Particulate emissions and respiratory exposure to hazardous chemical substances during additive manufacturing of sand moulds

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PREFACE

This mini-dissertation is written in accordance to the requirements of the journal *Annals of Work Exposures and Health*. The style of reference therefore follows that of *Annals of Work Exposures and Health*. Chapter 3 provides the guidelines for authors and referencing style.

The outline of this mini-dissertation is as follows:

- **Chapter 1**: Provides a background on additive manufacturing (AM) as well as a problem statement, main objectives and hypotheses.
- **Chapter 2**: Literature study which provides a thorough discussion on AM, feedstock materials used, physical and chemical characteristics of the feedstock, hazardous chemical substances present during AM and their related health effects as well as particle emissions.
- **Chapter 3**: An article on respiratory exposure to respirable crystalline silica and coinciding particulate emissions during coating of silica sand for additive manufacturing.
- **Chapter 4**: An article on emissions and personal respiratory exposure to hazardous chemical substances during additive manufacturing of sand moulds.
- **Chapter 5**: A conclusion of this study which provides a summary of results, recommendations, limitations and suggestions for future studies.

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AUTHOR'S CONTRIBUTION

This study was performed by a group of researchers. The contribution of each individual is outlined on Table 1.

Table 1: Contribution of authors

NAME	CONTRIBUTION
Mr NL Matlhatsi	• Planning and design of the study. • Literature study. • Conduct monitoring, data collection and analysis, article writing and formulation of recommendations. • Writing the mini-dissertation.
Dr SJL Linde	• Supervisor. • Assisted with planning and design of the study. • Provided feedback and recommendations. • Review the mini-dissertation.
Dr S du Preez	• Co-supervisor. • Assisted with planning and design of the study. • Provided feedback and recommendations. • Review the mini-dissertation.
Mr CJ van der Merwe	• Co-supervisor. • Assisted with planning and design of the study. • Provided feedback and recommendations. • Review the mini-dissertation.

The following is a statement from the co-authors confirming their individual roles in this study:

By signing below, I declare that I have approved the article and that my role in the study as indicated above is representative of my actual contribution. I hereby give my consent that it may be published as part of Ntoko Lucas Matlhatsi's MHSc (Occupational Hygiene) mini-dissertation.

Dr SJL Linde

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SUMMARY

Title: Particulate emissions and respiratory exposure to hazardous chemical substances during the additive manufacturing of sand moulds

Background: AM (Additive Manufacturing) is a process that produces three-dimensional (3D) parts via the layering of materials. To date, there has been little research on the health risks associated with the use of this technology to produce sand moulds for metal casting. Apart from the processing steps involving the AM machine, binder jetting (BJ) of sand moulds includes an additional step which involves the coating of virgin (new) silica sand with sulphonic acid prior to the AM processes. As yet, there is also no information available on the risks concerning the coating process. Both coating and AM processes involve the handling of silica sand, which may result in personal exposure to respirable crystalline silica and particulate matter. Also, furan resin binders used during processing may cause emission of volatile organic compounds (VOCs).

Objectives: This study was aimed at determining emissions of and personal respiratory exposure to hazardous chemical substances (respirable crystalline silica, VOCs and respirable particulate matter) during various phases of AM with silica sand as well as during the coating of silica sand prior to AM.

Methodology: Analysis of bulk silica sand was performed through the characterisation of particle size and shape using Malvern Morphologi particle analyser and scanning electron microscopy (SEM) while the X-ray diffraction (XRD) process was utilised to determine elemental composition. The Aerosol Particle Counter (APC) and Condensation Particle Counter (CPC) were used to quantify emissions of 0.3 - 10 µm (APC) and 0.01 - ~ 1.0 µm (CPC) sized particles during the coating process as well as pre-processing, processing and post-processing phases. Both personal and area monitoring were performed to measure airborne concentrations of respirable crystalline silica, VOCs and respirable particulate matter during the operator's shift. Three days were allocated to monitor emissions, personal exposure and area concentrations during coating, while monitoring of the AM process was conducted over a period of five days, where three identical parts were printed.

Results: Respirable sized particles were found in all three sand types (virgin, coated and used), with virgin sand having the highest respirable content compared to other sands; d(0.9) = 3.98 ± 0.72 µm vs d(0.9) = 115.00 ± 95.15 µm and d(0.9) = 6.51 ± 2.71 µm, respectively. The quartz content for the three sand types ranged from 92.6 to 97.6%, which

made it the dominant mineral. The coating and AM machines were confirmed to emit particles 0.3 µm, 0.5 µm, 1 µm and 0.01 - ~ 1.0 µm. in size. Particulate emissions data indicated that the particle emissions for particles 0.3 µm, 0.5 µm and 1 µm and 0.01 - ~ 1.0 µm in size, increased considerably during the cleaning of the coating machine filter as well as during the opening of the bay door. The particle number concentrations of 0.3 µm, 0.5 µm, 1 µm and 0.01 - ~ 1.0 µm sized particles were higher during the third day of printing compared to the other days, as a result of increased particle number concentrations during post-processing and pre-processing. When comparing the phases, the average particle number concentration was significantly higher during pre-processing compared to other phases. There were no significant differences in emission rates (ERs) but the average ERs for particles 0.3 µm and 0.01 - ~ 1.0 µm in size were slightly higher during pre-processing followed by post-processing and then processing. Personal exposure to respirable crystalline silica during cleaning of the coating machine with compressed air exceeded the South African time weighted average occupational exposure limit-control limit (TWA OEL-CL) of 0.1 mg/m^3 (0.112 mg/m^3). During cleaning of the AM machine, personal exposure to respirable crystalline silica surpassed the action level (0.07 mg/m^3). The personal exposures to HCS (respirable crystalline silica, respirable dust and VOCs) measured during the AM processes were below 10% of their respective OELs.

Conclusion: The feedstock material used (silica sand) was regarded as a primary source of exposure. The amount of respirable sized particles found in the silica sand coupled with quartz content of > 90%, made the feedstock material a risk to the health of the AM operator. Both the cleaning methods used during coating and printing led to increased personal exposure to respirable crystalline silica. The AM operator was overexposed to respirable crystalline due to the use of compressed air to clean the filter, and was exposed to respirable crystalline silica exceeding the action level due to the use of a broom when cleaning the AM machine room. The cleaning methods were therefore classified as tasks with the highest risks. Particulate emissions were higher during pre-processing compared to other processes and is of concern since emissions of particles 0.3 µm, 0.5 µm, 1 µm and 0.01 - ~ 1.0 µm in size are a risk to the health of the AM operator as they may deposit in the alveoli, resulting in respiratory dysfunctions.

In an attempt to minimise exposure to HCSs during the AM of sand moulds, 18 recommendations were made to the AM facility. Due to overexposure caused by cleaning activities using compressed air, the key recommendation made was for the AM operator to clean the filters in an isolated glove box in order to reduce exposure to respirable crystalline silica, a confirmed human carcinogen.

Key words

Sulphonic acid coating, additive manufacturing, quartz, personal exposure, particle number concentration, emission rates

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LIST OF SYMBOLS AND ABBREVIATIONS

>	Larger than
°C	Degrees Celsius
%	Percentage
±	Plus-Minus
<	Smaller than
Δt	Change in time
3D	Three dimensional
3DP	Three-Dimensional Printing
8-hour TWA	8-hour Time Weighted Average
ABS	Acrylonitrile Butadiene Styrene
ACGIH	American Conference of Governmental Industrial Hygienists
AER	Air Exchange Rate
AM	Additive manufacturing
ANOVA	Analysis of Variance
APC	Aerosol Particle Counter
ASTM	American Society for Testing and Materials
ATSDR	Agency for Toxic Substances and Disease Registry, USA
BJ	Binder jetting
BTEX	Benzene Toluene Ethylbenzene Xylene
CAD	Computer-Aided design

CC16	Club Cell Protein 16
CEN	European Committee for Standardization
C_{in}	Average concentration of the contaminant during printing
CO_2	Carbon Dioxide
CPC	Condensation Particle Counter
C_{peak}	Peak concentration of contaminants during printing
C_{out}	Outside concentration of the contaminant during printing
d	Diameter
DED	Direct Energy Deposition
DNA	Deoxyribonucleic Acid
e.g.	Example
EPA	Environmental Protection Agency, USA
ER	Emission Rates
etc.	Et cetera
FDM™	Fused Deposition Modelling
HCS	Hazardous Chemical Substances
HCSR	Hazardous Chemical Substances Regulations
HEPA	High-Efficiency Particulate Air
HVAC	Heating Ventilation Air Conditioning
i.e.	That is
IARC	International Agency for Research on Cancer
ISO	International Organization for Standardization
k	Rate of contaminant loss due to surface deposition

LEV	Local Exhaust Ventilation
MSDS	Material Safety Data Sheet
NIOSH	National Institute for Occupational Safety and Health, USA
NWU-HREC	North-West University Health Research Ethics Committee
OEL	Occupational Exposure Limit
OEL-CL	Occupational Exposure Limit-Control Limit
OEL-RL	Occupational Exposure Limit-Recommended Limit
OSHA	Occupational Safety and Health Administration, USA
p	P-value
PBF	Powder Bed Fusion
PLA	Polyactic Acid
PM	Particulate Matter
PPE	Personal Protective Equipment
PVC	Polyvinyl Chloride
PSD	Particle Size Distribution
RPE	Respiratory Protective Equipment
SDS	Safety Data Sheet
SEM	Scanning Electron Microscopy
sk	Skin Notation
SLM	Selective Laser Melting
SLS	Selective Laser Sintering
STL	Stereolithography
TLV®	Threshold Limit Value

TVOC	Total Volatile Organic Compounds
TWA-OEL-CL	Time Weighted Average-Occupational Exposure Limit-Control Limit
UFP	Ultrafine Particles
VOC	Volatile Organic Compounds
vs	Versus
WHO	World Health Organisation
XRD	X-ray Diffraction

STANDARD UNITS

$\mu g/m^3$	Micrograms per cubic metre
µm	Micrometre
L/min	Litres per minute
m	Metre
mg	Milligram
mg/kg	Milligram per Kilogram
mg/m^3	Milligram per Cubic Metre
mm	Millimetre
nm	Nanometre
p/cm^3	Particles per Cubic Centimetres
p/m^3	Particles per Cubic Metre
p/min	Particles per Minute
ppm	Parts per Million

CHAPTER 1

1.1 Introduction

Additive manufacturing (AM) is a process during which raw materials are layered together to create objects based on three-dimensional (3D) model data (Gibson *et al*., 2015). AM offers freedom of fabrication and is preferred to traditional manufacturing due to its ability to produce printed parts with complex and precise geometry (Wojtyla *et al*., 2017). The International Organization for Standardization/American Society for Testing and Materials (ISO/ASTM) 52900 (2015) classifies AM into seven distinct categories, which are: powder bed fusion (PBF), direct energy deposition (DED), material extrusion, vat photo-polymerisation, binder jetting (BJ), material jetting and sheet lamination. Each AM process uses a specific feedstock material, such as polymers, metallic substances and ceramics to mention a few. Due to its flexibility and versatility, AM has been adopted in many industrial sectors (Tofail *et al*., 2018). These sectors range from aerospace, automotive industry, bioengineering to sand casting (Muthu and Savalani, 2016; Zhao *et al*., 2018).

Application of AM to produce sand moulds (sand casting) has been adopted by various metal industries as there are insufficient AM technologies that can directly manufacture metal parts (Chhabra and Singh, 2011). Metal industries use sand moulds as a method to produce metal parts by pouring molten metal into the hollow cavity of the mould (Le Néel *et al*., 2018). Sands used for moulding include silica, chromite, zircon and olivine, but silica sand is preferred compared to other types of sand due to its widespread availability, low cost, and its ability to withstand high temperature and consume less furan resin (Nyembwe *et al*., 2016a Anakhu *et al*., 2018).

AM of sand moulds is achieved through the AM process, which consists of three phases: pre-processing, processing and post-processing (Gibson *et al*. 2015). But prior to pre-processing, virgin (new or unused) silica sand first needs to be coated with sulphonic acid, which acts as a catalyst during the processing phase (Nyembwe *et al*. 2016b). Sulphonic acid is used to change the chemical structure of the furan resin binder thus increasing the resin's ability to bind sand particles together and maintain the structure of the mould (Zhang *et al*., 2014). After the coating process, the coated silica sand can go through the AM processes.

The pre-processing phase involves creation of a print model using 3D Computer-Aided Design (CAD) followed by loading of the feedstock material (silica sand for sand moulding) into the AM machine. The processing phase involves the actual printing of the print part. This

phase is automated, and the printing occurs within an enclosed chamber. Post-processing involves cleaning of the printed materials using different methods such as brushing, sanding, grinding and driving out by compressed air (Deak, 1999; Bours *et al*., 2017; Voxeljet, 2018).

Despite its benefits to numerous industries, Afshar-Mohajer *et al*. (2015) stated that due to continuous movement of powder and injection of resin binder, BJ printers are a source of particulate matter (from powder) and volatile organic compounds (resin binder). Since the BJ processing is similar, it can be assumed that for BJ of silica sand moulds, respirable crystalline will be the main particulate matter emitted. Also, several studies have associated AM with exposure to hazardous chemical substances (Steinle, 2015; Azimi *et al*., 2016; Deng *et al*., 2016; Graff *et al*., 2016; Yi *et al*., 2016; Bours *et al*., 2017; Roth *et al*., 2019). According to Bours *et al*. (2017), exposure to hazards can occur during any of the three phases (pre-processing, processing and post-processing) depending on the activities performed during the phase. During pre-processing, handling of silica sand may lead to particles becoming airborne, possibly resulting in AM operator exposure to respirable crystalline silica. During processing, the application of the furan binder may lead to the emission of organic vapours, and during the post-processing phase, AM operators may also be exposed to airborne respirable crystalline silica due to various silica sand removal techniques such as sandblasting, grinding and brushing, that may release particles into the air. Since silica sand is the main feedstock material, it can be anticipated that it will be the primary source of exposure.

Prolonged exposure to airborne respirable crystalline silica leads to respiratory complications and toxicity to the macrophages. If airborne crystalline silica accumulates in the alveolar region it can cause fibrogenic silicosis (Schroder and Stanton, 2014). Fibrogenic silicosis is indicated by shortness of breath, fever, decreased lung elasticity due to increased surface tension as a result of reduced surfactant production, chest pains, susceptibility to tuberculosis and decreased capacity for physical work due to reduced lung capacity (NIOSH, 2004; Schroder and Stanton, 2014). Hazards concerning printing of moulds using silica sand may not only be limited to respirable crystalline silica exposure, but also include exposure to volatile organic compounds (VOCs) and particulate matter emissions.

AM operators might be at risk of VOC exposure during both the printing and coating processes. The use of sulphonic acid during coating can have negative health effects on AM operators. A material safety data sheet (MSDS) by Protea Chemicals (2017) indicated that sulphonic acid can cause eye damage, and skin and respiratory irritation if users are exposed to it for longer periods. During the AM process, VOCs may be present due to the use of furan resin binder on sand particles during the processing phase. The resin is

commonly used due to its excellent strength and its ability to cure rapidly. But usage of the resin binder has its own disadvantages. When heated, the binder decomposes and emits VOCs such as benzene, toluene, ethylbenzene and xylene (BTEX) which can be toxic to human health (Holtzer *et al*. 2016; Kmita *et al*., 2018). According to Holtzer *et al*. (2016), 1% of furan resin can emit BTEX concentrations of 0.70 mg/kg (0.70 ppm). Additionally, benzene is a confirmed grou≤one human carcinogen, making it highly hazardous among the VOCs emitted during the AM of sand moulds (IARC, 2012; Tsai, 2016).

The AM of sand moulds can be performed using either BJ or selective laser sintering (SLS) (Le Néel *et al*., 2018). Each process has the potential of emitting particulate matter. According to Afshar-Mohajer (2015), BJ is a potential source of fine particulate matter. Particulate matter emissions present during printing may include ultrafine particles (UFPs). UFPs can be defined as particles with aerodynamic measurement of < 100 nm. Studies conducted on other AM processes, such as fused deposition modelling (FDM™), have confirmed emission of UFPs (Steinle, 2015; Azimi *et al*., 2016; Stabile *et al*., 2016; Yi *et al*., 2016; Zhang *et al*., 2017). Once inhaled, UFPs can deposit deeper into the alveoli, where they translocate into the bloodstream. In the bloodstream, UFPs are distributed to various target organs, including the brain where they can disrupt cell functions (Cena *et al*., 2011; Mellin *et al*., 2016).

The physical and chemical characteristics of silica sand particles are also of importance when trying to completely understand operators' exposure. According to Adams (2016), there is a growing concern about the potential health effects of the physicochemical (physical and chemical) characteristics of silica sand on AM operators. Determining the particles' (silica sand particles) morphology will assist to comprehend their behaviour and the health risk they pose to AM operators. According to Fernandez and Casan (2012), deposition of particles into the lungs depends on various factors, but the most noticeable are size and shape. Respirable crystalline silica particles or other particulate matter can deposit in the nose and mouth, bronchioles or alveolar region, depending on their size. These size fractions can be classified as inhalable, thoracic or respirable (Brown *et al*., 2013). Inhalable refers to airborne particles that can be inhaled through the mouth and nose; thoracic as airborne particles that can penetrate beyond the larynx when inhaled; and respirable as airborne particles, when inhaled can penetrate deeper into the alveolar regions. Respirable airborne crystalline silica, when continuously inhaled during prolonged exposure, can therefore penetrate into the alveolar region resulting in fibrogenic silicosis (NIOSH, 1985; American Thoracic Society, 1997; Schroder and Stanton, 2014). Thus, due to their size,

respirable crystalline silica sand particles can, therefore, penetrate to the alveolar region of the respiratory tract and possibly cause pulmonary fibrosis.

Even with the information provided thus far, there is still insufficient literature regarding risks that AM poses to operators. Huang *et al* (2013) mentions that due to the lack of sufficient data on the impact of AM on operators, AM may create new health and environmental problems that occupational hygiene professionals are unaware of. Graff *et al*. (2016) also states that AM may bring about uncertainties regarding the health and safety of workers. As various feedstock materials are used for different processes, according to Bours *et al*. (2017) and AIG Emergind Risk Research (2018), every AM technology may endanger operators differently and commonly used feedstock can lead to health risks.

In addition, Bours *et al*. (2017) and Oskui *et al*. (2015) argue that a lack of information on the toxicity of printed parts is a problem on its own. According to Oskui *et al*. (2015), the toxicity of printed parts depends on how the parts are used and in what setting. After sand moulds have been produced using AM, they are used for metal casting in foundry industries. Studies conducted in foundries show that molten metal being poured into moulds results in the emission of hazardous vapours such as BTEX and fumes due to the decomposition of binders used during the processing phase of AM (IFC, 2007: Kmita *et al*., 2016; Chate *et al*., 2017). It is therefore evident that printed parts, depending on what they are used for, can present risks to other industry workers as well. Lastly, in a study by Huang *et al*. (2016), it is concluded that there is still a need for improved comprehension of the occupational hazards associated with AM, as well as the different materials used. With that in mind, it is evident that there is a still a gap in knowledge about health risks presented by AM.

Therefore, this study aims to assess the following: 1) the particulate emissions during the silica sand preparation process (coating) and three processing phases; 2) personal exposure and area airborne concentrations of hazardous chemical substances (HCSs) (respirable crystalline silica, VOCs and particulate matter emissions) during coating as well as BJ of sand moulds, and 3) the physical and chemical characteristics of the silica sand in order to improve worker health and safety.

1.2 Research aims and objectives

1.2.1 General aim

The aim of this study is to assess the emissions of and respiratory exposure to HCSs (airborne crystalline silica, VOCs and particulate matter) during the AM of sand moulds.

1.2.2 Specific objectives

- To determine the physical and chemical characteristics of virgin, coated and used silica sand using a Malvern Morphologi G3 particle analyser, Scanning Electron Microscope (SEM) and X-ray Diffraction (XRD) analyser.
- To quantify emissions of HCSs (airborne crystalline silica, VOCs and particulate matter) released during AM of sand moulds.

- To determine personal respiratory exposure of AM operators to airborne respirable crystalline silica, VOCs and particulate matter during the full shift.

1.3 Hypotheses

According to Nyembwe *et al*. (2016b) silica sand with high quartz content is refractory and best suited for casting alloys with high pouring temperatures. The authors also mention that larger particles negatively affect the surface finish of the mould. Additionally, according to Murthy and Rao (2016), small grain sizes are better at interlinking with inorganic or organic binders, as the investigated silica sand, Ferro-Chrome and Granulated Blast Furnace slag ranged from 35.49 - 45.52 µm in size.

- It is therefore hypothesised that the bulk silica sand contains silica sand particles with high quartz content and that are in the inhalable (or smaller) (< 100 µm) size range.

Adams (2016) conducted research on respiratory exposure to HCSs released during the production of sand moulds using AM. The results obtained show that exposure to respirable crystalline silica was the highest during pre-processing, compared to other phases, as the sand was sieved and poured into the AM machine. Afshar-Mohajer *et al*. (2015) noticed that during post-processing, peak emissions were 1.20×10^4 p/m^3 when the AM machine lid was opened and the excess powder of the printed part was cleaned using a brush. During post-processing of sand moulds, crystalline silica emissions may occur due to techniques used (cleaning by compressed air, brushing, polishing, sanding) to remove excess silica sand from parts. Stefaniak *et al*. (2018) observed that particle emissions decrease when the printer operates with the lid closed.

- It is therefore hypothesised that there is a statistically significant difference in particle emissions during each phase depending on the activities performed during each processing phase.

During a study on AM of sand casting moulds by Adams (2016), it was found that exposure to airborne respirable crystalline silica, VOCs and particulate matter was > 10% of the respective occupational exposure limits (OELs) and that exposure to respirable crystalline silica was the highest.

- Therefore, it is hypothesised that operators are exposed to respirable crystalline silica, VOCs and particulate matter at concentrations > 10% of the respective OELs but that exposure to respirable crystalline silica is most prominent.

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CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

This chapter discusses additive manufacturing (AM), sand casting, physical and chemical characteristics of silica sand and hazardous chemical substances (respirable crystalline silica, volatile organic substances and particulate matter) present during Binder Jetting (BJ). Additionally, the respiratory tract and the mechanisms of particulate matter deposition as well as the relevant occupational exposure limits (OELs) of the hazardous chemical substances (HCS) are discussed.

2.2 Additive manufacturing

Additive manufacturing (AM) refers to the techniques used to rapidly fabricate three-dimensional (3D) parts layer by layer (Ford and Despeisse, 2016). The term was defined by the International Organization for Standardization/American Society for Testing and Materials (ISO/ASTM) and it is the accepted terminology among AM industries (Gibson *et al*. 2015). AM emerged in the 1980s and is used to produce 3D parts on demand while minimising cost, energy consumption and material waste (Ford and Despeisse, 2016) when compared to traditional manufacturing techniques.

There is more to AM than producing parts for the manufacturing industry or foundries. AM has also been applied in the aerospace, automotive, food and medical sectors (Muthu and Savalani, 2016). The aerospace sector was one of the first sectors to apply AM in order to produce lightweight products that contribute to fuel efficiency (Huang *et al*., 2015; Gibson, 2017). AM has also been used in the automotive sector to fabricate parts suitable for performance testing and to produce engines with complex geometries (Gibson, 2017). The food industry has been applying AM to design food with enhanced nutritional value and texture (Lipton *et al*., 2015; Codoi *et al*., 2016). In the medical sector, AM has been used to produce custom made prostheses as well as the production of 3D models of the human anatomy in order to assist surgeons' planning prior to surgery (Onuh and Yusuf, 1999; Gibson *et al*, 2015). In addition, AM has also been used in tissue engineering to produce scaffolds that act like living tissue and allow cells to proliferate (Xiao *et al.*, 2012; Gibson *et al*., 2015; Senatov *et al*., 2016). AM has also been adopted in metal casting foundries to reduce the time taken to produce sand moulds, cost of production and energy consumption (Sivarupan *et al*., 2019). Despite AM having more benefits than traditional manufacturing, Klahn *at al*. (2015) states that it is unlikely that AM will replace it. AM will rather contribute to the portfolio of manufacturing technologies.

