MCHB-TS-TTE (40)

MEMORANDUM FOR Commander, U.S. Army Center Environmental Center, ATTN: SFIM-AEC-ETP (Kelly Rigano), Aberdeen Proving Ground MD 21010-5401

SUBJECT: Review of Tungsten

1. Per request for information regarding Tungsten please find the attached report.

2. The U.S. Army Center for Health Promotion and Preventive Medicine point of contact is Dr. Wilfred McCain at extension 5-3980.

FOR THE COMMANDER:

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Program Manager
Toxicity Evaluation

TUNGSTEN:
A REVIEW

I. Historical Background

General:

The history of the development of tungsten and its alloys for practical use is more than two centuries old. C.W. Scheele first discovered tungsten in 1781. J.J. and F. de Elhuyer published the first account regarding the isolation of tungsten from ore in 1783. It wasn't until 1847, however, when Oxiand patented processes describing the manufacture of two chemicals used as starting materials in tungsten metallurgy (tungstic acid and sodium tungstate) that industrialization of tungsten began in earnest. In the mid-1800's efforts to produce tungsten steel succeeded and the field developed rapidly from that point onward. The importance of tungsten hardened steel was recognized immediately, the manufacture of rails being the first practical application of that product.

A number of other practical applications followed. The Bethlehem Steel Co. exhibited tungsten high-speed steel tools at the Pads Exposition in 1900. The process for drawing tungsten filaments was patented in 1904, and development of the tungsten filament itself began 5 years later. The result of this invention is perhaps the single best known application that there is of tungsten light bulbs.

Further developments and applications of tungsten came about with the introduction of tungsten carbide, produced when tungsten is blended with carbon and heated to about 1,550ºC. The carbide is extremely hard, but it found few applications at first because of its brittleness. The discovery in Germany in the late 1920's that the properties of tungsten carbide were improved enormously upon addition of a cementing or bonding agent led to a significant 25 year period of development-the so-called "carbide era" (Li and Yu Wang, 1955).

Military Applications:

The development of armor-piercing tungsten carbide penetrators by Germany during World War II signaled the onset of an irreversible change in modern tank warfare-both in armor and in antiarmor weaponry. The use of high velocity tungsten carbide penetrators for the first time-by Rommel's forces against British armors cited by Li as a major contributor to Germany's near success in its North Africa campaign. Two years later, American forces perfected similar antiarmor penetrators that were highly effective against German armor.

The development of spaced array armor in the 1960's made tungsten carbide penetrators obsolete. The tungsten carbide rods were susceptible to breakage upon impact, even against a relatively thin plate. Metallurgical advances in the manufacture of tungsten alloys and adaptation of a new swaging process resulted in substantially improved performance of penetrators against the new challenge posed by the advanced armor systems (Davitt, 1980).

Tungsten alloy penetrators remained the mainstay of the Army's antiarmor ammunition until the end of the 1970's when production of the 105-mm M735 tungsten kinetic energy (KE) penetrator round was phased out, and depleted uranium (DU) KE penetrators were introduced, i.e., the 105-mm M774 (Coleman, 1995).

The U. S. Navy formerly used DU in Phalanx penetrator cartridges and switched back to tungsten alloy in 1990 (Coleman, 1995). The reasons for the changeover included the following: (1) for their purposes, a slight improvement was found in tungsten performance over depleted uranium; (2) transition to tungsten obviated the need for protective shielding, thus lowering costs; and (3) there are lower demilitarization costs for tungsten ammunition than for DU.

Industrial and Other Applications:

The physical attributes of tungsten alloys' density, hardness, and heat-resistance have led to a multitude of peacetime uses. Modern uses of tungsten alloys are in aircraft, automotive and power components, in light bulbs as filaments, for shielding and for arc welding. A further attribute of the metal that it is relatively inert-has resulted in its use as a Carrier of DNA for genetic engineering of plants and for research on advanced immunological techniques.

The use of tungsten or its alloys in our daily lives is becoming increasingly common: For instance, tungsten is used in the manufacture of some hand tools such as chisels and saw blades; in various types of sporting equipment, such as dart barrels and as weights in golf-club heads. It is also used for electrical lighting filaments, for automotive distributor points, as a flame-retardant for cellulose, and in x-ray and cathode ray tubes. In general, tungsten is used where metals with a high temperature tolerance and a low reactivity rate are needed.

A process for embedding tungsten in a polymeric matrix has recently been patented (USEPA, 1994). Items fabricated from the composite have the advantages of high density and absence of toxicity. The absence of toxicity in tungsten composites is particularly important because the new material provides environmental relief from the known toxicity of lead to wildlife.

II. Occurrence

Naturally occurring tungsten is found, for the most part, in the base ores wolframite ($(Fe, Mn)WO_4$), scheelite ($CaWO_4$), ferberite ($FeWO_4$), and hubnerite ($MnWO_4$). Worldwide, wolframite is the most important ore while sheelite is the principal domestic ore. The richest deposits are in China, Alaska, and Mexico. Worldwide production is around 50,000 metric tons per year. It has an abundance of 1 ppm in the earth's crust. Tungsten has also been found in drinking water at levels between 0.03 to 0.1 µg/l depending on sampling site. Atmospheric levels of tungsten are in the "very low" category (less than 1.5 ng/m^3) and are generally related to industrial emissions. Tungsten is found in rainwater at levels less than 0.1 µg/l. Nuclear explosions have produced tungsten radioisotopes. These are widely distributed in the environment, primarily as tungstic oxide.

