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TOXICITY OF TUNGSTEN, MOLYBDENUM, AND TANTALUM AND THE ENVIRONMENTAL AND OCCUPATIONAL LAWS ASSOCIATED WITH THEIR MANUFACTURE, USE, AND DISPOSAL

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This report gives an account of the toxicity of tungsten, molybdenum, and tantalum to humans. A brief summary of the environmental and occupational safety laws related to the manufacture, use, and disposal of these metals is provided.

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INTRODUCTION

The Life Cycle Readiness Office at the U.S. Army Armament Research, Development and Engineering Center, Picatinny Arsenal, New Jersey has requested that a literature survey be conducted to identify chemical toxicity problems associated with tungsten, molybdenum, tantalum, and their alloys. In addition, it was requested that the Environmental Protection Agency (EPA) and Occupational Safety and Health Administration (OSHA) laws governing the manufacture and use of these materials be identified.

TOXICITY AND HEALTH EFFECTS

Tungsten: Toxicity

Tungsten may be mildly toxic to humans depending on the route of exposure and the form that it is in. Typically, tungsten metal is poorly absorbed by the human body and is not considered to be an important human health hazard.

Epidemiological studies on tungsten are scarce. Back in 1912, Kruger fed patients 25 to 80 g of powdered tungsten metal by mouth in place of barium for radiological exams and observed no ill effects (ref 1). Much of what is known today about tungsten toxicity comes from industrial exposure.

There is significant evidence from industry that inhalation of certain tungsten alloys is hazardous. In humans, hard metal disease has been a problem for workers who manufacture tungsten carbide powders. However, since cobalt is used as a binder in this manufacturing process, many researchers believe that cobalt is actually the causative agent in hard metal disease--not tungsten (ref 2).

To get an idea of the industrial doses involved, the Handbook on the Toxicology of Metals (ref 1) describes the work of several researchers which are listed here for the reader's reference. Miller (1953) reported three cases of pneumoconiosis in 1,500 men working in the tungsten carbide tool industry. On average, these men breathed in 0.1 to 0.2 mg (Co)/m3 for a period of 2.5 to 7 yrs. Moschinski, et. al. (1959) investigated 331 hard metal workers and found evidence of pulmonary fibrosis in 59 of them. No dosages nor periods of exposure are given. Bech, et. al. (1962) described six cases of hard metal disease which they followed for 15 yrs. The subjects' symptoms included nonproductive coughing, expectoration, shortness of breath, and tightness in the chest. On average, the workers were exposed to 0.30 mg/m^3 of particles less than or equal to 5 μ in diameter. Of these particles, 90% were tungsten and 6% were cobalt.

Anionic, soluble tungsten compounds are more readily absorbed by the human body than cationic tungsten (i.e., tungsten metal) and thus are more toxic. In various rat feeding experiments, sodium tungstate, tungstic oxide, and ammonium paratungstate were found to be extremely toxic, causing death within days. Chronic tungsten toxicity was shown to retard growth in mammals (ref 3).

There is anecdotal evidence of tungsten being a teratogen or a substance which causes deformities in a developing fetus. However, other dietary and cultural factors could not be ignored in these studies. Thus, tungsten is considered to be an experimental teratogen that has experimental reproductive effects (ref 4).

In summation, the oral toxicity of tungsten metal is not a major health concern, but the inhalation of tungsten carbide, probably because of the cobalt binder, is known to cause hard metal disease. In dust form, tungsten is a skin and eye irritant and is flammable when exposed to flame. Powdered tungsten may ignite on contact with air or oxidants (e.g., bromine, fluorine, etc.)

Tungsten-Cobalt Heavy Alloys: Cobalt Toxicity

Since many researchers feel that cobalt is the culprit of hard metal disease in tungsten carbide workers, it stands to reason that tungsten-cobalt alloys, such as those used in projectiles, may be associated with various health effects in addition to hard metal disease. Since the toxicity of tungsten was discussed, the toxicity of cobalt is described here briefly.

Cobalt is a known carcinogen, but it is not a teratogen. The human body absorbs cobalt faster than it can eliminate it. Thus, cobalt can build up causing gastrointestinal, pulmonary, and myocardial disorders.

Cobalt allergy can cause dermatitis. Simply staying away from the cobalt metal prevents this disorder.

Acute oral cobalt poisoning can cause diarrhea, paralysis of limbs, low blood pressure, and low body temperature prior to death. Death is caused by the congestion of all organs.

Acute inhalation cobalt poisoning can cause acute lung irritation, edema and hemorrhage, hyperplasia of bone marrow, massive pericardial effusion, and loss of fluids from capillaries into the peritoneal cavity.

