VI. DEVELOPMENT OF STANDARD

Basis for Previous Standards

In 1967, the Threshold Limits Committee of the American Conference of Governmental Industrial Hygienists proposed a threshold limit value (TLV) of 5 mg of tungsten/cu m for tungsten and its insoluble compounds and a TLV of 1 mg of tungsten/cu m for soluble tungsten compounds [91]. These proposed limits were adopted by the ACGIH in 1969 [92]. The 1971 Documentation of the Threshold Limit Values for Substances in Workroom Air [93] cites a number of reports which were used to support the need for separate limits for soluble and insoluble tungsten compounds. Karantassis [45] found that the toxic single doses of sodium tungstate, administered intragastrically and subcutaneously to guinea pigs, were 0.55 and 0.45 g of tungsten/kg, respectively. These guinea pigs suffered from anorexia, colic, incoordination of movement, trembling, dyspnea, and weight loss before a delayed death. Kinard and Van de Erve [47] reported the LD50 of subcutaneously injected sodium tungstate for rats to be 0.14-0.16 g/kg and ascribed death to generalized cellular asphyxiation. Kinard and Van de Erve [48] suggested that, when administered orally to rats, sodium tungstate was more toxic than the insoluble compounds, tungsten trioxide and ammonium-p-tungstate.

Emphasizing the relatively low toxicity of the insoluble compounds, the documentation [93] also cited the studies of the following investigators to support separate standards for soluble and insoluble tungsten compounds: Kinard and Van de Erve [44] stated that female weanling rats fed a diet containing 2-10% of tungsten metal powder gained

15.4% less weight than did either female controls or male weanling rats on a tungsten-free diet. Frederick and Bradley [94] found that the LD50 of tungsten metal powder injected intraperitoneally in rats was 5 g/kg and that it did not produce a distinct fibrosis. Delahant [35] administered 150 mg of tungsten metal powder or tungsten carbide intratracheally to guinea pigs in three weekly doses and concluded that it did not irritate lung tissue. Schepers [36] examined the lungs of these guinea pigs microscopically and found that tungsten metal caused moderate interstitial cellular proliferation. He concluded that tungsten metal dust was relatively inert and that exposures of human beings to it would be relatively safe, though not wholly free from risk. Harding [95] reported no "unexpected" effects of intratracheal injections of tungsten metal and tungsten carbide powders on guinea pig lungs. Mezentseva [28] showed that, while rats given tungsten intratracheally had a proliferation of the intra-alveolar septa, those exposed by inhalation to dusts of tungsten, tungsten dioxide, and tungsten carbide had only minor changes in the lungs.

In 1976, the ACGIH also recommended short term exposure limits (STEL's) of 10 mg and 3 mg of tungsten/cu m of air for insoluble and soluble compounds, respectively [96]. The STEL was defined by the ACGIH as a maximum allowable concentration, or absolute ceiling, not to be exceeded at any time during a 15-minute excursion period.

The 1975 USSR maximum workplace concentrations were 6 mg/cu m for tungsten, tungsten carbide, and tungsten silicide, and 2 mg/cu m for tungsten carbonyl [97]. In 1970, the maximum allowable concentration (MAC) in Rumania for tungsten and tungsten carbide was 6 mg/cu m [98]. The 1973 standard for tungsten, tungsten carbide, and tungsten oxide in the German

Democratic Republic was an MAC of 6 mg/cu m with a 30-minute excursion limit of 12 mg/cu m [99]. No bases for these foreign standards have been found. Brakhnova [97] recommended standards for tungsten sulfide (6 mg/cu m), tungsten selenide (2 mg/cu m), and tungsten telluride (0.01 mg/cu m), but they seem not to have been approved yet by the USSR State Sanitary Inspection Office.

There is currently no US Federal Standard for tungsten or its compounds.

Basis for the Recommended Standard

(a) Permissible Exposure Limits

Almost all reports of human exposure to tungsten and its compounds deal with the effects observed after exposure to mixtures of dusts encountered in the hard-metal (cemented tungsten carbide) industry. The components of hard metal include tungsten carbide, cobalt, and sometimes tantalum, titanium, niobium, chromium, nickel, iron, or derivatives of these metals. Only two studies [27,28] were found which described the effects of occupational exposure to tungsten and its compounds without concurrent exposure to other toxic metals.

