



## Original article

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

Seungwhan Song<sup>1</sup>, Sunju Kim<sup>2</sup>, Donghyeon Kim<sup>1</sup>, Chungsik Yoon<sup>1,3,\*</sup><sup>1</sup> Department of Environmental Health Sciences, Graduate School of Public Health, Seoul National University, Seoul 08826, Republic of Korea<sup>2</sup> Center for Technology Innovation, Seoul Institute of Technology, Seoul 03909, Republic of Korea<sup>3</sup> Institute of Health and Environment, Seoul National University, Seoul 08826, Republic of Korea

## ARTICLE INFO

## Article history:

Received 6 October 2021

Received in revised form

8 April 2022

Accepted 25 April 2022

Available online 7 May 2022

## Keywords:

Exposure assessment

High-temperature insulation

Occupational exposure

Refractory ceramic fibers

Work environment

## ABSTRACT

**Background:** Refractory ceramic fibers (RCFs) are a suspected carcinogen but have been widely used as insulations. Depending on the temperature, RCFs can transform into crystalline SiO<sub>2</sub>, which is a carcinogen that can be present in the air during bulk RCF handling. This study analyzed the physico-chemical and morphological characteristics of RCFs at high temperatures and determined the exposure levels during the semiconductor scrubber maintenance.

**Methods:** Sampling was conducted at a company that manufactures semiconductor scrubbers using RCFs as insulation. Bulk RCF samples were collected both before and after exposure to a scrubber temperature of 700°C. Airborne RCFs were collected during scrubber maintenance, and their characteristics were analyzed using microscopes.

**Results:** The components of bulk RCFs were SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, having an amorphous structure. Airborne RCFs were morphologically different from bulk RCFs in size, which could negatively affect maintenance workers' health. 58% of airborne RCFs correspond to the size of thoracic and respirable fibers. RCFs did not crystallize at high temperatures. The exposure caused by airborne RCFs during the scrubber frame assembly and insulation replacement was higher than the occupational exposure limit.

**Conclusion:** Workers conducting insulation replacement are likely exposed to airborne RCFs above safe exposure limits. As RCFs are suspected carcinogens, this exposure should be minimized through prevention and precautionary procedures.

© 2022 Occupational Safety and Health Research Institute, Published by Elsevier Korea LLC. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

## 1. Introduction

Asbestos has been used in residential environments and industries for a long time, owing to its heat resistance and durability [1]. Since the carcinogenic threat of asbestos to humans was discovered, man-made vitreous fibers (MMVFs) have been used as a safe substitute [2]. MMVFs can be categorized into various types, such as glass wool, rock wool, and refractory ceramic fibers (RCFs), depending on their chemical composition. Of these, RCFs are fibers that contain silicon dioxide (SiO<sub>2</sub>) and aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) as their main components [3]. Compared to other MMVFs, RCFs have greater success in high-temperature environments, i.e., 1000 °C or

higher, owing to the presence of Al<sub>2</sub>O<sub>3</sub>, which accounts for more than 40% of the RCF's chemical composition [4].

Depending on the method of manufacturing, RCFs can be made either as blanket or roll insulations; these forms consist of individual fibers extruded in long structures with small diameters [5]. Workers may be exposed to these fibers when handling RCFs, despite the fact that RCFs are classified as Group 2B substances (a suspected carcinogenic agent that can cause lung disease if inhaled by humans) by the International Agency for Research on Cancer (IARC). The diameter of bulk RCFs is between 1.2–3 μm, which is smaller than that of other MMVFs [3,4]. These fibers, therefore, get deposited into the alveoli upon inhalation and may have the potential to cause adverse health effects [3,6].

Seungwhan Song: <https://orcid.org/0000-0001-6065-707X>; Sunju Kim: <https://orcid.org/0000-0001-9997-0776>; Chungsik Yoon: <https://orcid.org/0000-0001-7822-0079>

\* Corresponding author. Department of Environmental Health Sciences, Graduate School of Public Health, Seoul National University, Institute of Health and Environment, Seoul National University, 1, Gwanak-ro, Gwanak-gu, Seoul 08826, Republic of Korea.

E-mail address: [csyoon@snu.ac.kr](mailto:csyoon@snu.ac.kr) (C. Yoon).

2093-7911/\$ – see front matter © 2022 Occupational Safety and Health Research Institute, Published by Elsevier Korea LLC. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

<https://doi.org/10.1016/j.shaw.2022.04.005>

RCFs are composed of amorphous SiO<sub>2</sub>; however, previous studies have suggested that amorphous SiO<sub>2</sub> in RCFs can be crystallized depending on the heating temperature and time [7]. RCFs are known to change to various forms of crystalline SiO<sub>2</sub>, such as quartz, cristobalite, and tridymite, depending on the temperature [8,9]; crystalline SiO<sub>2</sub> is classified as a Group 1 human carcinogen by the IARC [10]. Interestingly, these studies were conducted under controlled temperature conditions, which do not reflect the high-temperature conditions of the scrubbers. Considering the fact that RCFs are used as insulation materials in the workplace, it is necessary to investigate the changes in RCF structure due to exposure to high temperatures.