AM has been part of the manufacturing sector since the 1980s but to date, the technology is still considered new in terms of adoption and research (Schniederjans and Yalcin, 2018). According to Steinle (2015), new technologies can raise issues regarding their possible risk to the health of workers. AM has been reported to release hazardous chemicals into the air (Stefaniak *et al*., 2018) and since AM is growing exponentially in many sectors (Wohlers and Caffrey, 2013), the growth also means that there is a possible increase in the emission of contaminants in the occupational environment which may lead to personal exposure (Stefaniak *et al*., 2018).

According to the ISO/ASTM 52900 (2015), AM can be classified into seven distinct process categories. These include: powder bed fusion (PBF), direct energy deposition (DED), material extrusion, vat photo-polymerisation, binder jetting (BJ), material jetting and sheet lamination. According to Bours *et al*. (2017), all these processes have a potential to present a hazard to the operator depending on the feedstock material used. These hazards include, but are not limited to, exposure to volatile organic compounds (VOCs), particulate matter emissions (including ultrafine particles) as well as physical and environmental hazards. For AM of sand moulds, these hazards may include exposure to respirable crystalline silica quartz.

2.2.1 Application of AM: Rapid sand casting

Sand casting is one of the earliest techniques that were used to manufacture metal parts. The process involves the making of sand moulds and cores that will be used at a later stage for metal casting. Firstly, the pattern (made of wood, metal or any suitable material) is designed to form a cavity in the premixed sand (Hawaldar & Zhang, 2018). Pattern making traditionally requires a skilled worker. After the pattern has been imprinted into the sand, it is removed and it leaves a cavity into which molten metal can be poured. After the metal has cooled off, it is removed taking the shape of the pattern (Holtzer *et al*., 2016). AM has made casting much more efficient. Since pattern making is a tedious procedure, with rapid casting, the pattern making step is skipped with the use of the three-dimensional computer-aided design system (3D CAD). With the 3D CAD system, moulds can be printed directly without the use of a pattern. Printed parts can now be easily manufactured whilst reducing lead time (Hackney and Woolridge, 2017). Two well-known processes adopted in foundries are BJ and PBF (Gunther and Mogele, 2016).

2.2.2 Binder jetting and Powder bed fusion

BJ and PBF are the two main AM processes used to produce sand moulds. Each process has its own, different technology that is utilised to produce sand moulds. PBF uses selective laser sintering (SLS) whereas BJ uses three-dimensional printing (3DP) (Zhao *et al*., 2018). Both processes and their technologies are discussed in the following section. It should be noted, however, that only BJ will be used during this study.

2.2.2.1 Binder jetting and three dimensional printing (3DP)

BJ is a process where a print head is used to deposit a binder (e.g., furan resin) onto the feedstock material (e.g., sand or powder) in order to create a desired shape (Le Néel *et al*., 2018). The 3DP process is the main technology of BJ and was developed at the Massachusetts Institute of Technology (MIT) and licensed to Soligen Corporation, Extrude Hone and Z Corporation of Burlington. It is based on inkjet technology and follows similar principles. The process begins with spreading of the feedstock on the build platform (a support base for the object being printed) using a roller. The jet nozzles then deposit droplets of binder onto the feedstock material, which functions as a glue that holds the feedstock together. The binder droplets are specifically deposited on the pattern where the printed part will take shape. The build platform is then lowered allowing another layer of feedstock to be spread onto it, and the binder is again deposited on this new layer (Vaezi *et al*., 2013). The process is repeated until the print part is completed (Zhao *et al*., 2018).

2.2.2.2 PBF and selective laser sintering (SLS)

PBF utilises a laser as a heat source to fuse the powder or sand particles together. A cross section is created on the feedstock material as the laser scans the material horizontally. The build platform is then lowered to allow for the deposition of another layer of feedstock material. This process is continued until a desired 3D shape printed part is attained (Roth *et al*., 2019).

SLS is a process of sintering (binding together via heat) feedstock material layer by layer until it forms a 3D part (Le Néel *et al*., 2018). The feedstock material is only fused together where the printed part will be built. A low powered carbon dioxide (CO_2) laser is commonly used because it can sinter the silica sand without any binder (Wang *et al*., 2003). The principle is to selectively sinter the feedstock uniformly until all layers are complete and the final part takes a 3D form.

Activities necessary to perform both BJ and PBF can be divided into three phases namely pre-processing, processing and post-processing. The following section discusses these phases and how they may impact on AM operator exposure.

2.2.3 AM phases

AM has three phases; pre-processing, processing and post-processing (Gibson *et al*., 2015). According to du Preez, *et al*. (2018a), AM operators can potentially inhale airborne feedstock particles during pre-processing, processing and post-processing phases. The three phases of the AM of sand moulds might be similar to the phases of other AM processes. There is, however, a slight variation which involves the coating of feedstock materials prior to pre-processing and the curing of the printed parts at the end of post-processing (Zhao *et al*., 2018).

2.2.3.1 Coating

Coating is a stand-alone process whereby un-coated silica sand (virgin sand) is coated with sulphonic acid. The acid acts as a catalyst to change the chemical structure of the furan resin binder in order to improve the mould's structure (Brown, 2000; Nyembwe *et al*., 2016a; Zhao *et al*., 2018). AM facilities can purchase already coated sand but due to financial constraints, some facilities choose to coat the sand themselves. Studies conducted on the risks associated with this process are unavailable; it is however possible that, due to the operators handling silica sand, exposure to respirable crystalline silica quartz might occur. Other than respirable crystalline silica, AM operators are at risk of sulphonic acid exposure.

The coating process has not been described in detail in other studies and it is a newly implemented process in the facility participating in this study. But based on observation at the facility where the study takes place, the process is as follows: the AM operator begins by cleaning the coating machine filter using compressed air; the operator then draws silica sand from the bulk bag using a flexible duct pipe; then the sand is transported into the hopper from where it is supplied to the screw conveyer; in the conveyer, the silica sand is continuously coated with liquid sulphonic acid via a pipe until the sand is collected in the bulk bag; the built-in dust extractor is used to collect free silica sand dust as it collects in the bag. The use of compressed air is a risk to the AM operator as it can liberate silica sand dust which leads to respirable crystalline silica exposure. Also, it is required of the AM operator to remain in the room until the procedure is completed, to ensure that the machine does not malfunction. Because the AM operator sits next to the machine, there is additional exposure

to silica sand dust that can not be captured by the built-in dust extractor, as well as exposure to sulphonic acid.

2.2.3.2 Pre-processing phase

Pre-processing begins with a creation of a model using a three-dimensional Computer-Aided Design (3D CAD). The 3D CAD model contains the information of the geometry of the print part to be built. The file is then converted into a stereolithography (STL) format which can be used by the AM machine. The AM machine can then be set up for a build (Gibson *et al*., 2015). Practical tasks involved in pre-processing may include handling and loading of silica sand into the AM machine as well as the cleaning it. While preparing the feedstock material, AM operators may be exposed to fine particulate matter. This makes pre-processing an integral step of AM where operators can be exposed to hazardous feedstock material.

2.2.3.3 Processing phase

The processing phase involves the automatic printing of parts. During the processing phase of BJ, the print head spreads a layer of feedstock material onto the powder bed. This is followed by the jet nozzles which deposit binder onto the feedstock, to bind material together. The binder is sprayed in a pattern which forms the basis of the print part. The powder bed is then lowered via a piston, and another layer of fresh feedstock is spread over the previous one followed by the deposition of the binder. Layering of the feedstock is repeated until the 3D shape is obtained (Vaezi *et al*., 2013). Although the process does not require constant monitoring, it still poses a risk to AM operators. According to Roth *et al*. (2019), the furan binder adds a potential risk of VOC exposure. Additionally, the furan resin binder is composed of furfural alcohol which can cause both eyes and respiratory irritations (NIOSH, 1989).

2.2.3.4 Post-processing

The post-processing phase involves removal of the part from the AM machine and cleaning the excess material using abrasive techniques such as sandpapering and polishing (Gibson *et al*., 2015). In a study by Scholz and Slavin (2007), on foundries, it was found out that quartz percentage in respirable dust is higher in the cleaning room where particles are more likely to be broken down via the techniques used. Abrasive techniques can break quartz and form smaller particles. Similar abrasive techniques, i.e. brushing of print part, are also used during post-processing. Thus it is possible that post-processing of sand moulds may lead to exposure to respirable crystalline silica with high quartz content as well as fine particulate matter as a result of abrasion. Roth *et al*. (2019) adds that the techniques used during this

phase also add other potential hazards. According to Kolb *et al*. (2017), manually performed tasks lead to an increase in particulate matter concentrations in the air, as peak concentrations during the PBF post-processing of stainless steel were reported to be 113331 p/cm^3. A study conducted by du Preez, *et al*. (2018b) on material extrusion indicates that the total volatile organic compounds (TVOCs) concentration in a small room increased when the 3D printer doors are opened. Since materials used for sand moulds contain plasters and furan resin binders (Adams, 2016), there is a possibility that opening the door after sand moulds were manufactured, may also lead to VOC emissions since furan resin binders have been found to emit VOCs when used (Kubecki *et al*., 2013; Holtzer *et al*., 2016; Hackney and Wooldridge, 2017).

As part of the post-processing phase, AM operators sometimes cure sand moulds (expose the mould to heat) in an oven if they are still wet after the processing phase (Hackney and Wooldridge, 2017). The moulds are cured at temperatures at or above 180 °C in order to order to avoid hot tearings of the moulds. The curing process therefore acts as an additional source of VOCs emission since higher temperatures can cause their emission.

2.2.4 Feedstock materials used in AM

Materials used in AM of sand moulds play a significant role in the mould's quality as they can affect the surface finish of the part. A well-casted mould should display the following properties: strength, hardness, permeability, dimensional accuracy, and low collapsibility (Nyembwe *et al*., 2016a). It is therefore crucial to choose the correct binder, sand material and additives when preparing for the production of sand moulds (Le Néel *et al*., 2018).

2.2.4.1 Silica sand

Silica sand (which is sand that contains silicon dioxide) is commonly used as refractory sand in both AM and foundries (EPA, 2014). There are two forms of silica: polymorphous (crystalline) and amorphous (non-crystalline) silica. Silica is found in its most common crystalline form of quartz, with less common silica forms being tridymite and cristobalite. Crystalline silica can be melted to form glass as well as be used to create jewellery or electronics (ATSDR, 2017). Other than silica, moulds can be produced by using chromite, zircon or olivine sand. Silica sand is however more commonly used as it is abundant and cost-effective. In addition, silica sand has more unique characteristics that sets it apart from other sands. These include thermal expansion, chemical purity, grain shape and size. Round and spherical silica sand grains produce denser and more rigid moulds while smaller sized sand grains ensure that the printed part has a good surface finish and dimensional accuracy.

These properties also ensure that silica consumes less furan resin and improves mould strength which leads to defect free parts (Nyembwe *et al*., 2016b).

Workers who have a high potential of being exposed to increased concentrations of respirable crystalline silica sand dust are miners, ceramic manufacturers as well as foundry and construction workers. Inhalation is the most common form of respirable crystalline silica exposure (ATSDR, 2017). According to the National Institute of Occupational Safety and Health (NIOSH) (2002), rare cases of dermal exposure to crystalline silica only occur when a worker has an open wound or cut. The focus of this study however, will be on the inhalation risks of respirable crystalline silica quartz associated with the AM of sand casting moulds.

2.2.4.2 Furan resin binder

Binders in AM and foundries are used to improve the strength and integrity of the mould. Furan and phenolic binders are the two most commonly used binders in AM of sand moulds (Le Néel *et al*., 2018). A study conducted by Snelling *et al*. (2014) reported that the use of furan resin binder leads to stronger parts compared to other binders i.e., phenolic binder, alkyd and sodium silicate, because of the binder's ability to maintain strength. Even though furan resin is well suited for the industry, it produces toxic vapours during casting that may pose a health risk to workers (Upadhyay *et al*., 2017).

Exposure to VOCs has been associated with both AM and foundry work. VOCs are defined as organic substances that have a high vapour pressure at normal atmospheric conditions due to their low boiling point. Emission of VOCs in foundries and AM is due to heating of binders applied to sand moulds (Zymankowska-Kumon, 2015).

2.2.4.3 Sulphonic acid

Sulphonic acid is used to coat virgin silica sand prior to the commencing of AM phases. It functions as a catalyst for the furan resin binder during the processing phase (Nyembwe *et al*., 2016a).

2.3 Health effects associated with AM materials

2.3.1 Crystalline silica and particulate matter (PM)

2.3.1.1 The physical and chemical characteristics associated with crystalline silica and PM

The particles' potential to induce toxicity on target organs is related to its physical and chemical characteristics. The physical and chemical characteristics of airborne particulate matter, specifically airborne crystalline silica, are of importance since they determine particle behaviour and the possibility to cause adverse health effects. Physical characteristics of a particle may include but not be limited to shape and size (Morakinyo *et al*., 2016), while the chemical properties refer to chemical composition (McClellan, 2002; Nazaroff, 2004; Estokova and Stevulova, 2012; Kelly and Fussell, 2014; Schroder, 2014; Morakinyo *et al*., 2016). The convexity (irregularity) and circularity (roundness) of particles also play important roles as they describe the shape of particles. Particle shape determines where the particles deposit in the respiratory tract (Sturm, 2012).

2.3.1.2 Physical characteristics

Particle size or aerodynamic diameter is significant as it determines where the particle will deposit in the respiratory tract (Wilson *et al*., 2002). To date, a significant number of studies have shown that adverse respiratory effects are related to particle size (Brown *et al*., 1950; Anderson *et al*., 2012; Upadhyay *et al*., 2014). According to Brown *et al*. (1950), induction of silicosis by airborne crystalline silica is predominantly dependant on the size of the silica particle. Additionally, McClellan (2002) states that, if the aerodynamic size of particle decreases, the possibility of it being respired becomes higher.

Particles can be divided into three fractions; inhalable, thoracic, or respirable (Brown *et al*., 2013). Inhalable dust (< 100 µm) refers to particles deposited in the mouth and nose following inhalation. Thoracic dust (< 10 µm) is classified as particles which can penetrate beyond the larynx up to the upper regions of the alveoli. Respirable dust (< 4 µm) poses a serious threat to human health as it is deposited in the unciliated alveoli sacs where it is not easily removed by the body's clearance mechanisms, resulting in accumulation of the dust (CEN, 1993; Brown *et al*., 2013; Schroder, 2014).

Deak (1999) stated that, during the post-processing phase, there is an increase in the emissions of PM. According to Schroder and Stanton (2014), PM emission is largely caused

by handling, crushing, grinding as well as pulverisation of organic and inorganic substances that can generate dust. Over the years, occupational hygienists have referred to inert and non-toxic PM as nuisance dust (McClellan, 2002). PM can be defined as airborne solid (fine [$PM_{2.5}$] or coarse [PM_{10}]), liquid or dust particles that can cause adverse health after exposure (Anderson *et al*., 2012; Kelly and Fussell, 2012; WHO, 2013; Upadhyay *et al*., 2014). $PM_{2.5}$ are particle fractions smaller than 2.5 µm whilst PM_{10} are particle fractions smaller than 10 µm (Panyacosit, 2000; Anderson *et al*., 2012). These definitions of size fractions are, however, mostly associated with outdoor air pollution or environmental exposure (McClellan, 2002).

In the workplace, PM is defined differently. The European Standard EN481:1993 (Workplace atmospheres – Size fraction definitions for the measurement of airborne particles), classifies particles in terms of sampling conventions which refer to the sampling specifications for each particle's aerodynamic diameter used by sampling instruments. According to these sampling conventions, inhalable dust sampling is classified as 50% of particles having an aerodynamic diameter of less than 100 µm, thoracic dust sampling as 50% of particles having an aerodynamic diameter of less than 10 µm and respirable dust sampling as 50% of particles having an aerodynamic diameter of less than 4 µm (CEN, 1993).

Long-term exposure to PM leads to respiratory as well as cardiovascular diseases and occasionally, premature death (Panyacosit, 2000; Silva *et al*., 2013). According to the WHO (2013), exposure to PM has no safe level. Workers who are asthmatic or allergic are most vulnerable to PM exposure as it can cause severe adverse health effects. Therefore, it is critical that workers' exposure should be kept as low as reasonably practicable.

Studies by McClellan (2002) and Kim *et al*. (2015a) found that, PM toxicity heavily depends on its size and chemical composition. The smaller the particle size, the deeper it penetrates into the gas exchange regions (Panyacosit, 2000; Kim *et al*., 2015a). This means that particles like ultrafine particles (UFPs) are a significant health concern due to their small size.

UFPs can be defined as particles with a diameter of less than 100 nm. Exposure to UFPs has been known to occur mainly via inhalation, as information on ingestion and dermal exposure is rarely documented. However, these exposure routes should not be overlooked (Oberdoster *et al*., 2005). After inhalation, due to the particles being nanosized, UFPs can easily penetrate the alveoli, move into the bloodstream and be distributed to various target organs, which may lead to deleterious effects (Cena *et al*., 2011). Moreover, according to

Oberdoster *et al*. (2005), UFPs can translocate into the central nervous system from the nasal regions via olfactory neurons, where they can cause neurodegenerative diseases.

2.3.1.3 Chemical characteristics: Crystalline silica

The chemical composition of crystalline silica forms the basis of the substance's toxicological properties (Key-Schwartz *et al*., 2003). According to Kelly and Fussell (2012) and Morakinyo *et al*. (2016), the ability of PM to induce toxicity in target organs is associated with the particles' composition. Particle composition is also an important factor to consider when it comes to determining behaviour of particles in relation to the causing of health problems. Crystalline silica particles released after grinding have been found to release oxygen radical species that potentiate silica's toxicity and carcinogenicity via free radicals. These oxidants may cause lung and cellular injury as well as damage to the deoxyribonucleic acid (DNA) (IARC, 2012).

2.3.1.4 Deposition of airborne particulate matter in the respiratory tract

PM matter originates from natural or man-made sources. These particles can be deposited either in the alveoli (respirable fractions), primary bronchi (thoracic fractions) or in the nasopharynx (nhalable fractions) (Kelly and Fussell, 2012).

Particle size is crucial in determining where the particle will settle in the respiratory tract as well as its potential to cause adverse health effects (Thomas, 2013). Deposition of particles into the respiratory tract also depends on several mechanisms of deposition, namely; inertial impaction, sedimentation and diffusion (Yeh *et al*., 1976) as is illustrated in Figure 2-1.

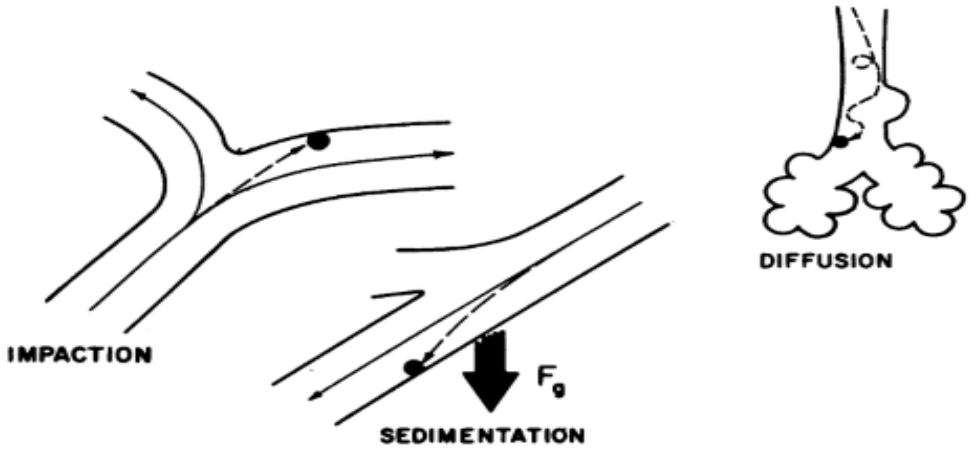

Figure 2-1: Respiratory tract deposition mechanisms (Yeh *et al*., 1976)

Inertial impaction is a mechanism that applies to deposition of particles ranging from 3 µm to larger than 20 µm in the upper region of the respiratory tract. This mechanism is predominantly effective with inhalable particle fractions. Sedimentation refers to a deposition mechanism by which particles deposit in the respiratory tract as a result of gravity. Particles deposited by sedimentation range from 0.1 µm to 50 µm in diameter. Thoracic particles are more likely to deposit into the lungs via this mechanism. Particles smaller than 0.5 µm can deposit into the respiratory tract mainly via diffusion. This mechanism is highly efficient when the particle size is small, ranging from 0.05 µm to 0.5 µm. Respirable particle fractions penetrate the alveolar regions via this mechanism (Lippmann *et al*., 1980; Stuart, 1984; Monjezi *et al*., 2012; Fernandez and Casan, 2012; Schroder, 2014).

2.3.1.5 Clearance of airborne particulate matter in the respiratory tract

Inhaled particles are deposited in specific sections of the respiratory tract depending on their size. However, the body has clearance mechanisms to assist in the elimination of these particles. Clearance mechanisms include mucociliary clearance, clearance by pulmonary alveolar macrophages and ingestion by macrophages and dissolution just to name a few (McClellan, 2002). After the particles have been cleared, they are transported either into the blood, lymphatic circulation, or gastrointestinal tract to be excreted (Stuart, 1984).

Mucociliary clearance is a type of clearance mechanism where particles deposited in the trachea and terminal bronchi are eliminated via mucus. The mucus layer on the walls of the respiratory tract traps the particles and they are carried to the gastrointestinal tract via the cilia. This mechanism, however, is less functional in the alveolar region, where cilia are absent. Particles deposited in the alveolar regions are cleared from the region by pulmonary alveolar macrophages. These cells entrap and phagocytize particles as they are rich lysosomes. However, this mechanism is not effective when continuous exposure to particulate matter leads to cell damage or proliferation (Stuart, 1984; Schroder, 2014).

Similar to deposition, clearance mechanisms depend on the size of particles in order to eliminate them successfully. According to Brown *et al*. (1950), the smaller the size of the particle is, the longer it will take to be eliminated from the respiratory tract. Accumulation of particles in a specific respiratory region leads to the inability of clearance mechanisms to function properly. Long term exposure to respirable airborne crystalline silica is associated with toxicity of the macrophages. This results in the inability of macrophages to eliminate the airborne crystalline silica particles leading to accumulation and the development of fibrogenic silicosis (NIOSH, 2004; Schroder and Stanton, 2014).

2.3.1.6 Respirable crystalline silica

In both foundries and AM, silica sand has been commonly used to produce sand moulds and cores. Foundry processes include sand preparation, mould and core making, mould cooling, shakeout, cleaning and finishing (NIOSH, 1985; Hawaldar & Zhang, 2018; Mgonja, 2018). AM processes include handling of silica, cleaning the AM machine, loading of a job box (filled with silica sand) into the AM machine and removal of excess silica sand from printed parts using various techniques. All these processes have a potential to expose workers to free airborne respirable crystalline silica quartz. In addition, according to Mgonja (2018), common illnesses in foundries are associated with respirable crystalline silica exposure. Prolonged exposure causes fibrogenic silicosis, chronic obstructive pulmonary disorders, lung cancer as well as increased potential risk of tuberculosis, kidney and autoimmune diseases (American Thoracic Society, 1997; ATSDR, 2017). Fibrogenic silicosis is an irreversible, progressive pulmonary disease and can lead to death. The development of fibrogenic silicosis is due to respirable crystalline silica quartz penetrating the alveolar section of the respiratory tract. After long term exposure to respirable crystalline silica, macrophages can be overwhelmed as a result of the quartz toxicity, thereby lose their effectiveness to clear out the quartz particles. As a result, this leads to accumulation of respirable crystalline silica quartz particles in the alveoli thereby causing fibrogenic silicosis. Additionally, as stated by Khoza *et al*. (2012), silicosis has a lengthy latency period and can cause harm decades after exposure has ceased. A study by Goldblatt and Rai (2017) is a good example of the statement by Khoza *et al*. The authors discussed the lawsuit of miners against gold mines on how exposure to respirable crystalline silica during their earlier employment still caused silicosis many years following exposure.

2.3.2 VOCs

Acute exposure to VOCs causes skin, eye and throat irritation and loss of coordination, whilst chronic exposure results in renal, hepatic and central nervous system damage. Symptoms may include dizziness, irritation, headaches, fatigue and allergic skin reactions (Chauhan, 2013; Shuai et al., 2018). Since VOCs are volatile, the main route of exposure during AM is via inhalation followed by dermal exposure and then ingestion.