In 1960, Mezentseva [28] reported that radiologic examination of 54 workers engaged in the production of malleable tungsten or in the early process stages of hard-metal production, where dust exposure was limited to tungsten trioxide, metallic tungsten, and tungsten carbide, showed early signs of diffuse pulmonary fibrosis in 9%. Total dust levels measured ranged from 1.3 mg/cu m in the breathing zone of workers loading furnaces for malleable tungsten production to 83 mg/cu m during loading and

unloading of mills in the production of hard metal. The diameters of 72-82% of the particles were less than 4 μm.

Kaplun and Mezentseva [27] compared results of periodic medical examinations of 36 workers in contact only with tungsten and its compounds with those of 247 workers exposed to dusts of mixed compounds (cobalt and tungsten carbide) in hard-metal production. Radiologic signs of early diffuse pulmonary fibrosis were found in 11% of the first group, while almost 50% of the second group showed damage to the upper respiratory tract in addition to a 13% incidence of pulmonary fibrosis. Subjective symptoms, such as loss of appetite, nausea, coughing, and olfactory disorders, were also reported for the second group, along with abnormalities, such as hypotension and blood changes, which were not limited to the respiratory system. Total concentrations of dust measured in areas where only tungsten compounds were released were 8.6-106 mg/cu m. The total concentrations of the mixed dusts in other parts of the plants were 3-186 mg/cu m, with cobalt content contributing 0.3-1.75 mg/cu m.

Studies with animals disclosed the effects of single and multiple exposures to tungsten and its compounds by inhalation, intratracheal administration, and ingestion. The major effects of inhalation and intratracheal administration were limited to the respiratory system, while the effects of ingestion were not so clearly apparent on any organ of the body. Although no report was found on the dermal effects of tungsten and its compounds in humans, exposure of rats to aerosols of tungsten hexachloride reportedly [41] caused irritation of the skin and mucosa.

In the inhalation study conducted by Mezentseva [28], rats were exposed to tungsten carbide at a concentration of 600 mg/cu m (77% of the

particles were less than 5 μm in diameter) for 1 hour/day for 5 months. Microscopic examination of the lungs showed proliferative reactions of the lymphoid histiocytic elements, particularly at sites of dust accumulation, and subsequent mild fibrosis. Thickening and homogeneity of the pulmonary walls were also noted. Mezentseva also reported that rats intratracheally exposed to a single 50-mg dose of metallic tungsten, tungsten carbide, or tungsten trioxide similarly showed no severe pulmonary changes upon microscopic examination. Totals of 150 mg of metallic tungsten dust or tungsten carbide dust introduced intratracheally in three equal doses at weekly intervals by Delahant [35] did not irritate the lungs of experimental animals. Miller et al [16] observed that 1 ml of a 10% suspension of tungsten carbide administered intratracheally to rats produced no changes in the lungs other than those typical of an inert dust after 18 weeks. Schepers [34] stated that intratracheal administration of tungsten carbide and carbon (in a 94:6 ratio), in three equal weekly doses totaling 150 mg, caused acute hyperemia, bronchial inflammation, and minor residual changes in the lungs, such as the development of subpleural fibrocellular granulomata. These reports suggest that tungsten and its compounds, when encountered without concomitant cobalt exposure, have a distinct but less severe toxicity than tungsten-cobalt mixtures.

The effects of exposure to mixed tungsten-cobalt dusts, reported almost exclusively from the cemented tungsten carbide industry, also relate to the respiratory system, with some effects seen on the skin. A number of reports of such studies identified pulmonary involvement as the outstanding result of the exposures [15,18,25,100]. The signs and symptoms included weight loss, exertional dyspnea, and cough which might progress to

extrinsic asthma [23], diffuse interstitial pneumonitis [18], or fibrosis [17,20,22]. The type of pneumoconiosis seen in the cemented tungsten carbide industry is referred to as "hard-metal disease" [21,25,101].

Skog [24] reported skin changes, including contact eczema, pruritus, folliculitis, and neurodermatitis, that affected 34 (9.4%) of 361 workers involved in production of hard metal. Contact eczema was observed mainly on the eyelids and between the fingers. Of the workers with contact eczema, 3 of 14 patch tested were allergic to cobalt. Although cobalt sensitization was apparent, Skog concluded that most of the cases of contact eczema were caused by the primary irritant effect of the combined metal dust.