III. Properties

Tungsten (Wolfram; W) metal is lustrous and silvery white in color and does not occur naturally in the environment. Tungsten containing ore is first converted to the trioxide and then reduced to the metal by reduction in hydrogen (carbon cannot be used as the very stable carbide would result). Tungsten metal is relatively inert, resisting attack by oxygen, acids and alkalis, although it will react with fused oxidizing alkali media. It has the highest melting point of all metals and, when pure, it can be worked with relative ease; the presence of impurities renders tungsten extremely brittle and, therefore, difficult to fabricate. Tungsten is a transitional element in group VIa of the periodic table and is therefore closely associated with the elements molybdenum and chromium.

The high melting point of tungsten makes it suitable for use as electric filaments (e.g. in light bulbs). It is also the basis of a range of alloys containing tungsten, copper and nickel which are used for radiation shielding as they provide a 50% increase in density compared to lead. Tungsten and its alloys also find uses in military applications as armor and ammunition. Tungsten carbide powder (with possible additions of titanium or tantalum carbides) along with nickel or cobalt powders, are compressed and sintered to produce cemented carbides. These products are used in place of high-speed steel to form the tip of the cutting and drilling tools, or for parts which will be subject to heavy usage.

Atomic Properties		
Atomic number	74	
Atomic radius	0.141 nm	
Atomic weight	183.85 amu	
Crystal structure	Body centered cubic	
Electronic structure	Xe $4f^{14}$ $5d^4$ $6s^2$	
Photoelectric work structure	4.55 eV	
Thermal neutron absorption cross-section	18.5 Barns	
Valences shown	2, 3, 4, 5, 6	
Natural Isotope distribution	Mass No.	%
	180	0.1
	182	26.3
	183	14.3
	184	30.7
	186	28.6

Ionization potential	No.	EV
	1	7.98
	2	17.7

Physical Properties	
Boiling point	5660°C
Density @ 20°C	19.3 g cm^{-3}
Melting point	3140°C

Electrical Properties	
Electrical resistivity @ 20°C	5.4 μΩcm
Temperature coefficient @ 0-100°C	0.0048 K^{-1}
Superconductivity critical temperature	0.0154 K
Thermal emf against pt (cold 0°C – hot 100°C)	+ 1.12 mV

Thermal Properties	
Latent heat of evaporation	4009 J gm^{-1}
Latent heat of fusion	192 J gm^{-1}
Linear expansion coefficient @ 0-100°C	4.5 x 10^{-6} K^{-1}
Specific heat @ 25°C	133 J K^{-1} kg^{-1}
Thermal conductivity @ 0-100°C	173 W m-1K^{-1}

Mechanical Properties			
Material condition	Soft	Hard	Polycrystalline
Bulk modulus			311 Gpa
Hardness (Vicker's)	360	500	
Poisson's ratio			0.28
Tensile modulus			411 GPa
Tensile strength	550-620	1920 MPa	
Yield strength	550 Mpa		

IV. Production

This section is excerpted from Gold and Los (1966).

Manufacturing:

Some physical and chemical properties of tungsten and the procedures necessary to purify intermediates when producing metallic tungsten are presented here as an aid to understanding tungsten metallurgy as it applies to kinetic energy penetrators.

Tungsten has an extremely high melting temperature (3,410± 200°C), the highest of all elements with the exception of carbon. [Tantalum carbide is one of the few carbides that has a higher melting point than tungsten (Rieck, 1967)] Because of tungsten's high melting point, methods involving chemical decomposition and purification must be used instead of ordinary processing techniques such as pyro-metallurgy. The purified powder can then be used for manufacturing penetrators or other Army materiel.

Ores containing tungsten are generally treated to obtain intermediates such as sodium tungstate, which must then be purified. A practical approach to purification is to first transform the sodium tungstate to ammonium paratungstate. This is digested, washed, and then redissolved in ammonia to reprecipitate ammonium paratungstate crystals. The process is repeated several times to obtain pure ammonium paratungstate which, after digestion with nitric and hydrochloric acids followed by drying, yields pure tungsten trioxide. Reduction of tungsten trioxide in a hydrogen atmosphere produces metallic tungsten powder. [Reduction of tungsten with carbon (e.g., lampblack or carbon black) in a hydrogen atmosphere between 1,450°C and 1,550^{o}C produces tungsten carbide (Li and Yu Wang, 1955).

The manufacture of penetrators involves compaction of a blend of metal powders in molds at high pressure (predominantly tungsten with lesser amounts of alloying metals). After they are removed from the molds, the compacts are sintered, annealed, swaged, and finally cut to a prescribed shape. These operations are described in greater detail.

<u>General</u>: Tungsten heavy alloys (WHA) are the materials of choice for tungsten-based penetrators. Tungsten carbide was used during WW II, but changes in target materials and design-as well as advances in metallurgy and processing techniques-shifted attention to tungsten heavy alloys. In addition to providing the hardness that was associated with tungsten carbide, these alloys have other noteworthy characteristics that affect penetrator performance and cost: (1) greater density, (2) increased strength and ductility, (3), machinability, (4) reasonable production costs, and (5) resistance to corrosion when stored, over long periods of time (German, 1992).