RCFs are used as insulation for semiconductor scrubbers that operate under high temperatures, i.e., 700°C or higher. The scrubber, which is maintained at this high temperature, is used to treat waste gases generated during the semiconductor manufacturing process [12]. Since the scrubber is in constant use, regular preventive maintenance is required to ensure safety, during which workers could get exposed to RCFs. However, there is still an insufficient number of studies on human exposure to hazards in the semiconductor preventive maintenance [13,14]. As the semiconductor industry continues to grow and the emission of gaseous pollutants generated from this growth increases, the demand for treatment by scrubbers will also increase [15,16]. This makes an assessment of the hazards of RCF exposure during semiconductor scrubber maintenance necessary.

The aim of this study is to analyze the physicochemical and morphological characteristics of bulk RCFs under high-temperature in a semiconductor scrubber manufacturing factory. In addition, this study investigates the characteristics and exposure levels of airborne RCFs in such workplaces arising from handling bulk RCFs.

## 2. Materials and methods

### 2.1. Subject of study

Sampling was carried out in July 2020 at a semiconductor scrubber factory located in South Korea. Blanket insulation using RCFs was used to wrap the heater inside the scrubber, and this insulation was handled by workers. The scrubber maintenance process was categorized into three tasks: scrubber frame assembly, insulation replacement, and the cleaning of scrubber parts. During scrubber frame assembly, two workers assembled or disassembled the scrubber frame and replaced the insulation. The scrubber parts were then cleaned by three workers. The scrubber maintenance was carried out in the workplace (Length × Width × Height = 24 m × 5.4 m × 3.8 m = 492.5 m<sup>3</sup>).

In this study, glass wool was used for insulation along with the RCFs. In the workplace, however, RCFs provided primary insulation for all scrubbers, which is why only the RCF content is presented in the main text of this study. The glass wool is further described in the supplementary material.

This study was conducted with the consent of the company and its workers. The research ethics was approved by the Seoul National University Institutional Review Board (IRB No. 2007/002-005).

### 2.2. Sampling strategy

Two types of bulk RCFs were collected: One set of unused insulation RCFs that had not been exposed to the scrubber's high temperatures and another of bulk RCFs that had been exposed to high temperatures while acting as insulation. Airborne RCFs were collected during the assembly of the scrubber frame, replacement of insulation, and cleaning of scrubber parts. Since these three tasks deal with RCFs, airborne RCFs were sampled by selecting workers

who perform these tasks. Additionally, sampling was conducted within the scrubber inspection workplace, the exhaust outside, the general outdoors, and locations where RCFs were 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 mixed cellulose ester (MCE; diameter 25 mm, pore size 0.8 μm) filters. After the pump (GilAir Sampling Pump; Sensidyne, Florida, USA) was connected to the cassette, the flow rate was 2 L/min. The pump was then attached to the worker to sample their breathing patterns.

Area samples of airborne RCFs were sampled using polycarbonate (PC; diameter 37 mm, pore size 0.8 μm), polyvinyl chloride (PVC; diameter 37 mm, pore size 5 μm), and MCE filters (SKC, Pennsylvania, USA). 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 to full-period consecutive sampling in which two samples were collected by dividing the working hour into morning and afternoon for three days. Temperature and relative humidity were measured using a thermo-hygrometer (TR-72Ui; T&D, Matsumoto, Japan); the general ventilation system in the workplace was investigated using a heated-element anemometer (TSI 9545; TSI, Minnesota, USA). The average temperature of the scrubber maintenance workplace was 24.6 ± 3.1°C, and the average relative humidity was 55.3 ± 9.7%. Average wind speed at the ground level of the workplace was 0.83 ± 0.5 m/s, while 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.

### 2.3. Analytical methodology

#### 2.3.1. Physicochemical and morphological characteristics

Bulk and airborne RCFs collected using PC filters were analyzed for their morphological and chemical composition using a field emission-scanning electron microscope (FE-SEM; MERLIN Compact; ZEISS, Oberkochen, Germany), along with an energy-dispersive X-ray spectroscopy (Ultradry EDS detector; Thermo fisher scientific, Massachusetts, USA). The bulk sample and parts of the PC filters were attached to carbon tape. Considering that they may be overlooked when counting airborne RCFs (n = 300) on PC filters, airborne RCFs on the walls of the conductive cassette were also attached to the carbon tape. This carbon tape was then attached to a stub, which was coated with Pt for 200 s at a current of 10 mA. The prepared sample was then analyzed for size distribution using FE-SEM; acceleration voltage was set to 15.0 kV, and the FE-SEM magnification ranged from 100 × to 20,000 ×. The chemical composition of the sample was also analyzed using EDS.

The structure of bulk and airborne RCFs collected with PVC filters was analyzed using a Raman microscope (DXR 3xi; Thermo Scientific, Massachusetts, USA), without any sample preparation. The images were then displayed using an electron-multiplying charge-coupled device; the laser wavelength was 532 nm, the laser power was 10 mW, and the magnification of the Raman microscope ranged from 100 × to 20,000 ×.