Similar dermatologic effects have not been reported from experiments on animals, but the effects of tungsten-cobalt mixtures on the respiratory system have been well documented. In animals injected intratracheally with suspensions of tungsten carbide and cobalt (in a 10:1 ratio), Schepers [37] noted a transient inflammatory response with residual fibrosis. The inhalation of tungsten carbide and cobalt in a 3:1 ratio produced acute inflammation, followed by focal pneumonitis with residual hyperplasia and metaplasia of the bronchial epithelium. The author emphasized that the unusual epithelial reaction was a unique feature of exposure to the tungsten carbide-cobalt mixture. Both Delahant [35] and Schepers [37] found that the intense irritant property of cobalt was dominant when cobalt was combined with tungsten carbide.

Since the use of tungsten in soluble form constitutes only 3% of the total usage of tungsten and its compounds [8], occupational exposures to soluble tungsten compounds are limited except in the early stages of

production of tungsten from its ores. Occupational exposure effects from the soluble compounds of tungsten are virtually unknown. However, comparisons have been made of the toxicity of soluble and insoluble tungsten compounds when administered to experimental animals. Karantassis [45] found that the lethal single doses of sodium tungstate, administered intragastrically and subcutaneously to guinea pigs, were 0.55 and 0.45 g of tungsten/kg of body weight, respectively. Guinea pigs given the toxic dose had anorexia, colic, incoordination of movement, trembling, dyspnea, and loss of weight before a delayed death. Death was attributed to generalized cellular asphyxiation. Kinard and Van de Erve [47] found that the LD50 of subcutaneously injected sodium tungstate in rats was 0.14-0.16 g/kg. Kinard and Van de Erve [48] concluded that, when administered orally to rats, tungsten trioxide and ammonium-p-tungstate were less toxic than soluble sodium tungstate. Comparing the LD50 values of orally administered sodium tungstate, sodium phosphotungstate, and tungstic oxide (WO3), Nadeenko [50] concluded that tungstic oxide was the least toxic of the three compounds. He suggested that the lower toxicity of WO3 was caused by its lower solubility.

Insoluble tungsten, soluble tungsten, tungsten carbide-cobalt mixtures, and the much less common tungsten carbide-nickel mixtures constitute four different potential exposures with different types and degrees of hazard for employees. NIOSH, therefore, recommends separate environmental limits on the following bases:

(1) Dusts of insoluble tungsten compounds pose a hazard considered to be somewhat greater than that of nuisance dust. Generally accepted characteristics of lung-tissue reaction to nuisance aerosols are:

the architecture of the air spaces remains intact; collagen (scar tissue) is not formed to a significant extent; and the tissue reaction is potentially reversible. The 9-11% incidence of pulmonary fibrosis in two studies [27,28] in which employees were exposed to tungsten without concomitant cobalt exposure indicates that the respirable fraction of insoluble tungsten compounds should be limited to below the respirable nuisance dust standard of 5 mg/cu m. Dust of insoluble tungsten compounds has been found to contain a high percentage of respirable particles (approximately 72-90% less than 10μm) [28,42,54]. In addition, collection of total dust is less difficult than size selective sampling. Therefore, NIOSH recommends that dust containing insoluble tungsten be limited to 5 mg/cu m measured as tungsten, which allows both a margin of safety and ease of sampling.

(2) Soluble tungsten compounds are considered to be potentially more toxic than insoluble compounds, although the magnitude of the difference is not precisely known. Comparison of acute toxicity of tungstic oxide and sodium tungstate in mice (oral LD50's of 840 mg/kg and 240 mg/kg, respectively) [50] gives a 3.5-fold difference. A calculated limit of 1.4 mg/cu m for soluble tungsten compounds is suggested when the ratio of the LD50's is applied to the recommended limit for insoluble compounds. In addition, the effects of insoluble tungsten compounds are confined to the respiratory system, while soluble sodium tungstate has been found to cause systemic effects involving the gastrointestinal tract and CNS in guinea pigs. [45]. NIOSH considers the broader range of toxic effects an indication of the need for a somewhat increased margin of safety beyond the 3.5-fold difference and therefore recommends a limit of 1

mg/cu m for soluble tungsten compounds.

