

Respiratory exposure during the additive manufacturing of sand casting moulds

GEM Adams

BSc; BSc Hons

25185942

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Supervisor: Prof. J.L. du Plessis

Co-supervisor: Mr. S.J.L. Linde

Assistant supervisor: Mrs. S. du Preez

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PREFACE

This mini dissertation was written in article format. For uniformity purposes, this mini-dissertation is written according to the guidelines of the journal, *Rapid Prototyping Journal*. References are listed using Harvard Style of abbreviation and punctuation. Citing publications in the text: (Adams, 2006) using the first named author's name or (Adams and Brown, 2006) citing both names of two, and (Adams *et al.*, 2006), when there are three or more authors. At the end of the paper a reference list in alphabetical order should be supplied. See Chapter 3: Instructions to authors, for more a detailed description on referencing styles. *Rapid Prototyping Journal* limits the word count of an article to 4 000 words.

Chapter 1 introduces the additive manufacturing (AM) of sand casting moulds and the possible health effects associated with respiratory exposure to the sand dust as well as the potential hazardous chemical substances, such as crystalline silica, polycyclic aromatic hydrocarbons, volatile organic compounds, furan resins and bonding agents released during each processing phase. The problem statement, research objectives and the research question are included in this section. Chapter 2 comprises a thorough discussion of the characteristics of the sand dust, such as sand type, composition and particle sizes as well as the possible hazardous chemical substances present during AM as a result of the processes and their possible health effects. Chapter 3 is written in article format. Tables and Figures are included in this section to present the findings of this study in a comprehensive format. Chapter 4 is the concluding chapter with recommendations and study limitations.

To prevent confusion, the following definitions as used in this mini-dissertation are explained:

Inhalable size fraction: All particles with an aerodynamic diameter of less than 100 µm (Capstick and Clifton, 2012).

Respirable size fraction: Particles with an aerodynamic diameter of less than 4 µm (Capstick and Clifton, 2012).

Additive manufacturing: Three-dimensional objects printed, layer-by-layer, from 3D model data (Manfredi *et al.*, 2014).

Sand casting: A process that uses a mould to create a negative impression, which is then filled with a molten metal and left to cool and solidify (Rao, 2003).

Quartz: A crystal structure made up of a continuous framework of SiO₄ silicon–oxygen tetrahedra, with each oxygen molecule being shared between two tetrahedra, giving an overall formula SiO₂. Quartz is the most abundant form of crystalline silica (Anderson and Anderson, 2010).

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AUTHOR'S CONTRIBUTION

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

Name	Contribution
Ms. G.E.M. Adams	1. Designing and planning of the study. 2. Literature research, interpretation of data and writing of the article. 3. Execution of monitoring processes. 4. Writing of mini-dissertation.
Prof. J.L. du Plessis	1. Supervisor. 2. Assisted with approval of protocol, the interpretation of results and documentation of the study. 3. Provided guidance with specific aspects of this study. 4. Assisted with the design and planning of the study. 5. Professional input and recommendations. 6. Assisted with communication with the universities. 7. Review of the mini-dissertation.
Mr. S.J.L. Linde	1. Co-supervisor. 2. Assisted with approval of protocol, the interpretation of results and documentation of the study. 3. Provided guidance with specific aspects of this study. 4. Assisted with the design and planning of the study. 5. Professional input and recommendations. 6. Review of the mini-dissertation.

Mrs. S. du Preez	1. Assistant supervisor. 2. Assisted with approval of protocol, the interpretation of results and documentation of the study. 3. Provided guidance with specific aspects of this study. 4. Assisted with the design and planning of the study. 5. Professional input and recommendations. 6. Review of the mini-dissertation.
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The following is a statement from the supervisors that confirms each individual's role in the study:

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

Prof. J.L. du Plessis

Mr. S.J.L. Linde

Mrs. S. du Preez

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Table of Contents

PREFACE	ii
REFERENCES.....	iii
AUTHOR'S CONTRIBUTION	iii
ACKNOWLEDGEMENTS.....	v
ABSTRACT	ix
OPSOMMING	x
LIST OF SYMBOLS AND ABBREVIATIONS.....	xi
STANDARD UNITS.....	xii
LIST OF TABLES.....	xiii
LIST OF FIGURES.....	xiv
CHAPTER 1: INTRODUCTION	1
1.1 Overview.....	1
1.2 Problem statement	1
1.3 Research aims and objectives	3
1.3.1 General aim:.....	3
1.3.2 Specific objectives:	3
1.4 Hypothesis.....	4
1.5 References	4
CHAPTER 2: LITERATURE REVIEW	8
2.1 Additive manufacturing and sand casting.....	8
2.1.1 AM techniques/technologies used in sand casting	9
2.2.2 Additive manufacturing processes, materials and health risks	9

2.3	Physicochemical characteristics of particulate matter	13
2.4	Deposition of airborne particulates in the respiratory tract	14
2.5	Respiratory defence mechanisms (clearance)	16
2.6	Health effects associated with particulate matter (PNOC and silica dust - crystalline/amorphous).....	17
2.7	Inhalation of hazardous vapours	18
2.7.1	Volatile organic compounds (VOC's)	19
2.7.2	Health effects associated with VOC's	19
2.7.3	Polycyclic aromatic hydrocarbons (PAHs)	20
2.7.4	Health effects associated with PAH's.....	20
2.8	Occupational Exposure Limits	22
2.9	Conclusion.....	24
2.10	References	24
CHAPTER 3: ARTICLE		40
Instructions to authors		40
Abstract.....		44
Introduction.....		44
Methodology.....		46
Sites and subjects		46
Ethical considerations		46
Physicochemical characterisation of particles.....		46
Respiratory exposure monitoring.....		47
Statistical analysis of results.....		48

Results.....	49
PSD and SEM analysis	49
XRD analysis for mineral composition	50
Exposure monitoring: PNOC	51
Exposure monitoring: Crystalline silica (Quartz)	51
Exposure monitoring: PAH's.....	51
Exposure monitoring: VOC's	52
Discussion.....	54
Conclusions.....	57
References.....	57
CHAPTER 4: CONCLUDING CHAPTER.....	61
4.1 Further discussion and summary of findings.....	61
4.2 Limitations of this study	63
4.3 Recommendations for occupational settings.....	63
Engineering and administrative control measures	63
Personal protective equipment (PPE).....	64
Education and training:.....	65
4.4 Recommendations for future studies	66
4.5 References	67
ANNEXURES.....	70
Certificate for english language editing:.....	70

ABSTRACT

Background: During additive manufacturing (AM) of sand casting moulds, potential dust species of unknown particle size or mineral composition, and hazardous chemical substances (HCS's) such as silica (crystalline), volatile organic compounds (VOC's) and polycyclic aromatic hydrocarbons (PAH's) are liberated/released during the pre-processing, processing and post-processing phases of manufacture. **Aims and Objectives:** Bulk sand samples were collected from two research facilities (Facility A and Facility B) in South Africa to determine particle size fractions and mineral composition. Respiratory exposure monitoring of HCS's was conducted. **Methods:** Physicochemical characterisation of new, used and mixed bulk sand samples through particle size distribution (PSD) analysis, scanning electron microscopy (SEM) analysis and X-Ray diffraction (XRD) was conducted to determine particle sizes and their mineral composition. Area and personal respiratory exposure monitoring of particles not otherwise classified (PNOC), crystalline silica (quartz), PAH's and VOC's was conducted for the duration of each process to determine concentration levels for comparison with national legislation. **Results and discussion:** For new sand, a mean particle size of 137.49 μm at Facility A and 282.70 μm at Facility B was found, indicating that both Facilities had particle sizes larger than the inhalable size fraction. However, 10% of particles at Facility A were smaller than 75.35 μm , indicating the presence of inhalable particles. The SEM imaging supported the abovementioned particle size findings, with particle sizes $> 100 \mu\text{m}$. XRD analysis indicated that sand at Facility A had a majority percentage of mullite present while sand at Facility B comprised of 100% crystalline silica (quartz). Respirable PNOC exposure was lower than the national occupational exposure limits (OEL) at both facilities. Respirable silica (quartz) time-weighted average (TWA) exposure at Facility B indicated a 0.06 mg/m^3 and 0.05 mg/m^3 for two operators respectively, which is below the South African OEL-CL of 0.1 mg/m^3 but at a concentration warranting further action. The only PAH compound present at either Facility was naphthalene, but with a TWA far below its OEL. Exposure to seven VOC's (acetone, pentane, hexane, benzene, toluene, cyclohexane and naphthas) indicated TWA's below their respective OEL's at both facilities. **Conclusions:** This is the first study of its kind to assess the physicochemical characteristics and the respiratory exposure to HCS's during the AM of sand casting moulds. This study is of imperative value, especially as the results have indicated exposure to respirable fractions of crystalline silica (quartz) at one Facility as well as low concentrations of naphthalene and other VOC's, indicating the need for biological monitoring. This study opens the doors to research other facets of exposure, such as assessing the inhalable and thoracic exposure and assessing furfuryl alcohol exposure.

Keywords: Silica, particle size fractions, occupational exposure, polycyclic aromatic hydrocarbons, volatile organic compounds, health effects, additive manufacturing

OPSOMMING

Agtergrond: Tydens dunlaagvervaardiging (DV) van sandgietsels word potensiële stof spesies van onbekende partikel groottes of mineraalsamestelling, en gevaarlike chemiese substansie (GCS's) soos kristallyne silika, polisikliese aromatiese koolwaterstowwe (PAK) en vlugtige organiese verbindings (VOV) bevry/vrygestel tydens die voor-verwerking, verwerking en na-verwerking fases van vervaardiging. **Doelwitte:** Grootmaat sandmonsters is versamel van twee navorsingsfasiliteite (Fasiliteit A en Fasiliteit B) in Suid-Afrika om partikel groottes en mineraalsamestelling te bepaal. Respiratoriese blootstellingsmonitering van GCS is uitgevoer. **Metodes:** Fisies-chemiese karakterisering van nuwe, gebruikte en gemengde grootmaat sandmonsters deur partikel grootte verspreiding (PGV) analise, skandeerelektronmikroskopie (SEM) analise en X-straaldiffraksie (XSD) is uitgevoer om partikel groottes en hul mineraal samestelling te bepaal. Area en persoonlike respiratoriese blootstellingsmonitering van partikels nie andersins klassifiseerbaar (PBAK), kristallyne silika (kwarts), PAK en VOV, is uitgevoer vir die duur van elke proses om konsentrasie vlakke te bepaal vir 'n vergelyking met die nasionale wetgewing. **Resultate en bespreking:** Vir nuwe sand, is 'n gemiddelde partikel grootte van 137.49 μm by Fasiliteit A en 282.70 μm by Fasiliteit B gevind, wat aandui dat beide fasiliteite partikel groottes groter as die inasembare grootte fraksie gehad het. Tien persent van die partikels by Fasiliteit A was egter kleiner as 75.35 μm , wat dui op die teenwoordigheid van inasembare partikels. Die SEM beelde ondersteun die bogenoemde partikelgrootte bevindings, met partikel groottes > 100 μm . XSD ontleding het aangedui dat sand by Fasiliteit A 'n meerderheid persentasie van "mullite" bevat het terwyl sand by Fasiliteit B uit 100% kristallyne silika (kwarts) bestaan het. Respirerbare PBAK blootstelling was laer as die nasionale beroepsblootstelling drempel (BBD) by beide fasiliteite. Tyd beswaarde gemiddeld (TBG) van respireerbare silika (kwarts) blootstelling by Fasiliteit B was 0.06 mg/m^3 en 0.05 mg/m^3 onderskudelik vir twee operateurs, wat laer is as die Suid-Afrikaanse BBD van 0.1 mg/m^3 , maar by 'n konsentrasie wat verdere aksie regverdig. Die enigste PAK teenwoordig by enige van die Fasiliteite was naftaleen, maar met 'n TBG ver onder sy BBD. Blootstelling aan seve VOV (asetoon, pentaan, hekasaan, benseen, tolueen, sikloheksaan en nafta) het aangedui dat die TBG onder hul onderskeie BBD was by beide fasiliteite. **Gevolgtrekkings:** Dit is die eerste studie van sy soort wat die fisies-chemiese eienskappe en die respiratoriese blootstelling aan GCS's gedurende die DV van sandgietsels evalueer. Hierdie studie is van imperatiewe waarde, veral omdat die een Fasiliteit se resultate die teenwoordigheid van respireerbare deeltjies van kristallyne silika (kwarts) asook lae konsentrasies van naftaleen en ander VOV's getoon het, dui dit op die noodsaaklikheid vir biologiese monitering. Hierdie studie maak die deure oop om ander fasette van blootstelling, soos die assessering van die inasembare en torakale blootstelling en die assessering van furfural alkohol blootstelling.

Sleutelwoorde: Silika, partikel grootte deeltjies, beroepsblootstelling, polisikliese aromatiese koolwaterstowwe, vlugtige organiese verbindings, gesondheids effekte

LIST OF SYMBOLS AND ABBREVIATIONS

ACGIH	American Conference of Governmental Industrial Hygienists
AM	Additive Manufacturing
AOEL	Acceptable Occupational Exposure Limit
ASTM	American Society for Testing and Materials
BDL	Below Detection Limit
CAD	Computer Aided Design
COPD	Chronic Obstructive Pulmonary Disease
DoL	Department of Labour
EPA	Environmental Protection Agency
IARC	International Agency for Research on Cancer
LOD	Limit of Detection
MSDS	Material Safety Data Sheet
NIOSH	National Institute for Occupational Safety and Health, USA
OEL	Occupational Exposure Limit
OEL-CL	Occupational Exposure Limit – Control Limit
OEL-RL	Occupational Exposure Limit – Recommended Limit
OSHA	Occupational Safety and Health Association, USA
PAH	Polycyclic Aromatic Hydrocarbons
PEL	Permissible Exposure Limit
PNOC	Particles Not Otherwise Classified
PPE	Personal Protective Equipment
PSD	Particle Size Distribution
RHCS	Regulations for Hazardous Chemical Substances
SEM	Scanning Electron Microscope
SKC	Manufacturer of air sampling equipment
STEL	Short Term Exposure Limit
TLV	Threshold Limit Value
TWA	Time Weighted Average
3D	Three dimensional
USA	United States of America
VOC	Volatile Organic Compounds

STANDARD UNITS

%	Percentage
<	Less than
>	Greater than
≤	Less or equal than
μg	Micrograms
μm	Micrometre
kg	Kilograms
m ³	Cubic metre
mg	Milligrams
mg/m ³	Milligram per cubic metre
mm	Millimetre
nm	Nanometre
ppm	Parts per million
p/cm ³	Parts per cubic centimetre
p/m ³	Parts per cubic metre

LIST OF TABLES

Chapter 2:

Table 1: Carcinogenic classification of selected PAHs by specific agencies.....	21
Table 2: Exposure limits for common VOC's set by three different occupational health agencies.....	23
Table 3: PAH exposure limits from various agencies.....	24

Chapter 3:

Table 1: Exposure monitoring strategy for HCS.....	48
Table 2: PSD (mean $\pm$ standard deviation) for sand (new and used) at Facility A and (new, used and mixed sand) Facility B	49
Table 3: Mineral composition types present in sand samples at each AM facility.	50
Table 4: PNO exposure at Facility A and Facility B.....	51
Table 5: Crystalline silica (quartz) exposure at both facilities	51
Table 6: PAH exposure at Facility A during processing and post-processing	52
Table 7: VOC exposure at Facility A	53
Table 8: VOC exposure at Facility B	53

Chapter 4:

Table 1: Observations and recommendations of PPE of operators at both facilities	64
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LIST OF FIGURES

Chapter 2:

Figure 2.1: Particle size considerations vital for deposition in the whole lung 15

Figure 2.2: The consequence of the size of particles on the sedimentationof aerosol particles in the
respiratory tract 16

Chapter 3:

Figure 1 (a): Facility A - New sand 49

Figure 1 (b): Facility A - Used sand 49

Figure 1 (c): Facility B - New sand 50

Figure 1 (d): Facility B - Mixed sand.....50

Figure 1 (e): Facility B - Used sand 50

CHAPTER 1: INTRODUCTION

1.1 Overview

Additive manufacturing (AM) is an innovative technology, now booming in industry for its ability to produce three-dimensional objects by printing them, layer-by-layer, from 3D model data (Manfredi *et al.*, 2014). This state-of-the art method of production has seen an annual global market growth of 20% and is utilised for its low cost and short manufacture time (Maxey, 2014). One of the many uses that AM has been called on for is the production of sand casting moulds for metal parts such as aluminium, magnesium, cast iron and steel (Radis, 2015).

