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Occupational Exposure to Refractory Ceramic Fibers in the Semiconductor Scrubber Manufacturing Industry

반도체 스크러버 제조 사업장에서 내화성 세라믹 섬유의 직업적 노출평가

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이 논문을 보건학석사 학위논문으로 제출함

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Abstract

Occupational Exposure to Refractory Ceramic Fibers in the Semiconductor Scrubber Manufacturing Industry

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Objective Refractory ceramic fibers (RCFs) are an International Agency for Research on Cancer Group 2B carcinogen, and have been used as insulation under high-temperature working conditions. Depending on the exposure temperature, RCFs could transform into crystalline SiO_2, a carcinogenic agent. In addition, RCFs can be present in the air as workers handle RCFs in bulk. The aims of this study are to analyze the physicochemical and morphological characteristics of RCFs involving high-temperature exposure and determine the occupational exposure levels of RCFs during several processes associated with scrubber maintenance.

Methods This study was conducted at a semiconductor scrubber manufacturing company using RCFs as insulation material. For bulk RCFs, samples were collected before and after exposure to a scrubber temperature of 700°C. For airborne RCFs, personal and area samples were collected during working hours in the scrubber maintenance process. The physicochemical and morphological characteristics of RCFs were analyzed using scanning electron microscope and Raman microscope. The collected airborne RCFs were counted using phase contrast microscope to determine the concentration. The exposure levels of airborne RCFs in the workplace were assessed using a statistical test.

Results Regardless of exposure to high temperature, the main components of bulk RCFs were SiO_2 and Al_2O_3, and the structure of these RCFs was amorphous. However, morphological differences were observed in airborne RCFs owing to the traverse breakage of RCFs in the process of handling bulk RCFs. Most airborne RCFs (n = 300) in the workplace corresponded to the size of respirable fiber. Airborne RCF concentrations were the highest for insulation replacement in both personal and area samples. The exposure levels to airborne RCFs observed in the workplace when performing insulation replacement were greater than the occupational exposure limit.

Conclusion RCFs were shown not to crystallize under high-temperature (700°C) treatment. However, airborne RCFs were morphologically different from bulk RCFs, particularly in terms of their size that could have an adverse impact on health. Workers performing insulation replacement may be exposed to airborne RCFs above the occupational exposure limit. As RCFs are suspected to be carcinogens, the exposure of workers to RCFs should be minimized through the prevention and precautionary principle.

Keyword: Refractory ceramic fibers, High-temperature insulation, Amorphous, Traverse breakage, Respirable fibers, Exposure assessment

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1. Introduction

Asbestos has been used in residential environments and industries for a long time owing to its heat resistance and durability. However, since the carcinogenic threat of asbestos to humans was discovered, man-made vitreous fibers (MMVFs) have been used as a substitute (Osinubi et al., 2000). MMVFs can be categorized into various types, such as glass wool, rock wool, slag wool, and refractory ceramic fibers (RCFs), depending on their chemical composition. Of these types, RCFs are fibers that contain silicon dioxide (SiO_2) and aluminum oxide (Al_2O_3) as the main components (NIOSH, 2006). Compared with other MMVFs, RCFs have greater favorability in high-temperature environments of 1000°C or higher owing to the presence of Al_2O_3, which accounts for more than 40% of the chemical composition of RCFs (IARC, 2002).

Depending on the manufacturing method, RCFs can be made in different forms, such as bats or blankets. These forms consist of individual fibers extruded in long structures having small diameters (Utell & Maxim, 2018). Workers may be exposed to these fibers upon handling RCFs. Meanwhile, RCFs are classified as Group 2B carcinogen by the International Agency for Research on Cancer (IARC), a suspected carcinogenic agent to humans that can cause lung disease if inhaled. The nominal diameter of bulk RCFs is 1.2–3 μm, which is smaller than that of other MMVFs (IARC, 2002; NIOSH, 2006). These fibers (length > 5 μm, diameter < 3 μm, aspect ratio ≥ 5:1), when inhaled becomes deposited into the alveolar region and cause adverse health effects (Maxim et al., 2006; NIOSH, 2006).

RCFs are composed of amorphous SiO_2. However, previous studies have suggested that amorphous SiO_2 in RCFs can be crystallized, depending on the heating temperature and time (Brown & Harrison, 2014). RCFs have been shown to change to forms of crystalline SiO_2, such as quartz, cristobalite, tridymite, and mullite, depending on temperature conditions (Comodi et al., 2010; Gualtieri et al., 2009), and crystalline SiO_2 is classified by the IARC as a Group 1 human carcinogen (IARC, 2012). However, these studies indicating form changes to crystalline SiO_2 were conducted under controlled temperature conditions, which do not reflect the high-temperature conditions of the workplace. Considering that RCFs are used as insulation to heat in the workplace, it is necessary to investigate the change in the structure of RCFs due to high-temperature exposure.

As mentioned above, RCFs have been used for insulation under high-temperature working conditions because of their superior insulating characteristics, as compared with other MMVFs (Maxim et al., 2008). Particularly, they are used as insulation for semiconductor scrubbers operating under high temperatures of 700°C or higher. The scrubber, which is maintained at a high temperature, is used to treat waste gas generated in the semiconductor manufacturing process (Arts et al., 2007). Therefore, with the use of a scrubber, regular preventive maintenance (PM) is required. During this process, workers can be exposed to RCFs. However, there is still an insufficient number of studies on worker exposure to hazards in the semiconductor PM process (Park et al., 2010; Yoon, 2012). As the semiconductor industry continues to grow and the emission of gaseous pollutants generated from the process increases, the demand for treatment by scrubbers will increase (Kim et al., 2012; Kim et al., 2018). For this reason, an assessment of the hazards of exposure to RCF during applications such as scrubber maintenance in semiconductor fabrication is necessary.

The aims of this study are to analyze the physicochemical and morphological characteristics of bulk RCFs under high-temperature exposure in a semiconductor scrubber manufacturing workplace. In addition, this study seeks to investigate the characteristics and exposure levels of airborne RCFs in the workplace that arises from handling bulk RCFs.

2. Methods

2.1. Study subject

Sampling was carried out in July 2020 at a semiconductor scrubber factory located in South Korea. Blanket insulation using RCFs was employed to wrap the heater inside the scrubber and the insulation was handled by workers. The scrubber maintenance process was categorized into three tasks: scrubber frame assembly, insulation replacement, and cleaning of scrubber parts. In the first process, two workers assembled or disassembled the scrubber frame and replaced the insulation. The scrubber parts were cleaned by three workers. The scrubber maintenance was carried out in a workplace having a length of 24 m, width of 5.4 m, and height of 3.8 m. The average temperature of the scrubber maintenance workplace was 24.6 ± 3.1℃ and the average relative humidity was 55.3 ± 9.7%. The average wind speed in the workplace at the ground-level was 0.83 ± 0.5 m/s and the wind speed measured at 1.5 m above the workplace floor was 0.18 ± 0.1 m/s. The workplace was a negative air pressure room.

In this study, glass wool was used for insulation along with RCFs. However, in the workplace, RCFs provided the primary insulation for all scrubbers. Therefore, in the main text of this paper, only the RCF content is presented. The glass wool is described in the Appendix.