(3) The majority of industrial exposures to tungsten and its compounds occur along with exposure to cobalt, used in cemented tungsten carbide in percentages ranging from 3-25%. Whenever employees are involved in the manufacture, use, storage, or handling of cemented tungsten carbide containing more than 2% cobalt, such exposures shall be limited to the current US federal standard for cobalt. If a future NIOSH recommendation for an occupational exposure limit for cobalt differs from the US federal standard for cobalt, this new recommendation should be considered to replace the current recommendation for an occupational exposure limit for dusts of cemented tungsten carbide containing more than 2% cobalt.

(4) Some cemented tungsten carbide is made with nickel or iron as the cementing substance. Iron dust constitutes no great hazard and can be controlled adequately by adherence to the occupational exposure limit for tungsten. Nickel presents a different sort of situation, however, because it seems to be able to induce pulmonary cancers. When nickel is used as a binder rather than cobalt and the nickel content of the mixture exceeds 0.3%, then the NIOSH recommended standard for nickel of 15 μg/cu m should apply [1].

(b) Sampling and Analysis

Personal sampling with a membrane filter is recommended, since most of the compounds in the industrial environment exist as aerosols. Analysis by atomic absorption spectrophotometry has been successfully used in monitoring air for tungsten and cobalt at the necessary sensitivity ranges. The method is relatively simple, quick, and highly sensitive. It has few

interferences, and they can be corrected. The method has not been tested by NIOSH, and it does distinguish insoluble from soluble tungsten compounds. In the absence of differential sampling and analysis, application of the environmental limits for insoluble or soluble tungsten compounds depends on knowledge of the processes within a building or independent structure. Plant observations [11] indicate that only insoluble compounds exist in some operations, and these will be adequately controlled by adherence to the recommended standard for insoluble tungsten compounds. However, when soluble compounds are final, intermediate, or starting products and sampling and analysis can be performed only for total tungsten, concern for worker health and safety dictates that the recommended standard for soluble tungsten compounds should apply throughout that building.

(c) Medical Surveillance and Recordkeeping

Preplacement medical screening is recommended to identify any preexisting pulmonary conditions that might make a worker more susceptible to exposures in the work environment. Periodic medical examinations will aid in early detection of any occupationally related illnesses which might otherwise go undetected because of either delayed toxic effects or subtle changes. Maintenance of medical records for a period of 30 years is recommended.

(d) Personal Protective Equipment and Clothing

Since much of the dust and mist generated in the tungsten industries falls within the range of particle sizes generally considered to include the respirable fraction, respiratory protective equipment may be used when necessary under the following conditions:

(1) During the time necessary to install or test the required engineering controls.

(2) For operations, such as maintenance and repair activities, that cause brief exposure at concentrations above the TWA concentration limits.

(3) During emergencies when airborne concentrations may exceed the TWA concentration limits.

Eye protection is required for operations which produce and scatter fine particles into the air, such as grinding, in accordance with 29 CFR 1910.133. Skin irritation may occur, especially in individuals sensitive to cobalt or to the abrasive action of hard-metal dust, even at environmental concentrations below the action level. Appropriate protective and therapeutic measures should be recommended by a physician. These may include fingerless gloves, protective sleeves, or creams.

(e) Informing Employees of Hazards

Employee awareness is important in an overall effort to reduce occupational injuries and illness. Therefore, employees should be informed through discussion and the Material Safety Data Sheet (see Appendix III) of the possible effects of exposure to tungsten compounds and to dust from cemented tungsten carbide and of the measures being taken to protect the workers against such exposures. In addition, labels and posters should be readily visible to employees.

(f) Work Practices

Exposures to tungsten and its compounds in occupational environments can best be prevented by engineering controls and good work practices. Since tungsten compounds and dusts from cemented tungsten carbide affect

chiefly the respiratory system, measures are recommended that will reduce the atmospheric concentrations of tungsten in the work atmosphere. Adoption of these measures during normal operations will also minimize the possibility of skin contact or accidental ingestion.

