

#### IV. ENVIRONMENTAL DATA AND ENGINEERING CONTROLS

##### Environmental Concentrations

Most of the environmental data available on tungsten and its compounds are derived from cemented tungsten carbide (hard-metal) industries (Table IV-1) [29,55-60]. Depending on the stage and type of the process, the proportions of tungsten, cobalt, and other components in the airborne dusts vary considerably [59]. The initial stages of processing the ore involve exposure to primary ore dusts, namely those of scheelite and wolframite. In the course of production and use of tungsten, aerosols of sodium tungstate ( $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ), ammonium-p-tungstate [ $5(\text{NH}_4)_2\text{O} \cdot 12\text{WO}_3 \cdot 11\text{H}_2\text{O}$ ], tungstic oxide ( $\text{WO}_3$ ), tungsten pentoxide ( $\text{W}_2\text{O}_5$ ), tungsten dioxide ( $\text{WO}_2$ ), metallic tungsten (W), tungsten carbide (WC), and their mixtures may be generated. In the stages following the preparation of tungsten or tungsten carbide, exposures may occur also to aerosols of such binder metals as cobalt and nickel and to other commonly added metals and their derivatives (Figure XII-1).

Except for the studies by Lichtenstein et al [29], Fairhall et al [56], and McDermott [60], very little information is available on the environmental concentrations of tungsten, cobalt, or total dust in the cemented tungsten carbide industry in the United States. Because of differences in work practices and engineering controls, it is not possible to extrapolate directly from the observations of foreign investigators on environmental concentrations in industry to occupational exposures in the United States. However, the basic steps in manufacturing cemented tungsten carbide are quite similar throughout the world, so that a review of foreign

reports would provide a valuable comparative assessment of potential exposure sites in the industry. A number of factors might contribute to the observed variations in the environmental concentrations of tungsten, cobalt, or total dust among the various studies. Values might be affected by the sampling zone selected, ie, breathing or general atmosphere, and by the sampling and analytical methods. In addition, Fairhall et al [56] suggested that individual plant structure, ventilation, layout of machines and processes, and the segregation of the dustiest operations from the others were factors influencing the environmental concentrations and operator exposures.

Fairhall et al [56] determined the average dust and cobalt content of air in powder processing and tool and die operations in three cemented tungsten carbide plants (Table IV-1). The total dust concentrations in the general atmosphere were 20% and 50% lower than the operators' exposures in the powder processing and tool and die operations, respectively. The cobalt concentrations in the powder processing and tool and die operations were, respectively, 10% and 5% of the total dust concentrations. The authors emphasized that the total dust values are given as averages and that there are operations, such as calcination of cobalt nitrate, which produced total dust concentrations as high as 123 mg/cu m with cobalt concentrations as high as 79 mg/cu m. Operations such as screening powders, weighing and milling, and cleaning the mills were also reported to produce excessive exposures to dust and cobalt. Powder processing was the dustiest operation surveyed. Fairhall and his colleagues also noted the presence of cobalt in all areas of the plants, including those where no manufacturing was done, a significant finding.

To determine typical dust exposures, McDermott [60] studied the atmospheric cobalt levels of various operations in seven cemented tungsten carbide plants. The cobalt concentrations in the 173 samples ranged from undetected to 0.8 mg/cu m. Basing his conclusions on the present United States Federal occupational environmental limit for cobalt (0.1 mg/cu m), he found that 70% of the samples represented acceptable working conditions.

