement, (n=30)

There is a significant, positive correlation ($r = 0.994$) between personal exposure to NO and NO_2 measured by means of active sampling as shown in Figure 1. There were no other significant correlations between personal exposures of the remaining blasting fumes.

Passive diffusive air sampling

Table 2: TWA exposure of Cheesa Stoping (CS A) and Cheesa Development (CD B) to NH_3 and NO_2 generated as by-products during blasting, measured by means of passive diffusive sampling as a single exposure measurement, (n=12)

	Ammonia (NH_3)	**Nitrogen Dioxide (NO_2)**
OEL-TWA (mg/m^3)	**17**	**5**
Sample number (n=12)	**TWA (mg/m^3)**	**TWA (mg/m^3)**
1	0.094	0.008
2	44.955	0.035
3	1.612	0.013
4	5.135	0.050
5	5.709	0.008
6	0.880	0.011
7	0.758	0.055
8	43.129	0.023
9	1.185	0.032
10	5.208	0.008
11	1.025	0.017
12	24.116	0.038
Mean(mg/m^3) (n=12)	**11.151**	**0.025**

The TWA personal exposure to NH_3 and NO_2 of Cheesa Stoping (CS A) and Cheesa Development (CD B) is shown in Table 2. The underground mine workers had a mean TWA exposure of 11.151 mg/m^3 (± 11.708) for NH_3 and 0.025 mg/m^3 (± 0.017) for NO_2 respectively.

Table 2 indicate that the mean TWA personal exposure to NH_3 is lower than the OEL of the Mine Health and Safety Regulations of the Mine Health and Safety Act (Act No. 29 of 1996), although three mine workers' exposure did exceeded the OEL-TWA. The highest level of exposure to NH_3 was 44.955 mg/m^3, while the lowest exposure to NH_3 was 0.094 mg/m^3. The mean TWA measured for NO_2 was lower than the OEL of the Mine Health and Safety Regulations of the Mine Health and Safety Act (Act No. 29 of 1996). None of the mine workers exceeded the OEL-TWA or the action level for NO_2. The highest level of exposure to NO_2 was 0.055 mg/m^3, while the lowest exposure to NO_2 was 0.008 mg/m3. The Kruskal-Wallis test indicated no statistical difference between the exposure to NH_3 or NO_2 between the three different groups.

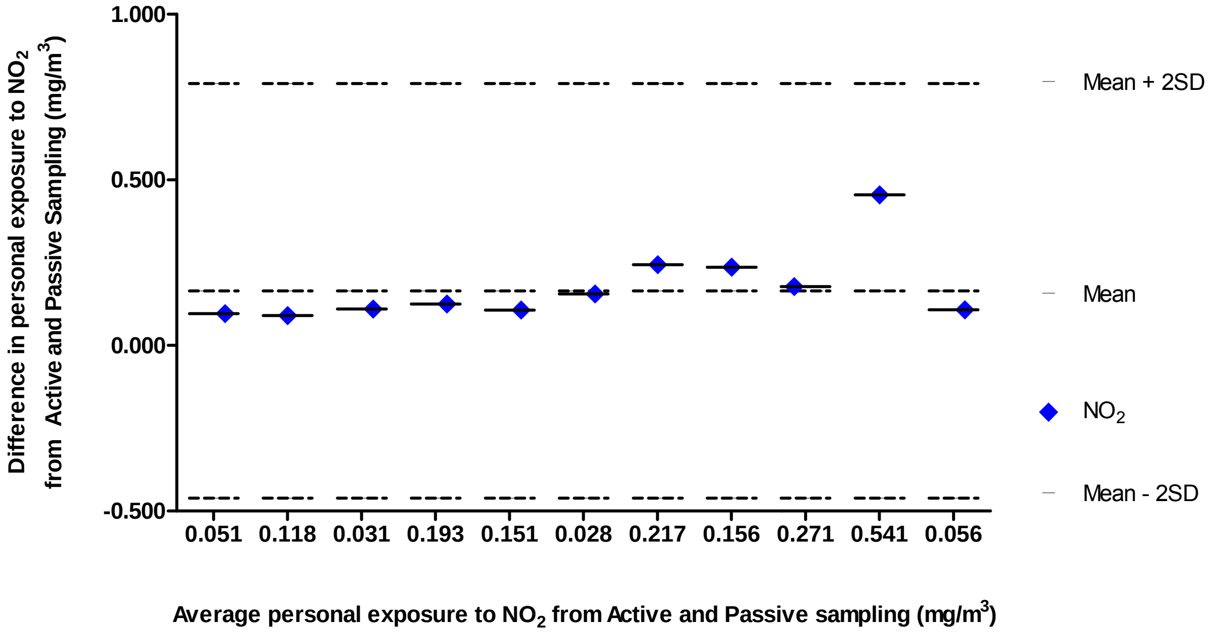

Figure 2: Limits of agreement between TWA personal exposure of Cheesa Stoping (CS A) and Cheesa Development (CD B) to NO_2 measured by active (n=12) and passive diffusive (n=12) sampling.

Figure 2 represents a Bland-Altman plot showing a comparison of personal exposure to NO_2 measured by active and passive diffusive sampling. The mean difference is 0.165 mg/m^3 with 95% confidence interval of 0.112 mg/m^3 to 0.234 mg/m^3. The limits of agreements are 0.791 mg/m^3 and 0.461 mg/m^3.

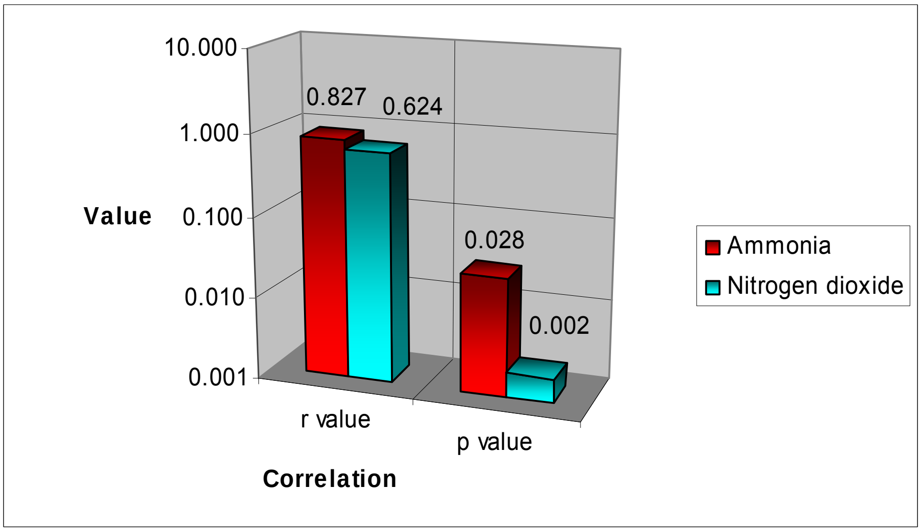

Figure 3: Positive correlation between TWA personal exposure of Cheesa Stoping (CS A) and Cheesa Development (CD B) to NH_3 and NO_2 measured by active (n=12) and passive diffusive (n=12) sampling.

Figure 3 reflects a significant correlation between personal exposure measured by active and passive diffusive sampling of NH_3 and NO_2. Both NH_3 (r = 0.827) and NO_2 (r = 0.624) indicated a positive correlation between the two different methods of determining exposure.

DISCUSSION

Studies indicate that underground mine workers handling explosives are potentially exposed to blasting fumes on a daily basis and cumulative exposure is therefore a major risk factor for decreasing their lung function.[4] Exposure to blasting fumes may also cause nasal mucosal swelling and increased levels of exhaled NO, indicating signs of upper and lower airway inflammation.[5]

Table 3: Components of blasting fumes' levels (TWA) recommended for human health [3,18]

	Mine Health and Safety Regulations, (Act No. 29 of 1996),	**American Industrial Hygiene Association (AIHA)**	**American Conference of Governmental Industrial Hygienists (ACGIH)**	**National Institute for Occupational Safety and Health (NIOSH)**	**Occupational Safety and Health Administration (OSHA)**
Blasting fumes	**mg/m^3**	**mg/m^3**	**mg/m^3**	**mg/m^3**	**mg/m^3**
Ammonia	17	17	17	17	35
Nitric oxide	30	-	31	31	31
Nitrogen dioxide	5	2	6	4	9

Note: There are no OELs specifically for blasting fumes

Active air Sampling

The TWA exposure to the blasting fumes measured by active sampling is lower than the South African legislation, as well as international OELs as depicted in Table 1 and Table 3. The measured concentrations complied with the OELs of the Mine Health and Safety Regulations, AIHA, ACGIH, NIOSH and OSHA.[3,18] This is an indication that the current 8-hour OELs do, in fact, offer adequate protection for underground mine workers handling explosives. None of the underground mine workers' exposure exceeded the action level. Although the average exposure over a period of 8-hours was lower than the OELs and action level, it must be emphasized that the short term exposure limit (STEL) is still unknown and it cannot be assumed that the STELs were not exceeded.