This study was conducted with the consent of the company and its workers. In addition, the research ethics was approved by the Seoul National University Institutional Review Board.

2.2. Sampling strategy

Two types of bulk RCFs were collected. One set of bulk RCFs was unused insulation that was not exposed to the high temperatures of 700°C. The other set of bulk RCFs was exposed to high temperatures as insulation. Airborne RCFs were collected during the assembly of the scrubber frame, replacement of insulation, and cleaning of scrubber parts. In addition, sampling was carried out at the scrubber inspection workplace, outside exhaust, and outdoors, locations where RCFs are not handled. Airborne RCF samples were measured by separating the samples into personal and area samples.

Personal samples for airborne RCFs were collected using a conductive polypropylene cassette equipped with 25-mm mixed cellulose ester (MCE) membrane filters (pore size 0.8 μm). After the pump (GilAir-3 Sampling Pump, Gilian, US) was connected to the cassette, the flow rate was 2 L/min. The pump was attached to the worker to sample from the worker's breathing zone.

Area samples of airborne RCFs were sampled with polycarbonate (PC; diameter 37 mm, pore size 0.8 μm), polyvinyl chloride (PVC; diameter 37 mm, pore size 5 μm), and MCE membrane filters. The PC filters were linked to the three-piece conductive polypropylene cassette, and the PVC filters were linked to the three-piece cassette. Each filter was connected to a pump, and sampling was performed at a height of 1.5 m from the floor of the workplace, with a pump flow rate of 2 L/min.

All samples were collected in the morning and afternoon during working hours for three days. The ventilation system in the workplace was investigated with a mist generator and a heated-element anemometer (Velocicalc Air Velocity Meter, TSI, US).

2.3. Analytical method

2.3.1. Physicochemical and morphological characteristics

Bulk and airborne RCFs collected using PC filters were analyzed for morphology and chemical composition using scanning electron microscope–energy dispersive x-ray spectroscopy (SEM-EDS, MERLIN Compact, ZEISS, Germany). The bulk sample and parts of the PC filters were attached to carbon tape. Considering that they may not have been sampled with PC filters, airborne RCFs on the walls of the conductive cassette were also attached to the carbon tape. The carbon tape was attached to a stub of diameter 25 mm and thickness 6 mm. The stub was coated with Pt for 200 s at a current of 10 mA. The prepared sample was analyzed using SEM. Table 1 shows the measurement conditions of the instrument. The image resolution of the SEM was set to 1024 × 768 pixels and the acceleration voltage was set to 15.0 kV. The magnification of the SEM ranged from a minimum of 100X to a maximum of 20,000X. The chemical composition of the sample was analyzed using EDS.

The structure of bulk and airborne RCFs collected with PVC filters was analyzed using Raman microscope (DXR 3xi, Thermo Scientific, US) without sample preparation. The images were displayed using an electron-multiplying charge-coupled device (EMCCD). The laser wavelength was 532 nm and the laser power was 10 mW. The wavenumber ranged from 3400 to 50 cm^{-1} and the magnification of Raman microscope ranged from 100X to 20,000X.

Table 1. Instrument measurement conditions

Field emission scanning electron microscope (MERLIN compact, ZEISS, Germany)	Detector	Ultra dry EDS detector (Thermo fisher scientific, US)
	Image resolution	1024 × 768
	Image pixel size	0.28 μm
	Acceleration voltage	15.0 kV
	Magnification	50-20,000X
Raman imaging microscope (DXR 3xi, Thermo fisher scientific, US)	Detector	EMCCD
	Laser wavelength	532 nm
	Laser power	10 mW
	Wavenumber range	3400-50 cm^{-1}
	Number of scans	300
	Exposure time	0.5 sec
	Magnification	10-100X
	Aperture	25 μm confocal pinhole
Phase contrast microscope (BH2, Olympus, Japan)	Objective lens	Olympus SPlan 40PL
	Reticle	Walton-Beckett graticule
	Magnification	400X

2.3.2. Airborne RCF counting

Sample preparation of airborne RCFs collected with MCE filters was based on National Institute for Occupational Safety and Health (NIOSH) method 7400 (NIOSH, 2019). The MCE filter placed on the microscope slide was pre-treated with acetone (Sigma–Aldrich, US) and triacetin (Kanto Chemical, Japan). Afterward, the glass was covered, leaving no air bubbles on the filter. The prepared MCE filter was analyzed using a phase contrast microscope (PCM, BH2, Olympus, Japan) equipped with a Walton–Beckett graticule. Respirable fibers (length > 5 μm, diameter < 3 μm, aspect ratio ≥ 5:1) based on the NIOSH 7400 B counting rule. The magnification of the PCM was 400X. The number of fibers over a total of 100 fields was counted and the PCM magnification was set to 400X. The fiber quantity, calculated as the airborne RCF concentration, was determined by applying the sampling flow rate and time using Equations 1 and 2 (NIOSH, 2019):

$$E = \frac{\left(\frac{F}{n_f}\right) - \left(\frac{B}{n_b}\right)}{A_f}, fibers/mm^2$$

Equation 1.

where E is the fiber density on the filter, F/n_f is the amount of fiber in the samples per counted graticule field, B/n_b is the amount of fiber in the blank sample per counted graticule field, and A_f is the area of the graticule of one field (0.00785 m^2).

$$Airborne\ RCFs = \frac{E \times A_c}{V \times 1000}, fibers/cc$$

Equation 2.

In Equation 2, A_c, which represents the area of a 25-mm filter, is 385 mm^2, and V is the sampling air volume. The limit of detection (LOD) was 0.00071 f/cc, which was calculated by dividing a minimum-detectable 0.5 fiber fields of PCM with the average sampling air volume. Values less than LOD were calculated as LOD/2 (Hornung & Reed, 1990).

2.4. Statistical analysis

The airborne RCF concentrations were compared for each process using statistical analysis. In the Kolmogorov–Smirnov test, the sampled airborne RCFs showed a log-normal distribution. Therefore, the airborne RCF concentration was expressed in terms of the geometric mean (GM) and geometric standard deviation (GSD). The comparison of concentrations for each task was statistically tested using the Mann–Whitney U test and Kruskal–Wallis test. The result of the statistical test was considered statistically significant when $p < 0.05$. The airborne RCF exposure variation within and between workers was analyzed by one-way analysis of variance. Statistical analysis was performed using the Statistical Package for the Social Sciences version 25 (IBM, US) and Excel Office 365 (Microsoft, US). The figures in this paper were created with Sigma Plot 12.5 (Systat Software, US).

Bayesian decision analysis was used to estimate the exposure range of airborne RCFs in the scrubber maintenance workplace. The upper confidence limit (UCL) of the estimated 95th percentile ($X_{0.95}$) was calculated based on professional judgment, sampling data, and the occupational exposure limit (OEL) of RCFs in the workplace (Hewett et al., 2006; Kim et al., 2014). The OEL of RCFs is 0.2 f/cc, as per the American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV)-time weighted average (TWA) for RCFs (ACGIH, 2020). The exposure range was confirmed by comparing the estimated $X_{0.95}$ with the American Industrial Hygiene Association exposure categories. The exposure categories were divided into four, corresponding to 1%, 10%, 50%, and 100% of OEL. Bayesian decision analysis was performed by an industrial hygiene data analyst-student 2020 (EASi, US).