Furan binders used in foundries and AM are reported to emit VOCs (Zhang *et al*., 2014). According to Zymankowska-Kumon (2015), of all the substances emitted, the BTEX (benzene, toluene, ethylbenzene and xylene) groups pose the most significant risks on workers. According to the Department of Employement and Labour (1995), both toluene and xylene have skin notations (sk), meaning that these substances have the ability to be

absorbed through the skin and cause deleterious effects. Shuai *et al*. (2018) states that, exposure to either toluene or xylene leads to neurosis. Long term exposure to xylene can also cause depression, insomnia and short-term memory loss, to name a few health effects (Kandyala *et al*., 2010). Chronic exposure to benzene may lead to leukemia as it is a confirmed human carcinogen (IARC, 2012).

2.3.3 Sulphonic acid

Sulphonic acid is a skin and respiratory irritant and continued exposure may cause drowsiness, dizziness or severe eye damage (Protea chemicals, 2017).

2.4 Occupational exposure

2.4.1 Occupational exposure in foundries

Pneumoconiosis, which is a lung disease caused by inhalation of dust, is prevalent in most foundry workers (Kayhan *et al*., 2013; Saraei *et al*., 2018). As a type of pneumoconiosis, silicosis has been found to be common in most foundry workers who handle silica sand with high respirable crystalline silica quartz content. Metal casting foundries engage in silica sand mould manufacturing which expose the workers to respirable crystalline silica dust. Chemical binders (phenolic, formaldehyde, furan resins etc.) added to sand moulds to bind the silica sand particles together prior to casting are also harmful (Kuo *et al*., 2018). A study conducted by Ahman *et al*. (1991) on obstruction of lung functions in foundry workers who handled furan resin, indicated that exposure to resin caused irritation of respiratory tract and mucous membranes of foundry workers. In addition, a study by Andersson *et al*. (2019) indicated that foundry workers who used furan resin had an increased secretion of CC16 (club cell protein 16), which is the protein secreted to mitigate inflammation and oxidation as well as to mark injury to the lungs. Both contaminants (respirable crystalline silica quartz and furan resin) have an impact on the respiratory tract, indicating that long term exposure may intensify respiratory dysfunctions. They have been reported to be present in refineries and may also be present in AM of sand moulds.

2.4.2 Occupational exposure during AM

There is a lack of information on personal exposure and emissions during AM of sand moulds. But other studies on various AM technologies have found that AM operators are exposed to hazardous emissions from AM machines. Although the emissions during AM of

sand moulds differ from other AM technologies due to feedstock materials used, the risk of using AM machines in general will be highlighted in the next section.

Studies have been conducted on emissions during AM, but the most prevalent studies are on material extrusion fused deposition modelling (FDM™) 3D printers. (Kim *et al*., 2015b; Steinle, 2015; Azimi *et al*., 2016; Mendes *et al*., 2017; Stefaniak *et al*., 2018). The FDM™ 3D printers are commonly used in indoor environments (offices, universities, homes or libraries) as they are easy to use and affordable (Mendes *et al*., 2017). FDM™ technique involves the extrusion of a thermoplastic material as a wire through the nozzle head. The head heats the material where after it is immediately hardened to form different layers required (Kim *et al*., 2015b; Azimi *et al*., 2016). The feedstock material mainly used in FDM™ 3D printers is acrylonitrile-butadiene-styrene (ABS) and polyactic acid (PLA) (Stephens *et al*., 2013; Kim *et al*., 2015b).

FDM™ 3D printers have been confirmed to emit UFPs. According to Stephens *et al*. (2013), FDM™ 3D printers utilising thermoplastics are considered high emitters of particulate matter, with UFPs emission rates of 10^{10-11} particles per minute (p/min). Afshar-Mohajer *et al*. (2015) also reported UFPs emission rates of $8 \times 10^3 – 4 \times 10^4$ p/min during BJ while utilising gypsum powder. FDM™ emissions vary between the feedstock materials used. A study conducted by Stephens *et al*. (2013) on identical FDM™ 3D printers indicated that, UFPs emission rates by ABS were higher than that of PLA ($1.8 – 2.0 \times 10^{11}$ p/min versus 1.9 - 2.0×10^{10} p/min). Vance *et al*. (2017) also found that, the average aerosol emission rates for ABS ($1.25 \times 10^{10} – 1.08 \times 10^{11}$ p/min) were higher compared to PLA ($1.10 \times 10^8 – 1.48 \times 10^{10}$ p/min). Other factors affecting particle emissions, such as printer brand, type of filament and colour, extruder nozzle temperature etc. were taken into account when conducting these studies. Kim *et al*. (2015b) conducted research on two different printer brands (Cube, 3D Systems and 3DISON Plus, Rokit, Korea) and the results were relatively similar to that of Stephens *et al*. (2013) and Vance *et al*. (2017) ABS had emission rates of 1.61 ×1 0^{10} p/min while PLA emission rates ranged from 4.27 - 4.89×10^8 p/min.

Yi *et al*. (2016) researched the effects of filament colour on particle emissions. The authors reported that blue ABS emitted the largest particles compared to black, which had the smallest particles. Also, it was observed that when using army green PLA, the printer had the highest particle number concentrations compared to ocean blue PLA, indicating that filament colour certainly has an effect on particles emitted. Stabile *et al*. (2017) performed a study to determine if extrusion temperature had an effect on emissions. It was found that the higher the extrusion temperature the higher the emissions. As an example, PLA emissions

extruded at 220 °C were less than those emitted at 240 °C (2.26×10^8 p/min compared to 3.33×10^9 p/min).

ABS can be classified as more hazardous than PLA due to its ability to emit higher numbers of particles. However, one study by Steinle (2015) indicated that PLA emissions should not be underestimated. The author reported that the UFPs emission rates while printing a standard object for PLA were higher than ABS (2.1×10^9 versus 2.4×10^8 p/min). ABS is more of a risk to AM operators compared to PLA as a result of its products, i.e; acrylonitrile, 1,3-butadiene and styrene. Acrylonitrile is regarded as a Group 2B possible human carcinogen while 1,3-butadiene is a Group 1 confirmed human carcinogen which can cause hereditary genetic damage with increased exposure while styrene is an eye and skin irritant (Kim *et al*., 2015b).

Studies on FDM™ 3D printers followed a similar trend: particle number concentrations reached a maximum when the printing process started and declined when it stopped (Kim *et* al., 2015b; Yi *et al*., 2016, Stabile *et al*., 2017). But three studies performed on BJ and selective laser melting (SLM) utilising powder showed a different trend. According to Afshar-Mohajer *et al*. (2015) fine particulate emissions during BJ increased at the end of the printing cycle and when the printed part was removed. This step also included cleaning of excess powder from the printed piece and transferring it into the bin for future prints (post-process). Mellin *et al*. (2016) observed that handling of powder (pre-processing) outside the SLM machine led to particulate matter emissions. Lastly, Graff *et al*. (2016) reported that during post-processing, particles ranging between 50 and 150 nm (0.05 and 0.150 µm) peaked at 1.6×10^{10} p/m^3 when cleaning of the machine took place. This indicates that exposure to particulate emissions is not limited to a single phase but all three phases of AM.

The results from these studies give a clear indication that particle emissions are present during AM. Even though they are not directly comparable with AM of sand moulds, they shed light on what kind of emissions can be anticipated during AM.

2.4.3 Occupational exposure limits (OELs)

Occupational exposure limits (OELs) are assigned to hazardous chemicals in order to maintain the workplace safe from those specific chemicals. OELs can be defined as maximum concentrations of a chemical substance that workers may be exposed to regularly in their various work practices without any negative health effects. They are used as guidelines to ensure that the concentrations of hazardous chemicals are kept as low as reasonably practicable in order to minimise workers' exposure. In South Africa, two types of

OELs can be assigned to chemical substances according to the Hazardous Chemical Substances Regulations: OEL-CL (control limit) or OEL-RL (recommended limit). A substance is assigned an OEL-RL if it will not lead to adverse health effects when exposure occurs at or below the limit (level). An OEL-CL is assigned to carcinogens and substances that have serious health effects on worker population. Some of the VOCs emitted by the furan resin binder are assigned an OEL-RL: ethylbenzene (435 mg/m^3), toluene (188 mg/m^3) and xylene (435 mg/m^3). Benzene (16 mg/m^3) and respirable crystalline silica (0.1 mg/m^3) are assigned an OEL-CL as they are confirmed human carcinogens (Department of Employment and Labour, 1995).

OELs vary from one country to another. The set time weighted average occupational exposure limit-control limit (TWA-OEL-CL) in South African legislation for respirable crystalline silica is 0.1 mg/m^3. The South African limit is similar to that of Australia and United Kingdom (0.1 mg/m^3) while the limit assigned to respirable crystalline silica by the Occupational Safety and Health Administration (OSHA, USA) is lower (0.05 mg/m^3) (Maciejewska, 2008). The American Conference of Government Industrial Hygienists' (ACGIH) threshold limit value (TLV®) for respirable crystalline silica is 0.025 mg/m^3, which is much lower than the South African exposure limit. However, this TLV is not meant to be used as a legal standard because they are health based (ACGIH, 2015). But in theory and practice, this does not disqualify TLVs® from being used as a standard.

Effects caused by substances due to exposure vary depending on the type of the substance. Some effects may occur after accumulated exposure while others are seen shortly after the individual has been exposed to the hazardous substance. For substances that have cumulative effects, a long-term (8-hour TWA) exposure limit is set. For substances that have acute effects, a short-term (15 minutes) exposure limit is set. Several substances, e.g., VOCs can penetrate the skin and be absorbed by the body (Schoeman and Schroder, 2014). These substances are assigned a skin notation (sk). Toluene and xylene are examples in this classification, which means that handling of such substances without proper gloves (nitrile gloves) may lead to the substances penetrating the skin and consequently causing dermatitis. Also, toluene and xylene are assigned a sk notation because vapours from these VOCs may also cause dermal exposure.

2.5 Conclusions

AM has found application in many sectors, one being metal casting. But the information on the risks associated with the manufacturing of sand casts for metal casting is minimal. Moreover, there is a lack of information on the health implications on AM operators posed by

the coating process. Both the coating of silica sand with sulphonic acid and the printing of sand moulds might be a risk to the AM operators' health due to the feedstock material used, i.e. silica sand, furan resin binder and sulphonic acid. It will therefore be beneficial to both AM operators and the AM community to investigate the exposures associated with these processes in order to contribute knowledge to already existing information on AM. This study will also be able to give recommendations of specific control measures and potentially help to improve working conditions for AM operators.

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CHAPTER 3: RESPIRATORY EXPOSURE TO RESPIRABLE CRYSTALLINE SILICA AND ASSOCIATED PARTICULATE EMISSIONS DURING THE COATING OF SILICA SAND FOR ADDITIVE MANUFACTURING

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'top 5' search terms (including 'number one') should each appear at least once in the abstract, with the 'top 3' appearing more than once if possible. It is important that your abstract is written in a naturalistic and engaging style that will encourage readers to follow up by reading the full paper. The 'bottom 5' search terms can then be added as keywords.

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Structure of paper: Papers should generally conform to the pattern: Introduction, Methods, Results, Discussion, and Conclusions, unless these are clearly inappropriate. A paper must be prefaced by an abstract of the argument and findings, which may also be arranged under the same headings.

Design and analysis: The quality of the data and analysis must always be good enough to justify the inferences and conclusions drawn. Particular attention should be given to design of sampling surveys, which should be planned using modern statistical principles, and to the treatment of results below the limit of detection.

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Jones and Brown (1995) and Hospath *et al* (2006) observed total breakdown of control..., or Total breakdown of control has sometimes been observed (Jones and Brown, 1995; Hospath *et al*., 2006).

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Examples:

Simpson AT, Groves JA, Unwin J, Piney M. (2000) Mineral oil metal working fluids (MWFs)—Development of practical criteria for mist sampling. Ann Occup Hyg; 44: 165–72. Vincent JH. (1989) Aerosol sampling: science and practice. Chichester, UK: John Wiley. ISBN 0 471 92175 0.

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RESPIRATORY EXPOSURE TO RESPIRABLE CRYSTALLINE SILICA AND COINCIDING PARTICULATE EMISSIONS DURING THE COATING OF SILICA SAND FOR ADDITIVE MANUFACTURING

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3.1 Abstract

Purpose: The coating process is a newly implemented procedure introduced by the additive manufacturing (AM) facility where the study took place, during which silica sand is coated with sulphonic acid and used to produce sand moulds with high structural integrity. The health risks associated with this specific coating process are not well known, thus it is the purpose of this study to determine respiratory exposure to and emission of airborne respirable crystalline silica and particulate matter during the coating process.

Methodology: Characterisation of particle size and shape of virgin (uncoated) and coated silica sand was conducted using Malvern Morphologi G3 particle analyser and scanning electron microscopy (SEM) while X-ray diffraction (XRD) was utilised to determine the mineral composition of the sand. The Aerosol Particle Counter (APC) and Condensation Particle Counter (CPC) were used to quantify emissions of particles ranging from 0.3 to 10 µm and from 0.01 - ~1.0 µm respectively. Both personal and area monitoring were performed to measure concentrations of respirable crystalline silica and respirable sized particulate concentrations during the AM operator's shift using standard occupational hygiene (OH) standard methods.

Results: The particle size distribution (PSD) indicated that the virgin sand comprised of more than 90% of respirable particles [d(0.9) = 3.98 ± 0.72 µm] while 50 - 90% of the coated sand were in the inhalable fraction range [d(0.5) = 26.76 ± 35.04 µm]. Both silica sand particles were smooth but not spherical. The quartz content of both the virgin and coated silica sands ranged from 92.6 to 97.3%. Real-time particulate emissions data indicated that the particle emissions for particles ranging between 0.3 and 1 µm, and between 0.01 - ~ 1.0 µm in size, increased considerably during the cleaning of the coating machine filter as well as during the opening of the room's bay door. Personal exposure to respirable crystalline silica during cleaning of the coating machine with compressed air was 0.112 mg/m³, which exceeded the South African TWA OEL-CL of 0.1 mg/m^3.

Conclusion*:* During cleaning of the coating machine, particles containing a high percentage of silica were released into the workplace air leading to an overexposure to crystalline silica, the leading cause of silicosis and a confirmed carcinogen.

3.2 Introduction

Additive manufacturing (AM) is defined as the layering of feedstock materials to produce a three-dimensional (3D) part. The introduction of this technology opened new doors for manufacturing industries, and it has been well implemented in the aerospace, automotive and medical sectors, amongst others (Gibson *et al*., 2015). The metal casting sector has also adopted the use of AM to manufacture sand moulds. Implementation of AM in metal casting means that sand moulds can now be manufactured easier, quicker and at a lower cost (Anakhu *et al*., 2018).

AM using silica sand involves three phases: pre-processing, processing and post-processing. Pre-processing includes cleaning of the AM machine and loading of the job box with the virgin (unused) silica sand into the AM machine. The processing phase involves printing of the actual part while the post-processing phase comprises of cleaning of the part as well as other finishing activities. With sand casting, there is an additional step involved prior to pre-processing. The uncoated silica sand needs to be coated with sulphonic acid to form a homogeneous mixture. This is a crucial part of the process as it helps harden the furan resin binder (Dady *et al*., 2019) which plays an important role in improving the integrity and strength of the sand mould (Shan *et al*., 2017).

There are two materials used during the coating process, namely silica sand and sulphonic acid. Usage of these materials can possibly result in airborne respirable crystalline silica and sulphonic acid exposure. Respirable crystalline silica (often referred to as quartz) exposure can cause silicosis, which is an irreversible chronic disease of the lungs associated with long term exposure. Silicosis results in coughing, decreased lung elasticity (due to increased surface tension as a result of low surfactant production), shortness of breath and chest pains (Schroder, 2014; Mgonja, 2017). Additionally, extended periods of personal exposure to respirable crystalline silica causes lung cancer International Agency for Research on Cancer (IARC) (2012). Exposure to sulphonic acid can result in respiratory, eye and skin irritation, drowsiness and dizziness (Protea Chemicals, 2017). Particle size is also another factor to consider as it determines the deposition of particles in the respiratory tract (Brown *et al*., 2013). As an example, respirable particles (< 4 µm) penetrate into alveolar region where they induce their toxicity (Wilson *et al*., 2002; Stacey *et al*., 2018). Respirable particles cannot be cleared from the lungs, therefore, they accumulate in the alveoli causing pneumoconiosis (Schroder, 2014).

There is no literature available concerning the health risks associated with the coating of silica sand used during AM to manufacture sand moulds. Thus, this study strives to shed

light on exposures associated with silica sand coating for AM. The objective of this study was to determine personal exposure to respirable crystalline silica and particulate matter during the coating process as well as to determine particulate emission concentrations and the physical and chemical characteristics of silica sand particles. The exposure to sulphonic acid is not discussed as it has low toxicity compared to crystalline silica.

3.3 Methodology

The study was conducted at an AM facility located on the campus of a South African tertiary education institution over a period of three days. One AM operator performed all the activities associated with the coating of the silica sand with sulphonic acid (Table 3-1). The room, in which the coating machine (Figure 3-1) was located, appeared to have been a storage facility (Figure 3-2). The housekeeping in this room was inadequate as there was loose silica sand on the floor. The only means of reducing airborne contaminants or introducing fresh air was a built-in dust extractor in the coating machine (Figure 3-1) and the occasional opening of the bay door (Figure 3-2). A full description of the activities performed during coating is supplied in Table 3-1. Figure 3-1 and Figure 3-2 show the structure of the coating machine and the layout of the coating room, respectively.

In addition to Table 3-1 and Figure 3-1, the following was observed with regard to the preforming of the process: firstly, the AM operator draws sand from a bulk bag using a built-in vacuum duct hose into the hopper. The sand then gradually flows from the hopper into the screw conveyor where a tube from a sulphonic acid container is then inserted supplying the sand with acid (in liquid form). The AM operator then places another empty bulk bag beneath the screw conveyor where coated sand is collected. The built-in dust extractor collects airborne dust particles released when sand is poured into the bulk bag, after which the bag is transferred to the outside the building using a forklift.

This study was classified as holding minimal risk and approved by the North-West University Health Research Committee (NWU-HREC) (NWU-00020-19-A1). Signed informed consent was obtained from the operator who participated in the study.

Table 3-1: Description of activities that occurred at the facility during the coating process

Activity	Day		
	1	2	3
The sand coating machine filter was cleaned using compressed air.	X		X
A built-in vacuum hose was utilised to transfer silica sand into the coating machine hopper.	X	X	X
The coating process was started by inserting a tube delivering sulphonic acid liquid into the mixer where the sand and the acid formed a homogeneous mixture.	X	X	X
The coated sand mixture was then deposited into a bulk bag.	X	X	X
The built-in dust extractor was operational but no natural ventilation was present in the coating area.	X	X	
During the coating process, other operators came in through the bay door with a forklift to collect a bulk bag that was filled with coated sand. The coating operator mentioned that since the built-in extractor transfers dust outside, it is possible for dust to be re-introduced again when the bay door opens as seen in Figure 3-2.			X
The room had means of natural ventilation due to the bay door opening.			X
The room had means of mechanical ventilation via the built-in dust extractor	X	X	X
The AM operator was wearing a PHUZA MOYA FFP2 half-face disposable respirator and latex gloves.	X	X	X

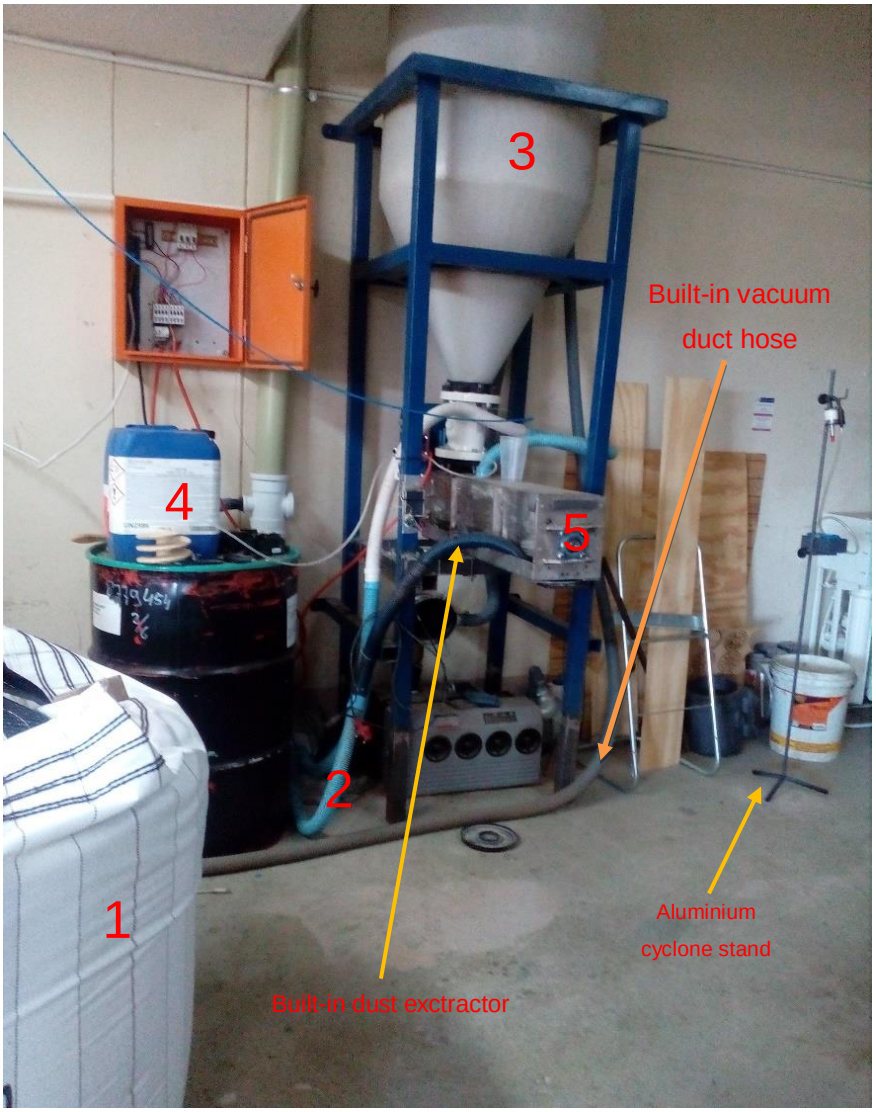

Figure 3-1: **The structure of the coating machine used for coating of silica sand with sulphonic acid. The components used in the coating process include; 1) bulk bag, 2) built-in vacuum extractor, 3) hopper, 4) sulphonic acid container and 5) screw conveyor. The figure also shows the area respirable particulate monitoring setup.**

Figure 3-2: **An image of the room where the coating process took place showing the bay door being opened as well as the placement of the direct reading instruments: airborne particle counter (APC) APC and condensation particle counter (CPC).**

3.3.1 Physical and chemical characterisation of silica sand

Bulk samples of two types of silica sand (virgin and coated) were collected separately into 50 ml vials. Virgin sand refers to new or unused sand. Sand that has been coated with sulphonic acid is classified as coated sand while sand that has been supplied to a AM machine during a previous build cycle is referred to as used sand according to the International Organization for Standardization/American Society for Testing and Materials (ISO/ASTM) 52900 (2015). The operator collected the different types of sand while wearing latex gloves. The Malvern Morphologi G3 (Malvern Instruments Ltd, UK) was used to quantify particle size distribution (PSD) and shape. Scanning Electron Microscopy (SEM) was used to determine the physical characteristics and external morphology while chemical composition was analysed using X-ray diffraction (XRD).

3.3.1.1 Particle size distribution (PSD) and shape analysis

The methodology used in this section of the chapter (PSD and shape analysis and elemental composition) were based on tha dsecribed by du Preez *et al*. (2018).

The Malvern Morphologi G3 automated microscope (Malvern Instruments Ltd., United Kingdom) was used to perform PSD and particle shape analysis. The 5 mm^3 samples were placed in a dispersion unit of the instrument. After the dispersion process, the images of individual sand particles were taken and analysed using the automated microscope. The samples were analysed in triplicate.

SEM analysis was performed by placing the sand samples on a double-sided tape stub where it was coated with an SPI Module sputter coater (SPI-Module$^{TM.}$ Sputter Coater, SPI Supplies, West Chester, PA, USA) fitted with gold-palladium alloys. Samples were then analysed using the software Phenom pro-desktop SEM (Phenom PRO Desktop SEM, Phenom-World B., Eindhoven, Netherlands) at a power of 5 kV. Magnifications were set to capture images of particles sizes ranging from 200 µm to 500 µm in order to capture images of particles smaller in size.