While there are various hazards associated with known components of AM of sand casting mould production, such as crystalline silica, liquid bonding agents and resins (ZCorp., 2007; Viridis3D, 2011); it is unknown whether/what other hazardous chemical substances (HCS's) might be present/released as a result of the effects of AM processes on these known raw materials. These include the possible release of certain polycyclic aromatic hydrocarbons (PAH's) and volatile organic compounds (VOC's) (Kubecki *et al.*, 2013; Holtzer *et al.*, 2014; Biache *et al.*, 2015). Health effects as a result of these substances include, but are not limited to, silicosis, respiratory dysfunction, granuloma formation, neurological and reproductive effects, cancer and renal failure; just to name a few (ATS, 1996; Hinwood *et al.*, 2007; Tibbetts, 2015).

1.2 Problem statement

As a relatively new branch of science and engineering, there is, at present, minimal local or international technical and scientific data available regarding the health risks associated with the pre-process, process and post-process of AM. Health and safety risks that arise for the operational workforce are a concern because of the lack of independent studies available (Klein, 2015).

Earlier methods of sand mould production often required hand carving and sanding the product for finishing. Because of human error and design flaws in these earlier processes, foundries have long been interested in the production of sand moulds through AM techniques, which allows casting directly from computer aided design (CAD) data sets. Patterns can now be fabricated with great precision and a substantial saving in cost, time and labour (Additively, 2015; Stratasys, 2015). Two prominent technologies are used for the AM of sand moulds, namely binder jetting and powder bed fusion. Binder jetting involves the deposition of a binder (a liquid bonding agent) through inkjet print heads into the raw material powder bed with a new layer being spread on top of the previous layer. The jetted binder then prints and stitches the new layer to the previous layer (DREAMS, 2015). Binder jetting does not use heat during the build process, which sets it apart from other AM processes (ExOne, 2014). Powder bed fusion, of which selective laser sintering is

the process used for sand cast production, is a process which uses various heat sources as a means of fusing powder sand particles. The temperature is controlled to just above the material's melting point. The process takes place in an enclosed chamber that contains nitrogen gas to reduce oxidation and degradation of the sand. A laser is usually utilised to melt the powder particles and then fuse the material together (Gibson *et al*, 2010; AMRG, 2015).

Some of the processes in AM technologies have overarching similarities to sand casting foundries in this field. These include the presence of heat, exposure to dust/powdered sand as well as exposure to resins/binding agents. Therefore, some of the processes in sand casting foundries can be examined and extrapolated to determine potential occupational exposures due to this limitation in the amount of information available with regards to the health effects of sand mould production using AM techniques (IARC, 2011; Stephens *et al.*, 2013; Lagnau, 2014).

Possible risks of exposure to each ingredient in AM materials, such as sand and resin binders, can be linked to the distinct phases of processing. During AM of sand casting moulds, three distinctive processes are evident for the construction of a mould. This includes a pre-processing phase which entails "loading" or pouring sand and resin into the printer. A processing phase wherein the build process occurs through the deposition of layers, one at a time, to construct the three-dimensional object; this process either does or does not utilise heat. Finally, the post-processing phase occurs wherein the printer/machine is opened and the completed mould is removed. This mould is finished off through sanding or dusting and the machine is then subsequently cleaned to prepare for the following production (Deak, 1999; Rechtenwald, 2013; Short *et al.*, 2015).

In the pre-processing phase, loading of the powdered sand material into the machine usually produces a dust cloud, which the operator could inhale. Loading of the liquid bonding agent into the machine in binder jetting could also involve possible VOC inhalation or dermal exposure. During processing utilising powder bed fusion, the vapours produced from the resins as a result of heat production, as well as the dust collected inside the machine are released when the machine is opened after the build process is complete. In the post-processing phase, dust is released during finishing (sanding down) of the completed product (Deak, 1999; Short *et al.*, 2015). VOC's may also be produced when the product must be baked in this final phase of production. Adverse health effects, as a result of dust and resin vapour exposure, as well as exposure to gases present inside the machine; encompass many possible respiratory and dermatological negative effects. These include, amongst others, silicosis (long term) if crystalline silica is present in the dust, respiratory dysfunction and contact dermatitis (Carex Canada, 2015). Respiratory dysfunction, nervous system dysfunction, kidney disease, cardiovascular disease and asthma are some of the adverse health effects associated with VOC exposure (Hinwood *et al.*, 2007; Tibbetts, 2015).

Because of a lack of information concerning the effects that the processing in AM has on each ingredient of the sand mixture, possible concerns arise from the potential effect that each individual ingredient has on the health of AM operators. AM machinery is most often sold without any filtration or exhaust ventilation fixtures (Stephans, 2013) and, as production is most often prioritised over the health and safety of the operators of the machinery, any ventilation equipment that is available is rarely utilised (Kramer, 2013). Both these factors are a cause for concern as exposure to the components in the powdered sand material is primarily respiratory by nature (Kruth *et al.*, 2004). A Material Safety Data Sheet (MSDS) is usually offered with the material that should specify all hazards, including respiratory hazards, related to the materials and chemicals. These MSDS' are at times out of date, inadequate and come in the form of a brochure rather than an official document regardless of legal requirements (Sentryair, 2014).

Due to a list of potential risks to the health of the AM operator in each phase of production as well as the evident lack of literature available on the topic, it is imperative that a study be conducted to assess the exposure of these operators to determine the subsequent urgency wherewith control measures need to be implemented. Accompanied by the usual lack of ventilation used with these printers and the prioritisation of production over safety, such a study becomes a matter of necessity. The study will be conducted at two facilities/institutions, Facility A and Facility B as both research institutions offer AM services to outside contractors and provide an adequate setting for testing the exposure of operations to AM operators. Each institution offers a certain AM technology namely, binder jetting and selective laser sintering.

1.3 Research aims and objectives

1.3.1 General aim:

- To assess the physicochemical characteristics of the sand and the occupational respiratory exposure of AM operators to HCS's (such as crystalline silica (quartz) in the respirable fraction, VOC's and PAH's) present during the pre-processing, processing and post-processing phases of the AM of sand moulds.

1.3.2 Specific objectives:

The specific objectives of this study were:

- To determine the physicochemical characteristics of the sand such as the particle sizes and the mineral composition of sand material used in AM. This was evaluated through particle size distribution (PSD), scanning electron microscopy (SEM) and X-Ray diffraction (XRD) analysis of collected bulk sand samples of new, mixed and used sand.
- To determine the concentration of respirable dust (particles not otherwise classified – PNOC and respirable crystalline silica), PAH's and VOC's that AM operators were

exposed to. This was done through the collection of personal exposure samples and static samples in closest proximity to the operator over the task-based period. Personal exposure samples of airborne particulate matter were collected during loading of the AM machine prior to processing, during processing and operation of the machine, and at the cleaning area after processing (post-processing).

1.4 Hypothesis

It is evident in literature that crystalline silica, particularly cristobalite and tridymite, is present in sand casting foundries especially during the cleaning processes of the moulds (NIOSH, 1998; Scholz *et al.*, 2007). Inhalable, thoracic and respirable particles are present in foundries as well as in some AM processes (Stephens *et al.*, 2013; Langnau, 2014).

It is hypothesised that AM operators are exposed to respirable concentrations of crystalline silica above the national TWA-OEL-CL of 0.1 mg/m³.

Literature also concludes that heat influences the release of VOC's as well as PAH's from the resins and silica sand respectively (Kubecki *et al.*, 2013; Biache *et al.*, 2015).

Powder bed fusion incorporates heat and thus it is hypothesised that, at Facility A, which uses powder bed fusion (or selective laser sintering), these VOC's and/or PAH's are present in the air that the AM operator inhales, in concentrations that exceed national OELs.

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CHAPTER 2: LITERATURE REVIEW

In Chapter 1, a brief overview was given to outline the problem presented in this study. In Chapter 2, the important key points of the study will be discussed in further detail. A more in-depth look will be focused on additive manufacturing (AM), the silica sand, the hazardous chemical substances present and the characterisation thereof. The respiratory deposition of particulate matter and the vapours of different hazardous chemicals will be discussed. These hazardous chemical substances will be defined based on each processing stage of AM of sand casting.

As very little information exists concerning the health effects of AM, particularly with its use in sand mould production, some of the processes in sand casting foundries can be examined and extrapolated to determine potential occupational exposures. Some of the processes in foundries have overarching similarities to AM technologies in this field. These include the presence of heat, exposure to dust/powdered sand as well as exposure to resins/bonding agents.

Most of the substances that pose possible health effects are in the form of hazardous chemical substances, of which inhalation is the main route of entry in this occupational and industrial environment (Thorne, 2003)

2.1 Additive manufacturing and sand casting

After more than 20 years of various and differing terminology, the American Society for Testing and Materials (ASTM) International F42 Committee on Additive Manufacturing Technologies defined additive manufacturing as the “process of joining materials to make objects from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing methodologies.” Other terms for these technologies were named including: rapid prototyping, direct digital manufacturing, solid freeform fabrication, additive fabrication, additive layer manufacturing, as well as a host of other names, of which a popular reference is “3D printing.” (Stucker, 2011). Additive manufacturing has been classified by many parameters, one of which is the material used. Either liquid based, solid based or powder based materials are incorporated in the process (Wong and Hernandez, 2012).

Sand casting is a process wherein metallic objects are formed through melting a metal and pouring it into a mould or cavity that is made from sand (due to its high tolerance of heat) and allowing solidification to occur. The processes involved in sand casting include making a pattern, preparing the sand, melting of the metal and pouring it into the mould, cooling, shake-out and finishing (Rao, 2003; ZCorp., 2007).

To reduce production time, the use of AM techniques was recruited for producing the sand moulds that otherwise had to be produced by hand, saving time and effort (Stratasys, 2015).

2.1.1 AM techniques/technologies used in sand casting

Two prominent technologies are used for the AM of sand moulds, namely binder jetting and powder bed fusion.

Binder-jetting techniques do not use the build material itself to form a mould but rather make use of nozzles to print the material with glue, deposited on each layer of powder, which forms a desired shape by holding the powder together (Gibson *et al.*, 2014). A thin layer of powder is first deposited as the process starts. The first layer is formed through a glue pattern being printed onto the powder by the print head. A new layer with this glue is deposited onto a new layer of powder, repeatedly, until a completed part is formed (Stucker, 2011). Thus, in short, binder jetting involves the deposition of a binder (a liquid bonding agent) through inkjet print heads into the raw material powder bed with a new layer being spread on top of the previous layer. The jetted binder then prints and stitches the new layer to the previous layer (DREAMS, 2015). Binder jetting does not use heat during the build process, which sets it apart from other AM processes (ExOne, 2014). This process was developed in the early 1990s, predominantly at Massachusetts Institute of Technology (MIT). This concept can be contrasted with powder bed fusion which uses various heat sources as a means of fusing powder particles (Gibson *et al.*, 2014).

Powder bed fusion, a selective laser sintering process, is a process which works similarly to binder jetting, however, instead of depositing glue onto a layer of powder; thermal energy (heat) is used to melt the powder into the required pattern (Stucker, 2011). The temperature in the chamber is controlled to just below the material's melting point (Wong and Hernandez, 2012). The process takes place in an enclosed chamber that contains nitrogen gas to reduce oxidation and degradation of the powder (AMRG, 2015). A carbon dioxide laser beam is usually utilised to sinter the powder particles and then fuse the material together (Gibson *et al.*, 2010). A piston controls a bed, in which the loose sand particles lie. This piston then lowers the bed at the same distance as one layer's thickness each time a layer is completed (Wong and Hernandez, 2012).

2.2.2 Additive manufacturing processes, materials and health risks

During AM of sand casting moulds, three distinctive processes are evident for the construction of a mould. This includes a pre-processing phase which entails "loading" or pouring powder and resin into the printer. A processing phase wherein the build process occurs through the deposition of layers, one at a time, to construct the three-dimensional object; this process either does or does not utilise heat. Finally, the post-processing phase occurs wherein the printer/machine is opened and the completed mould is removed. This mould is finished off through sanding or

dusting and the machine is then subsequently cleaned to prepare for the following production (Deak, 1999; Rechtenwald, 2013; Short *et al.*, 2015).

Materials used to create sand casting moulds is a mixture of foundry sand, plaster, and other ingredients such as resin binders that have been combined to provide strong moulds with a suitable surface finish. It is fabricated to withstand the heat necessary to cast non-ferrous metals (ZCorp, 2007). Various types of sand materials are used as the “ink” in the printer, usually present in powder form, and thus pose a potential risk for respiratory exposure to the operator (OSHA, 2002; Kruth *et al.*, 2004). In AM, foundry sand such as silica is often used, although other sand types such as olivine (a silica free, mineral mixture of iron and magnesium orthosilicates) and zircon (a compound constituting one-third silicon and two-thirds zircon oxide) are also used (Rao, 2003; Viridis3D, 2011).

Silica, the main constituent of sand, is chemically composed of silicon dioxide (an oxide of silicon). Silica exists in the earth’s crust in three main crystalline forms, namely quartz, cristobalite and tridymite, or in a non-crystalline structure. The most common natural form of silica is found in quartz which is the most well-known and one of the most abundant minerals in the earth’s crust. The crystalline, three-dimensional structure appears due to the framework of tetrahedral units wherein a silicon molecule is associated with four oxygen atoms. It is this crystalline structure that causes the hazardous biological effects that crystalline silica incurs on the human lung (Iler, 1979; Donaldson and Borm, 1998; Rao, 2003; Flörke *et al.*, 2008). Amorphous silica, a non-crystalline form of silica, may occur either naturally; as an intentionally manufactured synthetic silica or silica obtained under controlled conditions. Only synthetically produced amorphous silica is not contaminated with crystalline silica, while naturally occurring types are contaminated by up to 60 % with crystalline silica (Merget *et al.*, 2002).