3. Results

3.1. Effect of high temperature on the characteristics of bulk RCFs

3.1.1. Bulk RCF characteristics before high-temperature exposure

The bulk RCFs used were blanket-type insulation. Workers handled two types of RCFs during insulation replacement: RCFs before and after exposure to 700°C temperatures. The first type of RCFs represented new RCFs prior to wrapping inside the scrubber. The RCFs analyzed by SEM were in the form of an RCF bundle (Figure 1A). The manufacturer's nominal RCF diameter was 3 μm and the average bulk RCF ($n = 300$) diameter measured in this study was 2.6 ± 1.2 μm. The bulk RCFs had a length of 200 μm or greater; however, all fibers exceeded the area of the SEM lens. Thus, the exact length could not be measured. SiO_2 and Al_2O_3 comprise more than 89% of the total RCF composition, based on the weight percentage (Figure 1C). Si and Al, excluding oxides, showed similar proportions of 23% and 24%, respectively. The remaining components were small amounts of C, Cu, Zn, and Pt. The RCFs before exposure to high temperatures were amorphous (Figure 2A). Broad Si-O peaks in the Raman spectra were observed at 1080 cm^{-1}, 808 cm^{-1}, and 440 cm^{-1}.

3.1.2. Bulk RCF characteristics after high-temperature exposure

Workers disassembled the scrubber frame and removed the insulation exposed to the high temperature of 700°C. The average diameter of high-temperature-exposed RCFs ($n = 300$) confirmed by SEM was 2.9 ± 1.4 μm (Figure 1B). High-temperature-exposed RCFs were long fibers that exceeded the SEM lens area; thus, the exact length could not be measured. The main chemical components were SiO_2 and Al_2O_3, comprising 84% of the total (Figure 1D), with the proportions of Si and Al at 21% each. C, Cu, and Pt exhibited proportions of 6.0%, 3.0%, and 7.0%, respectively. Similar to RCFs before high-temperature exposure, broad Si-O peaks were observed at 1060 cm^{-1}, 806 cm^{-1}, and 442 cm^{-1} in Raman spectra (Figure 2B).

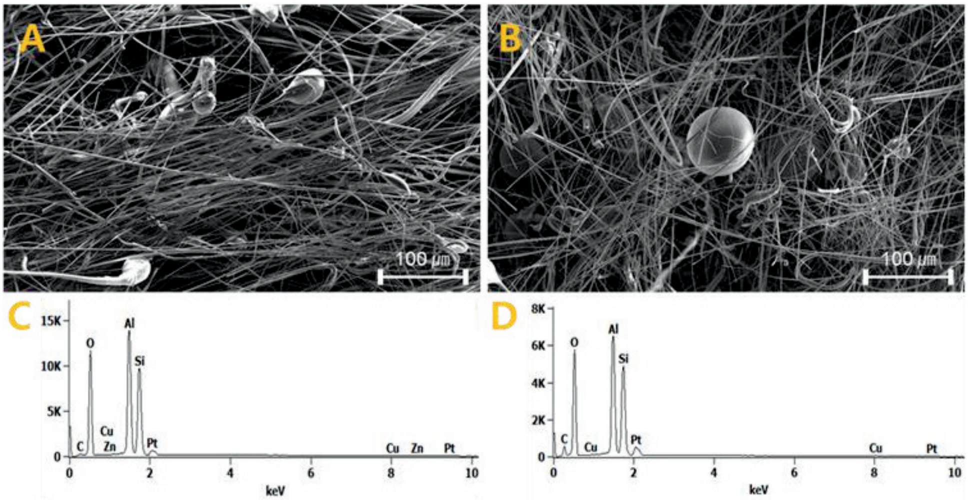

Figure 1. SEM images of bulk RCFs. A: Bulk RCFs before high-temperature exposure under 100X magnification; B: Bulk RCFs after high-temperature exposure under 100X magnification; C: SEM-EDS spectra of bulk RCFs before high-temperature exposure; D: SEM-EDS spectra of bulk RCFs after high-temperature exposure

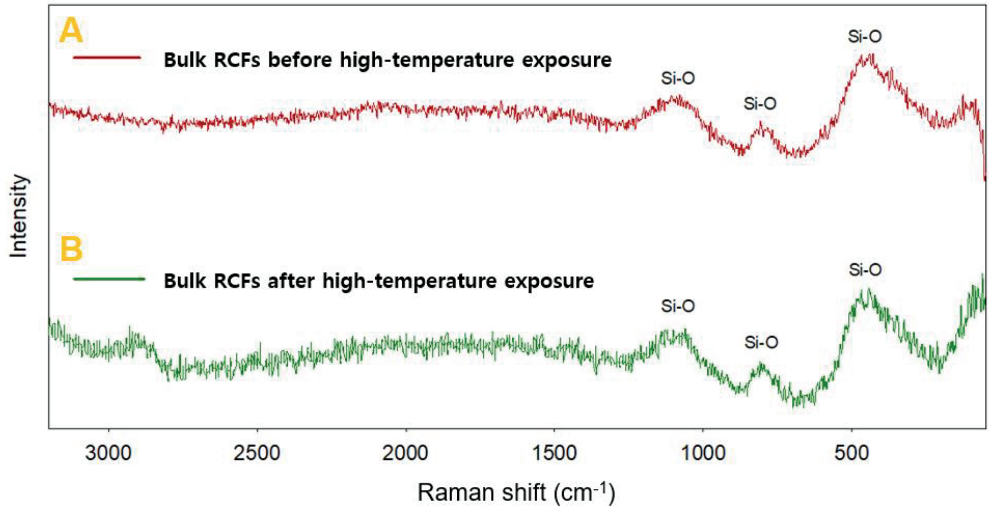

Figure 2. Raman spectra of bulk RCFs. A: Bulk RCFs before high-temperature exposure; B: Bulk RCFs after high-temperature exposure

3.2. Physicochemical and morphological characteristics of airborne RCFs

When replacing insulation, workers had to disassemble, assemble, and cut the insulation by hand. During this process, the form of RCFs was physically destroyed and released into the air. Airborne RCFs were morphologically different from bulk RCFs (Figure 3A). The diameter and length of airborne RCFs (n = 300) were GM 2.10(1.91) µm and GM 43.3(2.17) µm, respectively. Although the diameter of airborne RCFs was not significantly different from that of bulk RCFs, there was a significant difference in length ($p < 0.05$). The transverse breakage was demonstrated in the cross-section of airborne RCFs (Figure 3B).

The airborne RCFs comprised SiO_2 and Al_2O_3 (77%). Excluding oxides, both Si and Al made up 17% of the total composition. Other components were C, Pt, Cu, and Zn. In addition, the composition of Mg was analyzed to be ~0.04% (Figure 3C). The structure of airborne RCFs was amorphous, with a broad Si-O peaks at 1067 cm^{-1}, 789 cm^{-1}, and 436 cm^{-1} (Figure 3D).