3.3.1.2 Elemental composition

XRD analysis was conducted to determine the elemental composition of the two sand samples. The analysis was performed using the powder diffractometer (X' Pert Pro XRD PANalytical Instrument, Netherlands). The material was finely pulverised and undiluted sand samples were placed onto the spinner stage inside the XRD using a back-loading technique. The x-rays generated by a Cu Kα x-ray tube (PW3376/00 Co LFF tube, PANalytical, The Netherlands) were then used to scan the sand samples.

3.3.2 Particulate emissions

The real-time particulate emissions were measured using the Airborne Particle Counter (APC) (Aerotrak Portable Particle Counter model 9310 TSI Inc., MN, USA) and Condensation Particle Counter (CPC) (CPC model 3007 TSI Inc., MN, USA). The APC is used to characterise particles within the 0.3 - 10 µm size range and measures particles in specific size channels (0.3, 0.5, 1, 3, 5 and 10 µm). The CPC is used to quantify emissions of particles ranging from 0.01 - ~ 1.0 µm during the coating process and measures particles in a 0.01 - ~ 1.0 µm size range in a single channel with no specific upper cut off point. For each coating day, the APC collected data for 1 minute and the CPC for 10 seconds intervals, which was averaged to 1 minute. The background particle number concentrations were not

measured as the emission rates (ERs) were not calculated. Prior to use, both instruments were factory calibrated. Before sampling was performed, the alcohol capsule was filled to its specified volume. The alcohol cartridge was inserted into the CPC and then with the zero filter attached, it was allowed to run for 300 seconds until it was zeroed. The filter was then removed to allow sampling. During sampling, both the APC and CPC were placed on a table ±1 meter away from the source (Figure 3-2).

3.3.3 Personal and area monitoring

Personal respiratory exposure monitoring was conducted to determine personal exposure to airborne respirable crystalline silica and respirable sized particulate matter. An aluminium cyclone sampler containing a 37 mm polyvinyl chloride (PVC) filter with 5.0 µm pore size, attached to the GilianGilair plus (Sensidyne, Inc., LP, USA) air sampling pump with flexible tubing, was used to measure personal exposure in the worker's breathing zone. The sampling pump was calibrated using the Gilian Gilibrator-2 (Sensidyne, Inc., FL, USA) calibrator at a flow rate of 2.5 L/min in accordance with the National Institute for Occupational Safety and Health (NIOSH) method 0600 and 7500 (NIOSH, 1998; NIOSH, 2003). Area sampling was conducted in order to measure the concentrations of airborne respirable crystalline silica and respirable sized particulate matter in the area of the coating operation. The sampling train and calibration procedure were similar to that of personal monitoring. The air sampling train was placed on a tripod stand and positioned 1 m away from the source and 1.5 m above floor level (Figure 3-1). Following sampling, the samples were transported to an accredited analytical laboratory where crystalline silica was analysed for alpha quartz utilising XRD, according to the NIOSH method 7500 (NIOSH, 2003).

3.3.4 Statistical analysis of results

Descriptive statistics were utilised to calculate the mean and standard deviation of the PSD and shape of both virgin and coated silica sands. The mean particle sizes were classified as d(0.1) (10% of the particles were less than the stated diameter); d(0.5) (50% of the particles were less than this diameter) and d(0.9) (90% of the particles were less than the stated diameter). Tests for normal distribution of data were performed using the D'Agostino & Pearson test. The data was not normally distributed. The shape and PSD of both types of sand were compared to each other through unpaired t-tests using Graphpad Prism 8 (Graphpad Prism, version 8, GraphPad Software, La Jolla, USA). The mean, range and maximum for the number of particles measured during coating were obtained using descriptive statistics. Graphpad Prism 8 was again used to provide graphical representations of particle size data.. The statistically significant differences in particle number

concentrations measured on the three days were determined using Krustal-Wallis tests (non-parametric), followed by Dunn's multiple comparisons test. P-values of ≤ 0.05 were considered statistically significant.

3.4 Results

3.4.1 Physical and chemical characteristics of silica sand particles

Table 3-2 shows the PSD and composition for virgin and coated sand. The findings indicated that the virgin sand contained predominantly respirable fractions (< 4 µm) [d(0.9) = 3.98 ± 0.72]. For the coated sand more than 50% [d(0.5) = 26.76 ± 35.04] was within the inhalable fraction (< 100 µm). It was also observed that both virgin and coated sand particles were smooth, but not spherical (Table 3-2), which is supported by the SEM imaging (Figure 3-3). The silica sand particle sizes by SEM imaging were however larger than that of PSD. Both virgin and coated silica sand had > 92% quartz content. Mullite, aluminium oxide and graphite were also present in minute amounts.

Table 3-2: Particle size distribution (mean ± SD), shape and composition of virgin and coated sands

Sand type	N	PSD (µm)			Circularity number distribution	Convexity number distribution
		d(0.1)	d(0.5)	d(0.9)		
Virgin	**3**	1.16 ± 0.02	1.82 ± 0.13	3.98 ± 0.72	0.82 ± 0.03	0.99 ± 0.01
Coated	**3**	1.89 ± 0.89	26.76 ± 35.04	115.00 ± 95.15	0.79 ± 0.03	0.97 ± 0.01
		Particle composition (%)				
		Mullite	Aluminium Oxide	Graphite	Quartz	
Virgin	**1**	1.6	1.0	-	97.3	
Coated	**1**	-	0.1	7.3	92.6	

n – Number of repeated measurements; d(0.1) – 10% of the particles are smaller than the specified diameter; d(0.5) – 50% of the particles are smaller than the specified diameter; d(0.9) – 90% of the particles are smaller than the specified diameter; Circularity: The ratio of the perimeter of a circle with the same area as the particle divided by the perimeter of the actual image; Circularity values range from 0 - 1, a perfect sphere will have a circularity of 1; Convexity: The measured edge roughness of the particle. A smooth particle will have a convexity value close to 1 whereas an irregular particle will have a convexity value of 0.

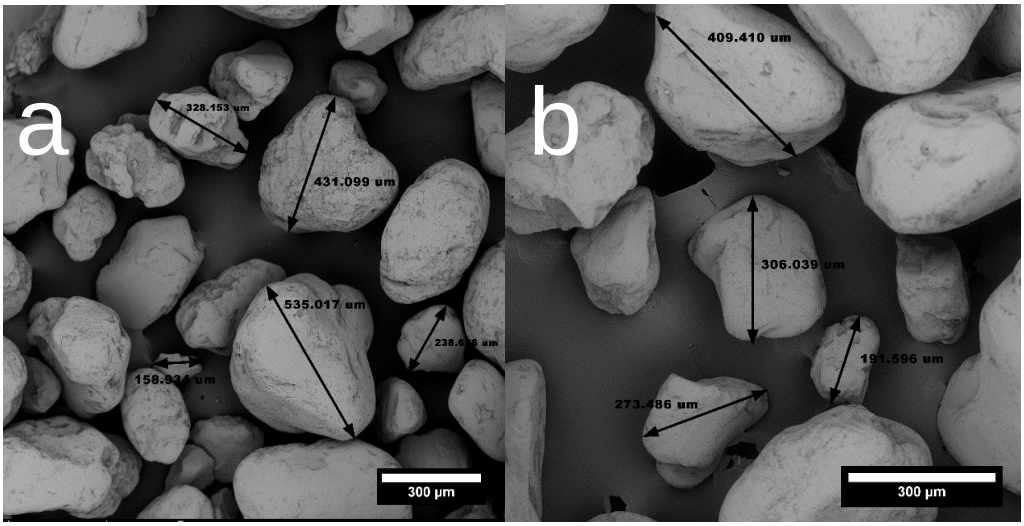

Figure 3-3: **SEM imaging of a) virgin and b) coated sand particles set at 300 µm scale.**

3.4.2 Particulate emissions

The coating process was monitored over a period of three days. Though the process is automated, the AM operator was required to remain in the room during coating to ensure that the machine does not malfunction. As is shown in Figure 3-4, the coating operation emitted the highest number concentrations of 0.3 µm sized particles, followed by 0.5 µm and 1 µm. Due to their low number concentrations, 3, 5 and 10 µm sized particle emissions will not be discussed further.

Table 3-3: **Peak particle number concentrations during certain activities**

	Day	Size of the particles (um)				Reason / Activity
		0.3	0.5	1.0	0.01 - ~ 1.0	
Particle number concentration (p/m^3)	1	1.44×10^8	1.39×10^8	1.16×10^8	1.65×10^{10}	Cleaning with compressed air
	2	8.71×10^7	4.39×10^7	2.49×10^7	3.81×10^{10}	Coating
	3	1.13×10^{10}	9.49×10^7	6.33×10^7	3.25×10^{10}	Cleaning with compressed air
	3	9.29×10^7	7.43×10^7	5.01×10^7	7.22×10^{10}	Opening bay door

On the first day of coating, the particle number concentrations of 0.3, 0.5, 1 µm and 0.01 - ~ 1.0 µm sized particles peaked at approximately (t = 5 – 7 minutes) when the operator used compressed air to clean the coating machine filter (Figure 3-4A and 3-4D).

On the second day of coating, 0.01 - ~ 1.0 µm sized particles reached a maximum at approximately (t ≈ 25 minutes).

On day three, particle number concentrations rapidly increased (t ≈ 6 min) when the coating machine filter was cleaned (0.3 µm = 1.13 × 10^{10}, 0.5 µm = 9.49 × 10^{7}, 1 µm = 6.33 × 10^{7} and 0.01 - ~1.0 µm = 3.25 × 10^{10} p/m^{3}). Opening of the bay door (between t ≈ 71 - 95 min) also caused an increase in the particle concentrations in the room (0.3 µm = 9.29 × 10^{7}; 0.5 µm = 7.43 × 10^{7}; 1 µm = 5.01 × 10^{7} and 0.01 - ~ 1.0 = 7.22 × 10^{10} p/m^{3}).

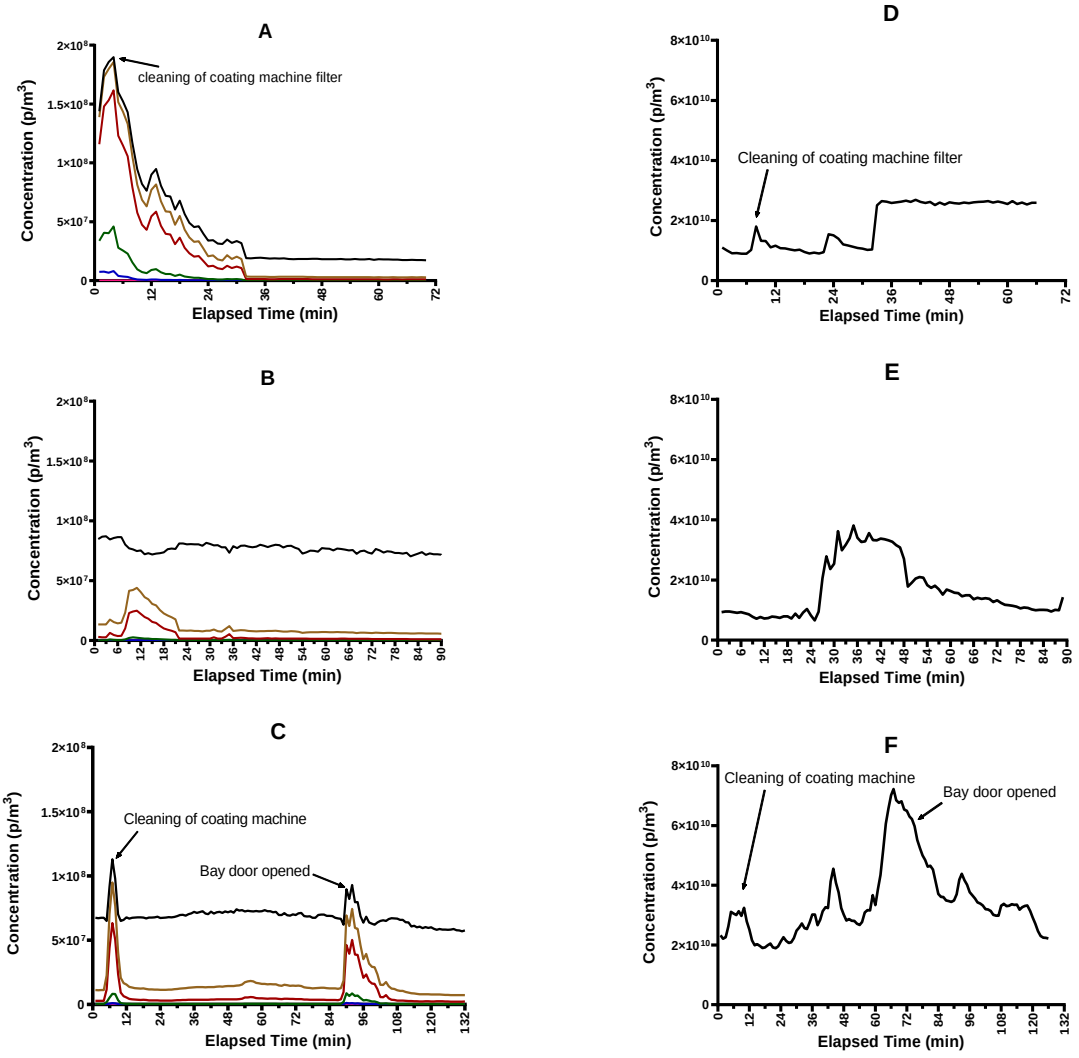

Figure 3-4: **Real time emissions of (A, B, C) 0.3 µm – 10 µm and (D, E, F) 0.01 - ~ 1.0 µm sized particles measured during day one (A & D); day two (B & E); day three (C & F) of coating.**

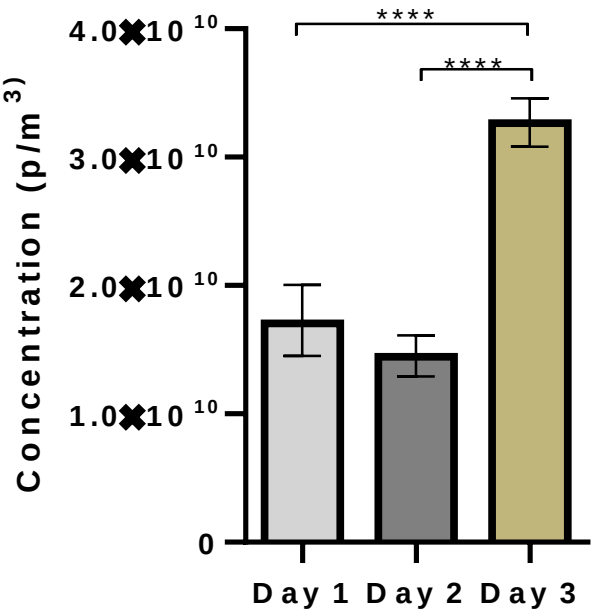

Figure 3-5: **Comparison of the particle number concentrations in 0.01 - ~ 1.0 µm size range between various days of coating. The columns represent the geometric means, and the lines represent 95% confidence intervals. **** Indicate statistical differences between the days ($p \leq 0.05$).**

The emission concentrations on different days were compared to one another and there was a statistically significant difference in particle number concentrations between the various days of coating (Figure 3-5). The emission concentration of 0.01 - ~ 1.0 µm sized particles on day three was significantly higher than that of day one ($p < 0.0001$) and two ($p < 0.0001$).

3.4.3 Personal exposure and area airborne concentrations of respirable crystalline silica and total respirable dust

Table 3-4: Personal exposure and area airborne concentrations of respirable crystalline silica and total respirable dust

Time (min)	Day	Activity	Total respirable dust (TWA mg/m^3)		Quartz (TWA mg/m^3)	
			Area	Personal	Area	Personal
205	1	Coating and cleaning	0.125	0.392	0.060#	0.112*
178	2	Coating	0.083	0.167	<0.003	0.007
250	3	Coating and cleaning	0.067	0.424	<0.003	0.009

Crystalline silica (quartz): TWA OEL-CL – 0.1 mg/m^3; Respirable dust TWA OEL-RL – 5 mg/m^3; # - Above the action level; * - Above the OEL

The coating process was measured over a period of three days. Though the process is automated, the operator was required to remain in the room during coating. The daily personal exposure to respirable crystalline silica during coating ranged from 0.007 to 0.112 mg/m^3. During the first day of coating, the personal exposure to respirable crystalline silica experienced by the operator exceeded the TWA OEL-CL (0.1 mg/m^3). Total respirable dust concentrations during personal monitoring ranged from 0.159 to 0.424 mg/m^3 which were less than 10% of the OEL-RL (5 mg/m^3).

3.5 Discussion

There is a lack of studies on the risks associated with coating of silica sand prior to use in AM. As such, this study was conducted to help determine respiratory exposure to particulates associated with this process. To help achieve this purpose, chemical and physical characteristics as well particulate emissions, area particulate concentrations and personal exposure were investigated.

3.5.1 Physical and chemical characteristics

According to the PSD analysis, more than 90% of virgin silica sand particles were respirable while 50 – 90% of coated silica sand comprised of inhalable sized particles. In contrast to the particle sizes reported in the PSD for coated silica sand, the SEM images indicated that the particles were larger, which could have resulted from agglomeration of smaller particles (not

shown in SEM) due to coating. The deviations between PSD and SEM are due to the method of analysis, where PSD analyses particles on a larger scale while SEM captures an image of a certain area on the stub.

Respirable crystalline silica can deposits in the alveolar region depending on the particles size, shape and behaviour in the tract. In the alveoli, respirable crystalline silica reduces the life expectancy of alveolar macrophages thereby decreasing the ability of macrophages to eliminate the silica particles. Inhalable sized particles can penetrate beyond the larynx (CEN, 1993). Exposure to these particles can cause sneezing or coughing, though repeated exposure can be hazardous to human health. Both coated and virgin silica sand predominantly comprised of quartz (92.6 - 97.3%). Exposure to respirable quartz (crystalline silica) is the primary cause of acute or chronic silicosis (Yassin *et al*., 2005). Due to size and quartz content, both virgin and coated silica sand pose a substantial risk to the AM operator. Since > 90% of virgin sand particles are classifiable as respirable, virgin sand poses a higher health risk compared to coated sand.

According to the facility where the research was conducted, the silica sand manufacturers could not provide a safety data sheet (SDS), thus it was not possible to compare findings of this study with the information on the SDS. Due to the absence of the SDS, the AM operator was possibly not aware of the possible risks associated with the use of the silica sand. Especially the high respirable crystalline silica quartz content of the sand should be communicated to the AM operator since it means that relatively low particulate exposure may lead to significant crystalline silica exposure, as was found on day one.

3.5.2 Day 1 of the coating process

Prior to the coating process, the AM operator cleaned the coating machine filter using compressed air. This caused the liberation of particles captured in the filter and a dust cloud was observed. As a result, there was a steep increase in particle number concentrations of 0.3 - 1 µm and 0.01 -~ 1.0 µm sized particles, which also reflected in the results of the personal and area monitoring.

The AM operator was exposed to a concentration of respirable crystalline silica above the OEL-CL as a result of filter cleaning using compressed air. This activity is concerning because particles released were predominantly composed of crystalline silica due to the high quartz content of the sand (> 90%). According to the International Agency for Research on Cancer (IARC) (2012) and Agency for Toxic Substances and Disease Registry (ATSDR)

(2017), in workplaces where silica sand is handled, exposure to respirable crystalline silica can lead to both silicosis and lung cancer.

The area airborne respirable crystalline silica concentration present during the cleaning was 0.06 mg/m^3. Area monitoring cannot be compared to the OEL-CL because it represents the concentrations of a hazardous substance in an area and the OEL is only applicable to personal exposure. Area concentrations were however still above the action level (50% of OEL). The reason it was compared to the OEL-CL is to indicate that respirable crystalline silica concentrations in the coating room were at a level that could place the AM operators' health at risk and action needs to be taken. The results from personal and area monitoring showed that cleaning of the coating machine and its filter should be classified as a high-risk activity.

3.5.3 Day 2 of the coating process

The particle number concentration of 0.5 and 1 µm sized particles peaked at (t ≈ 7 minutes) (Figure 3-4B). At approximately (t = 25 minutes) emission of 0.01 - ~ 1.0 µm sized particles rapidly increased during the coating process (Figure 3-4E). It is unknown what might have caused this drastic increase in particle number concentrations but it was observed that the same peak is absent on Figure 3-4B. Stefaniak *et al*. (2018) found that emission rates (ERs) for particles measured using the CPC were five to six times higher than the optical particle counter (OPC) (size range; 0.3 to > 20 µm), indicating that the dominant particles in that workplace were below 300 nm (0.3 µm). The CPC (0.01 - ~ 1.0 µm) shows a peak where the APC (0.3 µm, 0.5 µm, 1 µm, 3 µm, 5 µm and 10 µm) does not, which could also indicate the presence of particles between 0.01 and 0.3 µm in size.

This rapid increase in particle number concentration did however, not have a significant impact on the respirable dust and crystalline silica concentrations. This might be due to a high number of 0.3 µm sized particles in the room. Stefaniak *et al*. (2018) also observed that personal exposures to metal containing particles < 0.3 µm in size were below the NIOSH recommended exposure limit. Reason being that, particle mass decreases as size decreases. Compared to day one, the total respirable dust and crystalline silica exposure of the AM operator was lower (0.167 and 0.007 mg/m³, respectively). The reason being that on day two, cleaning of the coating machine filter was not performed which could be the reason for lower personal exposure concentrations.

3.5.4 Day 3 of the coating process

There was a drastic increase in 0.3 – 1.0 µm and 0.01 - ~ 1.0 µm sized particles (Figure 3-4C and 3-4F) when the AM operator cleaned the coating machine filter but the instantaneous peak concentrations were lower compared to day one. Later in the day, a second instantaneous peak occurred as a result of opening the bay door to remove the bulk bag with coated sand. This could be the reason why there was a statistical difference in particle number concentrations (0.01 - ~ 1.0 µm) between days three and one as well as between days three and two (Figure 3-5). Increased particulate matter and lower crystalline silica compared to day one points to dust (with a lower quartz content) from outside entering the room during opening of the bay door (Table 3-4).

The particulate emission results from the three days of coating show that cleaning of the coating machine filter using compressed air as well as the opening of the bay door caused increased airborne concentrations of particulates 0.01 - ~ 1.0 µm in size. Cleaning of the coating machine filter using compressed air led to personal crystalline silica exposure above the OEL-CL on day one. Since more than 90% of silica sand comprised of quartz, it means that the AM operator is at a risk of developing silicosis even if he is only exposed to relatively small concentrations of dust. Therefore, measures need to be implemented to reduce exposure.

3.6 Recommendations

Higher emissions of respirable crystalline silica were measured during cleaning of the coating machine filter. This is because the AM operator performed the task with the use of compressed air. According to the Regulation 13 (a) of the Hazardous Chemical Substances Regulations (HCSR) (Department of Employment and Labour, 1995), the use of compressed air to remove hazardous particles from any surfaces or person is strictly prohibited.

The following recommendations are made to help reduce emissions: 1) if available, a vacuum cleaner fitted with a high-efficiency particulate air (HEPA) filter can be used to clean the coating machine filters; 2) the coating machine fiters should be maintained and kept clean regularly to minimise accumulation of dust on the filter; 3) the facility can implement a small isolation chamber, like a glove box, where the filters can be cleaned without releasing particulates into the air; 4) it is advisable for the facility to improve the housekeeping of the coating room which will minimise contamination of workplace air caused by resuspension of silica sand dust; 5) a mobile dust extractor (Figure 5-1) can be placed around the coating machine to avoid the spread of crystalline silica particles into the room; 6) a heating,

ventilation and air conditioning (HVAC) is recommended because it can introduce fresh air which dilutes airborne particulate matter, thereby minimising particle accumulation in the room.

No SDS was provided by the silica sand manufacturer. It is recommended that the AM facility obtain an SDS because the AM operator was not aware of the dangers of working with silica sand. With SDSs, the AM operator will be able to gain information on how to handle and store silica sand as well as the dangers of exposure. It is also important for the facility to maintain good housekeeping by vacuuming the loose silica sand on the floor in order to minimise resuspension of settled silica sand particles. Lastly, the AM operator protected himself against respirable crystalline exposure by wearing half-face disposable respirators (PHUZA MOYA FFP-2) and latex gloves. For additional protection, the AM operator is advised to also wear standard industrial coveralls and safety shoes in order to avoid silica dust adhering to their casual wear thereby leading to cross-contamination.

