Improved Retrospective Exposure Assessment of Dust and Selected Dust Constituents in the Norwegian Silicon Carbide Industry from 1913 to 2005

Dissertation for the degree of
Philosophiae Doctor

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2. Summary

Aims

The main purpose of the study was to assess and characterize the exposure to dust and selected dust constituents in the Norwegian silicon carbide industry from 1913 to 2005 and construct a retrospective job-exposure matrix for use in epidemiological studies. The dust constituents were selected based on their known or suspected lung carcinogenicity and presence in the SiC industry.

Materials and methods

An exposure assessment based on repeated random personal sampling within a priori defined job groups was performed in the three Norwegian silicon carbide plants in 2001-2003. Total dust was sampled in parallel with respirable dust or fiber. Total dust and respirable dust was analysed gravimetrically and fibers were counted by phase contrast microscopy. The respirable dust was analysed for the content of quartz, cristobalite and silicon carbide by X-ray diffractometry. To characterize the morphology and chemical composition of the fibers, additional samples were analysed using a scanning electron microscope. Information on tasks performed and other possible determinants of exposure was collected and linear mixed effect models were used to identify predictors of reduced or increased exposure.

Exposure measurements and information on process and technological changes for the retrospective exposure estimation were obtained from available sources. As the majority of exposure measurements were of total dust, these were used as the basis for the retrospective exposure assessment. Linear regression models were developed to estimate total dust exposure for the time periods with exposure measurements (1967-2005). The exposure estimates were extrapolated backwards to periods without total dust measurements by applying multiplicators for relative changes in exposure due to process related changes and changes in working hours. The parallel sampling from the current study enabled us to construct linear mixed effect models to estimate the content of respirable dust, fiber, quartz, cristobalite and silicon carbide in total dust for the job groups and plants. These models were then applied to the total dust JEM. The performance of the models was evaluated with available historical exposure measurements of crystalline silica and fibers. PAH exposure was assessed semi-quantitatively and asbestos qualitatively.

Results

The fiber characterization in the furnace department showed that the silicon carbide fibers could be divided into eight groups based on morphology, in addition to cleavage fragments of silicon carbide. More than 90 % of the fibers in the furnace department were silicon carbide fibers, with less than two percent of cleavage fragments. In the processing department 82 % were silicon carbide fibers, of which cleavage fragments constituted 57 %. Exposure to sulphur dioxide, fiber, quartz and cristobalite was mainly restricted to job groups in the furnace department. Exposure to silicon carbide and total dust was significantly higher in the processing department than in the furnace and maintenance departments. The cleaner operator, charger and charger/mix operators were generally the highest exposed job groups in the furnace department, and the refinery crusher operator was the highest exposed job group in the processing department.

More than 3300 historical total dust exposure measurements were available from 1967-2005 and the current study added another 702 total dust measurements. The linear regression models of total dust described historical exposure best in the furnace department (R^2_{adj} = 0.49-0.74). Models in the other departments explained less variance (R^2_{adj} = 0.12-0.32). Exposure determinants and total dust exposure explained a substantial portion of the between- (70-100 %) and within-worker (8.0-54 %) variance in the mixed-effect models. The relative bias between the available historical dust measurements and the estimated exposure to dust components varied between -39 % (fiber) and 40 % (quartz). However corrections were not considered necessary due to limitations in the historical data. The $r_{Pearson}$ correlation coefficient for the exposure estimates were below 0.7 for all pairs with the exception of total dust and respirable dust ($r_{Pearson}$ = 0.84) and total dust and cristobalite ($r_{Pearson}$ = 0.72).

Job group was a strong determinant of exposure for all agents, explaining between 43-74 % of the between-worker variance. Determinants associated with increased exposure in the furnace department were performing the sorting of the crude silicon carbide inside the furnace hall, and the tasks cleaning, assisting in assembling and filling of furnaces and manual sorting. Filling and changing pallet boxes were important tasks related to increased exposure to total dust, respirable dust and silicon carbide in the processing department. Work in control rooms, laboratories, fresh air ventilated crane cabins, offices and maintenance outside the furnace hall and processing department were predictors of decreased dusts exposure. For maintenance workers, increased exposure to

fiber was associated with maintenance in the furnace department and increased exposure to SiC was related to maintenance in the processing department.

Conclusion

Workers in the silicon carbide industry are exposed to a mixture of several agents, including silicon carbide fibers, quartz, cristobalite, non-fibrous SiC and sulphur dioxide. The current exposure levels are generally below the current Norwegian OELs, however, high exposure to fibers and respirable dust still occur in the furnace department.

The increased number of total dust measurements and the comparative exposure study using parallel sampling of total dust, fibers and respirable dust with consecutive statistical modeling, made it possible to develop a new and improved JEM. Uncertainties remain in the exposure estimates, especially earlier than 1967 and for certain job groups without exposure measurements. The component specific metrices were sufficient different from each other to be used in component specific epidemiolocial analysis with the exception of total dust and respirable dust and total dust and cristobalite.

Job group was a strong determinant of exposure for all agents. Several tasks were associated with increased exposure, indicating possibilities for exposure control measures. Recommendations for exposure reduction based on this study are to (1) separate the sorting area from the furnace hall, (2) minimize manual work on furnaces and in the sorting process, (3) use remote controlled sanders/grinders with ventilated cabins, (4) use closed systems for filling pallet boxes, and (5) improve cleaning procedures by using methods that minimize dust generation.

3. Preface

The first Norwegian silicon carbide production plant started production in 1913 and was followed by two other plants in the 1960ies. Silicosis was a well known disease among miners, and silica dust was identified as the cause of silicosis already in the 1860ies [1]. The disease was until the 1940ies considered very rare in Norway despite industrial use of quartz. The first examination for silicosis in the Norwegian silicon carbide industry was performed in 1938 when the 32 workers with highest quartz exposure were X-rayed and no cases of silicosis observed [2]. However after the local general practitioner Andreas Samuelsen diagnosed a few cases of silicosis in 1940, a new examination was performed in cooperation with the labour inspectorate in 1941. At this time the radiograms of 91 workers were read by the inspectorate's consultant who found 42 affected cases, seven of these serious. He also re-examined the films from 1938 and found signs of silicosis in 18, four of these of grade III [2]. Preventive measures were then taken and affected workers were offered dust free work or retirement [2, 3]. The discovery of the many cases of silicosis, and the different interpretation of the radiograms lead to anxiety, agitation and distrust among the workers, and several workers resigned due to the fear of contracting silicosis. The plant was put under German administration in 1942, and due to Germany's need for silicon carbide, workers were now not allowed to resign from service unless they had been diagnosed with silicosis [2]. The plant was however closed down due a successful sabotage operation by the Linge Company (a British special operations executive group originally named Norwegian Independent Company 1, that performed commando raids in Norway during World War II [4]) on the 20th of November 1943, and did not start operating again until 1947. An examination of all the 222 workers in the plant during the years 1941-1947 resulted in 49 workers with pneumoconiotic changes, however pulmonary changes did also occur among workers that according to their occupational history only had been exposed to silicon carbide dust [3]. The author stated that the investigation indicated that many of these cases could be attributed to a considerable exposure to dust during the first years of operation, before adequate ventilation and exhaust had been installed, and that it now seemed that the risk of pneumoconiosis was virtually eliminated [3].

The Norwegian Cancer Registry and Arendal Smelteverk (now Saint-Gobain Ceramic Materials Arendal) initiated in 1983 an epidemiological study in the Norwegian

plants. The study was initiated in response to a report by the American Conference of Governmental Industrial Hygienists stating that the dust from the silicon carbide industry might be carcinogenic [5]. An increased risk of lung and lip cancer was found, but the study lacked information about exposure levels and recommended to perform epidemiological studies that included exposure estimates. The Cancer Registry of Norway performed a new study in 1999 where exposure data was included. The study revealed an excess incidence of lung and total cancer and increased mortality for workers in the Norwegian silicon carbide industry [6, 7]. This increased incidence was associated with cumulative dust exposure, however due to few exposure data and high correlation between the constituents in the dust, it was not possible to identify which constituent(s) that could explain this increased incidence. The results lead to an initiative from the Norwegian government to investigate these findings further. The Confederation of Norwegian Enterprise addressed the National Institute of Occupational Health with the proposal for a project that could identify the components of the dust that were responsible for the increased incidence. The project was financed by the Confederation of Norwegian Enterprise, the Research Council of Norway, the Ministry of Labour and Social Inclusion and the Norwegian Silicon Carbide industry. Project start was in 2001.

4. List of papers

The thesis is based on the following publications:

Paper I

Asbjørn Skogstad, Solveig Føreland, Erik Bye and Wijnand Eduard

Airborne Fibres in the Norwegian Silicon Carbide Industry.

Ann Occup Hyg. 2006;50(3):231-40

Paper II

Solveig Føreland, Erik Bye, Berit Bakke and Wijnand Eduard

Exposure to Fibres, Crystalline Silica, Silicon Carbide and Sulphur Dioxide in the Norwegian Silicon Carbide Industry.

Ann Occup Hyg. 2008;52(5):317-36

Paper III

Solveig Føreland, Merete Drevvatne Bugge, Berit Bakke, Erik Bye and Wijnand Eduard

A novel strategy for retrospective exposure assessment in the Norwegian silicon carbide industry

J Occup Environ Hyg. 2012;9(4):230-41

Paper IV

Solveig Føreland, Berit Bakke, Roel Vermeulen, Erik Bye and Wijnand Eduard

Determinants of Dust Exposure in the Norwegian Silicon Carbide Industry

Ann Occup Hyg. 2012 (submitted)

5. Abbreviations

AM	Arithmetic mean
ANOVA	Analysis of variance
AIC	Akaike information criterion
BW	Between-worker
d_{ae}	Particle aerodynamic diameter
GM	Geometric mean
GSD	Geometric standard deviation
JEM	Job-exposure matrix
LOD	Limit of detection
LOQ	Limit of quantification
MLE	Maximum likelihood estimation
NIOH	National Institute of Occupational Health
NP	Non-parametric
OEL	Occupational exposure limit
PAH	Polycyclic aromatic hydrocarbons
REML	Restricted maximum likelihood
SD	Standard deviation
SEM	Scanning electron microscopy
SiC	Silicon carbide
WW	Within-worker

6. Introduction

6.1. Silicon carbide

Silicon carbide (SiC) is a crystalline material composed of carbon and silicon that occurs in nature as the rare mineral moissanite found in meteoric rocks in Arizona and is also a common component in stardust [8, 9]. Dr. Edward Goodrich Acheson has been credited as being the first to produce synthetic silicon carbide, and the furnace used to produce SiC is named Acheson furnace after him [9]. He founded the Caborundum Company in 1891 and the production process that was patented by Acheson is in principle the same as is being used today. Silicon carbide has a tetrahedral crystal lattice with strong bonds between the carbon and silicon atoms and is one of the hardest synthetic materials. It is also brittle and crushes into very sharp grains. The most important area of application historically has been as abrasive grains and in cutting tools. Silicon carbide has a decomposition temperature of around 2825 °C, has high thermal conductivity and low thermal expansion, resists chemical and mechanical wear and is therefore used as construction and refractory materials and in composite armour [9]. It is also used as resistance heating elements for electric furnaces. SiC is a semiconductor and is being used in the semiconductor voltaic industry. Low quality SiC which is poorly crystallized is used as a silicon and carbon source for the metallurgic industry. The newest areas of applications are in diesel particle filters and in the wire saw used to produce silicon photovoltaic cells.

Silicon carbide production

The silicon carbide production process is shown in Figure 1. The raw materials are quartz (SiO_2) and petroleum coke (carbon source) that are mixed together according to weight. Used uncrystallized or poorly crystallized furnace mix may be recycled back into the mix of raw materials, and aluminium oxide might be added. Some factories use sawdust in the furnace mix to increase porosity. The Acheson furnace consists of a permanent electrode in each end and removable concrete side wall elements. The SiC production starts with assembling of the side elements and filling the furnace with furnace mix with a graphite core in the middle connecting the electrodes (Figure 2).

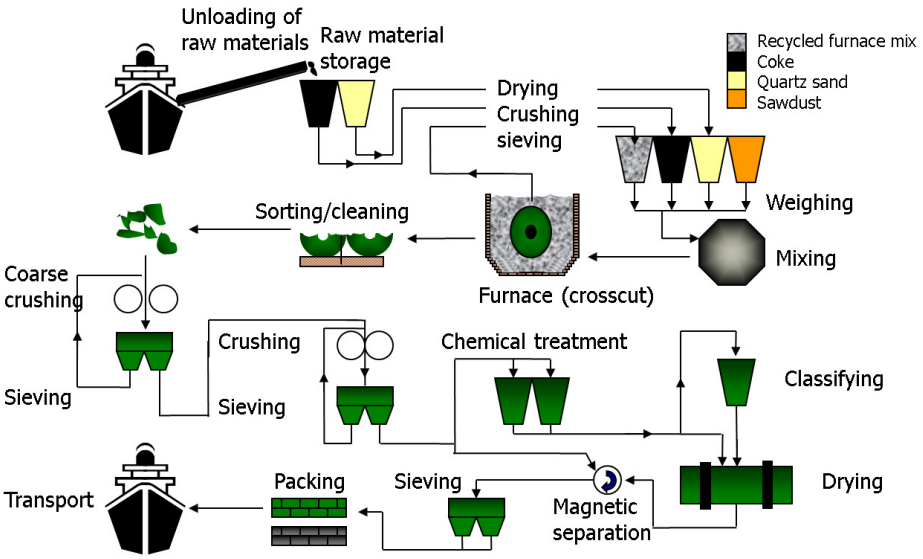

Figure 1. The silicon carbide production process, modified after Raaness *et al.* (1984) [10]

When electricity runs through the graphite core, the core functions as a resistance element and creates heat up to 3000 °C in the core. The heat in the furnace decreases with distance to the core. When quartz is heated it first dissociates into silicon monoxide gas and oxygen. The silicon monoxide gas then reacts with oxygen and carbon and forms silicon carbide and carbon monoxide.

Dissociation of SiO_2:

$$SiO_2 \rightarrow SiO + ½\ O_2$$

Reaction with coke:

$$SiO + ½\ O_2 + 3C \rightarrow SiC + 2CO$$

Total reaction:

$$SiO_2 + 3\ C \rightarrow SiC + 2\ CO$$

Due to its acute toxicity the carbon monoxide is ignited to oxidize it to carbon dioxide. SiC has two major crystalline forms, α-SiC that is hexagonal and β-SiC that is cubic. β-SiC is formed at 1520 °C and is formed first when carbon reacts with silicon oxide in the furnace, α-SiC is formed at temperatures greater than 1700 °C and is the wanted product

in the SiC industry. α-SiC is therefore found closest to the core, β-SiC and partly crystallized material further from the core and unreacted material at the perifery. After 40-48 hours the electricity is turned off, and the furnace is left to cool before being disassembled in stages. The disassembly includes moving the side elements, removing unreacted and poorly crystallized furnace mix, and transporting the crude SiC to the sorting area. The furnaces are organized in groups with 4-6 furnaces. The furnaces in a group will be in different stages of the furnace cycle, i.e. assembled and filled, heating, cooling or being emptied and disassembled.

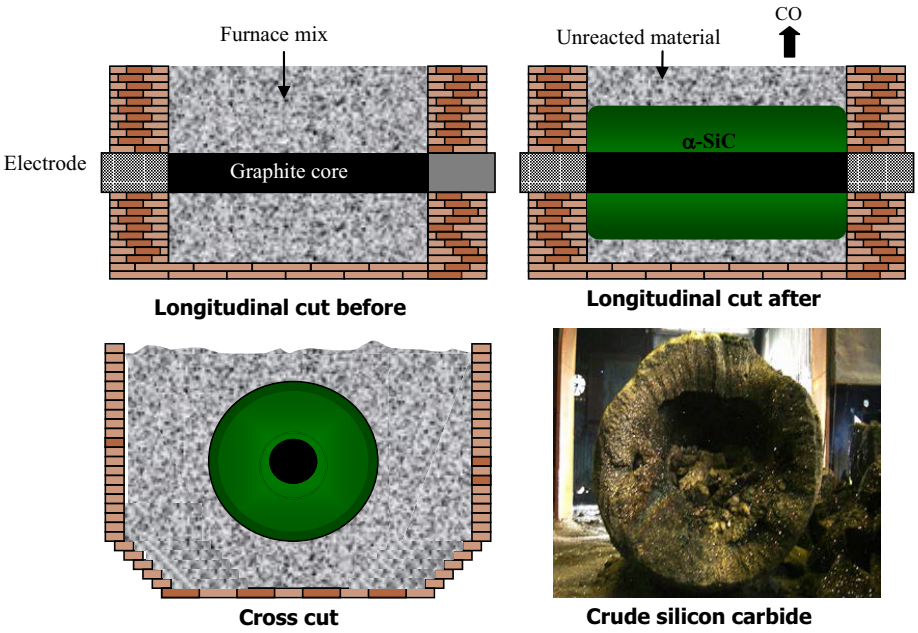

Figure 2. The Acheson furnace and the crude silicon carbide product

The crude SiC is transported from the furnace to the sorting area in big lumps by overhead cranes or pay-loaders. At the sorting areas a jack-hammer is used to divide the lumps into smaller parts. The outermost layer of the crude silicon carbide consisting of partly crystalized material and β-SiC, and is removed from α-SiC by handheld or machine controlled grinders and used in metallurgic industry or recycled into the furnace mix. α-SiC (hereafter referred to as SiC) is crushed and transported to the refinery.

In the refinery SiC is crushed further and sieved. It also treated chemically with pine oil, sulphuric acid and sodium hydroxide to remove silicon dioxide and carbon. Magnetic separation is used to remove metallic impurities mostly due to the wearing and

tearing of SiC on machinery and other metal parts. The products are grains which are separated and packed according to particle size and shape, with products ranging from 1 μm till 880 μm, and sold for further processing elsewhere.

Silicon carbide production in Norway

SiC production is energy intensive and Norway with its access to hydroelectric power was seen as an ideal place to start production. The production in Norway started with one plant in 1913. Two other plants started production in 1963 and 1965. The production was closed down during part of World War 2 due to a sabotage action. The production process in the furnace department has been relatively unchanged. The improvements in occupational hygiene conditions has thus mainly been achieved by reducing exposures by less manual work and less time spent in exposed areas, and by more work from control rooms, and ventilated cabins. The production development has been in the processing department. Historically the major abrasive products contained particles with a mean grain size larger than 45μm. Recently new technology has made it possible to produce finer grain fractions and the majority of SiC products have now mean grains sizes ranging from 45 μm to less than 1 μm. The plants have also started to import crude silicon carbide from other countries in addition to the crude silicon carbide produced in the furnace plant. This is partly due to current high prices of electricity in Norway, and low limits for emissions to the environment, especially of sulphur dioxide and dust.

Exposure and health effects

The production of silicon carbide generates several airborne contaminants and silicon carbide workers are not only exposed to the raw materials quartz and petroleum coke and the product, silicon carbide. The high temperatures in the furnace will transform some of the quartz into cristobalite [11, 12]. The petroleum coke contains sulphur impurities that are oxidized to sulphur dioxide in the furnace [13, 14]. Both gaseous and particulate PAHs are emitted from the petroleum coke when heated in the furnace [11, 14, 15]. Carbon monoxide is formed as a by-product in the furnace [14]. The occurrence of airborne SiC fibers during production of SiC was first reported in 1985 and later confirmed by several studies [12, 16, 17]. A characterization of these fibres showed that they have mainly cubic β-SiC crystal structure and they accumulated in the outermost layer of the crude SiC [18].

Crystalline silica (i.e. quartz and cristobalite) and PAH are classified as carcinogenic to humans [19, 20], and silicosis, lung cancer and pulmonary tuberculosis are associated with occupational exposure to quartz dust [21]. Silicon carbide fibres (whiskers) have shown carcinogenic properties in cell culture and animal experiments [22-25]. Experimental studies have shown that non-fibrous silicon carbide particles have low toxicity [26-28]. Some studies have indicated that silicon carbide dust may contribute to pneumoconiosis although this may be due to the presence of silicon carbide fibres in the dust [3, 29-31]. Sulphur dioxide is an irritating gas, and studies have shown that high short-term occupational exposures have lead to bronchial hyperactivity [32, 33]. The effect of chronic exposure to sulphur dioxide on the lungs has been a subject of controversy where some studies have found an association between lung impairment and occupational sulphur dioxide exposure and others have not [34-38]. The health effects of carbon monoxide are mainly related to the formation of carboxyhemoglobin, which impairs the oxygen carrying capacity of the blood [39]. Possible health risks related to the production of SiC has been discussed since Winslow et. al. [40] reported an increased risk of tuberculosis among silicon carbide workers. Silicosis was first diagnosed among workers in the Norwegian SiC plants in the 1940s [2, 3]. More recently increased risks for lung cancer and other lung diseases and decline in lung function were reported among workers in the Norwegian silicon carbide industry [6, 7, 41-43]. Studies of SiC workers from other countries have also found increased risks for lung cancer and decline in lung function [13, 34, 44].