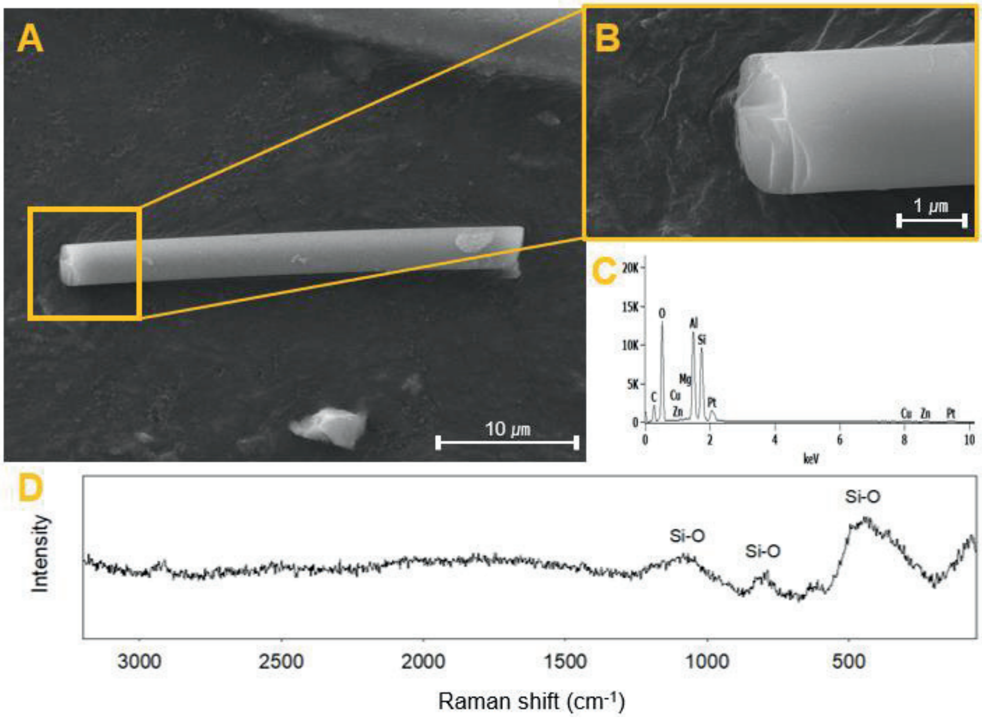

Figure 3. SEM and Raman microscope images of airborne RCFs. A: SEM images of airborne RCFs under 3,000X magnification; B: SEM images of airborne RCFs cross section under 20,000X magnification; C: SEM-EDS spectra of airborne RCFs; D: Raman spectra of airborne RCFs

3.3. Size distribution of airborne RCFs

The length and diameter of airborne RCFs (n = 300) sampled during the scrubber maintenance process were analyzed (Table 2). RCFs of length 5–20 μm constituted 17% of the total (n = 300). Airborne RCFs with lengths 21–50 μm, 50–100 μm, and > 100 μm constituted 42%, 22%, and 19% of the total, respectively. RCFs < 5 μm in length were not identified. Among airborne RCFs, fibers having a diameter 1–3 μm comprised 60% of the total. The fibers with diameter < 1 μm and > 3 μm constituted 11% and 29%, respectively. RCFs with lengths of 20 μm or greater and diameters of 3 μm or less constituted up 58% of the total. Of the 300 fibers, 8% (n = 24) was glass wool. The average diameters of bulk glass wool before and after high-temperature exposure were 9.25 ± 1.7 μm and 8.69 ± 2.0 μm, respectively (Appendix 1). RCFs and glass wool exhibited different fiber diameters; the two fibers were classified based on fiber diameter.

As shown in Figure 4, RCFs with an aspect ratio of 3–5 constituted 4% (n = 12) and that with an aspect ratio of 5–10 constituted 14% (n = 42) of the total (n = 300). RCFs with an aspect ratio of 10–50 accounted for the largest proportion, at 65% (n = 196). In addition, RCFs with an aspect ratio of 50 or greater constituted 16% (n = 47), whereas those with an aspect ratio of less than three constituted only 1% (n = 3) of the total.

Table 2. Size distribution of airborne RCFs released during insulation replacement (n = 300)

		Diameter			
		< 1 μm	1-3 μm	> 3 μm	Total
Length	< 5 μm	0 (0%)	0 (0%)	0 (0%)	0 (0%)
	5-20 μm	8 (3%)	31 (10%)	13 (4%)	52 (17%)
	21-50 μm	18 (6%)	90 (30%)	19 (6%)	127 (42%)
	51-100 μm	3 (1%)	34 (11%)	28 (10%)	65 (22%)
	> 100 μm	4 (1%)	26 (9%)	26 (9%)	56 (19%)
	Total	33 (11%)	181 (60%)	86 (29%)	300[a] (100%)

[a]Of the 300 fibers, 8% (n = 24) was glass wool.

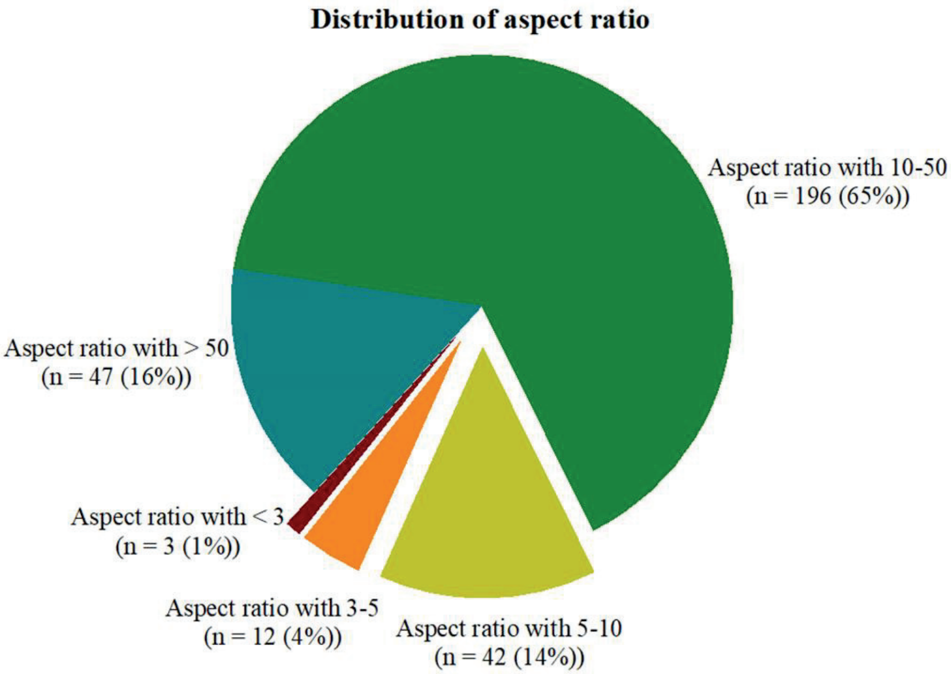

Figure 4. Aspect ratio distribution of airborne RCFs in insulation replacement workplace (n = 300)

3.4. Exposure level of airborne RCFs in the workplace

3.4.1. Airborne RCF exposure level comparison

As mentioned above, the scrubber maintenance process is divided into three sub-tasks: scrubber frame assembly, insulation replacement, and cleaning of scrubber parts (Table 3). The personal and area samples of airborne RCFs were measured for each task. However, for personal samples, the scrubber frame assembly and insulation replacement tasks were performed by the same workers. Therefore, in personal samples, the airborne RCF concentration was calculated by considering these two tasks as one.