3.7 Conclusion

There is very little information available on the risks associated with coating of silica sand used for AM of sand moulds, thus this study is aimed at providing information on the physical and chemical characteristics of silica sand particles as well as information on particle emissions and respiratory exposure to crystalline silica sand particles. The feedstock material is the primary source of exposure and virgin silica sand poses a greater risk as it is predominantly composed of respirable crystalline silica quartz (> 90%) particles. The AM operator was overexposed to respirable crystalline silica (0.112 mg/m^3) on day one of coating as a result of cleaning the coating machine filter using compressed air. Particle number concentrations of 0.3 – 1 µm and 0.01 - ~ 1.0 µm sized particles peaked due to cleaning activities and opening of the bay door. However, cleaning with compressed air should be regarded as the activity with the highest risk to the health of the operator during coating of silica sand for AM. The reduction of exposure during cleaning of the coating filter should be prioritised by the facility.

3.8 References

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CHAPTER 4: PARTICULATE EMISSIONS AND RESPIRATORY EXPOSURE TO HAZARDOUS CHEMICAL SUBSTANCES DURING ADDITIVE MANUFACTURING OF SAND MOULDS

PARTICULATE EMISSIONS AND RESPIRATORY EXPOSURE TO HAZARDOUS CHEMICAL SUBSTANCES DURING ADDITIVE MANUFACTURING OF SAND MOULDS

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4.1 Abstract

Background: AM is a process that produces three dimensional (3D) parts via the layering of materials. To date, there has been little research on the health risks associated with the use of binder jetting (BJ) to produce sand moulds for metal casting. This study is aimed at determining emissions of and personal respiratory exposure to respirable airborne crystalline silica, volatile organic compounds (VOCs) and respirable particulate matter during the BJ of silica sand moulds.

Methodology: Characterisation of silica sand particle size and shape was performed using Malvern Morphologi particle analyser and scanning electron microscopy (SEM) while the X-ray diffraction (XRD) process was utilised to determine elemental composition. The Aerosol Particle Counter (APC) and Condensation Particle Counter (CPC) were used to quantify emissions of 0.3 – 10 µm (APC) and 0.01 - ~ 1.0 µm (CPC) sized particles during the pre-processing, processing, and post-processing phases. Both personal and area monitoring were performed to measure concentrations of respirable crystalline silica, VOCs, and particulate matter during the AM operators' shift. The study was conducted over a period of five days, where three identical parts were printed.

Results: Quartz was the predominant mineral found in both coated and used silica sands (92.6% and 96.8%, respectively). Used silica sand contained 50 – 90% respirable particles (< 4 µm) [d(0.5) = 1.88 ± 0.12 µm and d(0.9) = 6.51 ± 2.71 µm] while > 10% of coated silica sand was respirable particles [d(0.1) = 1.89 ± 0.89 µm] and 50 – 90% was inhalable [d(0.5) = 29.76 ± 35.04 µm]. The particle number concentrations of 0.3 – 10 µm and 0.01 - ~ 1.0 µm sized particles were higher during the third day than any other day, as a result of increased particle number concentrations during pre-processing, processing, and post-processing. The average emission rates (ERs) of particles 0.3 µm and 0.01 - ~ 1.0 µm in size were the highest during pre-processing followed by post-processing and then processing. There were no significant differences in ERs of particles ranging from 0.01 - ~ 1.0 µm in size between the AM phases. During cleaning of the AM machine, personal exposure to respirable crystalline silica surpassed the action level (50% of OEL) (0.07 mg/m^3). The personal exposures to HCS (respirable crystalline silica, respirable dust and VOCs) measured during the AM processes were below 10% of their respective OELs.

Conclusion: The operator was exposed to respirable crystalline silica exceeding the action level due to the use of a broom when cleaning the AM machine room. This may lead to deleterious health effects as silica sand contained more than 90% of quartz. Small particle

size and high quartz content of the feedstock material increased the risk for the AM operator. Pre-processing had the highest particle emission compared to other processes.

4.2 Introduction

Additive manufacturing (AM), as termed by the American Society for Testing and Materials (ASTM), can be defined as a process of building a printed part layer upon layer until it is has taken a three-dimensional (3D) shape (Klahn *et al*., 2015; Le Néel *et al*., 2018). It is an umbrella term synonymous to rapid prototyping, rapid tooling, freeform fabrication and the most commonly used term, 3D Printing (Cozmei and Caloian, 2012; Jiminez *et al*., 2019). AM has been around for three decades and has gained recognition among companies and industries due to its ability to decrease costs, time and material wastage. Due to its flexibility and versatility, the technology has found its application in various industries such as aerospace, food industries, motorsport, and bioengineering, just to name a few (Tofail *et al*., 2018). One of the main applications of AM is manufacturing of sand moulds used for metal casting and AM has been utilised in this manufacturing sector as a more cost-effective method compared to traditional manufacturing methods (Chhabra and Singh, 2011).

There are two main techniques associated with AM of sand moulds, namely binder jetting (BJ) and selective laser sintering (SLS) (Le Néel *et al*., 2018). BJ (which is the main focus of this study) is a cold process which uses a furan resin binder to bind sand particles together, while SLS uses heat (carbon dioxide laser) to melt sand particles together (Hackney and Wooldridge, 2017). Though different, these techniques are similar in that they both have three phases, namely pre-processing [cleaning of the AM machine and loading of the feedstock material (silica sand) into the AM machine], processing (binding together of silica sand particles and print building) and post-processing (removal of excess silica sand using various cleaning techniques and curing of sand moulds). Silica sand is preferred over other materials such as zircon, olivine, and chromite due to its ability to consume less furan resin binder which results in defect-free moulds (Nyembwe *et al*., 2016a).

Although it is useful in this application, the usage of silica sand is a risk to the health of operators as they can be exposed to respirable crystalline silica particles (sometimes classified as quartz). When inhaled, these particles deposit in the alveoli where they induce their toxicity. Crystalline silica particles cause pulmonary inflammation and scarring which may result in silicosis. Silicosis is an incurable disease caused by prolonged exposure to respirable crystalline silica. Symptoms associated with this disease include coughing, fatigue, chest pains, fever as well as susceptibility to tuberculosis (Scholz and Slavin, 2007; Schroder, 2014).

Raw materials used for AM can cause adverse health effects in operators (Bours *et al*., 2017). For example, during the pre-processing and post-processing phases, handling of the feedstock material can lead to respiratory exposure to the material used which could lead to respiratory diseases (Du Preez *et al*., 2018a). In foundries, removal of excess silica sand following the manufacturing of the mould results in the substance becoming airborne, leading to possible respirable crystalline silica exposure (NIOSH, 1989). According to the Department of Labour (2007), long term exposure to more than 0.1 mg/m^3 of airborne crystalline silica increases the risk of pulmonary cancer by 30%. As a result, exposure respirable crystalline silica can cause both cancer (IARC, 2012) and silicosis. Health hazards associated with AM of sand moulds are not exclusively limited to respirable crystalline silica as resins used can lead to the emission of volatile organic compounds (VOCs) which can cause eye and skin irritation with a possibility of allergic reactions (Kellens *et al*., 2017). VOCs can also have an effect on the central nervous system (CNS), resulting in nausea, headaches, unconsciousness or dizziness, while some VOCs like benzene are carcinogenic to humans (IARC, 2012; Tsai, 2016; ToxTown, 2017; Shuai *et al*., 2018)

According to Adams (2016), there is a lack of in-depth knowledge regarding the physical and chemical characteristics of the feedstock material used in AM of sand moulds. Du Preez *et al*. (2018a) also states that size and composition of solid feedstock materials (powders/silica sand) are very important when determining workers' respiratory exposure. Deposition of particulate matter in the lungs is dependent on the size (Wilson *et al*., 2002; Kim *et al*., 2015) as well as the composition of particles (McClellan, 2002). Moreover, circularity and convexity can also be used to describe the shape of particles. Circularity describes the roundness of a particle while convexity refers to surface irregularity (Malvern Instruments Limited, 2015). Shape influences the deposition of a particle in the respiratory tract (Sturm, 2012). Therefore, physical and chemical characteristics of the silica sand used to manufacture AM sand moulds should be investigated when determining the risk to health associated with sand mould AM.

According to Stefaniak *et al*. (2018), AM is on the rise and with this increase in growth there is a potential of AM machines emitting contaminants that can lead to worker exposure. Thus this study was conducted with the aim of determining personal respiratory exposure of operators to respirable airborne crystalline silica, VOCs and particulate matter. The emission of these pollutants, during the pre-processing, processing and post-processing phases of AM as well as the physical and chemical characteristics of silica sand used for AM, are assessed in order to determine the factors that could negatively influence the health of the operators.

4.3 Methodology

4.3.1 AM facility and participants

The study was conducted over a period of five days: one day of cleaning and four days of printing. The AM machine was cleaned a day prior to the start of printing and three identical parts were printed over the next four days. It was not possible to perform sampling of all three AM phases in a single day because the sand moulds needed ± 12 hours to dry between the processing and post-processing phases. Thus, the post-processing for each print was performed on the day following pre-processing and processing. There was one operator working with the AM machine, however, on day two, two operators were involved in the printing of the sand moulds. The AM operator was tasked with printing three sand moulds of the same height and width so that the exposure scenario could be repeated three times. The printed sand moulds had a height, width and length of 33.5, 565.324 and 1000 mm respectively (Table 4-1).

This study was approved by the North-West University Health Research Committee (NWU-HREC) (NWU-00020-19-A1) and classified as holding minimal risk. Signed informed consent was obtained from the operators who participated in the study.

4.3.2 Physical and chemical characteristics of feedstock

A bulk sample of the coated (silica sand mixed with sulphonic acid) and used (excess silica sand removed from previously printed moulds) silica sand was collected separately using two sealable 50 ml storage vials by the operator, who wore latex gloves.

4.3.2.1 Particle size distribution (PSD) and shape analysis

The methodology used in this section of the chapter (PSD and shape analysis and elemental composition) were based on that dsecribed by du Preez *et al*. (2018b).

The Malvern Morphologi G3 automated microscope (Malvern Instruments Ltd, UK) was used to perform particle size distribution (PSD) and particle shape analysis. The 5 mm^3 samples were placed in a dispersion unit of the instrument. After the dispersion process, the images of individual sand particles were taken and analysed via automatic microscopic scanning. Samples were measured in triplicate.

The particle size and shape were studied visually using Scanning Electron Microscopy (SEM). The samples were placed on a piece of double-sided tape on a SEM sample stub.

The samples were then coated with an SPI Module sputter coater (SPI-Module$^{TM.}$ Sputter Coater, SPI Supplies, West Chester, PA, USA) fitted with gold-palladium alloys. This was used to visually represent the sample surface topography. The samples were then placed in the sampling chamber of a microscope for analysis using the software Phenom pro-desktop SEM (Phenom PRO Desktop SEM, Phenom-World B., Eindhoven, Netherlands) set at the magnification scale of 500 µm and 100 µm and power of 5 kV to enhance precision.

4.3.2.2 Elemental composition

The X-ray diffraction (XRD) (X' Pert Pro XRD PANalytical Instrument, Netherlands) was used to analyse the chemical composition of particles collected using a powder diffractometer. The back loading technique was required for sample preparation before the sample could be placed in the XRD spinner stage. After placing of the samples on the spinner stage, they were scanned using the x-rays from a Cu Kα x-ray tube (PW3376/00 Co LFF tube, PANalytical, The Netherlands).

4.3.3 Emission measurements

Table 4-1: Description of the activities that occurred at the facility during the AM process

Activity	Day				
	1	2	3	4	5
Pre-processing: • The AM machine was cleaned using a vacuum cleaner. The operator started by vacuuming the AM machine and ended with sweeping the floor using a broom.	X				
• Preparation of the print build, with regard to transferring CAD data into the AM machine and determining the print's dimensions.		X			
Pre-processing: • The AM operators checked if the hopper was working properly and able to supply the AM machine job box with the mixture of both used and virgin sands. Buckets full of previously used silica sand (beneath the hopper) were removed and empty ones were brought in.		X	X	X	
Processing: • After the print process was initiated, the AM operator left the room and returned periodically to monitor progress of the print. The print part (mould) was required to have a height, width and length of 33.5 mm, 565.324 and 1000 mm respectively. The size was identical throughout the study.		X	X	X	
Post-processing: • The operators unloaded the job box, placed it on the unpacking station and started cleaning of parts using brushes (post-process). • The unpacking station had openings beneath it that allowed excess silica sand to fall through and into the job box again, while a relatively small quantity was transported to the hopper to be mixed with virgin sand and reused again to print sand moulds. • The job box was then returned to the AM machine for the next print.			X	X	X
Ventilation: • The AM machine room had no means of natural ventilation, but there was movement in and out of the room via a door as the AM operator went in and out to ensure that the AM machine is functioning properly. This occurred throughout the study though not in a specific order. • There was a LEV (local extraction ventilation) system above the post-processing area as well as an air diluting ventilation system in the room but both were not operational.	X	X	X	X	X
Other information: • The AM machine side door was mistakenly left open during the processing phase		X			
• The background measurements inside the room were taken with the AM machine chamber open. The AM machine chamber door was already opened when the researcher arrived as the AM operator was already prepared to commence with post-processing.				X	
Personal protective equipment The AM operator wore casual clothing, latex gloves and PHUZA MOYA FFP2 half-face disposable respirators during the processes.	X	X	X	X	X

4.3.3.1 Particulate emissions

Figure 4-1: **Placement of the emission particle sampling instruments on the table 2 m from the AM machine door in the AM machine room at the facility where the study was conducted.**

The real-time emissions of particles ranging from 0.3 – 10 µm were measured using an Airborne Particle Counter (APC) (Aerotrak Portable Particle Counter model 9310 TSI Inc., MN, USA). The APC has different size channels in which various sized particles are measured (0.3 µm, 0.5 µm, 1 µm, 3 µm, 5 µm and 10 µm). The APC collected data for 1 minute during each phase of AM. Both the APC and CPC were factory calibrated prior to use. The particle number concentrations (particles/m^3) were measured throughout all the AM phases beginning with background measurements in the AM machine room prior to the start of the processing phase.

The Condensation Particle Counter (CPC) (CPC model 3007 TSI Inc., MN, USA) was used to quantify emissions of particles ranging from 0.01 - ~ 1.0 µm during the three phases of AM. The CPC does not have a specific upper cut-off point therefore it measures particles in the 0.01 - ~ 1.0 µm range. For each AM phase, the CPC collected data for intervals of 10

seconds, which were averaged to 1 minute. A zero filter was attached to the instrument and it was zeroed for 300 seconds. Thereafter, the filter was removed and sampling commenced.

The instruments were set on a table (Figure 4-1), approximately 2 metres away from the source (AM machine) (Figure 4-2, Area One) to allow the AM operator to use the trolley jack freely when loading and unloading the job box. Prior to the measurements of the print process, background measurements inside and outside the AM machine room were taken. Time was noted in order to record when each process started and ended, and measurements were taken in accordance to activities that occurred on each day of sampling. In total, the particle number concentrations from three identical printed parts over four days were measured.

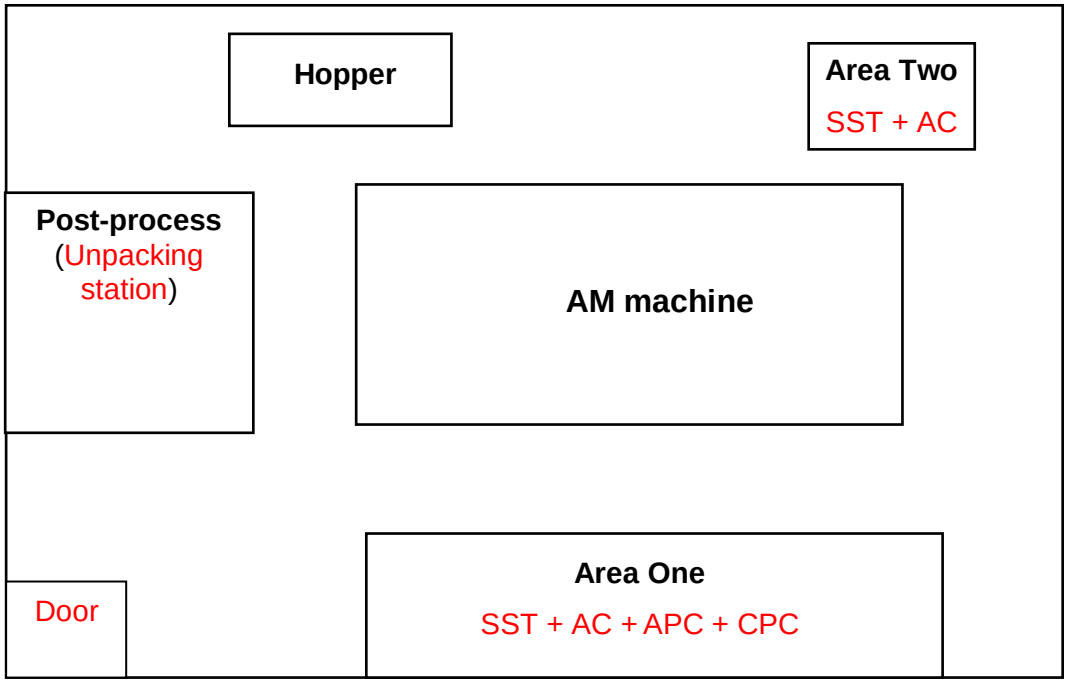

Figure 4-2: **A diagram illustrating the positioning of the sampling instruments during area monitoring. SST - solid sorbent tube; AC – aluminium cyclone; APC - Airborne Particle Counter; CPC- Condensation Particle Counter**

Emission rates (ER) for the emission of 0.3 – 10 µm and 0.01 - ~ 1.0 µm sized particles during each phase of AM were calculated using the following equation (He *et al*., 2004; Stabile *et al*., 2016; Stefaniak *et al*., 2018):

Equation 1:
$$ER = V \cdot \left[\frac{Cpeak - Cout}{\Delta t} + \overline{AER + k}.\,\overline{C}_{in} - \overline{AER}.\,C_{out} \right]$$

For this equation, V (m^3) = volume of the room; C_{peak} (p/m^3) = peak concentration of contaminants during printing; C_{out} (p/m^3) = outside concentration of the contaminant during printing (assumed to be equal to ambient concentration measured); Δt (min) = change in time between C_{peak} and C_{out}; $\overline{AER + k}.\overline{C}_{in}$ = average total removal rate of the contaminant (AER (h)= air exchange rate in the room, k = rate of contaminant loss due to deposition onto surfaces) and $\overline{C}_{in}$ = the average concentration of the contaminant during printing. Both AER and k are constants, with values of 0.22 and 1 respectively.

4.3.4 Personal exposure and area airborne particulate concentrations during the full shift of the AM process

Personal respiratory exposure monitoring was conducted to determine personal exposure to airborne respirable crystalline silica, respirable dust and VOCs during each day. The GilianGilair plus (Sensidyne, Inc., LP, USA) air sampling pump with an aluminium cyclone sampler and 37 mm PVC filter with pore sizes of 5.0 µm, was used to measure personal exposure to airborne respirable crystalline silica and respirable dust in the worker's breathing zone. The sampling pump drew air through the cyclone sampler set at a flow rate of 2.5 L/min in accordance with the NIOSH method 0600 (respirable dust) and 7500 (crystalline silica) (NIOSH, 1998; NIOSH, 2003). Calibration was performed with the use of the Gillian Gilibrator-2 (Sensidyne, Inc., FL, USA) calibrator. Following sampling, filters were sent to an accredited analytical laboratory where they were analysed for crystalline silica using XRD according to NIOSH method 7500 (NIOSH, 2003).

Personal exposure to VOCs was measured using a solid sorbent tube filled with 100/50 mg of coconut shell charcoal placed inside a sorbent tube holder. The sorbent tube collected VOCs from the workplace atmosphere as air was drawn through the tube by the GilianGilair plus the sampling pump was calibrated at a flow rate of 0.2 L/min. The sampling pump was calibrated using the Gillian Gilibrator-2 in accordance with the NIOSH methods 1501 and 1500. The sorbent tubes were then sent to an accredited analytical laboratory where analysis using gas chromatography-mass spectrometry took place.

As an addition to personal sampling, area sampling was also conducted in order to investigate concentrations of hazardous chemical substances (HCSs) (airborne crystalline silica, respirable dust and VOCs) in the work area. The sampling procedure was the same as that used for personal monitoring. The sampling trains were placed on stands at areas one and two (see Figure 4-2). Area one was in front of the AM machine (approximately 2 m from the AM machine door) and area two was behind the AM machine (approximately 1.2 m

from the back of the AM machine). Area two was included to determine if the hopper had an impact on the concentrations of airborne hazardous substances in the room. The individual stands were set at a height of approximately 1.5 m from the floor.

4.4 Statistical analysis of results

Basic descriptive statistics were used to calculate the mean and standard deviation of the particle size distribution of the coated and used sand as well as the mean, range and maximum for the number of particles released during the AM process. The mean particle sizes were classified as d(0.1) - 10% of the particles are less than the stated diameter; d(0.5) - 50% of the particles are less than this diameter and d(0.9) - 90% of the particles are less than the stated diameter. Tests for normal distribution of data were performed using the D'Agostino & Pearson test. The data was not normally distributed. Graphpad Prism 8 (Graphpad Prism, version 8, GraphPad Software, La Jolla, USA) was used to compare the PSD and shape of the silica sands collected with the use of unpaired t-tests. Graphical representations of the particle emission data were drawn using Graphpad Prism 8. In order to obtain significant differences in particle number concentrations between pre-processing, processing and post-processing as well as various printing days, a Kruskal-Wallis test was used followed by Dunn's multiple comparisons tests. Particle number concentrations in the various phases from the three repeats were also compared to one another utilising the Kruskal-Wallis and Dunn's multiple comparisons tests. For the analyses, $p \leq 0.05$ were considered statistically significant.