6.2. Quantitative exposure assessment for epidemiological studies

Occupational exposure assessment is important for several purposes e.g. risk assessment, compliance, epidemiological studies, source identification and identifying determinants of exposure. The strategy used in the exposure assessment will depend on the goal of the assessment but important steps in the exposure assessment process are to collect descriptive data, identify the hazard to be evaluated, form exposure groups, select the exposure metric and estimate the exposure as described in detail by Stewart and Stenzel (2000) [45]. The exposure assessment process is subject to error which can influence the results in subsequent epidemiological studies. The error is assumed to be non-differential, i.e. does not vary according to the health outcome, when the exposure is measured or assessed without knowing the health outcome for the person for which

exposure is being measured or assessed. The measurement error in numerical variables can be systematic (values are consistently high or consistently low compared to the expected value due to e.g. calibration error in the sampling equipment) or random (some values are underestimated and some overestimated, but the mean error is zero). If the systematic errors results in over-estimation of exposure, a decreased risk estimate will be the result, while under-estimation of exposure will give increased risk estimates.

An exposure assessment strategy can either focus on the individual worker or a group of workers. A strategy focusing on individual workers instead of groups of workers is time consuming, often inefficient and expensive as every worker has to be sampled on several occasions during a period of time. It can however be feasible when studying short-term effects of exposure e.g. cross-shift changes [46, 47]. The individual sampling strategy is primarily subject to a classical type of measurement error where the average of many replicate measurements of same true exposure would equal the true exposure [48]. Classical errors reduces study power and bias the regression coefficients towards zero and the association is described as attenuated [48]. The development of exposure groups is an important part of the exposure assessment process in most epidemiological studies. The intention is then to group subjects with similar exposures together so that the within group variance is low and the between group variance is high and hence the contrast between groups is high. Contrast in exposure levels between exposed groups is a requirement for detection of any exposure response relationship in an epidemiological analysis [49]. The grouping of workers with similar exposure is often based on common factors related to the work environment e.g. process, job-title, task or location. A random sample of workers within the group is selected for exposure measurements. The grouping sampling strategy is mainly subject to a Berkson type of random error where the same mean exposure is used for all subjects within the group and the true individual exposures vary randomly about this mean exposure [48]. Berkson type of error will also reduce study power, but will not lead to bias in linear regression coefficients, and little or no bias in logistic or log-linear regression coefficients [48].

Workers within the same department performing the same tasks in the same working environment can have considerable differences in average exposure levels (between-worker (BW) variance) and experience varying exposure concentrations from day-to-day (within-worker (WW) variance) [50]. Repeated measurements on the same worker make it possible to distinguish the BW and WW components of variance. Information on the BW and WW variance can be used for measurement strategies, in risk

assessment, in epidemiological studies and when identifying determinants of exposure. The sampling campaign should be spread out in time to cover seasonal and process changes and the days should be selected at random. However, selecting the days at random can be impractical in many cases, and the measurements are therefore often conducted during one or a few campaigns lasting a few days. Campaign sampling can still lead to valid inferences if the full range of activities giving rise to exposure is covered during the campaign [51].

In addition to exposure measurements, the sampling should also include collecting information on possible determinants of exposure. The identification of determinants of exposure aims at describing factors in the workplace that are associated with reduced or elevated exposure levels. The factors may include task [52-58], season and metrological conditions [54-56, 59-61], ventilation [55, 58, 60, 62], work practices [59, 61, 63], type of material and equipment used [57, 60, 61, 63, 64] and other work environment characteristics [57, 60, 61, 63, 65]. Determinants are important to identify priorities for reducing exposure and thereby reducing health risks. Determinants of exposure like task and production parameters can be used as an aid in the grouping process for epidemiological studies [66-68].

6.3. Qualitative and semi-quantitative exposure assessment

When exposure measurements can not be performed and there are none or few exposure measurements available, qualitative or semi-quantitative measures of exposure have to be used. Measurement error associated with categorical exposure variables (e.g. exposed versus non-exposed or high, medium or low exposed) are termed misclassification i.e. study subjects may be classified incorrectly, and will reduce the study power [48]. Dependent measurement error arises when the probability of a subjects misclassification on one variable (e.g. the exposure) depends on whether the subject was misclassified on a second variable (e.g. the disease) [69, 70]. Non-differential and independent error always biases the effect measure towards the null value when the exposure is measured on a dichotomous scale (exposed versus non-exposed) [48]. When there are more than two groups (polytomous scale), non-differential error biases downward estimates of trend across ordered groups, but comparisons between specific categories can be biased in either direction [48]. Non-differential and dependent misclassification can result in a falsely inflated association between exposure and outcome [69, 70].

Exposure experts have frequently been asked to estimate exposures for studies and time periods were measurements are limited or lacking. The expert-based methods are often not explicitly described and holds little opportunity for others to validate and reproduce the exposure estimation process [71]. As the inter-rater agreement has been shown to be poor in some studies [72, 73], using a panel of experts and consensus meetings has been recommended [72-74]. It is important that the experts are provided with detailed information about the workplace and become familiar with the jobs and exposures to be able to assess the exposure levels. An alternative to expert based exposure assessment is self-assessed which is widely used in community based case-control studies. In these studies several thousand jobs might have to be assessed, and expert based assessment will be extremely labour intensive. Recall bias in self reported exposure for subjects with disease is a concern in case-control studies, especially in cases where there have been a public awareness of the harmful effect of a particular exposure [75-77]. Recall bias occurs when recall of prior exposures is misclassified differentially for those with and without disease. The ability of subjects to accurately assess exposure varies with the agent of interest, and detailed and specific task based questions can improve the assessment [78, 79]. Bias from dependent errors can be a concern in studies providing data on both exposure and outcome from questionnaires. The basic source of dependent error is usually normal variation in certain personality traits, and can be eliminated by breaking the bond between information on exposure and outcome by gathering these data from separate sources [69, 70]. Methods to improve the expert and self-assessment procedure by making it more structured and less prone to subjectiveness, and more reproducible and more transparent has been developed [78, 80].

Surrogate measures as exposed yes/no, employment data, qualitative or semi-quantitative exposure data have been used in studies that have been able to find exposure-response relationships [73, 81, 82]. However, as pointed out by Stewart et. al. 1996 [71], there are several reasons that quantitative exposure assessment are more important today than earlier. One important reason is that the relative risks arising from exposures of concern today might be smaller than risks for exposures evaluated historically and the mechanism of disease might not be well understood and as straight forward as simply accumulated exposure over a subject's life time.

6.4. Retrospective exposure assessment

Retrospective exposure assessment is a reconstruction of historical exposure. It is an essential part of occupational epidemiology when studying risk factors with long latency time where prospective studies are not feasible or when studying processes or exposures no longer existing. Retrospective exposure assessment is a complicated and time consuming process that can be characterized as detective work where the aim is to find as much relevant information as possible on factors related to exposure for the process and time period studied. The available information is then used to construct exposure estimates for the component(s) and workers in question. The exposure assessment process depends on the type of study (e.g. community-based case-control studies or industry specific cohort studies) and the available data, and often involves a combination of different approaches.

Exposure estimates based on exposure measurements are commonly regarded as the "gold standard" however that relies on the nature, quality and quantity of the measurement data available. Factors like the type of aerosol samplers used, sampling strategy used and the use of area samples instead of personal samples can complicate the exposure assessment. When there are few or no exposure measurements, qualitative or semi-quantitative methods has to be used to estimate the exposure.

Exposure measurements of aerosols are performed using aerosol samplers. The first aerosol samplers were developed in the 1920-30ies, and sampling equipment and analytical methods have been further developed since then. There has been a rising concern during the last decades of the importance of using a metric for exposure measurements based on the site of deposition in the airways. The first internationally recognized recommendation of a definition of respirable aerosol, the so called Johannesburg convention was published as early as 1959 [83]. This aerosol fraction describes the particles that are expected to penetrate to the alveoli. A respirable particle was defined by a curve with a 50 % particle penetration at particle aerodynamic diameter (d_{ae}) of 5.0 µm. Other criteria have been published since, but by the late 1990ies general agreement had been achieved on a set of particle size-selective criteria for health-related aerosol exposure assessment at the workplace: the inhalable fraction, the thoracic fraction and the respirable fraction [84]. The respirable fraction is now defined as having a 50 % particle penetration at d_{ae} 4.0 µm instead of 5.0 µm. A number of different sampling heads have been developed to match the criteria, and have been used in different time periods.

Conversion methods are often needed in retrospective assessments of aerosol exposure to be able to convert measurements into the same metric when different sampling heads are used. Historical exposure measurements made with old sampling equipment, often only applicable for static measurements and with short sampling time, can be difficult to relate to modern sampling methods [84, 85]. The conversion from particle count analysis to gravimetric analysis is a particular challenge since particle counts are dominated by small particles whereas the particle mass is mainly determined by large particles. Measurements based on particle counting and gravimetric analysis are therefore expected to be poorly correlated. Conversion factors should preferably be derived from personal side-by-side sampling in the work place or industry in question as the particle size distribution in the work atmosphere may influence the sampling efficiency of different sampling heads differently.

Other factors complicating the use of historical exposure measurements are biased sampling strategies such as compliance based, task-specific sampling, worst-case sampling, and lacking data on the sampling strategy. Some studies have shown that a compliance based sampling strategy can result in overestimation of exposure probably caused by sampling concentrated on higher exposed tasks and not on a random selection of workers [86, 87]. Other studies have found that the sampling strategy was not a significant determinant of exposure after adjusting for other factors that might influence exposure levels [65, 88, 89].

Performing area measurements frequently on set locations have been a common sampling strategy in several industries, for long time periods. Personal exposure measurements are considered to be more representative of human exposure and risk than area measurements [85]. Area samples usually underestimate personal exposure, can in many cases not be easily linked to a specific job, and ignores worker-machine interactions [90]. A study from the European rubber industry found that personal measurements of inhalable dust were on average 2-4 times higher than stationary measurements in all but one country where the number of personal measurements was very limited [89]. Area measurements of formaldehyde in the reconstituted wood panel industry on the other hand were consistently higher than personal measurements [86]. In other instances no significant differences have been found between area and personal measurements [68]. Area measurements have been utilized in conjunction with personal exposure measurements and determinants of exposure to predict time trends where personal exposure measurements are few [91-93].

Measurements may be lacking for some agents, job groups and/or time periods. A current exposure assessment can be performed to increase the number of measurements available, to perform concurrent measurements of several agents, and to be able to estimate the exposure for job groups with few or lacking measurements if they still exists [88, 93-96]. The exposure estimates can be based on time spent in different areas compared to job groups with known exposure working in the same or similar area [88, 97, 98], with job groups performing similar tasks [88, 98, 99] or with stationary measurements [92, 100]. Measurements are often sparse in the earliest time of operation for a plant, and backwards extrapolation of the exposure estimates is then necessary. The backwards extrapolation can be adjusted by factors accounting for changes in the production, equipment, ventilation etc. The adjustment factors can be based on expert assessment [80, 88, 94, 97], simulation of working conditions and/or tasks [94, 95, 99, 101, 102] use of physiochemical models [80, 94], measurements of other agents [93, 96] or comparison with similar changes in other studies [94].

Use of statistical models to predict historical exposure

Statistical models like regression models and linear mixed effect models have been used as an objective tool to predict historical exposure in many studies where there has been a substantial number of exposure measurements available [65, 91, 92, 103-107]. Statistical models have the ability to borrow information to predict exposure levels for circumstances (e.g. job groups or years) where no or few measurements are available [97]. Determinants of exposure can be included as covariates in the statistical model to improve the models prediction abilities [65, 87, 92, 104]. Regression models incorporate covariates as fixed effects and makes the assumption that all measurements are independent. However, when the data contain e.g. repeated measurements on the same worker, this assumption is violated. Linear mixed effect models are able to incorporate such data using both fixed and random effects, and are therefore routinely used in exposure estimation [86, 87, 89, 97, 106]. An effect is classified as fixed effect when inferences are to be restricted to the levels that occur in the sample [106]. Normally covariates are introduced as a fixed effect into the models when the focus is on estimating the mean value for specified groups/levels represented in the data. When inferences are to be drawn to a population of all possible levels, the effects are considered to be random [106]. Random effects are used for controlling for lack of independence unaccounted for by other variables in the model [105, 106]. The worker can be treated as a random effect to control for correlation

between repeated measurements on the same worker and both within-worker (day to day variability) and between-worker variance components can then be accounted for. Random effects resulting from variation between workers and from variation within workers have been recognized for a long time, but several studies have also examined random effects for job groups, buildings, machines, rigs, plants, region/country and sampling campaigns [86, 87, 106, 108]. The mixed effect models will only provide exposure estimates for covariates offered as fixed effects in the model, for random effects only the variance estimates are provided. However, empirical Bayes estimates of exposure can be calculated for the random effects [105].

Bayesian statistical methods has gained popularity in occupational hygiene decision analysis due to its ability to combine exposure measurements with expert judgement or other sources of information, and is regarded to be most useful when the number of exposure measurements is small [109]. The Bayesian methods are based on the concepts of prior, likelihood and posterior distribution. In retrospective exposure assessment the prior can represent elements like the plant working conditions over its operating history, experts judgement and physical models of the exposure behaviour, that are updated using measurement data to form a posterior distribution of the parameters [110]. Bayesian methods have been used in a few retrospective exposure assessment studies [111, 112]. An alternative to the full Bayesian framework is to combine priori exposure intensity ratings from independently developed JEMS with exposure measurements in mixed models, a method that has been used in large population based studies [108, 113].

Occupational exposure measurements data are most often best described by a log-normal distribution and needs to be log-transformed prior to statistical modelling when using models that assume normally distributed data. When regression coefficients from log-transformed data are back-transformed, the resulting estimate is the GM. However, AM is considered to be the best summary statistics for estimating cumulative exposure [114]. In order to convert GM to AM an estimate of the variance is required. Different variance estimates can be used for different jobs and/or time periods, or a single estimate based on data least likely to be effected by error can be used on all jobs and time periods [97, 103]. When an accurate estimate of the GSD cannot be derived from the data, a value of 2.7 may be reasonably assumed [115].

Evaluation of statistical models and exposure estimates

An important step in retrospective exposure model development is evaluation of the performance of statistical models and the reliability and robustness of the exposure estimates [104, 116]. Internal evaluation of the performance of the models have been done by splitting the database randomly into a dataset used to create statistical exposure models and a dataset to evaluate the performance of these models. The two datasets can then be combined to derive final estimates of the model parameters [89, 91]. External evaluation on the other hand use measurements not used to develop the statistical models to evaluate the performance of the models. The external data can be from the same plants [92, 93, 117], from the same operation in a different country [118] or from similar plant(s) [104, 119]. The exposure estimates predicted by the statistical models have also been compared to those of an expert panel [104], to the exposure measurements used to create the model [89] or to model estimates bootstrapped 1000 times [86]. To assess the robustness of estimates from the statistical models, alternative models of exposure estimates can be explored. In a study of historical diesel exhaust exposure in underground mining two alternative sets of time trend models were explored [92]. Andersson et al (2011) created mixed models for respirable quartz exposure for different time periods for the Swedish iron foundries [117]. The mixed models for different time periods showed systematic changes in concentration levels, implying that extrapolation of exposure estimates outside the range of years covered by measurements may result in under- or overestimation of exposure.

Bias (average difference between predicted and observed exposure) and precision (standard deviation of the differences) can be used to compare estimates derived from different sources [120]. Predicted values should also be inspected to see if they are inside a range of possible exposure levels [104]. Pronounced variation in the exposure estimate from one year to another should be documented and explained to be accepted as plausible [121].

6.5. Measurements below the limit of detection

Measurements below the limit of detection (LOD) are commonly encountered in occupational exposure assessments, and the proportion of non-detectable samples appears to be increasing as the exposures in occupational environments are decreasing [122, 123]. Laboratories normally report measurement data below the LOD as not detected or <LOD

and this leads to left-censored data which are a challenge when performing statistical analysis.

The LOD for an analytical procedure is the lowest concentration of the analyst that can be distinguished with reasonable confidence from a field blank (often 3*SD of field blanks) [124]. Also some laboratories report results using a higher threshold called limit of quantitation (LOQ), practical quantitation limit or determination limit arguing that the analytt can be determined with a reasonable degree of precision only when present in levels above such a limit (often 10*SD of field blanks) [124]. Measurements below the LOQ are normally reported as <LOQ or the values of the measurements are reported with a remark [125].

There are different strategies to solve the problem of left-censored data (data with measurements <LOD/<LOQ), and they are commonly grouped into four main categories: substitution methods, regression on order methods (ROS), maximum likelihood estimation methods (MLE) and non-parametric methods (NP). One additional method is to use all values, even those below LOD. Several studies using either real, simulated or generated data have evaluated the different methods to handle censored data, but none of the methods have been shown to be superior to the others [122, 123, 126-128]. All methods have pros and cons depending on the dataset (e.g. number of measurements, degree of censoring, distribution and single or multiple LODs) and the statistics to be computed. When the percentage of censoring is too large, none of the methods will perform to a satisfactory degree [123, 125].

The substitution methods have been very popular since they are the easiest to perform and can handle multiple LODs. Each sample below the LOD is simply replaced by the chosen substitute and conventional statistical analyses can then be performed on the revised dataset. The missing values are normally replaced by zero [123], LOD [65, 123], LOD/√2 [86, 97, 122, 123] or LOD/2 [93, 122]. Substitution methods have been shown to perform poorly compared other methods on several occasions, and can result in substantial bias when the proportion of censored data is large [122, 123, 126, 128-130]. Especially substituting with 0 or LOD is disregarded in general, and substituting by LOD/√2 or LOD/2 when the proportion of measurements <LOD are more than 5-10 % [123, 128, 131].

The practice of laboratories to report measurement data below the LOD and/or LOQ as not detected or <LOD or <LOQ leads to censored data and a loss of information since censored data contain less information than data for which numbers are reported

even if some of the numbers are very imprecise [132]. All measurements are subjected to random error which contributes to the uncertainty of the result. It is, however, widely recognized that precision in an analytical system varies with analyte concentration, with higher relative precision for higher concentrations. The use of observed values even though they are below the limit of detection have been argued for by several authors [124, 132-135]. However, due to the high relative error and therefore low precision of these measurements, they are not considered useful by others [123, 136]. A limitation of the use of all values is that zero, negative, and unreadable measurements are possible, since if the constituent of interest is not present, one would expect negative values to occur as often as positive [123, 132]. Non-positive values can not be log-transformed; however, a solution could be to add a large constant (c) to all measurements to transform them to positive values (ln(y+c)). The fact that measurements below the limit of detection are not necessarily exclusively positive values was one of the reasons that this method was not recommended in the study by Antweiler and Taylor (2008) [123]. Another limitation is that most laboratories do not report the observed values that are below the detection limit, and it might be difficult to get hold of the observed values, in particular for historical data. Several publications have advocated a change in the laboratory report practise, so that the values below LOD are reported [124, 133, 134, 137].

Several statistical methods, e.g. linear mixed models, require explicit values for measurements below LOD (a dataset with values for all measurements both below and above LOD), and there has until recently been a lack of easy available alternatives to substitution of values below LOD to create complete dataset for censored data. MLE based multiple imputations of measurements <LOD can be used to create datasets with imputed values for measurements below LOD [128, 130, 138]. The MLE methods rely on knowing the distribution of the data. [128]. A value between 0 and LOD are imputed for each measurement below LOD assuming that the all measurements arise from the same distribution. The imputed datasets can then be used in further statistical analyses. It is, however, important to recognize that the imputed value does not represent a true value. By repeating the imputation and combining the results based on the imputed samples guarantees that the final results do not depend on a specific set of imputed values. The number of imputations needed to get a valid result depends on the proportion of measurements that has to be imputed. Based on relative efficiency, between 3-5 imputations has been recommended unless the proportion of data missing is great [139]. In simulation studies the regression coefficients have been shown to be essentially unbiased

with 3-5 imputations, even with up to 90 % missing data, but the statistical power decrease and the standard error and p-values increase with increased number of samples below LOD and decreased number of imputations [139].

6.6. Previous retrospective exposure assessment in the Norwegian silicon carbide industry

A previous study in the Norwegian SiC industry constructed a job-exposure matrix to assess the morbidity and mortality from cancer and other lung diseases [6, 7]. The study was based on historical exposure measurements and information on process changes and changes in work pattern. They had access to 4200 Watson thermal precipitator samples (short-term samples analyzed as particles/cm^3 air), 2062 gravimetric analyzed total dust samples, 216 short term fiber samples, 200 measurements of crystalline silica (quartz and cristobalite) and a few respirable dust samples. The content of SiC particles was estimated by subtracting the mass of crystalline silica from the mass of inorganic material. The arithmetic mean of total dust was calculated for periods with more than five gravimetric personal total dust measurements. The precipitator measurements were used together with changes in work patterns to indicate relative changes in exposure for the period 1950-1974. For the production period prior to 1950 the exposure was assigned on basis of changes in work pattern and process technology. The proportion of crystalline silica, SiC fibers and SiC particles in total dust was assumed to be constant in time with a few exceptions in the mix department. Because of a lack of measurements for maintenance workers, they were assigned percentages of the average exposure for workers in the furnace and process department based on estimates of the amount of time they spent in these departments. Exposure to asbestos was assigned qualitatively as exposed/unexposed. They found an excess incidence of lung and total cancer and increased mortality for workers in the Norwegian silicon carbide industry. However, due to strong correlation between the different exposures, they were not been able to identify the components most important for the increased mortality and morbidity. The uncertainties in the exposure assessment was highest for the fibres, crystalline silica and silicon carbide exposure due to the limited number of measurements available, and they suggested that a better characterization of the dust might enable a identification of the component(s) that is/are most important.

7. Aim

The main purpose of this study was to construct an improved retrospective JEM for selected dust constituents in the Norwegian SiC industry including known and suspected lung carcinogens, to be used in updated epidemiologic studies.