Lichtenstein et al [29] reported the airborne tungsten and cobalt concentrations in operations involving wet-grinding of tool bits and inserts made of two commercial grades of cemented tungsten carbide: one contained 72% tungsten carbide, 8% titanium carbide, 11.5% tantalum carbide, and 8.5% cobalt; the other contained 94% tungsten carbide and 6% cobalt. About 70% of the tool-grinding activity involved the latter grade. Approximately 75% of the tool-work involved regrinding old carbide tips, and 25% involved grinding new carbide tips. The air was sampled with filters in the workers' breathing zones, and the filters were analyzed for tungsten and cobalt by atomic absorption spectrometry. The concentrations of tungsten ranged between 0.2 and 12.8 mg/cu m, while those of cobalt were 0.04-0.93 mg/cu m. Mean concentrations were 5.16 mg/cu m for tungsten and 0.28 mg/cu m for cobalt. Of the 25 samples taken, 40% exceeded 5 mg/cu m for tungsten and 60% exceeded 0.1 mg/cu m for cobalt. Since such airborne levels of tungsten and cobalt could not be effectively controlled by an existing exhaust ventilation system, Lichtenstein et al designed an improved exhaust ventilation system which is described in the Engineering Controls section. A follow-up study done after the installation of the improved system reportedly showed cobalt concentrations well below the detection limit of an atomic absorption spectrophotometer and TWA exposures

one order of magnitude below the TLV for cobalt.

Reber and Burckhardt [57] evaluated the potential exposures of workers to airborne total dust, tungsten, and cobalt in operations such as mixing, die casting, forming, and grinding of sintered pieces in five Swiss hard-metal plants. The results showed that the cobalt limit of 0.5 mg/cu m was exceeded by 13% of the measurements in the mixing division and by 25% of the values in the forming area. However, cobalt concentrations in the die casting division never reached the limit. In comparison, the limit of 6 mg/cu m for tungsten was rarely exceeded in these operations. The authors attributed the high dust and cobalt concentrations in mixing and forming divisions to the machining of unfinished pieces with large diameters, a process which generates sufficiently large amounts of the dusts to exceed the capacity of the exhausts. In the grinding of sintered pieces, Reber and Burckhardt found that dry grinding produced high total dust and cobalt concentrations, and they suggested that wet grinding gave concentrations far below the appropriate limits.

Salikhodzhaev and Vengerskaya [59] examined the airborne concentrations of total dust, tungsten, and cobalt generated in various processing stages of hard-metal production in the USSR. During the powder processing stage, the dust levels were between 10 and 693 mg/cu m with averages of 3-130 mg/cu m for various operations. The dust levels were between 3.3 and 153 mg/cu m (averages 5.5-48 mg/cu m for various operations) during casting and between 3.3 and 32.5 mg/cu m (average 13 mg/cu m) during forming operations. Thus it appears that high levels of dust are generated during all stages of processing, although powder processing generated the highest levels. However, in all of the

operations, the average tungsten concentrations were well below the limit for tungsten. In the powder processing operation, the 0.5 mg/cu m limit for cobalt was exceeded. The authors did not explain why the tungsten concentrations were well below the limit when the dust levels were quite high in many of these operations.

In general, dust concentrations generated in hard-metal production were higher during the powder processing and forming stages than during either die casting or grinding of sintered products. The dust levels presented in Table IV-1 indicate that the highest exposures might occur in the powder processing and forming operations.

#### Engineering Controls

To decrease the concentration of tungsten to the recommended limit or below it, engineering controls must be instituted where the airborne concentrations of tungsten exceed the TWA concentration limits. Industrial experience indicates that closed-system operations are commonly used in manufacturing processes. Such systems must be used whenever feasible to control tungsten and its compounds wherever they are manufactured, processed, packaged, or used. Closed systems should operate under negative pressure whenever possible so that, if leaks develop, the flow of air will be inward. Closed-system operations are effective only when the integrity of the system is maintained. The system should be inspected frequently and leaks should be repaired promptly.