4.5 Results

4.5.1 Physical and chemical characteristics of silica sand particles

Table 4-2 shows the mean particle sizes and composition of the coated and used silica sands used by the facility. The mean particle diameter ranged from 1.89 µm [d(0.1)] to 115.00 µm [d(0.9)] for coated sand, while the mean diameter for used sand particles ranged from 1.14 µm [d(0.1)] to 6.51 µm [d(0.9)]. The SEM imaging however showed that coated silica sand particles were larger compared to the PSD analysis. Both used and coated silica sand particles had smooth surfaces (convexity number distribution = 0.97 ± 0.01 and 0.98 ± 0.00, respectively) (Table 4-2) and were non-spherical (circularity in Table 4-2 and Figure 4-3). The silica sand samples collected (coated and used) had high quartz content, ranging from 92.6 to 96.8% (Table 4-2). The quartz content of the used silica sand exceeded that of the coated sand. Graphite content of the sand decreased while aluminium oxide was not

detected after the silica sand was used for printing, thereby increasing the used sand's quartz content

Table 4-2: Particle size distribution (mean ± SD), shape and composition of coated and used silica sands

Type	n	PSD (µm) (mean ± SD)			Circularity number distribution (mean ± SD)	Convexity number distribution (mean ± SD)
		D(0.1)	**d(0.5)**	**d(0.9)**		
Coated	3	1.89 ± 0.89	29.76 ± 35.04	115 .00 ± 95.15	0.79 ± 0.03	0.97 ± 0.01
Used	3	1.14 ± 0.02	1.88 ± 0.12	6.51 ± 2.71	0.80 ± 0.01	0.98 ± 0.00
				Particle composition (%)		
		Mullite	Aluminium oxide	Graphite	Quartz (crystalline silica)	
Coated	1	-	0.1	7.3	92.6	
Used	1	-	-	3.2	96.8	

n – Number of repeated measurements; d(0.1) – 10 per cent of the particles are smaller than the specified diameter; d(0.5) – 50 per cent of the particles are smaller than the specified diameter; d(0.9) – 90 per cent of the particles are smaller than the specified diameter; Circularity: The ratio of the perimeter of a circle with the same area as the particle divided by the perimeter of the actual image. Circularity values range from 0 – 1, a perfect sphere will have a circularity of 1; Convexity: The measured edge roughness of the particle. A smooth particle will have a convexity value close to 1 whereas an irregular particle will have a convexity value of 0; - Not detected

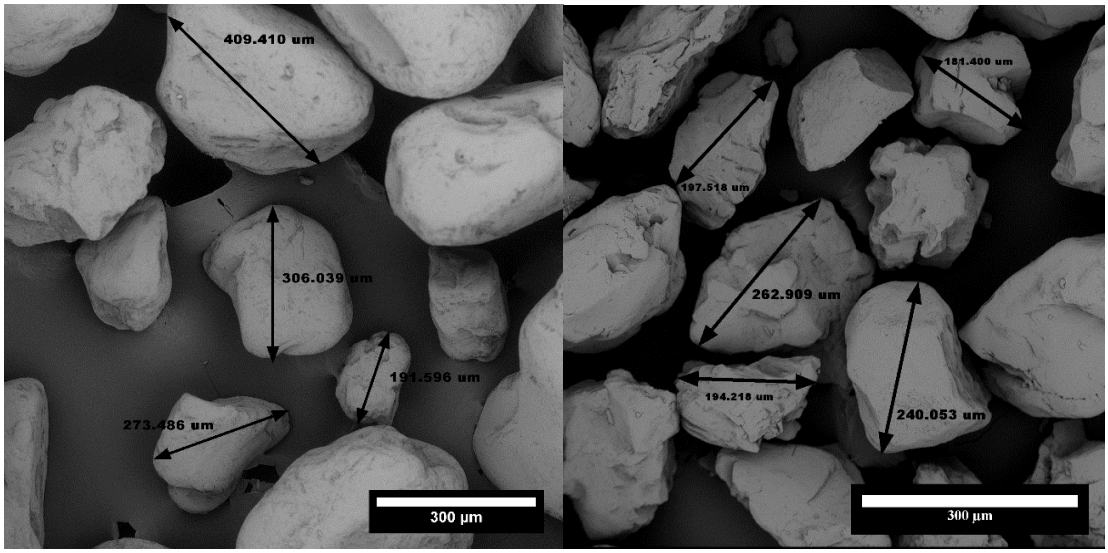

Figure 4-3: **SEM images of coated and used silica sands set on 300 µm scale; 2a – coated silica sand and 2b – used silica sand**

4.5.2 Emissions measured during the cleaning of the AM machine and the AM processes

Figure 4-4 is a representation of real-time emissions concentrations for 0.3 – 10 µm and 0.01 - ~ 1.0 µm sized particles during cleaning of the AM machine. Particle number concentrations gradually increased when the operator started cleaning and peaked towards the end of the procedure (peak: 0.3 µm = 8.71×10^7 p/m^3; 0.5 µm = 7.97×10^7 p/m^3; 1 µm = 6.27×10^7 p/m^3; and 0.01 - ~ 1.0 µm = 3.11×10^{10} p/m^3), during which the operator used a broom to sweep the AM machine room.

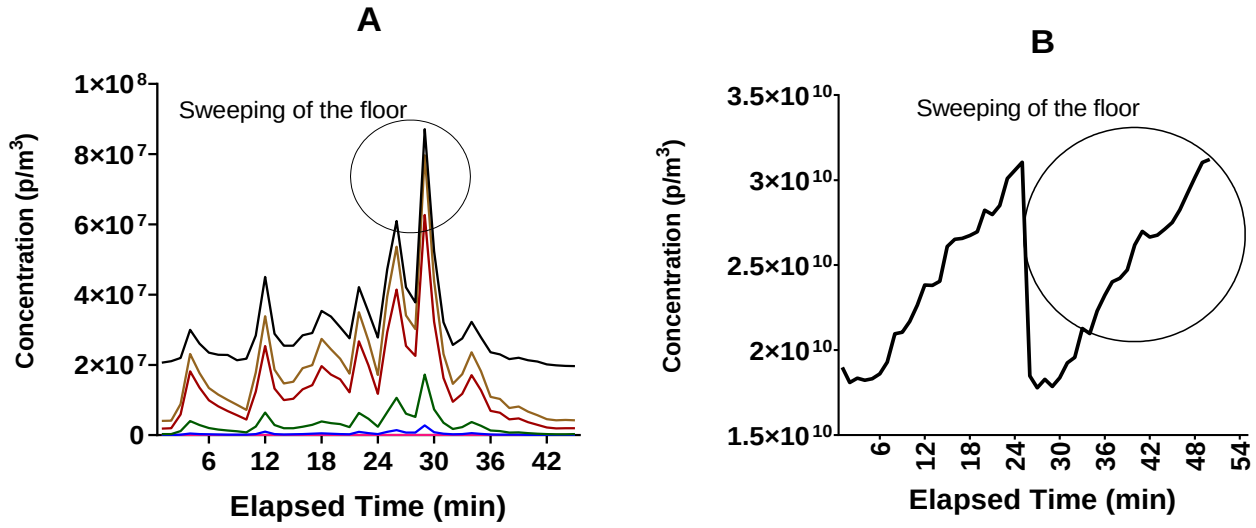

Figure 4-4: **Real-time emissions of particle concentrations for 0.3 - 10 µm (A) and 0.01 - ~ 1.0 µm (B) channel sizes during cleaning of the AM machine.**

Particle number concentrations of 0.3 – 10 µm and 0.01 - ~ 1.0 µm sized particles varied depending on the AM phases performed during each day (Figure 4-5). Figure 4-5 shows the measurements of day three, which is the best representation of the emissions measured on the days of printing. The rest are shown in the supplementary section at the end of the chapter (Figure 4-S1).

Concentrations of 0.3 µm sized particles were the highest compared to other sized fractions. Particles of 3, 5 and 10 µm in size were very low compared to 0.3 µm, 0.5 µm and 1 µm sized particles. Only 0.3 to 1 µm sized particles are shown and discussed.

Figure 4-5 shows that particle number concentrations increased above the background level when the AM operator started to clean the sand moulds (post-processing) printed on the previous day. Emissions further increased as the AM operator finished with cleaning and placed the build box back inside the AM machine (pre-processing). The particles of 0.3 µm in size reached a maximum of 9.38×10^{7} p/m^{3} while 0.01 - ~ 1.0 µm sized particles peaked at 7.76×10^{12} p/m^{3}, both during pre-processing (Figure 4-5). Particle emissions then decreased during processing.

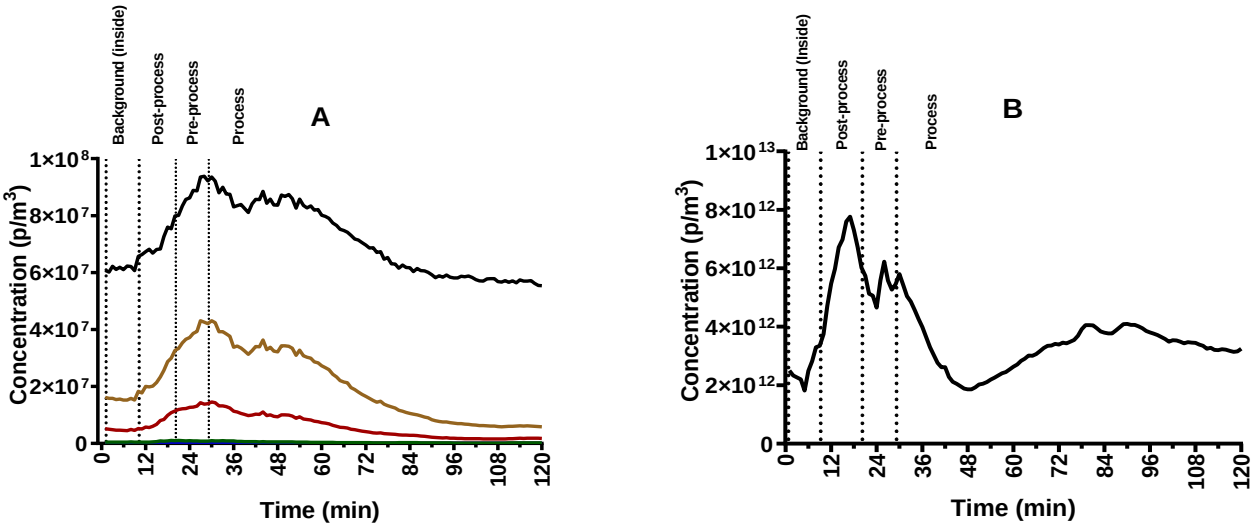

Figure 4-5: **Real-time emissions of particles for 0.3 – 10 µm (A) and 0.01 - ~ 1.0 µm (B) channel sizes during different phases of AM on day two of printing.**

Particle number concentrations of 0.01 - ~ 1.0 µm sized particles during each sampling day and during the various print phases of each day were compared to one another. The size channel 0.01 - ~ 1.0 µm was chosen because it is the fraction with the highest number concetration and therefore, the best representation of the emitted particles. There were statistical differences for comparisons made (Figure 4-6). Particle number concentrations on day three were significantly higher compared to other days. Pre-processing had the highest average particulate emissions while processing and post-processing were relatively similar (Figure 4-7).

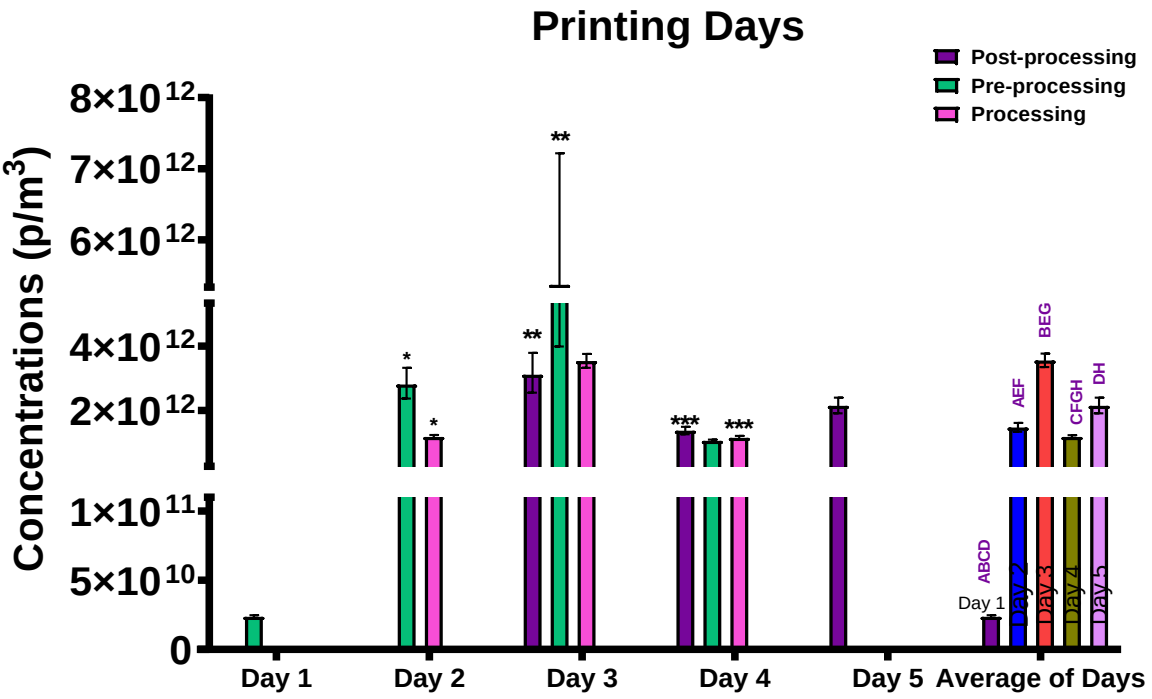

Figure 4-6: **Comparison of 0.01 - ~ 1.0 µm particle number concentrations during the different days and mean particle number concentrations of the various days. The columns represent mean particle number concentrations and the lines represent 95% confidence intervals. *, *, **, ***, A, B, C, D, E, F, G, and H indicate statistical differences ($p \leq 0.05$).**

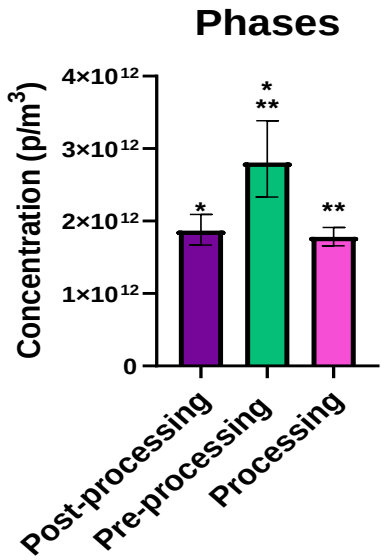

Figure 4-7: **Comparison of 0.01 - ~ 1.0 µm mean particle number concentrations of the various phases. The columns represent the mean particle number concentrations and the lines represent 95% confidence intervals. ***, **** indicate statistical differences ($p \leq 0.05$).**

The AM process consists of three phases (pre-processing, processing and post-processing) and the number of particles emitted per minute (emission rate) during each phase was calculated using Equation 1. In some instances, background measurements taken at the start of the day were higher than the peak measured concentration measured during the process phase causing the calculated emission rates to be negative. These results were not used for Table 4-S1 and, therefore, two measurements for pre-processing; three for processing and one for post-processing were used. The average emission rates for 0.01 - ~ 1.0 µm sized particles ranged from 9.17×10^{14} to 1.49×10^{15} p/min for pre-processing, 2.17×10^{14} to 1.05×10^{15} p/min for processing and 7.74×10^{14} p/min for post-processing. There were no observed statistically significant differences but pre-processing had higher ERs compared to processing and post-processing (Table 4-S1).

4.5.3 Personal exposure and area airborne concentrations of respirable crystalline silica dust, respirable dust and VOCs

Table 4-3 shows personal exposure and area airborne concentrations for respirable crystalline silica and respirable dust during cleaning of the AM machine and the various AM phases. On the day of cleaning, personal exposure to respirable dust and crystalline silica were found to be 0.159 and 0.070 mg/m^3 respectively. The operator was exposed to respirable crystalline silica exceeding the action level (half of the OEL: 0.05 mg/m^3). Personal exposure to crystalline silica on the days of printing was below the limit of detection.

Table 4-3: Personal exposure and area airborne concentrations for airborne silica dust and respirable dust during the AM process

Sampling time (min)	Day	Processing Phase/ Activity	Total respirable dust (TWA mg/m^3)				Alpha quartz (TWA mg/m^3)			
			A1	A2	P1	P2	A1	A2	P1	P2
47	1	Cleaning of the AM machine	**-**	**-**	0.159	-	-	-	0.070*	**-**
190	2	Pre-processing Processing	0.050	0.066	0.242	0.075	<0.003	<0.003	<0.003	<0.003
232	3	Pre-processing Processing Post-processing	0.266	0.042	0.100	-	<0.003	<0.003	<0.003	-
252	4	Pre-processing Processing Post-processing	0.175	<0.010	0.075	-	<0.003	<0.003	<0.003	-
47	5	Post-processing	0.192	0.117	0.200	-	<0.003	<0.003	<0.003	-

- Absent; * - Above action level; A1 – Area One (in front of AM machine); A2 – Area Two (behind AM machine); P1 - Operator 1; P2 – Operator Two; Crystalline silica (quartz) TWA OEL-CL – 0.1 mg/m^3; Respirable dust TWA OEL-RL – 5 mg/m^3. Note that area monitoring was not performed on day one.

Four VOCs (acetone, pentane, heptane and toluene) were detected for both personal and area monitoring (Table 4-4). Personal exposure to all individual VOCs was less than 0.1% of their respective OELs.

Table 4-4: Personal exposure to and area airborne concentrations for VOCs during the AM process

Time (min)	Day	Processing phase	Acetone (TWA µg/m^3)				Pentane (TWA µg/m^3)				Heptane (TWA µg/m^3)				Toluene (TWA µg/m^3)			
			Area		Personal		Area		Personal		Area		Personal		Area		Personal	
			A1	**A2**	**P1**	**P2**	**A1**	**A2**	**P1**	**P2**	**A1**	**A2**	**P1**	**P2**	**A1**	**A2**	**P1**	**P2**
191	2	Pre-process	46.10	57.45	< LOD	18.18	42.90	62.18	< LOD	13.89	15.47	15.47	< LOD	14.91	49.50	44.19	< LOD	25.53
		Process																
228	3	Pre-process																
		Process	43.81	56.03	< LOD	-	< LOD	41.05	< LOD	-	6.84	9.24	0.01	-	25.84	37.97	< LOD	-
		Post-process																
252	4	Pre-process																
		Process	< LOD	37.50	14.40	-	< LOD	14.38	< LOD	-	0.01	0.01	0.01	-	< LOD	4.69	< LOD	-
		Post-process																
36	5	Post-process	< LOD	< LOD	< LOD	-	< LOD	< LOD	< LOD	-	0.01	0.01	0.01	-	< LOD	< LOD	< LOD	-
		TWA-OEL (µg/m^3)		178000				180000				160000				188000		

- Absent; TWA-OEL – Time weighted average occupational exposure limit; < LOD – Below Limit of Detection; A1 – Area One; A2 – Area Two; P1 – Operator One; P2 – Operator Two

4.6 Discussion

This study investigated the physical and chemical characteristics of AM silica sand particles as well as emissions and personal respiratory exposure to HCSs during the pre-processing, processing and post-processing phases of AM.

4.6.1 PSD and particle shape

The size and shape of silica sand particles were determined to indicate whether the silica sand particles are either inhalable (< 100 µm), thoracic (< 10 µm) or respirable (< 4 µm), since this can determine the location in the respiratory tract where they are deposited (Brown, 2013). The PSD analysis indicated that 50 – 90% of coated silica sand particles were inhalable [d(0.5) = 29.76 ± 35.04 µm], though > 10% was respirable [d(0.1) = 1.89 ± 0.89 µm]. For used sand, > 50% of particles were in the respirable fraction [d(0.5) = 1.88 ± 0.12 µm] and are, therefore, able to penetrate to the alveoli. Deposition of respirable crystalline silica fractions deep into the lungs reduces the ability of clearance mechanisms to eliminate the particles and consequently increasing accumulation in the lungs (Schroder, 2014). Thoracic fractions (< 10 µm) also have a negative impact on the operator's health. According to Upadhyay *et al*. (2014), particles that have an aerodynamic diameter of < 10 µm can irritate the airways, induce coughing or lead to breathing difficulties.

According to Nyembwe *et al*. (2016b), used silica sand refers to the excess contaminated sand collected after parts are cleaned. It was anticipated that the SEM images (Figure 4-3b) would show agglomeration or residues of the furan resin on the particles as seen on the SEM analysis performed by Danko *et al*. (2016). There were neither residues nor agglomerations; rather, the used silica sand particles were smaller and smoother (Table 4-2 – convexity number distribution). It was not possible to observe the agglomerations due to the SEM method of analysis, which captures an image of a certain area on the stub. This is also noticeable when comparing the PSD data with SEM imaging for coated silica sand. The SEM images only displays larger particles compared to PSD. The reason being that, unlike SEM, PSD analyses particles on a larger scale. It is also noticeable on Chapter 3, Figure 3-4 that during coating, the dominant particles emitted were between 0.3 – 1 µm in size. This therefore increases the possibility of the presence of smaller particles even though the area captured by SEM does not.

4.6.2 Chemical composition

The coated and used silica sand consisted of 92.6 - 96.8% quartz (Table 4-2). Respirable crystalline silica in quartz form has an increased potential to cause pulmonary fibrosis compared to cristobalite and tridymite (Department of Labour, 2007). Also, according to the International Agency for Research on Cancer (IARC) (2012) and Agency for Toxic Substances and Disease Registry (ATSDR) (2017), respirable crystalline silica quartz causes lung cancer. Long term exposure to respirable crystalline silica leads to silicosis, the effects of which are irreversible and might lead to an untimely death (Mgonja, 2016).

The sand used as feedstock material therefore poses a substantial risk to the health of the AM operator due to its high quartz content and small particle size. Also, the manufacturers of the sand did not provide a safety data sheet (SDS), meaning that the AM operator was not aware of the potential dangers of silica sand.

4.6.3 Emissions of particles ranging from 0.3 – 1 µm and 0.01 - ~ 1.0 µm as well as personal exposure and area monitoring of hazardous chemicals

Day 1: Cleaning of the AM machine

The particle number concentrations of 0.3 - 1 µm and 0.01 - ~ 1.0 µm sized particles gradually increased as the AM machine was being vacuumed but peaked towards the end of cleaning when the AM operator used a broom to sweep loose silica sand from the floor. This resulted in a dust cloud inside the room, which was easily observed. Since the operator did not use a wet sweeping method, this increased the particle concentrations in the workplace atmosphere which was also seen in respirable crystalline silica concentrations from personal and area monitoring (Table 4-3). The operator's exposure to respirable crystalline silica exceeded the action level (0.05 mg/m³), [defined as 50% of the OEL (0.1 mg/m^3)] making the cleaning of the AM machine the activity with the highest personal exposure recorded in this study.

In comparison with the AM phases, cleaning was the only process where respirable crystalline silica was detected during personal or area monitoring (Table 4-3). The high quartz content of the sand (Table 4-2) means that exposure to relatively low concentrations of airborne dust during cleaning could lead to significant exposure to respirable crystalline silica.

Day 2: First day of printing

The particle number concentrations of 0.3 – 1 µm and 0.01 - ~ 1.0 µm sized particles peaked when pre-processing commenced (Supplementary Figure 4-S1), during which AM operators removed buckets of used silica sand (beneath the hopper) and brought in empty ones. Emissions were significantly higher during pre-processing compared to processing ($p \leq 0.0001$) (Figure 4-6). It is possible that when silica sand was collected into the buckets, sand particles became airborne which caused an increase in the particle number concentrations. Area two (behind the AM machine) had higher respirable dust concentrations than area one, indicating that the hopper was the possible source of increased airborne dust (Table 4-3). The AM operators were however exposed to concentrations of respirable crystalline silica below the limit of detection (< 0.003 mg/m^3). This low exposure to crystalline silica can be associated with the employees work pattern, as they move in and out of the room as well as perform activities short in duration.

Day 3: Second day of printing

During post-processing, the number of particles 0.3 – 1 µm and 0.01 - ~ 1.0 µm in size increased as a result of cleaning sand moulds (Figure 4-5A and 4-5B). Pre-processing followed and the mean particle number concentration measured was significantly higher than post-processing ($p = 0.0354$) (Figure 4-6). Since the extraction ventilation system was not operational during cleaning of the moulds, it is possible that airborne particles released during post-processing were still airborne during pre-processing of the next print. Day three also showed that pre-processing caused an increase in particle concentrations. Therefore, particles from post-processing could have increased the particle concentrations even further. Both processes could have contributed to increase in particle concentrations.

Area 1 (approximately 1 meter away from the unpacking station, where post-processing activities occurred) also had the highest respirable dust concentration of the four printing days (Table 4-3). Although not as severe as respirable crystalline silica, respirable dust is a risk to AM operators. According to Cherrie *et al*. (2013), respirable dust can cause chronic obstructive pulmonary disorders, such as emphysema and chronic bronchitis. These disorders lead to narrowing of the lung airways; as a result, airflow to the lungs is reduced. Therefore, caution should be taken when handling respirable feedstock material.

Day 4: Third day of printing

The background particle number concentration of 0.3 – 1 µm and 0.01 - ~ 1.0 µm sized particles was higher compared to pre-processing, processing, and post-processing (Supplementary Figure 4-S1, B and E). The reason behind this incidence is that, when background measurements were taken, the AM machine lid was already open as the AM operator was ready to commence with post-processing. This allowed particles to escape into the workplace atmosphere. This is comparable to a study by du Preez *et al*. (2018b) on PLA and ABS filaments. The authors found that, particle number concentrations increase when the cover of the AM machine is removed. The higher background particle number concentrations, however, did not have a significant effect on the concentrations of respirable crystalline silica in the workplace atmosphere as measured during personal and area monitoring (Table 4-3).

Day 5: Fourth day of printing

Similar to day four, the particle number concentrations of 0.3 – 1 µm and 0.01 - ~ 1.0 µm sized particles were also higher during background measurements compared to post-processing (Supplementary Figure 4-S1, C and F). However unlike on day four, the AM machine lid was closed. One possible explanation might be that, due to the lack of natural and mechanical ventilation in the room, there was particle build-up in the workplace atmosphere as air exchange was not possible. A study conducted by Zontek *et al*. (2016) reports that, poorly ventilated areas lead to an increase in particle concentrations while Zhang *et al*. (2017) also observes that adequate ventilation resulted in accumulation of fewer particles. Even though background particle number concentrations were high, post-processing was a source of exposure since it was the only process performed and personal and area monitoring was comparable to the other days (Table 4-3). However, respirable crystalline silica concentrations were low throughout the process (Table 4-3). But it is still necessary for the facility to incorporate LEV or HVAC systems in order to reduce particle build-up of both respirable and crystalline silica dust.