The concentration of personal samples of airborne RCFs in the scrubber maintenance process was GM 0.14(2.7) f/cc and was in the range of 0.028–0.61 f/cc during frame assembly and insulation replacement processes. In the cleaning process, the airborne RCF concentration was GM 0.017(2.3) f/cc and the concentration even reached as high as 0.055 f/cc. In the Mann–Whitney U test, there was a statistical significance in the concentration of personal samples in each process ($p < 0.001$).

In the area samples, the highest concentration of airborne RCFs was observed during the insulation replacement in the scrubber maintenance process. The airborne RCF concentration was GM 0.033(2.3) f/cc; it was in the range of 0.012–0.10 f/cc during the insulation replacement. During the scrubber frame assembly and cleaning, the airborne RCF concentration was GM 0.0023(8.9) f/cc and GM 0.011(2.2) f/cc, respectively. The Kruskal–Wallis test for the area samples of the three tasks showed a statistical significance in the concentration of airborne RCFs in each task ($p < 0.05$). The total concentration of airborne RCFs in the scrubber maintenance workplace was GM 0.039(3.9) f/cc in personal samples and GM 0.0054(4.6) f/cc in area samples. There was a statistical significance between the mean concentrations of personal samples and area samples ($p < 0.05$).

In the workplace where RCFs are not handled, the highest concentration of airborne RCFs, GM 0.0042(1.6) f/cc, was observed in the scrubber inspection workplace. However, based on of the median, the outside exhaust showed the highest concentration among the three samples at 0.0047 f/cc and even reached as high as 0.011 f/cc. Outdoors, the concentration of airborne fiber was GM 0.0017(3.8) f/cc. The total concentration in non-RCF-handling workplaces was GM 0.0029(3.0) f/cc, which was statistically significant when compared with the concentration in RCF-handling workplaces ($p < 0.001$).

Table 4 shows the variation in exposure of two workers to airborne RCFs during the scrubber frame assembly and insulation replacement; they were exposed to airborne RCF concentration of greater than OEL (0.2 f/cc) on days 1 and 3. The within-worker variance was 0.84 and the between-worker variance was 0.49. The three workers who cleaned the scrubber parts were exposed to airborne RCF concentration less than the OEL on all sampling days. The within-worker variance of the workers who performed this task was 0.58 and the between-worker variance was 0.2.

Table 3. Distribution of airborne RCF concentration in scrubber maintenance workplace

Sample type		Task type	n[a]	Sampling time (min)	Airborne RCF concentration (f/cc)[b]			p-value
					GM(GSD)	Median	Range	
Personal sample		Scrubber frame assembly and insulation replacement	12(12)[a]	177 ± 41	0.14(2.7)	0.14	0.028-0.61	$p < 0.001$[c]
		Cleaning of scrubber parts	18(18)[a]	165 ± 50	0.017(2.3)	0.020	0.0032-0.055	
		Total	30(30)[a]	170 ± 46	0.039(3.9)	0.037	0.0032-0.61	
Area sample	RCF handling workplace	Scrubber frame assembly	6(3)[a]	175 ± 49	0.0023(8.9)	0.0036	< LOD-0.062	$p < 0.05$[d]
		Insulation replacement	7(7)[a]	182 ± 50	0.033(2.3)	0.040	0.012-0.10	
		Cleaning of scrubber parts	11(11)[a]	172 ± 47	0.011(2.2)	0.0093	0.0024-0.031	
		Total	24(21)[a]	176 ± 46	0.0054(4.6)	0.011	LOD-0.10	
	Non-RCF handling workplace	Scrubber inspection	6(6)[a]	172 ± 52	0.0042(1.6)	0.0040	0.0023-0.0076	$p = 0.685$[d]
		Outside exhaust	12(10)[a]	167 ± 42	0.0031(3.3)	0.0047	< LOD-0.011	
		Outdoors	6(4)[a]	162 ± 42	0.0017(3.8)	0.0023	< LOD-0.0066	
		Total	24(20)[a]	167 ± 43	0.0029(3.0)	0.0036	< LOD-0.011	

[a]Values within parentheses indicate the number of samples excluding those with concentrations less than LOD among all samples. [b]Approximately 8% of airborne fiber was glass wool. [c]Mann–Whitney U test ($p < 0.05$), [d]Kruskal-Wallis test ($p < 0.05$)

Table 4. Airborne RCF exposure variation within worker and between workers

Task	k[a]	Day 1		Day 2		Day 3		Within worker	Between workers
		n[b]	GM(GSD)	n[b]	GM(GSD)	n[b]	GM(GSD)	Variance ± SD[c]	Variance ± SD[c]
Scrubber frame assembly and insulation replacement	2	4	0.21(3.6)	4	0.058(1.8)	4	0.2(1.4)	0.84 ± 0.9	0.49 ± 0.7
Cleaning of scrubber parts	3	6	0.019(2.7)	6	0.0092(2.0)	6	0.030(1.3)	0.58 ± 0.8	0.2 ± 0.4

[a]Number of workers, [b]Number of samples, [c]Standard deviation

3.4.2. Airborne RCF exposure range estimation

Bayesian decision analysis was performed on personal samples of five workers (Table 5). The $X_{0.95}$ value of airborne RCFs (n = 12) during the assembly of the frame and replacement of the insulation was 0.69 f/cc. The probability of $X_{0.95}$ exceeding 0.2 f/cc, which is the OEL for RCFs, was 100%. For workers A and B performing this task, the probability of $X_{0.95}$ value of exposure exceeding the OEL was 99.1% and 100%, respectively.

The $X_{0.95}$ value of airborne RCFs (n = 18) during cleaning the scrubber parts was 0.069 f/cc. The probability of $X_{0.95}$ exceeding the OEL was 0.8%; the probability of $X_{0.95}$ residing between 10% and 50% of the limit was 80.1% and that residing between 50% and 100% was 19.1%. For workers C, D, and E performing the cleaning task, the probability of $X_{0.95}$ being between 10% and 50% of the OEL was 54.4%, 97.3%, and 67.1%, respectively.