#### 2.3.2. Airborne RCF counting

Sample preparation of airborne RCFs, collected using MCE filters, was based on the National Institute for Occupational Safety and Health's (NIOSH) method 7400 [17]. The MCE filter placed on the microscope slide was pretreated with acetone (Sigma–Aldrich, Missouri, USA) and triacetin (Kanto Chemical, Tokyo, Japan); the prepared MCE filter was analyzed using a phase-contrast

microscope (PCM; BH2; Olympus, Tokyo, Japan) equipped with a Walton–Beckett graticule. The fibers (length  $>5 \mu\text{m}$ , diameter  $<3 \mu\text{m}$ , aspect ratio  $\geq 5:1$ ) were based on the NIOSH 7400 B counting rule, and the magnification of the PCM was  $400\times$ . The fiber quantity, calculated as the airborne RCF concentration, was determined by applying sampling flow rate and time [17].

The limit of detection (LOD) was  $0.00071 \text{ f/cc}$ , which was calculated by dividing a minimum-detectable  $0.5$  fiber fields of PCM with the average sample of air volume. Values less than LOD were calculated as  $\text{LOD}/2$  [18].

## 2.4. Statistical analysis

### 2.4.1. Distribution of airborne RCFs

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, airborne RCF concentration was expressed as 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  $p < 0.05$ . Variations in exposure to airborne RCFs within and between workers were analyzed by using a one-way analysis of variance. Statistical analysis was performed using the Statistical Package for the Social Sciences (Version 25; IBM, USA) and Excel (Office 365; Microsoft, Washington, USA); graphs were created using Sigma Plot (Version 12.5; Systat Software, Illinois, USA).

### 2.4.2. Airborne RCFs exposure assessment

Bayesian decision analysis was used to estimate the exposure range of airborne RCFs during scrubber maintenance. The upper confidence limit 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 [19,20]. The OEL of RCFs is  $0.2 \text{ f/cc}$ , as per the American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit of a value-time weighted average (TLV-TWA) for RCFs [21]. The exposure range was confirmed by comparing estimated  $X_{0.95}$  values with the American Industrial Hygiene Association exposure categories. The exposure categories were divided into four, corre-

sponding to 1%, 10%, 50%, and 100% of OEL, respectively. Bayesian decision analysis was performed using an industrial hygiene data analyst-student (Version 2020; EASi, USA).

## 3. Results

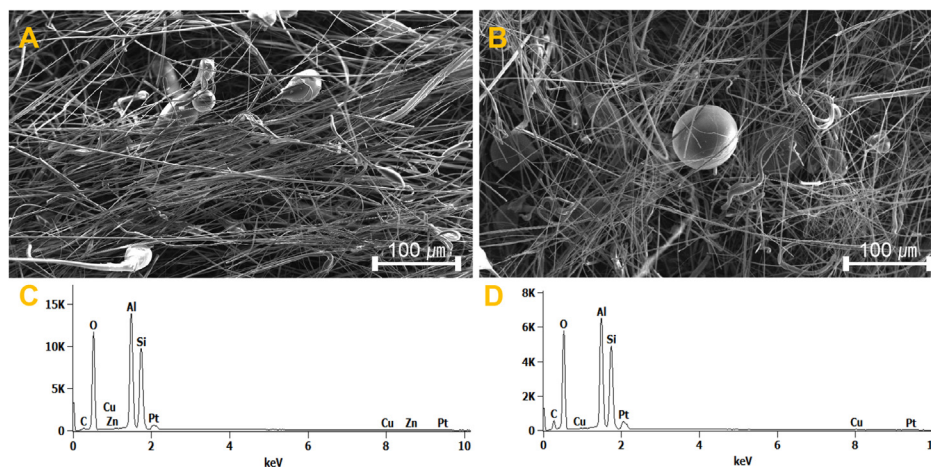
### 3.1. Effect of high temperature on the characteristics of bulk RCFs

The bulk RCFs that were used had blanket-type insulation. Workers handled two types of RCFs during insulation replacement: RCFs before and after exposure to  $700^\circ\text{C}$  temperatures; the former represents new RCFs prior to wrapping inside the scrubber, and the RCFs analyzed by the FE-SEM were in the form of an RCF bundle (Fig. 1(A)). The manufacturer's "normal" RCF diameter was  $3 \mu\text{m}$ , and the average bulk RCFs ( $n = 300$ ) diameter measured in this study was  $2.6 \pm 1.2 \mu\text{m}$ . Bulk RCFs had a length of  $200 \mu\text{m}$  or greater, but all fibers exceeded the area of the FE-SEM lens; thus, the exact length could not be measured.  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  comprised more than 89% of the total RCF composition, based on weight percentage (Fig. 1(C) and (D)). RCFs before exposure to high temperatures were amorphous (Fig. 2(A)). Broad Si–O peaks in the Raman spectra were observed at  $1080 \text{ cm}^{-1}$ ,  $808 \text{ cm}^{-1}$ , and  $440 \text{ cm}^{-1}$ .