(g) Monitoring and Recordkeeping Requirements

It is recognized that many workers are exposed to tungsten compounds or cemented tungsten carbide at concentrations considerably below the recommended TWA limits. Under these conditions, it should not be necessary to comply with many of the provisions of this recommended standard. However, concern for worker health requires that protective measures be instituted below the enforceable limits to ensure that exposures do not exceed the standards. For this reason, "Occupational exposure to tungsten and cemented tungsten carbide" has been defined as exposure above half the recommended TWAs, thereby delineating those work situations which do not require the expenditure of health resources for compliance with such provisions as performance of frequent environmental monitoring and associated recordkeeping. For cemented tungsten carbide products in which nickel is the binder, the NIOSH definition of occupational exposure to nickel shall apply [1].

To relate the employee's known occupational exposure to possible chronic sequelae which do not appear during the period of employment, records of environmental monitoring should be kept for the same 30-year period as the medical records.

VII. RESEARCH NEEDS

Proper assessment of the toxicity of tungsten and evaluation of its potential hazard to the working population require further animal and human study. The following aspects of epidemiologic and toxicologic research are especially important.

(a) Epidemiologic Studies

Further research is desirable to assess the effects of long-term occupational exposure to tungsten. Therefore, detailed long-term epidemiologic studies, retrospective and prospective, of worker populations exposed at or below the recommended environmental limits should be conducted. Such studies should consider the pulmonary, dermal, ocular, and metabolic effects of tungsten and should distinguish exposures to tungsten and its compounds from mixed exposures to tungsten and to compounds of tungsten and cobalt, nickel, vanadium, chromium, or other metals and compounds of these metals. As a minimum, these studies should include environmental air measurements, medical histories, pulmonary function studies, histories of known or suspected acute exposures to tungsten, and comparisons with morbidity and mortality information for the general population.

(b) Acute and Chronic Animal Studies

No definitive acute or chronic inhalation studies have been found for many of the tungsten compounds currently in use. There is some indication of the skin and eye irritation potential of tungsten hexachloride and of tungstic acid, respectively [41,102]. Hence, dermal and eye irritation studies should be undertaken to aid in evaluating the toxic effects of

tungsten and its compounds with and without concurrent exposure to cobalt or other metals commonly used in the production of hard metal. Some studies are available which indicate the possible effects of tungsten and its compounds on the liver, kidneys, adrenals [38,46], and central nervous system [50]; however, these studies are not conclusive. Hence, additional studies are needed to assess the toxic effects of tungsten and its compounds, especially on the liver, kidneys, adrenals, lungs, and central nervous system of various species. Studies should use exposure schedules simulating occupational exposure and should involve routes of exposure which are likely to occur in occupational contact with tungsten (ie, inhalation, ingestion, and absorption through the skin). These results may then provide insight into probable effects of tungsten on human health. Similar studies should also be planned to determine the synergistic or potentiating effects of other metals and compounds commonly found where tungsten and/or its compounds is used.

In experimental animals, high doses of tungsten have been incorporated into such enzymes as xanthine oxidase and sulfite oxidase by competing with molybdenum and producing inactive proteins [49,103-106]. Since xanthine oxidase affects purine and pyrimidine metabolism, a study of its effect through alterations in nitrogen metabolism may reveal some new information about the toxicity of tungsten.

(c) Studies on Carcinogenicity, Mutagenicity, Teratogenicity, and Effects on Reproduction

At present the available literature [25,26] does not supply the information necessary for an evaluation of the carcinogenic, mutagenic, or teratogenic potential of tungsten and its products. No studies were found

which addressed effects of tungsten on reproduction. Hence, further research concerning these possible effects of tungsten should be conducted. These studies should include microbial tests and extensive long-term and multigeneration experiments to evaluate the synergistic and carcinogenic actions, if any, of tungsten carbide. Properly designed and performed experiments can furnish information on all three types of effects resulting from reactions with nucleic acids.

(d) Sampling and Analysis

Investigations of sampling and analytical techniques are encouraged, especially those concerned with developing an analytical method which distinguishes aerosols of soluble tungsten compounds from those which are insoluble in water. NIOSH is currently conducting an analytical methods development project which will distinguish tungsten carbide and tungsten trioxide from sodium tungstate as examples of acid soluble, base soluble, and water soluble tungsten compounds.

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