The low 8-hour TWA exposure to blasting fumes could be a result of the underground mine workers' shift starting 12 hours after the previous blast, which resulted in sampling determining the background levels of blasting fumes the workers were being exposed to. The effectiveness of the ventilation system will also cause the blasting fumes to be diluted to very low concentrations before it reaches the mine workers' breathing zone.

The TWA exposure to NH_3 determined by active sampling shows a statistical difference between the two different groups. There was a significant difference ($p = 0.001$) between surface workers' (CG C, n=10) exposure and underground mine workers' exposure (CS A, CD B, n=20) to NH_3. Underground mine workers had a higher TWA mean exposure to NH_3 and this could be due to the handling of ANFO as expected. Exposure to NH_3 could cause inhibition in the activity of catalase enzymes, as well as an increase in the frequency of chromosome aberrations and sister chromatid exchanges.[12,14] NH_3 could also react with tissue water to form a strong alkaline solution ammonium hydroxide. This alkaline solution causes severe alkaline chemical burns to skin, eyes and respiratory system.[11,15] Thus, the occupational exposures of underground mine workers to NH_3 at the time of the study may have an adverse effect on their skin, eyes and respiratory system. Although the mean TWA is lower than legislative requirements, it is still necessary to determine the cumulative exposure of underground mine workers to NH_3. Cumulative exposure carries a great risk because employees could be exposed to high levels on a day- to-day basis over an extended period of time. This could lead to serious health effects mentioned previously.

The TWA exposure to NO_x determined by active sampling show no statistical difference between the exposure of Cheesa Stoping (CS A), Cheesa Development (CD B) and Surface workers (CG C). These results could be due to the high humidity and temperature at the time of the survey, which caused the mine workers to sweat profusely during their work shift. Underground mine workers also use water for drilling, as well as for controlling the dust generation during the charge up process. This led to many of the NO_x sorbent tubes being wet during sampling and made it difficult to analyze. The effectiveness of the ventilation system will also cause the blasting fume levels to be diluted to very low concentrations before it reaches the mine workers' breathing zone.

The TWA exposure showed no statistical difference between surface workers' (CG C, n=10) exposure and underground mine workers' exposure (CS A, CD B, n=20) to NO and NO_2 and could be due to the fact that there were no formation of NO and NO_2 during the charge up phase and the results obtained were NO_x in the background concentrations from blasting fumes from the previous blast. This limitation is explained in detail in Chapter 4.

There was a significant, positive correlation ($r = 0.994$) between personal exposure to NO and NO_2 measured by means of active sampling as indicated by Figure 1. This correlation could be a result of the chemical reaction taking place when NO or NO_2 is produced. A deficiency of oxygen favours the formation of carbon monoxide and produces little, if any, NO_x. An excess of oxygen produces more NO_x and less carbon monoxide.[7] This indicates that workers who were exposed to NO, were likely to be exposed to NO_2 as well, as indicated by the positive correlation. All of the subjects were exposed to both NO and NO_2 and had the same risk regarding their exposure. There were no other significant correlations between personal exposures of the remaining blasting fumes.

Passive Diffusive Sampling

If the TWA exposure of each worker to NH_3 measured by passive diffusive samplers is individually compared to OELs, three individuals exceeded the OELs (17 mg/m^3) of the Mine Health and Safety Regulations of the Mine Health and Safety Act (Act No. 29 of 1996), AIHA, ACGIH and NIOSH.[3,18] Three underground mine workers also exceeded the OSHA limits of 35 mg/m^3.[18] Control methods should therefore be implemented in the area where charge up takes place to eliminate or minimize the exposure of underground mine workers to NH_3. Underground mine workers handling explosives should always be aware of the risk involved in the exposure to NH_3 and act accordingly to help prevent further exposure by following safe work procedures. Evaluating the current charge up procedure and using a better quality explosive is only one of the engineering control measures that can be implemented to help minimize the exposure to NH_3. Adequate supply of information and training of underground mine workers to handle explosives could also be implemented to minimize exposure. Underground mine workers were exposed to a wide range of concentration with the highest level of exposure to NH_3 being 44.955 mg/m^3, while the lowest exposure to NH_3 being 0.094 mg/m^3.

The TWA exposure to NO_2 measured by passive diffusive sampling was lower than South African legislation, as well as international OELs as depicted in Table 2 and Table 3.

There was a strong agreement between personal exposure to NO_2 measured by means of active sampling and passive diffusive sampling as indicated by Figure 2. Bland-Altman plot indicated that passive diffusive sampling tends to give a lower reading, by between 0.112 mg/m^3 to 0.234 mg/m^3, but the limits of agreement were small enough to be confident that passive diffusive sampling can be used in place of active sampling.

The correlation between personal exposures to NO_2 measured by means of active sampling and passive diffusive sampling as indicated by Figure 3 was positive ($r = 0.624$), but not significant. This correlation could be a result of the high humidity, as well as their work shift starting 12 hours after the previous blast, which resulted in sampling determining the background levels of blasting fumes the workers were being exposed to. This study should be repeated with the tube holder measuring NO_x fitted with a dehumidifier at the distal end to prevent the sorbent tubes getting damp from the high humidity.

There was a significant, positive correlation ($r = 0.827$) between personal exposure to NH_3 measured by means of active sampling and passive diffusive sampling as indicated by Figure 3. This correlation could be a result of the NH_3 samples not being affected by the relative high humidity of the underground mining environment, thus ensuring the accuracy of the samples taken. This also proves that the two conventional approved methodologies are adequate to determine the exposure of underground mine workers to NH_3.

Results also indicated no statistical difference between the exposures of underground mine workers to blasting fumes between the four different levels which were identified and measured. The exposure of underground mine workers was therefore the same and was not influenced by the level where work was being done. This could be due to the ventilation system working properly in all different levels.

To minimize the production of NO_x and NH_3, the boreholes must be properly loaded with the appropriate amount, composition and proportion of ANFO.[8,9] Blasting off-shift or at restricted times, removing the fumes through local exhaust systems or auxiliary ventilation (dilution ventilation) could also be implemented for the control of blasting fumes.[13]

CONCLUSION

This study concludes that the TWA occupational exposure to NH_3, NO and NO_2 measured by active sampling of underground mine workers at a platinum mine in South Africa did not exceed the OELs of the Mine Health and Safety Regulations, AIHA, ACGIH, NIOSH or OSHA. Passive diffusive sampling indicated that the TWA occupational exposure to NH_3 of three underground mine workers responsible for charge did exceed the OELs of the Mine Health and Safety Regulations, AIHA, ACGIH, NIOSH or OSHA..However, this study does not exclude the short term exposure to very high concentrations exceeding legislation requirements. There was a significant, positive correlation in personal exposures to NH_3 between the two measurement methods. The correlation in personal exposures to NO_2 was positive, but not significant, with a strong agreement between personal exposure to NO_2 measured by means of active sampling and passive diffusive sampling as depicted in Figure 3. The correlation in parallel measurements of personal exposure by means of the active sampling and passive diffusive sampling were strong and indicated that any of these two approved conventional measurement methodologies could be used to determine the exposure of underground mine workers to NH_3 or NO_2, taking into account the influence of humidity on NO_2 sampling and the numerous limitations of active sampling.

REFERENCES

1 Mainiero RJ, Harris ML and Rowland JH. Dangers of toxic fumes during blasting. National Institute for Occupational Safety and Health (NIOSH) [Online]. 2006 [cited 2009 Apr 15];
Available from: URL:http://www.cdc.gov/niosh/mining/pubs/pdfs/dotff.pdf

2 Harris ML, Mainiero RJ. Monitoring and removal of CO in blasting operations. Saf Sci 2008;(46): 1393–1405.

3 Department of Minerals and Energy. South Africa. Mine Health and Safety Regulations (GN R904, 2 Jul 2002 as last amended by GN R94, 1 Feb 2008). Accessed on 26 Apr 2010. Pretoria: Government Printer.