This investigation was based on an existing JEM [6], refined through comprehensive exposure assessment in the Norwegian silicon carbide industry in the period 2001 – 2003, and recollection of information on historical exposure. The complete exposure assessment was performed for the years from 1913 to 2005.

To realize the aim we have:

1) Estimated the retrospective exposure to total dust based on statistical modelling of exposure measurements.
2) Developed a model to estimate the content of fiber, quartz, cristobalite, silicon carbide and respirable dust in total dust.
3) Estimated the retrospective exposure to PAH and asbestos semi-quantitatively
4) Summarized the retrospective exposure estimates a JEM that is used in epidemiological studies addressing mortality, cancer risk and lung function reduction.

As a further result of this study, exposure determinants was identified which can be used to implement control measures to reduce future exposure.

8. Materials and methods

8.1. Comparative exposure assessment and characterization

Sampling methods

The sampling for fibre characterization was performed in 2001 (Paper I), and the sampling of total dust, respirable dust, fibre and sulphur dioxide in 2002 and 2003 (Paper II and IV). Total dust was sampled in parallel with fibre or respirable dust, see Figure 3. The sampling strategy was based on random personal sampling within job groups in all three plants. Total dust samples were collected using 37-mm closed faced aerosol filter cassette. Respirable dust was collected using cyclones. Total dust and respirable dust particle mass was measured gravimetrically. The quartz, cristobalite and crystalline silicon carbide contents of the respirable dust were measured by X-ray diffraction. Fibers were collected on filters mounted in open-face aerosol filter cassettes made of conducting polypropylene and were analysed by scanning electron microscopy (Paper I) or counted with a light microscope (Paper II and IV). Sulphur dioxide was measured with a direct-reading electrochemical sensor with a data-logging facility.

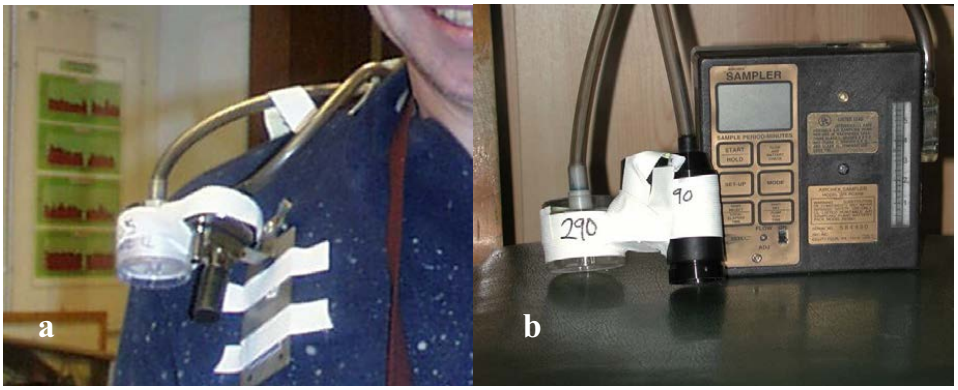

Figure 3. Parallell sampling of (a) total dust and respirable dust and (b) total dust and fibre

Data analysis

The fiber proportion data (Paper I) were transformed by the function arcsine prior to statistical analysis. Kolmogorov-Smirnov test was used to analyse the distribution of the fibre dimensions. Kruskal-Wallis test and subsequent Mann-Whitney test were used to compare the size distributions of the SiC fibre types. Analysis of variance (ANOVA) was

performed with plant as grouping variable and multiple regressions were applied with job group, plant and production parameters as independent variables on the fibre proportion data.

Cumulative probability plots showed that the exposure data in Paper II-IV were best described by lognormal distributions and the exposure data were log-transformed for statistical analysis. Standard measurements of central tendency and distributions were calculated (AM, SD, GM, GSD and 95th percentile). The significance of differences in exposure levels among the job groups and plants was evaluated using post hoc tests with Bonferroni adjustments in Paper II. Variance components and contrast between groups and workers were computed for the comparative study (Appendix I).

8.2. Retrospective exposure assessment

Developing exposure estimates (Paper III)

Historical exposure measurements and information on process and technological changes were obtained from company records, the Norwegian Labor Inspectorate records, studies performed by the National Institute of Occupational Health (NIOH) in Norway, plant personnel and from the paper describing the previous JEM [6]. As the majority of exposure measurements were total dust, total dust measurements were used as the basis for the retrospective exposure assessment. Only personal exposure measurements with a sampling time of more than four hours and were included in the exposure assessment process. Outliers were excluded based on z-scores and qualitative judgement. The estimates were developed following these steps:

1. Multiple linear regression models were developed to estimate total dust exposure estimates within the period with exposure measurements, one model for each department within each plant.
2. Exposure estimates in plant A were extrapolated backwards to periods without total dust measurements, by applying multiplicators for relative changes in exposure dependent on information on process related changes and working hour, resulting in a JEM with log-transformed total dust exposure estimates by year and job group from when the plants started operation to 2005.
3. The comparative data with parallel samples of total dust with fibre and respirable dust analysed for content of quartz, cristobalite and crystalline silicon carbide were used to develop mixed models with total dust and job group as a fixed effects. This

enabled us to estimate the exposure of these constituents from total dust exposure measurements.

4. The mixed models were then applied to the total dust JEM giving log-transformed estimates of the retrospective exposure to respirable dust, quartz, cristobalite, silicon carbide and fibre.
5. The resulting log-transformed estimates of total dust, respirable dust, fibre, quart, cristobalite and silicon carbide were converted to AM using the equation AM=exp(log-transformed estimate + $0.5*\sigma^2$).
6. The quartz and cristobalite exposure for job groups in the processing and maintenance department were calculated as a percentage of the respirable dust exposure in the comparative study due to a large proportion of measurements below LOD.
7. PAH exposure was categorized by four semi-quantitative exposure scores based on the available measurements.
8. Asbestos exposure was assigned qualitatively as exposed/non-exposed in relevant years due to lack of exposure measurements.

Evaluation of the exposure estimates:

The reliability of the total dust linear regression models were evaluated by a split-sample evaluation using a random 10 % of the measurements. A sensitivity analysis was performed to examine the effect of the magnitude of the process related adjustment factors, using different adjustment factors. The resulting exposure estimates for quarts, cristobalite and fibre were compared with the available historical exposure measurements using relative bias.

8.3. Determinants of current exposure

Collection of information on determinants of current exposure

Information on potential determinants of exposure was collected together with the exposure measurements during the exposure assessment in 2002 and 2003 (Paper IV). The workers provided information about type and duration of tasks performed during sampling by filling out plant and department specific forms. The industrial hygienist performed walk through surveys of the premises and recorded information such as type of equipment used and organization of work. The foremean in the furnace and processing departments filled out a form on each shift when sampling was performed providing

information on department specific production parameters. Table 1 provides a summary of the determinants explored.

Statistical modelling

To account for the correlation between the repeated measurements, linear mixed effect models were used with exposure as the dependent variable. Possible determinants of exposure were treated as fixed effects, whereas worker was treated as a random effect. Variables with p-values<0.2 in univariate models were included in multivariate analysis. Multivariate models were built forward stepwise starting with the variable with lowest p-value in the univariate models. Akaike's information criterion (AIC) was used to determine the optimal combination of exposure determinants in the model. Variables were kept in the multivariate model if they improved the fit of the model. Tasks were modelled as dichotomous variable (task performed yes/no). To quantify the contribution of the fixed effects to the between-worker (BW) and within-worker (WW) variance components, values of the variance components obtained under the mixed effect model were compared with those from a mixed effect model without the fixed effects. Separate models were constructed for total dust, respirable dust, quartz, cristobalite, SiC and fibres.

Table 1 Determinants of current exposure were modelled on three levels, general, department and job group

	Level		
	General	Department	Job group
Data	All measurements	Measurements from one department	Measurements from one job group*
Determinants	Plant, department, job group and season	Plant, job group, season, shift and department specific parameters	Shift, task and location of sorting area

* Charger, mix and charger/mix operators were combined into one job group (charger/mix)

8.4. Measurements below the limit of detection

Values below the LOD were treated as follows: In paper II readable values below the LOD (i.e. fibers counted or a positive identification of a peak in the 2Θ region for quartz,

cristobalite or silicon carbide) were used unchanged in calculations, and non-readable values (i.e. fiber samples with zero fiber count and the crystalline samples with no peak identified) were replaced by the lowest readable value divided by √2 [133, 140]. In paper III and IV: A multiple imputation approach based on maximum-likelihood estimation and a log-normal distribution was conducted to assign values to samples below LOD [128].

A comparison of the two methods to handle measurements below LOD was performed in a subanalyse in Appendix II. The same linear mixed models of determinants of exposure were computed on two datasets only differing in how measurements below LOD were handled.

9. Summary of results

9.1. Current exposure assessment

The fibre characterisation in the furnace department showed that the silicon carbide fibres could be divided into eight groups based on morphology in addition to cleavage fragments of silicon carbide (Figure 4). The different morphologies were also manifested by different diameter distributions. Cleavage fragments are fragments of silicon carbide with size characteristics of fibers, but that probably originate from cleavage of non-fibrous SiC crystals. These were most frequently found in samples of the sorting operators and of job groups in the processing department. 93 % of the fibres in the furnace department were silicon carbide fibres, with the K4 category being most common. The other fibre types found were carbon fibres, silicon oxide fibres, silicon fibres, man-made vitreous fibers and vanadium rich fibres (Figure 5). Samples from the processing department showed that 25 % of the fibres were silicon carbide fibres, 57 % were cleavage fragments and organic fibres constituted 17 %. GM length of all fibres with length>5 μm was 9.5 μm with a range of 5.0–900 μm and GM diameter of all SiC fibres was 0.39 μm and ranged from the detection limit of the SEM of 0.07 to 2.90 μm. The proportions of the different SiC fibre categories differed between plants, job groups and production parameters.

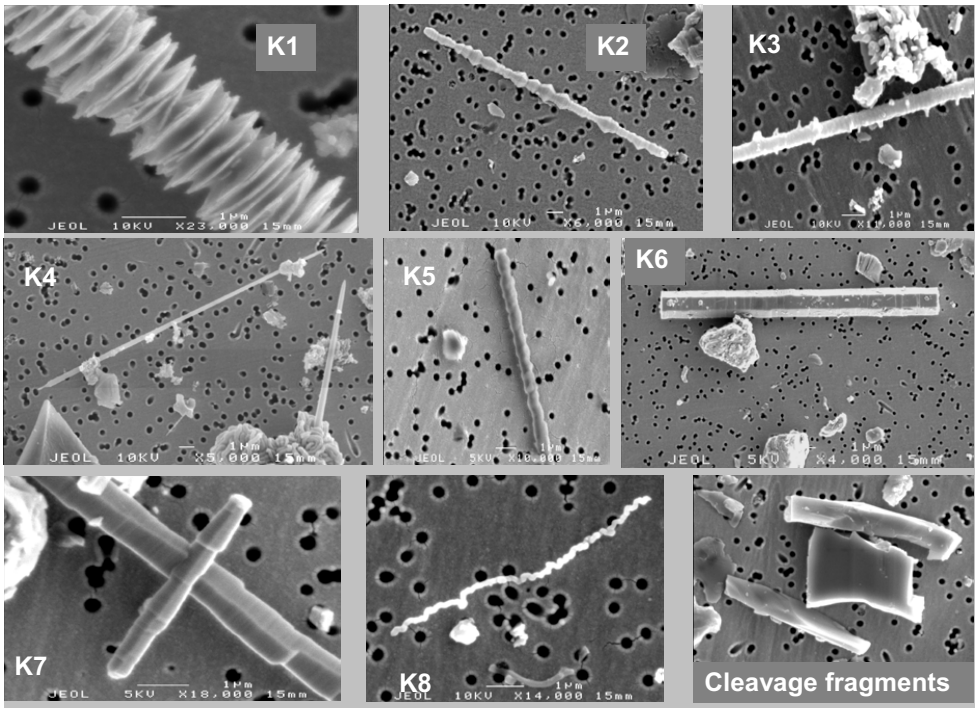

Figure 4. SEM images of the eight different SiC fibre categories, K1-K8 and SiC cleavage fragments. Scale bars represent 1 µm. In courtesy of Asbjørn Skogstad, NIOH, Norway.

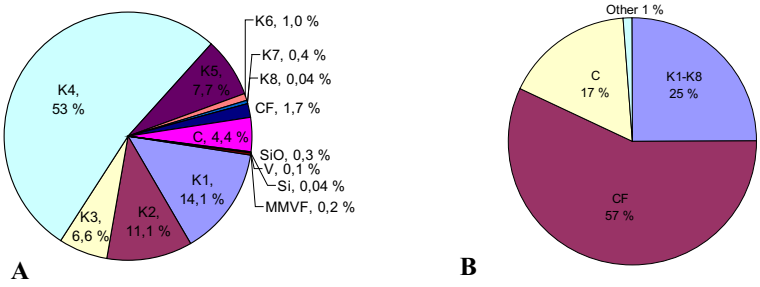

Figure 5. Proportions of SiC fibre categories and other fibre types in the furnace (A) and processing (B) department. K1-K8 are SiC fibre categories, CF are SiC cleavage fragments, SiO are silicon oxide fibres, V are vanadium rich fibres, Si are silicon fibres and MMVF are man-made vitreous fibres

The sorting operators from all plants, control room and cleaning operators in Plant A and charger, charger/mix and pay loader operators in Plant C had the highest exposure to fiber (Figure 6). The cleaner operators in Plant A had the highest GM exposure to respirable quartz (20 μg m^{-3}). The charger/mix operators in Plant C had the highest GM exposure to respirable cristobalite (38 μg m^{-3}) and the refinery crusher operators in Plant A had the highest GM exposure to non-fibrous SiC (0.65 mg m^{-3}) (Figure 7). Exposure to crystalline silica and non-fibrous SiC was generally low and between 0.4 and 2.1 % of the measurements exceeded the OELs. The cleaner operators in Plant A had the highest GM exposure to respirable dust (1.3 mg m^{-3}) and total dust (21 mg m^{-3}) (Figure 8 and Figure 9). GM exposures for respirable dust above the Norwegian SiC industry-specific OEL of 0.5 mg m^{-3} were also found for refinery crusher operators in all plants and mix, charger, charger/mix and sorting operators in Plant C. Only 4 % of the total dust measurements exceeded the OEL for nuisance dust of (10 mg m^{-3}). Exposure to sulphur dioxide was generally low. However, peaks in the range of 10–100 ppm were observed for control room and crane operators in Plants A and B and for charger and charger/mix operators in Plant C. The grouping of workers into job groups reduced the between-worker variance and resulted in higher contrast between groups than having plant or department as grouping variable (Appendix I).

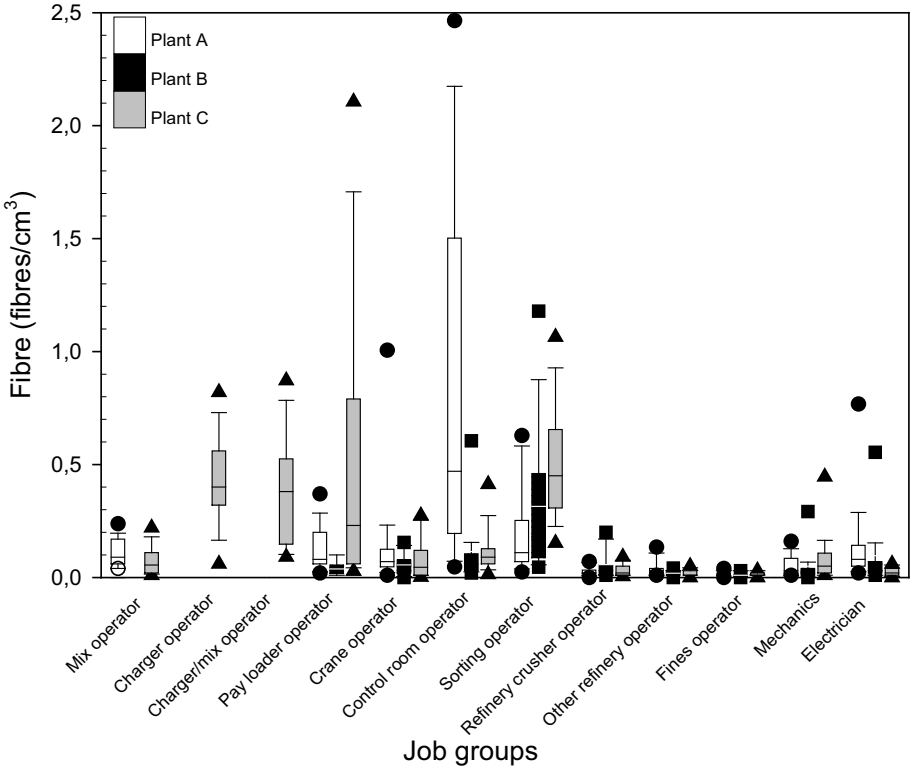

Figure 6. Box plot of fiber exposure in fibres/cm^3 for job groups in Plants A, B and C. The exposure for the cleaning operator is not included due to too few exposure measurements. The box bounds the 25th and 75th percentiles, encompassing 50 % of the data and includes the median (solid line within the box). Dispersion above and below this range is marked by whiskers that extend to the 10th and 90th percentiles. Points above or below the whiskers represents the 95th and 5th percentiles.

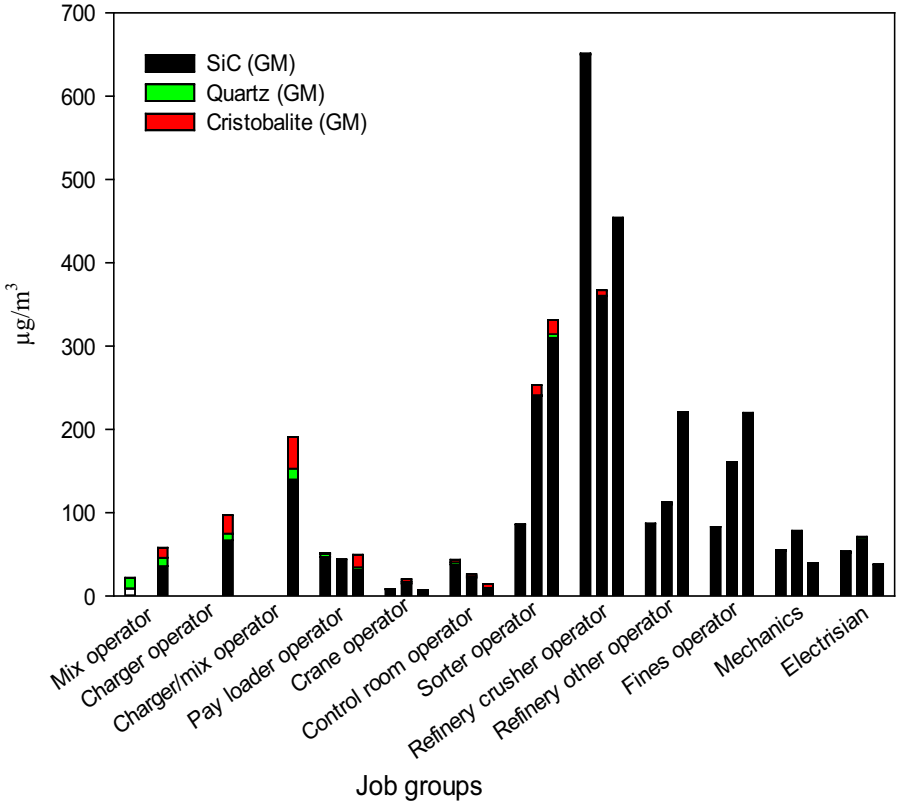

Figure 7. Graphic comparison of the geometric mean silicon carbide, quartz and cristobalite exposure levels in µg/m^3 for job groups in Plants A, B and C.

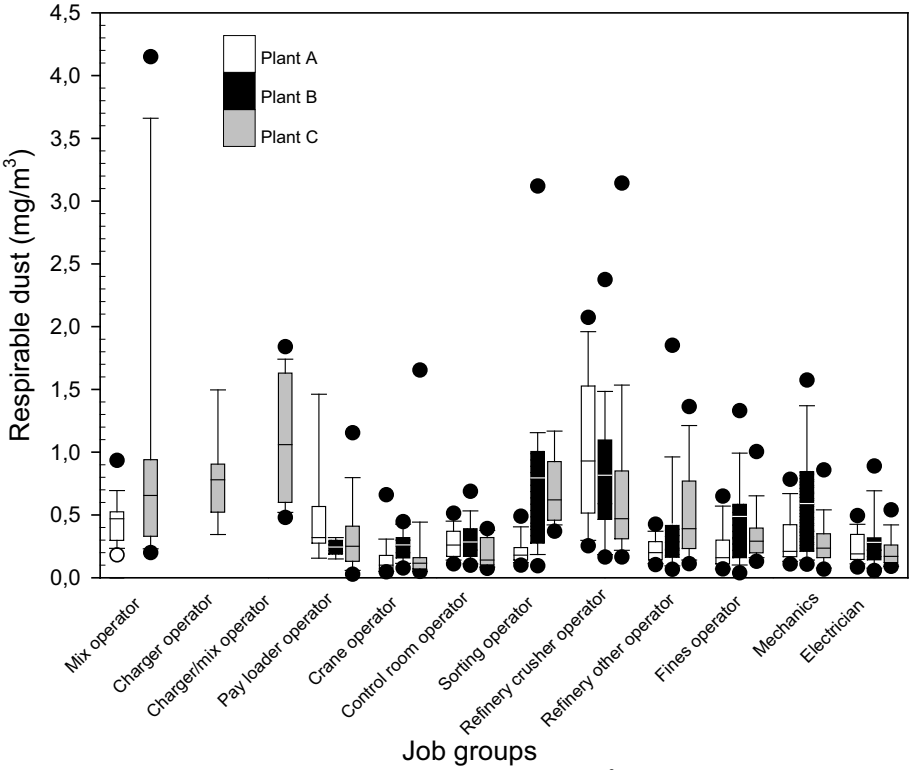

Figure 8. Box plot of respirable dust exposure in mg/m^3 for job groups in Plants A, B and C. The description of the box plot is the same as in Figure 6.

