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Presence of Airborne Fibers in Tungsten Refining and Manufacturing Processes: Preliminary Characterization

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In tungsten refining and manufacturing processes, a series of tungsten oxides (WO_x) are typically formed as intermediates in the production of tungsten powder. Studies in the Swedish tungsten refining and manufacturing industry have shown that intermediate tungsten refining processes can create WO_x fibers. The purpose of the present study was to identify and provide a preliminary characterization of airborne tungsten-containing fiber dimensions, elemental composition, and concentrations in the U.S. tungsten refining and manufacturing industry. To provide the preliminary characterization, 10 static air samples were collected during the course of normal employee work activities and analyzed using standard fiber sampling and counting methods. Results from transmission electron microscopy analyses conducted indicate that airborne fibers with length >0.5 μm, diameter >0.01 μm, and aspect ratio ≥3:1, with a geometric mean (GM) length of ~2.0 μm and GM diameter of ~0.25 μm, were present on 9 of the 10 air samples collected. Energy dispersive X-ray spectrometry results indicate that airborne fibers prior to the carburization process consisted primarily of tungsten and oxygen, with other elements being detected in trace quantities. Results from an air sample collected at the carburization process indicated the presence of fibers composed primarily of tungsten with oxygen and carbon, and traces of other elements. Based on National Institute for Occupational Safety and Health standard fiber counting rules, airborne fiber concentrations ranged from below the limit of detection to 0.14 f/cm³. The calcining process was associated with the highest airborne fiber concentrations. More than 99% (574/578) of the airborne fibers identified had an aerodynamic diameter ≤10 μm, indicating that they were capable of reaching the thoracic regions. Until more is known about the durability and potential health effects associated with airborne tungsten-containing fibers, it would be prudent to take steps to limit or eliminate occupational exposures.

Keywords electron microscopy, hard-metal manufacturing, occupational exposure, thoracic, tungsten blue oxide, tungsten oxide bronze

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The findings and conclusions in this report are those of the authors and do not necessarily represent the views of the National Institute for Occupational Safety and Health.

INTRODUCTION

Tungsten (W) is a naturally occurring element that can be refined and alloyed in production processes to provide products with unique physical and chemical properties well suited to industrial applications. For example, tungsten alloys tend to be strong and flexible, resist wear, and conduct electricity well. Tungsten and its alloys are used as light bulb filaments, as the target anode in X-ray tubes, as catalysts for chemical reactions, as a component of steel in high-speed tools, as welding electrodes, and as gyroscope wheels. Sintered mixtures of tungsten carbide and other metals, referred to as cemented tungsten carbide or hard-metal, are the most common tungsten products produced.⁽¹⁾ Because of the numerous and diverse applications of tungsten in industrial and commercial products, it is estimated that in 2002, approximately 800,000 workers potentially came into contact with or were exposed to tungsten compounds in ~50,000 workplaces throughout the United States.⁽²⁾ Approximately 4500 of these workers are potentially exposed to tungsten in the refining and manufacturing industry.⁽²⁾

The purpose of the present study was to identify and provide a preliminary characterization of dimensions, elemental composition, and concentrations of airborne tungsten-containing fibers in the U.S. tungsten refining and manufacturing industry.

A majority of the exposures to tungsten and its compounds in occupational environments occur during production of tungsten metal from the ore, and preparation of tungsten carbide powders in the tungsten refining and manufacturing industry.⁽¹⁾ Dusts and mists of tungsten and its compounds are produced during crushing, mixing, ball milling, sintering, cutting, sandblasting, and grinding operations.⁽³⁾

Although hard-metal lung disease in the tungsten refining and manufacturing industry is well known, historically, health effects have been attributed to the presence of cobalt because of its solubility and known properties as an irritant and promoter of asthma.^(4,5) In tungsten refining and manufacturing processes, a series of tungsten oxides (WO_x) are typically formed as intermediates in the production of tungsten powder. For example, tungsten oxides are formed when calcining ammonium paratungstate (APT). Two primary forms of tungsten oxide are (1) the trioxide (WO_3), or yellow oxide, because of its characteristic color, and (2) the blue oxide, which is a mixture of tungsten oxide species (i.e., $WO_{3.0}$, $WO_{2.9}$, $WO_{2.82}$, $WO_{2.72}$, and so on), tungsten bronze [$(NH_4)_n WO_n yH_2O$], and an amorphous fraction.⁽⁶⁾

The fractional molar ratios expressed are reduced versions of the chemical formula (i.e., $WO_{2.72} = W_{18}O_{49}$). The actual proportion of oxides in tungsten blue oxide varies and is dependent on conditions in the calcining furnace, such as temperature, pressure, and heating time. Tungsten blue oxides with varying molar ratios of oxygen and tungsten yield tungsten powders with differing properties, such as grain size, size distribution, and compaction.

Studies in the Swedish tungsten refining and manufacturing industry have shown that calcining APT and reducing tungsten blue and yellow oxides result in the formation of airborne WO_x fibers.⁽⁷⁻⁹⁾ Leanderson and Sahle⁽¹⁰⁾ were able to produce WO_x fibers by combining WO_2 and WO_3 , and heating the mixture for 3 days at 900°C. The product was an oxide with nominal composition of $WO_{2.72}$. The median length (L), diameter (D), and aspect ratio (AR) of fibers produced were 23.9 micrometers (μm), 0.96 μm , and 26.1, respectively. WO_x fibers, which are also referred to as whiskers or needles, are thought to be more toxic than nonfibrous WO_x , based on their ability to produce free radical damage in vitro.⁽¹⁰⁾ It has been suggested that the generation of free radicals contributes to the development of pulmonary fibrosis.⁽¹¹⁾

The existence of airborne tungsten-containing fibers in the tungsten refining and manufacturing industry has not been investigated in the United States. Although there are recommended occupational exposure limits for soluble and insoluble tungsten compounds, there are no occupational exposure limits (OELs) specifically for tungsten-containing fibers.^(12,13) A number of OELs based on varying toxicological end points exist for man-made fibers, ranging from 0.2 fibers per cubic centimeter of air (f/cm³) for refractory ceramic fibers to 3 f/cm³ for fibrous glass dust.⁽¹²⁻¹⁴⁾

Since the toxicological end point of tungsten-containing fibers such as WO_x fibers is unknown, the use of these OELs is restricted to providing an approximate guide to

airborne concentration results. Since this work was limited to characterizing airborne fibers in the tungsten refining and manufacturing industry, it is beyond the scope of this research to develop an OEL for tungsten-containing fibers.