4 Bakke B, Ulvestad B, Stewart P, Eduard W. Cumulative exposure to dust and gases as determinants of lung function decline in tunnel construction workers. Occup Environ Med 2004;(61):262-69.

5 Ulvestad B, Lund MB, Bakke B, Djupeslandz PG, Kongerud J, Boe J. Gas and dust exposure in underground construction is associated with signs of airway inflammation. Eur Respir J 2001;(17): 416–21

6 Ulvestad B, Bakke B, Melbostad E, Fuglerud P, Kongerud J, Lund, MB. Tunnel workers are at increased risk of obstructive pulmonary disease. Thorax. 2000 Jan 7;55:277-82.

7 Pike J. Global Security. Explosives - ANFO (Ammonium Nitrate - Fuel Oil). [Online]. 2009 [cited 2010 Jan 28]; Available from: URL:http://www.globalsecurity.org/military/systems/munitions/explosives-anfo.htm

8 Mainiero RJ, Harris ML, Rowland JH. Dangers of toxic fumes during blasting. National Institute for Occupational Safety and Health (NIOSH) [Online]. 2006 [cited 2009 Apr 15]; Available from: URL:http://www.cdc.gov/niosh/mining/pubs/pdfs/dotff.pdf

9 Eltschlager KK, Shuss W, Kovalchuk TE. Carbon Monoxide Poisoning at a Surface Coal Mine - A Case Study. National Institute for Occupational Safety and Health (NIOSH) [Online]. 2006 [cited 2009 Apr 13]; Available from: URL:http://www.arblast.osmre.gov/downloads/OSM%20Reports/ISEE%202001-CO3.pdf

10 Jarvis DL, Leaderer BP, Chinn S, Burney PG. Indoor nitrous acid and respiratory symptoms and lung function in adults. Thorax. 2005;60:474-79.

11 Patniak P. A comprehensive guide to the hazardous properties of chemical substances. 2nd ed. New York: Wiley; 1999. p. 371-373.

12 Hamid HA, El-Gazzar RM. Effect of occupational exposure to ammonia on enzymatic activities of catalase and mono amine oxidase. Egypt Public Health Assoc. 1996;71(5-6):465-75.

13 De Souza E, Katsabanis, PD, Roberts W, Heidrich H. Proceedings of the 6th US mine ventilation symposium. 6th. Ed. Utah (Salt Lake City): Littleton Colo; 1993.

14 Yadav JS Kaushik VK. Genotoxic effect of ammonia exposure on workers in a fertilizer factory. Indian J Exp Biol. 1997 May;35:487-92.

15 Issley S, Lang E. Toxicity, Ammonia. [Online]. 2009 [cited 2009 Oct 13]; Available from: URL:http://emedicine.medscape.com/article/820298-overview

16 National Institute for Occupational Safety and Health. Manual of Analytical Methods (NMAM), Fourth Edition. Cincinnati: Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health. DHHS (NIOSH) Publication NIOSH 6014 (NO_x)

17 National Institute for Occupational Safety and Health. Manual of Analytical Methods (NMAM), Fourth Edition. Cincinnati: Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health. DHHS (NIOSH) Publication NIOSH 6015 (Ammonia)

18 National Institute for Occupational Safety and Health. NIOSH Pocket Guide to Chemical Hazards. Cincinnati: Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health. DHHS (NIOSH) Publication 2005-149.

CHAPTER 4

METHODS FOR MEASURING MINE BLASTING FUMES

METHODS FOR MEASURING MINE BLASTING FUMES

1. Introduction

Traditional techniques for the experimental determination of toxic fumes produced by the detonation of high explosives are not applicable to blasting agents, because of the lack of practicality when it comes to the underground mining conditions. Alternative techniques are therefore required for the experimental determination of the exposure of underground mine workers to blasting fumes. Underground mine workers handling explosives are potentially exposed to blasting fumes on a daily basis. These blasting fumes in an underground mine produced by blasting operations includes both oxides of nitrogen (NO_x), ammonia (NH_3) and carbon monoxide (CO). These blasting fumes are highly toxic to the human body and can have a negative effect on the health of the human body.[8,9] It is therefore important to determine the exposure of underground mine workers to blasting fumes on a regular basis. Although these by-products of blasting can be measured individually by means of approved NIOSH methods, these measuring methods do not provide adequate techniques for the sole purpose of measuring blasting fumes as a whole. There is currently no known method for measuring blasting fumes as a whole and this chapter discusses a proposed method for measuring blasting fumes as a whole, thus intensifying and adapting the existing NIOSH method of each individual fume.

A study done by Mainiero used the following procedure to develop a technique for measuring toxic gases produced by blasting agents.[1] He built a chamber for detonating explosives under controlled environments. After detonation of the explosive, a fan was run for approximately 10 minutes to uniformly mix the atmosphere in the chamber. NO_x and NH_3 were taken out of the chamber through a 0.6-cm Teflon sampler hole to minimize loss of these constituents to absorption on the tube surface. These sampler bags were then sent away for analysis. Vacutainer samples were also taken and sent to the analytical laboratory for analysis; but this technique was not amenable to analysis for NO_x and NH_3 and these were instead absorbed into chemical solutions in bubbler trains.[1] Although this is a technique developed to measure toxic gases produced by blasting agents, this technique is not sufficient to determine the personal exposure of underground mine workers to blasting fumes as a whole, because the underground mine workers are not allowed underground for a minimum of three hours after the detonation took place. Measuring the personal exposure of underground mine workers to blasting fumes as a whole can only be achieved by developing a technique that is specific and practical to blasting fumes measurements during routine underground work being performed by underground mine workers. By obtaining accurate and specific data regarding the exposure of underground mine workers to blasting fumes, only then can precise and inaugurated results be concluded, as well as abatement of NH_3 emissions. This could have a very positive impact on the way blasting fumes are perceived today and lead to a better understanding of the dangers and risks involved in the handling, storage, transportations and better control of explosives. The health and safety of each individual mineworker is very important and should always be a top priority when investigating the working environment of explosive handling. To better understand the control measurements that are needed for the minimization and possible elimination of blasting fumes, it is necessary to begin at the root of the problem to better understand the workings of blasting fumes. A thorough and updated evaluation of NH_3, NO_x and CO measurement techniques related to blasting fumes will benefit users and researchers in selecting, employing, and developing such methods.

2. Previous studies

In none of the following studies that are presented here were NH_3, NO_x and CO measured simultaneously for the sole purpose of measuring the exposure of workers to blasting fumes in an underground mining setup.

2.1 Ammonia

In a previous study done by Rahman, Bratveit and Moen, they measured personal exposure to NH_3 during a full shift using a PAC III direct reading instrument and DrÃger diffusion tubes.[10]

Although Bai et al did not measure personal exposure to NH_3, they did measure NH_3 in ambient air using a KC-6D atmosphere sampler developed by Qingdao Lao Mountain electronic instrument factory in China. This atmospheric sampler was used for sampling and determining of NH_3 in chambers or rooms.[10]

Suh et al have done a study to determine the personal exposure to NH_3 of children living in Pittsburg. Personal sampling was done by attaching a personal monitor to the shoulder strap of a backpack containing padding. Each personal monitor also required the use of a sampling pump and a battery pack. The children were instructed to carry the sampler throughout the sampling period which started at 8 am in the morning and ended at 8 pm in the evening. Each child was monitored twice on two different days. Personal samples were collected at a flow rate of 4 l/min using the personal annular denuder system (PADS). This PADS consists of an inlet, two impactor plates, two coated multi annular denuders and three-stage filter pack connected in series. NH_3 was collected on the second denuder, which is coated with citric acid in a glycerol/methanol solution. After sampling was completed, the denuders were extracted with 5 mL of ultrahigh-purity water and analyzed using ion chromatography.[12]

Table 6: An overview of techniques applied to measure NH_3 concentrations [13]