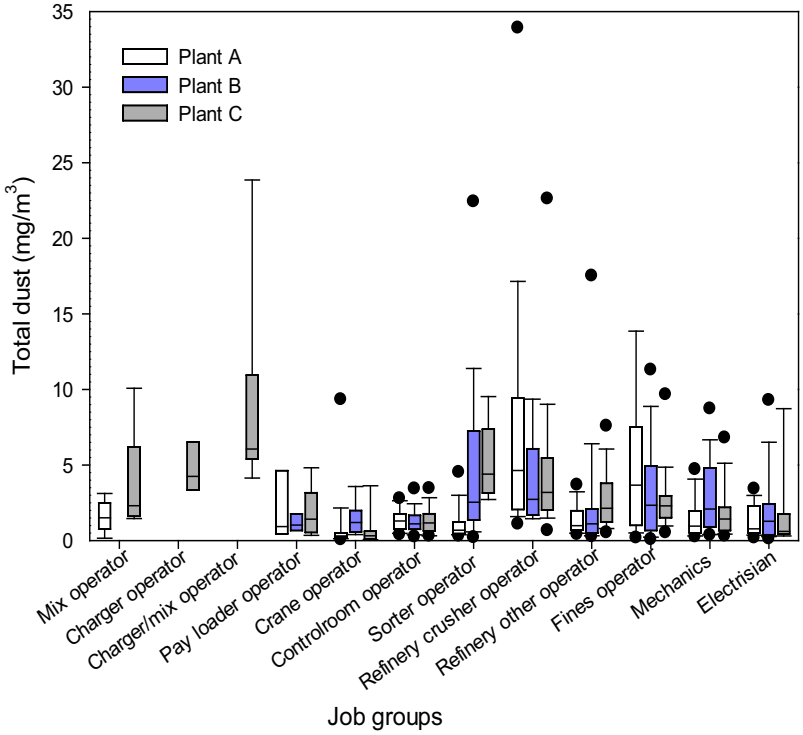

Figure 9. Box plot of total dust exposure in mg/m^3 for job groups in Plants A, B and C. The description of the box plot is the same as in Figure 6.

9.2. Retrospective exposure assessment

The data collection process resulted in a substantial number of total dust measurements, Figure 10 gives an overview over the personal and stationary total dust measurements in Plants A, B and C respectively. As much as 72 % of the samples were personal measurements. After excluding measurements due to stationary sampling, small sampling time and outliers, and including total dust measurements from the comparative study, a total of 4047 total dust measurements were available for construction of regression models covering the years 1967-2005. The regression models explained a substantial portion of the variance in the furnace department (R^2_{adj} ranging from 0.47-0.74). The explained variance was less in the processing department (R^2_{adj} ranging from 0.27-0.32) and maintenance department (R^2_{adj} ranging from 0.12-0.30). Job group was a significant determinant of exposure in the models, explaining on average 44 % of the

variance (ranging from 5-75 %). The evaluation of the regression models by remodelling without 10 % of the measurements (split-sample evaluation) resulted in similar exposure estimates as the estimates from the full model. The mean relative bias was 0.76 %, ranging from -12 % to 12 %. The sensitivity analysis for the backward extrapolation of total dust measurements applying different multiplicators, resulted in highly correlated exposure estimates ($r_{Pearson}$ = 0.96). The regression models generally predicted a reduction in exposure over time as illustrated for two job groups in Figure 11.

In addition to the total dust measurements, more than 4100 particle count data from thermal precipitator samples were available from the years 1942-1973 as a job groups AM for a year or 10-year period. The number of measurements included in the AM was only known for 54 % of the data, and varied from 1 to 89 measurements. A flaw in the in the analytic process prior to 1951 resulted in that only measurements from 1951 to 1973 could be used. No clear trends could be ween on the plots of particle counts over time, except for high exposure estimates in the earliest years for two job groups that were confirmed by information on process related changes. Particle counts are dominated by small particles whereas the particle mass is mainly determined by large particles. Measurements based on particle counting and gravimetry are therefore expected to be poorly correlated. Due to the uncertainty in the particle count data, these data were omitted from the study and information on process realted changes and working hours were instead used to indicate relative changes in exposure in the time period without total dust exposure measurements.

Total dust exposure and job group explained between 70-100 % of the BW variance and 8.0-54 % of the WW variance in the linear mixed effect models of the constituents of the dust. Regression coefficients of total dust were all lower than one, indicating that the content of agents that were quantified in the respirable dust decreased with increasing exposure levels of total dust. The estimated fibre concentration were generally lower and estimated quartz and cristobalite concentration were generally higher than existing historical measurements, but the relative bias (-39 % (fiber), 1% (cristobalite) and 40% (quartz)), were comparable to results from other studies. The $r_{Pearson}$ correlation coefficient between the exposure estimates for the agents were less than 0.70 for all but total dust and respirable dust (0.84) and total dust and cristobalite (0.72).

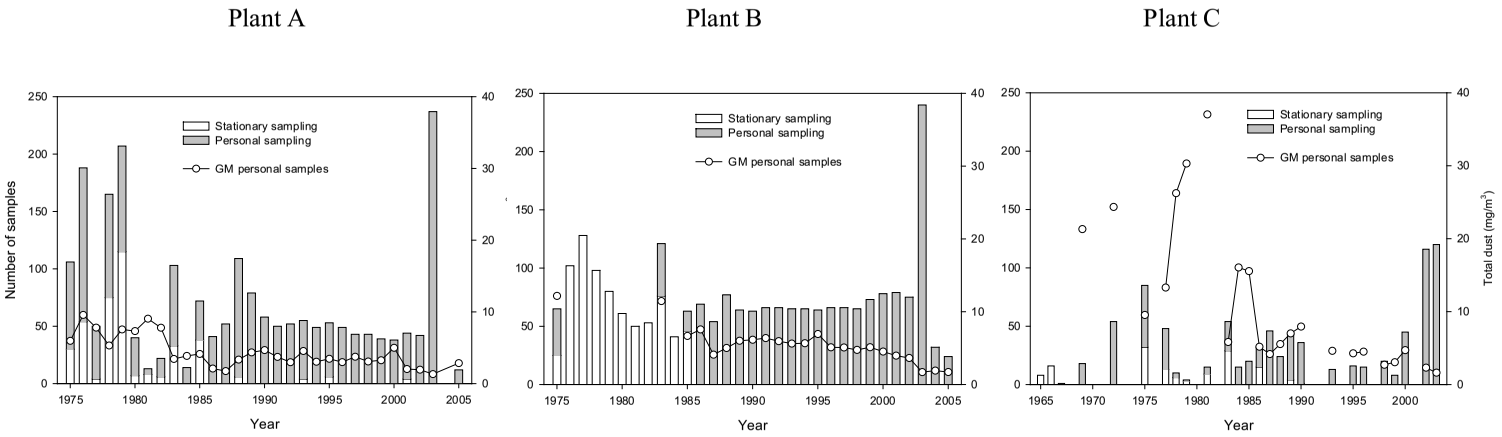

Figure 10. Geometric mean total dust exposure and number of measurements by year for plant A, plant B and plant C.

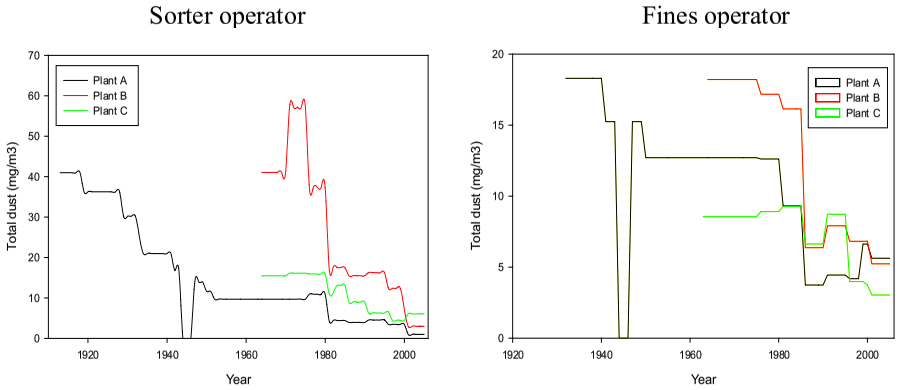

Figure 11. Estimated arithmetic mean total dust exposure from 1912-2005 for sorter and fines operators.

9.3. Determinants of current exposure

Plant was a poor predictor of exposure explained less than 5 % of the between-worker (BW) variance. Department was a major predictor of SiC and fiber exposure (38-70 % of the BW variance explained), but a poor predictor of total and respirable dust exposure (< 10 % of the BW variance explained). Work in the furnace department was associated with the highest exposure to fibers, quartz and cristobalite, while work in the processing department was associated with the highest SiC, total and respirable dust exposure. Job group was a strong determinant of exposure for all agents, explaining 43-74 % of the BW variance. Working night shift was a determinant of lower exposure to most agents in the furnace department and for total dust in the processing department. Having the sorting area inside the furnace hall was a predictor of increased exposure. Several tasks were identified as predictors of exposure. Assisting with assembling and filling of the furnaces resulted in 1.9-8.0 fold increased exposure for the charger and mix operator. Cleaning lead to a 1.3-6.2 fold increase in exposure for operators in the furnace department, but a decreased exposure for other refinery workers. Filling of pallet boxes with SiC resulted in a 1.6-2.7 fold increased exposure for operators in the refinery and changing of pallet boxes resulted in 1.5-2.4 fold increased exposure for fines operators. Maintenance in the furnace hall resulted in a 3.9-4.8 fold increase in fiber exposure, and maintenance in the processing department resulted in a 1.7-2.1 fold increase in exposure to SiC. Work in control rooms, laboratories, fresh air ventilated crane cabins, offices and maintenance outside the furnace hall and processing department were predictors of decreased dusts exposure by 26-86 %.

The sub-analyze using the dataset from Paper II found that with the exception of pay loader operator (cristobalite and SiC) and control room operator (cristobalite), the same tasks were significant predictors of exposure (Appendix II).

10. Discussion

The study was initiated as a result of a previous study revealing an excess incidence of lung cancer and total cancer and increased total mortality and mortality of respiratory diseases for workers in the Norwegian silicon carbide industry [6, 7]. This increased incidence was associated with exposure to cumulative dust, however due to limited exposure data and high correlation between the dust constituents, they were not able to identify which component(s) of the dust that could explain this increased incidence. We therefore performed a comparative study to characterise the exposure to selected components in the dust and we investigate the chemical composition and morphology of the airborne fibers. The improved dust characterization was used together with collected historical exposure measurements of total dust and information on changes in work hours and technology and process to construct a new job-exposure matrix covering the years 1913-2005. The comparative study also aimed at identifying possible determinants of exposure.

10.1. Exposure assessment

Sampling strategy

A group based sampling strategy based on a priori defined job groups from job titles and tasks were chosen, as this information was available for the historical exposure measurements. An individual based strategy was not feasible as the historical exposure measurements were mostly without individual identification infomation. Randomly selected workers within the job groups were selected for repeated exposure measurements to be able to assess WW and BW variance. Job group was a strong determinant of exposure for all agents, explaining between 43 and 74 % of the BW variance, and the contrast between groups was much higher when job group was the grouping variable compared to using plant or department as grouping variable. This supports that the grouping performed was successful.

Fiber counting

Fibers are normally counted with a phase contrast light microscope, which does not provide information on the fiber type, and fibers thinner than around 0.25 μm are not visible. A substantial number of fibers present in the working atmosphere in the silicon carbide

industry are therefore not possible to detected with the light microscope. The visibisily limit of scanning electron microscopy (SEM) is around 0.07 μm. However, since a large proportion of fibers were close to this limit, it is likely that a substantial number of fibers remained undetected even with the SEM. This will lead to a underestimation of the fiber exposure for thin fibers. However this measurement error is likely less than for asbestos fibers as asbestos fibers, unlike SiC fibers, tend to split into thinner fibrils of similar length probably resulting in a larger proportion below the LOD of SEM.

Health based particle size fraction

When performing exposure assessment it is important to sample the fraction of the dust that correspond to the part of the lung where one expects that the dust has its toxic effect. Lung cancer and respiratory diseases mainly develop in the alveolar and bronchial region of the lungs and dust reaching these parts of the lung should therefore be sampled. We sampled respirable dust with a cyclone constructed to comply with the respirable convention, and that has shown reasonable compliance with the convention. However, the other dust fraction was sampled with a so called total dust cassette. When comparing the sampling efficiency of the total dust cassette with the inhalable and thoracic penetration curve convention, it lies in-between the inhalable and thoracic curve. [141, 142]. The reason for using the total dust in this case was that it has been used regularly in the Norwegian SiC plants since the 1960ies. We needed parallel measurements with total dust to be able to estimate the exposure to the dust constituents from historical total dust measurements. Ideally we should have sampled the thoracic fraction parallel as well but it was not considered feasible due to economic constrains. The strong correlation between total dust and respirable dust indicates that thoracic dust also would be strongly correlated to total dust and respirable dust making total dust exposure a good proxies of thoracic dust exposure.

The crystalline components of the dust were assessed in the respirable fraction as this was the standard method at the laboratory. If the focus is on alveolar lung diseases like silicosis, the respirable fraction is the correct exposure measure. Lung cancer can however occur in the bronchial as well as in the alveolar region of the lung, and the thoracic fraction could be a better measure of exposure.

Components in the dust not characterized

The exposure assessment was concentrated on known and suspected lung carcinogens that were known to be present in substantial amounts in the SiC industry. Previous studies

have shown that the workers in the silicon carbide industry are exposure to PAH, carbon monoxide, asbestos and organic dust in addition to the components in the dust characterized in the present study. Asbestos is a known lung carcinogen, but due to asbestos being banned from use in the 1980ies, the exposure is no longer present in the plants and could therefore not be assessed in the comparative study. Only 17 exposure measurements of PAH were available, however, the exposure level were low, 2.0 $\mu g/m^3$ or less for personal measurements. It was decided to not include PAH measurements in the comparative study. PAH was assessed semi-quantitatively based on these measurements and asbestos exposure by classification as exposed/non-exposed in the retrospective exposure assessment.

The content of organic dust in the samples could have been estimated in combination with the analysis of the crystalline components. This was unfortunately not performed in the comparative study. Two measurement reports from the plants reported that the organic dust content of total dust in the furnace department was 0-87 % and 2-84 % in the processing department.

The content of various elements was analyzed in total dust from the furnace hall and raw material area in all three plants in 1983, and in the furnace and processing department of plant C in 2001 (Appendix III). The levels of all analyzed elements were very low compared to the OELs.

There has lately been much focus on health effects and exposure to particles in the ultrafine size range (particles less than 100 nm). The sublimation process in the furnace will produce particles in the ultrafine size-range. In addition will use of diesel vehicles inside the furnace hall be a source to ultrafine particles from diesel exhaust particles. Maintenance work can involve hot processes like welding and torch cutting that will lead to exposure to ultrafine particles.

Exposure to sulphur dioxide was assessed in the furnace department using direct reading instrument in the comparative study. Sulphur dioxide is known to be able to cause respiratory symptoms, and it would be preferable to have estimates of the historical sulphur dioxide exposure. The assessment of sulphur dioxide exposure was however not originally planed, and was included just before the start of the exposure assessement. There was therefore no time to design a sampling strategy to be able to assess the retrospective sulphur dioxide exposure. The exposure to carbon monoxide was not assessed due to its mainly acute toxicity not expected to be related to the diseases of interest for the epidemiological study.

10.2. Methodological considerations

Fiber toxicity

SiC fibers used to investigate the toxicological properties are mostly SiC whiskers that are not formed as a byproduct in the Acheson process, but produced by other methods. In paper I we compared the morphology of the SiC whiskers used in *in vivo* test of the carcinogenic potency of fibrous minerals [22, 143] and found that these fibers showed similarities to the material found in the Norwegian plants both with regard to morphology and size distribution.

A recent study comparing the *in vivo* carcinogenicity of SiC whiskers with fiber formed cleavage fragments of SiC (length > 5 μm, diameter < 3 μm and aspect ratio > 1/3 as defined in the WHO fiber criteria), found that the carcinogenic potency was much lower for SiC fragments than for whiskers [28]. They concluded that the main reason for the difference in carcinogenicity was the difference in length and aspect ratio between the cleavage fragments and the whiskers, and that the carcinogenicity was mainly related to fibers longer than 10 μm and thinner than about 1 μm. Results from several studies of the carcinogenicity of fibrous minerals supports the findings of higher carcinogenicity of thinner and longer fibers compared shorter and thicker fibers [22, 143, 144]. By using the WHO definition of fibers the exposure estimates of fibers will be biased if only SiC fibers longer than 10 μm and thinner than 1 μm have carcinogenic properties, which results in biased exposure response relationship.

Respiratory protection

The use of respiratory protection was not accounted for in the exposure estimates. Use of respirators will lead to a lower actual exposure if worn according to specifications, however, the effectiveness of respirators depends on several factors, such as type of respirator used, how well it fits the face, training on proper wearing, actual use in high exposure situations and the efficiency of the mask [145]. Studies of workplace performance of respiratory protective equipment have shown that the effectiveness of respirators can be substantially lower than laboratory performance and thus lower than the nominal protection factor [146]. Some studies have chosen to apply a reduction factor that takes into account the use of respirators [147, 148]. Not adjusting for use of respirators will lead to an overestimation of exposure, especially for the recent years. We had limited information on historical respirator use except that the use of respirators was more frequent in the recent years as use of respirators have

become mandiatory in many areas of the plants. The respirators have also improved during the years, so the exposure estimates will be mostly influenced in the latest years and not so much in the earliest years which probably is most important with regard to the development of cancer.

Model evaluation

An important step in retrospective exposure model development is evaluation of the model [104, 116]. The total dust models in the current study had to be extrapolated back in time to periods without exposure measurements, and the models estimating the content of the constituents of dust in total dust were based on measurements performed during 2002-2003. Andersson *et al.* (2011) created mixed models for respirable quartz exposure for different time periods for the Swedish iron foundries [117]. The mixed models for different time periods showed systematic changes in concentration levels, implying that extrapolation of exposure estimates outside the range of years covered by measurements may result in under- or overestimation of exposure.

To evaluate the performance of our models of the constituents of the dust the quartz, cristobalite and fiber models were evaluated by comparing the model estimates with available historical measurement data. The relative bias between the estimated exposure and the measured exposure varied between -39 % and 40 %. The biases was lower than what was found for the historical model in the iron foundries (between -220 and -140 %) and during asphalt paving (between -70 % and -51 %), but similar to the bias found in saw mills (between -33 % and 2 %) and mines (between -48 % and 20 % for respirable elemental carbon and -25 % to 49 % for CO area) [118, 119, 149]. In the asphalt paving and saw mills studies the measurements used for evaluation were from a different plant or sampling campaign which probably will increase the bias compared to using measurements from the same plants for evaluation. The extrapolation of the total dust estimates could not be evaluated by exposure measurements and it was not considered feasible to conduct experimental studies to assess these factors as has been done to some degree in a few studies [99, 101, 102]. These factors were based on professional judgment only. The robustness was evaluated by applying different adjustment factors which yielded estimates that were highly correlated with the original estimates ($r_{Pearson} = 0.96$).

The total dust regression models were evaluated by split-sample validation using a random 10 % of the measurements. The relative bias of predicted total dust exposure was

between -12 % and 12 %, which is, not surprisingly, substantially lower than the relative bias for the constituent models.

An alternative method were explored for modeling time trend in the total dust models by using splines within the five-year period instead of categorical variables [97], but this approach did not result in major differences in exposure estimates, and it did not improve the fit of the models. Since the original model was divided in so narrow time periods, it is probably limited how much more a spline model can explain. Furthermore, exposure changes may occur step-wise rather than continuously when due to (not anticipated) process changes.