Important parameters in the determination of fiber toxicity are airborne concentration (i.e., dose), dimensions, and durability. These three parameters are used to characterize the potential pulmonary hazard presented by fibers.^(15,16) The airborne concentration of fibers required to elicit an adverse health effect are dependent on the two other factors of dimensions and durability. The potential for health effects from exposure to tungsten-containing fibers is suggested, based on past studies linking exposure to man-made or natural mineral fibers to adverse health effects.^(9-11,14-25)

The current state of knowledge of the adverse health effects caused by inhaled durable fibers is based, for the most part, on asbestos studies. These studies implicate thoracic fibers (i.e., having an aerodynamic diameter $\leq 10 \mu m$) with dimensions $L > 2 \mu m$ and $D < 3 \mu m$.^(15,16,20-26) Fibers with $L > 2 \mu m$ and $D > 0.15 \mu m$ are associated with pulmonary fibrosis, while fibers with $L > 5 \mu m$ and $D < 0.10 \mu m$ are associated with mesothelioma.⁽¹⁶⁾ Fibers with $L > 10 \mu m$ and $D > 0.15 \mu m$ are associated with lung cancer. The durability provides a measure of the persistence (i.e., a measure of solubility and resistance to clearance mechanisms) of fibers once they are inside the body. Bulk solubility tests indicate that WO_x is insoluble in water and organic solvents.⁽²⁷⁾ However, additional solubility and mechanistic clearance research in simulated human lung fluid and in vivo is needed. Such research will address the question of whether tungsten-containing fibers can persist in the lung, increasing their potential to induce cell damage.⁽¹⁰⁾

Previous Research in the Tungsten Refining and Manufacturing Industry

Results from a preliminary fiber assessment conducted near the reduction process in a Swedish tungsten refining and manufacturing facility indicated that all fibers observed were respirable, with about 80% having a physical diameter $\leq 0.3 \mu m$.⁽⁹⁾ In an additional exposure assessment conducted by Sahle and colleagues,⁽⁷⁾ 32-hr air samples were collected near the reduction process in one tungsten refining and manufacturing facility in Sweden. Transmission electron microscopy (TEM) analysis of the 10 air samples collected indicated a mean airborne WO_x fiber concentration of 0.08 f/cm³ for fibers with $L \geq 5 \mu m$, $D \leq 3 \mu m$, and $AR \geq 5:1$. Examination revealed both straight and curved WO_x fibers. In these air samples, thin and short fibers were predominate. Occasionally, thick fibers ($D \sim 2.0 \mu m$) were observed. Both single and aggregates of fibers were common.

In follow-up studies, Sahle and colleagues⁽⁸⁾ also detected respirable WO_x fibers ($L \geq 5 \mu m$, $D \leq 3 \mu m$, and $AR \geq 5:1$) in static and personal samples collected at two Swedish factories for calcining and reduction processes. The carburizing process was also sampled, but fibers were not found near this process. The first factory processed APT and blue oxide ($WO_{2.9}$) into tungsten powder. The second factory processed yellow oxide

(WO_{3,0}) into tungsten powder. The AM ± SD airborne WO_x fiber concentration among all samples in the first factory was 0.06 ± 0.03 f/cm³ [range 0.002–0.2 f/cm³; N = 24]. In the second factory where yellow oxide was used, only positions near the reduction furnaces were monitored. At these positions, AM ± SD airborne WO_x fiber levels were 0.04 ± 0.03 f/cm³ [range 0.001 – 0.1 f/cm³; N = 18].

In Sahle and colleagues⁽⁸⁾ research, workers were noted to be exposed to airborne WO_x fibers during charging of raw materials, transporting, sieving, maintenance, and handling of leftovers. When blue oxide was loaded in the calcining furnace, the airborne particles generated were fibrous, while particles from APT and yellow oxide were not. However, the process of calcining APT, and reducing blue and yellow oxides did generate WO_x fibers.

METHODS

A walk-through survey was conducted by the National Institute for Occupational Safety and Health (NIOSH) investigators to identify processes that potentially produce airborne fibers in a U.S. tungsten refining and manufacturing facility. Subsequently, a preliminary exposure assessment was conducted in two buildings at the facility based on information gathered during the walk-through survey, and on limited published data from Sahle and colleagues.^(7–9) A flow diagram of the processes present in the tungsten refining and manufacturing facility is provided in Figure 1. To characterize process effluents, static (i.e., area) air samples were collected and analyzed using standard fiber sampling and counting methods to determine dimensions, elemental composition, and airborne fiber concentrations associated with selected processes.^(28,29) Processes selected for monitoring are identified in bold in Figure 1. In addition to the calcining and reduction processes indicated by Sahle and colleagues, the carburizing process was included in the preliminary characterization due to the extent of powder handling by employees near the process.⁽⁸⁾

Air Sampling and Analysis for Fibers

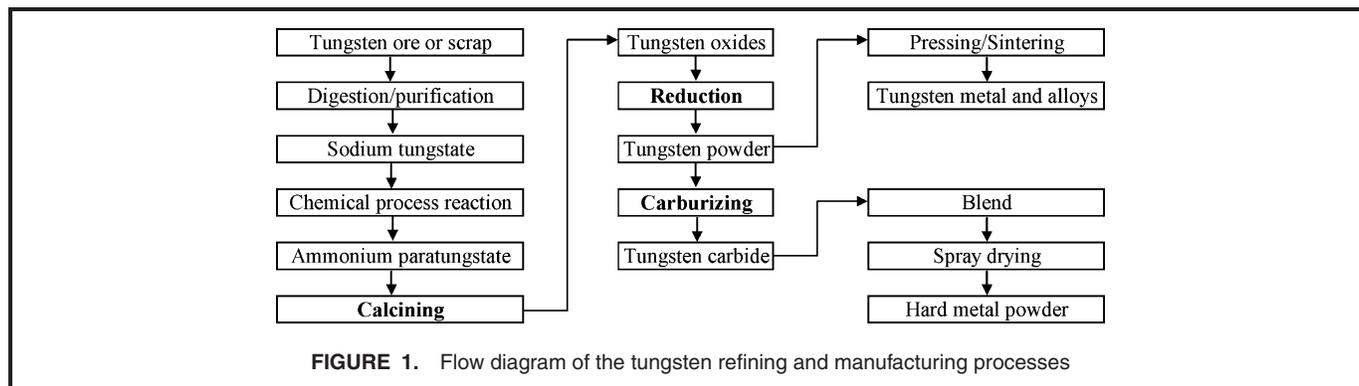
Air samples were collected in accordance with NIOSH Methods 7400: Asbestos and Other Fibers by Phase Contrast

Microscopy,⁽²⁸⁾ and Method 7402: Asbestos by Transmission Electron Microscopy (TEM).⁽²⁹⁾ These are standard methods for sampling and analysis of airborne asbestos-containing fibers, synthetic vitreous fibers, man-made vitreous or mineral fibers (MMMF), and refractory ceramic fibers (RCF).⁽¹⁴⁾ These analytical methods were selected for their strengths in providing information on analytes expected to be present in low concentrations and for their ability to provide spectrographic analyses for fiber structures.