Method	**Sampling / measuring device**
Wet Chemistry	Titrimetry Photometry & colorimetry Conductimetry pH paper pHydrion test strips Ammonia Quick Test
Gas detection tubes	Dräger tube Kitagawa tube Gastec tube Sensidyne tube MSA tube SKC 226-10-06
Fourier Transform Infrared Spectroscopy (FTIR)	M 2401 Spectrometer K300 Spectrometer Bomen-100 Spectrometer
Non-dispersive Infrared analyzer	PAS Type 1302 Rosemount; Beckman
Ultra Violet - Differential optical absorption spectroscopy system	Opsis monitor WSU system
CL NO_x analyzer	Monitor-Labs analyzer THIS analyzer Thermo Environmental analyzer API analyzer
Electrochemical sensor	Dräger sensor Quadscan gas monitor Twistik Transmitter
Chemcassette Monitor	Single Point Monitor
Solid-state sensor	Solidox sensor IMEC sensor

2.2 Oxides of nitrogen

In a previous study done by Ulvestad and Bakke, they measured NO_2 with a direct reading instrument: Neotox-xl personal single gas monitor developed by Neotronics. Electrochemical sensors with a data logging facility were built into the direct reading instrument and calibrated with gases of known concentrations every two months. A sampling rate of one reading every two minutes was selected.[2]

Another study was also done by Ulvestad and Bakke to determine the exposure of underground construction workers to NO and NO_2. They used the same sampling method for NO_2 as mentioned in the previous study, but only calibrated the sensors every three months. For personal air sampling of NO, they used a chemiluminescence's analyser: LR 2000 developed by Logan Research. The sampling rate of the analyser for all measurements was set to 250 ml/min. The analyser was calibrated on a daily basis using certified NO mixtures of 100 parts per billion (ppb) in nitrogen. Ambient air sampling of NO was also recorded on a daily basis. Exhaled and nasal measurements of NO were also performed in accordance with recommendations outlined in the European Respiratory Society's Task Force Report. This report indicates that measurements were made through a Teflon mouthpiece by slow exhalation of 20 – 30 s from total lung capacity. A mild resistance of mouth pressure of 4 to 5 cmH_2O were also implemented during exhalation to avoid nasal NO contamination. End-expiratory NO values were measured at the plateau level of the last part of the exhalation curve. The subject was required to hold his/her breath, while a Teflon tube was inserted into one of the nares (nostrils or nasal passages) and the values of the last plateau part of the trace were recorded. Three technically acceptable measurements were obtained for both exhaled and nasal measurements of NO and the mean of the two closest measurements was reported.[3]

The use of passive samplers to sample NO_2 where only used in two studies. Both these studies used Palmes' diffusive sampler (diffusive sampler incorporating a fixed path length) to determine NO_2 concentrations. Palmes' diffusive sampler is based on the principle of molecular diffusion. Its response to fluctuating concentrations can be analysed theoretically using a mathematical method defined by Hearl and Manning to resolve Fick's second law of diffusion.[4,5]

In a former study Dahmann et al used chemoluminescence devices that were more sensitive for NO_x in low exposure environments such as workshops. However, they concluded that these chemoluminescence devices could generally not be applied in mining because of explosion hazards and the extremely rough environmental conditions prevailing in most workplaces in an underground mining setup.[6] They also reported that if a person carried a gas sensor developed by Multiwarn, it cannot be used according to well established standardized procedures, because these gas sensors are characterized by a relative sturdy design, but low sensitivity. To guarantee their proper use, very high quality control efforts are also needed, because cross sensitivities between some of the components like NO, CO and humidity may play a part.[6] It is therefore necessary to put special emphasis on the calibration procedures and use commercially available calibration gases to calibrate the instruments in the laboratory. A direct reading instrument with a data logging facility was also used to sample NO and NO_2. A sampling rate of one reading every minute was chosen.[7]

2.3 Carbon monoxide

Carbon monoxide can be measured by means of two approved conventional measurement methodologies. The first method incorporates the use of a small portable instrument that measures the concentration of CO in exhaled air at any given time, being at the beginning or at the end of a work shift. A very accurate instrument that can be used to measure the amount of CO in exhaled air is demonstrated a study which used a portable Bedfont EC50 analyzer developed by Bedfont Technical Instruments Ltd in the United Kingdom. Subjects were asked to exhale fully, inhale deeply and hold their breath for 20 seconds before exhaling rapidly into a disposable mouthpiece. This procedure was repeated three times, with 1 minute of normal breathing between each repetition. The mean value was used for analysis. Prior to the start of the study, the analyzer was calibrated with a mixture of 50 ppm CO in air. Exhaled CO concentration measured by the Bedfont EC50 analyzer correlated closely with blood carboxyhemoglobin concentration over the range of values encountered in smokers and non-smokers, as well as the cigarette consumption.[14]

Wilson and Monster also used a direct reading instrument containing electrochemical sensors to determine CO in exhaled air. This sampling method involved breathing directly into an electrochemical detector through a nasal catheter. The instrument automatically measured CO, as well as carbon dioxide (CO_2), in exhaled air. They also used a diode laser as a direct reading instrument to determine CO in exhaled air. A Diode laser is a multicomponent gas analyser based on tunable diode lasers and uses lead salt diode lasers of different spectral regions from 4 μm to 12 μm that operate at liquid nitrogen temperatures. The technique might have applications in the biomedical area for the simultaneous detection of gases such as CO, NH_3, and NO.[15] The use of indirect methods generally involves collecting and trapping the breath sample and subsequently transferring it to an analytical instrument for analysis. A 500 ml Mylar bag could be used as a device. Sampling should be done by using reheated cell methanol or Fourier transform infrared. This method has a detection limit of 0.2% for CO. It is moderate easy to use and is commercially available.[15]

Mainero and Harris used Testo 3501 electrochemical cell-based gas analyzers (direct reading instrument) to determine periodical concentration of CO, NO and NO_2. The instruments were allowed to sample for more than 2 min at a rate of 1.2 l/min.[16]

Another study measured CO in ambient air using 2 different instruments. The first instrument was a battery-operated electrochemical sensor with data logging functions developed by Dräger, while the second instrument was a CO passive diffusion (colour stain) tube also developed by Dräger. In addition to the area monitoring, personal exposure was also determined using a passive diffusive Dräger CO tube. The passive diffusive CO tube was attached to the clothing in the chest area and worn by the mother and her child.[17]

Alm et al have also reported that personal CO measurements were carried out with a passive electrochemical monitor (Personal Alarm Monitor model 2140) developed by Interscan Corporation, California, USA. The monitor was connected to a data logger (Digital Data Recorder) also developed by the same company. The monitor continuously stored 1-min average values with each reading. All the monitors were zeroed on a daily basis and calibrated weekly with bottled CO gas.[18]

Harrison et al used infrared spectrophotometer (TECO model 48C) to measure CO in ambient air. Personal exposure to CO was monitored with a sampling pump drawing air at a constant flow rate of 75 ml/min for one hour periods into 5 litre gas bags. Particles were removed using a PTFE filter. The bags were worn around the waist with inlets were attached to the breathing zone. After collection, the air was analysed with the TECO model 48C analyser, providing an average CO concentration for the hour's sampling.[19]

3. Ammonia: NIOSH 6015 [20]

3.1 Sampling and measurement

The sampler used is a sulphuric acid treated silica gel sorbent tube with a flow rate of 0.1 to 0.2 l/min. A minimum and maximum volume of 0.1 L and 96 L should be sampled. Samples should be analyzed by visible absorption spectrophotometry. The precision for this method is not yet determined and no interference has been identified.

3.2 Equipment

- A 37-mm cellulose ester membrane filter can be used as a prefilter to remove particulate interferences
- 6.0 cm long sulphuric acid-treated silica gel sampling tubes
- Personal sampling pump calibrated to 0.1 to 0.2 l/min
- Flexible tubing and a stopwatch

3.3 Sampling technique

- Each personal sampling pump should be calibrated with the representative sampler in line.
- Sample at a known flow rate between 0.1 and 0.2 l/min for a total sample size of 0.1 to 96 L.
- Cap the sampling tubes with plastic caps immediately after sampling.
- Pack securely for routine shipment.

4. Nitric oxide and nitrogen dioxide: NIOSH 6014 [21]

4.1 Sampling and measurement

The sampler used for this method contains 3 sorbent tubes. The first sorbent tube is an oxidizer and the remaining 2 sorbent tubes are triethanolamine-treated (TEA) molecular sieve sorbent tubes. When sampling nitric oxide individually, the method requires a flow rate of 0.025 l/min, but when sampling nitric oxide and nitrogen dioxide simultaneously, a flow rate of 0.025 to 0.200 l/min is required. A minimum and maximum volume size of 1.5 L and 6 L should be sampled. Samples should be analyzed by visible absorption spectrophotometry. The precision for this method is 0.061 for nitric oxide and 0.026 for nitrogen dioxide respectively. Any compound which reacts with the colorimetric reagents will interfere.