The use of crystalline silica is common in sand casting foundries - foundry processes being a good industry to compare AM processes with due to the similar chemicals and materials present - with many studies revealing the exposure of operators to this form of silica (OSHA, 2002; Scholz *et al.*, 2007; Derbyshire, 2012). Respiratory exposure to crystalline silica can cause silicosis and it has been classified as a known human carcinogen (Class 1) by the International Agency for Research on Cancer (IARC) (IARC, 1997; NIOSH, 2002). In foundries, cleaning and smoothing any abnormalities of castings is a primary source of exposure to crystalline silica and could also feature in the post processing phase of AM manufactured sand moulds (NIOSH, 1998).

One of the dustiest operations in sand casting foundries includes mixing of dry sands for mould making (Chastain, 2004). This operation could extend and relate to potential risks involved during loading of the printer with the powdered sand material in AM production. Working with powders

during the pre-processing phase has implications based on the size of the particles and its chemical composition (Scholz *et al.*, 2007).

Some manufacturers leave selective laser sintering printer vats open, which contain the sand powder (ExOne, 2014; Sentryair, 2014). These powders, especially quartz powder, are free to infiltrate the air. The grain size used in AM powder materials is usually between 90 and 250 μm , but the presence of smaller particles is unknown (Voxeljet, 2013).

Some AM techniques used in the production of sand casting moulds operate through lasers, which produce heat (Beaman *et al.*, 1994). In a study conducted by Zihms *et al.* (2013), the effect that high temperature processes have on silica sand and the potential risks or hazards these changes produce, were assessed. These include alterations in the mineralogy of the sand as well as instability in the silicon dioxide resulting in the formation of silica polymorphs such as cristobalite and tridymite, although a study conducted by Wahl *et al.* (1961) notes the inability to produce tridymite by heating quartz (Di Benedetto *et al.*, 2016). These two forms of silica are crystalline in structure and result in serious adverse health effects (ATS, 1996). There is also a possibility of grain fracturing due to the high temperatures, resulting in finer sand particles which, during handling, could release the finer particles into the air as dust (Zihms *et al.*, 2013).

Sand has a high melting point and is thus resistant to high temperatures but the resins that are used to bind the moulds for improved strength and finish could be influenced by the heat produced (ZCorp., 2007). The sand and resin binders are exposed to temperatures that range from 100 °C to 250 °C inside the machinery (Song *et al.*, 2007). During the actual processing, the powder bed of constituents can be preheated up to 400 °C (Tang *et al.*, 2003). In some processes, printed moulds must be baked in an oven at 180 °C for four to eight hours after removal from the printer to remove excess moisture from the mould before the metal can be poured (Snelling *et al.*, 2013). A study conducted by Kubecki *et al.* (2013) investigated the influence of temperature on the formation of volatile organic compounds (VOC's) from furan resins. This study investigated the release of VOC's as a result of high temperatures (500 °C to 1200 °C) during the pouring of molten metals into the casting. Toluene, ethylbenzene and xylenes were of the vapours formed in high concentrations even at lower temperatures (Kubecki *et al.*, 2013). Although much higher temperatures were used than those produced by a 3D printer, it could indicate a possible result of the influence of heat on resins during the AM process.

Polycyclic Aromatic Hydrocarbons (PAH's) (a mixture of chemicals produced during the incomplete combustion of fuels) are also likely to be found in sand or soil matrices as microscopic crystallites (Sluszný *et al.*, 1998). Silica sand is a good adsorbent of PAH's and can thus be contaminated with them. A study conducted in 2014 by Smol *et al.* tested the adsorption of six carcinogenic PAH's in quartz sand namely benzo(b)fluoranthene, benzo(k)fluoranthene,

benzo(a)pyrene, dibenzo(a,h)anthracene, ideno(1,2,3,c,d)pyrene and benzo(g,h,i)perylene. The results showed a removal of PAH's from the quartz sand through a desorption process, thus concluding that quartz is a good sorbent of PAH's. These PAH's are desorbed or released at a low temperature of between 100 °C and 300 °C as was concluded in a study by Biache *et al.* (2015). A certain amount of PAH's could thus be released by the sand particles as a vapour, or through adsorption onto the particles, due to the heat exposure from the AM process (Holtzer *et al.*, 2014).

Foundries often use carriers or reducers in their sand casting processes, which is a liquid phase of the coating, used to dilute it. A layer of refractory solids stays behind, when the carrier evaporates, and acts as a barricade between the molten metal and the sand. These carriers also determine how deep the coating penetrates the sand. Naphtha, an aliphatic hydrocarbon, is often used as a carrier or reducer in the sand casting processing in foundries to improve the drying and removal process of the metal from the sand cast, through improvement of the solubility of the coating binder. (HA-International, 2006). Exposure routes for naphtha includes, ingestion, dermal or eye contact resulting in irritation of the eyes, nose and throat; dizziness, drowsiness, headache and biliousness as well as dehydrated, cracked/fractured skin (NIOSH, 2016).

During the post process of AM the core moulds are removed from the machine, cleaned, finished, smoothed and bonded (Langnau, 2014). Respiratory and dermatological exposure to dust particles would be prevalent during the removal process, as removing the mould from the powder build material by hand and then simply dusting it off is common as an extraction method. This allows the dust to infiltrate the air easily. Sanding of the object is done to remove excess build material, unwanted surface textures and improve the appearance of the surface which would allow for further dust exposure. (Langnau, 2014; Stratasys, 2015).

To print within a small build volume and reduce the printing time, many AM systems split and print many individual parts that make up the whole structure simultaneously (Langnau, 2014). Bonding of individual parts of the mould to build the product into its completed 3D structure and to improve the durability of the mould, makes use of super glue (cyanoacrylate), chemical solvents and epoxy based bonding (Stratasys, 2015).

In the sintering process (the actual building process of the material), the working space is isolated in a gas chamber to prevent oxidation of the materials due to the high temperatures produced. This gas chamber could be filled with nitrogen or argon (Tang, 2003). Some printers contain cabinet enclosures that isolate the vat of powdered or liquid materials and the laser beam when the laser fires. Trapping of the vapours can occur inside the cabinets that, upon opening of the lid, will be released when retrieving the final printed object (Sentryair, 2014).

2.3 Physicochemical characteristics of particulate matter

Particulate matter has physical characteristics which include the particle size, number, shape, concentration of particles in the air, surface area and aerodynamic diameter (Dockery and Pope, 1994; McClellan, 2002; Wilson *et al.*, 2002; Kim and Hu, 2006). One of the chemical characteristics most important for this study includes the silica composition of sand particles such as a crystalline structure (McClellan, 2002; Nazaroff, 2004). Particle size, number, aerodynamic diameter and the silica composition of particles is, therefore, important in determining the risk for causing adverse health effects in humans (Nazaroff, 2004; Scheckman and McMurry, 2011). In this study the focus will fall on the particle sizes as well as the sand mineral composition of the particulate matter present in the air.

Mortality and morbidity among humans exposed to airborne particles is greatest when exposed to respirable particles as they are smaller in size. As particle size decreases, the exposure level to particles will increase because a decreasing particle size has a resultant increase in the surface area per unit mass. This leads to a heightened toxicity of the particulate through greater and deeper lung deposition (Lippmann, 1999; Greenberg, 2003; Kim and Hu, 2006; Khettabi *et al.*, 2010).

Deposition of particles in the human lung can occur as a result of inertial impaction, diffusion, gravitational settling, electrostatics and interception (Scheckman and McMurry, 2011). Particle size distribution shifts and a change in the shape of particles (through the formation of clusters) can occur when particulate matter coagulates (Tsuda *et al.*, 2013).

Three main areas or regions of the respiratory tract have been distinguished for classification, specifically useful for determining particle size deposition locations. These include the head, the tracheobronchial regions and the gas exchange region. Size, structure and function are the basis for these classified regions (Brown *et al.*, 2013). The inhalable size fraction is that particle size that has an aerodynamic diameter (the diameter of a unit density microsphere that settles with the same terminal velocity as the particle in question) of less than 100 μm and is usually trapped in the throat and nose. These particles usually do not enter the deeper parts of the lung due to their larger sizes (Ivester *et al.*, 2014; Brown *et al.*, 2013). During inhalation, certain particle sizes can pass further than the larynx and respiratory airways/pathways that are ciliated. These particle size fractions include the thoracic size fraction and the respiratory size fraction. The thoracic size fraction, which includes those particles that pass further than the larynx and can deposit anywhere in the airways of the lung or in the deeper regions of the lung, such as the gas exchange region. These particles have an aerodynamic diameter of less than 10 μm which thus includes the respirable and UFP size fractions (Capstick and Clifton, 2012; Brown *et al.*, 2013).

The respirable size fraction, those particles that have an aerodynamic diameter of less than 4 µm, and can be deposited in the deepest areas of the lung, such as the gas exchange region, could allow for deposition into the alveoli (Capstick and Clifton, 2012; Brown *et al.*, 2013). These respirable particles are considered the most dangerous due to their slow clearance rate and their small sizes relative to other particles of the same chemical composition, allowing them to penetrate the deepest regions of the lung which results in a more significant reaction to clear these particles (CCOHS, 2012).

2.4 Deposition of airborne particulates in the respiratory tract

The respiratory tract is continuously exposed to about 10 000 – 20 000 litres of ambient air daily due to its large surface area (Schlesinger, 1988). Particle sizes have been categorised and defined by the occupational health community based on their biological region of deposition in the respiratory tract. These particle sizes can be classified as inhalable, thoracic and respirable size fractions based on the diameter of each particle (Brown *et al.*, 1950; Miller *et al.*, 2012). There is much variation in the physiological characteristics between individuals, such as their lung anatomy and capacity, differences in lifestyle as well as genetic variance (Kuempel *et al.*, 2001; Sleeth, 2013). These differences play a significant role in the deposition of particles in the respiratory system, the retention of these particles as well as the respiratory systems' ability for clearance (Kuempel *et al.*, 2001; Oberdörster *et al.*, 2013). Particle size, shape, chemical composition and physiological characteristics are the key determinants for the depth/site of deposition at which these particles will settle in the lungs (McClellan, 2002; Heyder, 2004; Maynard and Kuempel, 2005; Trakumas and Salter, 2009; Oberdörster *et al.*, 2013). Deposition of particles in the respiratory system occurs when the particles encounter any airway surface (Thomas *et al.*, 2008; Méndez *et al.*, 2010).

Inhalation of particles through the nose and/or mouth is the main route of human exposure to particles (Vincent, 2007).

The respiratory tract can be divided into three main compartments based on structure, size and function namely: the nasopharyngeal region (the head), which includes the area from the nose/mouth to larynx, the tracheobronchial region (also known as the conducting airways) which includes the area from the larynx to the terminal bronchioles and the alveolar region (the gas exchange region) which includes the area from the respiratory bronchioles to the alveolar ducts as indicated in Figure 2.1 (Vincent, 2007; Brown *et al.*, 2013; Oberdörster *et al.*, 2013; Fröhlich and Salar-Behzadi, 2014).

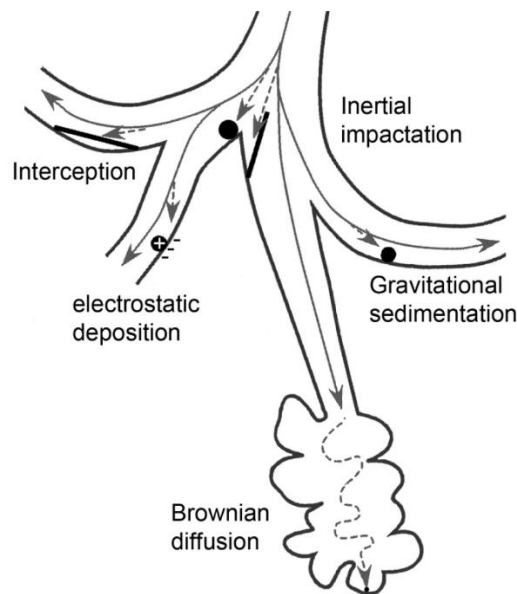


Figure 2.1: Particle size considerations vital for deposition in the whole lung (Fröhlich and Salar-Behzadi, 2014).

Inhalation occurs through the nose or mouth and thus, initially, the particles reach the nasopharyngeal region (Vincent, 2007). Inertial impaction (the deposition of large particles on airway surfaces where the airway direction changes) and gravitational sedimentation (settling of particles due to gravity) are the main means of deposition for larger particles that get trapped/settle in the nose and throat (Heyder, 2004; Oberdörster *et al.*, 2005; Martin and Finlay, 2006; Vincent, 2007; Yang *et al.*, 2008). Diffusion (the dispersion over a surface due to random Brownian movements which causes relocation of particulate matter from the airstream to the surface of the respiratory tract) and electrostatic forces (the attraction or the repelling of particles due to their electric charges) are the main means of deposition of smaller particles as depicted in Figure 2.1 (Heyder, 2004; Vincent, 2007; Carvalho *et al.*, 2011; Fröhlich and Salar-Behzadi, 2014; Schröder, 2014).

Inertial impaction is often a property of larger particles while gravitational sedimentation and diffusion is what allows smaller particles to deposit in the alveoli. Charged particles often undergo electrostatic deposition (Fröhlich and Salar-Behzadi, 2014). Due to forces that act upon particles in the lung through their carriage with the tidal air (normal, resting breathing), particle trajectories are often not the same as the air stream lines. Sedimentation, impaction, and diffusion are how particles are shifted off torrent lines and transported toward the surfaces of the respiratory tract. Gravity, inertia, and impulse transfer from collisions with gas molecules are the most important mechanical forces acting on particles in the respiratory airways (Heyder, 2002; Ricard, 2003).

As previously mentioned, certain particle sizes can pass further than the larynx and respiratory airways/pathways that are ciliated. These particle size fractions include the thoracic size fraction and the respiratory size fraction. The thoracic size fraction, which includes those particles that pass further than the larynx and can deposit anywhere in the airways of the lung or in deeper regions of the lung, such as the gas exchange region. The respirable fraction of particles penetrates to the alveolar region of the lungs as depicted in Figure 2.2 (Wilson *et al.*, 2002; Patton and Byron, 2007; Pickford and Davies, 2007; Capstick and Clifton, 2012).

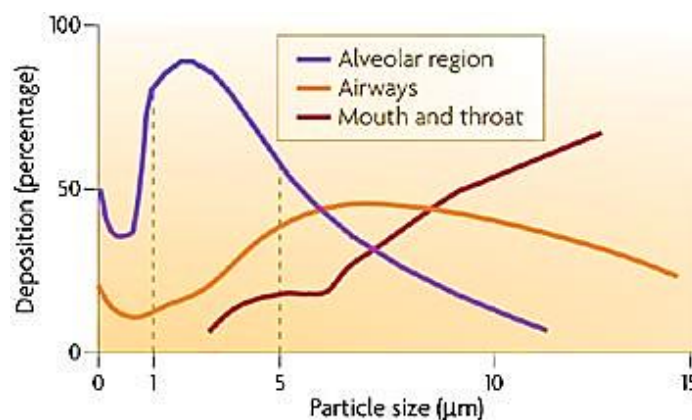


Figure 2.2: The consequence of the size of particles on the sedimentation of aerosol particles in the respiratory tract (Patton and Byron, 2007).