All static air samples were collected on 25 mm diameter conductive cassettes preloaded with mixed cellulose ester (MCE) 0.45 μm pore-size membrane filters (SKC Inc., Eighty Four, Pa.). Air sampling was conducted through the use of battery operated pumps calibrated at a flow rate of 2.5 liters per minute (L/min) using a standard flow calibration device (Bios International Corp., Butler, N.J.). Static air samples were collected over 1–5 hr. These static samples were collected near processes being conducted by workers to characterize airborne fiber emissions and provide an estimate of potential exposures.

Each MCE filter was removed from its sample cassette and prepared for analysis using the direct transfer method outlined in NIOSH Method 7402.⁽²⁹⁾ After preparation, each sample was individually loaded into the TEM (Model CM 12; Philips, Eindhoven, Netherlands) for analysis at an accelerating voltage of 100 kV and a magnification of ≥ 10,000×. The elemental composition of fibers were determined using an energy dispersive X-ray (EDX) spectrometer (Gresham Light Element Detector, Model 510 with IXRF software; Houston, Texas) connected to the TEM. The “foil” (i.e., thin film) EDX algorithm was used to quantify elemental composition by weight percentage. At a minimum, EDX counts were collected over 100 sec. The EDX detector can qualitatively identify elements having atomic numbers ≥ 4 (beryllium), and quantitatively identify elements with atomic numbers ≥ 6 (carbon). Selected area electron diffraction (SAED) was conducted to determine the crystalline structure of the fibers observed.

NIOSH Method 7400 counting rules “A” and “B,” and the rule for glass wool fibers were used to classify the fibers identified on the samples. The “A” rule prescribes counting all fibers that lie in the field of view that have L > 5 μm,



$D > 0.25 \mu\text{m}$, with $AR \geq 3:1$.⁽²⁸⁾ The “B” rule prescribes counting all fiber ends that lie in the field of view and have $L > 5 \mu\text{m}$, $D < 3 \mu\text{m}$, with $AR \geq 5:1$.⁽²⁸⁾ The counting method for glass wool fibers prescribes counting all fibers that lie in the field of view that have $L \geq 10 \mu\text{m}$, $D \leq 3.5 \mu\text{m}$, with $AR \geq 3:1$.⁽¹³⁾

Since there is limited information in the literature regarding the dimensions of airborne tungsten-containing fibers, such as WO_x , a slight modification was made to counting rule “A” to provide improved characterization of the fiber dimensions from the samples. Fiber classifications of $L > 0.5, > 2, > 5, > 10$, and $> 15 \mu\text{m}$, with $D > 0.01, > 0.1, > 0.3, > 1$, and $> 3 \mu\text{m}$ were added to provide for comparison of data to previous study results, and information on health effects associated with fiber dimensions.^(7–9,16) Fiber counting was conducted using the TEM as indicated in NIOSH Method 7400 and 7402.^(28,29) The recommended quantitative working range of the method is 0.04 to 0.5 f/cm³ per 1000 L air sample. The limit of detection (LOD) was estimated based on the assertion in NIOSH Method 7402 that the TEM can resolve one fiber above 95% of the expected mean blank value. Equation 1 provides the LOD for filters with light to moderate fiber loading.

$$\text{LOD (f/cm}^3\text{)} = \frac{A}{V} \left(\frac{F}{C \cdot O} \right) \quad (1)$$

- A = Collection surface area of 25 millimeter filter; 385 square millimeters (mm²)
- V = Air volume sampled; cm³
- F = Number of fibers above 95% of the expected mean blank value; 1 fiber (blanks negative)
- C = Number of grid openings counted; 40 openings
- O = Size of grid opening; ~0.01 mm²

The maximum likelihood estimate (MLE) was used to provide descriptive statistics for airborne fiber concentrations in the presence of nondetectable values.⁽³⁰⁾ When less than half of the sample results were above the LOD, only the range and number of detectable samples were reported. All calculations and descriptive statistics were conducted using either SAS (SAS 9.1.3; SAS Institute, Cary, N.C.) or Excel (Excel 2003; Microsoft Corp., Redmond, Wash.).

Equation 2 provides the orientation-averaged aerodynamic diameter (AD) that was used to determine the aerodynamic size, in centimeters (cm), of each fiber meeting the counting criteria above.⁽³¹⁾

$$\text{AD (cm)} = D[0.75\sqrt{\rho(\ln \beta - 0.11)} + 0.53\sqrt{\rho(\ln \beta + 0.87)}] \quad (2)$$

- D = Fiber diameter; cm
- ρ = Fiber density; 10.8 grams per cubic centimeter (g/cm³)
- β = L/D
- L = Fiber length; cm

Fiber density (ρ) was derived from the CAS registry number 12036-22-5 for tungsten (IV) oxide [$\text{WO}_{2.0}$].^(1,27) This AD equation was applied because it provides the average of the aerodynamic diameter for motion parallel and perpendicular

to the fiber axis. Both orientations are observed during fiber transport in the tracheobronchial and alveolar (i.e., thoracic) regions of the respiratory tract. The orientation of the fiber axis is likely parallel to the flow in the tracheobronchial region of the lung where air velocities are high and could be either parallel or perpendicular to the flow in the alveolar region of the lung where air velocities are low. The orientation-averaged AD is important because it provides a metric to assist in determining the fraction of fibers that could potentially reach the thoracic regions.

RESULTS

Air Sampling and Analysis for Fibers

Table I provides summary results for measured airborne fiber concentrations using modified NIOSH “A” and “B” rule counting, as well as the counting method for glass wool fibers. A test for normality of the airborne fiber concentration data was conducted using PROC CAPABILITY in SAS. Test results indicate that the concentration data for the modified NIOSH “A” and “B” rule were log-normally distributed. Airborne fiber concentrations determined using the “A” rule ranged from $< \text{LOD}$ (calcining, product; carburizing, feed) to 0.14 f/cm³ (calcining, product). The MLE-estimated GM (GSD) of airborne fiber concentrations among all monitored processes was 0.0048 f/cm³ (4.1) [N = 10]. Airborne fiber concentrations determined using the “B” rule ranged from $< \text{LOD}$ (calcining, product; carburizing, feed) to 0.13 f/cm³ (calcining, product). The MLE-estimated GM (GSD) of airborne fiber concentrations among all monitored processes was 0.0037 f/cm³ (4.1) [N = 10]. Airborne fiber concentrations for four samples exceeded the LOD using the counting method for glass wool (calcining, product; reduction, feed; reduction, product). The highest airborne fiber concentration for this method was 0.015 f/cm³ (calcining, product). The range of airborne fiber concentrations among the monitored processes with results $> \text{LOD}$ was 0.0012–0.015 f/cm³ [n = 4].

Table II provides a characterization of airborne fiber dimensions using the modified NIOSH counting rule “A.” A normality test of the distribution of fiber length, diameter, and aerodynamic diameter variables was conducted using PROC CAPABILITY in SAS. Test results indicate that these variables were log-normally distributed. Results from the 578 fibers counted indicate that the GM (GSD) fiber length from all sampled processes was 1.8 μm (1.9), and the diameter was 0.24 μm . Of all the airborne fibers identified, $> 99\%$ (574/578 fibers) were determined to be thoracic.⁽¹²⁾ Notably, the GM (GSD) aerodynamic diameter among all processes surveyed was 1.6 μm (1.9).