A ventilation system may be required if a closed system proves to be impractical, and is desirable as a standby if the closed system should

TABLE IV-1  
 CONDITIONS OF TUNGSTEN-COBALT EXPOSURES  
 IN THE HARD-METAL INDUSTRY

Type of Operation	Total Dust Concentration (mg/cu m)	Tungsten (mg/cu m)	Cobalt (mg/cu m)	Sample Type*	Location	Reference
Powder processing	14.9	7.7	0.95	G	Austria	55
(Stages from	10. - 14	-	1.05 - 1.67	B	United States	56
Ammonium paratungstate	2.0 - 3.3	-	0.12 - 0.22	G	"	56
to tungsten carbide are	0.3 - 9.8	1.8 - 8.24	0 - 0.55	B	Switzerland	57
shown on Figure XII-1)	1.1 - 32.0	0.88 - 25.6	0.09 - 2.72	"	Sweden	58
	3.1 - 130.3	2.2 - 3.5	1.8 - 2.0	G	USSR	59
	-	-	0.01 - 0.8	B	United States	60
	-	-	0 - 0.14	G	"	60
105 Tool and die operations	1.0 - 5.0	-	0.05 - 0.23	B	"	56
	0.5 - 2.2	-	0.01 - 0.07	G	"	56
Casting	0.22 - 7.5	0.52 - 4.56	0 - 0.41	B	Switzerland	57
	15	12	0.21	"	Sweden	58
	0.7 - 3.0	0.6 - 2.6	0.04 - 0.19	G	"	58
	5.5 - 47.7	1.4 - 2.1	6.8	"	USSR	59
	21.5	17.6	1.14	"	Austria	55
	-	-	0 - 0.08	B	United States	60
Forming	0.5 - 24.6	0.97 - 26.7	0.03 - 1.75	"	Switzerland	57
	0.1 - 7.5	0.08 - 5.9	0.008 - 0.56	"	Sweden	58
	0.2 - 0.7	0.17 - 0.58	0.01 - 0.04	G	"	58
		3.3 - 32.5	-	"	USSR	59
	11.1	8.8	1.12	B	Austria	55
	-	-	0.001 - 0.8	"	United States	60
	-	-	0.01 - 0.15	G	"	60
Grinding of sintered pieces						
Dry grinding without exhaust	6.6 - 44	-	0.04 - 2.44	B	Switzerland	57
Wet grinding without exhaust	-	0.2 - 12.8	0.04 - 0.93	"	United States	29

\* B = breathing zone; G = general air

fail. The principles set forth in Industrial Ventilation--A Manual of Recommended Practice [61] published by the American Conference of Governmental Industrial Hygienists, Fundamentals Governing the Design and Operation of Local Exhaust Systems, ANSI Z9.2-1971 [62], published by the American National Standards Institute, and NIOSH's Recommended Industrial Ventilation Guidelines [63] should be applied to control workplace atmospheric concentrations of tungsten. These principles and guidelines have been used to control the concentrations of aerosols in the cemented tungsten carbide industry [29,57,60]. Because large accumulations of fine dust in dust collectors may pose a fire hazard, such systems should be located away from the other structures and areas where employees may be exposed. Internal sprinkler systems with fusible-link activation should also be considered.

From the data collected during a survey of five Swiss cemented tungsten carbide plants, Reber and Burckhardt [57] found that wet-grinding of sintered pieces produced cobalt concentrations far below the recommended limit of 0.5 mg/cu m. Although no exhaust was required for automatic machinery, grinding machines with manual adjustment reportedly required an efficient localized exhaust system. The authors concluded that individual exhaust pipes, with suction systems similar to vacuum cleaners which are attached directly to the lathe or grinding machine, are best for dust removal. They also recommended daily clean-up of the system to ensure its continuing efficiency. Reber and Burckhardt noted that the use of an exhaust ventilation system in an operation liberating total dust concentrations of 6 mg/cu m (of which 10% was cobalt) reduced the dust levels to 0.3-0.6 mg/cu m. They also mentioned that too small exhaust pipe

inlets, improper adjustment of exhaust pipe inlets, cut grinding, and machining of large pieces contributed to the buildup of high dust concentrations. Although Salikhodzhaerv and Vengerskaya [59] gave no details of the ventilation system, they stated that, in the work places equipped with a local dust extraction system, the dust concentration was reduced from 153 mg/cu m to 28 mg/cu m and the tungsten level decreased from 3 to 0.3 mg/cu m. They recommended mechanization of the processes, hermetic sealing of the sifting devices, and use of local dust extraction systems as measures to control dust concentrations.