4.2 Equipment

- Three sorbent tubes (SKC-226-40). Tube A and C: 400 mg TEA molecular sieve, Tube B: 800 mg chromate oxidizer.
- Personal sampling pump calibrated to 0.025 to 0.200 l/min
- Flexible tubing and a stopwatch

4.3 Sampling technique

- Each personal sampling pump should be calibrated with the representative sampler in line.
- Immediately before sampling, break ends of sampler and attach to pump. Nitrogen dioxide collects on the first tube (Tube A) and is thereby separated form nitric oxide, which is oxidized by Tube B and then collected on Tube C.
- Sample at an accurate flow rate of 0.025 l/min for a total sample size of 1.5 to 6 L.
- Cap the sampling tubes with plastic caps immediately after sampling.
- Pack securely for routine shipment.

5. Carbon monoxide: NIOSH 6604 [22]

5.1 Sampling and measurement

The sampler used for this method is a portable direct reading CO monitor with built in data logging facilities. The minimum and maximum volume is dependent on the instrument itself and therefore irrelevant. Samples should be analyzed with an electrochemical sensor built into the monitor itself. The precision for this method is 0.035 at 20 ppm, 0.012 at 50 ppm and 0.008 at 100 ppm. NO_2 and SO_2 may cause interference at levels over 5 ppm. If these gasses are present, a monitor with a chemical interference scrubber over the sensor should be used.

5.2 Equipment

- Carbon monoxide monitor: Envirocheck I single sensor CO Monitor (Quest Technologies) or
- MiniCO (MSA) or
- Electrochemical CO monitor with equivalent performance specifications
- Personal sampling pump, 0.250 l/min, with inlet and outlet, used for bag filling and sample analysis when off-site analysis is needed
- Air bags, aluminized, 2-L, or other appropriate sizes (optional)
- Replacement batteries or battery charger appropriate for monitor

5.3 Sampling technique

- If possible, zero the CO monitor in CO-free air at the same temperature and relative humidity as the work environment. Note: Monitors are more sensitive to temperature variations than to humidity variations, but most monitors have temperature compensating circuitry.
- For personal monitoring, locate the monitor as near to the worker's breathing zone as possible.
- For area monitoring, locate monitor in an area with good air circulation about 1.5 to 1.7 meters above the floor. Note: Make sure that the sensor is not obstructed in either of the two applications.

6. Limitations between NIOSH 6014, NIOSH 6015 and NIOSH 6604 methods [20,21,22]

The methods prescribed by NIOSH are sufficient for measuring NH_3, NO_x and CO as individual gases, but when it comes to blasting fumes there is a lack of practicality when measuring NH_3, NO_x and CO at the same time. NIOSH 6014 and NIOSH 6015 indicate that a very low flow rate should be used during the sampling period, thus requiring the use of a low flow module which is mounted on top of the sampling pump. NIOSH 6604 on the other hand doesn't require the use of any flow rate, because it is not necessary for air to flow through a sampling media. This forces the researcher to use two different approved conventional measurement methodologies to measure these three gases at the same time. In terms of financial reasons this could be a possible drawback. NIOSH 6014 and NIOSH 6015 requires the use of flexible tubing with a smaller diameter and is not readily available as it should be.

NIOSH 6014 and NIOSH 6015 requires the use of a low flow calibrator to calibrate the sampling pumps and could be a possible problem when finances are limited due to the fact that it has to be bought separately. NIOSH 6604 requires that the CO monitor should be calibrated with a standard calibration mixture of CO in air from a pressurized cylinder at the CO level recommended by the monitor manufacturer. This is normally 20 to 50 ppm CO. The monitor should be calibrated at the temperature and relative humidity as near as possible to that of the work environment in which it will be used. Calibration should be checked daily and recalibrated whenever the monitor reading varies from the span gas by 5% or more. This forces the researcher to use two different calibration procedures to calibrate these three instruments at the same time.

NIOSH 6014 and NIOS 6015 requires the use of a double tube holder for simultaneous sampling of blasting fumes, because NH_3 should be sampled in the one tube holder, while NO_x is being sampled in the other tube holder. The tube holder which samples NO_x contains three sorbent tubes connected in series to each other and in effect makes the tube holder 25 cm long and very impractical because the tube holder can't be placed in the breathing zone of the mineworker. The two tube holders are also very large and uncomfortable. The use of a double tube holder, combined with low flow rate, makes it very difficult to calibrate the sampling pumps to the desired flow rate because of the sensitivity of the double tube holder to adjust the flow rate at very low flow rates. Although NIOSH methods are individually tested for reproducibility, combining two NIOSH methods could lead to complications during the use of double tube holders set at a low flow rate. NIOSH 6604 doesn't require any tube holder, but only requires the sensor to be attached in the worker's breathing zone.

Performing hard labour underground is already a strain on the human body. Sampling methods and instruments should therefore be ergonomically designed not to interfere with a worker's normal working regime during the sampling period. A lot of the workers complained about the size and number of instruments they had to wear during the sampling period, because many of them were working in the stoping area and by attaching a double tube holder with a sampling pump, as well as passive diffusive samplers in their breathing zone complained that it would interfere with their range of movement in an already confined space during work. It is therefore very important to keep in mind the conditions the workers have to endure while working underground, all the while when they have to wear sampling media at the same time. As a result sampling media should be small, light and ergonomical and should interfere as little as possible with the range of motion of the worker.

According to NIOSH 6014 and NIOSH 6015 when sampling NH_3 and NO_x simultaneously, the average time of sampling should be 180 minutes and should never exceed 240 minutes at any time because of the possibility of a breakthrough occurring on one of the sorbent tubes. Depending on the time it takes to charge up the rock face with explosives, this is not efficient to determine the exposure of the mine workers over a full work shift of 8 hours. The charge up of the rock face with explosives usually takes about 120 to 180 minutes, thus leaving approximately a period of six hours when no explosives are handled. During this period of six hours, the exposure to ANFO fumes would be minimal, because of the explosives only arriving at the site of charge up right before charge up takes place. This required us to identify 180 minutes where exposures to blasting fumes were at a maximum and then time weighted the concentration to an 8-hour TWA to compare results with available OELs. The OEL-TWA according to the Mine Health and Safety Regulations of the Mine Health and Safety Act (Act No. 29 of 1996) for NH_3, NO, NO_2 and CO is as follows: 17 ppm for NH_3, 30 ppm for NO, 5 ppm for NO_2 and 50 ppm for CO.[23] This OEL-TWA is determined over an 8 hour period. Although the results obtained were time weighted to an 8-hour TWA, the results are not a true representation of a full working shift of 8 hours. Rather than time weighting the OEL to an 8-hour TWA, the researcher recommends that a new OEL-TWA is determined over a period of 240 minutes by using Brief and Scala method. Exposure of workers to blasting fumes in an underground mining setup could then be measured for a maximum of 240 minutes and compared to a new established OEL as mentioned previously.

The researcher found it unnecessary to measure blasting fumes over a period of 8 hours, because the exposure to blasting fumes is only limited to 240 minutes at a time, during which the charge up usually takes place. By measuring an underground mineworker for a period of 240 minutes and comparing it to a 4h OEL-TWA will ensure that a more accurate representation of the exposure to blasting fumes is reported. As indicated by NIOSH 6014 and NIOSH 6015, it is therefore impossible to measure blasting fumes over a period of 8 hours, because there will always be the possibility of a breakthrough occurring on the tubes, which will cause inaccurate results. One solution would be the use of two sets of sorbent tubes, but due to financial limitations, this option was not available for this present study. It is highly recommended by the researcher that a new occupational exposure limit specific for blasting operations, for a period of 240 minutes it approximately takes for charge up to take place, is determined and implemented in the applicable legislation like the Mine Health and Safety Regulations. Exposure of workers to blasting fumes in an underground mining setup could then be compared to these new OELs.

After sampling took place and the samples were sent to the laboratory, it was noted that many of the NO_x sorbent tubes where completely wet due to the underground conditions. The high humidity underground, together with water being used for drilling, as well as controlling the dust generation during the charge up process resulted in NO_x sorbent tubes being wet and difficult to analyze. The temperature was also high and the mine workers sweated profusely during their working shift

Blasting fumes are unique in the sense because of the surrounding circumstances they are usually produced in. Underground mining environments are confined spaces and in conditions where ventilation are limited and humidity and temperatures are usually high, it is necessary to implement a different perspective when sampling blasting fumes as a whole.