Table 5. Bayesian decision distributions of exposure to airborne RCFs by task and worker in scrubber maintenance workplace

Worker	Task	n	Airborne RCF concentration (f/cc)			$X_{0.95}$[a] (f/cc)	Bayesian decision analysis exposure rating (%)			
			GM(GSD)	Median	Range		1[b]	2[c]	3[d]	4[e]
A	Scrubber frame assembly and insulation replacement	6	0.11(3.1)	0.11	0.028-0.61	0.66	0	0	0.9	99.1
B		6	0.18(2.3)	0.19	0.052-0.54	0.70	0	0	0	100
Total	Scrubber frame assembly and insulation replacement	12	0.14(2.7)	0.14	0.028-0.61	0.69	0	0	0	100
C	Cleaning of scrubber parts	6	0.017(2.9)	0.028	0.0032-0.042	0.10	0	54.4	35.4	10.1
D		6	0.020(1.4)	0.020	0.014-0.036	0.034	0	97.3	2.3	0.4
E		6	0.014(2.8)	0.019	0.0035-0.055	0.081	0.1	67.1	27	5.8
Total	Cleaning of scrubber parts	18	0.017(2.3)	0.020	0.0032-0.055	0.069	0	80.1	19.1	0.8

[a]Upper confidence limit of the estimated 95th percentile, [b]1% OEL < $X_{0.95}$ ≤ 10% OEL (Highly-controlled), [c]10% OEL < $X_{0.95}$ ≤ 50% OEL (Well-controlled), [d]50% OEL < $X_{0.95}$ ≤ 100% OEL (Controlled), [e]100% OEL < $X_{0.95}$ (Poorly-controlled)

4. Discussion

In the United States, furnace lining accounts for more than 60% of the demand for RCFs (as cited in IARC, 2002). Additionally, in Europe, 50% of RCFs are used in furnaces, heaters, and related applications, and 15% are used for high-temperature applications, such as fire protection and heat shields (as cited in IARC, 2002). Under these varied circumstances, RCFs may have different characteristics and concentrations to which workers are exposed, depending on the temperature conditions and handling methods in the work environment. The present study reveals whether the structure of RCFs changes at a high temperature of 700℃ and examines the morphological differences between bulk RCFs and airborne RCFs. Furthermore, the exposure level to airborne RCFs is assessed by task and worker.

This study shows that there are no physicochemical or morphological differences between bulk RCFs before and after high-temperature exposure. This is due to the fact that when RCFs are used as heat insulation materials for heaters in scrubbers, no physical force is applied, except the high-temperature exposure. In the bulk RCFs used in this study, the main components were SiO_2 and Al_2O_3 with similar proportions. The proportions of the components were determined to be the same before and after high-temperature exposure.

In this study, it was expected that bulk RCFs as blanket-type insulation would crystallize when exposed to the scrubber temperature condition of 700°C. However, the RCF structure remained the same, before and after high-temperature exposure. In fact, the Raman spectra for both examples showed a broad peak in a similar wavenumber region. Recent evidence shows that the four amorphous silicates exhibited a broad Si-O peak in similar peak positions as those exhibited by crystalline silicates with different degrees of polymerization; in contrast, sharp Si-O peaks were observed for crystalline silicates (Fu et al., 2017). It is believed that the temperature was not high enough to crystallize the structures of the RCFs. Comodi et al. (2010) showed that RCFs began to crystallize into mullite at 950°C and cristobalite and tridymite at 1350°C. In addition, Gualtieri et al. (2009) revealed that amorphous RCFs crystallized to cristobalite when exposed to 1200°C or higher.

Workers could be exposed to airborne RCFs while handling bulk RCFs. The airborne RCFs observed in the workplace were shorter owing to the traverse breakage of bulk RCFs. Crystalline minerals, such as asbestos, have structural properties that cause longitudinal fracture due to mechanical stress, resulting in smaller diameters; The MMVFs, such as RCFs, become transversely fractured owing to their amorphous structure, resulting in shorter lengths (NIOSH, 2006). In this study, the airborne fibers with a diameter of 1–3 μm constituted 60% of the total number of fibers (n = 300). Linnainmaa et al. (2007) determined the diameter distribution of airborne RCFs in the metal industry using RCFs and demonstrated that 51% of the airborne fibers had a diameter of 1–3 μm, similar to the results of this study. Respirable fibers with a diameter of 1–3 μm can reach the alveolar region through inhalation (Costa & Orriols, 2012). Among the fibers accumulated in the distal pulmonary and alveolar regions, fibers with lengths of 20 μm or greater may be toxic to the respiratory system (Greim et al., 2014). Because the diameter of pulmonary macrophage is 14–21 μm, fibers larger than the diameter of pulmonary macrophage are not completely engulfed by macrophages (Utell & Maxim, 2018). Therefore, RCFs may not be removed by phagocytosis of macrophages; during this process, macrophages may be destroyed, causing additional inflammation in the deposited alveolar region (Zhu et al., 2018). In addition, long fibers deposited in the alveolar region can break into short fibers through dissolution and breakage, increasing the possibility for further toxic effects (Maxim et al., 2006). However, according to a study using the computational fluid dynamics model to study the deposition pattern of carbon fibers in the respiratory airway, fibers greater than 100 μm were not deposited in the lung region, and glass fibers with greater densities and diameters than carbon fibers were accumulated in the nasal cavity (Inthavong et al., 2013). In addition, the deposition rate of fibers in the human body is affected not only by the fiber dimension but also by the breathing path and inspiratory flow rate (Su & Cheng, 2006). Therefore, according to previous studies, airborne RCFs, which account for 40% of the total (n = 300), maybe more harmful than fibers of other sizes when exposed to workers.

The exposure level of airborne RCFs in each scrubber maintenance task revealed that the personal samples were highly concentrated during the frame assembly and insulation replacement processes. In area samples, high concentrations of airborne RCFs were identified during insulation replacement. Insulation replacement is a process in which workers disassemble, assemble, and cut insulation. Since the task was carried out by hand, relatively high levels of airborne RCFs were confirmed in the workplace, despite the presence of a ventilation system. During this task, airborne RCF concentration was observed to reach as high as 0.61 f/cc, exceeding the TLV-TWA of 0.2 f/cc for RCFs (ACGIH, 2020).

The variation in exposure to personal samples of five workers demonstrated that the within-worker variance was greater than the between-worker variance. Therefore, the daily exposure difference to airborne RCFs was greater than the difference in exposure between workers doing the same work. This is due to the difference in the amount of scrubber handled for maintenance from day-to-day. During the sampling period, the amount of scrubber handled was different for each working day. However, the relationship between workload and exposure level of airborne RCFs was not described in this study because specific workload information was not known.

Bayesian decision analysis demonstrated that workers who perform insulation replacement may be frequently exposed to high concentrations of airborne RCFs exceeding 0.2 f/cc. However, relatively low concentrations of airborne RCFs were found in the personal samples of workers who cleaned the scrubber parts and in all area samples. In addition, from the Bayesian decision analysis of the cleaning task, it was estimated with a greater than 50% probability that the personal exposure of airborne RCFs would be 10%–50% of TLV-TWA.

According to previous studies, occupational exposure concentrations of airborne RCFs were GM 0.10(5.3), 0.58(6.15), and 1.17(3.54) f/cc in TWA for the assembly, installation, and removal of RCFs, respectively (D. L. Maxim et al., 1999; NIOSH, 2006). Furthermore, Maxim et al. (2008) identified that when occupational exposures to RCFs over 10 years were classified according to functional job categories, RCFs were shown to be exposed above the exposure standard (0.2 f/cc) during finishing, installation, and removal. In this study, it was assumed that the worker replacing insulation could assemble, install, and remove RCFs at the same time; hence, they could be exposed to high concentrations of airborne RCFs. The high concentration of airborne RCFs in the workplace was influenced not only by the type of task but also by the type of ventilation system. The ventilation system in the workplace is a structure that collects air from the floor of the workplace and exhausts it through the wall outlet. However, there was no air exerting pressure downward from the upper part of the workplace and the airflow in the downstream direction was weak; thus, it was not possible to prevent exposure from the scattering of RCFs. The airborne RCFs was observed outside at the exhaust, despite the high efficiency particulate air filter of the ventilation system.