Lichtenstein et al [29] successfully used a local exhaust ventilation system to control worker exposures to tungsten and cobalt during wet - grinding. Well-fitted hoods, equipped with sliding doors controlling the designed air quantity of 400 cu ft/min, were installed around tool grinding wheels. Each hood was connected to a bench plenum by short flexible ducting with a smooth-walled interior, and each outlet was provided with an individual blast gate. All branch plena were connected to a main plenum. The measured air transport velocities of both the main and branch plena exceeded 4,500 ft/min. To allow for the draining of the coolant used in grinding and to reclaim the diamond dust from grinding wheel breakdown, swing check valves were provided in the plena. The plena also had provisions for cleanout. The authors recommended that regular maintenance and cleaning schedules be adopted for the exhaust system to prevent its degradation.

McDermott [60] recommended an efficient low-volume-high-velocity ventilation system (Figure XII-2) to reduce worker exposures to total dust and cobalt in the cemented tungsten carbide industry. In this system, the



exhaust fittings, because of their small duct size, are mounted near the dust source. According to McDermott, the system has significant advantages: an improved recovery rate for valuable material which would reduce the additional cost of such equipment; and, in climates where compensating makeup air must be tempered, a smaller volume of makeup air units to control specific operations, thus resulting in greater conservation of energy. The latter advantage may take on added importance, since many jurisdictions do not permit recirculation of toxic dusts.

Ventilation systems of this type will require regular inspection and maintenance to ensure effective operation. A program of scheduled inspection should be established in which the ventilation systems are checked routinely. These routine checks should include face velocity measurements of the collecting hood, inspection of the air mover and collector, and measurements of workroom airborne concentrations. Any changes which may affect the ventilation system or the operations being ventilated must be assessed promptly to ensure that engineering controls continue to provide adequate protection of employees.

#### Sampling and Analysis

In general, two types of sampling methods, electrostatic precipitation and filtration, have been reported for collecting dusts in industrial atmospheres that contained tungsten and its compounds. Electrostatic precipitators have been used to collect general room dust samples and samples taken near the breathing areas of employees [16,56,60]. Total air volumes of 45-180 cu ft were sampled within 15-60 minutes (85 liters/min) [60]. Although some tasks would allow positioning of the

sampler in the general breathing area of an employee, electrostatic precipitators are generally used for area monitoring.

Filter sampling, using glass fiber [64], paper [54,58], and membrane filters [10,29], has been applied to the collection of area air samples and to personal monitoring. In one study [54], an average of 3 cu m of air/hr (50 liters/min) was drawn through 9-cm filter papers, except in areas where dust concentrations were low, where flowrates up to 6 cu m of air/hr (100 liters/min) were used. In another study, Lundgren and Ohman [58] collected general air samples and samples close to the breathing areas of employees for several hours through filter paper at a flowrate of 25 liters/min. The specific sampling time and collection efficiency data were not provided. However, these high flowrates are not suitable for personal monitoring.

Measurements of general airborne dust concentrations only indicate possible employee exposure. The concentrations of tungsten dust close to a machine or process may be quite different from that in the breathing zone of an employee. Therefore, collection of breathing zone samples is essential if one is to determine employee exposure. A breathing zone sampling device should be small enough to be conveniently attached to an employee's clothing without interfering with that person's normal activities and should ideally contain no fragile glassware or liquids. Membrane filter collection of dust using a battery-operated personal sampling pump satisfies these conditions.

Personal sampling has been performed using membrane filters at flowrates of 2-2.5 liters/minute for 2-6 hours [11]. Lichtenstein et al [29] reported using Millipore Type AA membrane filters at a flowrate of 4.3 liters/minute to sample the general room air and at a flowrate of 2.5

liters/minute for 2-4 hours to obtain breathing zone samples.