Larger particles deposit in the airways or mouth and throat, whereas smaller particles deposit in the alveolar region. Particles $<1 \mu\text{m}$ are very light and can thus be exhaled due to their low inertia, thereby reducing deep-lung deposition (Patton and Byron, 2007; Yang *et al.*, 2008).

2.5 Respiratory defence mechanisms (clearance)

Different lung clearance mechanisms are available to defend the respiratory system and keep airways surfaces free from inhaled particles. These mechanisms, however, have some limitations (McClellan, 2002; Maynard and Kuempel, 2005; Oberdörster *et al.*, 2005). Each site of deposition in the respiratory system has a specific method of clearance (Méndez *et al.*, 2010).

An inhaled particle that enters the nose or mouth (upper respiratory tract) is cleared through blowing of the nose or through coughing (involves respiratory muscular effort). The coughing mechanism occurs through particles being trapped on a mucus layer that is secreted by cells in the airways. This mucosal layer covers tiny, muscular, hair-like projections known as cilia that project out of the epithelial layer of the upper respiratory tract and the cilia move the mucus layer

at about 0.5 to 1 cm per minute. The particles that are trapped in the liquid mucus are coughed out and/or moved upward to the larynx and the mouth, and swallowed into the gastrointestinal (GI) tract (mucociliary escalator). Particles that bypass this ciliated system and enter into the lungs are not deposited in the nasopharyngeal region (McClellan, 2002; Vincent, 2007). Clearance of deposited particles in the tracheobronchial region of the lungs is also achieved through this mucociliary escalator by the same trapping of particles in the mucus (Eschenbacher *et al.*, 2000; Pickford and Davies, 2007).

Alveoli are, however, not protected by mucus and cilia due to gas exchange requirements. The mucus is thick and is thus a hindrance to the movement of oxygen and carbon dioxide (Lechtzin, 2016). The alveoli, therefore, make use of another, much slower, defence mechanism that utilises phagocytic macrophages on the alveolar surface. Macrophages are scavenger cells that kill particles (dust or microorganisms) through digestion (Kelly, 2002; Oberdörster *et al.*, 2005; Vincent, 2007). These particles (usually respirable) are then carried upwards to the mucociliary escalator, by the moving cilia, into the tracheobronchial region and eventually swallowed (Maynard and Kuempel, 2005; Oberdörster *et al.*, 2005; Vincent, 2007). The efficiency of this mechanism is greatly dependent on the ability of the macrophages to detect the settled particles and there is also a possible risk of pulmonary inflammation if the phagocytosed particles persist in the alveoli resulting in lysis of the macrophages (Kuempel *et al.*, 2001; Oberdörster *et al.*, 2005; Vincent, 2007).

2.6 Health effects associated with particulate matter (PNOC and silica dust - crystalline/amorphous)

According to the British Standard Institute, dust is an overarching and colloquial term for suspensions of fine particles in the atmosphere that are often smaller than 75 µm in diameter. These small solid particles either remain suspended in the atmosphere for some time or they settle out due to their own weight (BSI, 1994; Petavratzi *et al.*, 2005).

The region in the human respiratory tract where particles deposit will determine the pathogenic potential of inhaled particulate matter (Asgharian, 2001). Acute respiratory health effects (instantaneous pathogenesis such as irritation) or chronic respiratory health effects (development over years such as chronic bronchitis) may occur due to the deposition of particulate matter in the respiratory system (Balásházy *et al.*, 2003; OSHA, 2010). According to OSHA, some particulate matter, including crystalline silica, can be classified as a respiratory sensitiser (a chemical or particulate matter causing an allergic reaction due to repeated respiratory or skin exposure and may lead to an exacerbation of symptoms such as asthma, chronic obstructive pulmonary disease and rhinitis) (OSHA, 2015). Irritation, inflammation and damage to the lungs are also a possibility,

causing obstructive changes in pulmonary function as well as chronic bronchitis which may result in chronic emphysema. It may also cause pneumoconiosis and lung cancer (mainly caused by respirable particles) (Kim and Hu, 2006; IARC, 2007; Zhang *et al.*, 2010; Brown *et al.*, 2013).

It is a well-known fact that exposure to crystalline silica dust in foundry workers carries a high risk for silicosis (fibrosis of the lungs caused by the inhalation of dust containing crystalline silica). This was indicated in a 29-year cohort study published by Zhang *et al.* (2010) which pointed to a significant proportion of foundry workers, who were exposed to crystalline silica dust, and their development of silicosis. (Zhang *et al.*, 2010; DOL, 2011). Sandblasting and sand-casting foundry procedures are processes that are historically associated with elevated incidences of silicosis (OSHA, 2002).

Most adverse health effects attributed to amorphous silica are due to its combined presence with crystalline silica. The inhalation of synthetically produced amorphous silica has only indicated health effects such as inflammation that is partially reversible, emphysema and granuloma formation but no fibrosis formation in the lung tissue. Data is, however, limited, therefore, chronic obstructive pulmonary disease (COPD), emphysema or chronic bronchitis cannot be ruled out (Merget *et al.*, 2002).

Airborne particulate matter, particularly generated dust (dust produced through mechanical processes) or nuisance dust may lead to various health effects which are not limited to the respiratory tract only. Working in close proximity to processes that release particles may lead to exposure of the eyes, skin and respiratory tract of workers and this could cause damage to the skin (dermatitis), eyes, nose and throat (Petavratzi *et al.*, 2005).

Exposure limits have been determined for particles not otherwise classified or regulated (PNOC/R). This is due to the evolution of mass sampling technology and its ability to determine the respirable dust concentrations of all nuisance dust (coarse particles that reduce visibility or cause irritation). Nuisance dust includes PNOC / dust concentrations containing less than 5 % crystalline silica and do not lead to the development of disabling lung disease (Hearl, 1998).

2.7 Inhalation of hazardous vapours

The lungs and airways are continuously exposed to non-toxic, or irritant and toxic gases or vapours through inhalation. Exposures to oxidising, electrophilic, acidic, or basic gases/vapours recurrently transpire in occupational and ambient environments. Toxic properties of hazardous vapours can induce either acute or chronic adverse effects on the human body through inhalation. These effects are carried out through actions in the tissue outside the lungs, or through preventing oxygen from reaching the alveolar region of the lungs either individually or through synergistic

means (Krotoszynski *et al.*, 1979; Patnaik, 2007; Bessac and Jordt, 2010). These effects extend over to include mutagenicity, carcinogenicity, teratogenicity (reproductive and developmental effects), corrosivity and irritation (Bessac and Jordt, 2010).

Receptor systems in the respiratory tract detect chemicals present in the airways which usually induce a protective behavioural and physiological response. These responses include conscious, autonomic, involuntary or inflammatory reactions (Taylor-Clark and Undem, 2006). At only trace levels, some of these hazardous vapours are detectable through slight smell, while others are pungent and can induce irritant reactions such as coughing, sneezing, tearing and upper respiratory inflammation. Irritant vapours inside an inflammatory response through dissolving in the respiratory tract mucosa (Pisi *et al.*, 2009; Bessac and Jordt, 2010).

Individuals who suffer from pre-existing conditions such as asthma are known to be more at risk for subsequent attacks if exposed to some hazardous vapours allowing for further development of bronchitis, reactive airway dysfunction syndrome and other chronic airway diseases (Nowak, 2002; Francis *et al.*, 2007; Springer *et al.*, 2007).

2.7.1 Volatile organic compounds (VOC's)

VOC's are found in many man-made chemicals throughout industry and are classified as high vapour pressure, low water solubility compounds. The Environmental Protection Agency (EPA) has defined VOC's as "Any organic compound that participates in atmospheric photochemical reactions except those designated by the EPA as having negligible photochemical reactivity." (Owens, 2009; EPA, 2016). VOC's that are commonly present in industry include carbonyl compounds such as benzene, toluene, ethyl benzene, and xylenes (BTEX), styrene, naphthalene and chlorobenzene which can be released directly into the air that workers breathe (Duarte *et al.*, 2014).

2.7.2 Health effects associated with VOC's

Exposure to these VOC's can be through inhalation, ingestion, and skin contact. Due to the extensive list of harmful substances compiled by the EPA, the level of toxicity that VOC's present is evident (EPA, 2016). "Sick building syndrome" (SBS) and "building related illness" (BRI) are both wholly related to VOC's and affect a large working populace (Owens, 2009).

Health effects associated with VOC's range from carcinogenic effects, e.g. benzene, (EPA, 2006; Duarte *et al.*, 2014) to non-carcinogenic effects such as respiratory dysfunction, nervous system dysfunction (central nervous system depressants), kidney disease, cardiovascular disease and asthma with symptoms ranging from euphoria to headache, eye irritation, nose and throat uneasiness, vertigo, sensitised allergic skin reactions, biliousness, and dizziness; while pregnant

women are at high risk due to effects on the unborn foetus. These effects include low birth weight and reduced foetal growth (Hinwood *et al.*, 2007; Duarte *et al.*, 2014; Tibbetts, 2015; TOXNET).

2.7.3 Polycyclic aromatic hydrocarbons (PAH's)

PAH's are a large group of organic compounds consisting of two or more fused benzene rings arranged in many different configurations and are known for their potentially carcinogenic/mutagenic effects. These molecules are mostly associated with incomplete combustion of fossil fuels and produced in a variety of industrial processes (Dzombak and Luthy, 1984; Vo-Dinh, 1990; Sluzny, 1998; Unwen *et al.*, 2006; Ki-Hyun Kim *et al.*, 2013). They are major persistent organic pollutants, and are widely found in various environmental substances such as air, sediments and soils with many studies published on the content of PAH's in sediments (Mastrangelo *et al.*, 1996; Wang *et al.*, 2012).

Most PAHs are released into the atmosphere from pyrogenic sources and are regularly reallocated between gas and particle phases because of their chemical and physical properties (Vardar and Noll, 2003; Wang *et al.*, 2016). As a result of their low vapour pressure and aqueous solubility, most PAH's are inclined to get absorbed/incorporated into particles (such as soils, sediments, and dust) instead of remaining in their gaseous phase. This is particularly true with the more harmful, high molecular weight PAH's (HAPAHs, generally PAH's with >4 benzene rings). This is because of a dependence on the physiochemical properties (such as the finer particles) of the PAH's for the region of their deposition in the lungs. The higher the molecular weight and the finer the particles, the deeper the penetration into the lungs (Yu *et al.*, 2015; Wang *et al.*, 2016). Dust and soil containing silica can thus potentially contain accumulated PAH's, and is, therefore, an important consideration regarding human health in the AM processes of sand mould production. (Kang *et al.*, 2010; Wang *et al.*, 2016).

Exposure to PAH's occur through water, air, soil and food for most people (ACGIH, 2005; Chen and Liao, 2005; ATSDR, 2009; Yu *et al.*, 2015). The main exposure routes to occupational and non-occupational PAH's has been assumed to be inhalation, ingestion and dermal exposure and some exposures may involve more than one route at the same time (Venkataraman and Raymond, 1998; Tsai *et al.*, 2001; Chen and Liao, 2005; ATSDR, 2009; Ruby *et al.*, 2016).

2.7.4 Health effects associated with PAH's

The main route of exposure for PAH's is through inhalation, however, exposure to PAH's is never to one single type, but exposure to many in a mixture, aiding in their toxicity profile. The most serious toxic effect of PAH's lies in that these compounds are termed complete carcinogens (a substance capable of triggering changes in cells at all three stages of tumour progression) (Kent, 1998). There are, however, other toxic effects such as immuno-toxicity, skin/eye irritation and

developmental toxicity such as involvement of the gastrointestinal, pulmonary, dermatological and renal systems (Flowers *et al.*, 2002; Chen and Liao, 2005; Carex, 2015). The carcinogenic potential of these compounds is shown in their association with skin, lung and bladder cancer in occupational settings (Boffetta *et al.*, 1997; Armstrong *et al.*, 2004; ATSDR, 2009). In terms of developmental toxicity, many studies have also indicated that PAH's have been associated with reproductive outcomes, DNA adduct formation in new-borns as well as premature birth and intrauterine growth constraints (Perera *et al.*, 2002; Somers *et al.*, 2002, 2004; Chen and Liao, 2005).

The IARC has classified individual PAH species in groups 1 (Carcinogenic to humans), 2A (Probably carcinogenic to humans), 2B (Possibly carcinogenic to humans) and 3 (Not classifiable regarding carcinogenicity to humans) based on the carcinogenicity of the various types in human and animal studies (Friesen, 2003; IARC, 2010; 2011). The EPA of the United States has listed 16 individual PAHs as priority pollutants (Sun, *et al.*, 1998).

Table 1: Carcinogenic classification of selected PAHs by specific agencies (Kim *et al.*, 2013).

Order	Agency	PAH compound(s)	Classification group
1	Agency for Toxic Substances and Disease Registry (ATSDR)	Benz(a)anthracene Benzo(b)fluoranthene, Benzo(a)pyrene, Dibenz(a,h) anthracene, Indeno(1,2,3-c,d)pyrene Benz(a)anthracene	Known animal carcinogen Probably carcinogenic to humans
2	International Agency for Research on Cancer (IARC)	Benzo(a)fluoranthene, Benzo(k)fluoranthene and Indeno(1,2,3-c,d)pyrene Anthracene, Benzo(g,h,i)perylene, Benzo(e)pyrene, Chrysene, Fluoranthene, Fluorene, Naphthalene Phenanthrene, and Pyrene Benzo(a)pyrene	Not classifiable as to their carcinogenicity to humans Carcinogenic to humans
3	U.S. Environmental Protection Agency (EPA)	Benz(a)anthracene, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Chrysene, Dibenz(a,h)anthracene, and Indeno(1,2,3-c,d)pyrene. Acenaphthylene, Anthracene, Benzo(g,h,i)perylene,	Probable human carcinogens Not classifiable as to human carcinogenicity

Furthermost, exposures to PAH's and VOC's often occur in intricate mixtures of multiple components, all with varying toxicity profiles and carcinogenic potency. As potency can be influenced based on bioavailability, carcinogenic action, metabolism and rivalry for binding sites; uncertainty remains in the valuations of certain PAH mixtures. These mixtures have been associated with cancer, DNA strand impairment and respiratory illness, amongst others, and the risks of exposure to these mixtures are difficult to estimate due to the multiplexity of the mixtures and each individual compound working additively or synergistically with one another (Petry *et al.*, 1996; Jarvis *et al.*, 2014). Concern can thus be induced in terms of combinations of total aliphatic and aromatic hydrocarbons. In terms of mixtures of hydrocarbon solvents, specifically aliphatic hydrocarbons, these mixtures can be complex and can differ quite pointedly in composition. Hydrocarbons are often described as naphthenic, aromatic or aliphatic but may comprise of a host of these products collectively, which lead us to consider additivity critically. The main additive toxicological effect of the constituents of hydrocarbons solvents is acute central nervous system (CNS) depression (McKee *et al.*, 2005).