Figures 2–5 provide EDX spectra and TEM micrographs of fibers from 4 of the 10 area air samples collected. In Figure 2, the EDX spectrum and micrograph from an area sample collected at the product side of the reduction process indicate that the fiber pictured was composed of tungsten (W) and oxygen (O). Figure 3 provides an EDX spectrum and micrograph for an airborne fiber collected at the feed side of

TABLE I. Airborne Fiber Concentration and Elemental Composition by Tungsten Refining and Manufacturing Process

Building	Process		Airborne Concentration (f/cm ³) ^A				Elemental Analysis	
			LOD ^B	Fibers with Dimensions				
				L > 5 μm AR ≥ 3:1 ^C	L > 5 μm D < 3 μm AR ≥ 5:1 ^D	L ≥ 10 μm D ≤ 3.5 μm AR ≥ 3:1 ^E	Anticipated	Detected
A	Calcining	Product	0.0075	0.14	0.13	0.015	W, O	W, O
A	Calcining	Product	0.050	<0.050	<0.050	<0.050	W, O	W, O ^F
B	Carburizing	Feed	0.0014	<0.0014	<0.0014	<0.0014	W, C	ND
B	Carburizing	Product	0.0018	0.0092	0.0055	<0.0018	W, C	W, C, O
A	Reduction	Feed	0.0057	0.011	0.0057	0.011	W, O	Mo, W, O
A	Reduction	Feed	0.0012	0.0037	0.0025	0.0012	W, O	W, O
A	Reduction	Feed	0.0013	0.0027	0.0027	<0.0013	W, O	W, O
A	Reduction	Feed	0.0011	0.0034	0.0034	<0.0011	W, O	W, O
A	Reduction	Product	0.0012	0.0024	0.0024	<0.0012	W	W, O
A	Reduction	Product	0.0012	0.0024	0.0012	0.0012	W	W, O
	Range (number > LOD)			0.0024–0.14 (8)	0.0012–0.13 (8)	0.0012–0.015 (4)		
	AM ± SD ^G			0.013 ± 0.022	0.010 ± 0.017	—		
	GM (GSD) ^G			0.0048 (4.1)	0.0037 (4.1)	—		
	NIOSH REL (refractory ceramic) ^{D,H}			0.5				
	NIOSH REL (fibrous glass dust, mineral wool, Man-made mineral fibers, rock wool, slag wool) ^{D,H}			3				
	ACGIH TLV (refractory ceramic) ^{C,I}			0.2				
	ACGIH TLV (cont. filament glass, glass Wool, rock wool, slag wool, special purpose glass) ^{C,I}			1				

ND = Fibers not detected.

^A=The recommended quantitative working range of NMAM 7400 is 0.04 to 0.5 f/cm³ for a 1000-L air sample with a preferable fiber concentration range of 100 to 1300 f/mm² on the media.⁽²⁸⁾

^B=Limit of detection; calculated based on NMAM 7402, 1 confirmed f/mm² above 95% of expected mean blank value.⁽²⁸⁾

^C=NMAM 7400 counting rule "A."⁽²⁸⁾

^D=NMAM 7400 counting rule "B."⁽²⁸⁾

^E=Using NMAM 7400.⁽²⁸⁾

^F=Elemental content of fibers with L ≤ 5 μm.

^G=Estimated airborne concentrations using MLE method.⁽³⁰⁾ When less than half of the sample results were above the LOD, only the range and number of detectable samples were reported.

^H=Airborne concentration for up to a 10-hr work shift during a 40-hr workweek.

^I=Airborne concentration for a conventional 8-hr workday and a 40-hr workweek.

the reduction process. The EDX spectrum indicates that the fiber pictured was composed of W and O.

In Figure 4, the EDX spectrum and micrograph from the area sample collected at the product side of the carburizing process indicates the fiber pictured was composed mainly of tungsten, with amounts of carbon (C) and O above background. The EDX spectrum and micrograph in Figure 5 are from an area sample collected at the product side of the calcining process. The EDX spectrum indicates the needle-like fiber in the micrograph was composed of W and O. These micrographs provide a good illustration of the variety of ways fibers were found on the filter substrates.

The 23 remaining EDX spectra and micrographs (27 conducted, three from each sample containing fibers) indicated the

presence of tungsten with oxygen, tungsten with oxygen and carbon, or molybdenum (Mo) with oxygen. Fibers consisting of tungsten and oxygen were predominant. The presence of oxygen and carbon in a tungsten matrix was found in the sample collected near the product side of the carburizing process. Fibers consisting of molybdenum and oxygen were identified in a sample collected near the feed side of the reduction process. EDX results do not provide information on the tungsten valence level, or information to accurately determine stoichiometry (i.e., ratio of tungsten to oxygen) of the sampled fibers. Selected area electron diffraction (SAED) results were inconclusive as to the crystalline structure of the fibers.

Elements that were determined to be part of the fiber matrix or TEM grid were labeled in the EDX spectra. The labeled

TABLE II. Airborne Fiber Dimensions by Tungsten Refining and Manufacturing Process

Building	Process			Length (μm)			Diameter (μm)			Aerodynamic Diameter (μm) ^A		
	Name	Side	n'	Range	AM \pm SD ^{C,D}	GM (GSD) ^{E,F}	Range	AM \pm SD ^{C,D}	GM (GSD) ^{E,F}	Range	AM \pm SD ^{C,D}	
A	Calcining	Product	100	0.64–16	3.1 \pm 2.3	2.4 (2.0)	0.064–1.3	0.27 \pm 0.19	0.22 (1.9)	0.49–8.0	1.9 \pm 1.3	
A	Calcining	Product	100	0.51–3.2	1.2 \pm 0.6	1.1 (1.6)	0.064–0.76	0.16 \pm 0.10	0.14 (1.7)	0.44–4.4	1.1 \pm 0.57	
B	Carburizing	Feed	ND	—	—	—	—	—	—	—	—	
B	Carburizing	Product	18	1.9–8.9	4.0 \pm 2.0	3.6 (1.6)	0.32–2.5	0.88 \pm 0.54	0.76 (1.7)	2.2–15	5.4 \pm 3.1	
A	Reduction	Feed	12	1.1–19	4.4 \pm 5.4	2.8 (2.4)	0.13–3.5	0.86 \pm 1.1	0.51 (2.7)	0.90–20	5.4 \pm 6.4	
A	Reduction	Feed	115	0.64–19	2.4 \pm 1.9	2.0 (1.7)	0.064–1.6	0.34 \pm 0.23	0.29 (1.7)	0.46–9.9	2.3 \pm 1.5	
A	Reduction	Feed	64	0.64–5.1	1.8 \pm 1.0	1.6 (1.7)	0.064–0.95	0.27 \pm 0.16	0.24 (1.7)	0.46–6.1	1.8 \pm 1.0	
A	Reduction	Feed	102	0.64–7.0	2.1 \pm 1.0	1.9 (1.5)	0.064–0.83	0.30 \pm 0.15	0.27 (1.6)	0.49–5.4	2.0 \pm 0.93	
A	Reduction	Product	49	0.51–6.4	2.0 \pm 1.4	1.6 (1.9)	0.064–0.76	0.28 \pm 0.17	0.23 (2.0)	0.44–4.6	1.9 \pm 1.1	
A	Reduction	Product	18	0.64–11	2.3 \pm 2.4	1.7 (2.1)	0.13–2.2	0.38 \pm 0.53	0.24 (2.3)	0.81–14	2.4 \pm 3.3	
Overall			578	0.51–19	2.2 \pm 1.9	1.8 (1.9)	0.064–3.5	0.31 \pm 0.30	0.24 (2.0)	0.44–20	2.0 \pm 1.8	

^A Orientation averaged.