7. Differences between NIOSH 6014, NIOSH 6015 and NIOSH 6604[20,21,22]

Table 7: Differences between NIOSH methods for measuring blasting fumes

	NIOSH 6015 Ammonia	**NIOSH 6014 Nitric oxide and Nitrogen dioxide**	**NIOSH 6604 Carbon monoxide**
Method	Sorbent tubes	Sorbent tubes	Direct reading instrument
Sample stability	Not determined	Stable for 7 days at 25 ºC	Stable for 7 days at 25 ºC
Blanks	2 to 10 field blanks per set	3 to 6 field blanks per set	Fresh air or compressed CO-free air from cylinder
Range study	Not studied	NO: 11-48 ppm for 1.5 L sample NO_2: 2-12 ppm for 3 L sample	0 – 200 ppm
BIAS	Not determined	NO: 1.4% NO_2: -2%	- 1.7%
Overall precision	Not determined	NO: 0.083 NO_2: 0.063	0.022
Accuracy	Not determined	NO: 20.4% NO_2: 14.6%	6.0%

As seen from Table 7, there is very limited information about the sampling method of NH_3 (NIOSH 6015) and this should be resolved by obtaining results where information is lacking. By gaining more information about the sampling method of NH_3, only then can an accurate comparison of the three methods be made, but until then it remains uncertain which method is sufficient for measuring blasting fumes. There is ample information about the sampling method of oxides of nitrogen and this is due to the fact that more research has been done on the exposure assessment of workers to NO_x, than NH_3. There is also insufficient information about the sampling methods for CO as well as the effects of exposure on the human body.

8. Alternative methods for measuring blasting fumes

8.1. Solid sorbent tubes

When solid sorbent tubes are the only option available to the researcher as in this case, it is advisable to do the following. An underground mine worker's full shift consists of approximately 8 hours, although the physical handling and charge up with explosives only last about a maximum of 180 minutes. Rather than using one set of solid sorbent tubes to identify when the mine workers maximum exposure to blasting fumes will be, use two sets of solid sorbent tubes for a period of 240 minutes each. If the aim of the study were to compare occupational exposure levels to existing legislation, the problem is solved by combining the two concentrations together for an 8-hour TWA. It is therefore not recommended to identify a maximum period of exposure to blasting fumes and time weighting it to an 8-hour TWA, because this will not be representative of a full shifts work activities. The same method as described in NIOSH 6014, NIOSH 6015 and NIOSH 6604 should be used.

Workers are handling explosives in a non consistent manner and it is therefore not advisable to measure blasting fume exposure with solid sorbent tubes, because this will only give the TWA exposure of each mineworker and not a STEL value. This method should only be used when no other options are available to the researcher and is therefore not recommended for measuring the exposure of workers to blasting fumes in an underground mining setup.

8.2. Direct reading instruments

The best method for measuring blasting fumes in an underground mining setup would be to use a direct reading instrument fitted with electrochemical sensors with built in data logging facilities. The researcher recommends the use of a miniRAE 3000 portable monitor developed by RAE systems. It is very tough, waterproof, lightweight and has an extended range between 0 and 15 000 ppm,. Before sampling takes place, the researchers should identify which blasting fumes have to be sampled. By identifying these blasting fumes, the researcher is then able to determine and install the necessary electrochemical sensors for each blasting fume. This direct reading instrument will be able to sample for the whole duration of the full work shift. By adjusting the settings on the direct reading instrument to measure a reading every 15 seconds for 480 minutes, a representation of the full day's work can be achieved. By downloading these measurements to a computer and plotting it on a graph, a very fair representative of not only the TWA could be determined, but also the STEL values. Only by means of this measuring technique can an accurate exposure assessment be made.

8.3. Exhaled air

Another method for measuring the exposure of underground mine workers to CO are the use of biological sampling. Exhaled air at the end of the shift can also be measured by means of a direct reading instrument measuring CO in exhaled air. These direct reading instruments are very accurate. It is also very simple and easy to use and readings can be done quickly. The direct reading instruments are rather expensive and will be limited to the funds available.

8.4 Passive samplers

When the researcher decides to make use of passive samplers to determine blasting fumes in an underground mining setup, it is recommended that an adsorbing cartridge fitted into a diffusive body, which is screwed onto a supporting plate and labelled with a self adhesive sticker is used. Each worker should then be fitted with the diffusive sampler developed by Radiello. The adsorbing cartridge for NH_3 is made of microporous polyethylene impregnated with phosphoric acid and the adsorbing cartridge for NO_2 is made of mycroporous polyethylene coated with triethanolamine (TEA). These diffusive samplers only measure NH_3 and NO_2 at present, but with further advances in technology, it will soon be possible to measure CO and NO as well. These diffusive samplers will be able to sample for the whole duration of the work shift. A time saving aspect of using a diffusive sampler is that no calibration is required. Another advantage of the diffusive technology used is that the effect of temperature, humidity and air speed has little effect on the sampling-rate of the compound of interest, or can be compensated for, e.g. temperature for NO_2 sampling. The diffusive sampler should then be fitted in the breathing zone on the right side of the mineworker's collar. One diffusive sampler was used at a time and fitted before charge up took place. After the mine workers finished with the charge up, the diffusive sampler should be removed and placed into a tube and labelled. The Radiello diffusive samplers should then be sent to an accredited laboratory for analysis.

The researcher recommends that a direct reading instrument should be used to measure blasting fumes in the future. The use of passive diffusive samplers could also be used to determine the exposure of underground mine workers to blasting fumes. Direct reading instruments are more expensive than passive diffusive samplers, but if this option is available to the researcher, it is recommended that direct reading instruments are used because they can detect low concentrations without being exhausted. Both these methods are also very user-friendly and very easy to use, especially when considering the underground mining setup, because both of these instruments are waterproof. Both these methods also have a very good accuracy, as long as the correct sampling procedure is followed.

9. Conclusion

Although NIOSH methods are up to standard to measure a great deal of different fumes, the limitations of these methods for the experimental determination of the exposure of underground mine workers to blasting fumes as a whole are numerous. Without robust actions to specify an alternative method for measuring blasting fumes as a whole, we must rely on the current methods to provide us with adequate information about the blasting process and the exposure of underground mine workers to blasting fumes as a whole. It remains to be seen whether the occupational health and safety (OH&S) professionals will drive this issue any further than in the past. At the same time, the OH&S networks (NIOSH, OSHA, ACGIH) that have evolved through the regional initiatives can hopefully advance OH&S professional training through their combined efforts at national and international level. If, in ten years from now, there are still only these methods available to measure blasting fumes, occupational hygiene measurement to determine blasting fume exposure will indeed be a 'nice to have' and not be a priority.

10. References

1. Mainero J. A technique for measuring toxic gases produced by blasting agents. National Institute for Occupational Safety and Health (NIOSH) [Online]. 2006 [cited 2009 Sept 23]; Available from: URL:http://www.cdc.gov/niosh/mining/pubs/pdfs/tfmt.pdf

2. Ulvestad B, Bakke B, Melbostad E, Fuglerud P, Kongerud J, Lund, MB. Tunnel workers are at increased risk of obstructive pulmonary disease. Thorax. 2000 Jan 7; 55:277-82.

3. Ulvestad B, Lund MB, Bakke B, Djupeslandz PG, Kongerud J, Boe J. Gas and dust exposure in underground construction is associated with signs of airway inflammation. Eur Respir J. 2001 Sept 14;17:416–21.

4. Oglesby L, Künzli N, Monn C, Schindler C, Ackermann-Liebrich U, Leuenberger P, and the SAPALDIA Team. Validity of annoyance scores for estimation of long term air pollution exposure in epidemiologic studies. Am J of Epidemiol. 2000; 152:75–83.

5. Jarvis DL, Leaderer BP, Chinn S, Burney PG. Indoor nitrous acid and respiratory symptoms and lung function in adults. Thorax. 2005; 60:474-79.

6. Dahmann D, Monz C, Sönksen H. Exposure assessment in German potash mining. Int Arch Occup Environ Health. 2007 Jun 14; 81:95–107.