2.8 Occupational Exposure Limits

Occupational exposure limits (OEL's)/threshold limit values (TLV's) have been designed and then designated to many hazardous or toxic products due to evident adverse effects present in human health from toxic substances. This has been done to protect workers from exposure to these toxic/hazardous substances by providing a maximum concentration value of air contaminants to which an unprotected employee may be exposed. These OEL's have been defined through exposure times during normal work activities. These times include: a long-term exposure limit calculated as an 8-hour time weighted average (TWA) and a short-term exposure limit (STEL) a shorter period of time allowing a maximum concentration measurement (usually 15 min for measurement of task-based exposure) (Duarte *et al.*, 2014; ACGIH, 2016).

A few OEL's have been set in South African legislation for the various compounds whose possible presence in AM technologies pose a risk to human health such as:

Silica - the current time weighted average occupational exposure limit - control limit (TWA OEL-CL) in South Africa for respirable crystalline silica is 0.1 mg/m³ (HCSR, 1995). This South African limit is higher in comparison to other countries such as Finland and the Netherlands with 0.05 mg/m³ and 0.075 mg/m³ respectively (IMA-Europe, 2014) as well as the recent change by OSHA for the American standard (which took effect on June 23rd, 2016), where the permissible exposure limit (PEL) was reduced to 0.05 mg/m³ over an 8-hour shift (HCSR, 1995; OSHA, 2016). The amorphous silica, TWA OEL-RL is 6 mg/m³ for total inhalable dust not containing any crystalline silica and 3 mg/m³ for total respirable dust (HCSR, 1995).

For VOC's, the South African TWA OEL-RL (recommended limit) for toluene is 180 mg/m³, for ethylbenzene and xylene both at 435 mg/m³ (HCSR, 1995). Table 2 has a list of regulations for these, and other common VOC's, set by other international occupational health agencies.

Table 2: Exposure limits for common VOC's set by three different occupational health agencies (OSHA, 1993; HCSR, 1995; EU-OSHA, 2004, 2007; NIOSH, 2007; Duarte, 2014)

VOC's (mg/m ³)	HCSR		NIOSH		OSHA		EU-OSHA	
	TWA	STEL	TWA	STEL	TWA	STEL	TWA	STEL
Benzene	16	-	0.319	3.19	3.19	15.95	3.25	12.8
Ethyl benzene	435	545	435	545	435	-	442	884
Styrene	420	1050	215	425	425	852*	-	-
Toluene	188	560	375	560	754	1131*	192	384
Xylenes	435	650	435	655	435	-	221	442

*Ceiling values; TWA, 8-h limit value; STEL., Short-term limit value (15 min); BTEX - benzene, toluene, ethylbenzene, and xylenes

While South African legislation does not provide for OELs for individual PAH's, the National Institute for Occupational Safety and Health (NIOSH), the Occupational Safety and Health Administration (OSHA) and the American Conference of Governmental Industrial Hygienists (ACGIH) do have regulations concerning some PAH's (Van Niekerk *et al.*, 2002). This list can be seen in Table 3.

The exposure limits for PAH's has been regulated under OSHA Air Contaminants Standard for substances termed coal tar pitch volatiles (CTPVs) and coke oven emissions (Buha, 2011). The exposure limit set for PAH's (benzene soluble fraction) by OSHA in the workplace for 8-hour TWA-PEL (time weighted average - permissible exposure level) is 0.15 mg/m³ for coke oven emissions in 1978 (OSHA, 1978; Van Niekerk *et al.*, 2002). NIOSH has recommended that the workplace exposure limit for PAH's be set at the lowest detectable concentration, which is 0.1 mg/m³ recommended exposure limit (REL) for CTPV agents for an 8-hour workday (NIOSH, 2007).

Table 3: PAH exposure limits from various agencies (NIOSH, 1977; OSHA, 1978; NIOSH, 1994; ACGIH, 2016).

PAH	OSHA	NIOSH	ACGIH
Acenaphthene	-	-	-
Acenaphthylene	-	-	-
Anthracene	0.2 mg/m ³	-	-
Benz[a]anthracene	-	-	-
Benzo[b]fluoranthene	-	-	-
Benzo[k]fluoranthene	-	-	-
Benzo[g,h,i]perylene	-	-	-
Benzo[a]pyrene	0.2 mg/m ³	0.1 mg/m ³	-
Benzo[e]pyrene	-	-	-
Chrysene	0.2 mg/m ³	-	-
Dibenz[a,h]anthracene	-	-	-
Fluoranthene	-	-	-
Fluorine	-	-	-
Indeno[1,2,3-cd]pyrene	-	-	-
Naphthalene	50 mg/m ³	50 mg/m ³	52 mg/m ³
Phenanthrene	0.2 mg/m ³	-	-
Pyrene	-	-	-

2.9 Conclusion

Clearly, a whole host of possible health effects could be present during the processes of AM, attributable to the substances used and the possible effect that temperature may have on them. Due to the lack of information pertaining to the health effects of the powdered substances used in AM, it is crucial that a study be conducted. This study could determine whether AM operators are exposed to these substances in concentrations exceeding those stipulated in South African Occupational Health and Safety legislation and whether adequate, or more stringent, safety measures should be implemented.

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CHAPTER 3: ARTICLE

Instructions to authors

Rapid Prototyping Journal is the world's leading journal covering additive manufacturing (AM) and related technologies. The journal concentrates on development in a manufacturing environment but covers applications in other areas, such as medicine and construction. All papers published in this field are scattered over a wide range of international publications, none of which specialises in this discipline.

Title, article and format: A title of not more than eight words should be provided. Articles should be between 2000 and 4000 words in length. This includes all text including references and appendices. Please allow 280 words for each figure or table. Article files should be provided in Microsoft Word format. LaTeX files can be used if an accompanying PDF document is provided. PDF as a sole file type is not accepted, a PDF must be accompanied by the source file. Acceptable figure file types are listed further below.

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Maximum is 250 words in total (including keywords and article classification, see below). Authors should avoid the use of personal pronouns within the structured abstract and body of the paper (e.g. "this paper investigates..." is correct, "I investigate..." is incorrect).

Research funding: Authors must declare all sources of external research funding in their article and a statement to this effect should appear in the Acknowledgements section. Authors should

describe the role of the funder or financial sponsor in the entire research process, from study design to submission.

Headings: Headings must be concise, with a clear indication of the distinction between the hierarchies of headings. The preferred format is for first level headings to be presented in bold format and subsequent sub-headings to be presented in medium italics.

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Tables: Tables should be typed and included in a separate file to the main body of the article. The position of each table should be clearly labelled in the body text of article with corresponding labels being clearly shown in the separate file. Ensure that any superscripts or asterisks are shown next to the relevant items and have corresponding explanations displayed as footnotes to the table, figure or plate.

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Examples:

For books: Harrow, R. (2005), *No Place to Hide*, Simon & Schuster, New York, NY.

For book chapters: Calabrese, F.A. (2005), "The early pathways: theory to practice – a continuum", in Stankosky, M. (Ed.), *Creating the Discipline of Knowledge Management*, Elsevier, New York, NY, pp. 15-20.

For journals: Capizzi, M.T. and Ferguson, R. (2005), "Loyalty trends for the twenty-first century", *Journal of Consumer Marketing*, Vol. 22 No. 2, pp. 72-80.

For published conference proceedings: Jakkilinki, R., Georgievski, M. and Sharda, N. (2007), "Connecting destinations with an ontology-based e-tourism planner", in *Information and communication technologies in tourism 2007 proceedings of the international conference in Ljubljana, Slovenia, 2007*, Springer-Verlag, Vienna, pp. 12-32.

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For archival or other unpublished sources: Litman, S. (1902), "Mechanism & Technique of Commerce", Unpublished Manuscript, Simon Litman Papers, Record series 9/5/29 Box 3, University of Illinois Archives, Urbana-Champaign, IL.

Note to the reader: Chapter 3 is written in article format. Tables and Figures are included in this section to present the findings of this study in a comprehensive format. The length of the article exceeds 4000 words. Elaboration was necessary for examination purposes but the word count will be reduced prior to submission to the journal. The title length exceeds the eight-word limitation, however, many other articles submitted to the *Rapid Prototyping Journal* has been published with titles longer than eight words.

Respiratory exposure during the additive manufacturing of sand casting moulds

GRACE EM ADAMS, STEPHANUS JL LINDE, SONETTE DU PREEZ, JOHANNES L DU
PLESSIS

Occupational Hygiene and Health Research Initiative (OHHRI), North-West University
Potchefstroom Campus, South Africa.

Corresponding author:

Prof Johan du Plessis

Occupational Hygiene and Health Research Initiative (OHHRI)

North-West University

Potchefstroom

2520

South Africa

Tel. +27 18 299 2436

Fax. +27 87 230 1925

E-mail: Johan.duPlessis@nwu.ac.za

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Keywords: Silica, particle size fractions, occupational exposure, polycyclic aromatic hydrocarbons, volatile organic compounds, health effects

Abstract

Purpose: During additive manufacturing (AM) of sand casting moulds, dust species of unknown particle size and mineral composition, as well as other hazardous chemical substances (HCS's) are potentially liberated/released. The occupational respiratory exposure of AM operators, at two research facilities, to HCS's was assessed. **Methodology:** Physicochemical characterisation of sand particles through particle size distribution (PSD) analysis, scanning electron microscopy (SEM) analysis and X-Ray diffraction (XRD) was conducted to determine particle sizes and their mineral composition. Static and personal respiratory exposure monitoring was conducted on AM operators to determine concentration levels of particles not otherwise classified (PNOC), silica, polycyclic aromatic hydrocarbons (PAH's) and volatile organic compounds (VOC's) for comparison with legislation. **Findings:** Mean particle sizes of sand at both facilities were above the inhalable size fraction ($>100\ \mu\text{m}$) which was supported by SEM imaging, however, particles $< 100\ \mu\text{m}$ were also detected at one facility. Mullite and quartz were major composites of the sand. The time-weighted average (TWA) respirable silica (quartz) exposure of the AM operators was between 0.03 and $0.06\ \text{mg}/\text{m}^3$. PAH exposure was limited to naphthalene but at concentrations $< 0.001\ \text{mg}/\text{m}^3$. Exposure to seven VOC's (acetone, pentane, hexane, benzene, toluene, cyclohexane and naphthas) occurred, but at very low concentrations. **Originality/Value:** This is the first study of its kind to assess the physicochemical characteristics and the respiratory exposure of AM operators to HCS's during the AM of sand casting moulds.

Introduction

Additive manufacturing (AM) is an innovative technology, now booming in industry for its ability to produce three-dimensional objects by printing them from 3D model data (Manfredi *et al.*, 2014) and has officially been defined as the “process of joining materials to make objects from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing methodologies.” One of the many uses that AM has been called on for is the production of sand casting moulds for metal parts (Radis, 2015).

Health and safety risks that arise for the operational workforce in AM are a concern because of the lack of independent studies available (Klein, 2015). As a relatively new branch of science and engineering, there is, at present, minimal local or international technical and scientific data available regarding the health risks associated with AM. These processes include the pre-process (refilling the AM printer, in preparation for a build, with sand/sieving the sand), process (building process of a new sand casting mould) and post-process (removal of the completed build product, cleaning of the machinery, baking of the mould) of AM. Some of the processes in AM technologies have overarching similarities to sand casting foundries. These include the presence of heat, exposure to dust/powdered sand as well as exposure to resins/binding agents. Therefore,

some of the processes in sand casting foundries can be examined and extrapolated to determine potential occupational exposures due to this limitation in the amount of information available with regards to the health effects of sand mould production using AM techniques (IARC, 2011).

Materials used to create sand casting moulds are a mixture of foundry sand (usually containing crystalline silica), plaster and resin binders that have been combined to provide strong moulds with a suitable surface finish. It is fabricated to withstand the heat necessary to cast non-ferrous metals (ZCorp, 2007). Various types of sand materials are used as the “ink” in the printer, usually present in powder form, and thus pose a potential for respiratory exposure risk to the operator (OSHA, 2002; Rao, 2003; Kruth *et al.*, 2004; Viridis3D, 2011). The use of crystalline silica is common in sand casting foundries with many studies revealing the exposure of workers to this form of silica (OSHA, 2002; Scholz *et al.*, 2007; Derbyshire, 2012). Respiratory exposure to crystalline silica can cause silicosis and it has been classified as a Class 1 human carcinogen by the International Agency for Research on Cancer (IARC) (IARC, 1997; NIOSH, 2002).

Some AM techniques used in the production of sand casting moulds operate through lasers, which produce heat (Beaman *et al.*, 1994). In a study conducted by Zihms *et al.* (2013), the effect that high temperature processes have on silica sand and the potential risks or hazards these changes produce, was assessed and included alterations in the mineralogy of the sand, grain fracturing resulting in smaller particle sizes, as well as instability in the silicon dioxide resulting in the formation of silica polymorphs such as cristobalite and tridymite, two forms of silica that are also crystalline in structure (ATS, 1996; Zihms *et al.*, 2013).

Polycyclic Aromatic Hydrocarbons (PAH's) (a mixture of chemicals produced during the incomplete combustion of fuels) are also likely to be found in sand or soil matrices as microscopic crystallites (Sluszný, 1998). Silica sand is a good adsorbent of PAH's and can thus be contaminated with them. A study conducted by Smol *et al.* (2014) tested the adsorption of six carcinogenic PAH's to quartz sand and the subsequent removal thereof through desorption in the presence of heat (Holtzer *et al.*, 2014).

Kubecki *et al.* (2013) investigated the influence of temperature on volatile organic compound (VOC) formation from furan resins. Toluene, ethylbenzene and xylenes were of the vapours formed in high concentrations during pouring of the molten metal into the sand cast (Kubecki *et al.*, 2013).

While there are various diseases such as fibrotic lung disease, respiratory dysfunction and nervous system dysfunction associated with known products used in AM of sand casting mould production, such as crystalline silica, liquid bonding agents and resins (ZCorp., 2007; Viridis3D, 2011; Duarte *et al.*, 2014); it is unknown whether or what other hazardous chemical substances

(HCS's) might be present/released because of the effects of AM processes on these known raw materials. These include the possible release of certain PAH's and VOC's (Kubecki *et al.*, 2013; Stephens *et al.*, 2013; Holtzer *et al.*, 2014; Biache *et al.*, 2015). Health effects associated with silica, PAH's and VOC's include, but are not limited to, silicosis, respiratory dysfunction, granuloma formation, neurological and reproductive effects, cancer and renal failure; just to name a few (ATS, 1996; Hinwood *et al.*, 2007; Tibbetts, 2015).

As very little information exists pertaining to the physicochemical characteristics of the sand used in AM of sand casting moulds, as well as a lack of information concerning the effects that the processing in AM has on each ingredient of the sand mixtures used in the processes; possible concerns arise from the potential effect that each individual ingredient may have on the health of AM operators. This study, therefore, aimed to assess the physicochemical characteristics of the sand and the occupational respiratory exposure of AM operators to HCS's (such as crystalline silica, VOC's and PAH's) present during the pre-processing, processing and post-processing phases of the AM of sand moulds.

Methodology

Sites and subjects

Two AM facilities in South Africa utilising powder bed fusion (Facility A) and binder jetting (Facility B) were included in this study. Facility A had one AM operator (n=1), and Facility B had two (n=2). At both facilities, AM was conducted in an enclosed room without ventilation (natural or mechanical) on the machine itself or inside the room.