Modern tungsten-based alloy penetrators are manufactured by a powder metallurgy process that involves compaction of tungsten powder (the primary phase) with alloying (binding or cementing) elements such as nickel and iron and possibly cobalt (the secondary phase). In general, tungsten particles with diameters in the nominal range less than 5 p are used. Recent efforts have focused on smaller grain sizes, including ultrafine dimensions, to improve tungsten alloys (Dowding, 1991).

The manufacturing process described here for large-diameter penetrators was used by Teledyne Firth Sterling, LaVergne, Tennessee (Brooks, 1986).

<u>Powder blending and compaction</u>: Tungsten Powder was blended with sieved matrix elements such as nickel and iron (and possibly cobalt) with the aid of a V-blender equipped with a central high-speed intensifying bar to improve efficiency. The amount of tungsten powder in the blend is high, up to 97%; nickel and iron powders are widely used in the industry in an optimum ratio of 7:3 (Dowding, 1991), though other ratios are also used.

Approximately 15 lb. (7 kg) of blended powder was-fed to a rubber mold which in turn was surrounded by a steel casing to ensure accurate shaping during pressing. Each rubber mold was then sealed and the compact cold-pressed isostatically. This involved sealing the molds inside a chamber where they were exposed to water pressure up to 2,000 bar (30 ksi). The process was termed "wet-bag" inasmuch as the molds were in direct contact with pressurized water. As many as 250 large-diameter penetrator compacts could be processed simultaneously in the pressure chamber used by Teledyne, a converted 16-in. gun.

Small penetrator rods (⅛ in. to 1 in. diameter) were produced automatically in a dry-bag pressing device. The process consisted of compaction of powder in forms placed inside a bag within a bag. Only the outside bag was exposed to the hydrostatic fluid (a water and soluble oil mixture) at about 2,000 bar (30 ksi). Components could be loaded into the dry-bag instrument and cold pressed, all within a 45-sec interval.

Sintering: Liquid phase sintering consisted of bringing the compact to a temperature at which it would liquefy and then maintaining the compact at that temperature so that the metallic secondary phase elements remained liquid throughout all or most of the process. As a consequence of this process: (1) a portion of the tungsten was dissolved in the liquid fraction; (2) upon cooling, there was a substantial increase in the diameter of the undissolved tungsten particles. The compact was strengthened and densified by this operation.

Sintering at Teledyne was carried out in semi-automatic twin-muffle electric furnaces which were equipped to provide three individually controlled temperature zones in a hydrogen atmosphere. Penetrators were sintered in alumna boats (to avoid contact with carbon) at temperatures in the range of 1,350 to 1,560ºC and higher for alloys that contained more than 97% tungsten.

Alloys with less than 95% tungsten required a shorter exposure interval at lower temperatures and a maximum temperature of approximately 1,500ºC. Teledyne used other suitable furnaces for sintering such alloys.

Heating in appropriate furnaces as performed by Teledyne is one kind of sintering process used in the powder metallurgy industry. Resistive heating is another. In resistive heating, a current is passed through a compacted preformed item. At suitable electrical current and resistance levels, a temperature greater than 2,500ºC is obtained and the powder is fully sintered within minutes. The resulting product is suboptimum from the viewpoint of ductility at room temperature, however, and requires cold work such as rolling or swaging and elevated temperatures to improve its properties (Dowding, 1991).

An experimental approach taken by other investigators to improve properties of tungsten heavy alloys involved liquid phase sintering in a vacuum. Alloys sintered in a vacuum were compared with alloys sintered in a heated dry hydrogen atmosphere. Improvements attributable to vacuum sintering included, production of an alloy with a density that approached the theoretical value and strength and ductility values comparable to the best reported. A disadvantage, however, was that prolonged sintering in a vacuum resulted in loss of matrix phase metals through vaporization (Bose et al, 1987).

Annealing: Special vacuum furnaces capable of heating 9 tons of sintered rods at once were used at Teledyne. This post-sintering operation was designed to remove residual hydrogen, which, if left behind, could have resulted in penetrator embrittlement. Ductility was improved by annealing. If impurities were present at the surface of the penetrator they were redistributed back into the nickel-iron binder during the annealing process.

Swaging: Large penetrators were swaged in a fixed-die 600-ton swaging machine. Bars were held between centers and rotated while passing through a set of four die segments that have a stroke of approximately 2 mm. A single pass through the machine sufficed to obtain the desired final diameter.

Machining: The bars were cut to length and milling of the ends was begun. Further machining was done on a lathe by securing a large rod in a chuck at one end and a center at the other. As an example of the extent of machining required to produce a finished penetrator, a bar 25-in. long (650 mm) with a diameter of about 2 in. (50 mm) was machined down to a diameter of 1.444 in. (36.7 mm). Additional metal shaping involved machining buttress grooves on the penetrator. The quantity of metal removed in this machining step was dependent on the configuration of grooves on the penetrator, which varied according to proprietary customer specifications.