Measurements below the limit of detection

The number of measurements below the LOD was relatively high for fiber, quartz and cristobalite, especially for job groups in the processing and maintenance department. We had access to all values below the LOD and in paper II we choose to use all readable values as long as there was a positive identification in the 2θ region for the crystalline samples or fibres were counted, even if the measurements were below the LOD. Non-readable values were substituted by the lowest readable value/√2 which is the recommended substitution method for data below the LOD that are not highly skrewed [122]. This reduced the number of values that had to be substituted from 72 % to 19 % for cristobalite, 48 % to 9 % for quartz, 31 % to 9 % for fiber and 12 % to 0 % for SiC. The bias due to substitution is therefore probably limited for quartz, fiber and SiC, but the percentage of measurements substituted for cristobalite was higher than prefered. There has been a lack of available alternatives to the substitution and using the readable values methods when performing linear mixed models (MIXED procedure in SAS). However in recent years several papers have been published that presents methods for handling censored data based on MLE when performing non-linear mixed effect modeling (NLMIXED procedure in SAS) or regression modeling (LIFEREG procedure in SAS) [128-130, 150]. MLE based multiple imputation of values <LOD have been use to create datasets for statistical modeling [128, 130, 138]. The MLE methods relay on knowledge of the distribution of the data. As the substitution methods are considered inferior to the other methods, and occupational exposure data often follow a log-normal distribution we chose to use the multiple imputation approach based on MLE and log-normal distribution in paper III and IV [128]. A value between 0 and LOD is imputed for each measurement below LOD assuming that the all measurements arise from the same distribution. The imputed datasets can then be used in further statistical analyses. It is, however, important to recognize that the imputed value does not represent a true value, and by

repeating the imputation process and combining the results from several imputed data sets guarantees that the final result does not depend on a specific set of imputed values. It has earlier been recommended that 3-5 imputations would be sufficient based on relative efficiency. Results from a recent simulation study suggests that regression coefficients are essentially unbiased even with few imputations, but more imputations are needed than predicted by relative efficiency to ensure unbiased estimates of standard errors and p-values for regression coefficients [139]. The number of imputations needed are depended upon the number of measurements below LOD and the sample size [128]. We used nine or ten imputations in our studies, which are more than predicted by relative efficiency, to account for the bias in estimates of standard errors and p-values shown with fewer imputations. The same number of imputations has been used in other recent studies with similar fractions of missing data [128, 138], but 100 imputations was used in a study in the underground non-metal mining facilities with around 40 % missing data [92]. The simulation study recommended between 20 to 100 imputations depending on the proportion of missing data, however that was primarily based on the rate of power falloff for small effect sizes [139]. To evaluate the method of treatment for measurements below LOD a sub-analysis was performed on the final models for determinants on job group level using the dataset with readable values and LOD/√2 substitution from Paper II (Appendix II). These were the models with fewest exposure measurements, and where therefore expected to be most vulnerable to measurements below LOD. It was reassuring to find that with a few exceptions, the same tasks were found to be significant predictors of exposure.

Estimating the arithmetic mean from the geometric mean

The AM is considered to be the best summary statistics for estimating cumulative exposure. However in order to estimate AM from the log-transformed regression coefficients a estimate of the variance is needed [114]. We chose to use the total dust models as a basis for calculating the AM since they include measurements from a wide time period (1967-2005), and include more measurements than the models from the specific components. This will result in more robust variance estimates that are valid for the whole time period. In addition there were a substantial number of measurements with values below LOD for some of the components, in particular quartz, cristobalite and fiber, which will result in variance estimates that are less reliable. A final issue is that the mixed models include total dust as a determinant, and we are worried that this will invalidate the residual variance as an estimate of exposure variability of the dust constituents. A study in the diatomaceous earth industry

also used a variance estimate that was assumed least likely to be affected by error [103]. We believe that the total dust regression models are less likely to be affected by error than the constituent models for the reasons mentioned above. However the variance of dust constituents may deviate from the variance of total dust. Considering the data from the comparative study (Paper II) the median GSD for the job was 2.7 for fiber, 2.9 for quartz, 2.8 for cristobalite, 2.5 for SiC, 2.0 for respirable dust and 2.3 for total dust. Using the variance estimates from the total dust models indicate overestimating of the variance estimates for respirable dust by 10 % and underestimation for the constituents of the dust by 8-25 %.

10.3. Exposure estimates in the improved JEM compared to the previous JEM

The total dust exposure estimates were generally higher in the current JEM than in the previous JEM by Romundstad *et al.* (2001) [6]. The current JEM was based on almost twice as many total dust exposure measurements, a substantial number of these were historical measurements. The increased number of measurements willl lead to more reliable exposure estimates. By applying statistical modelling instead of calculating AM directly from exposure measurements as in the previous study, we were able to adjust for measurement strategy, and to predict exposure levels for job groups and/or years with few available measurements.

The exposure estimates for the constituents of the dust were lower in the current JEM compared to the previous JEM. However, the exposure estimates for crystalline silica in the previous JEM was based on analysis of crystalline silica in total dust, while crystalline silica was analysed in respirable dust in the current study. The content of crystalline silicon carbide was estimated indirectly as the difference between the amount of total dust and the amount of crystalline silica and organic dust in the previous JEM, while it was determined directly in the respirable fraction by X-ray diffraction in the current study [151]. Unless all the crystalline silica and SiC is in the respirable size range, which is unlikely, this will lead to higher exposure estimates for the crystalline components when estimated in total dust instead of respirable dust, and may partly explain the higher estimates in the previous JEM. When the fiber estimates from the statistical models were compared to the existing historical exposure measurements, the relative bias was -39 % indicating that the predictive models underestimated the exposure compared to the exposure measurement. The fiber exposure estimates was also generally higher in the previous JEM. As the historical exposure measurements were the same measurements that were used in the exposure estimation in the previous JEM, it was not surprising that the predicative models underestimated both the actual

exposure measurements and the exposure estimates in the previous JEM. This difference is most likely due to the representative sampling strategy aimed at in the exposure modelling compared to a task-based sampling strategy with short sampling duration for the historical measurements.

10.4. Strengths and limitations of the retrospective study

Strengths of the study

The aim of the study was to construct an improved JEM for the Norwegian silicon carbide industry. The exposure estimates have been improved in several ways. The number of measurements used to construct the total dust exposure estimate was increased from 2062 to 4047, and nine years of exposure estimates was added. The number of measurements was increased for all job groups still existing in the plant, and especially job groups in the maintenance department where few historical measurements were available. The statistical model allowed us to adjust the total dust estimates for measurements performed for compliance reasons.

More than 700 new measurements of each of the constituents of the dust resulted in improved characterization of these, and the parallel sampling with total dust allowed us to construct predictive models of the dust components in total dust. Historically measurements of components of the dust were available to evaluate the performance of some of the predictive models.

The fiber characterization with SEM enabled us to study the morphology and chemical composition of the fibers.

SiC exposure was analysed directly in the respirable dust which had not been performed earlier on measurements from the Norwegian SiC industry.

Semi-quantitative exposure estimates of PAH was based on the few historical exposure measurements available and were added to the job-exposure matrix. Exposure to PAH was not assessed in the previous JEM.

The correlation between the exposure estimates were sufficient different from each other ($r_{Pearson} < 0.7$) to enable component specific epidemiologic analyses with the exception of total dust and respirable dust ($r_{Pearson} = 0.84$) and total dust and cristobalite ($r_{Pearson} = 0.72$).

Limitations of the study

Despite the large number of total dust measurements, the quantitative exposure estimates are uncertain, particularly for the period prior to exposure measurements, and for job groups with few or no measurements. The exposure estimates with the poorest certainty are from 1913 to 1967 due to the lack of quantitative exposure data to assess the accuracy of the exposure adjustment factors that were applied.

Measurements for evaluation of the fiber and crystalline silica models were not available prior to 1980. Most of the historical crystalline silica had been analyzed in the total dust fraction and had to be transformed to the respirable dust fraction prior to validation. The historical fiber measurements were performed using a task based sampling strategy that could lead to biased estimates compared to the representative sampling strategy used in the comparative study. In spite of this differences, the observed bias was not larger than in reported similar studies, and we could at least partly account for these biases.

Asbestos and PAH was estimated qualitatively and semi-quantitatively respectively, and exposure misclassification is therefore a major concern.

Even though the crystalline silica, silicon carbide and fiber content of the dust were analyzed, there is still a large fraction of the dust that is unidentified.

Sulphur dioxide exposure can cause respiratory dieasase, but was not included in the retrospective exposure assessment.

10.5. Determinants of exposure

Job group and department were identified as important determinants of exposure in Paper IV. These were among the few determinants that were also available for the retrospective exposure assessment. Several tasks were identified as predictors of increased or decreased exposure and enabled us to suggest measures for exposure reduction. Having the sorting area inside the furnace hall resulted in increased exposure to all agents for the sorting operator, but not for the other job groups working in the furnace hall. This suggests that the exposure to the general furnace hall athmosphere results in higher exposure for the sorter operator, but the dust created by the sorting process does not affect the other workers in the furnace hall to a great extent. The production specific determinants like production volume and number of furnaces burning were not important determinants of exposures for any of the agents. Production rate has been shown as a predictor of exposure in several studies [59-61, 152]. The production specific parameters in the SiC industy are probably most important for the general

work atmosphere. This suggests that the work performed by the worker is a more important predictor of exposure than parameters influencing the general work athmosphere.

11. Conclusion

The comparative exposure study using parallel sampling of total dust, fibers and respirable dust, the larger number of total dust measurements and the consecutive statistical modeling, made it possible to develop a JEM with improved estimates for total dust and the constituents of the dust. Uncertainties remain in the exposure estimates, especially for the earliest period where no exposure measurements exists, and for certain job groups without exposure measurements. The correlation between the exposure estimates were sufficient different from each other ($r_{Pearson} < 0.7$) to enable component specific epidemiologic analyses with the exception of total dust and respirable dust ($r_{Pearson} = 0.84$) and total dust and cristobalite ($r_{Pearson} = 0.72$).

Workers in the silicon carbide industry are exposed to a mixture of several agents including silicon carbide fibers, quartz, cristobalite, non-fibrous SiC and sulphur dioxide. Exposure levels today are generally below the current Norwegian OELs; however, high exposure to fibers and respirable dust still occurs in the furnace department. Having the sorting area inside the furnace hall and the tasks cleaning, assisting with assembling and filling of furnaces, manual sorting and filling and changing pallet boxes were identified as predictors of increased exposure.

12. Practical implications

The retrospective exposure assessment could not be performed without the large numbers of routine exposure measurements performed by the plants. For epidemiological studies of diseases with long latency time, this kind of data is vital. It is seldom that this kind of exposure data is available for epidemiological studies, and unfortunately the current trend is that the number of exposure measurements performed is declining [85]. The plants are encouraged to continue the routine sampling to enable updated epidemiological studies later in order to evaluate the risks at lower exposure levels.

The plants should implement exposure reduction measures to ensure that the exposure levels are kept below the OELs and as low as possible. Possible exposure reduction measures identified in this study are:

- Separate the sorting area from the furnace hall
- Minimize manual work on furnaces and in the sorting process
- Use remote controlled sanders/grinders with ventilated cabins
- Transfer silicon carbide into pallet boxes in closed systems
- Improve cleaning procedures by using methods that minimize dust generation

The study design and data analysis used in this study can serve as an example for other retrospective exposure assessment studies in other industries.

13. Future perspectives

- Study the short-term health effects of the peak exposure to sulphur dioxide observed in the furnace department.
- Characterize the exposure to ultrafine particles in the SiC industry and compare with the exposure levels and particle size distribution found in other industrial settings.
- Epidemiological studies of respiratory cancer incidence and mortality with updated exposure and health data in order to evaluate the risks at lower exposure levels and the possible role of organic components, sulphur dioxide and ultrafine particles.

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Appendix I

Variance components of current dust exposure

Table I. Variance components of total and respirable dust

Grouping variable	N[a]	Total dust					Respirable dust				
		BG[b]	BW[c]	WW[c]	Contrast[e] group	Contrast[f] worker	BG[b]	BW[c]	WW[c]	Contrast[e] group	Contrast[f] worker
Worker only		NA[g]	0.13	0.13	NA[g]	0.49	NA[g]	0.073	0.084	NA[g]	0.46
Plant	3	0.003	0.12	0.13	0.02	0.49	0.025	0.071	0.084	0.025	0.46
Department	3	0.011	0.12	0.13	0.08	0.47	0.021	0.072	0.084	0.021	0.46
Job group	13	0.055	0.072	0.13	0.43	0.35	0.032	0.041	0.085	0.44	0.32

[a] Number of groups
[b] Between-group variance
[c] Between-worker variance or within group variance
[d] Within-worker variance
[e] Contrast between groups: between-group variance/sum between-and within-group variance
[f] Contrast between workers: BW variance/ BW + WW variance
[g] Not applicable

Table II. Variance components of fiber and silicon carbide

Grouping variable	N[a]	Fiber					SiC				
		BG[b]	BW[c]	WW[c]	Contrast[e] group	Contrast[f] worker	BG[b]	BW[c]	WW[c]	Contrast[e] group	Contrast[f] worker
Worker only		NA[g]	0.27	0.17	NA[g]	0.61	NA[g]	0.29	0.13	NA[g]	0.70
Plant	3	0.023	0.24	0.17	0.086	0.59	0.001	0.29	0.13	0.004	0.70
Department	3	0.17	0.095	0.17	0.64	0.35	0.11	0.18	0.13	0.38	0.59
Job group	13	0.21	0.056	0.17	0.79	0.24	0.22	0.075	0.13	0.74	0.37

[a] Number of groups
[b] Between-group variance
[c] Between-worker variance or within group variance
[d] Within-worker variance
[e] Contrast between groups: between-group variance/sum between-and within-group variance
[f] Contrast between workers: BW variance/ BW + WW worker variance
[g] Not applicable

Table III. Variance components of quartz and cristobalite

		Quartz					Cristobalite				
Grouping variable	N[a]	BG[b]	BW[c]	WW[c]	Contrast[e] group	Contrast[f] worker	BG[b]	BW[c]	WW[c]	Contrast[e] group	Contrast[f] worker
Worker only		NA[g]	0.17	0.32	NA[g]	0.35	NA[g]	0.70	0.32	NA[g]	0.68
Plant	3	0.015	0.16	0.32	0.089	0.33	0.046	0.65	0.32	0.067	0.67
Department	3	0.040	0.13	0.32	0.24	0.29	0.27	0.43	0.32	0.38	0.57
Job group	13	0.085	0.087	0.32	0.50	0.21	0.47	0.23	0.32	0.67	0.42

[a] Number of groups
[b] Between-group variance
[c] Between-worker variance or within group variance
[d] Within-worker variance
[e] Contrast between groups: between-group variance/sum between-and within-group variance
[f] Contrast between workers: BW variance/ BW + WW variance
[g] Not applicable

Appendix II

Sub-analyze to evaluate the impact of measurements below the limit of detection for the task performed models.

Introduction

Measurements below the limit of detection are commonly encountered in occupational exposure measurement series. This leads to left-censored datasets which represent a challenge when performing statistical analysis. Several methods have been proposed to treat left-censored data. Two different methods were used in this thesis, readable values were used unchanged in Paper II and unreadable values were substituted with the lowest readable value divided by √2. In Paper III and IV an imputation procedure was used for measurements below LOD. To evaluate if the method for treating the values below LOD would impact the results of the modeling, the method from Paper II were also used on the final models on job group level in Paper IV.

Methods

A sub-analyze was performed where the final models for determinants on job group level also were computed with the dataset used in Paper II where readable values below the LOD were used unchanged, and non-readable values were replaced by the lowest readable value divided by √2.

Results

With the exception of pay loader operator (cristobalite and SiC) and control room operator (cristobalite) the same tasks were found to be significant predictors of exposure when using the readable values dataset (results not shown).

Discussion

It was reassuring to find that with a few exceptions, the same tasks were found to be significant predictors of exposure when using the readable values dataset. The pay loader operator was the job group with fewest measurements, and is therefore likely to be most vulnerable to changes in concentrations, and also to artificial results due to chance. Operating the crane resulted in a significant decrease in cristobalite exposure for the control room operator when using the readable values dataset ($p<0.05$), but not when using the imputed dataset ($p=0.08$) even though the fit of the model was improved. The control room operator had the lowest exposure to cristobalite and more than 30 % of the measurements were below the LOD which might partly explain the differences. The models on job group level were the

ones with fewest measurements and would therefore be more prone to be impacted by measurements below LOD. These results suggests that the method used for replacing measurements below LOD does not have a great influence on the results. Cristobalite with most measurements below the LOD would be most prone to be affected by the values below LOD.

Appendix III

Element analysis performed in 1983 and 2001

Element	1983 ($\mu g/m^3$)	2001 ($\mu g/m^3$)	OEL ($\mu g/m^3$)
Number of measurements	14	7	
Cu	<LOD-1.8	<LOD	100
Ni	0.013-4.16	0.05-15.4	50
Al		7.2-55.9	5000
Ca		<LOD-55	
Fe		17.4-177	3000
Mg		2.0-8.72	
Pb	<LOD-0.57	<LOD	50
Cd	<LOD-0.13	<LOD	50
Mn	0.013-0.79	0.2-0.99	100
Zn	0.046-0.68	<LOD-2.0	
B		<LOD-2.0	
Co		<LOD-0.6	20
K		<LOD-12.0	
Ti		0.7-10.5	
Zr		<LOD-2.99	5000
Ba		<LOD-1.6	500
Cr	<LOD-5.17	0.6-1.4	500
Na		3.6-35.4	
Si		69.1-568	10000
V	<LOD-18	0.5-18.9	50

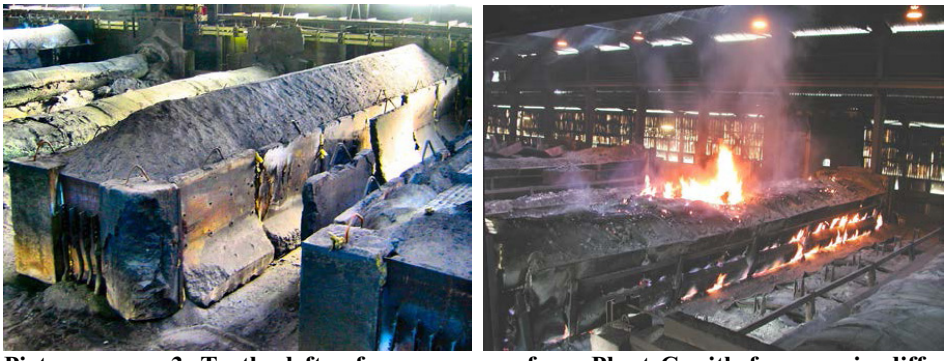
Ag, As, Bi, Hg, La, Li, Mo, Sb, Se, Sn, Sr, Ta, W and Y were below the limit of detection.

Appendix IV

Illustrations

Picture group 1. The raw materials in the silicon carbide production, quartz sand (left) and petroleum coke (right).

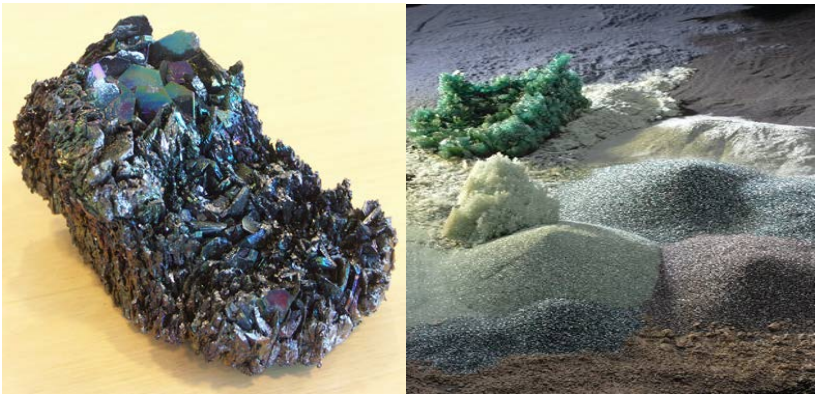
Picture group 2. To the left a furnace worker from Plant A, year unknown. In courtesy of Aust-Agder kulturhistoriske senter. To the right a charger operator assisting in laying the graphite core in Plant C in 2003.



Picture group 3. To the left a furnace group from Plant C with furnaces in different stages. The furnace in the middle has just been started and it is surrounded by furnaces in different stages of cooling and disassembling. To the right a furnace during a blow-out in Plant A. The pictures have been provided by Washington Mills AS and Saint-Gobain Ceramic Materials.

Picture group 4. Sorting the crude SiC. The picture to the left is manual sorting in 1952, the picture in the middle shows manual sorting in 2003 and the picture to the right shows sorting in cabin in 2003. In courtesy of Aust-Agder kulturhistoriske senter.

Picture group 5. Packing of SiC product in 25 kg bags (left) and big bags (right).



Picture group 6. Silicon carbide. To the left a silicon carbide lump from the furnace hall prior to crushing. In courtesy of Erik Bye, NIOH, Norway. To the right silico carbide lumps and final products with different grain sizes. In courtesy of Saint-Gobain Ceramic Materials.

Picture group 7. Silicon carbide workers from Plant A in 1913 (left) and 1919 (right). In courtesy of Aust-Agder kulturhistoriske senter.

Papers I-IV

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Exposure to Fibres, Crystalline Silica, Silicon Carbide and Sulphur Dioxide in the Norwegian Silicon Carbide Industry

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Objectives: The aim of this study was to assess personal exposure to fibres, crystalline silica, silicon carbide (SiC) and sulphur dioxide in the Norwegian SiC industry.

Methods: Approximately 720 fibre samples, 720 respirable dust samples and 1400 total dust samples were collected from randomly chosen workers from the furnace, processing and maintenance departments in all three Norwegian SiC plants. The respirable dust samples were analysed for quartz, cristobalite and non-fibrous SiC content. Approximately 240 sulphur dioxide samples were collected from workers in the furnace department.