Ethical considerations

This study was approved by the Health Research Ethics Committee (HREC) of the North-West University (NWU-00056-16-A1).

Physicochemical characterisation of particles

Bulk samples of the raw and used material (new, used and mixed sand) were taken at the pre-processing and post-processing phases and collected into sample storage vials for analysis. Particle size distribution (PSD) analysis, scanning electron microscopy (SEM) and X-Ray diffraction (XRD) analysis was conducted to determine the particle sizes and the mineral composition (in particular, crystalline silica) present.

PSD analysis was conducted using a Malvern Mastersizer 2000 particle size analyser (Malvern Instruments Ltd., United Kingdom). Results were obtained with software for the Mastersizer 2000 version 5.31. The sand samples were analysed individually by mixing each with a dispersing agent (1 ml of 99.9% purity ethanol). Prior to every measurement, background measurements

were taken. After completion of the background measurement, a sufficient quantity of the raw material was added to render an obscuration of 10-20%, where after, the particle size measurement was made. Samples were analysed in triplicate.

SEM analysis was conducted by preparing the specimens for observation of their surface morphology by coating using an SPI Module sputter coater (SPI-Module™. Sputter Coater, SPI Supplies, West Chester, PA, USA) fitted with a gold palladium source, and specimens were then studied using a Phenom pro-desktop SEM (Phenom PRO Desktop SEM, Phenom-World B., Eindhoven, Netherlands) at a power of 5 kV.

XRD analysis was also conducted on the sand samples to determine their mineral composition. This was performed using a powder diffractometer (X'Pert Pro XRD, PANalytical, Almelo, Netherlands). The preparation method involved finely pulverising the material and placing the undiluted powder samples, using a back-loading technique, onto a spinner stage inside the XRD. The samples were then scanned using X-rays generated by a Cu X-Ray tube (PW3376/00 Co LFF tube, PANalytical, Almelo, Netherlands).

Respiratory exposure monitoring

Personal exposure monitoring was carried out on each operator working with the AM technology in sand casting. This sampling approach was used to determine the exposure to crystalline silica, dust (PNOC – particles not otherwise classified), PAHs and VOC's. Static area monitoring (an alternative to personal exposure monitoring) was performed in the vicinity of the workstations, where the highest potential release of HCS's for all three phases of processing was anticipated, and was placed at closest proximity to the breathing zone of the AM operator (1.5 m from the floor). Both the static and personal samples were collected for the duration of each process. The detection limits for silica was 0.005 mg/sample and 0.003 mg/sample for PNOC.

Exposure monitoring and laboratory analysis for each specific HCS was carried out according to the standardised methodologies indicated by the National Institute for Occupational Safety and Health (NIOSH) Manual of Analytical Methods (NMAM, 2016) and Occupational Health and Safety Administration (OSHA) methods, and analysed by a SANAS (South African National Accreditation System) accredited laboratory. No PAH exposure monitoring was conducted at Facility B or during the pre-processing phase at Facility A, due to the absence of heat. A summary of the exposure monitoring strategy for each HCS is indicated in Table 1.

Exposure monitoring pumps were calibrated at the respective flow rates of the different samplers by means of a Gillian Gilibrator-2 (Gillian Gilibrator-2, Sensidyne Inc., FL, USA) in line with the specific sampler for the various HCS's. Pump calibration took place before and after exposure monitoring for verification of flow rates. VOC badges were used for passive exposure monitoring

wherein air is naturally diffused through the permeable carbon membrane after removing both strips. For static sampling the VOC badges were placed at 1.5 m from the floor. The VOC badges were placed into a plastic container and stored in sealed bags at room temperature.

Field blanks were used. The field blanks were handled, stored and transported in the same manner as the sampling media. One field blank was taken for each of the three samples per process. The exception was for the PAH sampling which had eight blank samples taken (used for solvent selection during analysis).

Statistical analysis of results

Basic descriptive statistics (mean and standard deviation) were used for interpretation of results. Measured values that were below the limit of detection (LOD), were substituted with values that were calculated using the “LOD divided by the square root of two” method as most data collected during this study was below the LOD and the small number of samples prevented the use of β -substitution (Ganser and Hewett, 2010). Time-weighted averages (TWA) were calculated from the concentration results (mg/m^3) where $TWA = \frac{C_1T_1 + C_2T_2 + C_nT_n}{T_1 + T_2 + T_n}$. TWA is used to calculate an operators' daily exposure to HCS's in the workplace over an 8-hour work day, considering the time exposed and the average concentrations of each substance. This calculated TWA was used for comparison to TWA occupational exposure limits (OEL's) to determine whether operator exposures were compliant with HCS Regulations. TWA's consisted of measurements from all three phases of processing.

Table 1: Exposure monitoring strategy for HCS

HCS	n	Sampler	Flow rate	Filter used	Sample handling technicalities	Analysis
Silica and PNOC (respirable)	21	10-mm nylon Aluminium cyclone	2.5 l/min	*PVC filter supported with backup pad in a two-piece cassette. 37 mm, 5.0 μm pore size	Cyclone placed in an upright position, disallowing inversion during sampling	Gravimetric analysis (NIOSH 0501, 2015; NIOSH 7602, 2003)
VOC's	15	OVM Traceair 521 Fast Sampling Rate Badge, VOC badges (passive sampler)	N/a	300 mg coconut-based charcoal strips	Both end of badge covers removed before sampling, then replaced after and placed into a supplied plastic container at room temperature	The badges were analysed for VOC's by solvent desorption and gas chromatography (NIOSH 1500, 2003).
PAH's	4	Closed face three-piece cassette with tube	2.0 l/min	#PTFE-laminated membrane filter, 2 μm pore size, 37 mm in line with a washed XAD-2 resin tube (front 100 mg; back 50 mg)	The cassette and filter as well as the XAD-2 tubes were wrapped in aluminium foil and transported at 0 °C	Extraction with benzene & gravimetric analysis (OSHA 58) for total mass of PAH °BSF. XAD-2 tubes - solvent desorption (NIOSH 5515, 2003; OSHA 58, 1986).

n – number of samples N/a – Not applicable *PVC – Polyvinyl chloride #PTFE – Polytetrafluoroethylene °BSF – Benzene soluble fraction

Results

The PSD, SEM, XRD analysis and exposure to PNOC, crystalline silica, PAH's and VOC's were determined for the pre-processing, processing and post-processing phases of AM at both Facility A and Facility B.

PSD and SEM analysis

Mean particle sizes of all sand at both facilities were larger than 100 μm (Table 2) which is supported by the SEM images (Figures 1(a)-(e)). New and used sand at Facility A, however, contained particles smaller than 100 μm , with 10% of the particles smaller than 75.35 μm and 81.19 μm for new and used sand respectively. The mean particle sizes at Facility A were below the manufacturers specified mean particle size (137.49 μm vs 170 μm) while the mean particle sizes at Facility B were above the manufacturers specified particle size range (282.70 μm vs 90-200 μm).

Table 2: PSD (mean $\pm$ standard deviation) for sand (new and used) at Facility A and (new, used and mixed sand) Facility B.

Facility	n	Sample	Particle size distribution (μm)				
			Volume Weighted Mean	d (0.1)	d (0.5)	d (0.9)	Manufacturer particle size
A	1	New	137.49 $\pm$ 0.81	75.35 $\pm$ 15.22	135.14 $\pm$ 2.61	209.63 $\pm$ 14.45	170 mean (EOS, 2016)
	1	Used	168.12 $\pm$ 24.107	81.19 $\pm$ 4.23	147.87 $\pm$ 6.69	276.47 $\pm$ 61.10	N/a
B	1	New	282.70 $\pm$ 3.141	199.46 $\pm$ 1.82	274.44 $\pm$ 2.74	376.25 $\pm$ 6.05	90 – 200 (Voxeljet, 2012)
	1	Mixed	279.68 $\pm$ 1.299	184.80 $\pm$ 4.63	268.12 $\pm$ 0.33	390.48 $\pm$ 9.55	N/a
	1	Used	289.41 $\pm$ 10.256	199.77 $\pm$ 3.63	279.82 $\pm$ 9.13	391.13 $\pm$ 19.08	N/a

- New (Unused powder, as purchased from the manufacturer); Used (Recycled and reused powder); d(0.1) – 10% of the particles are smaller than this diameter; d(0.5) – the median diameter; d(0.9) – 90% of particles are smaller than this diameter; N/a – Not applicable; n=number of samples

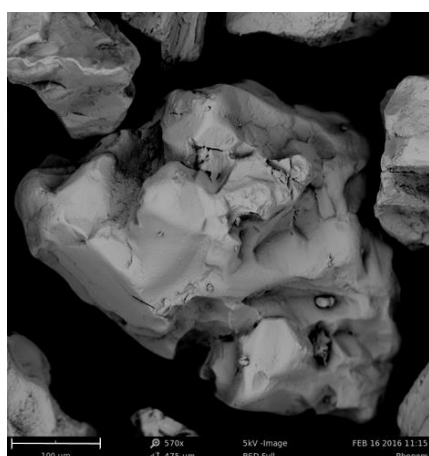


Figure 1(a): Facility A - New sand

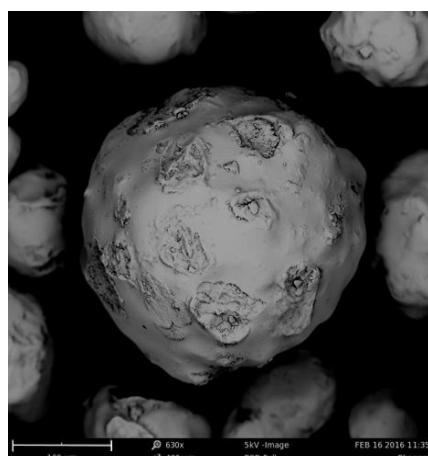


Figure 1(b): Facility A - Used sand

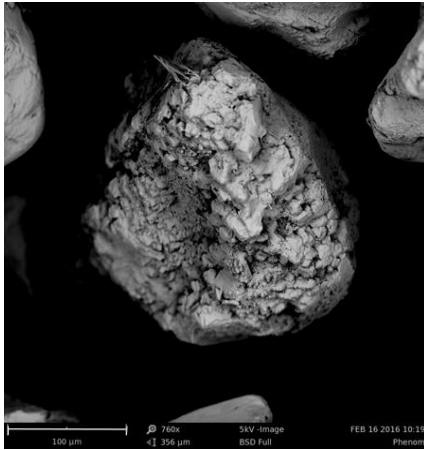


Figure 1(c): Facility B - New sand

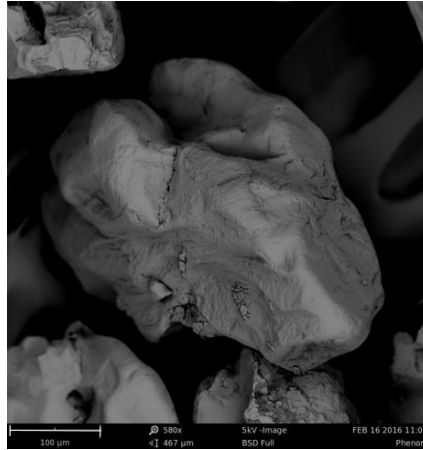


Figure 1(d): Facility B - Mixed sand

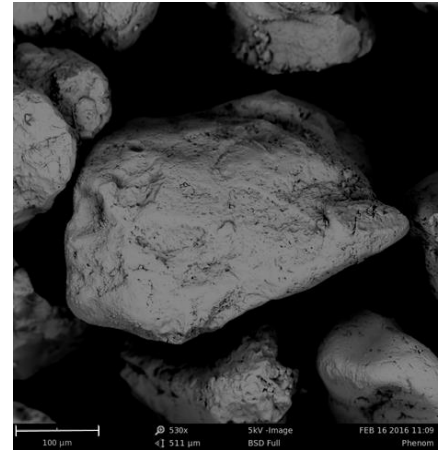


Figure 1(e): Facility B - Used sand

XRD analysis for mineral composition

Table 3: Mineral composition types present in sand samples at each AM facility.

Facility	Sand type	Mineral composition (%)				Manufacturer
		Corundum	Graphite	Mullite	Crystalline silica (quartz)	
A	New sand	1.7	-	94.0	4.3	Mullite (EOS, 2016).
	Used sand	1.5	-	94.7	3.8	
B	New sand	-	-	-	100	Silica and kerphalite (Voxeljet, 2012).
	Mixed sand	-	-	-	100	
	Used sand	-	1.4	-	98.6	

- Not detected; Corundum – An aluminium oxide, rock forming mineral; Graphite – Crystalline form of carbon; Mullite – A man made, aluminium oxide silicate; Quartz – Most common form of crystalline silica; Kerphalite – natural aluminium silicate.

Facility A's sand was predominantly comprised of mullite and 4.3% or less of quartz (silica), while Facility B's new and mixed sand contained 100% quartz silica. Used sand remained very similar to new sand in its mineral composition. According to the manufacturers, sand at Facility A is comprised of mullite, while sand at Facility B is comprised of silica and kerphalite, a natural aluminium silicate (Voxeljet, 2012). Percentage composition of minerals were not provided by the manufacturers.

Exposure monitoring: PNOC

Table 4: PNOC exposure at Facility A and Facility B

Facility	Process phase	n	Area		n	Personal	
			mg/m ³	TWA mg/m ³		mg/m ³	TWA mg/m ³
A	Pre-processing	1	0.40		1	0.58	
	Processing	1	0.03*	0.16	1	0.32*	0.42
	Post-processing	1	0.21		1	0.20*	
B	Pre-processing	1	0.32*		2	0.57*/1.99	
	Processing	2	0.06*/0.06*	0.09	1	0.27*	*0.22/°0.60
	Post-processing	1	0.12*		2	0.12*/0.14*	

PNOC: Time-weighted Average-Occupational Exposure Limit-Recommended Limit (TWA-OEL-RL) = 5 mg/m³ respirable dust; LOD is 0.03 mg/sample; *Concentration calculated from LOD; $\text{mg/m}^3 = \frac{0.03}{\sqrt{2}} / \text{volume}(m^3)$; °TWA for Operator 1; °TWA for Operator 2; n – number of samples

Table 4 indicates that the PNOC personal exposure of AM operators for the different processing phases ranged between 0.12 and 1.99 mg/m³ for both facilities, while area concentrations ranged between 0.03 and 0.4 mg/m³. The TWA exposure of AM operators ranged between 0.22 and 0.60 mg/m³. The area exposure was lower than the operators' personal exposure.

Exposure monitoring: Crystalline silica (Quartz)

Table 5 indicates that the crystalline silica (quartz) personal exposure of AM operators for the different processing phases ranged between 0.02 and 0.11 mg/m³, while area concentrations ranged between 0.01 and 0.06 mg/m³. The TWA exposure of AM operators ranged between 0.03 and 0.06 mg/m³. The area exposure was lower than the operators' personal exposure.