Airborne tungsten present in work areas is predominantly in the form of highly dispersed aerosols of negligible volatility. For the collection of these aerosols, personal monitoring by the membrane filter method (described in NIOSH Method No. P & CAM 173 [65]) is recommended. This method for the collection of aerosols containing tungsten and its compounds consists of drawing a known volume of air through a membrane filter as described in Appendix I. Although this sampling method has not been evaluated by NIOSH for this specific application, it is recommended for metals in general.

The analytical chemistry of tungsten has been reviewed, including detailed discussions on the precipitation, gravimetric, colorimetric, polarographic, amperometric, emission spectroscopic, atomic absorption, X-ray fluorescence, and neutron activation methods [66,67]. Of the methods available for determining tungsten, colorimetric [68-70], emission spectrographic [71], atomic absorption [10,29], neutron activation [72-77], and X-ray fluorescence [78] analyses have been used to determine its concentrations in air. Most of these methods were applied to multi-elemental analysis with no special modification for tungsten determination.

The colorimetric method is based on the principle that, in hydrochloric acid or in a sulfuric/hydrochloric acid solution, tungsten(VI) forms a yellow complex with thiocyanate in the presence of a reducing agent such as stannous or titanous chloride. The complex contains tungsten(V) and has a maximum absorption at about 400 nm [66]. Salyamon and Krashenitsyna [68] studied the usefulness of two thiocyanate methods, using either titanium trichloride or stannous chloride as a reducing agent, to

analyze tungsten and its compounds in air. In the method which used titanium trichloride, the color was stable for 4 hours with a minimum detection limit of 0.5  $\mu\text{g}$ . The color developed by stannous chloride reduction was stable for only 1.5 hours with a minimum detection limit of 0.1  $\mu\text{g}$ .

Urusova [70] reported that when stannous chloride was used, although most of the tungsten was converted to the colored complex after 1 hour, the intensity of the color continued to increase even after 2 hours. However, when titanium(III) was used as the reducing agent, the color developed more rapidly and stabilized sooner. Urusova stated that the sensitivity of the method was 5  $\mu\text{g}$  of tungsten in the colorimetric volume. Peregud and Gernet [69] reported the sensitivity of the method to be 0.1 mg/cu m, using stannous chloride as the reducing agent, and they found no interferences in the method from titanium, cobalt, iron, vanadium, molybdenum, manganese, chromium, and thorium. Fogg et al [79] concluded from a review of literature that vanadium, iron, and molybdenum interfered with the method. Sample preparation for the method generally involved ashing the filter containing the sample in a muffle furnace at 500-600 C until tungstic oxide was formed [68,69]. Urusova [70] believed that, in samples containing mixtures of cobalt, titanium, and tungsten, protective coatings might be formed when they were ashed. Hence, the author recommended that, for a complete decomposition of such samples, concentrated sulfuric acid and ammonium sulfate be used.

Seeley and Skogerboe [71] described the use of an emission spectrographic method to determine atmospheric concentrations of several elements, including tungsten. Porous cup graphite spectrographic

electrodes were used as filters for atmospheric particles, collected at 1 liter/minute for 30 minutes, to determine concentrations of less than 0.1  $\mu\text{g}/\text{cu m}$ . The samples were analyzed directly by a spectrograph (with an absolute detection limit of 5 ng) at 400.8 nm for tungsten and with a precision and an accuracy of 10-20% of the amount present. The authors found that, for the spectrographic determination, vaporization of refractory elements such as tungsten was not completely effective because the bottom of the electrode did not reach a sufficiently high temperature. This problem was corrected by forming metal chlorides with the vapor of hydrochloric acid in the sample chamber.

A nondestructive neutron activation analytical procedure for the determination of 33 elements, including tungsten, in air polluting particles was reported by Dams et al [73] and Linch et al [76]. Aerosols were sampled by using a polystyrene filter with a flowrate of 12 liters/minute/sq cm. The samples were irradiated for 5 minutes at a flux of  $2 \times 10^{12}$  neutrons/sq cm/second (\* means "to the power of") and counted in a Ge(Li) detector. Tungsten in the irradiated samples was measured at photopeaks of 479.3 and 685.7 Kev as  $^{187}\text{W}$  having a half-life of 24 hours. The detection limit for tungsten was 0.005  $\mu\text{g}$ , and the minimum concentration detected in a 24-hour urban air sample was 0.0005  $\mu\text{g}/\text{cu m}$ . These reports [73,76] indicated that the standard deviations of the analysis were greater than 40% when the elements were in concentrations near the limit of detection. However, the authors did not report specific deviations for tungsten analysis.