Figures 4-6 and 4-7 show that the results of the individual phases and days showed statistical differences. Day one (cleaning) had lower emissions for 0.3 – 1 µm and 0.01 - ~ 1.0 µm sized particles than other days (printing) but personal exposure to respirable crystalline silica was higher compared to printing days due to release of larger particles by cleaning activities (Figure 4-4A). When comparing printing days to

each other, particle emissions on day three (all phases) were significantly higher than day two and four. Pre-processing on day three was also the highest compared to other days where pre-processing was performed. It is noteworthy that the mean particle concentrations measured on day three for all phases were the highest recorded for each individual phase. Additionally, respiratory particles at area 1 (close to where post-processing took place) were also the highest on day three. It should be noted that pre-processing was undertaken directly after post-processing. Therefore, the particle emissions from post-processing might have influenced the particle number concentrations measured during pre-processing (and processing). Overall, the average particle number concentrations for pre-processing were significantly higher compared to processing ($p \leq 0.0001$) and post-processing ($p = 0.0003$), making pre-processing the highest emitter of 0.3 – 1 µm and 0.01 - ~ 1.0 µm sized particles during this study. It is however not possible to conclude that the particle emissions were chiefly from pre-processing since the phases were performed in succession. When phases are performed in succession, emissions from one phase may influence those measured during the next phase. Even if the prints were identical, Figure 4-S2 indicates that emissions from different repeats for each phase varied significantly, which suggests that the emissions from the identical prints are not necessarily identical. This is an important result since, in real-world, the phases follow each other because performing each phase on a separate day will be too time consuming. The emissions from the phases are influenced by 1) other activities and phases taking place on the same day, 2) ventilation (or the lack thereof), etc. This leads to emissions not being identical even when the print job is.

4.6.4 Emission rates of particles 0.3 – 1 µm and 0.01 - ~ 1.0 µm in size during pre-processing, processing, and post-processing

The high ER measured during the background could be ascribed to the LEV system that was not operational at the time of the sampling. There were no statistical differences in the average ERs of particles 0.3 µm, 0.5 µm, 1 µm and 0.01 - ~ 1.0 µm in size. But slight variations in the ERs were observed. The average ERs for 0.3 µm sized particles were relatively similar across all phases, as well as those for particles 1 µm in size. The ERs during pre-processing and post-processing, for 0.5 µm sized particles, were one order of magnitude higher than processing. For particles 0.01 - ~ 1.0 µm in size, the average ERs during pre-processing were also one order of magnitude higher compared to processing and post-processing.

The ERs of 0.01 - ~ 1.0 µm and 0.3 – 1 µm sized particles of this study were compared to those of Stephens *et al*. (2013) and Hayes *et al*. (2020) respectively. Hayes *et al*. (2020) reports ERs of 5.4×10^5 p/min for hydroperm, 1.0×10^6 p/min for zeolite and 2.2×10^7 p/min for LHS-1 for particles 0.3 – 0.9 µm and 0.5 – 8.3 µm in size. In comparison to our study, the ERs were 7 – 9 orders of magnitude lower. Although Hayes *et al*. (2020) is a chamber study, it was used for comparison due to feedstock used (powder), which is relatable to silica sand. The high background particle concentrations were the significant contributing factor when calculating ERs as they resulted in high ERs calculations.

The average ERs of particles 0.3 µm, 0.5 µm and 1 µm were however comparable to that of Stephens *et al*. (2013), which ranged from 2.0×10^{10} p/min for PLA to 1.9×10^{11} p/min for ABS for ultrafine particles (UFPs). The difference, depending on the particle size, was one or two orders of magnitude lower than Stephens *et al* (2013) study. It is therefore possible to conclude that the ERs is at high end of AM ERs since it is only 1 – 2 orders of magnitude lower than that of UFPs emitted when PLA and ABS are used in material extrusion (ME) AM.

4.6.5 Personal exposure to, and area airborne concentrations of VOCs

Four VOCs (acetone, pentane, heptane and toluene) were detected, with the area airborne concentrations being higher than that of personal exposure. VOC concentrations were higher on day two in comparison with other days as a result of the AM machine side door mistakenly being left open by the AM operator. This is possible because according to the study conducted by du Preez *et al*. (2018b), opening of the AM machine door resulted in the increase concentrations of VOCs. Thus, VOCs emission can be ascribed to the processing phase because of the binder being added to the sand to form the printed object. This is supported by area monitoring on day five, where VOC concentrations were below the detection limit when processing was not performed.

The concentrations of the individual VOCs were however considerably below their respective OELs (< 0.1%). Stefaniak *et al*. (2018) as well as Adams (2016) obtained similar results, meaning that it is unlikely for the AM operator to be overexposed to VOCs during the printing process. The measured VOCs mainly act as irritants (skin, eye, nose or lung irritation) (Kim *et al*., 2012; NIOSH, 2019). Even though these VOCs are a risk at high concentrations, in this case, there is no risk during exposure

due to low VOCs concetrations. It is therefore possible consider the existing controls to the individual VOCs adequate.

4.7 Recommendations

Exposure to respirable crystalline silica can cause deleterious health effects. Thus, it is important for the management of the facility to ensure that the AM operator is protected against exposure. The following recommendations can be implemented to help reduce emissions in the specific facility: 1) engineering controls such as mechanical extraction ventilation are recommended in order to reduce accumulation of respirable airborne particles in the room; 2) a vacuum cleaner equipped with a high-efficiency particulate air (HEPA) filter can be used, instead of a broom, throughout the cleaning procedure since cleaning using a broom was the activity that resulted in the highest personal exposure to crystalline silica; 3) if a vacuum cleaner is not available or feasible, wet sweeping methods can be utilised to reduce resuspension of silica sand dust in the air; 4) the AM operator needs to be provided with training sessions and information on the type of feedstock material they use, preferably via SDSs, to help them understand the risks of handling, storage and usage of silica sand and what the correct procedures are; 5) lastly, throughout the study, the AM operator was wearing personal protective equipment (PPE) i.e. PHUZA MOYA FFP2 half-face disposable respirator and latex gloves, to help protect them from respirable crystalline silica exposure. Additional protection i.e. standard overalls and safety boots, is also required to prevent silica sand dust adhering to surfaces of the AM operators' casual clothing and to improve the general housekeeping in the facility.

4.8 Limitations

There were discrepancies when performing background measurements using direct reading instruments. On day two, the particle number concentrations for 0.01 - ~ 1.0 µm sized particles during background measurements were low (7.62×10^{11} p/m^3). As sampling continued, the background concentrations increased with each day (Day five = 4.74×10^{12} p/m^3). Due to sampling being conducted on five consecutive days, particle built-up in the room over the study period had an effect on background particle number concentrations. This also applies to particle number concentrations measured during each phase as particle emissions from each phase had an influence on the next. This is an important factor to consider for future studies. It is therefore recommended for future studies that a day should be allocated

between sampling days where the AM machine room can be ventilated in order to allow airborne particle concentrations to return to as low as possible. This being said, the results of this study have shown the real-life workplace exposure situations are influenced by the activities that were performed on the days leading up to the specific activities.

4.9 Conclusion

There are few studies on health risks associated with AM of sand moulds, and therefore, this study investigated the physical and chemical properties of the silica sand and quantified particulate emissions and personal exposure to HCSs during the different phases of AM of sand moulds.

The feedstock material used contained respirable as well as thoracic sized silica sand with quartz content of more than 90%. Quartz is a confirmed class one human carcinogen and the high quartz content of the sand along with the small particulate size increases the risk of exposure and the development of both cancer and silicosis. Emission of particles 0.3 µm and 0.01 - ~1.0 µm in size were low during cleaning but personal exposure to respirable crystalline silica was higher than during printing. The cleaning of the AM machine was notably the task with the highest risk regard to personal exposure compared to printing of sand moulds; therefore, the cleaning technique used should be adapted to keep exposure as low as reasonably practicable. The average particle emissions were significantly higher during pre-processing compared to other phases. ERs of 0.3 µm and 0.01 - ~ 1.0 µm sized particles were also higher during pre-processing than processing and post-processing. It is however possible that post-processing might have influenced the particle number concentrations measured during pre-processing. The emissions for days when the identical print parts were printed differed. Exposure to VOCs albeit it low took place during the processing phase, but as a result of low concentrations, it means there was no risk at exposure.

4.10 References

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4.11 Supplementary materials

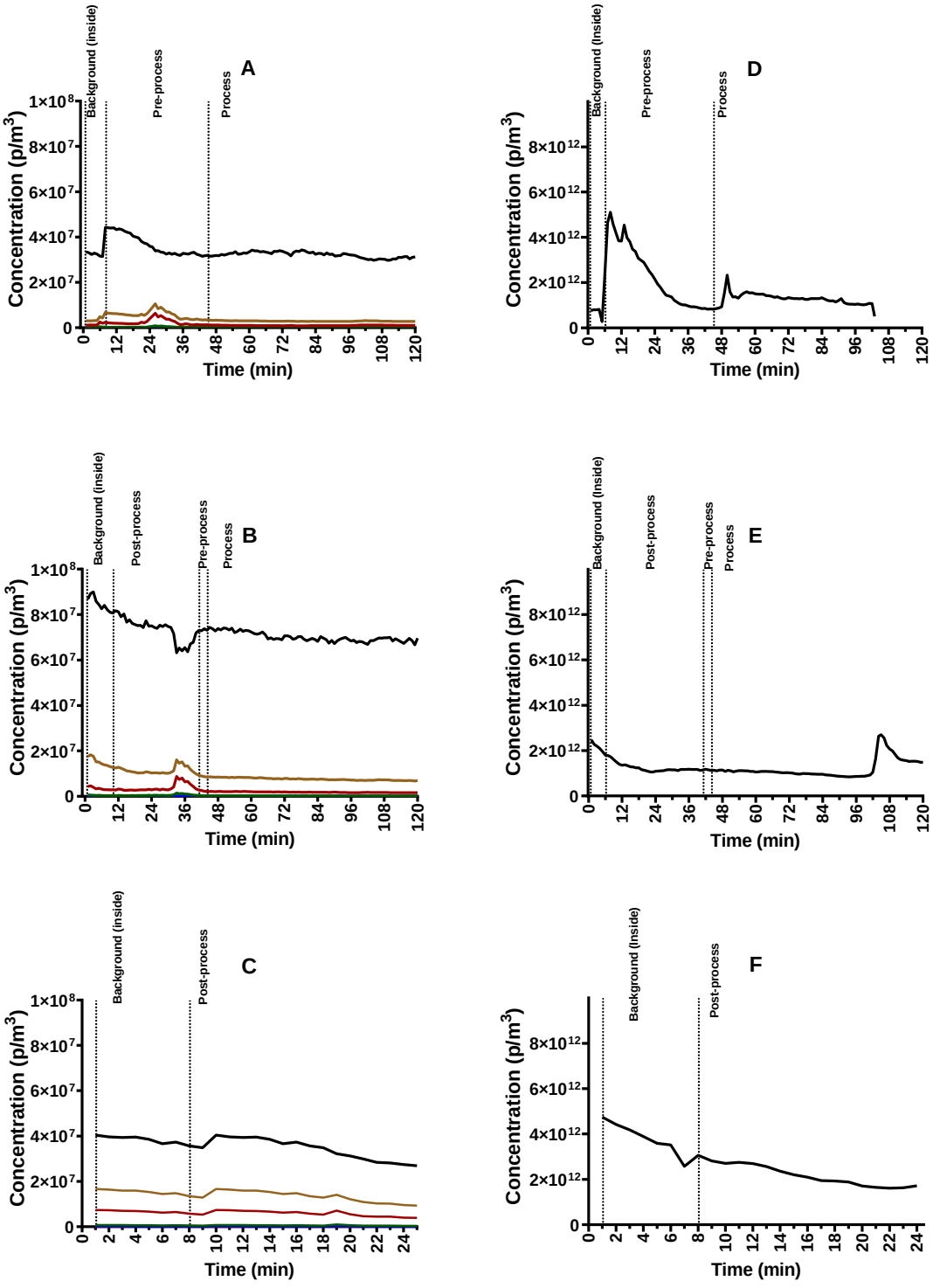

Figure 4-S1: **Real-time emissions of particles for 0.3 – 10 µm channel sizes (A-C) and 0.01 - ~ 1.0 µm channel sizes (D-F) during different phases of AM. A&D - Day two; B&E – Day four; C&F – Day five.**

Table 4-S1: Average ERs, average particle number concentrations and peak particle concentrations

Phases	0.3 µm			0.5 µm			1 µm			0.01 - ~ 1.0 µm		
	Ave. ERs (p/min)	Ave. p/m^3	Peak p/m^3	Ave. ERs (p/min)	Ave. p/m^3	Peak p/m^3	Ave. ERs (p/min)	Ave. p/m^3	Peak p/m^3	Ave. ERs (p/min)	Ave. p/m^3	Peak p/m^3
Pre-process	1.6 2× 10^{10}	4.7 × 10^7	9.40 × 10^7	9.12 × 10^9	1.1 × 10^7	4.3 × 10^7	3.14 × 10^9	4.19 × 10^6	1.43 × 10^7	1.2 × 10^{15}	3.14 × $10^{12\ a,b}$	5.98 × 10^{12}
Process	1.53 × 10^{10}	5.8 × 10^7	9.40 × 10^7	9.81 × 10^9	8.05 × 10^6	4.31 × 10^7	3.26 × 10^9	2.64 × 10^6	1.45 × 10^7	5.27 × 10^{14}	2.17 × $10^{12\ a}$	7.76 × 10^{12}
Post-process	1.13 × 10^{10}	5.1 × 10^7	8.17 × 10^7	6.34 × 10^9	1.3 × 10^7	3.27 × 10^7	2.6 × 10^9	5.42 × 10^6	1.19 × 10^7	7.74 × 10^{14}	1.98 × $10^{12\ b}$	3.74 × 10^{12}

- a,b – statistically significant difference ($p \leq 0.05$); Ave - average; p/min – particles per minute; p/m^3 – particles per cubic meter; For some calculations, the background measurements were higher than the peak values. The average emission rates (ERs) were therefore calculated using a specific number of repeats for each phase; For 0.01 - ~ 1.0 µm sized particles; 2 repeats from pre-processing, 3 from processing and 1 repeat from post-processing were used; For average emission rates of 0.3 µm sized particles, 2 repeats from each phase were used; For average emission rates of 0.5 µm and 1 µm sized particles, 2 repeats from pre-processing, 1 from processing and 3 from post-processing were used.

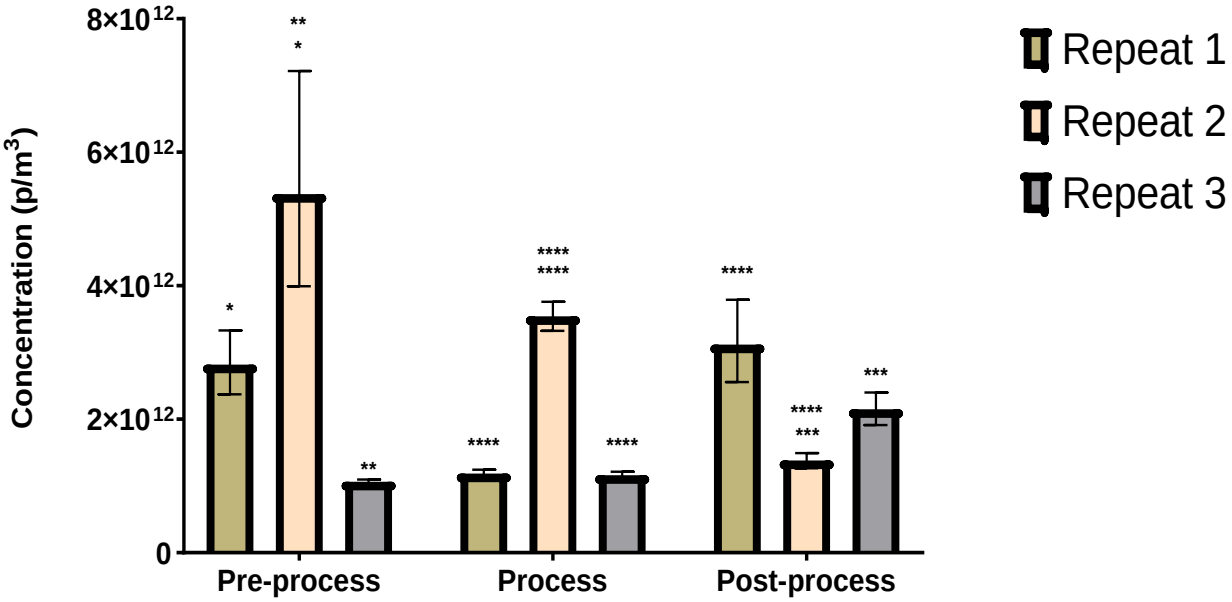

Figure 4-S2: **Comparison of mean particle number concentrations of 0.01 - ~ 1.0 µm sized particles in three repeats. The columns represent the mean particle number concentration and the lines represent 95% confidence intervals. * Indicates statistical differences between repeats ($p \leq 0.05$).**

CHAPTER 5: CONCLUSIONS

The following chapter gives a summary of the main findings of this study. The main objectives are listed and assessed. The hypotheses are evaluated to indicate whether they have been accepted or rejected. A total of 18 recommendations are provided to assist employers reducing exposure to hazardous chemicals at the facilities. The limitations of this study are also addressed and recommendations for future studies are provided.

5.1 Background

Additive manufacturing (AM) is globally known as the process of creating three dimensional (3D) structures layer by layer (Gibson *et al*., 2015; Upadhyay *et al*., 2017). AM has found applications in many industries, one of which being sand mould production via binder jetting (BJ) and selective laser sintering (SLS). BJ does not make use of a heat source and uses a binder (furan resin) while SLS uses heat from a CO_2 laser to bind sand particles together (Le Néel *et al*., 2018). Silica sand is the feedstock material preferred to olivine, zircon and chromite due to its availability, lower cost, the ability to withstand high temperature and less furan resin consumption (Nyembwe *et al*., 2016; Anakhu *et al*., 2018). The manufacturing of sand moulds using binder jetting requires silica sand coated with sulphonic acid which has the ability to act as a catalyst during the processing phase of AM. To date, there is limited information on the health risks associated with AM of sand moulds.

The manufacturing of sand moulds for metal casting is traditionally performed in foundries but, AM has introduced new processes which can be used to manufacture sand moulds. Since sand moulds can be manufactured using both AM and foundry processes, a comparison can be made between these processes in terms of exposure to hazardous chemicals. In foundries, the use and handling of silica sand during metal casting (which is also necessary during the AM of sand moulds) have been shown to lead to exposure of workers to respirable crystalline silica (Omidianidost *et al*., 2016). AM uses similar feedstock materials and binders and has similar processes (pre-processing and post-processing) to those of foundries. Therefore, it is likely that there is exposure to similar hazardous chemicals during AM. It was, therefore, the purpose of this study to investigate whether AM workers are also exposed to hazardous chemicals as has been reported for foundries (Omidianidost *et al*., 2016), by determining the following: 1) the physical and chemical characteristics of the silica sand used as feedstock during AM; 2) the hazardous chemical substance (HCS) emissions during the AM of sand moulds; 3) the personal respiratory exposure of the AM operators to airborne crystalline silica, VOCs and particulate matter. These tasks have been performed in order to determine exposure and make recommendations that could improve the working conditions of workers. The facility where the study has been conducted coat silica sand with sulphonic acid using their own improvised coating machine (Chapter 3). This method has

provided the opportunity to assess exposure associated with the coating process as well as the three AM processing phases.

5.2 Main findings

5.2.1 Physical and chemical characteristics of silica sands

Deposition of particles into the respiratory tract primarily depends on their size and shape (Panyacosit, 2000). But also, these characteristics determine where the particles will induce toxicity (McClellan, 2002), i.e. respirable fractions tend to accumulate in alveoli where they can damage macrophages (Schroder, 2014). The first objective of this mini-dissertation was to determine the physical and chemical characteristics of virgin, coated and used sand using a Malvern Morphologi G3 particle analyser, scanning electron microscopy (SEM) and x-ray diffraction (XRD) analyser. Three types of silica sand were collected; virgin, coated and used. The particle size distribution (PSD) analysis indicated that the virgin silica sand contained > 90% respirable particles [d(0.9) = 3.98 ± 0.72]. More than 10% of particles present in coated silica sand were respirable [d(0.1) = 1.89 ± 0.89] and > 50% were inhalable [d(0.5) = 26.76 ± 35.04]. Used silica sand contained 50 – 90% respirable particles [d(0.5) = 1.88 ± 0.12] (Chapter 3, Table 3-2; Chapter 4, Table 4-2). Coated sand contained less respirable particles compared to virgin and used sand. It is possible that this was due to the application of sulphonic acid that caused the silica particles to agglomerate. Inhalable sized particles (< 100 µm) penetrate through nose and mouth; thoracic sized particles (< 10 µm) penetrate beyond the larynx while respirable sized particles (< 4 µm) penetrate into the alveoli (Brown *et al*., 2013). The quartz content of the three silica sand samples ranged from 92.6 - 97.3%. High respirable particle content means that virgin and used sand are most likely to deposit in the alveoli region and with a high quartz percentage, the chance for the development of silicosis and pulmonary cancer increases, as respirable crystalline silica is a confirmed human carcinogen (International Agency for Research on Cancer (IARC), 2012; Schroder, 2014).

The physical and chemical characteristics of the silica sands were determined; thus the first objective has been achieved. The small particle size and high quartz content of samples mean that the there is an inherent health risk associated with working with silica sand feedstock material.

It was hypothesised that *the bulk silica sand contains silica sand particles with high quartz content and that they are in the inhalable (or smaller) (< 100 µm) size range.* The silica sands (virgin, coated and used) were all found to have a quartz content of > 90%. The coated silica sand mostly comprised of particles in the inhalable fraction while virgin and used silica sands contained particles < 10 µm. The hypothesis is therefore accepted.

5.2.2 Particle emissions during pre-processing, processing and post-processing of sand moulds

Information regarding the hazardous chemical emissions during AM of sand moulds is limited. According to Huang *et al*. (2013), various challenges regarding the health of AM operators may arise due to AM processes. Bours *et al*. (2017) states that hazardous feedstock material (e.g., silica sand) is present during the processing (printing) phase, while du Preez *et al*. (2018) mentions that operators may be exposed to feedstock material during pre-processing and post-processing phases. The second objective was to quantify emissions of HCSs (airborne crystalline silica, VOCs and particulate matter) released during AM of sand moulds.

5.2.2.1 Coating

The coating process was investigated to observe if the process caused emission of particles. This study confirms the emission of 0.3 µm, 0.5 µm, 1 µm and 0.01 - ~ 1.0 µm sized particles during the coating process. The initial increase in particle number concentrations measured on day one and three was attributed to the use of compressed air to clean the coating machine filter. When the AM operator used compressed air, there was dust visible in the workplace which indicated increased particle emissions. The second increase in particle number concentrations measured on day three, during mid-coating, was linked with opening of the room's bay door (Chapter 3, Figure 3-4). There is a possibility that dust from outside influenced the particle number concentration in the room. As a result, the particle number concentrations of 0.01 - ~ 1.0 µm sized particles on day three, reached the highest maximum compared to other days of coating. Compressed air was not utilised on day two, however, there was an increase in concentrations of particles 0.01 - ~ 1.0 µm in size as opposed to 0.3 µm, 0.5 µm and 1 µm. Though unconfirmed, it was suspected that it might have been caused by resuspension of particles < 0.3 µm in size. This corresponded with the air monitoring results, which indicated that personal respiratory exposure to respirable dust concentrations measured on day two were low in contrast to day one and three where compressed air was used (Chapter 3, Table 3-4). The use of compressed air can thus be regarded as the primary source of particle emissions during the coating process, followed by indirect increase in particle number concentrations due to the bay door opening. Lastly, the presence of particles < 0.3 µm in size poses a risk to AM the operator as these particles can remain suspended in the air for longer periods and inhalation can lead to their deposition in the alveoli.

5.2.2.2 Printing

The monitoring of particle number concentrations was conducted on five consecutive days (one day of cleaning the AM machine and four days of AM processes) using direct reading instruments. During this study, it was evident that the AM machine emitted particles 0.3 µm, 0.5 µm, 1 µm and 0.01 - ~ 1.0 µm in size.