Table 5: Crystalline silica (quartz) exposure at both facilities

Facility	Process phase	n	Area		n	Personal	
			mg/m ³	TWA mg/m ³		mg/m ³	TWA mg/m ³
A	Pre-processing	1	0.02*		1	0.02*	
	Processing	1	0.01*	0.01	1	0.06*	0.03
	Post-processing	1	0.01*		1	0.04*	
B	Pre-processing	1	0.06*		2	0.11*/0.09*	
	Processing	2	0.01*/0.01*	0.01	1	0.11	*0.06/°0.05
	Post-processing	1	0.02*		2	0.02*/0.03*	

Silica (Quartz): TWA-OEL-CL = 0.1 mg/m³; *Concentration calculated from LOD $\text{mg/m}^3 = \frac{0.005}{\sqrt{2}} / \text{volume}(m^3)$; LOD is 0.005 mg/sample; °TWA for Operator 1; °TWA for Operator 2

Exposure monitoring: PAH's

OSHA method 58 and NIOSH method 5515 were both used for the analysis of 18 PAH species. No exposure monitoring for PAH's was conducted at Facility A as the process did not involve heat, which is necessary to liberate PAH's. Only one of the 18 PAH species analysed (naphthalene) was detected above the LOD but at a concentration < 0.001 mg/m³ (Table 6). The total PAH exposure was below 0.001 mg/m³. The particulate phase results of OSHA method 58 were all below the LOD of 0.05 mg/sample.

Table 6: PAH exposure at Facility A during processing and post-processing

Exposure type	n	Process phase	Naphthalene		Total PAH	
			mg/m ³	TWA mg/m ³	mg/m ³	TWA mg/m ³
Area	2	Processing	<0.001	<0.001	<0.001	<0.001
		Post processing	<0.001		<0.001	
Personal	2	Processing	<0.001	<0.001	<0.001	<0.001
		Post processing	<0.001		<0.001	

BSF; TWA-OEL-RL naphthalene = 50 mg/m³; ACGIH – Total PAH = 5 mg/m³ Benzene Soluble Fraction (BSF); n = number of samples

Exposure monitoring: VOC's

NIOSH method 1500 was used for the exposure monitoring and analysis of forty VOC's. Only seven of the forty VOC's were above the LOD. These seven compounds were acetone, pentane, hexane, benzene, toluene, cyclohexane and naphthas (a mixture). The personal exposure concentrations of AM operators at Facility A (Table 7) during all three processing phases ranged between 0.07 and 0.27 mg/m³ for acetone, 0.01 and 0.26 mg/m³ for pentane, 0.69 and 2.12 mg/m³ for hexane, 0.08 and 0.21 mg/m³ for toluene, 0.12 and 0.33 mg/m³ for benzene, 0.20 and 0.51 mg/m³ for cyclohexane 0.67 and 7.50 and 14.77 mg/m³ for naphthas. The TWA exposure for acetone, pentane, hexane, benzene, toluene, cyclohexane and naphthas were 0.04, 0.04, 0.21, 0.03, 0.05, 0.09 and 2.92 mg/m³ respectively. The area exposure was lower than the personal exposure for all the VOC's with a TWA of 0.03, 0.026, 0.25, 0.03, 0.05, 0.07 and 1.92 mg/m³ respectively. The exposure of AM operator 1 at Facility B during all three processing phases ranged between 0.17 and 1.24 mg/m³ for acetone, 0.13 and 1.19 mg/m³ for pentane, 0.73 and 3.40 mg/m³ for hexane, 0.08 and 0.37 mg/m³ for toluene, 0.04 and 0.57 mg/m³ for benzene, 0.20 and 1.38 mg/m³ for cyclohexane and 14.17 and 19.41 mg/m³ for naphthas respectively.

The exposure of AM operator 2 at Facility B (Table 8) during the pre-processing and post-processing phases ranged between 0.54 and 1.07 mg/m³ for acetone, 0.28 and 1.17 mg/m³ for pentane, 0.94 and 1.94 mg/m³ for hexane, 0.10 and 0.21 mg/m³ for toluene, 0.32 and 0.33 mg/m³ for benzene, 0.37 and 0.74 mg/m³ for cyclohexane and 13.68 and 35.91 for naphthas respectively. The TWA exposure for operator 1 for acetone, pentane, hexane, benzene, toluene, cyclohexane and naphthas was 0.15, 0.10, 0.30, 0.03, 0.06, 0.10 and 3.50 mg/m³ respectively. The TWA exposure for operator 2 for acetone, pentane, hexane, benzene, toluene, cyclohexane and naphthas was 0.12, 0.09, 0.21, 0.02, 0.05, 0.08 and 3.44 mg/m³ respectively. The area exposure was higher than the personal exposure with TWA for acetone, pentane, hexane, benzene, toluene, cyclohexane and naphthas at 0.92, 0.96, 0.37, 0.03, 0.07, 0.10 and 4.80 mg/m³ respectively.

Table 7: VOC exposure at Facility A

Exposure type	Process	n	VOC													
			Acetone		Pentane		Hexane		Toluene		Benzene		Cyclohexane		Naphthas*	
			mg/m ³	TWA mg/m ³	mg/m ³	TWA mg/m ³	mg/m ³	TWA mg/m ³	mg/m ³	TWA mg/m ³	mg/m ³	TWA mg/m ³	mg/m ³	TWA mg/m ³	mg/m ³	TWA mg/m ³
Area	Pre-processing	1	0.05*		0.05*		0.48*		0.05*		0.09		0.11		3.90	
	Processing	1	0.01	0.03	0.01	0.03	0.10	0.25	0.01	0.03	0.02	0.05	0.03	0.07	0.67	1.92
	Post-processing	1	0.02*		0.02*		0.25*		0.03		0.02		0.03		1.96	
Personal	Pre-processing	1	0.07*		0.07*		0.69*		0.08*		0.12		0.20		7.50	
	Processing	1	0.27	0.04	0.26	0.04	2.12*	0.21	0.21*	0.03	0.33	0.05	0.51	0.09	14.77	2.92
	Post-processing	1	0.18		0.19		1.19*		0.13*		0.33		0.51		12.82	
TWA-OEL-RL (mg/m ³)			1780		1800		70		16		340		188		350	

*Indicates results below the LOD

Table 8: VOC exposure at Facility B

Exposure type	Process	n	VOC													
			Acetone		Pentane		Hexane		Toluene		Benzene		Cyclohexane		Naphthas*	
			mg/m ³	TWA mg/m ³	mg/m ³	TWA mg/m ³	mg/m ³	TWA mg/m ³	mg/m ³	TWA mg/m ³	mg/m ³	TWA mg/m ³	mg/m ³	TWA mg/m ³	mg/m ³	TWA mg/m ³
Area	Pre-processing	1	0.25		0.21		0.73*		0.08*		0.12*		0.209		12.50	
	Processing	1	0.71	0.915	0.66	0.96	2.65	0.37	0.29*	0.03	0.445*	0.07	0.81	0.10	31.130	4.80
	Post-processing	2	1.23/1.50		1.31/1.59		0.45/0.42*		0.04/0.04*		0.05/0.05*		0.08/0.06		2.71/3.50	
Personal	Pre-processing	2	1.24/1.07		1.19/1.171		3.40*/1.94		0.37*/0.21*		0.57*/0.32*		1.38/0.74		19.41/35.91	
	Processing	1	0.85	°0.15 °0.12	0.81	°0.10 °0.09	1.59*	°0.30 °0.21	0.17*	°0.03 °0.02	0.04*	°0.06 °0.05	0.50	°0.10 °0.08	16.09	°3.50 °3.44
	Post-processing	2	0.17/0.54		0.13/0.28		0.73*/0.94*		0.08*/0.10*		0.15/0.33		0.20/0.37		14.17/13.68	
TWA-OEL-RL (mg/m ³)			1780		1800		70		16		340		188		350	

*Indicates results below the LOD; ° TWA for Operator 1; ° TWA for Operator 2; (where results are separated by a " / " indicates two operators sampled and their results); n=number of samples

Discussion

This study was conducted to determine the physicochemical characteristics of the sand used in AM, as well as the respiratory exposure to HCS's present in AM of sand casting moulds during each processing phase of manufacture, namely pre-processing, processing and post-processing. The aerodynamic diameter of airborne particulate matter plays an important role in the deposition, and subsequent clearance, of particulate matter in the respiratory tract. Inhalable particles ($< 100\ \mu\text{m}$) deposit in the upper respiratory tract (nose and throat) and the respirable particles ($< 4\ \mu\text{m}$) deposit in the alveolar region of the lungs. (Méndez *et al.*, 2010; Brown *et al.*, 2013).

The results from the PSD analysis (Table 2) indicated that at Facility A, 10% of the particles for both the new and used sand were $< 75.35\ \mu\text{m}$ and $81.19\ \mu\text{m}$ respectively. At both facilities, the mean particle size ranges were $> 100\ \mu\text{m}$, which was supported by the SEM imaging (Figure 1 a-e). There was also a resemblance in the size of new, used and mixed sand indicating that sand casting processes did not alter the physical size of the sand particles. The area of concern lies in the presence of the inhalable size fraction of particulate matter as indicated through the results of the PSD analysis (Table 2). Inhalation of inhalable size fraction dust can cause coughing and mild irritation and could potentially aggravate pre-existing respiratory conditions (Brown *et al.*, 2013). There were discrepancies noticed between the mean particle sizes from the PSD analysis in comparison to the manufacturers' details provided. At Facility A, the mean particle sizes were in a size range below the mean particle sizes given by the manufacturer. At Facility B, the particle sizes were larger than the range which the manufacturer specified. This leads to questioning of the validity of MSDS's. In this case, the employer/AM operators are under the impression that there is no risk of inhalation, yet a fraction of the particles is inhalable (providing a false sense of security). Implications extend beyond incorrect risk estimations, as it may contribute to incorrect exposure monitoring strategies and consequential control measures. Irrespective, it places the operator at risk.

The XRD results (Table 3) indicate the presence of quartz in both sand types at Facility A and Facility B, with percentages ranging between 3.8% and 100%. Sand at Facility A consisted of a high percentage of mullite (94% and 94.7%). Mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$), a man-made aluminium silicate used for its high melting point, poses a health hazard as it may contain traces of crystalline silica. The PSD results indicated the existence of inhalable sand particles at Facility A containing crystalline silica (quartz) (4.3%). Mineral composition provided by the manufacturer was accurate for Facility A (mullite), except for silica, which was not reported, while Facility B's manufacturer stated silica and kersalite as the mineral composition of the sands used. XRD results indicate only silica and not kersalite, an aluminium silicate. There is, therefore, both particle size and mineral composition discrepancies.

The Hazardous Chemical Substances Regulations (HCS, 1995), states that where there is no indication of the need for a lower value, personal exposure to respirable dust (PNOC) should be kept below 5 mg/m³ respirable TWA. The results from the gravimetric analysis of the collected samples (Table 4) indicated that AM operators had a low TWA exposure to PNOC, ranging between 0.22 and 0.60 mg/m³. The area exposure was lower than the operators' personal exposure. Facility A had a higher exposure to PNOC (area TWA of 0.16 mg/m³) than Facility B (area TWA of 0.12 mg/m³) and pre-processing had the highest overall exposure in comparison with the other three processing phases at both facilities, which included operations such sieving the sand and pouring it into the AM machinery. Exposure to respirable fractions of PNOC at both Facility A and Facility B was at low concentrations, below the national TWA-OEL-RL.

The results from the gravimetric analysis of the collected samples (Table 5) indicated that exposure of AM operators to crystalline silica (quartz) for the different processing phases ranged between 0.02 and 0.11 mg/m³, while the area exposure ranged between 0.01 and 0.06 mg/m³. The TWA exposure of AM operators ranged between 0.03 and 0.06 mg/m³. The area exposure was lower than the operators' personal exposure. Facility B had the highest crystalline silica exposure (0.06 mg/m³) between the two facilities (0.03 mg/m³ TWA at Facility A). At Facility B, the TWA exposure was 0.06 mg/m³ for operator 1 and 0.05 mg/m³ for operator 2. While these exposures are below the South African TWA-OEL-CL of 0.1 mg/m³ they are above the action limit (50% of the TWA-OEL-CL) and at or above both the ACGIH threshold limit value (TLV) and the OSHA Permissible Exposure Limit (PEL) of 0.05 mg/m³ respirable fraction. The action limit, which is calculated as an 8-hour time-weighted average, is used by OSHA to express the presence of a physical hazard and to indicate the level of a harmful substance that requires medical surveillance, increased hygiene monitoring or biological monitoring and is usually lower than the PEL (OSHA, 2016). This is cause for concern as Facility B has a mineral composition of 100% quartz as indicated by Table 3 even though particle sizes were > 100 µm (Table 2). This indicates that AM operators' exposure to crystalline silica, a known human carcinogen (causing lung cancer) and a cause of silicosis, was above international OEL's. Also, even though the particle size analysis indicated the particles were > 100 µm, respirable sized particles were still being generated to which workers were exposed. This warrants introduction of control measures to protect the operators at these facilities by reducing the silica exposure as far as is reasonably practicable, such as installing adequate ventilation systems into the enclosed work space.

PAH's are likely to be found in sand or soil matrices as microscopic crystallites (Sluszný, 1998). Silica sand is a good adsorbent of PAH's and can thus be contaminated with them. Some PAH's are desorbed or released at a low temperature of between 100 °C and 300 °C as was concluded in a study by Biache *et al.* (2015). A certain amount of PAH's could thus be released by the sand particles as a vapour, or through adsorption onto the particles due to the heat exposure from the

AM process (Holtzer *et al.*, 2014). Naphthalene was the only PAH detected during two phases of manufacture (processing, and post-processing) at Facility A ($< 0.001 \text{ mg/m}^3$) (Table 6), which was at concentrations 50 000 times lower than the South African TWA-OEL-RL of 50 mg/m^3 . At this low concentration, there is a very low risk to the health of the AM operators. Other than the release of naphthalene from the sand particles due to the heat exposure from the AM process, another possible reason for the presence of naphthalene, in these low concentrations, is indicated in studies concluding that naphthalene regularly occurs in environmental/outdoor and indoor air, especially in urban areas that are near industries involved in burning processes and motor vehicle traffic or inside buildings where people smoke tobacco (Preuss *et al.*, 2003). As for the total PAH results per the NIOSH method 5042, the results fall far below the OEL of 5 mg/m^3 . It can be concluded that PAH's are released at insignificant concentrations in the sand used at Facility A.

Only seven of the forty VOC's analysed for were above the LOD. These seven compounds were acetone, pentane, hexane, benzene, toluene, cyclohexane and naphtha (a mixture). Of these VOC's, expected compounds included benzene, toluene and naphthalene. Unexpected VOC's, not previously alluded to in literature to be present during AM processes included acetone, pentane, hexane and cyclohexane. A study conducted by Kubecki *et al.* (2013) investigated the influence of temperature on the formation of VOC's from resins. Resins are used in sand casting processes to bind the sand particles together for a better finish. Foundries often use carriers or reducers in their sand casting processes. Naphtha, an aliphatic hydrocarbon, is often used as a carrier or reducer in the sand casting processes in foundries to improve the drying and removal process of the metal from the sand cast, through improvement of the solubility of the coating binder (HA-International, 2006).