Peirson and associates [77] similarly analyzed atmospheric trace elements by neutron activation analysis and found that the concentrations

of tungsten ranged from less than 0.1 to 0.3 ng/kg of air (0.12-0.36 ng/cu m). There were no data on the sensitivity or precision of the method in determining tungsten. Pszeny and Russell [75] also determined environmental levels of various elements using neutron activation analysis. However, they ashed the filter paper containing the sample in a furnace at 450 C before irradiating for 8 hours in a flux of  $2 \times 10^{13}$  neutrons/sq cm/sec. The elements, including tungsten, were assayed by a high-resolution gamma-ray spectroscope using a Ge(Li) detector. The concentrations of airborne tungsten were between 19 and 25 ng/cu m with a standard deviation of greater than 50%. Because of the high resolution of the method, Mamuro and his colleagues [72] recognized the usefulness of neutron activation analysis in the determination of tungsten in airborne dust, yet they believed that it was not suited for routine evaluation of air contaminants.

Dzubay and Stevens [78] and Roberts [74] discussed the usefulness of X-ray fluorescence analysis for determining trace elements in aerosols. Although the authors stated that it was one of the most sensitive available methods, its application for determining tungsten was not discussed in either report. The method requires a homogeneous sample for better reproducibility and hence a special sampling device that separates the dust particles by size [11,78].

In general, neutron activation, emission spectrographic and X-ray fluorescence analyses are sensitive methods. However, no reports were found in which any of these methods were examined for their ability to determine tungsten in samples of air from industrial environments. In addition, the methods were used primarily for general analysis of trace

elements, so any interferences in determining tungsten alone, accuracy for tungsten, or details of specific sample preparation for tungsten were not discussed. Such information is required to assess the suitability of these methods for determining environmental concentrations of tungsten in industrial atmospheres.

Although a colorimetric method using thiocyanate was successfully used by Russian investigators [68-70] to determine tungsten in air, there are potential interferences in the method if the sample contains vanadium, iron, or molybdenum. Other variables, such as the type of reducing agent used in developing the colored complex and sample preparation, have substantial influence on the tungsten values and have not been adequately investigated. Thus, although the colorimetric method may be useful for determining tungsten at the recommended TWA concentration, interferences and lack of standardized procedures would make this method unacceptable unless improvements were made and procedures were standardized.

Of all the analytical methods discussed in the recent literature, atomic absorption stands out as the most acceptable, particularly because it is simple, rapid, sensitive, selective, and suited for use with generally available laboratory equipment and personnel. Lichtenstein et al [29] successfully analyzed hard-metal workplace breathing zone air samples by atomic absorption. The membrane filter containing tungsten carbide and cobalt was divided into two portions which were separately analyzed for tungsten and cobalt. For analyzing tungsten, the filter and sample were digested in aqua regia and brought up to 10-ml volume by adding deionized water. The solution was analyzed by atomic absorption spectrophotometry against known concentrations of each metal. The accuracy of the method was

noted to be  $\pm 0.1$  mg in the total sample. In the cemented tungsten carbide industry, the authors found that tungsten concentrations were 0.2-12.8 mg/cu m.