V. Environmental Levels and Exposures

Standards and Regulations:

MSHA STANDARD (air):	TWA 1 mg/m^3 (soluble)
MSHA STANDARD (air):	TWA 5 mg/m^3 (insoluble)
OEL-DENMARK	TWA 5 mg/m^3
OEL-RUSSIA	STEL 2 mg/m^3
OEL SWEEDEN	TWA 5 mg/m^3
OEL-UNITED KINGDOM	TWA 5 mg/m^3
	STEL 10 mg/m^3

NIOSH Documents:

NIOSH REL to Tungsten:insoluble (air)	TWA 5 $mg(W)/m^3$
	STEL 10 $mg(W)/m^3$
Soluble (air)	TWA 1 mg(W)/m3
	STEL 3 mg(W)/m3
National Occupational Exposure Survey (1983):	Hazard Code 74980

National Occupational Exposure Survey (1983): Hazard Code X5928
National Occupational Exposure Survey (1983): Hazard Code X7685
National Occupational Hazard Survey (1974): Hazard Code 74980

Status in the United States:

EPA TSCA Section 8(b) Chemical Inventory
EPA TSCA Section 8(d) Unpublished Health / Safety Studies
EPA TSCA Test Submission (TSCATS) Database, April 1997
NIOSH Analytical Method, 1994: Tungsten (Soluble and Insoluble), 7074
U.S. Army: Approved Health Hazard Assessment of the 120 mm Armor Piercing, Fin Stabilized, Detachable Sabot-Tracer, Kinetic Energy-Tungsten (APFSDS-T, KE-W) round.
U.S. Fish and Wildlife Service has approved the use of tungsten-iron shot for waterfowl hunting. 1997
USEPA has approved replacement of lead sinkers with tungsten for fishing 1997

VI. Background Levels in Humans

Webster and his colleagues (1973), using neutron activation analysis, determined the serum concentration of tungsten in humans. The concentration was 5.8 (±3.5) ng/ml in eight healthy subjects.

VII. Potential Exposure (Forms of Tungsten and Route of Entry)

Recent studies at Oak Ridge National Laboratories and Picatinny Arsenal have indicated that only insoluble forms of tungsten are generated from small caliber rounds. These forms include tungsten metal (W), oxides of tungsten (tungsten trioxide, WO_3; tungsten hemipentoxide, W_2O_5; and tungsten dioxide, WO_2), and tungstic (VI) acid (H_2WO_4). It is unlikely that salts of tungsten (Na and Ca) will be formed either from the manufacturing process or normal use of small caliber tungsten rounds. Insoluble forms of tungsten are generally less toxic than are the soluble forms.

Studies conducted by the Close Combat Arms Center (CCAC) indicated that airborne levels of tungsten did not exceed the Threshold Limit Value (TLV) set by the American Congress of Governmental Industrial Hygienists (ACGIH) or Permissible Exposure Level (PEL) set by the Occupational Safety and Health Administration. In fact, the airborne levels of tungsten produced from firing 30 rounds of 5.56 mm tungsten ammunition was two to three orders of magnitude lower than the 5.0 mg/m^3 TLV or PEL. Investigators from the CCAC have indicated that little or no soluble forms of tungsten are produced during live fire exercises.

Several epidemiological studies measured airborn concentrations of tungsten during the manufacturing process. Kaplum and Mezentseva (1959) reported airborne concentrations of tungsten in various processing operations between 8.6 and 107 mg/m^3. Another study conducted in 1975 reported concentrations of tungsten in the grinding process between 0.2 and 12.8 mg/m^3.

The most likely route of entry for tungsten from manufacturing or use of the small caliber rounds is the pulmonary route. This route may be more problematic in the manufacturing process than from firing small caliber rounds. In both cases, however, areosols containing tungsten will be produced. Because of the density of tungsten (19.3 g/cm^3), only particles 5 µm or less will remain airborne for extended periods of time. Dusts containing smaller particles (0.5 to 1 µm) may be produced around powdered metallurgy operations where mixing, milling, shaping, and grinding of tungsten and its alloys occur.

The dermal or ocular routes of exposure are also relevant. Deposition of tungsten on the exposed surfaces of the body is likely in manufacturing operations. Deposition may also occur at indoor firing ranges where the concentration of minute particles of tungsten may be concentrated.

Ingestion is another potential route of entry for tungsten, although it is not considered to be of great importance. Inhaled tungsten particles may be carried to the gastrointestinal tract by the mucociliary escalator. This mechanism is important in both the removal of inhaled tungsten particles from the respiratory system as well as providing a secondary route of exposure for tungsten.

VIII. Metabolism (Absorption, Distribution and Elimination)

The disposition of tungsten in the body has been evaluated by several investigators. In rats, 40 percent of ingested ^{185}W was excreted in the urine after 24 hours and 58 percent had either been eliminated in the feces or remained unabsorbed in the gut. Only 2 percent remained in the tissues (Ballou, 1960). The absorption in dogs of inhaled ^{181}W-labeled tungstic oxide indicated that 60 percent of the activity was deposited in the respiratory tract. One third of the activity was cleared to systemic circulation within ten days and the remaining two thirds was cleared to the gastrointestinal tract (Aamodt, 1975).

The distribution of ingested tungsten metal, tungstic oxide, sodium tungstate and ammonium-*p*-tungstate was evaluated by Kinard and Aull (1945). The principal sites of deposition were bone and spleen. With less than 1 percent deposited in the kidney, liver, and, in some animals, the blood lung muscle, and testes. These investigators indicated that there was essentially no difference in distribution among the compounds evaluated. The Aamodt study (1975), where labeled tungsten was inhaled, indicated that the highest concentration of tungsten was found in the lung and the kidney 165 days after exposure,. Concentrations in bone, gall bladder, liver, and spleen were approximately one order of magnitude less than that found in the lung and kidney. When this data is examined as organ burden, the highest activity levels were found in bone (37%) and lung (31%).