The respective personal exposure TWA's for acetone, pentane, hexane, benzene, toluene, cyclohexane and naphtha was higher at Facility B than at Facility A indicating that the presence of heat has very little effect on the liberation of VOC's during AM, as Facility A made use of selective laser sintering AM processes (heat), while Facility B made use of binder jetting (no heat). All exposure results were, however, below the South African TWA-OEL's. Very little risk to the health of the worker was thus present. Biological monitoring will need to be conducted as per the HCS regulations which states that if an assessment is made wherein it is indicated that the operator may be exposed to certain VOC's (benzene, hexane and toluene – substances listed in Table 3 of the HCS's Regulations), the employer must ensure that biological monitoring/medical surveillance is carried out and that the exposure must be adequately controlled. (HCSR, 1995). An explanation for the presence of very low concentrations of benzene detected during analysis could also be due to residual concentrations from furnishing and building materials, environmental tobacco smoke, floor adhesives, photocopiers and paints to name a few (Duarte-Davidson *et al.*,

2001). As a final note, all AM operators wore the recommended personal protective equipment (PPE) including examination gloves, dust masks, overalls and safety shoes.

Conclusions

No prior knowledge existed about the particle size fractions after processing using mixed or used sand, airborne particle size fractions, the mineral composition of the sand used or the presence (and concentrations) of HCS's during AM of sand casting moulds. This study aimed to provide information on the respiratory exposure levels during AM processes, namely pre-processing, processing and post-processing at two South African research facilities. Various particle size fractions, mineral composition, silica and dust concentrations as well as other HCS's (PAH's and VOC's) present were assessed. Of concern was that this study found that both facilities had mean particle sizes and mineral compositions that deviated from the manufacturers' details of the sand. Facility A contained inhalable particle sizes, of which the sand was comprised of 4.3% crystalline silica. Facility B's sand had a 100% crystalline silica composition and a respirable crystalline silica TWA exposure of 0.05 and 0.06 mg/m³ TWA. This is above the action limit (0.05 mg/m³) and at or above other international OEL's. Exposure to PNOC, PAH's and VOC's were very low, well below the respective OEL's. The findings of this study have spread light on the health risks involved with AM of sand casting moulds. These include discrepancies between manufacturer details, actual sand particle sizes and mineral composition, the presence of inhalable sized sand particles, the presence of respirable crystalline silica and the low effect heat has on the liberation of VOC's during AM of sand casting moulds. Other health risks that were observed include a lack of any natural or mechanical ventilation in the enclosed rooms that contain the AM technology, no signs were available indicating any exposure to silica/quartz at Facility B, and there was no indication of a respirator zone. All personnel did, however, wear the recommended personal protective equipment.

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CHAPTER 4: CONCLUDING CHAPTER

4.1 Further discussion and summary of findings

The general aim of this study was to determine the occupational respiratory exposure of AM operators to HCS's (crystalline silica, VOC's and PAH's) present during the pre-processing, processing and post-processing phases of AM of sand moulds. This was achieved through the evaluation of two objectives. The first objective was to determine the physicochemical characteristics of the sand, such as the particle sizes and the mineral composition of sand material

used in AM. This was evaluated through PSD, SEM and XRD analysis of collected bulk sand samples from the pre-processing and post-processing phases of manufacture. The results of these analysis indicated that for new sand, the mean particle size was 137.49 μm at Facility A and 282.70 μm at Facility B, indicating that both Facilities had particle sizes larger than the inhalable size fraction. However, 10% of particles at Facility A were smaller than 75.35 μm , indicating the presence of inhalable particles. The SEM imaging supported the above, with particle sizes > 100 μm . XRD analysis indicated that sand at Facility A had a majority percentage of mullite (94%) and a presence of silica (4.3%) present while sand at Facility B comprised of 100% crystalline silica (quartz). Therefore, the first objective was met.

The second objective was to determine the concentration of respirable nuisance dust, crystalline silica, VOC's and PAH's that AM operators were exposed to. This was done through the collection of personal exposure samples as well as static samples in closest proximity to the operator over the task-based period to assess exposure. Personal exposure samples of airborne particulate matter, VOC's and PAH's was collected during loading of the AM machine prior to processing, during processing and operation of the machine, and at the cleaning area after processing (post-processing). The results of these analysis indicated that respirable PNOC exposure was lower than the national OEL at both facilities. Respirable silica (quartz) TWA exposure at Facility B indicated a 0.06 mg/m^3 and 0.05 mg/m^3 for two operators respectively, which is below the South African OEL-CL of 0.1 mg/m^3 but at a concentration warranting further steps. The only PAH compound present at either Facility was naphthalene, but with a TWA far below its OEL. Exposure to seven VOC's (acetone, pentane, hexane, benzene, toluene, cyclohexane and naphthas) indicated TWA's below their respective OEL's at both facilities. Therefore, the second objective was met. Based on the above, the aim of this study was met.

Two hypothesis were formulated for this study. The first hypothesis was that AM operators are exposed to respirable concentrations of crystalline silica (quartz) above the national OEL-CL of 0.1 mg/m^3 . This study proved that AM operators were not exposed to respirable fractions of crystalline silica (quartz) or to PNOC in concentrations, at either facility, above the national OEL's. The operators at Facility B were, however, exposed to silica (quartz – a type of crystalline silica) above the action level, and at and above, the international OEL of 0.05 mg/m^3 . This hypothesis is thus rejected.

The second hypothesis was that powder bed fusion incorporates heat and thus it is hypothesised that, at Facility A, which uses powder bed fusion (or selective laser sintering), VOC's and/or PAH's are present in the air that the AM operator inhales, in concentrations that exceed national OELs. During this study, AM operators were exposed to one PAH (naphthalene) and seven VOC's but not above the national OEL's and that operators at both facilities were exposed to VOC's regardless of whether the AM process utilised heat or not. This hypothesis is therefore rejected.

There were discrepancies noticed between the mean particle sizes from the PSD analysis and the mineral composition from the XRD analysis, in comparison to the manufacturers' details provided. At Facility A, the mean particle sizes were in a size range below the mean particle sizes given by the manufacturer. At Facility B, the particle sizes were larger than the range which the manufacturer specified. Mineral composition provided by the manufacturer was accurate for Facility A (mullite), except for silica which was not reported, while Facility B's manufacturer stated silica and kersalite as the mineral composition of the sands used. XRD results indicate only silica and not kersalite, an aluminium silicate. This leads to questioning of the validity of MSDS's. In this case the employer/AM operators are under the impression that there is no risk of inhalation (providing a false sense of security), yet a fraction of the particles is inhalable. Implications extend beyond incorrect risk estimations as it may contribute to incorrect exposure monitoring strategies and consequential control measures. Irrespective, it places the operator at risk.

4.2 Limitations of this study

AM is still a relatively new branch of science and engineering and the occupational health of AM operators surrounding these processes has not been extensively studied yet. There is thus very little, if no, literature available to indicate exposure concerns during these sand casting processes. There are usually only one or two operators for many different AM processes like sand casting, plastics and metals. These AM operators are usually skilled and trained to work with these machines. AM is a highly specialised and expensive technology. Not many facilities are thus expected wherein exposure monitoring can take place, resulting in very few operators available to assess. This limits comparative or larger studies from being executed.

4.3 Recommendations for occupational settings

Engineering and administrative control measures

Observations made during exposure monitoring at both facilities included observation that all the operators performing the AM processes at both facilities wore the recommended PPE. There was a lack of any natural or mechanical ventilation in the enclosed rooms that contain the AM technology. No signs were available indicating any exposure to silica/quartz at Facility B, and there was no indication of a respirator zone. Facility A made use of compressed air to clean the sand mould, which is prohibited according to Section 13 (a) of the HCS's Regulations. Recommendations to rectify these observations include using local exhaust and extraction ventilation, especially during the pre-processing and post-processing phases of manufacture to control air contaminants at or below acceptable exposure limits/guidelines. Provision for an extracted flanged welding hood attached to a flexible arm, or a mobile unit can be considered and installed in the enclosed room above the AM machinery. Supplementary controls to limit exposure

to crystalline silica (due to its confirmed classification as a human carcinogen) may include installation of dust collection systems and use of high efficiency particulate air (HEPA)-filtered vacuuming instead of compressed air (Kyanite Mining Corporation, 2015).

Where there is a potential exposure to crystalline silica, the following warnings should be readily visible and posted near entrances, work areas and the respirator zone: “WARNING! FREE SILICA WORK AREA. Unauthorized persons keep out. No entry without respiratory protective equipment. The following warning should be posed within the work area where potential exposure may occur: WARNING! FREE SILICA WORK AREA. Avoid breathing dust. May cause delayed lung injury (silicosis)” (NIOSH, 1974; HCS, 1995; OSHA, 2014).

Personal protective equipment (PPE)

Table 4: Observations and recommendations of PPE of operators at both facilities

Observation	Recommendation
Operators were equipped with the following PPE: <u>Facility A:</u> • Dust mask: EOS e-manufacturing solutions, Respirator Full Face Mask (Gases and vapour filter). • Latex examination gloves • Overalls • Steel toe-capped shoes <u>Facility B:</u> • Dust mask: DroAir EN 149:2001 + A1:2009 FFP2, with an active carbon moulded respirator (disposable) • Nitrile Examination gloves • Overalls • Steel toe-capped shoes	PPE worn by the operators could be reevaluated to assure sufficient protection and safe work practices implemented. This may include: • Under dusty conditions, operators should wear overalls or other appropriate workplace clothing without turn-ups or pockets • Contaminated clothing must be vacuumed before being removed and the last piece of clothing to be removed should be the respiratory protection. Under no circumstances should dusts be removed from clothing by blowing or shaking. • Practice good housekeeping. • Wash contaminated clothing thoroughly before re-wearing. • Do not take clothing, contaminated with silica, home (Kyanite Mining Corporation, 2015).

Education and training

Section 3 (1) of the HCS's Regulations states that employers must adequately train and inform the employees before they are exposed to any HCS's, and thereafter, at regular intervals. All employees working with the AM processes or those near the processes should be educated on the associated particle size exposure as well as the HCS's present, including how they infiltrate the airways, their distribution in the respiratory tract and the negative health effects they may pose. This allows for AM operators to understand the need for engineering, administrative controls or correct PPE to be worn. Engineers and floor managers should also be trained with respect to the exposures present to enforce the recommendations. If the employer is not knowledgeable enough to provide training him/herself, then the employer must obtain the use of a relevant service provider to conduct the necessary training.

The operator must be made aware of the generation of respirable silica dust exposure during all three phases of AM processes and where highest exposure occurs, such as during pre-processing wherein the sand is sieved and poured into the AM machine. The operator must be educated on the necessity of personal air sampling as well as medical monitoring such as chest x-rays. Education on the potential risks to their health caused by exposure, such as the risk of developing lung cancer/silicosis (OSHA, 2015). They must be trained in the selection, correct use (donning and doffing) and maintenance of a dust mask/respirator during which a physical demonstration of fitting should be conducted ensuring that there are no gaps around the bridge of the nose or around the chin area. This is done by the inhale-exhale test. Operators must be instructed on personal hygiene and good housekeeping, such as operators with facial hair being instructed to shave before donning of the dust mask and exposure.

The operators must be made aware of the presence of naphthalene and the other seven VOC's present, especially benzene, hexane and toluene as exposure to these compounds require biological monitoring, even at very low concentrations. The operator must be educated on the health effects of exposure to the PAH's and VOC's present such as such as respiratory dysfunction, nervous system dysfunction (central nervous system depressants), kidney disease, cardiovascular disease and asthma, sensitised allergic skin reactions, biliousness, and dizziness; while pregnant women are at high risk due to effects on the unborn foetus such as low birth weight and reduced foetal growth (Hinwood *et al.*, 2007; Duarte *et al.*, 2014; Tibbetts, 2015; TOXNET).

These operators must be instructed to subject themselves to biological monitoring by an occupational medicine practitioner provided by the employer. They must undergo biological monitoring for hexane, toluene and benzene to establish whether their total body burden (exposure via all routes) is below the biological exposure indices (BEI's). Operators must also be

trained on awareness and the correct interpretation of signage of respirator zones as well as the labelling, handling and storage of sand.

4.4 Recommendations for future studies

Future studies should include both inhalable and thoracic size fractions of dust to determine operator exposure as these size fractions still pose a significant risk to respiratory health, especially with the evident presence of quartz sand and the evidence of inhalable particle sizes at Facility A. The inhalable size fraction is that particle size that has an aerodynamic diameter (the diameter of a unit density microsphere with the same terminal velocity as the particle in question) of less than 100 µm and is usually trapped in the throat and nose. These particles usually do not enter the deeper parts of the lung due to their larger sizes (Capstick and Clifton, 2012; Brown *et al.*, 2013). The thoracic size fraction, which includes those particles that pass further than the larynx and can deposit anywhere in the airways of the lung or in the deeper regions of the lung, such as the gas exchange region. These particles have an aerodynamic diameter of less than 10 µm which thus includes the respirable and UFP size fractions (Capstick and Clifton, 2012; Brown *et al.*, 2013).

Exposure to ultrafine particles (UFP's) should also be investigated as there is a potential risk for the presence of submicron or UFP's (particles in the nano size range less than 100 nm in diameter) in the AM process. According to a study by Stephens *et al.* (2013), desktop 3D printers that utilised heat and a thermoplastic material had a resultant UFP emission in the office space and were characterised as high emitters of these UFP's. This could pose a problem in AM processes for sand mould production that use heat in the process, as heat can change the structure of silica sand (Nazaroff, 2004; Zihms *et al.*, 2013).

Various adverse health effects are associated with silica UFPs (both crystalline and amorphous) such as decreasing lung cell viability and increasing lung cell cytotoxicity and genotoxicity through the effects of reactive oxygen species (ROS), although most of these effects are still being investigated. This is because the toxicological mechanisms behind some of these health effects are still unknown, unclear or only supposed (McCarthy *et al.*, 2012; Mu *et al.*, 2012). The effects of these UFPs are due to their ability to deposit in the nasal, tracheobronchial and alveolar lung regions through diffusion and, because of their small size, their ability to translocate/escape from the lungs into the blood stream, or into the central nervous system through the olfactory nerve (Oberdörster *et al.*, 2004; Donaldson *et al.*, 2005). Health effects due to these particles include potential cardio-respiratory mortality, aggravated asthma symptoms, inflammation, immune system impairment, chronic bronchitis and stroke (Stephens *et al.*, 2013; Behera *et al.*, 2015).

Exposure to furan resins, measured as furfuryl alcohol, should also be implemented per NIOSH method 2505 or OSHA method 72 (NIOSH, 2016; OSHA, 1988) as the VOC exposure monitoring could not analyse for this compound specifically. Biological monitoring will need to be conducted as per section 7 (b) of the HCS regulations which states that if an assessment is made wherein it is indicated that the operator may be exposed to VOC's listed in Table 3 of the HCS's Regulations such as benzene, hexane and toluene (which were evident during this study), the employer must ensure that biological monitoring/medical surveillance is carried out and that the exposure must be controlled. (HCS, 1995).

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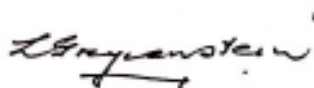
ANNEXURES

Certificate for english language editing:

CERTIFICATE FOR ENGLISH LANGUAGE EDITING

This is to certify that the mini-dissertation written by Ms. G. Adams

Has been English Language edited by Prof. L.A. Greyvenstein.



PROF. LESLEY ANN GREYVENSTEIN

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