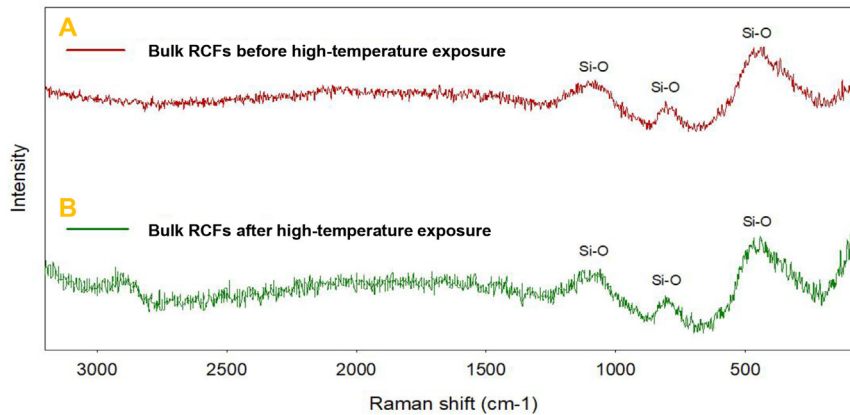
Workers disassembled the scrubber frame and removed the insulation that had been exposed to  $700^\circ\text{C}$ . The average diameter of high-temperature exposed RCFs ( $n = 300$ ) was confirmed by FE-SEM as  $2.9 \pm 1.4 \mu\text{m}$  (Fig. 1(B)). The main chemical components were  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , comprising 84% of the total (Fig. 1(D)). Similar to RCFs before high-temperature exposure, broad Si–O peaks were observed at  $1060 \text{ cm}^{-1}$ ,  $806 \text{ cm}^{-1}$ , and  $442 \text{ cm}^{-1}$  in Raman spectra (Fig. 2(B)).

### 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, RCFs were physically destroyed and released into the air. Airborne RCFs were morphologically different from bulk RCFs (Fig. 3(A)). The diameter and length of airborne RCFs ( $n = 300$ ) were GM  $2.10$  ( $1.91$ )  $\mu\text{m}$  and GM  $43.3$  ( $2.17$ )  $\mu\text{m}$ , respectively. Although the diameter of airborne RCFs was similar to that of bulk RCFs, there was a significant difference in length



**Fig. 1.** FE-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) FE-SEM-EDS spectra of bulk RCFs before high-temperature exposure; (D) FE-SEM-EDS spectra of bulk RCFs after high-temperature exposure.



**Fig. 2.** Raman spectra of bulk RCFs. (A) Bulk RCFs before high-temperature exposure; (B) Bulk RCFs after high-temperature exposure.

( $p < 0.05$ ). Transverse breakage was demonstrated in the cross-section of airborne RCFs (Fig. 3(B)). Airborne RCFs comprised  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  (77%) and had an amorphous structure, with broad Si-O peaks at  $1067\text{ cm}^{-1}$ ,  $789\text{ cm}^{-1}$ , and  $436\text{ cm}^{-1}$  (Fig. 3(D)).

### 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 1); RCFs of length  $5\text{--}20\text{ }\mu\text{m}$  constituted 17% of the total ( $n = 300$ ). Airborne RCFs with lengths  $21\text{--}50\text{ }\mu\text{m}$ ,  $50\text{--}100\text{ }\mu\text{m}$ , and  $>100\text{ }\mu\text{m}$  constituted 42%, 22%, and 19% of the total, respectively. Among airborne RCFs, fibers having a diameter  $1\text{--}3\text{ }\mu\text{m}$  comprised 60% of the total. Fibers with diameters  $<1\text{ }\mu\text{m}$  and  $>3\text{ }\mu\text{m}$  constituted 11% and 29%. Thoracic and respirable sized-RCFs with lengths  $>20\text{ }\mu\text{m}$  and diameters  $<3\text{ }\mu\text{m}$  constituted up to 58% of the total.

As shown in Fig. 4, RCFs with an aspect ratio of  $3\text{--}5$  constituted 4% ( $n = 12$ ), and those with an aspect ratio of  $5\text{--}10$  constituted 14% ( $n = 42$ ) of the total ( $n = 300$ ). RCFs with an aspect ratio of  $10\text{--}50$  accounted for the largest proportion, i.e., 65% ( $n = 196$ ). Additionally, RCFs with an aspect ratio of 50 or greater constituted 16% ( $n = 47$ ).

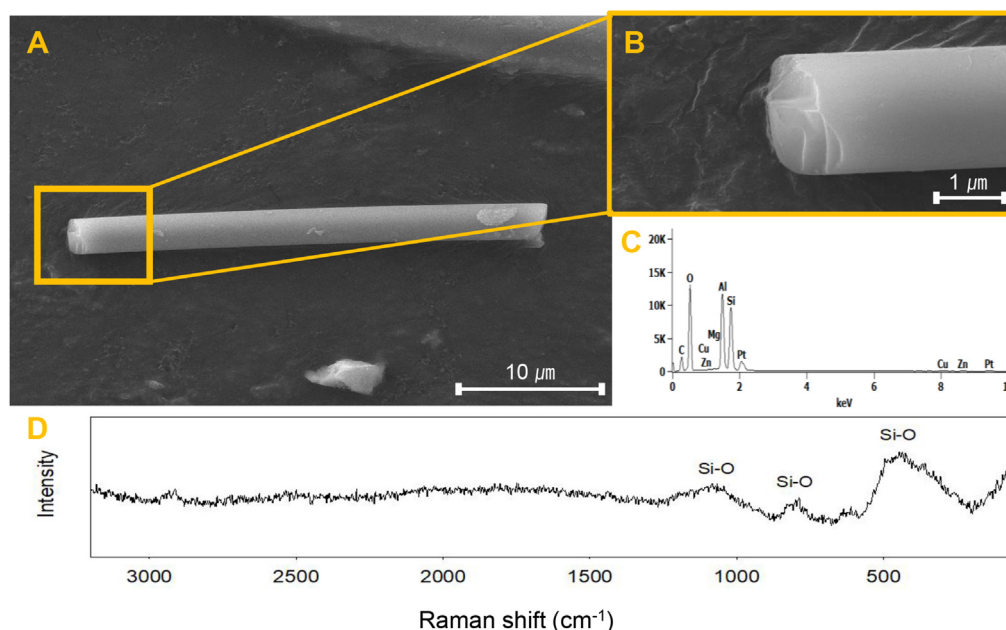
Of the 300 fibers, 8% ( $n = 24$ ) were glass wool. The average diameters of bulk glass wool before and after high-temperature exposure were  $9.25 \pm 1.7\text{ }\mu\text{m}$  and  $8.69 \pm 2.0\text{ }\mu\text{m}$ , respectively (Fig. S1). RCFs and glass wool exhibited different fiber diameters; the two were classified based on diameter.