The primary route of elimination for both soluble and insoluble forms of tungsten is the urine. This type of elimination is rapid for tungsten. Following intravenous injection of ^{185}W-labeled sodium tungstate, 91 percent was eliminated within 24 hours. The rate of decrease in blood activity of inhaled ^{181}W-labelled tungstic oxide was lower than that for injected sodium tungstate. This phenomenon may have been due to the extended rate of absorption of tungsten to blood from the lungs. The daily excretion rate for ten workers exposed to tungsten carbide was 490 µg W/24 hours (Barborik, 1972). A study of urinary and fecal elimination of tungsten was conducted on four healthy young adults. With only small variations, tungsten elimination was equivalent to tungsten ingested from the diet.

The biological half life of inhaled metallic tungsten has been determined for dogs. More than 94 percent of the inhaled metal was removed within nine hours. The longest half life was 139 days for the final 1.6 percent.

IX. Toxicity Information

Data:

Information evaluated on the toxicity of tungsten for this review falls into two major categories. One type of data includes information on human worker exposure. Toxicologists, industrial hygienists, and occupational health physicians have reviewed historical data, coupled with ambient workplace levels of tungsten and its alloys. The interpretation of many of the studies, which focused on tungsten alloys, is difficult due to the presence of other, more toxic, materials such as cobalt and nickel. Severe adverse health effects have, for the most part, have been attributed to the presence of cobalt and nickel in the alloyed product. The National Institute of Occupational Safety and Health (NIOSH), in order to develop workplace exposure criteria, reviewed this type of information as well as pertinent information obtained from animal studies. The second type of data includes studies on the toxicity of tungsten in both humans and animals. This type of specific information is scanty at best. Environmental studies are also considered in this category. Other studies in which tungsten was used but not evaluated as a toxicant were reviewed as well. Care was taken to evaluate only studies that examined only the effects of insoluble forms of tungsten and tungsten metal.

General toxicity information:

The median intraperitoneal toxic dose (LD_{50}) for tungsten in rats is 5000 mg/kg and the estimated LD_{50} for humans is between 500 and 5000 mg/kg. This range is between an ounce and a pound for a 70 kg (154 lb.) individual. However, no ill effects were observed in a patient given 25-80 grams of tungsten metal orally as a substitute for barium in radiological examinations. The LD_{50} for tungstic oxides and tungstic acid are approximately 1000 mg/kg in the rat via the oral route.

Tungsten metal and insoluble forms of tungsten have not been shown to be mutagenic or carcinogenic. Tungsten has a reproductive hazard rating of B- (few reproductive effects in animals but no human data) and a general toxicity hazard rating of 1 (may cause reversible effects that are not life threatening) according to REPROTEXT®. The toxicity hazard rating of 1 for tungsten is due more to its effects as a mechanical irritant than to the toxicity of the compound.

Respiratory toxicology:

Almost all human studies are of tungsten carbide and its alloys in connection with its use in the hard metal industry. Hard metal disease, a form of debilitating pulmonary fibrosis, occurs in persons chronically exposed to the mixed dust of cobalt-cemented metal carbides. However, pure tungsten did not cause pneumoconiosis, and hard metal disease is believed to be caused by cobalt (ACGIH, 1986; Friberg *et al*, 1986).

Respirable particles less than 10 µm Mean Mass Aerodynamic Diameter (MMAD) pose the greatest danger to health. The deposition of particles in the respiratory system is influenced by four mechanisms: impaction, sedimentation, interception, and diffusion. The MMAD of a particle will also influence where is deposited within the respiratory system and, to some extent, the rate of its elimination. The respiratory characteristics for humans and particle clearance phases are tabulated below:

Respiratory Characteristics for Humans

Respiratory Region	Number	Diameter (mm)	Flow Speed (cm/sec)
Trachea	1	18	390
Main Bronchus	2	12	430
Terminal Bronchioles	66,000	0.6	5
Alveoli	3×10^8	0.3	~0

(Kennedy and Valentine, 1994)

Particle Clearance Phases:

Anatomic Region	Clearance Mechanism	Approximate Clearance Half-time
Nasopharynx	Mucociliary transport	Minutes
Tracheobronchial	Mucociliary transport	Minutes to hours
Alveolar	Macrophages	Days to weeks
Pulmonary	Interstitial migration	Months
Pulmonary	Dissolution	Months to years

(Kennedy and Valentine, 1994)

The International Commission on Radiologic protection (ICRP) has developed a model for the deposition of particles in humans. The collective data indicates that deposition is at a minimum with particles approximately 0.3-0.5 µm MMAD. Particles in this size range are affected the least by deposition mechanisms and particles greater than 30 to 80 μm are not inhalable through the nose. As indicated in the particle clearance chart, above, particle size greatly affects clearance of material from the respiratory system and the clearance mechanism utilized.

Studies in animals have indicated that morphological changes occur in the respiratory system after exposure to tungsten. Four months after intertracheal instillation of tungsten metal, rats displayed an increase in macrophage infiltration in proximity to pulmonary blood vessels. At six months, there was distinct cellular proliferation around the blood vessels with overlying collagenous fibers. At this time, there was also a swelling of the endothelium and a thickening of the walls of the small blood vessels. Some lymph nodes contained free particles of tungsten carbide (Mezentseva, 1967). Rats inhaling tungsten carbide dust (600 mg/m^3) remained healthy and displayed no morphological changes at this concentration (Mezentseva, 1967).