Generally, the toxicity of RCFs is related to the dose, diameter, and durability of fibers, known as the 3Ds (Cannizzaro et al., 2019; Costa & Orriols, 2012; Greim et al., 2014; Maxim et al., 2006; Utell & Maxim, 2018). RCFs with diameters of 1–3 μm can accumulate in high concentrations in the body through the respiratory system, leading to large deposition of RCFs in the alveolar region (Maxim et al., 2006). The deposited RCFs can cause inflammations in the alveolar regions. Considering the morphological characteristics and exposure levels of airborne RCFs identified in this study, RCFs exposed by scrubber maintenance workers have the 3D toxicity characteristics mentioned above. Falzone et al. (2016) reported that the mechanism of toxicity caused by MMVFs occurs after an incubation period of 20 to 60 years after continuous exposure. Therefore, since RCFs are suspected carcinogens, the exposure of workers to RCFs should be minimized through prevention and precaution principle.

PM is an essential aspect of the semiconductor manufacturing process. In this study, RCFs that may be exposed during semiconductor scrubber PM were studied; it is to be noted that workers may also be exposed to other hazardous chemicals. In general, semiconductor scrubber PM is performed by employees of outside contractors that supply scrubbers to semiconductor companies, rather than employees of semiconductor companies themselves (Park et al., 2010). However, studies assessing the hazards of exposure to RCFs during semiconductor scrubber PM remain insufficient. The occupational exposure assessments for various hazards that may result from scrubber PM should be carried out continuously.

A limitation of this study is that the number of samples was small, as the study considered only one company. However, the characteristics of RCFs under high-temperature exposure were analyzed by three microscopy methods. In addition, it is meaningful that a small number of samples were analyzed from various perspectives, confirming the exposure level of and variation in RCFs in workers through statistical analysis. It is necessary to further study the characteristics of and occupational exposure to RCFs by conducting research in other types of workplaces that handle RCFs under high temperatures.

5. Conclusion

Bulk RCFs handled in an industrial workplace were found to not differ physicochemically or morphologically before and after exposure to a scrubber temperature of 700°C. The airborne RCFs had the same amorphous SiO_2 structure and chemical composition as the bulk RCFs; however, the morphology differed from that of bulk RCFs, owing to the traverse breakage of fibers during the RCF handling process. Most of the airborne RCFs sampled consisted of respirable fibers. Workers were exposed to the greatest concentration of airborne RCFs during insulation replacement, in which the disassembly, assembly, and cutting of RCFs were performed by hand. It is estimated that workers doing this task were exposed to RCF levels above the OEL.

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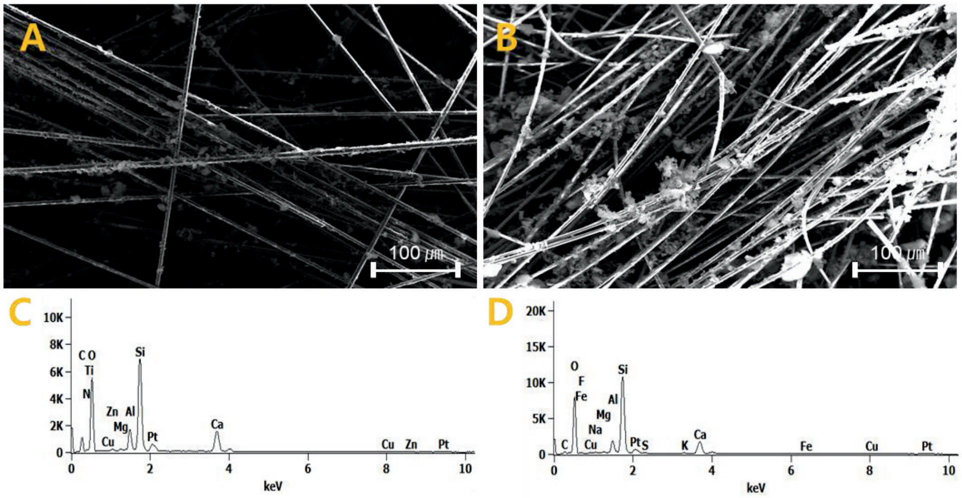
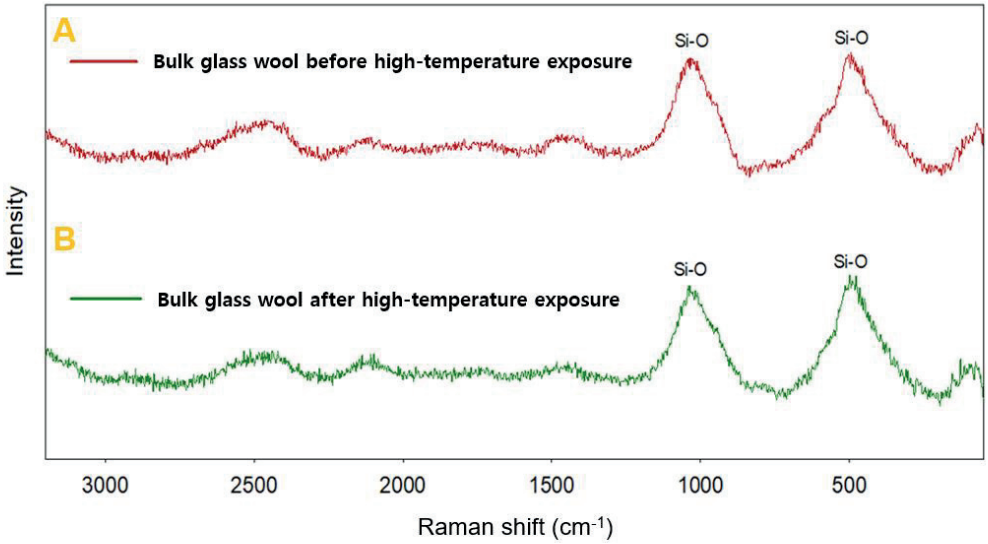
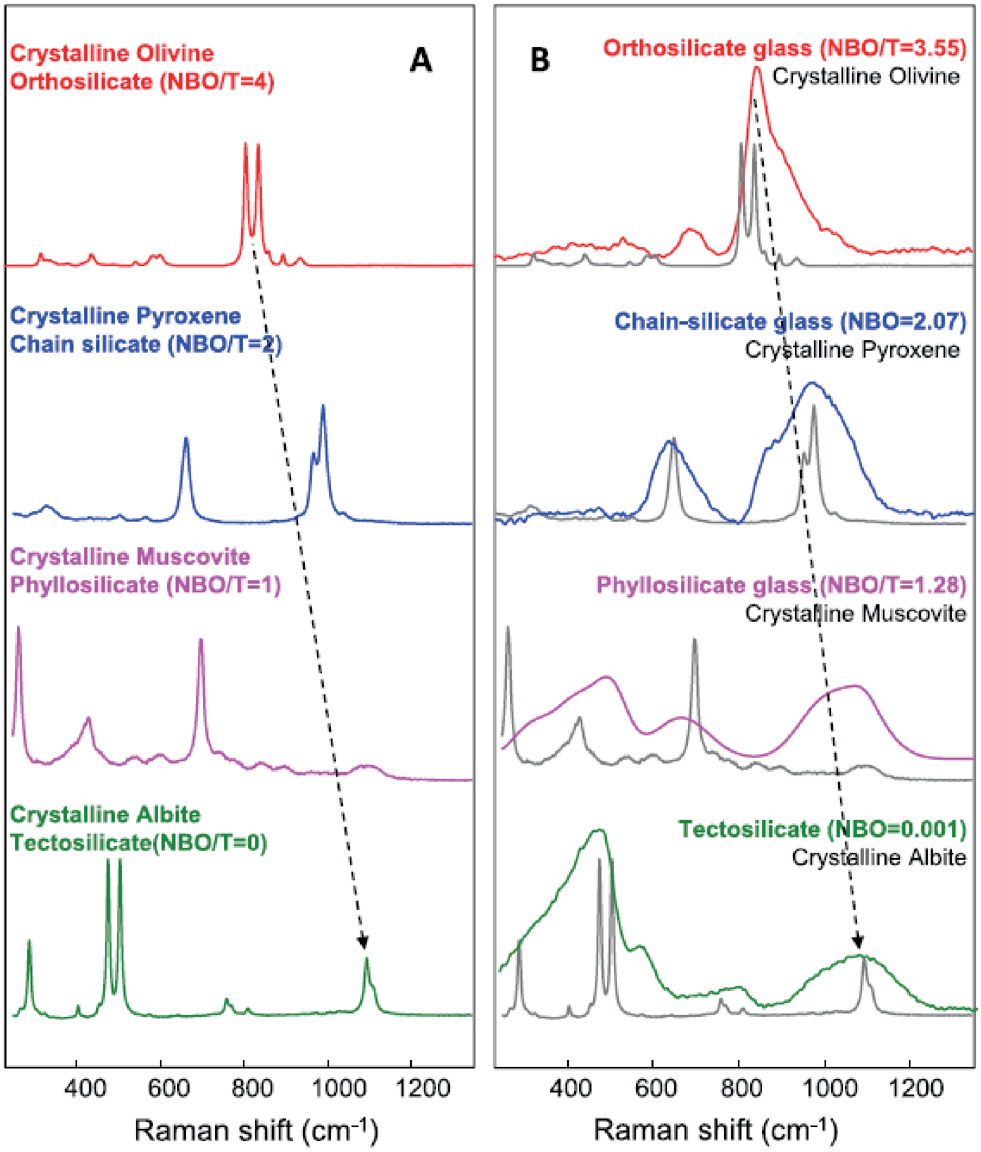
Appendix