^B n' = Number of fibers with dimensions $L > 0.5 \mu\text{m}$, $D > 0.01 \mu\text{m}$, and $AR \geq 3:1$.

^C AM = Arithmetic mean.

^D SD = Standard deviation.

^E GM = Geometric mean.

^F GSD = Geometric standard deviation.

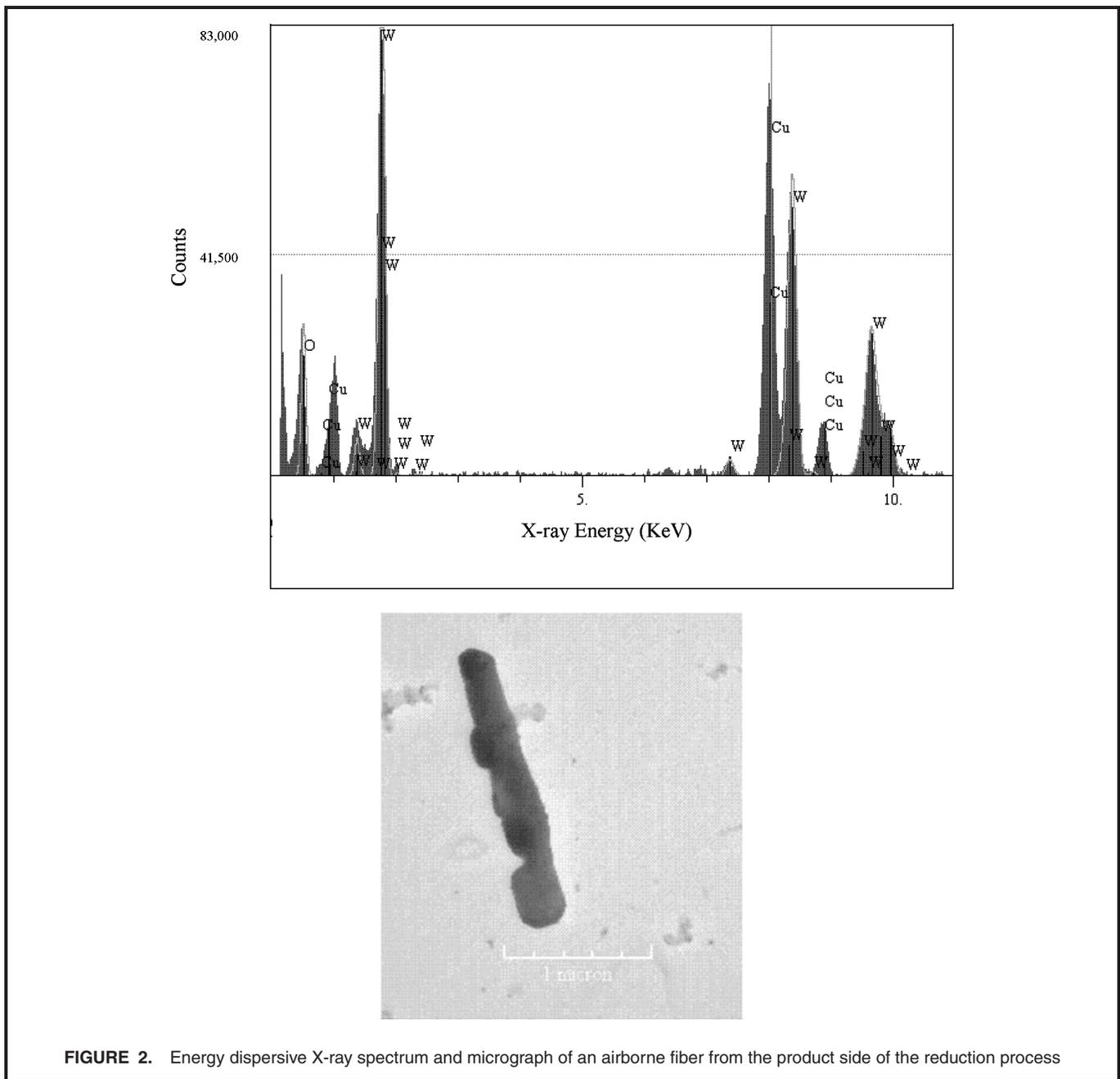


FIGURE 2. Energy dispersive X-ray spectrum and micrograph of an airborne fiber from the product side of the reduction process

peak for copper (Cu) in each spectra was expected, as it was present in the TEM grids used. Other elements were present in the spectra at trace quantities. These were determined to be part of the sample preparation (i.e., elements in the sample holder, pole piece, and so on) by the analytical operator.

DISCUSSION

Minor differences were observed between the airborne concentration results obtained when using either NIOSH counting rule “A” or “B.” Results indicate that the airborne fiber concentrations from the area samples collected

at the facility surveyed are below NIOSH and American Conference of Governmental Industrial Hygienists (ACGIH[®]) OELs for man-made fibers (range 0.2 to 3 f/cm³). It is not known if these OELs are applicable to the fibers identified due to potential differences in pulmonary health effects. Therefore, these limits provide an approximate guide for comparison to the airborne concentration results.