In two other plants producing cemented tungsten carbide, atomic absorption was used to determine levels of airborne tungsten [11]. The levels of tungsten found in these plants were 2.6-36.3 mg/cu m and 0.13-1.3 mg/cu m. The details of analysis were not available for one plant, but at the other the filter was dissolved in a suitable acid and tungsten was determined by using a reducing nitrous oxide-acetylene flame. Husler [80] recommended dissolution of the tungsten sample in a mixture of nitric and hydrofluoric acids as particularly advantageous since this reagent keeps tungstic oxide from precipitating out of solution. Edgar [81] showed that tungsten samples contaminated with molybdenum, chromium, manganese, vanadium, and nickel gave 50-60% higher absorbance readings and that the addition of 2% of sodium sulfate eliminated such interference and enhanced the sensitivity of tungsten absorbance. In most of these studies, the fuel was acetylene and the oxidant was nitrous oxide.

Since analysis by atomic absorption is generally available to industry, possesses the required precision and sensitivity, and has been successfully used by several companies in the cemented tungsten carbide industry to determine concentrations of airborne tungsten, the method outlined in Appendix II is recommended for use in determining adherence to the recommended standard. The recommended procedure is based on Method No. P & CAM 173 of the NIOSH Manual of Analytical Methods [65] with suggested modifications derived from other appropriate literature [80-84]. The recommended procedure is a synthesis of the best available methods, but it



has not been validated by NIOSH. The disadvantages of this method include its inability to determine tungstic oxide, an acid-insoluble compound, and to distinguish insoluble compounds from water soluble ones. Methods shown to be at least equivalent in precision and sensitivity to the recommended method may also be used.

## V. WORK PRACTICES

Most exposures to tungsten compounds in the occupational environment occur during the production of tungsten metal from the ore and in the preparation of tungsten carbide powders. Exposures to cemented tungsten carbide occur in the manufacturing and grinding of cemented tungsten carbide (hard-metal) parts [9]. Dusts and mists of tungsten and its compounds or cemented tungsten carbide are produced during crushing, mixing, ball milling, loading and unloading, sintering, and grinding operations. Because of the high melting points of tungsten compounds and of cobalt, exposure to their vapors or fumes is negligible. Exposures to sodium tungstate, a soluble compound, are limited and occur primarily during the first few stages of processing the ore (see Figure XII-1). Although NIOSH is aware that exposures also occur during filament manufacture and that processes such as high-voltage smelting and wire-drawing pose specific safety problems, it is not possible to elaborate on control measures for these operations because of lack of access to this portion of the industry.

To control the exposure of employees to tungsten compounds and cemented tungsten carbide in these industries, engineering controls and work practices should be designed and applied to minimize or prevent inhalation or ingestion of, or skin contact with, the aerosols.

Properly designed and maintained ventilation systems will minimize dispersal of tungsten compounds and cemented tungsten carbide in the work atmosphere, not only controlling exposure to the airborne compounds but also reducing their accumulation on surfaces. These systems will minimize

maintenance problems and the chance of redispersal during cleanup. Ventilation practices and principles to control workplace air concentrations of tungsten should be based on those set forth in the ACGIH manual Industrial Ventilation: A Manual of Recommended Practice [61], Fundamentals Governing the Design and Operation of Local Exhaust Systems (ANSI Z9.2-1971) [62], and NIOSH's Recommended Industrial Ventilation Guidelines [63]. Exhaust air should be adequately cleaned before it is discharged outside the plant to ensure that it meets applicable federal, state, and local air standards. The airflow, static pressure, and leakage of the ventilation system should be monitored frequently by trained personnel to ensure proper functioning of the system. A logbook showing the airflow design and the results of periodic ventilation monitoring measurements should be maintained. In areas where crushing, mixing, ball milling, loading and unloading, sintering, and grinding operations are performed, local exhaust ventilation should be located as close to the operation as feasible and in accordance with good industrial hygiene engineering practices [61-63]. Alternate means of control for certain processes may include the reduction in density of production equipment and a decrease in equipment speed. Mechanization and enclosure of processes offer additional engineering controls which may be effectively used under some circumstances [11].