Results: The sorting operators from all plants, control room and cleaning operators in Plant A and charger, charger/mix and payloader operators in Plant C had a geometric mean (GM) of fibre exposure above the Norwegian occupational exposure limit (OEL) (0.1 fibre cm^{-3}). The cleaner operators in Plant A had the highest GM exposure to respirable quartz (20 $\mu g\ m^{-3}$). The charger/mix operators in Plant C had the highest GM exposure to respirable cristobalite (38 $\mu g\ m^{-3}$) and the refinery crusher operators in Plant A had the highest GM exposure to non-fibrous SiC (0.65 mg m^{-3}). Exposure to the crystalline silica and non-fibrous SiC was generally low and between 0.4 and 2.1% of the measurements exceeded the OELs. The cleaner operators in Plant A had the highest GM exposure to respirable dust (1.3 mg m^{-3}) and total dust (21 mg m^{-3}). GM exposures for respirable dust above the Norwegian SiC industry-specific OEL of 0.5 mg m^{-3} were also found for refinery crusher operators in all plants and mix, charger, charger/mix and sorting operators in Plant C. Only 4% of the total dust measurements exceeded the OEL for nuisance dust of (10 mg m^{-3}). Exposure to sulphur dioxide was generally low. However, peaks in the range of 10–100 p.p.m. were observed for control room and crane operators in Plants A and B and for charger and charger/mix operators in Plant C.

Conclusion: Workers in the SiC industry are exposed to a mixture of several agents including SiC fibres, quartz, cristobalite, non-fibrous SiC and sulphur dioxide. Exposure levels were generally below the current Norwegian OELs; however, high exposure to fibres and respirable dust still occurs in the furnace department.

Keywords: cristobalite; exposure assessment; fibres; quartz; respirable dust; silicon carbide; sulphur dioxide; total dust

INTRODUCTION

Silicon carbide (SiC) is produced by mixing quartz sand and petrol coke in an electric resistance furnace (Smoak *et al.*, 1978). Small-scale production of SiC was started by Edward Goodrich Acheson in the 1891 and has risen steadily since then (Smoak *et al.*, 1978). The global SiC production capacity was 1 010 000 metric tons in 2002, of these the Norwegian plants accounted for ~8% (US Geological Survey, 2004). Important areas of application are as abrasive grains, construction and refractory materials, for metallurgical purposes, in diesel particle filters and in slicing of silicon wafers for the photovoltaic and semiconductor industry.

In the SiC production process, crystalline silica, SiC fibre, non-fibrous SiC, polycyclic aromatic

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hydrocarbons (PAHs), sulphur dioxide (SO_2) and carbon monoxide (CO) are released into the work environment (Smith *et al.*, 1984; Bye *et al.*, 1985; Dufresne *et al.*, 1987; Scansetti *et al.*, 1992; Petry *et al.*, 1994; Dion *et al.*, 2005). Many of these exposures have been linked to malignant and non-malignant respiratory diseases (Bruusgaard, 1948; Osterman *et al.*, 1989; Marcer *et al.*, 1992; Infante-Rivard *et al.*, 1994; Romundstad *et al.*, 2001, 2002). Several studies have reported an increased risk for pulmonary impairments, pneumoconiosis and lung cancer; however, specific exposure agents have not been linked to these outcomes.

The main objective of this study was to provide an overview of the contemporary dust, fibre and sulphur dioxide exposure levels in the SiC industry in Norway. This information will be used to improve a previously developed retrospective job-exposure matrix (Romundstad *et al.*, 2001), which will be applied in an ongoing epidemiological study on lung cancer and non-malignant respiratory diseases in the Norwegian SiC industry. The results may also be useful for risk assessment.

MATERIALS AND METHODS

SiC production

SiC appears in two different crystalline forms. The hexagonal α-SiC is the main product, while the cubic β-SiC is formed at lower temperatures and is used in the metallurgic industry or recycled into the furnace mix. SiC is produced as either green or black crystals from a mixture of high-grade quartz sand and petrol coke. In the production of black SiC product, reclaimed furnace mix and aluminium oxide may be added to the furnace mix, and sawdust is sometimes added to improve porosity of the furnace mix. The furnace mix is transported to the furnace building and loaded into an electrical resistance furnace with a graphite core in the centre. The furnace mix is heated electrically by the graphite core that functions as a resistance element. Quartz (SiO_2) will react with carbon and form α-SiC and carbon monoxide (CO) at temperatures >1700°C according to the chemical reaction:

$$SiO_2 + 3C \rightarrow SiC + 2CO.$$

After the completion of a furnace cycle (8–10 days), unreacted material is removed and returned to the mix area, while the crude SiC is transported to the sorting area. In the sorting area β-SiC is removed from α-SiC. α-SiC is then crushed and transported to the processing department where it is crushed further and treated chemically with pine oil, sulphuric acid and sodium hydroxide to remove unreacted crystalline silica, silicon and carbon. Metallic impurities are removed by magnetic separation. SiC is then sieved and classified into size fractions (grits) with a mass median particle size ranging from 0.1 to 880 μm. The high temperatures in the furnace will transform quartz into cristobalite, another crystalline form of silica. Sulphur impurities in the coke will lead to emission of sulphur dioxide.

A SiC plant can be divided into three different departments: furnace department where the crude SiC is produced, processing department where the SiC grits are manufactured and maintenance department responsible for maintenance work in all parts of the plant, see Fig. 1 and Table 1.

Plant characteristics

Exposure assessment was performed in all three Norwegian SiC plants. One plant is located in central Norway, while the two other plants are located in the southern part of Norway. The three plants employ a total of ~350 production and maintenance workers. The furnaces are located inside a furnace hall building. Differences between plants are described under the job groups in Table 1.

Sampling strategy

The agents that were measured were fibres, respirable quartz, respirable cristobalite, respirable non-fibrous SiC, respirable dust, total dust and sulphur dioxide. Other agents known to be present in the work atmosphere in the SiC industry are carbon monoxide, PAHs and amorphous silica. Carbon monoxide was not measured, as this gas was not expected to induce chronic respiratory effects. Amorphous silica was not analysed due to analytical limitations. PAHs were not quantified due to relative low levels reported in other studies (Dufresne *et al.*, 1987; Petry *et al.*, 1994).

Walk-through surveys of the plants were performed by one of the authors and information on jobs and tasks was collected. Workers were then divided into job groups performing similar tasks in similar work conditions. The jobs were categorized as described in detail in Table 1.

A random sample of workers from each group was invited to participate in the study and all except one agreed to participate. Exposure to dust and gas was determined by means of personal sampling. The aim was to measure two or more agents for each person for at least 2 days. Workers were interviewed after sampling for their perception of the work conditions and respirator use. There were no criteria given for stating normal/worse/better working conditions other than the workers' own perception of the work on that specific day

The sampling duration for sulphur dioxide, total dust full-shift samples and respirable dust was close to a full work shift (6–8 h). Sampling duration for total dust short-term and fibre samples was limited

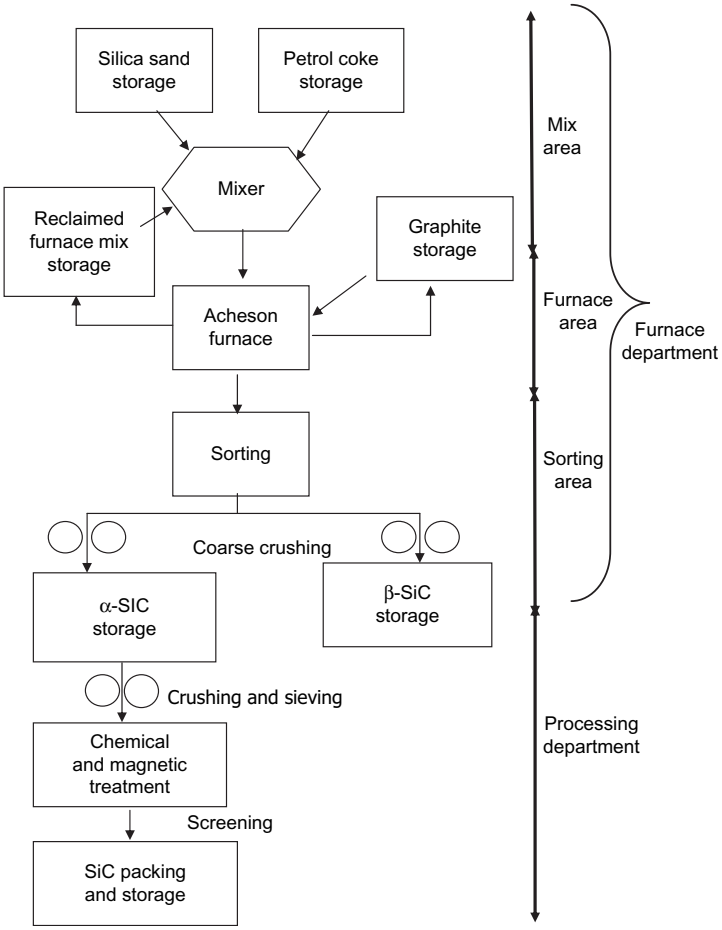

Fig. 1. Flow diagram over the SiC production.

to 0.5–3.5 h to avoid particle overload of the filter used for fibre analyses.

The sampling was performed between November 2002 and December 2003 and included two sampling periods of two work weeks (total 10 days). One sampling period was during autumn/winter (November–February) and the second period during spring/summer (May–August).

The work was organized as daytime only, two-shift schedule per day (morning and afternoon) or three-shift schedule per day (morning, afternoon and night). Sampling was evenly divided on morning and afternoon shifts. In addition, four night shifts per agent per job group were included in each plant.

Sampling methods and analysis

Total dust full-shift samples were collected on 37-mm cellulose acetate filters (Millipore Corporation, Bedford, NY, USA), with a 5.0-μm pore size, whereas the total dust short-term samples were collected on 37-mm Teflon (polytetrafluoroethylene) filters (Millipore Corporation). Both filters were fitted in 37-mm closed-faced aerosol filter cassettes (Millipore Corporation) applying a sampling flow rate of 2 l min^{-1}. Respirable dust was collected on 37-mm cellulose acetate filters with a pore size of 5.0 μm (Millipore Corporation) using a cyclone (Casella T13026/2, London, UK) at a sampling flow rate of 2.2 l min^{-1}. The particle mass was measured with a microbalance Sartorius Micro MC 210 P (Sartorius AG, Goettingen, Germany), with a detection limit of 0.06 mg. The detection limit with 8-h sampling time was therefore 0.063 mg m^{-3} for total dust and 0.057 mg m^{-3} for respirable dust. The amount of quartz, cristobalite and non-fibrous SiC in the respirable dust was determined by the use of X-ray powder diffractometry, applying Philips PW1729 X-ray generator, Phillips PW 1710 diffractometer control and Phillips APD software. The crystalline silica was determined by the use of standard methods (Bye, 1983; NIOSH, 1998) with

Table 1. Occupational job groups in the Norwegian SiC industry

Job groups	Description of work
Furnace department	
Mix operator (Plants A and C)	The mix operator is in charge of the mix building where the furnace mix is made from quartz sand, coke and recycled furnace mix. He supervises the process from a control room, but regular rounds inside the mixing plant are necessary. Raw materials are transported on elevators and transport bands and when there are jams or leaks, the mix operator has to clean up.
Charger (Plant C)	The charger operator is involved in construction of furnaces. He inserts insulation material between the elements in the furnace wall. He assists the crane operator in assembling the furnace and loads it with furnace mix and graphite while standing beside the furnace giving directions or inside the furnace steering the gondola when the graphite core is laid down. He also helps the crane operator to change equipment on the crane. He waits in the control room in the mix building when there is an intermission in the work.
Charger/mix operator (Plant C)	In the second sampling period, the plant had combined the charger and mix operator jobs into one job done by one person on each shift.
Crane operator (Plants A, B and C)	The crane operator works in fresh air-supplied closed cabins located close to the roof of the furnace plant. The crane transports furnace mix to furnaces being constructed and removes fully and partially reacted materials from the furnaces. Sometimes the operator has to leave the cabin in order to do manually work on the furnaces.
Payloader operator (Plants A, B and C)	The payloader operator transports raw materials (petrol coke and quartz sand) from storage rooms to elevators connected to the furnace building. When the elevators jams up or spills, he cleans up. Usually that means getting out of the payloader and doing it manually. He is also involved in emptying of the furnace by removing unreacted furnace mix from the furnace floor. He transports crude SiC from the furnace hall to the sorting building (Plant A) and transports coarse crushed SiC to the processing department. The payloader vehicles used are closed cabin vehicles.
Control room operator (Plants A, B and C)	The control room operator controls the furnaces and the dust release to the environment from a control room. He spends much of his time in the control room, but performs inspection rounds in the furnace plant and works in cranes and on furnace plant floor occasionally. He also has to connect and disconnect the furnace to the power line. The control room is either situated in the furnace building (Plant B) or in a separate building close to the furnace building (Plants A and C).
Cleaning operator (Plant A)	The cleaning operator performs manual cleaning of the area where reclaimed furnace mix is stored.
Sorting operator (Plants A, B and C)	The sorting operator sorts the furnace product so that partially reacted material is removed from the fully reacted SiC. The sorting department is either situated in a separate building (Plant A) or inside the furnace building (Plants B and C). The operators in Plants A and B work in closed cabin vehicles most of the time, most with fresh air supply. The operator in Plant C works in a closed cabin vehicle or in a fresh air-supplied room situated inside the furnace plant.
Processing department	
Refinery crusher operator (Plants A, B and C)	The crusher operator is the first operator to come in contact with the SiC transported from furnace department. He controls the crushing process. Other tasks are performed as well, depending on plant (e.g. sieving, cleaning and truck driving).
Refinery other operator (Plants A, B and C)	Other refinery workers grind, clean and screen the SiC from the furnace plant into various sizes. The product is then either transported to the fines area for further processing or packed into bags ready for sale.
Fines operator (Plants A, B and C)	The fines operator crushes, grinds, cleans and screens the SiC from the refinery area further into various sizes. The end product is packed into 25 or 1000 kg bags and stored ready for sale.
Maintenance department	
Mechanics (Plants A, B and C)	The mechanics do mechanical maintenance work in the furnace department, processing department, outdoor and in repair shops.
Electricians (Plants A, B and C)	The electricians do electrical maintenance work in the furnace department, processing department, outdoors and in the repair shop.

some modifications due to the presence of graphite in samples from the furnace hall. Graphite interferes with quartz in the analyses and was removed by high-temperature ashing (700°C). The detection limit for quartz was 5 μg, which amounts to 5.2 μg m^{-3} with 8-h sampling time, and for cristobalite 10 μg, which amounts to 10.4 μg m^{-3} with 8-h sampling time. Non-fibrous SiC was determined by a corresponding X-ray method developed in our laboratory (E Bye *et al*, in press). Pure SiC

products from the three plants were used for calibration purposes. The detection limit for SiC was 12 μg which amounts to 0.013 mg m^{-3} with 8-h sampling time. Due to the detection limits of the XRD analytical methods, dust samples were combined if there was not enough dust to ensure sufficient material for analysis (>0.7 mg). Samples were combined within plant and job groups, preferably from the same persons. The detection limits apply to the combined samples and the detection limit for the individual samples would be lower depending on the amount of dust in the sample. The total number of samples was 680 and they were combined into 272 analyses.

Fibres were collected on 25-mm cellulose acetate filters (Millipore Corporation) with a pore size of 1.2 μm using an open-face aerosol filter cassette of conducting polypropylene (Gelman Sciences, Ann Arbor, MI, USA) at a sampling flow rate of 1 l min^{-1}. The fibres were counted with a light microscope according to World Health Organization (WHO) counting criteria (WHO, 1997) with a detection limit of four fibres which amounts to 0.016 fibres cm^{-3} with a sampling time of 2 h.

The samples were collected in parallel with a cyclone and a total dust cassette, or a fibre cassette and a short-term total dust cassette placed side by side on the worker. The two parallel cassettes were connected to the same high-flow pump through a hose with a Y-passage (SKC Inc., Eighty Four, PA, USA).

Sulphur dioxide was measured with direct-reading electrochemical sensors with a data-logging facility built into the instrument (PAC III Dräger Aktiengesellschaft, Lübeck, Germany). An averaging period of one reading every 10 s was selected. The detection limit was 0.2 p.p.m. for each 10-s period.

Quality control

One field blank was taken to the plants per day for every 10 particulate samples, with at least one blank per day. The average mass change of 1-day blanks were subtracted from the mass change for samples collected that day. The quality control procedures for the gravimetric measurements also included measuring two weights, at the beginning of each weighing session. The Norwegian Metrology Service calibrated the balances annually. The response factors of the electrochemical sensors were calibrated before each sampling period with calibration gas obtained from Hydrogass Norge AS, Oslo, Norway. Crystalline silica analyses were controlled by participation in an inter-laboratory proficiency-testing programme (Grunder, 2003).

Data analysis

Using cumulative probability plots, the exposure data were found to be best described by lognormal distributions and were $\log_{10}$ transformed before the statistical analyses. Standard measures of central tendency and distributions [arithmetic mean (AM), geometric mean (GM) and geometric standard deviation] were calculated. The GM was also calculated using mixed effect models, as was the 95th percentile. The mixed effects models were constructed with the exposure as the dependent variable. Exposure determinants were treated as fixed effects, whereas worker was treated as random effects. For sulphur dioxide measurements the highest value recorded for a 10-s averaging period within a work shift was registered as the maximum peak value.

Values below the limit of detection were treated as follows: readable values above the background noise level were directly applied in calculations and modelling, while non-readable values were substituted with the lowest readable value divided by the square root of two (Eduard, 2002).

The significance of differences in exposure levels among the job groups and plants was evaluated using *post hoc* tests with Bonferroni adjustment. In order to investigate whether the short-term samples were representative of full-shift exposure, we calculated the ratio of the adjusted GMs of short-term and full-shift total dust samples for each job group in all three plants.

The software package SPSS version 15.0 for Windows (SPSS Inc., Chicago, IL, USA) and SAS version 9.1 (SAS Institute Inc., Cary, NC, USA) was used for statistical analysis.

RESULTS

All measurements were carried out between November 2002 and December 2003. Most of the workers (77%) were monitored on more than one occasion. Results are shown in Tables 2–9 and Figs 2 and 3, and the GM referred to in the following text is the GM adjusted with mixed effect models.

Fibres

Most of the fibre sampling (90%) was initiated during the first half of the shift due to practical considerations. A total of 40% of the samples were below the detection limit. However, the fibre count was zero in only 9% of the samples. The fibre exposure levels are shown in Fig. 2 and Table 2. Highest GM of fibre exposures was found in the furnace and sorting areas in all plants, and the cleaning operators in Plant A had the highest exposure to fibres (2.7 fibres cm^{-3}). The control room, cleaning and sorting operators in Plant A, sorting operators in Plant B and charger, charger/mix, payloader and sorting operators in Plant C had all GM exposures of 0.1 fibres cm^{-3} or more. The sorting operators had significantly higher exposure in Plant C compared to the

Table 2. Summary of fibre levels by plant and job group, exposure intensity in samples collected with 0.5–3.5 h sampling time

Job group	Fibres (fibres per cm^3)																			
	Plant A							Plant B							Plant C					
	Unadjusted					Adjusted[a]		Unadjusted					Adjusted[a]		Unadjusted					Adjusted[a]	
	N[b]	K[c]	AM	GM	GSD[d]	GM	P95[e]	N[b]	K[c]	AM	GM	GSD[d]	GM	P95[e]	N[b]	K[c]	AM	GM	GSD[d]	GM	P95[e]
Furnace																					
Mix	14	3	0.11	0.097	1.8	0.096	0.25								10	5	0.072	0.046	3.0	0.047	0.22
Charger															10	4	0.43	0.36	2.0	0.36	0.82
Charger/mix															11	5	0.39	0.31	2.2	0.31	0.88
Payloader	10	2	0.12	0.086	2.5	0.086	0.37	5	1	0.037	0.025	2.9	0.025	0.098	18	6	0.58	0.24	4.3	0.24	2.4
Crane	21	8	0.18	0.082	2.9	0.081	0.25	19	7	0.056	0.036	3.0	0.037	0.16	14	7	0.082	0.039	4.3	0.037	0.28
Control room	21	5	0.87	0.46	3.8	0.46	2.2	20	5	0.11	0.062	2.5	0.061	0.61	19	8	0.12	0.080	2.8	0.078	0.48
Cleaning	2	1	2.8	2.7	1.6	2.7	3.7														
Sorting	19	5	0.21	0.13	2.8	0.13	0.66	21	4	0.32	0.19	2.7	0.18	1.1	21	9	0.50	0.43	1.9	0.43	0.97
Processing																					
Refinery																					
Crusher	29	14	0.029	0.022	2.4	0.022	0.073	15	2	0.058	0.037	2.5	0.040	0.21	19	6	0.032	0.021	2.7	0.019	0.097
Other	29	13	0.050	0.030	2.4	0.031	0.12	27	13	0.019	0.015	2.3	0.015	0.044	32	8	0.019	0.013	2.7	0.013	0.048
Fines	36	21	0.015	0.011	2.2	0.011	0.044	60	23	0.010	0.007	2.3	0.007	0.034	49	19	0.014	0.011	2.2	0.011	0.035
Maintenance																					
Mechanics	48	18	0.057	0.034	2.9	0.035	0.16	47	16	0.050	0.017	4.0	0.017	0.24	27	9	0.092	0.049	3.0	0.051	0.42
Electrician	21	7	0.15	0.086	2.6	0.085	0.39	22	7	0.096	0.041	3.0	0.043	0.23	10	5	0.025	0.017	2.6	0.018	0.059

The Norwegian OEL for SiC fibre is 0.1 fibre per cm^3 (The Norwegian Labour Inspection Authority, 2007).
[a]Adjusted with mixed effect models.
[b]Number of measurements.
[c]Number of persons.
[d]Geometric standard deviation.
[e]95th percentile.