7. Dahmann D, Morfeld P, Monz C, Noll B, Gast F. Exposure assessment for nitrogen oxides and carbon monoxide in German hard coal mining. Int Arch Occup Environ Health. 2009 Apr 8;82:1267–79.

8. Mainiero RJ, Harris ML, Rowland JH. Dangers of toxic fumes during blasting. National Institute for Occupational Safety and Health (NIOSH) [Online]. 2006 [cited 2009 Oct 26]; Available from: URL:http://www.cdc.gov/niosh/mining/pubs/pdfs/dotff.pdf

9. Eltschlager KK, Shuss W, Kovalchuk TE. Carbon Monoxide Poisoning at a Surface Coal Mine - A Case Study. National Institute for Occupational Safety and Health (NIOSH) [Online]. 2006 [cited 2009 Oct 25]; Available from: URL:http://www.arblast.osmre.gov/downloads/OSM%20Reports/ISEE%202001-CO3.pdf

10. Rahman H, Bratveit M, Moen BE. Exposure to ammonia and acute respiratory effects in a urea fertilizer factory. Int. J. of Occup. Med. Environ. Health. 2007 April 1; 13:153-59.

11. Bai Z, Dong Y, Wang Z, Zhu T. Emission of ammonia from indoor concrete wall and assessment of human exposure. Environ Int. 2006; 32:303–11.

12. Suh HH, Spengler JD, Koutrakls P. Personal Exposures to Acid Aerosols and Ammonia. Environ. Sci. Technol. 1992;26: 2507-17.

13. Heber AJ, Ni J. Sampling and Measurement of Ammonia Concentration at Animal Facilities – A Review. The Society for engineering in agricultural, food, and biological systems. Paper Number: 01-4090. American Society of Agricultural Engineers Annual International Meeting; 2001 July 30 – August 1; USA: Sacramento, California; 2001. p. 1-43.

14. Yamaha M, Sekizawa K, Ishizuka S, Monma M, Mizuta K, Sasaki H. Increased Carbon Monoxide in Exhaled Air of Subjects with Upper Respiratory Tract Infections. Am J Respir Crit Care Med 1998 Feb 24;158:311–14.

15. Wilson HK, Monster AC. New technologies in the use of exhaled breath analysis for biological monitoring. Occup Environ Med 1999;56:753–57.

16. Harris ML, Mainiero RJ. Monitoring and removal of CO in blasting operations. Saf Sci 2008; 46:1393–1405.

17. Naeher LP, Smith KR, Leaderer BP, Neufeld L, Mage DT. Carbon monoxide as a tracer for assessing exposures to particulate matter in wood and gas cookstove households of Highland Guatemala. Environ. Sci. Technol. 2001; 35: 575-81.

18. Alm S, Mukala K, Tiittanen P, Jantunen MJ. Personal carbon monoxide exposures of preschool children in Helsinki, Finland - comparison to ambient air concentrations. Atmos Environ 2001;35: 6259–66.

19. Harrison RM, Thornton CA, Lawrence RG, Mark D, Kinnersley RP, Ayres JG. Personal exposure monitoring of particulate matter, nitrogen dioxide, and carbon monoxide, including susceptible groups. Occup Environ Med 2002;59:671–79.

20. National Institute for Occupational Safety and Health. Manual of Analytical Methods (NMAM), Fourth Edition. Cincinnati: Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health. DHHS (NIOSH) Publication NIOSH 6015 (Ammonia)

21. National Institute for Occupational Safety and Health. Manual of Analytical Methods (NMAM), Fourth Edition. Cincinnati: Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health. DHHS (NIOSH) Publication NIOSH 6014 (NO_x)

22. National Institute for Occupational Safety and Health. Manual of Analytical Methods (NMAM), Fourth Edition. Cincinnati: Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health. DHHS (NIOSH) Publication NIOSH 6604 (CO)

23. Department of Minerals and Energy. South Africa. Mine Health and Safety Regulations (GN R904, 2 Jul 2002 as last amended by GN R94, 1 Feb 2008). Accessed on 26 Apr 2010. Pretoria: Government Printer.

CHAPTER 5

FURTHER DISCUSSION AND RECOMMENDATIONS

FURTHER DISCUSSION AND RECOMMENDATIONS

1. Introduction

A summary of the main findings, conclusions, standpoints and recommendations will be given in this chapter. This chapter will provide a better and deeper understanding of the conclusions arrived at in the previous chapters and will be used to make a final conclusion on the essence of the present study. Results will also be compared to the relevant literature. This chapter will also provide a viewpoint in retrospect of the general and specific findings and will conclude with the final synthesis of the main findings. General deficiencies in the literature will also be discussed, as well as if researchers' objectives were met. Recommendations will also be made for future studies on the occupational exposure of underground mine workers to blasting fumes and particular recommendations for the mining industry will also be made.

2. Summary of the main findings

The general aim of the present study was to determine the exposure of mine workers to NO_x and NH_3 from blasting fumes in an underground mine over an 8-hour work shift. The specific aims of this study were to:

- asses the occupational exposure by a single exposure measurement of underground mine workers' exposure to NO_x and NH_3 generated as by-products during blasting, 12 hours after the previous blast;
- determine the difference in occupational exposure levels to NO_x and NH_3 between two different groups of mine workers working underground and on the surface respectively;
- determine the difference between parallel measurements by means of two approved conventional measurement methodologies for NH_3 and NO_2.

It was hypothesised that:

- o Underground mine workers will be exposed to NO_x and NH_3 concentrations exceeding OELs during an 8-hour work shift.

Results indicated that the TWA occupational exposure to NH_3, NO and NO_2 measured by active sampling of underground mine workers complied with the OELs of the Mine Health and Safety Regulations (Act No. 29 0f 1996), AIHA, ACGIH, NIOSH and OSHA. Passive diffusive sampling indicated that the TWA occupational exposure to NH_3 of three underground mine workers responsible for charge did exceed the OELs of the Mine Health and Safety Regulations, AIHA, ACGIH, NIOSH and OSHA.[1,2] The hypothesis is thus accepted. Control methods should therefore be implemented in the area where charge up takes place to eliminate or minimize the exposure of underground mine workers to NH_3. The low 8 hour exposure is probably due to the high humidity at the time of the survey as well as the 3-hour exposure which had to be time weighted to an 8-hour value in order to comply with OEL-TWA. The effectiveness of the ventilation system will also cause the blasting fumes to be diluted to very low concentrations before it reaches the mine workers' breathing zone. It has to be emphasized that this study did not determine the STEL to blasting fumes and could therefore not exclude the short term exposure to very high concentrations exceeding legislation requirements. Cumulative exposure to low concentrations of blasting fumes should also be determined over a period of time to determine the effects of blasting fumes exposure on a day to day basis, because this could have a negative effect on the human body

The TWA exposure to NH_3 determined by active sampling show a statistical difference between the three different groups. The occupational exposures of underground mine workers to NH_3 at the time of the study may have an adverse effect on their skin, eyes and respiratory system.[3,10] According to the Kruskal-Wallis test, results indicated no statistical difference in the exposure to NO or NO_2 between the three different groups. This could be explained by the relative low concentrations the workers between the three different groups were exposed to at the time of the study.

Results also indicated a significant, positive correlation ($r = 0.994$) between personal exposure to NO and NO_2 measured by means of active sampling. This correlation could be a result of the chemical reaction taking place when NO or NO_2 is produced and the way in which NO_x is sampled in the same tube holder. Because the oxygen concentration is a constant in the formula, the amount of NO and NO_2 being produced will always be in relation to each other. This emphasises that there is a very strong relation between the exposure and not necessarily a strong agreement between them. Although there was a strong relation between the exposures, it doesn't necessarily mean that there was conformity between these two gases.

Results indicated a significant correlation between personal exposure measured by active and passive diffusive sampling of NH_3 and NO_2. Both NH_3 ($r = 0.827$) and NO_2 ($r = 0.624$) indicated a positive correlation between the two different methods of determining exposure. This proved that the two conventional approved methodologies are adequate to determine the exposure of underground mine workers to NH_3. This correlation between the two methods for measuring NO_2 was lower than for NH_3, but the limits of agreement were small enough to prove that any of the two conventional methodologies are adequate to determine the exposure of underground mineworkers.

3. Comparison with present literature

There is limited occupational exposure data available on the incidents of so-called “gassing cases”, i.e. excessive exposure to gasses associated with the use of explosives in an underground mining setup, although such cases do occur on a regular basis in an underground mining setup. If the results from this study were compared to results found in the literature, it was evident that some of the findings contradicted those found in the literature.