### 3.4. Exposure levels 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 2). 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 all performed by the same workers; their airborne RCF concentration was calculated by considering these tasks as one.

The concentration of personal samples of airborne RCFs in the scrubber maintenance process was  $\text{GM } 0.14$  ( $2.7$ )  $\text{f/cc}$  and was observed to reach as high as  $0.61\text{ f/cc}$ , exceeding the TLV-TWA of  $0.2\text{ f/cc}$  for RCFs [21], during the scrubber frame assembly and



**Fig. 3.** FE-SEM and Raman microscope images of airborne RCFs. (A) FE-SEM images of airborne RCFs under 3,000X magnification; (B) FE-SEM images of airborne RCFs cross section under 20,000X magnification; (C) FE-SEM-EDS spectra of airborne RCFs; (D) Raman spectra of airborne RCFs.



**Table 1**  
Size distribution of airborne RCFs released during insulation replacement

		Diameter			Total
		<1 $\mu\text{m}$	1-3 $\mu\text{m}$	>3 $\mu\text{m}$	
Length	<5 $\mu\text{m}$	0 (0%)	0 (0%)	0 (0%)	0 (0%)
	5-20 $\mu\text{m}$	8 (3%)	31 (10%)	13 (4%)	52 (17%)
	21-50 $\mu\text{m}$	18 (6%)	90 (30%)	19 (6%)	127 (42%)
	51-100 $\mu\text{m}$	3 (1%)	34 (11%)	28 (10%)	65 (22%)
	>100 $\mu\text{m}$	4 (1%)	26 (9%)	26 (9%)	56 (19%)
Total		33 (11%)	181 (60%)	86 (29%)	300* (100%)

\* Of the 300 fibers, 8% ( $n = 24$ ) was glass wool.

insulation replacement processes. During cleaning, airborne RCF concentration was GM 0.017 (2.3) f/cc, and the concentration even went as high as 0.055 f/cc. In the Mann–Whitney  $U$  test, there were statistically significant concentrations of personal samples in each task ( $p < 0.001$ ).

In area samples, the highest concentration of airborne RCFs was observed during the insulation replacement of the scrubber maintenance process. 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, 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 area samples of the three tasks showed statistically significant concentrations 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 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, i.e., GM 0.0042 (1.6) f/cc, was observed in the scrubber inspection workplace. The total concentration in non-RCF-handling workplaces was GM 0.0029 (3.0) f/cc, which was statistically significant when compared to the concentration in RCF-handling workplaces ( $p < 0.001$ ).

#### 3.4.2. Airborne RCF exposure range estimation

Bayesian decision analysis was performed on personal samples of five workers (Table 3). 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 the  $X_{0.95}$  value of exposure exceeding the OEL was 99.1% and 100%, respectively.

The  $X_{0.95}$  value of airborne RCFs ( $n = 18$ ) during the cleaning of 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 cleaning, the probability of  $X_{0.95}$  between 10% and 50% of the OEL was 54.4%, 97.3%, and 67.1%, respectively.

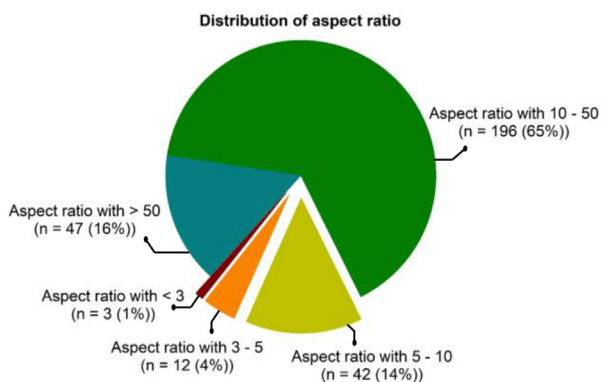
## 4. Discussion

This study shows that there are no physicochemical or morphological differences between bulk RCFs before and after high-temperature exposure because of the fact that no physical force is applied when RCFs are used as heat insulation materials for heaters in scrubbers except the high-temperature exposure. In the bulk RCFs used in this study, the main components were  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , with similar proportions. The proportions of the components were the same before and after high-temperature exposure.