Table 3. Summary of respirable quartz levels by plant and job group, exposure intensity in samples collected with 6–8 h sampling time

Job group	Respirable quartz (μg m^{-3})																			
	Plant A							Plant B							Plant C					
	Unadjusted					Adjusted[a]		Undjusted					Adjusted[a]		Unadjusted					Adjusted[a]	
	N[b]	K[c]	AM	GM	GSD[d]	GM	P95[e]	N[b]	K[c]	AM	GM	GSD[d]	GM	P95[e]	N[b]	K[c]	AM	GM	GSD[d]	GM	P95[e]
Furnace																				
Mix	13	3	14	13	1.5	13	22								9	4	15	10	2.4	9.6	30
Charger															9	5	10	8.0	2.0	8.0	58
Charger/mix															10	5	21	13	2.9	12	12
Payloader	7	2	4.0	3.3	2.0	3.1	7.9	5	1	NA	NA	NA	NA	NA	17	9	3.5	2.5	2.4	2.5	33
Crane	23	7	NA	NA	NA	NA	NA	17	5	3.6	2.1	3.5	2.1	11	13	5	3.4	1.1	3.1	1.1	6.5
Control room	19	6	3.0	2.5	2.0	2.3	7.0	19	5	2.6	1.9	2.4	1.9	11	19	7	2.1	1.7	2.0	1.7	6.5
Cleaning	2	1	23	20	2.1	20	34														
Sorting	20	5	NA	NA	NA	NA	NA	18	4	2.4	1.2	4.3	1.2	8.7	18	9	6.6	4.3	3.4	4.4	22
Processing																					
Refinery																					
Crusher	29	11	2.8	1.2	4.9	1.2	9.0	13	3	1.7	0.51	7.2	0.49	8.4	19	6	2.6	1.8	2.8	1.9	9.8
Other	27	11	NA	NA	NA	NA	NA	26	14	1.8	0.90	4.5	0.88	6.1	31	8	2.3	0.93	6.5	1.1	6.5
Fines	20	14	NA	NA	NA	NA	NA	56	22	1.5	0.42	7.8	0.44	5.1	48	15	NA	NA	NA	NA	NA
Maintenance																					
Mechanics	47	17	1.8	0.67	5.3	0.75	5.1	48	18	17	1.5	5.2	1.5	45	28	9	NA	NA	NA	NA	NA
Electrician	20	7	2.3	1.5	2.8	1.5	8.0	20	7	17	2.3	7.3	2.4	123	10	5	NA	NA	NA	NA	NA

The Norwegian OEL for respirable quartz is 100 μg m^{-3} (The Norwegian Labour Inspection Authority, 2007).
NA, not applicable, all measurements below limit of detection (5.2 μg m^{-3} for 8-h sampling time).
[a]Adjusted with mixed effect models.
[b]Number of measurements.
[c]Number of persons.
[d]Geometric standard deviation.
[e]95th percentile.

Table 4. Summary of respirable cristobalite levels by plant and job group, exposure intensity in samples collected with 6–8 h sampling time

Job group	Respirable cristobalite (μg m^{-3})																			
	Plant A							Plant B							Plant C					
	Unadjusted					Adjusted[a]		Unadjusted					Adjusted[a]		Unadjusted					Adjusted[a]	
	N[b]	K[c]	AM	GM	GSD[d]	GM	P95[e]	N[b]	K[c]	AM	GM	GSD[d]	GM	P95[e]	N[b]	K[c]	AM	GM	GSD[d]	GM	P95[e]
Furnace																					
Mix	13	3	NA	NA	NA	NA	NA								9	4	36	12	4.7	11	148
Charger															9	5	31	22	2.4	23	102
Charger/mix															10	5	46	38	2.0	35	98
Payloader	7	2	4.9	1.5	8.9	0.99	20	5	1	NA	NA	NA	NA	NA	17	9	26	15	2.8	15	116
Crane	23	7	1.6	0.55	3.4	0.55	10	17	5	4.2	3.0	2.4	2.9	14	13	5	12	2.2	3.7	2.1	135
Control room	19	6	3.9	3.1	2.0	2.9	11	19	5	3.5	2.2	2.6	2.1	16	19	7	5.6	4.7	1.9	4.7	14
Cleaning	2	1	29	29	1.2	29	33														
Sorting	20	5	NA	NA	NA	NA	NA	18	4	27	12	3.5	12	115	18	9	19	17	1.5	17	39
Processing																					
Refinery																					
Crusher	29	11	NA	NA	NA	NA	NA	13	3	9.9	6.4	2.7	6.4	36	19	6	4.1	2.5	2.7	2.6	24
Other	27	11	NA	NA	NA	NA	NA	26	14	3.1	1.6	3.3	1.6	13	31	8	NA	NA	NA	NA	NA
Fines	20	14	NA	NA	NA	NA	NA	56	22	NA	NA	NA	NA	NA	48	15	NA	NA	NA	NA	NA
Maintenance																					
Mechanics	47	17	1.4	0.50	6.0	0.52	2.6	48	18	2.8	0.87	6.0	0.74	9.8	28	9	1.7	0.31	12	0.33	6.5
Electrician	20	7	NA	NA	NA	NA	NA	20	7	1.7	0.80	4.0	0.79	7.1	10	5	NA	NA	NA	NA	NA

The Norwegian OEL for respirable cristobalite is 50 μg m^{-3} (The Norwegian Labour Inspection Authority, 2007).
NA, not applicable, all measurements below limit of detection (10.4 μg m^{-3} for 8-h sampling time).
[a]Adjusted with mixed effect models
[b]Number of measurements.
[c]Number of persons.
[d]Geometric standard deviation.
[e]95th percentile.

Table 5. Summary of respirable non-fibrous SiC levels by plant and job group, exposure intensity in samples collected with 6–8 h sampling time

Job group	Respirable non-fibrous SiC (mg m^{-3})																			
	Plant A							Plant B							Plant C					
	Unadjusted					Adjusted[a]		Unadjusted					Adjusted[a]		Unadjusted					Adjusted[a]	
	N[b]	K[c]	AM	GM	GSD[d]	GM	P95[e]	N[b]	K[c]	AM	GM	GSD[d]	GM	P95[e]	N[b]	K[c]	AM	GM	GSD[d]	GM	P95[e]
Furnace																					
Mix	13	3	0.014	0.009	2.6	0.010	0.72								9	4	0.066	0.036	3.0	0.034	0.22
Charger															9	5	0.075	0.067	1.7	0.068	0.16
Charger/mix															10	5	0.18	0.14	2.1	0.13	0.53
Payloader	7	2	0.17	0.047	6.9	0.033	0.071	5	1	0.046	0.044	1.4	0.044	0.052	17	9	0.046	0.032	2.4	0.032	0.17
Crane	23	7	0.014	0.008	2.6	0.008	0.097	17	5	0.019	0.015	2.2	0.015	0.052	13	5	0.016	0.004	3.2	0.004	0.16
Control room	19	6	0.044	0.038	1.8	0.035	0.097	19	5	0.034	0.022	2.5	0.022	0.16	19	7	0.011	0.008	2.1	0.008	0.029
Cleaning	2	1	0.54	0.49	1.9	0.49	0.77														
Sorting	20	5	0.10	0.086	1.7	0.083	0.26	18	4	0.48	0.24	3.1	0.22	3.6	18	9	0.35	0.31	1.7	0.31	0.68
Processing																					
Refinery																					
Crusher	29	11	0.89	0.65	2.4	0.65	2.1	13	3	0.54	0.36	2.5	0.39	2.1	19	6	0.69	0.45	2.4	0.46	3.8
Other	27	11	0.11	0.087	2.0	0.087	0.30	26	14	0.26	0.11	3.6	0.11	1.2	31	8	0.38	0.22	2.8	0.27	1.4
Fines	20	14	0.12	0.083	2.3	0.081	0.41	56	22	0.29	0.16	3.1	0.18	0.98	48	15	0.29	0.22	2.0	0.22	0.84
Maintenance																					
Mechanics	47	17	0.098	0.054	3.0	0.053	0.40	48	18	0.14	0.076	3.1	0.079	0.52	28	9	0.075	0.039	2.8	0.042	0.28
Electrician	20	7	0.068	0.052	2.2	0.052	0.17	20	7	0.12	0.068	2.5	0.067	0.55	10	5	0.086	0.038	3.9	0.038	0.33

There is no Norwegian OEL for respirable SiC; however, American Conference of Industrial Hygienists have suggested a threshold limit value of 3 mg m^{-3} (ACGIH, 2007).
[a]Adjusted with mixed effect models.
[b]Number of measurements.
[c]Number of persons.
[d]Geometric standard deviation.
[e]95th percentile.

Table 6. Summary of respirable dust levels by plant and job group, exposure intensity in samples collected with 6–8 h sampling time

Job group	Respirable dust (mg m^{-3})																			
	Plant A							Plant B							Plant C					
	Unadjusted					Adjusted[a]		Unadjusted					Adjusted[a]		Unadjusted					Adjusted[a]	
	N[b]	K[c]	AM	GM	GSD[d]	GM	P95[e]	N[b]	K[c]	AM	GM	GSD[d]	GM	P95[e]	N[b]	K[c]	AM	GM	GSD[d]	GM	P95[e]
Furnace																					
Mix	13	3	0.45	0.41	1.6	0.41	0.99								10	4	1.2	0.72	2.7	0.72	4.2
Charger															9	5	0.80	0.70	1.7	0.70	1.8
Charger/mix															10	5	1.1	0.99	1.7	0.93	1.8
Payloader	7	2	0.54	0.40	2.2	0.38	1.7	5	1	0.24	0.23	1.4	0.23	0.32	18	9	0.33	0.22	2.7	0.21	1.3
Crane	23	7	0.17	0.12	2.2	0.12	0.50	17	5	0.26	0.23	1.7	0.23	0.45	14	5	0.25	0.13	2.5	0.12	2.0
Control room	18	5	0.28	0.25	1.6	0.25	0.55	19	5	0.28	0.24	1.8	0.24	0.76	19	7	0.20	0.17	1.8	0.17	0.40
Cleaning	2	1	1.3	1.3	1.1	1.3	1.4														
Sorting	20	5	0.22	0.19	1.6	0.19	0.49	20	4	0.79	0.48	2.8	0.45	3.1	19	9	1.4	0.75	2.2	0.74	13
Processing																					
Refinery																					
Crusher	29	11	1.1	0.86	2.0	0.85	2.00	13	3	0.82	0.63	2.1	0.68	2.6	19	6	0.80	0.55	2.3	0.56	4.3
Other	27	11	0.23	0.21	1.6	0.20	0.41	27	15	0.43	0.27	2.5	0.28	1.7	31	8	0.54	0.40	2.2	0.45	1.4
Fines	30	17	0.81	0.19	3.0	0.20	0.65	56	22	0.49	0.30	2.7	0.34	1.3	49	15	0.37	0.30	1.8	0.30	1.0
Maintenance																					
Mechanics	49	17	0.31	0.25	1.9	0.25	0.77	48	18	0.59	0.41	2.4	0.40	1.5	28	9	0.28	0.22	2.0	0.23	0.85
Electrician	20	7	0.24	0.21	1.7	0.21	0.49	23	7	0.28	0.21	2.2	0.21	0.82	10	5	0.21	0.18	1.7	0.18	0.54

The Norwegian OEL for respirable dust is 0.5 mg m^{-3} in the furnace department and 5.0 mg m^{-3} in other areas (The Norwegian Labour Inspection Authority, 2007).
[a]Adjusted with mixed effect models.
[b]Number of measurements.
[c]Number of persons.
[d]Geometric standard deviation.
[e]95th percentile.

Table 7. Summary of total dust full-shift levels by plant and job group

Job group	Total dust (mg m^{-3})																				
	Plant A							Plant B							Plant C						
	Unadjusted					Adjusted[a]		Unadjusted					Adjusted[a]		Unadjusted					Adjusted[a]	
	N[b]	K[c]	AM	GM	GSD[d]	GM	P95[e]	N[b]	K[c]	AM	GM	GSD[d]	GM	P95[e]	N[b]	K[c]	AM	GM	GSD[d]	GM	P95[e]
Furnace																					
Mix	13	3	1.5	1.0	3.7	1.1	3.3								9	4	3.9	3.0	2.1	2.8	10
Charger															8	5	4.6	4.1	1.7	4.2	7.4
Charger/mix															10	5	9.3	7.6	1.8	7.3	24
Payloader	7	2	2.7	1.3	3.6	1.1	10	5	1	1.2	1.1	1.8	1.0	1.9	18	9	2.0	1.3	2.6	1.3	6.7
Crane	23	7	0.85	0.37	2.7	0.37	2.5	17	5	1.5	1.1	2.2	1.1	5.2	13	5	0.72	0.29	3.5	0.29	5.6
Control room	19	6	1.3	1.2	1.7	1.1	2.8	20	5	1.3	1.1	2.0	1.0	3.0	19	7	1.3	1.1	2.0	1.1	3.5
Cleaning	2	1	22	21	1.3	21	25														
Sorting	20	5	1.1	0.82	2.1	0.82	3.9	20	4	5.0	2.9	3.2	2.7	17	18	9	5.3	4.8	1.6	4.5	11
Processing																					
Refinery																					
Crusher	28	11	7.4	4.8	2.5	4.8	30	12	3	4.0	3.2	2.0	3.5	9.8	19	6	4.7	3.4	2.2	3.5	23
Other	25	11	1.4	1.1	1.9	1.1	3.5	27	14	2.5	1.2	3.1	1.1	9.3	31	8	2.7	2.1	2.1	2.4	6.3
Fines	32	17	9.2	3.0	4.3	2.9	47	57	23	3.7	1.7	4.3	1.9	11	49	15	3.3	2.2	2.2	2.2	7.4
Maintenance																					
Mechanics	48	17	1.5	1.0	2.5	1.0	4.7	47	18	3.1	2.0	2.8	2.0	7.9	28	9	1.8	1.3	2.3	1.4	6.7
Electrician	20	7	1.3	0.95	2.3	0.97	3.2	23	7	2.0	1.1	3.1	1.1	7.7	10	5	1.8	0.88	3.0	0.88	9.3

The Norwegian OEL for total dust is 10 mg m^{-3} (The Norwegian Labour Inspection Authority, 2007).
[a]Adjusted with mixed effect models.
[b]Number of measurements.
[c]Number of persons.
[d]Geometric standard deviation.
[e]95th percentile.

Table 8. Summary of total dust short-term levels by plant and job group, exposure intensity in samples collected with 0.5–3.5 h sampling time

Job group	Total dust short-term (mg m^{-3})																			
	Plant A							Plant B							Plant C					
	Unadjusted					Adjusted[a]		Unadjusted					Adjusted[a]		Unadjusted					Adjusted[a]	
	N[b]	K[c]	AM	GM	GSD[d]	GM	P95[e]	N[b]	K[c]	AM	GM	GSD[d]	GM	P95[e]	N[b]	K[c]	AM	GM	GSD[d]	GM	P95[e]
Furnace																				
Mix	13	3	2.3	1.4	2.9	1.5	8.6								10	5	3.0	1.3	3.0	1.3	20
Charger															10	4	7.3	6.9	1.4	6.9	11
Charger/mix															11	5	6.2	5.1	1.7	5.3	23
Payloader	10	2	2.2	1.1	3.6	1.1	7.9	5	1	6.7	2.3	6.3	2.3	22	18	6	2.3	1.2	3.3	1.2	8.5
Crane	20	8	0.57	0.42	1.9	0.42	2.2	19	7	0.84	0.52	3.0	0.61	2.9	14	7	0.52	0.38	2.4	0.37	1.5
Control room	21	5	1.9	1.3	2.5	1.3	4.2	19	5	1.5	1.2	1.9	1.2	4.6	18	8	1.2	0.81	2.7	0.85	4.7
Cleaning	1	1	3.9	3.9		3.9	3.9														
Sorting	19	5	1.5	1.0	2.3	0.99	7.1	20	4	4.3	2.7	2.6	2.5	13	21	9	7.5	5.4	2.1	5.2	23
Processing																				
Refinery																				
Crusher	25	14	5.3	3.8	2.4	3.6	13	15	2	5.0	3.7	2.4	3.6	13	19	6	2.3	1.7	2.2	1.6	9.1
Other	28	12	1.3	0.98	2.3	0.87	3.4	27	13	1.3	0.94	2.3	0.95	4.1	32	8	2.4	1.8	2.3	1.9	8.0
Fines	31	21	5.8	2.4	4.2	2.5	24	60	23	2.7	1.3	3.5	1.5	9.0	49	19	3.1	1.8	2.8	1.8	11
Maintenance																				
Mechanics	47	18	1.2	0.75	2.8	0.76	3.8	47	16	2.0	1.1	3.2	1.0	7.5	27	9	1.9	1.4	2.3	1.4	4.6
Electrician	21	7	0.85	0.65	2.0	0.63	2.7	22	7	1.1	0.41	4.4	0.43	2.4	10	5	0.74	0.34	3.2	0.36	4.1

[a]Adjusted with mixed effect models.
[b]Number of measurements.
[c]Number of persons.
[d]Geometric standard deviation.
[e]95th percentile.

Table 9. Summary of sulphur dioxide exposure levels by plant and job group, actual concentrations after 6–8 h sampling time

Job group	Sulphur dioxide (p.p.m.)																						
	Plant A								Plant B								Plant C						
						Maximum peak value[a]								Maximum peak value[a]								Maximum peak value[a]	
	N[b]	K[c]	GM	GSD[d]	GM	GM[e]	GM	P95[f]	N[b]	K[c]	GM	GSD[d]	GM[e]	GM	GM[e]	P95[f]	N[b]	K[c]	GM	GSD[d]	GM[e]	GM	GM[e]	P95[f]
Furnace																							
Mix	12	3	0.001	11	0.001	0.45	0.45	2.3									10	4	0.008	3.4	0.007	0.63	0.62	3.0
Charger																	10	4	0.37	2.1	0.37	5.0	5.0	11
Charger/mix																	10	5	0.37	1.9	0.37	6.9	7.1	18
Payloader	9	2	0.002	15	0.002	0.72	0.72	3.6	5	1	0.006	25	0.006	0.42	0.42	0.90	18	7	0.065	2.8	0.065	0.74	0.73	2.2
Crane	23	8	0.016	3.6	0.016	2.3	2.3	8.1	22	6	0.28	2.3	0.28	9.6	9.6	19	12	6	0.013	3.7	0.013	2.0	2.0	6.7
Control room	20	6	0.036	3.6	0.036	3.2	3.2	58	20	5	0.27	2.9	0.27	13	13	36	17	8	0.061	2.6	0.061	4.0	4.0	17
Cleaning	1	1	NA	NA	NA	NA	NA	NA																
Sorting	3	2	NA	NA	NA	NA	NA	NA	19	4	0.19	4.0	0.19	2.7	2.7	24	20	9	0.12	4.1	0.12	2.0	2.1	6.0

The Norwegian OEL for sulphur dioxide is 2 p.p.m. (The Norwegian Labour Inspection Authority, 2007).
NA, not applicable, all measurements below limit of detection, a measurement is below the limit of detection when all its 10-s reading periods are <0.2 p.p.m.
[a]Maximum observed peak value for a 10-s averaging period within shift measurements.
[b]Number of measurements.
[c]Number of persons.
[d]Geometric standard deviation.
[e]GM adjusted with linear mixed effect models.
[f]95th percentile adjusted with linear mixed effect models.

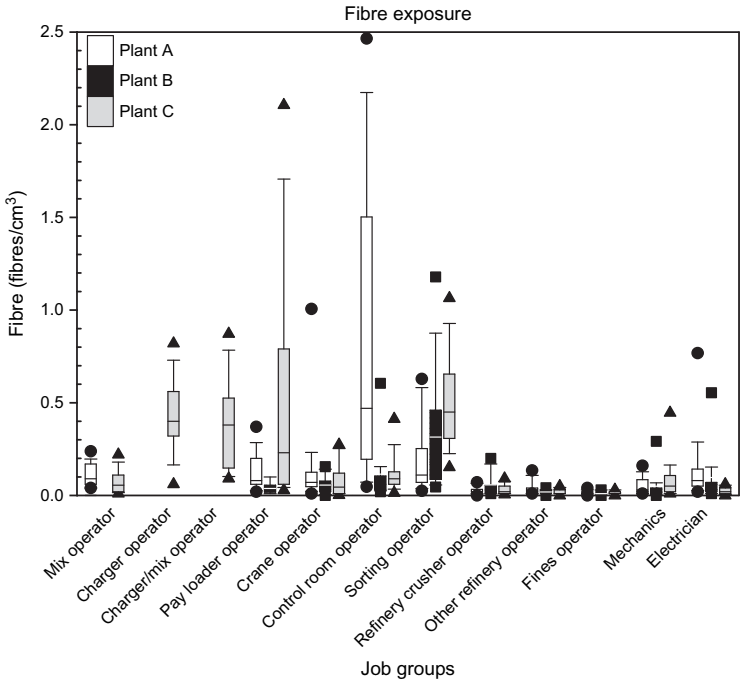

Fig. 2. Box plot of fibre exposure in fibre per cm^3 for job groups in Plants A, B and C. The exposure for the cleaning operator is not included due to too few exposure measurements. The box bounds the 25th and 75th percentiles, encompasses 50% of the data and includes the median (solid line within the box). Dispersion of the data above and below this range is marked by whiskers that extend to the 10th and 90th percentiles. Points above or below the whiskers represent the 95th and 5th percentiles.

other plants ($P < 0.05$). Control room operators had significantly higher exposure to fibres in Plant A compared to the two other plants ($P < 0.05$). The Norwegian occupational exposure limit (OEL) for SiC fibres of 0.1 fibre cm^{-3} was exceeded by 53% of the samples from the furnace department and 17% of the samples from the maintenance department (The Norwegian Labour Inspection Authority, 2007). Only 0.2% of the samples from the processing department exceeded the OEL.