Appendix 1. SEM images of bulk glass wool. A: Bulk glass wool before high-temperature exposure under 100X magnification; B: Bulk glass wool after high-temperature exposure under 100X magnification; C: SEM-EDS spectra of bulk glass wool before high-temperature exposure; D: SEM-EDS spectra of bulk glass wool after high-temperature exposure



Appendix 2. Raman spectra of bulk glass wool. A: Bulk glass wool before high-temperature exposure; B: Bulk glass wool after high-temperature exposure



Appendix 3. Raman spectra of crystalline silicates and synthesized glasses. (a) Raman spectra of silicate minerals. (b) Comparison of Raman spectra of crystalline silicates and synthesized glasses. Reprinted from "Characterizing amorphous silicates in extraterrestrial materials: Polymerization effects on Raman and mid-IR spectral features of alkali and alkali earth silicate glasses," by Fu, X., Wang, A. & Krawczynski, M. J., 2017, *Journal of Geophysical Research: Planets*, 122(5), page 844 (https://doi.org/10.1002/2016JE005241). Copyright 2017 by the American Geophysical Union. Reprinted with permission.

국문초록

반도체 스크러버 제조 사업장에서 내화성 세라믹 섬유의 직업적 노출평가

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연구 배경: IARC Group 2B인 내화성 세라믹 섬유(Refractory ceramic fibers, RCFs)는 고온작업환경에서 단열재로 사용되어 왔다. RCFs는 노출온도에 따라 발암성 물질인 결정형 SiO_2로 결정화 될 수 있으며, 근로자가 RCFs 고형시료를 취급하는 과정에서 공기 중으로 RCFs가 비산될 수 있다. 본 연구의 목적은 RCFs의 물리화학적, 형태학적 특성을 확인하고 스크러버 유지보수 공정 내 작업 별 공기 중 RCFs의 직업적 노출 수준을 평가하는 것이다.

연구 방법: RCFs를 단열재로 사용하는 반도체 스크러버 제조 사업장에서 연구를 진행하였다. 고형시료는 스크러버 온도조건인 700℃ 노출 전, 후의 RCFs를 채취하였다. 공기 중 RCFs는 스크러버 유지보수 공정에서 작업시간동안 개인시료와 지역시료를 채취하였다. 주사전자현미경과 라만현미경을 이용해 RCFs의 물리화학적, 형태학적 특성을 분석하였으며 채취한 섬유는 위상차현미경으로 계수하여 공기 중 농도를 구하였다. 작업장 내 공기 중 RCFs 노출수준은 통계분석을 이용하여 평가하였다.

연구 결과: RCFs 고형시료는 고온노출에 관계없이 주요 화학적 구성 성분은 SiO_2와 Al_2O_3이었으며 결정구조는 비결정이었다. 그러나 근로자가 RCFs 고형시료를 취급하는 과정에서 RCFs가 가로방향으로 파괴되어 공기 중 RCFs에서 형태학적 차이가 관찰되었다. 대부분의 작업장 내 공기 중 RCFs (n = 300)는 호흡성 섬유 크기에 포함되었다. 공기 중 RCFs 농도는 개인시료, 지역시료 모두 단열재 교체 작업에서 가장 높게 확인되었다. 단열재 교체 작업을 할 때 작업장에서 확인된 공기 중 RCFs는 직업적 노출 기준 이상이었다.

결론: 본 연구의 고온 노출 조건(700℃)에서 RCFs는 결정화되지 않았다. 그러나 RCFs 고형시료 취급과정에서 발생한 공기 중 RCFs는 고형시료와 형태학적 차이가 있었으며 이러한 공기 중 RCFs는 건강 악영향을 끼칠 수 있는 유해한 크기였다. 단열재 교체 작업을 하는 근로자는 노출 기준 이상으로 공기 중 RCFs에 노출될 수 있다. RCFs는 발암성 의심물질이기 때문에 예방과 사전주의 원칙을 통해 근로자의 RCFs 노출을 최소화해야 한다.

주요어: 내화성 세라믹 섬유, 고온 단열재, 비결정, 횡단 파괴, 호흡성 섬유, 노출평가

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