First of all, the AM machine was cleaned, and the particle number concentrations increased when the AM operator performed dry sweeping techniques. The sweeping caused a visible dust cloud which caused peak particle number concentrations during this procedure. Due to lack of ventilation in the AM machine room, the inability to remove or decrease the particle concentration in the air increased the AM operator's respiratory exposure to respirable particulates (possibly including crystalline silica).

The particle number concentrations averaged according to the days, indicated statistically significant differences between the days as well as amongst the various phases. On day three the particle number concentrations, were the highest during each phase in comparison to the same phases performed on other days. This resulted in day three having the highest average particle number concentrations compared to other printing days (Chapter 4, Figure 4-6). Particle emissions during post-processing might be the reason for this occurrence. Reason being that, both processing and pre-processing were performed directly after post-processing, therefore particle emissions from post-processing possibly influenced the particle number concentrations of both processing and pre-processing. It is evident, as shown in Chapter 4, Figure 4-6 that increased post-processing emissions led to increased average particle number concentrations on both day three and five, while the opposite occurred for particle emissions on day four.

Regarding the phases, the average particle number concentrations for pre-processing were statistically significantly higher than processing and post-processing (Chapter 4, Figure 4-7). The aforementioned explanation could also be applied to this scenario where it is possible that increased emissions during post-processing could have influenced the average particle number concentrations measured during subsequent pre-processing phases. However, no statistical significant differences were found between emission rates of different phases. The second objective was thus met.

It was hypothesised that *there is a difference in particle emissions during each phase which depends on the activities performed during each shift*. There was a statistical difference in the average particle number concentrations of 0.01 - ~ 1.0 µm sized particles between the different phases. Pre-processing was higher than processing and post-processing, while the latter were relatively similar. Furthermore, particle number concentrations also differed between the three repeats of a similar phase (Chapter 4, Figure 4-S2). This is an indication that activities or conditions during each phase influenced the particle emissions measured. There was however no difference in emission rates between phases (Chapter 4, Table S1). The hypothesis is therefore partially accepted.

5.2.3 Respiratory exposure to respirable crystalline silica, VOCs and particulate matter during full shift

Sand mould manufacturing is mainly an automatic process; however, AM operators still come into direct contact with feedstock materials which may pose a risk to their health. The use and handling of silica sand may lead to exposure to respirable crystalline silica and particulate matter. Also, binders used during processing can result in VOCs exposure (Roth *et al*., 2019). Thus, the third objective of this study was to determine respiratory exposure of AM the operators to airborne respirable crystalline silica, VOCs and particulate matter during the full shift.

5.2.3.1 Coating

On the first day of coating, the operator was exposed to a respirable crystalline silica concentration of 0.112 mg/m^3 while 0.060 mg/m^3 was measured in the coating area. Increased respirable crystalline silica exposure was attributed to the use of compressed air to clean the coating machine filter, which released silica sand particles from the filter. The AM operator was over-exposed to respirable crystalline silica which put the AM operator at risk of developing adverse effects associated with respirable crystalline silica exposure. Also, with inadequate ventilation in the room, this meant that the released airborne particles were present throughout the shift. This was reflected in the area airborne concentrations, which indicated that the workplace concentrations for respirable crystalline silica were above the action level [> 50% of the occupational exposure limit (OEL)] for the shift (Chapter 3, Table 3-4). Personal exposure to respirable dust on day one and three were higher than day two. Compressed air was used on both days, which have been shown to increase particle number concentrations (Chapter 3, Figure 3-4). Respirable dust concentrations on day three were however slightly higher than day one which could be ascribed to dust from the outside entering the room during opening of the bay door.

5.2.3.2 Printing

The cleaning of the AM machine resulted in increased exposures to respirable crystalline silica (above the action level) compared to the printing days (below the detection limit) (Chapter 4, Table 4-3). Area airborne concentrations for respirable dust at area 1 (in front of the AM machine), during days when post-processing was performed, were higher compared to area 2 (behind the AM machine). This indicated that post-processing activities contributed to the respirable dust concentrations and particulate emissions measured during the printing days. Low concentrations of hazardous chemical substances (HCSs) were measured during the printing days. VOCs concentrations were < 0.1% of OELs, while respirable crystalline silica concentrations were below the detection limit and respirable dust concentrations were < 10% of the OEL. It was evident that high personal exposure to, as well as area airborne concentrations of respirable crystalline silica during the coating process and cleaning of the AM machine, were a result of the cleaning

techniques used (dry sweeping and compressed air). This indicated that the methods used for cleaning need to be revised/improved to help minimise the risk of exposure. The third objective is met.

In addition, it was hypothesised that *there is exposure to respirable crystalline silica, VOCs and particulate matter > 10% of the OEL, but respirable crystalline silica is the most prominent*. Personal exposure to respirable crystalline silica (quartz) during the coating process (0.112 mg/m^3) was above the national occupational exposure limit-control limit (OEL-CL) (0.1 mg/m^3). Area airborne concentrations during the coating process (0.06 mg/m^3), as well as personal exposure during the cleaning of the AM machine (0.07 mg/m^3) indicated that the quartz concentrations were above the action level (> 0.05 mg/m^3). But the quartz concentrations for both area concentrations and personal exposure during the AM processes, as well as the last two days of coating were below 10% of the OEL. Acetone, pentane, heptane and toluene were < 0.1% of their respective OELs. In general, during printing, all the concentrations were < 10% of the OELs but during cleaning of the AM machine and the coating machine, it was > 10% of the OEL. This hypothesis is therefore partially accepted.

5.3 Further discussion

The feedstock material was the primary source of exposure to respirable crystalline silica. The high quartz content (> 90%) and small particles (most notably, respirable particles) posed a potential health risk to the AM operator. This indicates that there is a health risk associated with working with the silica sand used for AM. The increased particle number concentrations as well as high personal exposures to respirable crystalline silica linked to the cleaning of the coating machine filter and AM machine indicates that these activities should be classified as the activities with the highest risk. The increase in particle number concentrations in both the coating and AM machine rooms due to lack of fresh air introduction and extraction ventilation indicate the inadequacy of ventilation system in the facility. It is therefore important for the facility to prioritise improving ventilation and reducing exposure during cleaning tasks. This will help the facility to minimise exposure to HCSs to as low as reasonably practicable.

5.4 Recommendations for AM facilities printing silica sand moulds

Control measures are essential in the workplace to help reduce exposure of workers to HCSs. According to the South African Hazardous Chemical Substances Regulations (HCSR), exposure to Table 1 substances with an OEL-CL should be kept as low as possible (Department of Employment and Labour, 1995). It is of utmost importance for employers to implement occupational control measures according to the hierarchy of control: 1) elimination 2) substitution 3) engineering controls 4) administration controls 5) education, information and training 6) housekeeping and 7) personal protective equipment. In this study, handling silica sand was the

primary cause of exposure. Elimination or substitution of the feedstock material would be the most effective way to protect the operator. That it is not possible because the silica sand is specifically chosen for its physical and chemical characteristics making it a useful material in terms of the AM of sand moulds for metal casting. The following section addresses control measures that can be implemented by the facility to help protect workers from hazardous substances.

5.4.1 Engineering controls

Engineering controls are effective but very expensive. The employer therefore needs to do a cost-benefit analysis prior to implementing these control measures. The facility also needs to assess the building and verify if installing a new local extraction ventilation (LEV) system will be possible. The site where this study took place is a former library building, and consequently it was not meant to house industrial-scale AM machines. This situation makes installing industrial sized ventilation systems or similar control measures difficult.

5.4.1.1 The coating room

1. High exposures to respirable crystalline silica occurred during the cleaning of the filter using compressed air. According to the Regulation 13 (a) of the hazardous Chemical Substances Regulations (HCSR) (Department of Employment and Labour, 1995), the use of compressed air is strictly prohibited. Therefore, the most effective way to reduce exposure is controlling emissions at the source. The facility can enclose the cleaning process by using a glove box isolating the source of exposure from the AM the operator. This measure allows filters to be cleaned inside the box, minimising exposure. Dust is then captured by a filtering system. The gloves are attached to the box and remain inside after cleaning is done, meaning no silica sand dust will adhere to the AM operator's clothing.

2. If the glove box cannot be implemented, the AM operator can use vacuum cleaners fitted with highly-efficiency particulate air (HEPA) filters instead to clean the coating machine filter rather than compressed air. HEPA filters have been reported to capture particles 0.3 - 0.5 µm in size (Lioy *et al*., 1999). This will also reduce free airborne silica sand dust and avoid formation of dust clouds.

3. A mobile dust extractor (Figure 5-1) can also be effective as it captures silica sand dust from the source of exposure. The dust extractor can be moved around as well as the hood, which can be placed as close to the source of emission (coating machine).

4. The room had a heating, ventilation and air conditioning (HVAC) system that was not operational (Chapter 3, Figure 3-2). HVAC systems are used to provide fresh clean air to the room. Repairing the HVAC system may assist with introducing fresh air to the room, thus improving the air quality. It should be noted that the duct expelling the dust from LEV

systems should not be located close to any ducts introducing air into the room as it may lead to silica dust particles being reintroduced into the room. This can be accomplished by verifying the effectiveness of engineering controls after every 24 hours, as per Section 12 of the HCSR.

Figure 5-1: The PA series mobile dust extraction (Climavent, UK).

5.4.1.2 The AM machine room

5. The LEV system in the room was present; however, it was not operational. It was therefore not possible to extract silica sand dust during the post-processing phase, leading to the accumulation of airborne particulate matter in the room. It is recommended that the management of the facility repair the LEV systems (non-operational) or switch it on, during the pre- and post-processing to help reduce silica sand dust and keep exposures as low as reasonably practicable. This is a cost-effective method rather than installing new engineering controls. According to the Hazardous Chemical Substances Regulations (HCSR) Section 12, all control systems should be kept in good working order and examined every 24 hours.

6. HVAC systems were also available in the AM machine room but not operational. The facility should repair the HVAC systems as they supply the room with clean fresh air. This will dilute the air and help decrease built-up particle concentrations in the AM machine room. It is also important for the facility to implement a maintanance schedule for the HVAC system to improve its life expectency.

5.4.2 Administrative controls

5.4.2.1 The coating room

7. Safety data sheets (SDSs) are information sheets supplied by the manufacturer containing information about chemicals to be used by workers. SDSs provide detailed information on the work practices and health risks associated with the chemical (Schroder and Stanton, 2014). Providing SDSs will ensure that the AM operator is knowledgeable about the task they perform, and the hazards involved.

5.4.2.2 The AM machine room

8. The cleaning method used resulted in high particulate emissions during this study. It is therefore recommended to place warning signs where cleaning is performed in the facility, in order to notify the AM operator and other workers that the area is contaminated with silica dust and respiratory protective equipment (RPE) is required before entry. The sign can display: “WARNING! Silica sand work area” (NIOSH, 1974).

9. The facility should ensure that SDSs are available to inform workers. This will provide knowledge of the task they are performing. SDSs are valuable sources of information about the hazard involved with the tasks, health effects and work practices needed to ensure reduced exposure to the hazard in question (Schroder and Stanton, 2014).

5.4.3 Education, information, and training

10 The AM operator should be educated on crystalline silica exposure, its risks, health effects and how to reduce exposure. It is also imperative for employers to provide information on how to handle silica sand safely and store it properly. This can be accomplished by providing the AM operators with SDSs. According to the HCSR, the employer is required to provide the employees with SDSs.

11. The AM operator should be trained on how to use the ventilation systems and understand the necessity of these systems to minimise personal exposure during coating and the AM process.

12. The AM operator should also be trained on how to use and select the correct respiratory protective equipment (RPE).

13. The AM operator should be educated and trained on how to maintain both RPE and ventilation systems.

5.4.4 Housekeeping

Both the AM and sand coating machines rooms had silica sand on the floor and furniture (Chapter 3, Figure 3-2; Chapter 4, Figure 3-1). This may increase the chances of silica sand becoming airborne when stepped on or moving equipment on top of furniture. The AM operator needs to keep the rooms tidy and free of silica sand.

14. Vacuum cleaners equipped with HEPA filters should be used to clean the floor. This will reduce the likelihood of silica dust cloud formation compared to the use of compressed air or dry sweeping methods for cleaning.

15. If vacuum cleaners fitted with HEPA filters are not available, the AM operator should use wet cleaning methods to sweep silica sand off the floor. This method is less costly than buying vacuum cleaners but not as effective. However, it will minimise the resuspension of silica sand particles in the workplace air.

16. Wet cloths should be used to wipe off silica sand on furniture. The silica sand particles can adhere to the surface of the wet cloths, reducing any possibility sand particles' suspension.

5.4.5 Personal protective equipment (PPE)

17. PPE is the last form of protection against HCSs. It is used as the last resort when all other control measures cannot be or have already been implemented. PPE is more effective in conjunction with good engineering controls. The AM operator at the research facility wore PHUZA MOYA FFP2 dust masks to help protect against crystalline silica exposure. The FFP2 masks can reduce exposure to fine particulates by 10 times and is therefore appropriate for this situation. Even though FFP1 can reduce exposure to fine particulates by 4 times (Lee *et al*., 2016), respirable crystalline silica is a confirmed human carcinogen and the additional protection of the FFP2 is recommended. Since the AM operator may also be exposed to minute concentrations of VOCs during printing, the employer should supply the AM operator with respirators that are designed to protect against both VOCs and dust. Although the exposure to VOCs was low, respirators that protect against both HCSs serve the double function of protecting the AM operator against possible respirable crystalline silica exposure and possible VOC exposure.

18. The AM operator wore casual clothing instead of standard industrial overalls, which may contaminate their clothes with silica sand dust when taken home. It is

recommended that during work, the AM operator wears overalls and safety shoes to prevent take-home exposures.

5.5 Limitations of this study

- The SDSs for the silica sand sampled were not provided by the suppliers of the virgin silica sand. It was therefore not possible to compare the chemical composition of the sand used in this study with that of the manufacturers.

- The three processing phases (pre-processing, processing, and post-processing) were monitored on the same day and directly following one another, as is the common procedure in the facility. Process phases performed first influenced the particle number concentrations measured during the process phases that followed. This caused uncertainties due to particulate emissions that could not be associated solely with a single AM phase.

- It was difficult to obtain proper background levels as sampling was affected by real-work circumstances where conditions vary with each day. This made it difficult to calculate the ERs as well as discuss their results.

5.6 Recommendations for future studies

- Studies conducted on 3D desktop printers have found that these printers emit ultrafine particles (UFPs) (Steinle, 2015; Azimi *et al*., 2016; Yi *et al*., 2016). UFPs can be defined as particles < 100 nm (Cena *et al*., 2011). There is a lack of information on emission of UFPs during AM of sand moulds and SEM analysis did not reveal nano sized particles. But SEM analysis alone is not enough to dismiss the possibilities that UFPs might be present during AM of sand moulds. Both the coating and AM processes confirmed the emission of particles 0.01 - ~ 1.0 µm in size, meaning UFPs may also be present. Future studies can, therefore, investigate the emission of UFPs during the printing of silica sand moulds. The use of a nanoparticle respiratory deposition (NRD) sampler is recommended for personal exposure to < 0.3 µm sized particles.

- It was not possible to distinguish particle emissions between phases as the phases were performed directly after one another. Other phases might have influenced particle number concentrations of subsequent phases. It is therefore recommended for future studies that phases should be performed on separate days to eliminate uncertainties.

- It is also recommended that one or two days to be allocated between sampling days in which sampling will not be conducted. This will allow the room to be ventilated and particle

number concentrations to fall as low as possible, thereby avoiding increased background measurements when sampling takes place.

- The results of this study indicate that particle emissions still differ for similar printed parts. It is, therefore, recommended for future studies to investigate the influence of print size on the emission of particles during the AM of sand moulds' particle number concentrations.

5.7 References

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ANNEXURE A: ETHICS CLEARANCE CERTIFICATE

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Health Sciences Ethics Office for Research, Training and Support

North-West University Health Research Ethics Committee (NWU-HREC)
Tel: 018-285 2291
Email: Wayne.Towers@nwu.ac.za

Dr SJL Linde
Occupational Hygiene
OHHRI

21 May 2019

Dear Dr Linde

APPROVAL OF YOUR APPLICATION BY THE NORTH-WEST UNIVERSITY HEALTH RESEARCH ETHICS COMMITTEE (NWU-HREC) OF THE FACULTY OF HEALTH SCIENCES

Ethics number: NWU-00020-19-S1

Kindly use the ethics reference number provided above in all future correspondence or documents submitted to the administrative assistant of the North-West University Health Research Ethics Committee (NWU-HREC) secretariat.

Study title: Particulate emissions and respiratory exposure to hazardous chemical substances during additive manufacturing of sand moulds

Study leader: Dr SJL Linde

Student: NL Matihatsi-25257536

Application type: Single study

Risk level: Minimal (monitoring report required annually)

Expiry date: 31 May 2020 (monitoring report is due at the end of May annually until completion)

You are kindly informed that after review by the NWU-HREC, Faculty of Health Sciences, North-West University, your ethics approval application has been successful and was determined to fulfil all requirements for approval. Your study is approved for a year and may commence from 21/05/2019. Continuation of the study is dependent on receipt of the annual (or as otherwise stipulated) monitoring report and the concomitant issuing of a letter of continuation. A monitoring report should be submitted two months prior to the reporting dates as indicated i.e. annually for minimal risk studies, six-monthly for medium risk studies and three-monthly for high risk studies, to ensure timely renewal of the study. A final report must be provided at completion of the study or the NWU-HREC, Faculty of Health Sciences must be notified if the study is temporarily suspended or terminated. The monitoring report template is obtainable from the Faculty of Health Sciences Ethics Office for Research, Training and Support at Ethics-HRECMonitoring@nwu.ac.za. Annually, a number of studies may be randomly selected for an internal audit.

The NWU-HREC, Faculty of Health Sciences requires immediate reporting of any aspects that warrants a change of ethical approval. Any amendments, extensions or other modifications to the proposal or other associated documentation must be submitted to the NWU-HREC, Faculty of Health Sciences prior to implementing these changes. These requests should be submitted to Ethics-HRECApply@nwu.ac.za with a cover letter with a specific subject title indicating, "Amendment request: NWU-XXXXX-XX-XX". The letter should include the title of the approved study, the names of the researchers involved, the nature of the amendment/s being made (indicating what changes have been made as well as where they have been made), which documents have been attached and any further explanation to clarify the amendment request being submitted. The amendments made should be indicated in yellow highlight in the amended documents. The *e-mail*, to which you attach the documents that you send, should have a *specific subject line* indicating that it is

an amendment request e.g. "Amendment request: NWU-XXXXX-XX-XX". This e-mail should indicate the nature of the amendment. This submission will be handled via the expedited process.

Any adverse/unexpected/unforeseen events or incidents must be reported on either an adverse event report form or incident report form to Ethics-HRECIncident-SAE@nwu.ac.za. The *e-mail*, to which you attach the documents that you send, should have a specific subject line indicating that it is a notification of a serious adverse event or incident in a specific project e.g. "SAE/Incident notification: NWU-XXXXX-XX-XX". Please note that the NWU-HREC, Faculty of Health Sciences has the prerogative and authority to ask further questions, seek additional information, require further modification or monitor the conduct of your research or the informed consent process.

The NWU-HREC, Faculty of Health Sciences complies with the South African National Health Act 61 (2003), the Regulations on Research with Human Participants (2014), the Ethics in Health Research: Principles, Structures and Processes (2015), the Belmont Report and the Declaration of Helsinki (2013).

We wish you the best as you conduct your research. If you have any questions or need further assistance, please contact the Faculty of Health Sciences Ethics Office for Research, Training and Support at Ethics-HRECApply@nwu.ac.za.

Yours sincerely

Prof Wayne Towers
Chairperson: NWU-HREC

Prof Minrie Greeff
Head of Health Sciences Ethics Office for Research, Training and Support

Current details: (23239522) G:\My Drive\8. Research and Postgraduate Education\9.1.5.3 Letters Templates\9.1.5.4.1_Approval_letter_HREC.docm
30 April 2018

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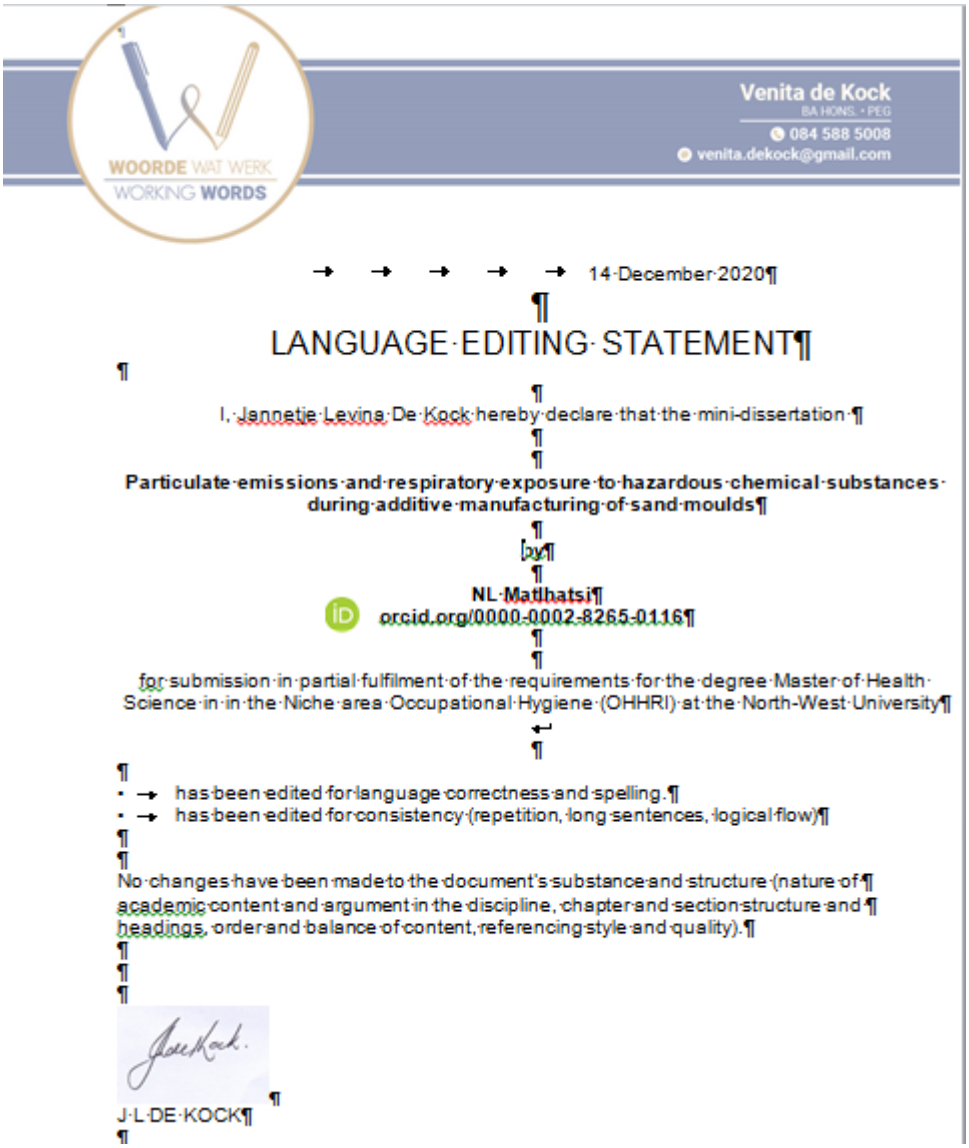
ANNEXURE B: LANGUAGE EDIT STATEMENT



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WOORDE WAT WERK
WORKING WORDS

14 December 2020

LANGUAGE EDITING STATEMENT

I, Jannetje Levina De Kock hereby declare that the mini-dissertation

Particulate emissions and respiratory exposure to hazardous chemical substances during additive manufacturing of sand moulds

by

NL Matlhatsi
orcid.org/0000-0002-8265-0116

for submission in partial fulfilment of the requirements for the degree Master of Health Science in in the Niche area Occupational Hygiene (OHHRI) at the North-West University

- has been edited for language correctness and spelling.
- has been edited for consistency (repetition, long sentences, logical flow)

No changes have been made to the document's substance and structure (nature of academic content and argument in the discipline, chapter and section structure and headings, order and balance of content, referencing style and quality).

J L DE KOCK