While crystallization of the silica in RCFs is not anticipated at 700°C, the typical temperature in this application, we examined the morphology of the RCF after-use for crystallinity because of the uncertainty in the specific attributes of the application. The RCF structure remained the same before and after high-temperature exposure. The Raman spectra for both examples showed a broad peak in similar wavenumbers. 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 [22]. This may be since the temperature was not high enough to crystallize the RCF's structures. Comodi et al. [8] showed that RCFs began to crystallize into mullite at 950°C and cristobalite and tridymite at 1350°C. Additionally, Gualtieri et al. [9] revealed that amorphous RCFs crystallized to cristobalite when exposed to 1200°C or higher. The company's safety officer and workers handling RCFs in this study were concerned that the blanket-type insulation would crystallize when the temperature of the scrubber exceeded 700 °C. Contrary to the controlled laboratory conditions of previous studies [7–9], the temperature might be higher in the workplace because the temperature is not precisely controlled. Additionally, there are few field studies on crystallization in the field. Therefore, this study tried to evaluate whether the structure of RCFs could be changed under these conditions in the workplace.

Workers were exposed to airborne RCFs while handling bulk RCFs. 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; MMVFs, such as RCFs, become transversely fractured owing to their amorphous structure, resulting in shorter lengths [3]. Linnainmaa et al. [23] determined the diameter distribution of airborne RCFs in the metal industry by using RCFs, and demonstrated that 51% of airborne fibers had a diameter of 1–3  $\mu\text{m}$ , similar to the results of this study; thoracic and respirable fibers with diameters <3  $\mu\text{m}$  reach the lower respiratory tract through inhalation [3].

The level of exposure to airborne RCFs in each scrubber maintenance task revealed that personal samples were highly concentrated during the scrubber frame assembly and insulation replacement processes. In area samples, high concentrations of airborne RCFs were identified during insulation replacement, which is a process in which workers disassemble, assemble, and cut insulation. Since the task was carried out manually, relatively high levels of airborne RCFs were confirmed in the workplace, despite a functioning 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 [21]. When using RCFs, typical tasks that were easily exposed to RCFs include assembly, auxiliary,



**Fig. 4.** Aspect ratio distribution of airborne RCFs in insulation replacement workplace.

**Table 2**  
Distribution of airborne RCF concentration in scrubber maintenance workplace

Sample type	Task type	n <sup>*</sup>	Sampling time (min)	Airborne RCF concentration (f/cc) <sup>†</sup>					p-value
				AM±SD	95% CI	GM(GSD)	Median	Range	
Personal sample	Scrubber frame assembly and insulation replacement	12 (12) <sup>*</sup>	177 ± 41	0.20 ± 0.19	0.083, 0.33	0.14 (2.7)	0.14	0.028-0.61	<i>p</i> < 0.001 <sup>‡</sup>
	Cleaning of scrubber parts	18 (18) <sup>*</sup>	165 ± 50	0.022 ± 0.014	0.015, 0.030	0.017 (2.3)	0.020	0.0032-0.055	
	Total	30 (30) <sup>*</sup>	170 ± 46	0.096 ± 0.15	0.040, 0.15	0.039 (3.9)	0.037	0.0032-0.61	
Area sample RCF handling workplace	Scrubber frame assembly	6 (3) <sup>*</sup>	175 ± 49	0.013 ± 0.024	-0.012, 0.038	0.0023 (8.9)	0.0036	<LOD-0.062	<i>p</i> < 0.05 <sup>§</sup>
	Insulation replacement	7 (7) <sup>*</sup>	182 ± 50	0.043 ± 0.033	0.013, 0.074	0.033 (2.3)	0.040	0.012-0.10	
	Cleaning of scrubber parts	11 (11) <sup>*</sup>	172 ± 47	0.014 ± 0.011	0.0073, 0.022	0.011 (2.2)	0.0093	0.0024-0.031	
Non-RCF handling workplace	Total	24 (21) <sup>*</sup>	176 ± 46	0.022 ± 0.025	0.012, 0.033	0.0054 (4.6)	0.011	LOD-0.10	<i>p</i> = 0.685 <sup>§</sup>
	Scrubber inspection	6 (6) <sup>*</sup>	172 ± 52	0.0045 ± 0.0021	0.0024, 0.0067	0.0042 (1.6)	0.0040	0.0023-0.0076	
	Outside exhaust	12 (10) <sup>*</sup>	167 ± 42	0.0049 ± 0.0036	0.0026, 0.0072	0.0031 (3.3)	0.0047	<LOD-0.011	
	Outdoors	6 (4) <sup>*</sup>	162 ± 42	0.0030 ± 0.0029	0.000011, 0.0061	0.0017 (3.8)	0.0023	<LOD-0.0066	
Total	24 (20) <sup>*</sup>	167 ± 43	0.0043 ± 0.0031	0.0030, 0.0056	0.0029 (3.0)	0.0036	<LOD-0.011		

\* Values within parentheses indicate the number of samples excluding those with concentrations less than LOD among all samples.

<sup>†</sup> Approximately 8% of airborne fiber was glass wool.

<sup>‡</sup> Mann–Whitney *U* test (*p* < 0.05).