The aerodynamic diameter (AD) was used to determine the number of fibers that potentially reach the thoracic regions of the respiratory tract.⁽²⁶⁾ In addition to the AD, the physical L and D of inhaled durable fibers have been shown by other researchers to be essential parameters in evaluating the potential risk of developing respiratory diseases. A review of

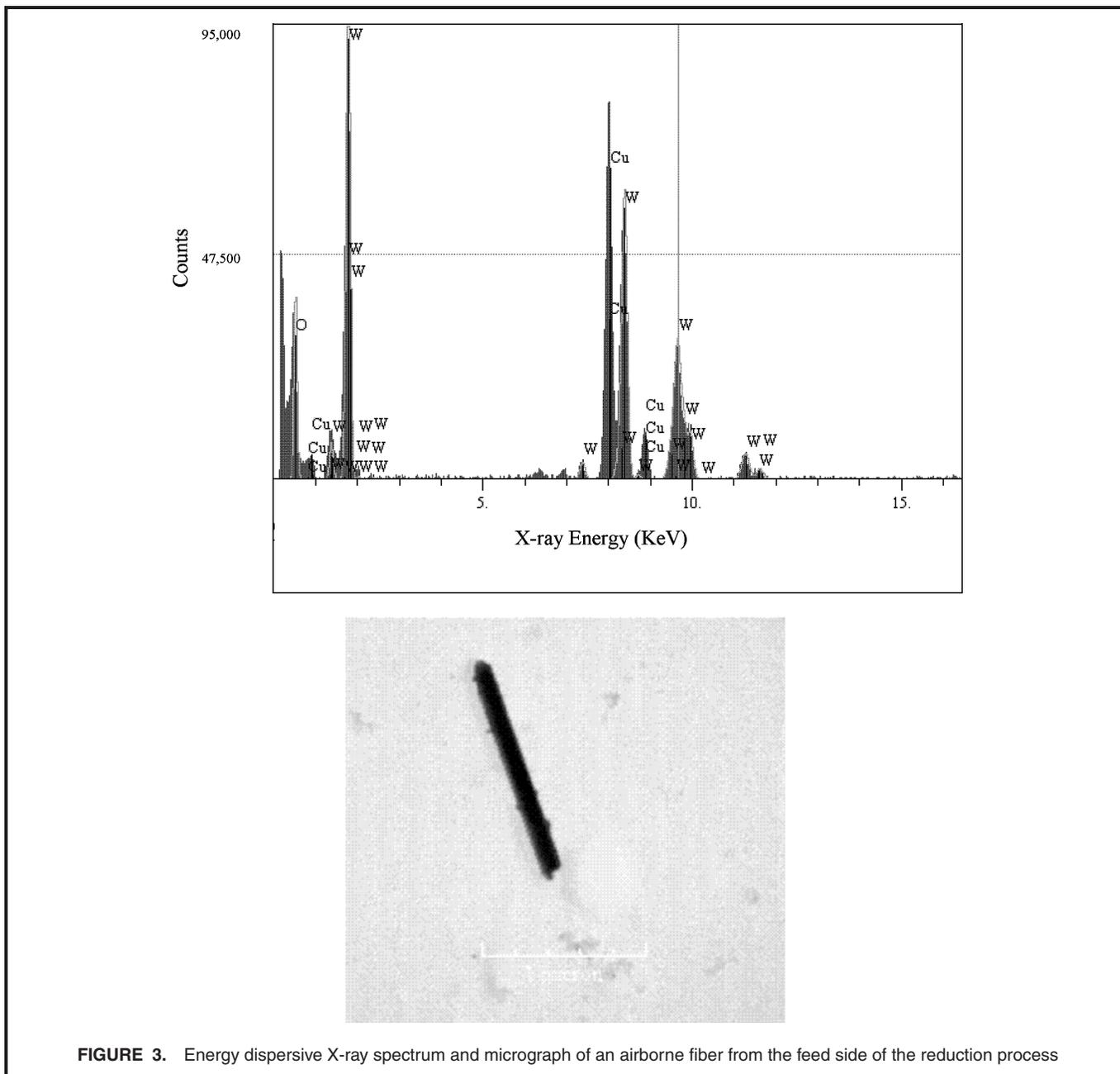


FIGURE 3. Energy dispersive X-ray spectrum and micrograph of an airborne fiber from the feed side of the reduction process

the health effects linked to durable fibrous material inhalation indicates a significant association between fiber dimensions and adverse effects.^(9–11,14–25)

Thoracic fibers with dimensions associated with adverse health effects were present in the air near the three processes surveyed. From Table III, 38% of the thoracic fibers from this study meet the L, D, and AD criteria associated with pulmonary fibrosis. Additionally, a small percentage of the fibers counted meet the criterion for cancer and mesothelioma, 0.5% and 0.3%, respectively. However, it is unknown if tungsten-containing fibers are durable and remain in the respiratory tract for a period of time associated with the development of adverse effects.

Determining the chemistry and crystallinity of the airborne fibers detected is important in that it would provide information on fiber durability in the respiratory tract. EDX systems, like the one used in this research, provide elemental characterization of the sample; however, they do not directly provide stoichiometric information. In addition to the EDX analyses, SAED analyses to determine fiber crystallinity were inconclusive. Information on the crystallinity of the fibers detected would have provided information on stoichiometry, since few tungsten oxide species are known to exist in a crystalline state. Obtaining satisfactory SAED results are effected by a number of factors, including but not limited to the thickness of the fiber being analyzed, the operating voltage