Chronic cobalt poisoning can cause polycythemia, hyperplasia of bone marrow and thyroid gland, pericardial effusion, and pancreatic damage. Heart tissue is highly susceptible to cobalt toxicity.

Dietary cobalt compounds are not carcinogenic in mammals, but parenteral injection of cobalt metal powder, oxides, sulfides, and other compounds causes malignant tumors in animals at the site of injection, in the thyroid glands, and other organs (ref 3).

Molybdenum: Toxicity

Molybdenum is poisonous by intraperitoneal (stomach lining) and intratracheal routes of exposure (ref 4). In humans, pneumoconiosis and hard metal disease formed in workers exposed to 1 to 19 mg Mo/m3 in the form of molybdenum metal and molybdenum trioxide (MoO_3) over a period of 3 to 7 yrs. The ratio of blood to uric acid values were raised in these workers and gout-like symptoms appeared. This phenommena has also been found in residents of Armenia in the 1960s living in areas that had soil containing high amounts of molybdenum (77 mg Mo/kg soil) and relatively low amounts of copper (39 mg Cu/kg soil) (ref 1).

Molybdenum metal, molybdenum trioxide, and sodium molybdate (Na_2MoO_4) are readily absorbed by the human body through inhalation and ingestion. The molybdenum then concentrates in the kidneys, liver, and bones. It is usually eliminated through urination within several weeks.

Molydenum is not a known carcinogen. It can, however, cross the mammalian placenta. Mutation data was reported and it is considered to be a teratogen. However, it has not caused any embryological effects (miscarriages).

Symptoms of acute molybdenum poisoning include severe gastrointestinal irritation with diarrhea, coma, and death from heart failure.

Chronic molybdenum poisoning leads to anemia, poor growth, weight loss, male sterility due to testicular degeneration, poor conception and deficient lactation in females, osteoporosis, and bone-joint abnormalities (ref 1).

Tantalum: Toxicity

There is very little data on the toxicity of tantalum in standard toxicological information sources (refs 3 and 5). This probably means that tantalum and its common compounds are relatively innocuous (ref 6). However, absence of information does not equal complete safety and it always pays to remain vigilant.

According to Sax and Lewis (ref 4), "Some industrial skin injuries from tantalum have been reported," though what these skin injuries were and who reported them is unknown. Tantalum is an experimental tumorigentic or tumor causing substance. However, overall systemic industrial poisoning is apparently unknown.

Tantalum and its common compounds are not listed as either presumptive or possible human carcinogens in the U.S. federal registry of suspected human carcinogens. However, under unusual circumstances following the implantation of tantalum in animal tissue, it has caused cancer (ref 3). Apparently, the smoothness of the implanted tantalum sheet plays a role--with highly polished surfaces potentially leading to cancer in animals. Thus, sometimes tantalum is listed as being a nonspecific, surface carcinogen.

Tantalum salts are non-toxic when taken orally because they are poorly absorbed and quickly eliminated from mammals. Tantalum is inert enough to be used as an implant material for humans. Inhaling tantalum oxide (Ta_2O_5) has caused transient bronchitis and interstitial pneumonitis with hyperemia in mammals. No adverse effects due to tantalum have been reported from industrial exposure--which is usually the most common source of epidemiological information.

EPA LAWS GOVERNING THE MANUFACTURE, USE, AND DISPOSAL OF MOLYBDENUM, TANTALUM, AND TUNGSTEN

The Toxic Substances Control Act (TSCA) of 1976, the Resource Conservation and Recovery Act (RCRA) of 1976 , the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund) of 1980 , the Clean Water Act (CWA) of 1977 , the Safe Drinking Water Act (SDWA) of 1974 and 1986, and the Clean Air Act (CAA) of 1970 are all acts that have at least a few laws governing the manufacture, use, and disposal of molybdenum, tantalum, and tungsten and their compounds. All of the following information was taken from the Environmental Law Handbook (ref 7).

Toxic Substances Control Act (TSCA) of 1976

All three metals: tungsten, tantalum, and molybdenum are listed in the TSCA inventory. Thus, TSCA is triggered, which ensures that the OSHA must set permissible exposure limits (PEL) for work place exposure within an 8-hr period. These are listed in the section on OSHA regulations in this report.