The effect of tungsten metal dust on the respiratory system was evaluated in guinea pigs (Delahant, 1955). His findings one month after intertracheal instillation were similar to those of Mezentsva and included macrophage infiltration and focal cellular lesions around capillary blood vessels of the lung. Guinea pigs examined one year after intertracheal instillation of tungsten metal dust displayed focal, interstitial cellular infiltration caused by retained particles.

<u>Reproductive and teratogenic toxicity</u>:

No information exists at this time on the effects of tungsten on reproductive performance in humans. One study currently in progress is an evaluation of birth rates among women in the tungsten mining industry in China. No data is available at this time.

A study conducted by Wide (1984) indicated that mice given intravenous sodium tungstate on day eight resulted in increased fetal resorptions. Sodium tungstate, however, is a soluble form of tungsten and not a potential chemical of concern for this review. It is the results of this study that classified tungsten as a B- reproductive toxicant.

Dulak and his colleagues (1984) found no treatment related effects in female rats fed a high tungsten diet. The study was conducted to assess the effect of a sulfite oxidase-deficient rat model rather than to observe the effects of dietary tungsten. A developmental trend was was observed in anophthalmia (complete absence of eyes) in tungsten treated rats, however, the observation was not significantly different from control animals.

<u>Dermal and ocular toxicity (acute exposure)</u>:

The standard Draize test was conducted on New Zeland white rabbits. There was a mild reaction to tungsten metal on shaved rabbit skin following an exposure of 500 mg for 24 hours. There was also a mild reaction 24 hours after placing 500 mg of tungsten in the rabbit's eyes. A few (20 of 1200) workers at a cemented tungsten manufacturing plant had erythemateous, papular dermatitis. Patch tests demonstrated that these workers were not sensitive to tungsten metal or tungsten oxides but positive reactions followed exposure to cobalt and cobalt chloride.

Systemic toxicology:

There are certain properties of an element that determine its biological behavior. These include the stable oxidation state of an element or compound at body pH, the solubility of the stable state, the tendency to be incorporated into organic molecules, and the tendency to associate with specific proteins.

Tungsten is capable of replacing the molybdenum molecule in several protein systems responsible for oxygen modification. These enzyme systems include xanthine dehydrogenase, xanthine oxidase, sulfite oxidase, aldehyde oxidase, and nitrate reductase. In a study conducted by Matsubara and his colleagues, tungsten displayed a protective effect against paraquat induced toxicity in rats by inhibiting xanthine oxidase. This was determined by examining S-phase chromosomes from liver and lung cells 1, 3, and 5 days after exposing the rats to paraquat. Rats fed a standard diet displayed an increase in S-phase cell populations in the lungs while rats given a tungsten-enriched diet displayed no increase in S-phase cell populations. A tungsten enriched diet fed to rats for 4 weeks diminished xanthine oxidase and lessened the rise in intracellular hydrogen peroxide production after lippopolysaccharide treatment. Liver damage, as assessed by serum transaminase levels, was also ameliorated by the tungsten-enriched diet.

Although no studies have indicated that tungsten is mutagenic or carcinogenic, it could potentially contribute to these effects. One study (Kirsch-Volders *et al*, 1997) indicated that although tungsten carbide did not cause single strand breaks in DNA, in cultured human peripheral lymphocytes, it may allow some uncoiling of the chromatin. This effect may lead to an increased DNA sensitivity to clastogenic effects. In another study, tungsten carbide alone does not produce DNA single strand breaks while tungsten carbide cobalt produced more ssb than cobalt alone. One indication is that the WC, when mixed with Co, increases the production of hydroxyl radicals. Furthermore, WC may modify the structure of chromatin, leading to increased DNA sensitivity to clastogenic effects (Anard,1997).This information concurs with results of the comet assay (single cell gel electrophoresis) where tungsten cobalt did not induce DNA strand breakage in human leukocytes.

Recently, a case study appeared in *The Lancet* (Marquet *et al*, Oct., 1996) which implicated tungsten in the illness of a young soldier. This soldier, and others, had ingested wine poured through the barrel of a 155 mm artillery piece after several shots had been fired. The soldier was admitted unconscious and with seizures to the hospital. The soldier suffered anuric renal failure after three days and was placed on hemodialysis. Renal biopsy demonstrated extensive tubular necrosis. The soldier was released completely recovered 35 days after being admitted to the hospital. Inductively coupled plasma emission spectrometry indicated that there was a high level of tungsten in the wine (1540 mg/l) and in all biological samples measured. Dr. Lison (*The Lancet*, Jan., 1997), who suggested that there was no causal relationship between tungsten and toxicity, questioned the validity of Dr. Marquet's assessment. No animal or human data supports the nephrotoxic activity of tungsten. Nephrotoxicity as well as neurotoxicity has, however been associated with some nitroaromatics used as a propellants for large caliber artillery rounds and could explain, in part, some of the effects noted in this particular soldier. This argument was refuted by Dr. Marquett (*The Lancet*, Jan., 1997).