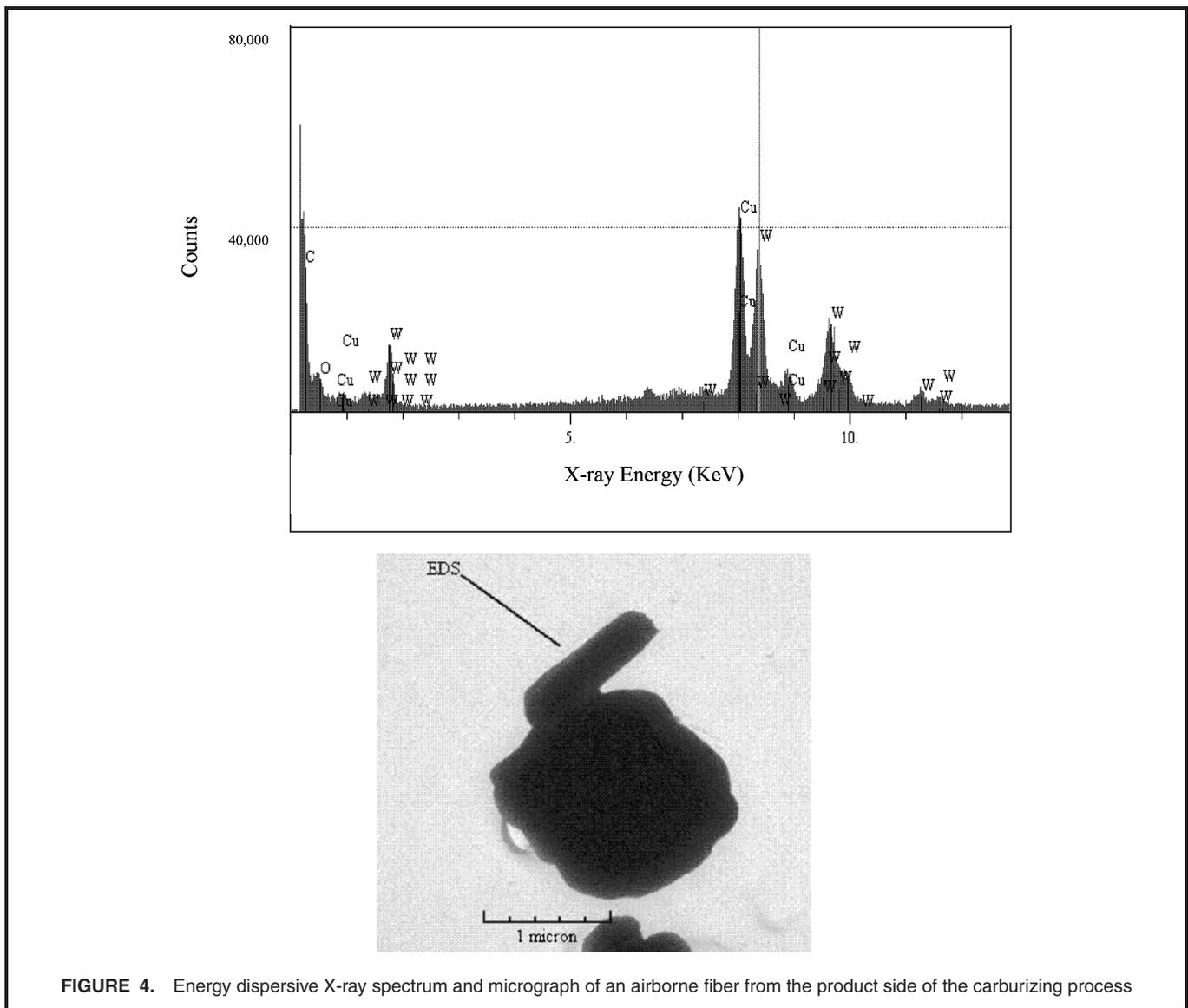


FIGURE 4. Energy dispersive X-ray spectrum and micrograph of an airborne fiber from the product side of the carburizing process

of the TEM beam, and the uniformity of crystal growth within the fiber (i.e., the crystal is coated with a layer of amorphous growth, or there is discontinuous crystalline growth).

From Table II, 18 airborne tungsten-containing fibers were detected on one air sample collected from the product side of the carburizing furnace, which is beyond the intermediate stages of tungsten powder production. It is notable that the airborne fibers collected near the carburizing process had a tendency to be longer, with greater physical and aerodynamic diameters than those collected near the calcining and reduction processes. Further research is required to determine why airborne fibers were detected near the carburizing process, and the reason for their dimensional differences when compared with airborne fibers collected near other processes.

Fiber concentrations that are outside of the recommended quantitative working range of the methods used (i.e., <0.04 f/cm³) have greater than optimal variability and are potentially biased.⁽²⁹⁾ The potential for bias in determining the number of

fibers on a sample can occur due to not counting fibers close to the upper or lower visibility limit at a given microscope magnification setting. This counting bias can be either negative (undercounting) or positive (overcounting) depending on the size distribution of the fibers present on the sample. Potentially biased results included airborne fiber concentration results from all but one sample (i.e., calcining, product). With the limited air sampling data currently available to researchers, it is difficult to estimate the mean airborne fiber concentrations and dimensions associated with domestic tungsten refining and manufacturing processes.

Previous Exposure Assessments in the Tungsten Refining and Manufacturing Industry

In Sahle's⁽⁹⁾ initial research, approximately 80% of the respirable WO_x fibers detected near a reduction furnace had $D \leq 0.3 \mu\text{m}$. For comparison, approximately 66% of the fibers associated with the reduction process from the present

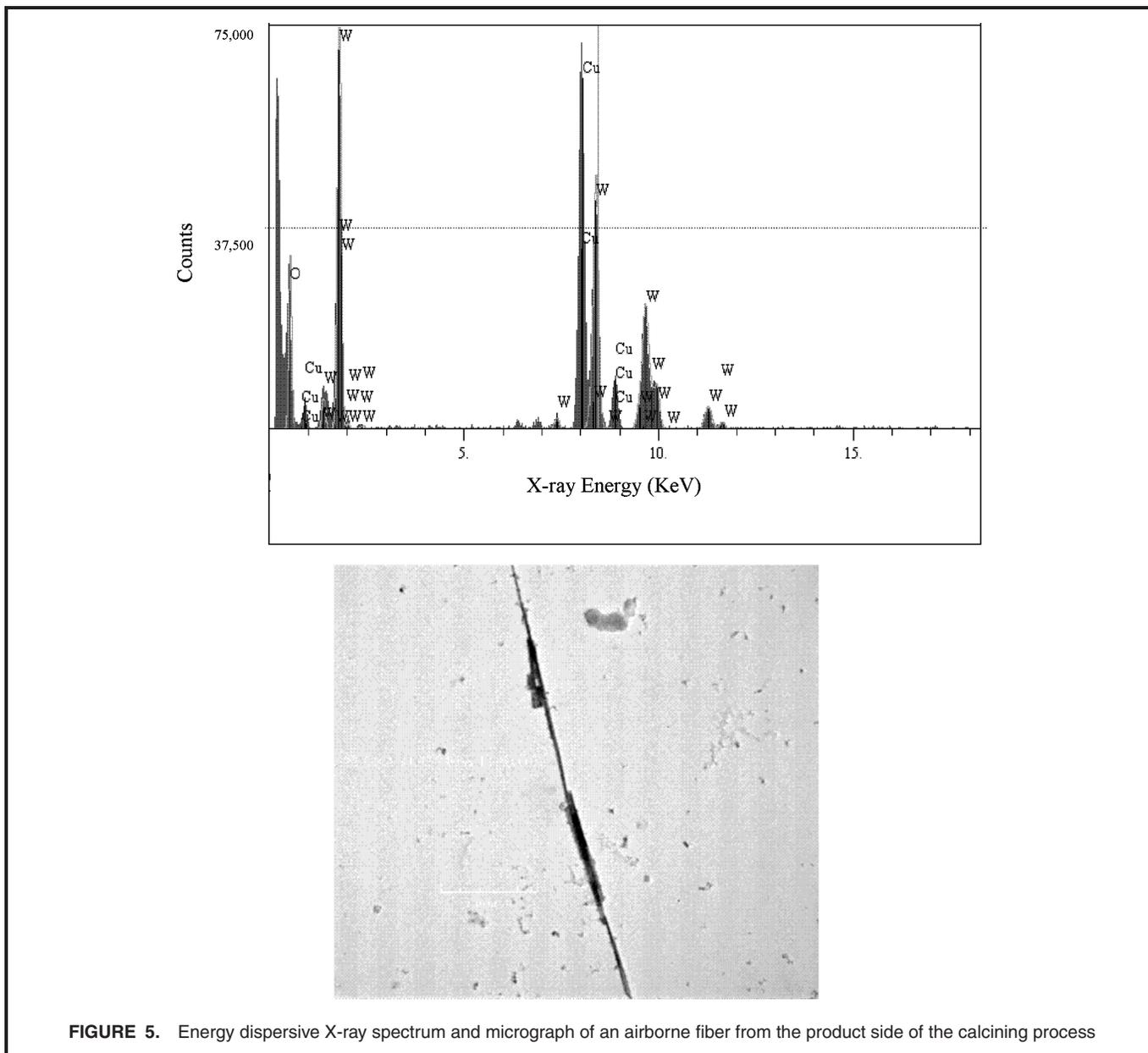


FIGURE 5. Energy dispersive X-ray spectrum and micrograph of an airborne fiber from the product side of the calcining process

assessment had $D \leq 0.3 \mu\text{m}$ ($L > 0.5 \mu\text{m}$, $D \leq 3 \mu\text{m}$, and $AR \geq 5:1$).⁽³²⁾