Since all three metals are listed on the TSCA inventory, it is not necessary to notify the EPA with a Premanufacture Notification (PMN) unless the items being made are a "new use which increases human or environmental exposure." If an item is a new use, it falls under the Significant New Use Regulation (SNUR). It is up to the EPA to decide if an item is a new use and falls under SNUR or not, and sometimes the EPA can be irregular in making this decision. Generally, new use includes not simply new uses of a chemical, but also increased production volumes, increased quantity or duration of human and environmental exposure, and hazards associated with manufacturing and distribution.

Generally, if SNUR applies, the EPA will look at the following factors:

- Projected volume of manufacturing and processing of a chemical substance

- The extent to which a use changes the type or form of exposure of humans or the environment to a chemical substance

- The extent to which a use increases the magnitude and duration of exposure of humans or the environment to a chemical substance

- The reasonably anticipated manner and methods of manufacturing, processing, distribution in commerce, and disposal of a chemical substance

If SNUR applies, the EPA will require the PMN. If a PMN is required, one must consult an environmental attorney because the complexity of this law is staggering. For example, if a PMN is required, a company would have to submit health and environmental effects data (which may be expensive to obtain), and record keeping and recording of environmental fate data would be necessary. All of this information would have to be sent in to the EPA in their suggested format. Manufacturers who produce less than 1,000 kg/yr of either molybdenum, tantalum, or tungsten may be able to have their PMN review expedited.

Resource Conservation and Recovery Act (RCRA) of 1976

The RCRA is a regulatory statute designed to provide cradle-to-grave control of hazardous waste by imposing management requirements on generators and transporters of hazardous waste and upon owners/operators of treatment, storage, and disposal (TSD) facilities.

The RCRA would apply if tungsten, molybdenum, and tantalum or their compounds are considered by the EPA to be solid and hazardous wastes. Once hazardous wastes have been identified, the EPA must be notified of hazardous waste activities. People who generate these wastes must comply with RCRA, Section 3002, to handle wastes properly and prepare manifests to track the shipment of the waste to the TSD facility. State programs may supersede the EPA program if they are more rigorous. Thus, the state a generator/ transporter/TSD operates in may have to be notified of hazardous waste activity as well.

A generator is allowed to accumulate hazardous waste on-site without a RCRA permit for storage in two types of cases. The first case, the generator can accumulate up to 55 gal of the hazardous waste near the point of generation in a satellite accumulation area. In the second case, once the 55 gal containers are filled they need to be moved to storage for up to 90 days maximum before being taken away by a transporter to a TSD.

The generator needs to report to the EPA on hazardous waste generation activities and efforts being made at waste minimization. These reports include (1) name, address, and EPA ID number of generator; (2) EPA ID number of transporter; (3) name, address, and ID number of TSD facility used; and (4) waste ID information including DOT hazard class, EPA hazardous waste ID number, and the quantity of waste. Use EPA Form 8700-13A or latest revision.

Penalties for not obeying RCRA are harsh, oftentimes involving heavy fines and, in extreme cases, jail sentences.

Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)

The CERCLA was devised to provide funding and enforcement authority for cleaning up hazardous waste sites and for responding to hazardous substance spills. CERCLA's scope includes water, aquifers, air, and soil. CERCLA is triggered when there is a release or threat of release into the environment of a hazardous substance, pollutant, or contaminant. The definition of these terms is broad.

Since molybdenum, tantalum, and tungsten are included in the TSCA inventory, their release into the environment would trigger CERCLA. Since molybdenum, tantalum, and tungsten may be hazardous substances, as defined by law, private parties are liable for cleanup costs and natural resource damage only to the extent that the said hazardous substances are involved. These private parties are also responsible for reporting releases of the said hazardous substances.

What to do if a release occurs during generation, transportation, or disposal is simply beyond the scope of this paper. Obviously, cleanup and remediation would have to be performed (and paid for). The cleanup and remediation efforts are usually described as massive and complex legal/scientific/engineering/construction undertakings, and are performed with the EPA's knowledge and guidance. The EPA needs to determine how bad the release was and whether it should be listed on the National Priorities List (Superfund site), and how best to cleanup the site based on a remedial investigation/feasibility studies (RI/FS), which lists remediation options and costs. The EPA then publishes a Record of Decision (ROD), in which it tentatively selects its RI/FS option. Public comments are invited in response to the ROD. This is only the start--the cleanup then commences and the legal/scientific/engineering/construction undertakings continue.

During and even after the cleanup is complete, many legal questions remain. For example, are there any other parties involved who might be held liable for cleanup? Will the EPA reopen the issue and require further cleanup at some point in the future? How clean is clean?