Some neurotoxic effects have been associated with the use of tungsten. Tungsten metal has been used as a research tool to produce epilepsy in cats. A 0.02 ml gel placed on the surface of the cortex produced abnormal electroencephalogram (EEG) activity within 20 to 30 minutes which eventually produced ictal (acute epileptic seizures) activity. This system is used currently to model epilepsy. An evaluation of memory deficits was conducted in 12 former hard metal workers who had been exposed primarily to tungsten carbide and cobalt. These workers obtained lower verbal memory index scores and had lower attention span than did non-exposed workers. Their visual-spatial memory was unaffected. The contribution of cobalt to these memory defecits is unknown.

X. Environmental Effects of Tungsten

Tungsten has few noticable effects on plants. According to one study, tungsten inhibited trace metal uptake in plants. Studies on tungsten uptake by bean plants were conducted at Oak Ridge National Laboratory. These studies indicated that bean plants are capable of accumulating tungsten from the soil. The uptake of tungsten powder was greater than that for tungsten trioxide. This phenomenon may be due more to particle size than to chemical properties of the materials

Tungsten has been found to be a suitable replacement for lead and steel shot for waterfowl hunting. Embedded tungsten/bismuth/tin shot, as compared to steel resisted corrosion and induced comparatively mild inflammatory responses in mallard muscle tissue according to Krabbel and his colleagues at the Colorado Division of Wildlife.

A study was conducted for the U.S. Army to determine the effect of soil type (dry vrs. moist) on deposition concentration of tungsten. The authors concluded that in dry soil, the concentration would not be greatly reduced in 100 years while a substantial reduction would occur in moist soil. Studies are currently being conducted at Oak Ridge National Laboratories to determine mobility and corrosion of tungsten under various conditions (Louden, 1998). This information will add to the existing database on environmental fate of tungsten.

The EPA does not list tungsten as an environmental contaminant and no studies have indicated that it is environmentally unsafe. There is some concern on the effect of tungsten on the spectacled eider and, for that reason, tungsten shot is not currently allowed in the Yukon-Kuskokwim Delta region of Alaska. Toxicity testing is in progress that will determine tungsten's effect on this bird.

XI. Environmental Assessments Involving Tungsten

Environmental assessments have been conducted at two sites where tungsten was thought to be a problem. An environmental assessment, which focused on tungsten, was conducted at the Kerr Reservoir. Although lead was found at unacceptable levels, tungsten was not found at levels high enough to be considered problematic. The Li Tungsten Corporation site in Glen Cove, NY was placed on the National Priority List (NPL) in 1992. Tungsten was not found at levels that were of concern to the U.S. Environmental Protection Agency (EPA). The Li Tungsten site was placed on the NPL due to the presence of several other materials such as arsenic, cadmium, chromium, lead, and mercury.

XII. Data Gaps

Although there are a vast number of papers exist on tungsten and its alloys in the medical literature, no papers were found that specifically examine tungsten/tin or tungsten/nylon, the materials selected for the small caliber rounds. It is unlikely that these alloys would be any more insidious than tungsten metal, its oxides or its acids.

It is unknown if the tungstate ion is formed from firing tungsten bullets, although this is unlikely, due to the chemical properties of tungsten metal and its low reactivity at low temperatures. If this ion is formed, further assessment will have to be performed in order to determine the amount of ion formed and potential exposure.

XIV. Conclusions

Exposure to tungsten dust is highly probable in both manufacturing and, to a far less extent, firing of small caliber munitions. The most likely route of exposure is through the respiratory system followed by dermal contact and ingestion. Once in the body, tungsten is, for the most part, rapidly eliminated by the urinary system. The small fraction remaining is incorporated primarily in bone, lung, and kidney from which it is released at a slower rate. The application of appropriate engineering methodologies and the use of personal protective equipment will significantly reduce exposure to tungsten aerosols.

The effects of insoluble tungsten on biological systems are minimal. It displays some systemic toxicity in that it can inhibit the activity of some molybdenum-containing enzymes. This capability has led to tungsten's use in the treatment of paraquat toxicity and ischemia-reperfusion injury induced from organ transplants. Although insoluble tungsten has not been identified as being mutagenic or carcinogenic, it may contribute to clastogenic damage of DNA by causing partial uncoiling of chromatin. Tungsten is a mechanical irritant when inhaled and produces a generalized response by the body to foreign material. This effect, whether produced by tungsten or some other compound, presents some cause for concern. Although adverse reproductive effects have been noted for sodium tungstate, there is no information on the adverse reproductive effects of tungsten metal or insoluble forms of tungsten.

The acceptance of tungsten as a replacement for lead is indicated by recent policy decisions of the U.S. Fish and Wildlife Service and the U.S. Environmental Protection Agency. These decisions are based on the relative safety of tungsten as an environmental toxicant when compared to lead. Increased use of tungsten products by the public is indicated by a wider range and increased sales of tungsten products.

Based on the evaluation of the available data, there appears to be minimal risk associated with the use of tungsten bullets. On a comparative basis, tungsten is far less toxic to humans and the environment than the copper/lead currently used.

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APPENDIX II:
SOLUBILITY OF SELECTED TUNGSTEN COMPOUNDS

Adapted from NIOSH Publication No. 77-127, *Criteria for a Recommended Standard. Occupational Exposure to Tungsten and Cemented Tungsten Carbide*, September 1977.