<sup>§</sup> Kruskal–Wallis test (*p* < 0.05).

finishing, installation, mixing forming, and removal [3]. Insulation replacement in this study was a task type similar to assembly, installation, and removal in a previous study. 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 [3,24]. Furthermore, Maxim et al. [11] identified that when occupational exposures to RCFs over 10 years were classified according to functional task categories, RCFs levels were above the OEL 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.

In this study, Bayesian decision analysis was used to statistically estimate the exposure range based on expert judgment and sampling results using the number of limited samples. Bayesian decision analysis demonstrated that workers who perform insulation replacement might be frequently exposed to high concentrations of airborne RCFs exceeding 0.2 f/cc; however, relatively low concentrations of airborne RCFs were found in personal samples of workers who cleaned 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. Since the exposure level was evaluated with the ACGIH OEL of 0.2 f/cc in this study, it was inferred that some workers could be exposed to RCFs above the exposure limit. Exposure limits for RCFs vary by

country and institution; France, Germany, and Norway are 0.1 f/cc; the Republic of Korea, Sweden, and ACGIH are 0.2 f/cc; Australia, Austria, Belgium and NIOSH are 0.5 f/cc; Denmark, Netherlands, and the United Kingdom: 1.0 f/cc [25]. If the exposure limit for exposure assessment is set to 0.5 and 1.0 f/cc, all RCFs exposure levels in this study were within the exposure limit. However, considering the handling method of RCFs in this workplace, a strict exposure limit was used because sufficient human exposure to RCFs was suspected. In addition, NIOSH suggested a recommended exposure limit for RCFs of 0.5 f/cc but emphasized an exposure level of less than 0.2 f/cc in the workplace because of the residual risk of cancer due to RCFs [3].

The high concentration of airborne RCFs in the workplace was influenced both by the type of task and the type of ventilation. The general 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. Airborne RCFs were observed at the exhaust, despite the high-efficiency particulate air filter of the general ventilation system.

Generally, the toxicity of RCFs is related to the dose, diameter, and durability of fibers, known as the 3Ds [3,5,6]. RCFs with diameters <3 μm can accumulate in high concentrations in the body through the respiratory system, leading to a large deposition of RCFs in the alveolar region [6], which can cause inflammation.

**Table 3**  
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 <sub>0.95</sub> <sup>*</sup> (f/cc)	Bayesian decision analysis exposure rating (%)			
			GM(GSD)	Median	Range		1 <sup>†</sup>	2 <sup>‡</sup>	3 <sup>§</sup>	4 <sup>  </sup>
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

\* Upper confidence limit of the estimated 95th percentile, <sup>†</sup>1% OEL < X<sub>0.95</sub> ≤ 10% OEL, <sup>‡</sup>10% OEL < X<sub>0.95</sub> ≤ 50% OEL, <sup>§</sup>50% OEL < X<sub>0.95</sub> ≤ 100% OEL, <sup>||</sup>100% OEL < X<sub>0.95</sub>.

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. [26] 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 the prevention and precaution principle.

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 using three microscopies; FE-SEM, Raman microscope, and phase-contrast microscope. Additionally, it is useful that a few samples were analyzed from various perspectives, confirming the exposure levels of RCFs in maintenance workers through Bayesian decision analysis. It is necessary to further study the characteristics and occupational exposure to RCFs by conducting research in other workplaces that handle RCFs under high temperatures.

## 5. Conclusions

Bulk RCFs handled in an industrial workplace were found to be physicochemically and morphologically similar before and after exposure to scrubber temperatures of 700°C. The airborne RCFs had the same amorphous SiO<sub>2</sub> structure and chemical composition as bulk RCFs; however, their morphology differed from that of bulk RCFs owing to the traverse breakage of fibers during the handling process. More than 50% of the airborne RCFs sampled consisted of thoracic and respirable-sized fibers. Workers were exposed to the greatest concentrations of airborne RCFs during the scrubber frame assembly and insulation replacement, in which the disassembly, reassembly, and cutting of RCFs were done manually. It is estimated that the workers involved were exposed to RCF levels higher than the OEL.

## Conflicts of interest

The authors declare no conflict of interest.

## Acknowledgments

This study was supported by the Ministry of Education of the Republic of Korea and the National Research Foundation of Korea (BK21 FOUR 519990214126). We thank the Research Institute of Advanced Materials for facilitating FE-SEM analysis and Thermo Fisher Scientific Korea for facilitating Raman microscopy.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.shaw.2022.04.005>.