In addition to using sound engineering controls, employers should institute a program of work practices which emphasizes good sanitation and personal hygiene. These practices are important in preventing skin and respiratory irritation caused by tungsten compounds or cemented tungsten carbide. Skin irritation has not been found to be a problem with insoluble

tungsten compounds in the occupational environment, but the dermatologic problems observed in cemented tungsten carbide workers were attributed in part to the abrasiveness of the powder. In experimental animals, tungsten hexachloride, a soluble tungsten compound, caused necrosis of the skin and membranes [41]. Workers handling soluble tungsten compounds or cemented tungsten carbide must thoroughly wash their hands and face before drinking, eating, or smoking. Employees must not store and use food, beverages, tobacco, or other materials that may be placed in the mouth, in these exposure areas. Rest areas, eating facilities, and smoking areas should be physically separated from these work areas. In addition, workers should be advised to shower or bathe after the workday. If skin irritation is observed, the employee should be referred to a physician for appropriate protective measures.

Respirators should not be used as a substitute for proper engineering controls in normal operations. However, during emergencies and during nonroutine repair and maintenance activities, exposures to airborne dusts or mists of tungsten compounds or cemented tungsten carbide might not be reduced either by engineering controls or by administrative measures to the levels specified in Chapter I, Section 1(a). If this occurs, then respiratory protection may be used only: during the time necessary to install or test the required engineering controls; for operations such as maintenance and repair activities causing brief exposure at concentrations above the TWA concentration limits; and during emergencies when airborne concentrations may exceed the TWA concentration limits. Respirators conforming to the Respirator Selection Guides in Tables I-1, I-2, and I-3 should be provided to employees, and a respiratory protective program

meeting the requirements of 29 CFR 1910.134 should be established. The Respiratory Protective Devices Manual [85] should be consulted for further information on respirators. Emphasis should be placed on providing clean, well-maintained, well-fitted respirators for use in unusual circumstances and emergencies. Contamination of the interior of the facepiece should be guarded against.

Eye irritation has rarely been a problem for employees involved in handling tungsten compounds or cemented tungsten carbide [15], but operations, such as grinding, which produce and scatter fine particles into the air, require eye protection in accordance with 29 CFR 1910.133. Both individual sensitivity to cobalt and the abrasiveness of powdered metals may contribute to skin irritation [14,24]. Gloves or other protective clothing may be helpful, but employees experiencing skin irritation should be referred to a physician to ensure effectiveness of the protective measures.

Spills of tungsten compounds or cemented tungsten carbide should be promptly cleaned up to minimize inhalation or contact. Liquid material spills should be copiously flushed with water and channeled to a treatment system or a holding tank for reclamation or proper disposal. Spills of dry material should be removed by vacuuming, wet mopping, or hosing, first with a mist of water that dampens the spilled material and then with a more forceful stream that flushes it into a holding tank or other facility for handling contaminated water. No dry sweeping or blowing should be permitted. All waste material generated in the handling of tungsten compounds or cemented tungsten carbide should be disposed of in compliance with local, state, and federal regulations.

Most tungsten compounds pose no fire or explosive hazards. However, powders of submicron-size tungsten metal or tungsten-aluminum-titanium alloys, tungsten metal powders of less than 100 mesh, and ferrotungsten powders of less than 200 mesh are classified as actively combustible [86] and should be handled with caution. Lamprey and Ripley [87] reported that tungsten powder of submicron size which came in contact with hot chlorine gas in a large glass receiver reacted violently and shattered the equipment. These materials should be stored in tight drums under argon or helium gases. The drums should never be vented in air. Great care must also be exercised in handling hexamethyl tungsten, since it is potentially explosive [88,89]. Similarly, tungsten carbonyls were reported to be moderate fire hazards when exposed to flame [90].

Warning labels indicating the potential fire or explosion hazards, skin and respiratory effects, and ventilation requirements should be placed on containers used to transport tungsten compounds or cemented tungsten carbide. In all industries where soluble tungsten compounds or cemented tungsten carbide are handled, written instructions informing employees of the particular hazards of these materials, the methods of handling, procedures for cleaning up spilled material, and the use of personal protective equipment must be on file and available to employees. Employers may use the Material Safety Data Sheet in Appendix III as a guide in providing the necessary information.