Compound Name	Chemical Formula	Solubility (g/100cc H_2O) *
Ammonium metatungstate	$(NH_4)_6H_2W_{12}O_{40}$	Soluble
Ammonium paratungstate	$(NH_4)_{10}(H_{10}W_{12}O_{46})$	Insoluble
Ammonium phosphotungstate	$(NH_4)_3P(W_3O_{10})_4$	Soluble
Cadmium tungstate	$CdWO_4$	0.05
Calcium tungstate	$CaWO_4$	0.00064 @ 15ºC 0.00323 @ 25ºC
Calcium tungstate (Sheelite)	$CaWO_4$	0.013 @ 20ºC 0.0002 @ 90ºC
Calcium metatungstate	$Ca_3H_4[H_2(W_2O_7)_6]\cdot{}_{27}H_2O$	Decomposes in acid
Cerium (III) tungstate	$Ce_2(WO_4)_3$	-
Cesium tungstate	$CsWO_4$	85.6 @ 17ºC
Cobalt tungstate	$CoWO_4$	Insoluble
Copper (III) tungstate	$CuWO_4\cdot{}_4H_2O$	0.1 @ 15ºC
Cyclopentadienylbitungsten Hexacarbonyl	$(C_5H_5)_2W_2(CO)_6$	-
Iron (II) tungstate	$FeWO_4$	-
Lead tungstate	$PbWO_4$	0.00159 @ 25ºC
Lithium tungstate	Li_2WO_4	Very soluble
Magnesium tungstate	$MgWO_4$	Insoluble
Mercury (I) tungstate	Hg_2WO_4	Insoluble
Mercury (II) tungstate	$HgWO_4$	Insoluble
Mesitylene-tungsten tricarbonyl	$(CH_3)_3C_6H_3W(CO)_3$	-
Metatungstic acid	$H_2W_4O_{13}\cdot 9H_2O$	88.57 @ 22ºC
Phosphotungstic acid	$H_3[P(W_3O_{10})_4]\cdot 14H_2O$	Soluble
Phosphotungstic acid	$H_3[P(W_3O_{10})_4]\cdot 24H_2O$	Soluble
Potassium tungstate	$K_2WO_4\cdot 2H_2O$	51.5
Potassium metatungstate	$K_6(H_2W_{12}O_{40})\cdot 18H_2O$	Soluble
Silicotungstic acid	$H_8SiW_{12}O_{42}$	961.5 @ 18ºC
Silver tungstate	Ag_2WO_4	0.05 @ 15ºC
Sodium tungstate	Na_2WO_4	57.5 @ 0ºC 73.2 @ 21ºC
Sodium tungstate, dihydrate	$Na_2WO_4\cdot 2H_2O$	41.0 @ 0ºC
Sodium metatungstate	$Na_2O\cdot WO_2\cdot 10H_2O$	Soluble
Sodium paratungstate	$Na_6W_7O_{24}\cdot 16H_2O$	8
Strontium tungstate	$SrWO_4$	0.14 @ 15ºC
Tungsten (Wolfram)	**W**	**Insoluble**

* insoluble compounds have a water solubility of less than 0.01g/100cc

SOLUBILITY OF SELECTED TUNGSTEN COMPOUNDS

Adapted from NIOSH Publication No. 77-127, *Criteria for a Recommended Standard. Occupational Exposure to Tungsten and Cemented Tungsten Carbide*, September 1977.

Compound Name	**Chemical Formula**	**Solubility (g/100cc H2O)***
Tungsten arsenide	WAs_2	Insoluble
Tungsten diboride	WB_2	Insoluble
Tungsten dibromide	WBr_2	Decomposes
Tungsten pentabromide	WBr_5	Decomposes
Tungsten hexabromide	WBr_6	Insoluble
Tungsten carbide	WC	Insoluble
Tungsten dicarbide	WC_2	Insoluble
Tungsten carbonyl	$W(CO)_6$	Insoluble
Tungsten dichloride	WCl_2	-
Tungsten tetrachloride	WCl_4	-
Tungsten pentachloride	WCl_5	-
Tungsten hexachloride	WCl_6	Decomposes
Tungsten hexafluoride	WF_6	Decomposes
Tungsten diiodide	WI_2	Insoluble
Tungsten tetraiodide	WI_4	Insoluble
Tungsten dinitride	WN_2	Decomposes
Tungsten dioxide	WO_2	Insoluble
Tungsten trioxide (Wolframite)	WO_3	Insoluble
Tungsten pentoxide	W_2O_5 or W_4O_{11}	Insoluble
Tungsten dioxydibromide	WO_2Br_2	-
Tungsten oxytetrabromide	$WOBr_4$	Decomposes
Tungsten oxytetrachloride	$WOCl_4$	Decomposes
Tungsten dioxydichloride	WO_2Cl_2	Soluble
Tungsten oxytetrafluoride	WOF_4	Decomposes
Tungsten phosphide	WP	Insoluble
Tungsten phosphide	WP_2	Insoluble
Tungsten phosphide	W_2P	-
Tungsten silicide	Wsi_2	Insoluble
Tungsten disulfide (Tungstenite)	WS_2	Insoluble
12-Tungstophosphoric acid	$P_2O_5{\cdot}24WO_3{\cdot}45H_2O$	86.75 @ 92ºC

* insoluble compounds have a water solubility of less than 0.01g/100cc