Although this study focused on the production of NO_x from blasting fumes, one study concluded that diesel engines were the main source of NO, while the main source of NO_2 was due to explosives.[4] This is contradicted by the present study because the mean TWA for NO_2 was lower than the OELs stipulated by legislation, although there was a definite transport, handling and storage of explosives when sampling took place.

Both NO and NO_2 are highly toxic gasses and is a strong irritant to the eyes, nose and throat.[3,5] Although this symptoms cannot be measured by means of approved conventional methodologies, a lot of the underground mine workers did indeed complain about irritation to the eyes, nose and throat which led them to cough and produce frothy sputum. This was however only an observation made by the researcher by questioning the underground mine workers during sampling. It was not determined if methemoglobinemia occurred in the underground mine workers, because no biological samples were obtained during the sampling period and the exposure to NO were also substantially low.[3] Spirometric data of the underground mine workers were not obtained and it could therefore not be concluded that the cumulative exposure to blasting fumes had an effect on their lung function.[6,7,8]

4. Conclusion

Results indicated that the TWA occupational exposure to NH_3, NO and NO_2 measured by active sampling of underground mine workers complied with the OELs of the Mine Health and Safety Regulations (Act No. 29 0f 1996), AIHA, ACGIH, NIOSH and OSHA. Passive diffusive sampling indicated that the TWA occupational exposure to NH_3 of three underground mine workers responsible for charge did exceed the OELs of the Mine Health and Safety Regulations, AIHA, ACGIH, NIOSH and OSHA.[1,2] This study however does not exclude the effect of cumulative exposure to blasting fumes over an extended period of time. Short term exposure is also a major concern when working with toxic fumes and should be determined. Blasting fumes are highly toxic and even though only three mineworkers exceeded the TWA for NH_3, the STEL could be exceeded and could lead to possible gassing incidents, although the measured concentrations of these blasting fumes do not seem to pose any short-term threat to the underground mine workers in the platinum mine.

5. Recommendations

The following recommendations are suggested to improve and retain occupational health and safety of underground mine workers handling explosives.[9]

- Manufacturers of explosives should evaluate the effectiveness of their safety programs for their explosives. The following should be used to ensure that the hazard analyses include: the examination of the quantity/distance requirements, underground setup and design, human factors and incident reports.
- Procedures, chemical hazards and safety information regarding the process should be communicated in a language that is fully understood by underground mine workers involved in transporting or handling of explosives.
- Training and certification programs for underground mine workers and supervisors using explosives should provide and demonstrate a basic understanding of explosive safety principles and job specific knowledge.
- Explosives safety programs should provide an understanding of the hazards and control if the detonation sources including foreign objects in raw materials, the use of substitute raw materials, specific handling requirements for raw materials, tools or equipment used, impingement, friction, sparking and static discharge from equipment.[9]

6. Limitations

The following limitations were experienced during this study and must be taken into consideration for future studies.

Conventional methods required:

- A very low flow rate was used during the sampling period, thus requiring the use of a low flow module.
- The use of flexible tubing with a smaller diameter is not readily available.
- The use of a low flow calibrator to calibrate the sampling pumps which is very sensitive to any interferences.
- The use of two tube holders which are 25 cm long are very impractical because the tube holder can not be placed in the breathing zone of the mineworker. By attaching a dehumidifier at the distal end to prevent the sorbent tubes getting damp from the high humidity, will further contribute to the sorbent tube not being placed in the workers breathing zone.

- Attaching a double tube holder with a sampling pump, as well as passive diffusive samplers in their breathing zone interfered with their range of movement in an already confined space during work.
- The average time of sampling should be 180 minutes and is not efficient to determine the exposure of the mine workers over a full work shift of 8 hours. Although underground mine workers responsible for charge up only works during the charge up process, they are not exposed during the remainder of the five hours. The results obtained were time weighted to an 8-hour TWA, but is not a true representation of a full work shift of 8 hours.
- Number of subjects per group should be sufficient to identify and include the maximum risk employee or at least a group of employees believed to have the greatest exposure. If a maximum risk worker cannot be selected with reasonable certainty, then it is necessary to resort to random sampling of a group of workers by means of sampling a homogeneous group of workers. This procedure involves randomly sampling of a group of subjects whose members have a similar expected exposure risk. The objective of this procedure is to select a subgroup of adequate size so that there is a high probability that the random sampling will contain at least one worker with the highest exposure.

The following recommendations are suggested to improve future studies to determine the exposure of underground mine workers handling explosives, because there is a lack of practicality when measuring blasting fumes as a whole.

- Sampling methods and instruments should therefore be ergonomically designed not to interfere with a workers normal working regime during the sampling period. Sampling media should be small, light and ergonomical and should interfere as little as possible with the range of motion of the worker.
- Rather than time weighting the OEL to an 8-hour TWA, the researcher recommends that a new OEL-TWA is determined over a period of 240 minutes using Brief and Scala method. Exposure of workers to blasting fumes in an underground mining setup could then be measured for a maximum of 240 minutes and compared to a new established OEL as mentioned previously. It is highly recommended by the researcher that a new occupational exposure limit specific for blasting operations, for a period of 240 minutes it approximately takes for charge up to take place, is determined and implemented in the applicable legislation such as the mine Health and Safety Regulations. Exposure of workers to blasting fumes in an underground mining setup could then be compared to these new OELs.

Blasting fumes are unique because of the surrounding circumstances they are usually produced in. Underground mining environments are highly confined spaces and in conditions where ventilation is limited and humidity and temperatures are usually high, it is necessary to implement a different perspective when sampling blasting fumes as a whole. Measuring blasting fumes as three separate gases could have a detrimental affect on the occupational hygiene industry and especially in the way we perceive blasting fumes.

Direct reading instruments should be used to measure blasting fumes in the future. The use of passive diffusive samplers could also be used to determine the exposure of underground mine workers to blasting fumes. Direct reading instruments are more expensive than passive diffusive samplers, but it is recommended that direct reading instruments are used because they can detect relatively small amounts, without being inundated. Both these methods are also very user-friendly, especially when considering the underground mining setup, because both of these instruments are waterproof. Both these methods also have a very good accuracy, as long as the correct sampling procedure is followed.

7. References

1. Department of Minerals and Energy. South Africa. Mine Health and Safety Regulations (GN R904, 2 Jul 2002 as last amended by GN R94, 1 Feb 2008). Accessed on 26 Apr 2010. Pretoria: Government Printer.

2. National Institute for Occupational Safety and Health. NIOSH Pocket Guide to Chemical Hazards. Cincinnati: Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health. DHHS (NIOSH) Publication 2005-149.

3. Patniak P. A comprehensive guide to the hazardous properties of chemical substances. 2nd ed. New York: Wiley; 1999. p. 371-373.

4. Dahmann D, Morfeld P, Monz C, Noll B, Gast F. Exposure assessment for nitrogen oxides and carbon monoxide in German hard coal mining. Int Arch Occup Environ Health. 2009 Apr 8;82:1267–79.

5. United States Environmental Protection Agency. Nitrogen Dioxide – An Introduction to indoor Air Quality. [Online]. 2009 [cited 2010 Jan 27]; Available from: URL:http://www.epa.gov/iaq/no2.html

6. Ulvestad B, Lund MB, Bakke B, Djupeslandz PG, Kongerud J, Boe J. Gas and dust exposure in underground construction is associated with signs of airway inflammation. Eur Respir J. 2001 Sept 14;17:416–21.

7. Bakke B, Ulvestad, B, Steward P, Eduard W. Cumulative exposure to dust and gases as determinants of lung function decline in tunnel construction workers. Occup Environ Med. 2003 Jul 21; 61:262-69.

8. Bakke B, Ulvestad B, Stewart P, Lund MB, Eduard W. Effects of blasting fumes on exposure and short-term lung function changes in tunnel construction workers. Scand J Work Environ Health 2001; 27(4):250—57.

9. United States Chemical and Hazard Investigation Safety Board. Recommendations – Sierra and explosives Manufacturers. [Online]. 2009 [cited 2010 March 21]; Available from: URL:www.csb.gov

10. Issley S, Lang E. Toxicity, Ammonia. [Online]. 2009 [cited 2009 Oct 13]; Available from: URL:http://emedicine.medscape.com/article/820298-overview