## References

- [1] Lee JE, Yoon CS, Ham SH, Tsai PJ. Optimal treatment condition for changing characteristics of naturally occurring asbestos. *Aerosol Air Qual Res* 2015;15: 2332–45.
- [2] Osinubi OY, Gochfeld M, Kipen HM. Health effects of asbestos and nonasbestos fibers. *Environ Health Perspect* 2000;108:665–74.
- [3] National Institute for Occupational Safety and Health. Occupational exposure to refractory ceramic fibers [Internet]; 2006 [cited 10 Oct. 2020], <https://www.cdc.gov/niosh/docs/2006-123/default.html>.
- [4] International Agency for Research on Cancer. IARC monographs on the evaluation of carcinogenic risks to humans, Volume 81, Man-Made Vitreous Fibres [Internet]; 2002 [cited 10 Oct. 2020], <https://publications.iarc.fr/99>.
- [5] Utell MJ, Maxim LD. Refractory ceramic fibers: fiber characteristics, potential health effects and clinical observations. *Toxicol Appl Pharmacol* 2018;361: 113–7.
- [6] Maxim LD, Hadley JG, Potter RM, Niebo R. The role of fiber durability/bio-persistence of silica-based synthetic vitreous fibers and their influence on toxicology. *Regul Toxicol Pharmacol* 2006;46:42–62.
- [7] Brown TP, Harrison PT. Crystalline silica in heated man-made vitreous fibres: a review. *Regul Toxicol Pharmacol* 2014;68:152–9.
- [8] Comodi P, Cera F, Gatta GD, Rotiroti N, Garofani P. The devitrification of artificial fibers: a multimethod approach to quantify the temperature–time onset of cancerogenic crystalline phases. *Ann Occup Hyg* 2010;54: 893–903.
- [9] Gualtieri AF, Foresti E, Lesci IG, Roveri N, Gualtieri ML, Dondi M, Zapparoli M. The thermal transformation of Man-Made Vitreous Fibers (MMVF) and safe recycling as secondary raw materials (SRM). *J Hazard Mater* 2009;162:1494–506.
- [10] International Agency for Research on Cancer. IARC monographs on the evaluation of carcinogenic risks to humans, Volume 100C, Arsenic, metals, fibres and dusts [Internet]; 2012 [cited 27 Oct. 2020], <https://publications.iarc.fr/120>.
- [11] Maxim LD, Allshouse J, Fairfax RE, Lentz T, Venturin D, Walters TE. Workplace monitoring of occupational exposure to refractory ceramic fiber—a 17-year retrospective. *Inhal Toxicol* 2008;20:289–309.
- [12] Yoon JH, Kim YB, Song HW. Numerical and experimental analysis of thermal-flow characteristics in a pyrolysis reactor of a gas scrubber designed based on similitude theory. *J Air Waste Manage Assoc* 2020;70:532–43.
- [13] Park DU, Yang HS, Jeong JY, Ha KC, Choi SJ, Kim CY, Yoon CS, Park DY, Paek DM. A comprehensive review of arsenic levels in the semiconductor manufacturing industry. *Ann Occup Hyg* 2010;54:869–79.
- [14] Yoon CS. Much concern but little research on semiconductor occupational health issues. *J Korean Med Sci* 2012;27:461–4.
- [15] Kim HJ, Han BW, Kim YJ, Yoa SJ, Oda T. Integration of a nonmetallic electrostatic precipitator and a wet scrubber for improved removal of particles and corrosive gas cleaning in semiconductor manufacturing industries. *J Air Waste Manage Assoc* 2012;62:905–15.
- [16] Kim HJ, Han BW, Woo CG, Kim YJ. NOx removal performance of a wet reduction scrubber combined with oxidation by an indirect DBD plasma for semiconductor manufacturing industries. *IEEE Trans Ind Appl* 2018;54:6401–7.
- [17] National Institute for Occupational Safety and Health. NIOSH manual of analytical methods 7400-asbestos and other fibers by PCM [Internet]; 2019 [cited 8 Jul. 2020], [https://www.cdc.gov/niosh/nmam/5th\\_edition\\_web\\_book.html](https://www.cdc.gov/niosh/nmam/5th_edition_web_book.html).
- [18] Hornung RW, Reed LD. Estimation of average concentration in the presence of nondetectable values. *Appl Occup Environ Hyg* 1990;5:46–51.
- [19] Hewett P, Logan P, Mulhausen J, Ramachandran G, Banerjee S. Rating exposure control using Bayesian decision analysis. *J Occup Environ Hyg* 2006;3: 568–81.
- [20] Kim SW, Jang JY, Kim GB. Development and validation of exposure models for construction industry: tier 1 model. *J Korean Soc Occup Environ Hyg* 2014;24: 208–18.
- [21] American Conference of Governmental Industrial Hygienists. Threshold limit values for chemical substances and physical agents and biological exposure indices. Cincinnati: ACGIH; 2020. 57 p.
- [22] Fu X, Wang A, Krawczynski MJ. Characterizing amorphous silicates in extra-terrestrial materials: polymerization effects on Raman and mid-IR spectral features of alkali and alkali earth silicate glasses. *J Geophys Res Planets* 2017;122:839–55.
- [23] Linnainmaa M, Kangas J, Mäkinen M, Metsärinne S, Tossavainen A, Sääntti J, Veteli M, Savolainen H, Kalliokoski P. Exposure to refractory ceramic fibres in the metal industry. *Ann Occup Hyg* 2007;51:509–16.
- [24] Maxim LD, Venturin D, Allshouse JN. Respirable crystalline silica exposure associated with the installation and removal of RCF and conventional silica-containing refractories in industrial furnaces. *Regul Toxicol Pharmacol* 1999;29:44–63.
- [25] Social Europe. Recommendation from the scientific committee on occupational exposure limits for refractory ceramic fibers [Internet]; 2011 [cited 23 Dec. 2021], <https://ec.europa.eu/social/BlobServlet?docId=7371&langId=en>.
- [26] Falzone L, Marconi A, Loreto C, Franco S, Spandidos DA, Libra M. Occupational exposure to carcinogens: benzene, pesticides and fibers. *Mol Med Rep* 2016;14:4467–74.