Obviously, the point is to not release molybdenum, tantalum, and tungsten into the environment. It is unclear how the EPA would rule if these metals were used to defend the nation and releases occurred as a result of war fighting. It is the opinion of this author that the public would demand that these and other hazardous materials be cleaned up should this scenario ever occur.

Clean Water Act (CWA) of 1977

The CWA is triggered when a priority pollutant or a certain industry plans to dispose of waste into a waterway. It may not be as applicable as TSCA, RCRA, or CERCLA.

There are 126 priority toxic pollutants listed in the CWA. Molybdenum, tungsten, and tantalum are not listed, but organic and inorganic nickel compounds are listed. Sometimes, tungsten heavy alloys contain nickel. The amount of nickel in tungsten heavy alloys is enough to trigger CWA. Also, industry categories such as nonferrous metals manufacturing and foundries trigger CWA.

When CWA is triggered, it means that "if there is a discharge of a pollutant or pollutants into any waters of the U.S. from any point source" a National Pollution Discharge Elimination System (NPDES) permit must be applied for and obtained from the EPA. Most established manufacturers are well aware of NPDES permits and probably already have them if they are in one of the industry categories listed under the CWA.

Applying for a NPDES permit is time-consuming and complex. It involves filing the proper paperwork with the EPA 180 days before the proposed discharge has commenced. The EPA will ask the company to fill out a new source questionnaire and prepare an environmental assessment. Various government agencies (example: Corps of Engineers) will review the application and make comments.

The NPDES permits require (1) specific levels of performance the discharger needs to maintain and (2) requires the discharger to report failures to meet the discharge requirements.

Safe Drinking Water Act (SDWA) of 1986

Only molybdenum is listed as one of the 83 contaminants required to be regulated under the SDWA. Under this act, the EPA is mostly keeping an eye on public water systems (the municipal government) not industry. However, SDWA has an effect on hazardous waste disposal through underground injection control (UIC). The UIC is the subsurface placement of fluid through a dug hole whose depth is greater than its width. Molybdenum should not be disposed of using UIC. Also, sole source aquifers should not be contaminated with molybdenum or severe penalties will result and RCRA will be triggered.

Clean Air Act (CAA) of 1970

Specifically, section 112 of the CAA calls for the regulation of toxic air pollutants. In the case of the manufacture of tungsten, molybdenum, and tantalum, however, it is not really the metals which present the most concern. Instead, it is the entire inventory of solvents, chemicals, and fuels used throughout the manufacturing cycle which are of greatest concern with respect to the CAA. Air permits are needed when there is a release of fossil fuels and toxic pollutants. These permits are issued by the EPA.

The CAA affects industry, not just by what it emits, but also by where the industry is located. Ironically, industries in urban areas are sometimes made to operate under more stringent rules than industries in rural areas. The size of the company and the state that it is located in also determines how stringently CAA is applied Heavily polluted states need to come into compliance with EPA/Congressionally mandated regulations and, thus, companies in these states may be required to use more pollution controls and meet tighter emissions requirements.

There are too many variables involved with the CAA to provide a concise discussion of it with respect to the manufacture of tungsten, tantalum, and molybdenum products. Such as, where they will be manufactured, the size of the company tasked to produce them, and what chemicals the company will use during manufacture.

OCCUPATIONAL SAFETY AND HEALTH (OSH) ACT

The OSH Act is administered by OSHA. OSHA is involved with many aspects of manufacturing such as worker protection, ergonomics, hazard communication, and monitoring safety at work sites. Since tungsten, tantalum, and molybdenum are all listed in the TSCA inventory, OSHA must set PELs for workers over an 8-hr period. The PELs for all three metals are given below:

Tantalum: OSHA PEL:	Total weight allowance (TWA)	5 mg/m3
Molybdenum: OSHA PEL:	TWA soluble compounds	5 mg/m3
	TWA insoluble compounds	15 mg/m3
Tungsten: OSHA PEL:	TWA soluble compounds	5 mg/m3
	TWA insoluble compounds	1 mg/m3

Generally, OSHA regulations require the use of local exhaust ventilation or personal respirators when working with these metals, especially when they are in particulate form. It is suggested that workers wear protective clothing and wash thoroughly after the end of the work shift. Hazard safety communication and material safety data sheets need to be used to inform workers of inhalation, ingestion, and skin irritation dangers. This simply scratches the surface, there are other rules and regulations that may need to be followed and implemented. Industrial hygienists and OSHA regulators need to be contacted for more site specific information.

CONCLUSIONS

It is hoped that this paper has provided an overview of the toxicity of tungsten, molybdenum, and tantalum and the environmental and worker safety regulations related to the manufacture, use, and disposal of these metals.

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