An additional study by Sahle and colleagues⁽⁷⁾ was conducted to characterize fibers from the reduction process in one Swedish tungsten refining and manufacturing facility. The analysis included WO_x fibers meeting the NIOSH “B” rule criteria. If the research presented here were restricted to fibers with these dimensions in the reduction process, the GM (GSD) airborne concentrations were 0.0027 f/cm^3 (1.7) for fibers with comparable dimensions [$N=6$]. This is considerably less than the results of 0.08 f/cm^3 published by Sahle and colleagues. Less than 1% of the fibers associated with this process had $L > 5 \mu\text{m}$ and $D \leq 0.3 \mu\text{m}$; however, 53% had $L \leq 5 \mu\text{m}$ and $D \leq 0.3 \mu\text{m}$. These results tend to support Sahle’s finding that thin and short airborne fibers are predominate.

Sahle and colleagues also indicated that the WO_x fibers they identified were either straight or curved, and both single fibers and agglomerates were common. Airborne tungsten-containing fibers detected in the processes surveyed in the present study were straight, and both single fibers and agglomerates were found. Occasionally, nodules were observed along the length of the fiber.

In follow-up studies, Sahle and colleagues⁽⁸⁾ also detected respirable WO_x fibers in static and personal air samples collected at two Swedish factories—one that processed APT and blue oxide, and another that processed yellow oxide into tungsten powder. The analysis was restricted to WO_x fibers meeting the NIOSH “B” rule criteria. In the present survey, the facility processed APT into tungsten powder. At positions away from the calcining furnaces in the same building (i.e., near

TABLE III. Airborne Thoracic Fiber Dimensions and Associated Potential Adverse Health Effects for Monitored Tungsten Refining and Manufacturing Processes

Diameter (μm)	Length (μm)					Total
	>0.5	>2	>5	>10	>15	
>0.01	37	5	2	—	—	44
>0.1	246	58	9	1	1	315
>0.3	66	127	15	—	—	208
>1	—	2	4	—	1	7
>3	—	—	—	—	—	0
Total	349	192	30	1	2	574
<i>Bold Italic</i>	Pulmonary fibrosis					
█	Mesothelioma					
▭	Cancer					

Note: L > 0.5 μm , D > 0.01 μm , AR \geq 3:1, and AD \leq 10 μm .⁽¹⁶⁾

the reduction furnace), the GM (GSD) airborne concentrations for fibers with comparable dimensions were 0.0027 f/cm³ (1.7) [N = 6]. The corresponding GM (GSD) values for areas near the calcining furnaces were 0.058 f/cm³(2.4) [N= 2]. The GM (GSD) airborne fiber concentrations for fibers with comparable dimensions among all samples collected were 0.0037 f/cm³(4.1) [arithmetic range = 0.0012–0.13 f/cm³; N = 10].

For comparison, results from the present survey were similar to those reported by Sahle and colleagues for locations away from the calcining process, and less than those reported near the reduction process. Geometric mean results from the present survey were greater than those reported by Sahle and colleagues near the APT calcining process. In addition, results from the present survey indicate airborne fibers near the carburizing process, which were not reported by Sahle and colleagues. The GM airborne fiber concentration among all processes in the present survey was less than that reported by Sahle and colleagues.

In their report, Sahle and colleagues⁽⁸⁾ noted that workers were exposed to airborne WO_x fibers during charging of raw materials, transporting, sieving, maintenance, and handling of leftovers. Highest exposures were associated with charging of raw material, changing of the hammer, emptying and cleaning the cyclone and microfilters, and cleaning and maintenance of the furnaces. In the present survey, it was found that calcining, reduction, and carburizing were associated with airborne tungsten-containing fibers, although not necessarily in quantifiable concentrations (Tables I and II).

Caution is advised in directly comparing Sahle and colleagues^(7–9) results with those from this domestic survey. From examining the Swedish body of work, it appears that many of the samples collected were for nonproduction or nonroutine tasks, possibly to assess the worst case scenarios for potential exposure. Although Sahle and colleagues chose

a number of short-term processes based on the belief that they had high exposure, data from the survey presented here are for typical production operations. Therefore, the data from the preliminary exposure assessment conducted in the United States provide a more realistic characterization of potential exposures that exist in day-to-day operations.

CONCLUSIONS

Results indicate that nearly all of the airborne tungsten-containing fibers meeting the modified NIOSH “A” rule counting criteria associated with the calcining, reduction, and carburizing processes monitored were thoracic. It is unknown if the fibers identified are durable and remain in the respiratory tract for a period of time associated with the development of adverse effects. The range of airborne fiber concentrations identified was <0.0011 to 0.14 f/cm³. These results indicate that fiber concentrations from the area samples collected are below the OELs for man-made fibers recommended by NIOSH and the ACGIH. These OELs provide a relative magnitude of airborne concentration results. However, it is not known if these limits are directly applicable to airborne tungsten-containing fibers, since their in vivo pulmonary toxicity has not been assessed.

Results from the present study indicate airborne fibers near the carburizing process, which were not reported by Sahle and colleagues. These fibers had different dimensional properties than those associated with calcining and reduction. The GM airborne fiber concentration among all processes in the present survey was less than that reported by Sahle and colleagues. Fibers detected in the present study consisted primarily of tungsten and oxygen. On average, these fibers were thoracic with physical characteristics of L ~ 2.0 μm and D ~ 0.25 μm , and AR \geq 3:1.

Among the samples analyzed, those collected from high-temperature processes involved in the oxidation of APT to tungsten oxides (calcining), or reducing tungsten oxides to pure tungsten powder (reduction), were associated with the highest airborne fiber concentrations. Further exposure assessment and engineering studies are needed to better understand the production process conditions (time, temperature, and oxygen content) under which fibers are formed. Adjustment of the operating conditions at these processing steps may eliminate the formation of fibers.

Although reported airborne fiber concentrations may be biased in the present assessment, airborne tungsten-containing fibers were detected in the U.S. tungsten refining and manufacturing industry. The results from this survey indicate the potential for airborne tungsten-containing fibers within and beyond the intermediate stages of tungsten powder production. This was unexpected, and further research is required to determine the source and characteristics of the airborne fibers detected near the carburizing process. Considering this, as well as the limited number of area samples collected, additional sampling is necessary to better characterize airborne tungsten-containing fibers. Until more is known about the durability

of tungsten-containing fibers in the lung, and potential health effects associated with exposure, it would be prudent to take steps to limit or eliminate potential occupational exposures.

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