Crystalline silica

The cleaning operators in Plant A had the highest GM exposure to respirable quartz (20 μg m^{-3}). The GM exposure of the mix operators in Plants A and C and charger/mix and charger operators in Plant C varied between 13 and 8.0 μg m^{-3}, while all other job groups had a GM exposure of <5 μg m^{-3} (Table 3). The sorting operators in Plant C had a significantly higher exposure to quartz than the sorting operators in the two other plants ($P < 0.05$). The quartz exposures were generally low and <1% of the samples exceeded the OEL of 100 μg m^{-3} (The Norwegian Labour Inspection Authority, 2007). The samples exceeding the OEL were all from the maintenance department in Plant B.

The job group exposed to the highest levels of respirable cristobalite was the charger/mix operators in Plant C (GM = 35 μg m^{-3}) (Table 4). GM exposures >10 μg m^{-3} were found among the cleaning operators in Plant A, sorting operators in Plants B and C and the mix, charger and payloader operators in Plant C. The mix operators, crane and sorting operators had significantly lower exposure in Plant A compared to the two other plants ($P < 0.01$). The OEL of 50 μg m^{-3} was exceeded in 2.1% of the samples (The Norwegian Labour Inspection Authority, 2007).

The crystalline silica exposures for workers in the processing department and in the maintenance department were generally low. More than 90% of the cristobalite samples from each of these departments were below the detection limit and the corresponding results for quartz exposure levels in these departments were 65 and 58%, respectively.

Respirable non-fibrous SiC

The highest GM exposure to respirable non-fibrous SiC was found among the crusher operators (GM = 0.39–0.65 mg m^{-3}) and the cleaning operators in Plant A (GM = 0.49 mg m^{-3}) (Table 5). The mix, sorting and fines operators had a significantly lower

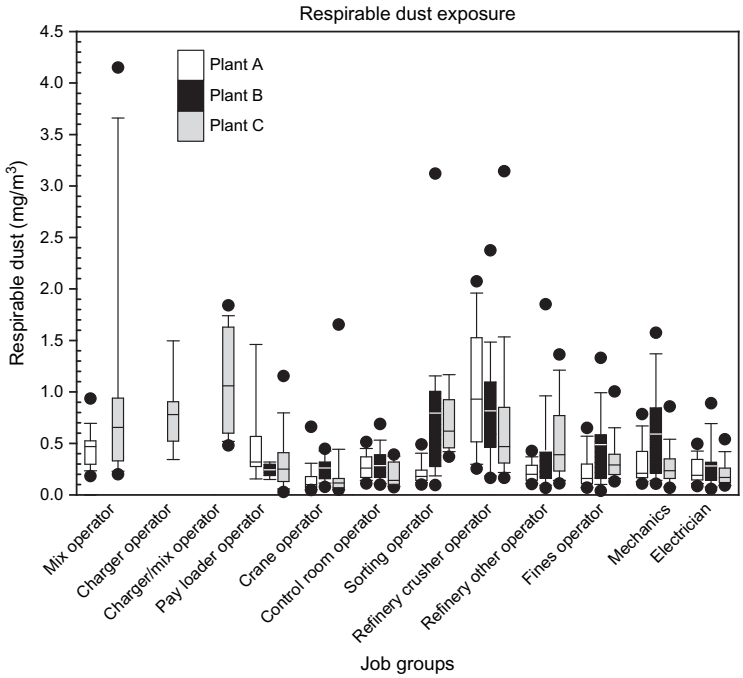

Fig. 3. Box plot of respirable dust exposure in mg m^{-3} for job groups in Plants A, B and C. The exposure for the cleaning operator is not included due to too few exposure measurements. The description of the box plots is the same as in Fig. 2.

exposure in Plant A compared to the two other plants ($P < 0.05$). The control room operators had a significantly lower exposure in Plant C compared to the two other plants ($P < 0.001$). Norway does not have a specific OEL for respirable non-fibrous SiC. The American Conference of Industrial Hygienists has recommended a threshold limit value of 3 mg m^{-3} (ACGIH, 2007) and only 0.4% of the measurements exceeded this limit.

Quantified crystalline components

The respirable dust in the furnace department contained on average 18% SiC, 1.1% quartz and 2.1% cristobalite. In the respirable dust from the processing department, we found 57% SiC, 0.2% quartz and 0.1% cristobalite, while the respirable dust in the maintenance department contained 21% SiC, 0.5% quartz and 0.2% cristobalite.

Respirable dust

The respirable dust exposure levels are shown in Fig. 3 and Table 6. The highest GM exposures to respirable dust (>0.5 mg m^{-3}) were found among cleaning operators in Plant A, mix, charger, charger/mix and sorting operators in Plant C and crusher operators in all plants. When comparing plants, sorting operators in Plant A had significantly lower exposure levels than the sorting operators in the other plants ($P < 0.05$) and the mechanics in Plant B had a significantly higher exposure than the other two plants ($P < 0.05$). The Norwegian OEL for mixed respirable dust is 0.5 mg m^{-3} in the furnace department and furnace-related areas of the SiC industry (The Norwegian Labour Inspection Authority, 2007). A total of 26% of the samples from the furnace department and 15% of the samples from maintenance workers performing maintenance in the furnace department exceeded this limit. Since there is no specific OEL for respirable dust in the processing department, the OEL for nuisance respirable dust of 5 mg m^{-3} was applied here (The Norwegian Labour Inspection Authority, 2007). Only 0.4% of the samples in the processing department and none of the samples from maintenance workers performing maintenance work in the processing department exceeded this limit.

Total dust

Cleaning and crusher operators in Plant A and charger, charger/mix and sorting operators in Plant C had GM exposures to total dust of 4 mg m^{-3} or higher (Table 7). The cleaning operators had four times higher GM exposure than any of the other

job groups, but this observation was based on only two measurements. The sorting operators had a significantly lower exposure in Plant A compared to Plants B and C ($P < 0.001$) and the crane operators in Plant B had a significantly higher exposure compared to crane operators in the two other plants ($P < 0.001$). As there is no specific OEL for total dust in the SiC industry, the Norwegian OEL for nuisance total dust of 10 mg m^{-3} was applied here (The Norwegian Labour Inspection Authority, 2007). This OEL does not take into account that the dust might contain harmful components. Four per cent of the samples were above the OEL and two-thirds of these were from the fines or refinery crusher operators.

Table 8 summarizes the total dust short-term exposure levels. The job group GM ratios of short-term to full-shift total dust samples varied from 0.19 to 1.4 in Plant A, 2.3 to 0.55 in Plant B and 0.4 to 1.2 in Plant C. However, the GM ratios for the separate plants were close to 1; 0.9 for Plant A and C and 1.0 for Plant B.

Sulphur dioxide

Sulphur dioxide exposure was assessed for job groups in the furnace hall. The mean exposure to sulphur dioxide over a full shift was generally low. The charger and charger/mix operators had the highest measured GM (0.37 p.p.m.), which is one-fifth of the OEL of 2 p.p.m. (Table 9) (The Norwegian Labour Inspection Authority, 2007). The highest GM for maximum peak value was found among the control room operators in Plant B (13 p.p.m.) (Table 9). The crane and control room operators in Plant B had a significantly higher maximum peak value compared to the same job groups in the other plants ($P < 0.05$). The sorting operators in Plant A had a significantly lower exposure than the sorting operators in the two other plants ($P < 0.001$).

Use of respirators

Respirators were available for all workers. The use of respirators was mandatory for workers in the furnace hall and for some operations in the refinery department (e.g. packing and cleaning). Different types of respirators were used [i.e. disposable half-masks with P2 or P3 particulate filters, half-masks with particulate filter and gas filter for acid gases (SO_2), powered air-purifying respirators, compressed air-fed respirators and self-contained breathing apparatus (when concentrations of CO were high)]. Most of the workers (74%) reported using respirators some or all of the time during the sampling. The use of respirators varied between plants, and 79% of the workers in Plant C used respirators all or some of the time compared to ~50% of the workers in Plants A and B. The use also varied within plants with 78% of the workers in the furnace department using respirators some or all of the time compared to 46% in refinery and maintenance departments. When measurements exceeded the OEL, between 79 and 100% of the workers had used respirators some or all of the time depending on component. The GM exposure for total dust was 79% higher among workers using respirators all the time, and 65% higher among workers using respirators some of the time compared to workers not using respirators. Similar trends were seen for all other agents.

Work conditions

Ninety-three per cent of the workers reported their perception of the work conditions of the shift. Of these, 84% reported that the conditions were normal, 6% reported it to be worse than normal and 10% reported better than normal.

DISCUSSION

The workers in the SiC industry are exposed to many different agents. In the present investigation, relatively high levels of fibres, quartz, cristobalite and sulphur dioxide were found in the furnace department while the highest exposure levels to non-fibrous SiC dust were observed in the processing department. Exposure levels were generally below the current Norwegian OELs, except for operators in the furnace department where 53% of the fibre and 26% of the respirable dust samples exceeded the OEL. Overall the operators reported that 85% of the measurements were performed under what they considered as normal work conditions. Previous studies of personal exposure in the SiC industry have been carried out in Canada and Norway (Smith *et al.*, 1984; Dufresne *et al.*, 1987; Romundstad *et al.*, 2001; Dion *et al.*, 2005). These studies reported exposure levels of one or more of the agents investigated in the present study; however, the job groups studied were not always comparable to the job groups in the present study.

Exposure to fibres was mainly found among workers in the furnace department. Gunnæs *et al.* (2005) found that airborne SiC fibres in the three Norwegian SiC plants mainly consisted of cubic β-SiC. They also found accumulation of the same β-SiC fibres in the outermost layer of the crude SiC. This layer is removed from the α-SiC in the sorting area prior to transport of α-SiC to the processing department. The sorting operators were therefore likely to be exposed to fibres and they were the highest exposed workers in Plants B and C. Compared to earlier studies, the fibre exposure levels found for sorting operators were lower than those reported by Romundstad *et al.* (2001) (AM = 0.8–1.8 fibres cm^{-3}). Dion *et al.* (2005) found similar levels for sorting operators as in Plant C (AM = 0.5

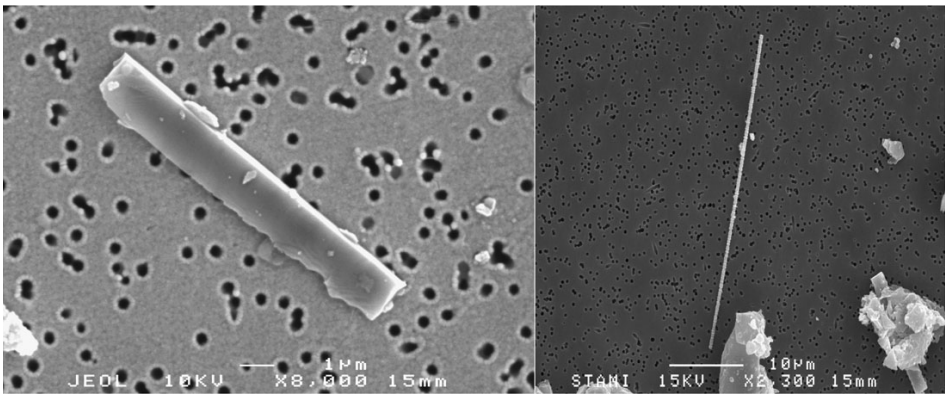

Fig. 4. SEM image of a SiC cleavage fragment to the left and a SiC fibre to the right. The scale bar represents 1 μm on the image to the left and 10 μm on the image to the right. In courtesy of Asbjørn Skogstad, National Institute of Occupational Health, Norway.

fibres cm^{-3}). The charger and charger/mix operators in Plant C were also highly exposed (AM = 0.43 and 0.39 fibres cm^{-3}, respectively) probably because the β-SiC is recycled into the furnace mix and these operators are involved in assembling and loading of furnaces. Romundstad *et al.* (2001) reported an AM of 0.4 fibres cm^{-3} for the charger operators in Plant C, which is similar to what we found. The control room operators in Plant A had a six times higher fibre exposure than the control room operators in the two other plants. This is probably because the control room operators in Plant A supervise the automatic feeder of reclaimed materials to the furnace mix. When there are leaks or jams in this system, the control room operators also cleans up spills. Dion *et al.* (2005) reported a GM of 0.06 fibres cm^{-3} among control room operators, which is similar to Plant B. The cleaning operators in Plant A had a high exposure of fibres, which is probably due to the fibre content of the reclaimed furnace mix that is stored in the area he is responsible for cleaning. The exposure levels of refinery operators were similar to the values reported by Romundstad *et al.* (2001) (AM = 0.04 fibres cm^{-3}) and Dion *et al.* (2005) found similar levels for maintenance operators as observed in Plant A (AM = 0.09 fibres cm^{-3}).

Fibres were counted with a light microscope, which does not provide information on the fibre types present or fibres thinner than ∼0.25 μm. However, Skogstad *et al.* (2006) characterized fibres from the furnace department in the Norwegian SiC plants by scanning electron microscopy (SEM)–energy dispersive spectroscopy. They found that >93% of the fibres were SiC fibres and that the SiC fibres could be divided into eight categories based on their morphology. They also found that <2% of the fibres in the furnace department were fragments of SiC satisfying the WHO counting criteria for length, diameter and aspect ratio (WHO, 1997). These SiC structures probably originate from cleavage of non-fibrous SiC crystals and were most frequently found in samples of the sorting operators. Figure 4 shows SEM micrographs of a SiC fibre and a SiC cleavage fragment. Samples from the processing department showed that 25% of the fibres were SiC fibres, 57% were cleavage fragments and organic fibres constituted 17% (Skogstad, personal communication). This suggests that the OEL for SiC fibres is not applicable to the samples from the processing department. Skogstad *et al.* (2006) further reported that the GM length of all fibres >5 μm was 9.5 μm with a range of 5.0–900 μm and GM diameter of all SiC fibres was 0.39 μm and ranged from the detection limit of the SEM of 0.07 to 2.90 μm. They found that 33% of the fibres had a diameter between 0.07 and 0.25 μm (Skogstad, personal communication). Thus, a substantial number of fibres were not detected in the light microscope counts. Moreover, as a large proportion of fibres were close to the visibility limit of the scanning electron microscope, it is likely that a substantial number of fibres remained undetected even with the SEM.

Exposure to crystalline silica was generally low, <2% of the samples exceeded the OEL. The highest GM exposures to crystalline silica were found in the cleaning, mix, charger and charger/mix operators who work in close contact with raw materials or furnace mix. Quartz sand is one of the raw materials and is transformed to cristobalite at the high temperature in the furnace. Reclaimed unreacted and partly reacted furnace mix that is reused in the new furnace mix therefore represents a source of cristobalite emission. The exposure to crystalline silica was low in the processing department, with the highest levels among crusher operators. The crusher operators have the first contact with SiC that is transported from the sorting area and are therefore exposed to impurities, e.g. quartz that is removed later in the process. The content of crystalline silica in the respirable dust in the SiC industry has been reported in three Canadian studies. Two of the studies report

exposure to both quartz and cristobalite (Dufresne *et al.*, 1987; Dion *et al.*, 2005) and one report the quartz exposure levels (Smith *et al.*, 1984). The GM exposure to quartz was between 2 and 10 times higher for all job groups in the Canadian plants compared to our results. The mix and sorting operators in Plant C had a similar GM cristobalite exposure as the mix and sorting operators in the Canadian studies, while the charger operators in Plant C had a two times higher GM exposure. The GM cristobalite exposure for crane, refinery and maintenance workers were all higher in the Canadian studies compared to our results.

The processing operators had the highest exposure to crystalline non-fibrous SiC. This is as expected since furnace operators are exposed to raw materials and furnace mix, while operators in the processing department are handling mainly pure SiC.

The content of non-fibrous SiC in airborne respirable dust has earlier been studied in two Canadian plants (Dufresne *et al.*, 1987). In general, the observed levels of SiC exposure in the furnace and maintenance operators in the Canadian studies were higher than in our study, while exposure in the refinery department was similar. The proportion of non-fibrous SiC in the respirable dust for sorting operators varied between 41 and 50% in our study, which was fairly similar to the Canadian plants (44–78%). The difference is therefore mainly due to higher dust levels. Other job groups in the furnace department were also exposed to respirable dust with a similar content of SiC in our study (2–10%) as the Canadian study (6–9%). The SiC content of the respirable dust that refinery crusher operators were exposed to was lower in the Canadian study (32%) compared to our results (57–81%). The Canadian results were, however, only based on three samples.

The GM for total dust varied from 0.29 mg m^{-3} for crane operators in Plant C to 21 mg m^{-3} for cleaning operators in Plant A. The GM for respirable dust varied from 0.12 mg m^{-3} for crane operators in Plant A to 1.3 mg m^{-3} for cleaning operators in Plant A. The low exposure of the crane operators is likely because they spend most of their work time inside closed cabins supplied with fresh air. The high exposure found for the cleaning operators was based on only two measurements and could be a chance finding; however, both measurements were reported to be representative for this task.

The measured total dust levels in the furnace department in the present study were 35–86% lower than the levels Romundstad *et al.* (2001) reported from the same plants. The generally lower exposure in the present investigation may partly be explained by introduction of remote controlled equipment and separation of exposure sources from the workers. The exposure levels in the processing department were similar or higher in Plant A, 50% lower in Plant B and ~25% lower in Plant C compared to the earlier study (Romundstad *et al.*, 2001). Three Canadian studies have reported respirable dust exposure levels in two SiC plants (Smith *et al.*, 1984; Dufresne *et al.*, 1987; Dion *et al.*, 2005). They reported higher levels of respirable dust in crane operators (GM = 0.42 mg m^{-3} compared to GM = 0.12–0.23 mg m^{-3}) and mix operators (GM = 1.01 mg m^{-3} compared to GM = 0.41–0.72 mg m^{-3}). Exposure levels for other job groups were essentially similar with those reported in our study.

The short-term measurements of total dust were considered to be representative for full-shift exposure since the mean ratios of short-term to full-shift total dust samples were close to one. This implies that the fibre measurements which were sampled in parallel with the short-term total dust samples can be considered to be representative for full-shift exposure.

Exposure to sulphur dioxide in the furnace hall was generally low with GM <0.4 p.p.m. and well below the Norwegian OEL of 2 p.p.m. However, short-term peaks in the range 10–100 p.p.m. were observed for control room and crane operators in Plants A and B, charger and charger/mix operators in Plant C. These are all operators that occasionally work near by operating furnaces and may be exposed to the gas produced during the thermal process.

Smith *et al.* (1984) found the exposure to sulphur dioxide among furnace workers in a Canadian SiC plant to be between 1.0 and 1.5 and ≤ 0.2 p.p.m. for sorting operators and maintenance workers. The exposure to sulphur dioxide in the Canadian study was based on a different sampling technique. Instead of using direct-reading electrochemical sensors as in the present study, the air was drawn through two midget impingers in series, each containing hydrogen peroxide, and SO_2 was measured by titration of the resulting sulphuric acid solution. The sampling system was said to be inconvenient to use and resulted in collection of limited samples. The authors therefore referred to it as tentative SO_2 exposure. The level of sulphur dioxide released is dependent upon the sulphur content of the coke used, which varies depending on the supplier and the availability of low-sulphur coke.

The most important exposure differences between Plants A, B and C was seen for the sorting operators. The operators in Plant A had lower exposure to most components compared to the other plants. This is probably most likely because the sorting area in Plant A was located in a separate building while the sorting area in Plants B and C was located inside the furnace hall. The sorting operators in Plants B and C were thus exposed to the contaminated ambient air in the furnace hall as well.

There was also a large difference between the exposure to cristobalite, total dust and non-fibrous SiC among mix operators. The operators in Plant A had a significantly lower exposure than in Plant C. This

can be ascribed to the fact that the mix operators in Plant A only handled raw materials, i.e. quartz and petrol coke. In Plant C, the mix operators handled the reclaimed furnace mixture as well. The differences in exposure for mix operators may also partly be explained by the location of the mix area. In Plant A, it was located in a building ~100 m away from the furnace hall, while in Plant C it was in a building with entrance from the furnace hall building and the mix operators in Plant C regularly entered the furnace hall.

Respirators were used by 74% of the workers some or all of the time. The actual exposure levels were therefore lower than indicated by the measurements and will also vary according to type of respirators used (e.g. disposable half-masks with P2 particulate filters versus compressed air-fed respirators).

CONCLUSION

SiC workers are exposed to a complex mixture of several agents. The highest exposures to fibres, crystalline silica and sulphur dioxide were found among operators in the furnace department. The cleaner operators in Plant A and charger and charger/mix operators in Plant C were generally the highest exposed job groups in the furnace department. Exposure to non-fibrous SiC and total dust was significantly higher in the processing department compared to the furnace and maintenance departments and the refinery crusher operators were the highest exposed job group. The exposure levels found in this study were comparable to or lower than the levels reported in previous studies. Exposure levels were generally below the current Norwegian OELs. However, 53% of the fibre samples and 26% of the respirable dust samples from the furnace department exceeded the OELs. The results suggest that a better control of exposure is needed.

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PAPER III

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PAPER IV

Submitted manuscript