Tungsten: Occurrence, Chemistry, Environmental and Health Exposure Issues

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Abstract: Tungsten also called wolfram is a steel gray to tin-white metal with a high melting point and good electrical conductivity. Tungsten occurs both naturally and can be manufactured commercially. Because of its unique physical and chemical properties tungsten has been used extensively both in industry and other electrical and high temperature application. The production and massive applications of tungsten are also of environmental and health concerns. This paper reviews the historical occurrence of tungsten, the unique physical and chemical properties and environmental fate and health exposure issues of tungsten.

Key words: Tungsten, toxicology, environment, health, contamination

INTRODUCTION

Tungsten occurs as Wolframite (FeWO₄). This wolframite occurs in close association with cassiterite (Tin Ore) in the greisens and quartz veins found in younger Granite complexes of Nigeria [1]. Although, it is widespread, only a few payable deposits of the mineral have been found. Wolframite mineralization is sporadic and becomes economic only when it carries substantial cassiterite. It does not survive in the alluvial environment hence its production depends mainly on the primary source in the biotite granite. Only a systematic exploration of the biotite granite phases of the younger granites can reveal more deposits. Unfortunately, such an exercise has ceased for a long time for many reasons [1]. Not the least among them is the lack of exploration funds and of entrepreneurship in the private sector and the parastatals charged with the responsibility of mineral development.

Moreso, it occurs in scheelite, huebuerite and ferberite. Its important deposits occur in California, Colorado, South Korea, Bolivia, Russia and Portugal. China is reported to have about 75% of the world's tungsten resources [2]. Natural tungsten contains five stable isotopes, twenty one other unstable isotopes are recognized. The metal is obtained commercially by reducing tungsten oxide with hydrogen or carbon [3]. It has some physical and chemical properties which makes the element unique.

Properties of tungsten: Pure tungsten as it is called by Swedish, “heavy stone”, is a steel-gray to tin-white metal. It can be cut with a hacksaw, forged, spun, drawn and extruded. The impure metal is brittle and can be worked only with difficulty. Tungsten has the highest melting point (3410°C - 3422°C), of all metals and at temperatures over 1650°C has the highest tensile strength. The metal oxidizes in air and must be protected at elevated temperatures. It has excellent corrosion resistance and is attacked only slightly by most mineral acids. The thermal expansion is about the same as borosilicate glass, which makes the metal useful for glass – to – metal seals [3].

At ordinary temperature, tungsten is stable in dry air. At red heat, tungsten forms trioxide. At room temperature, it is attacked by fluorine; at 250°C - 300°C, it is attacked by chlorine, producing hexachloride in the absence of air and trioxide and oxychloride in the presence of air. Tungsten is oxidized to dioxide by steam but is very stable to acids [4]. It strongly reacts with bromine trifluoride and chlorine trifluoride with fluorine, the reaction may be luminescent. Sodium tungstate effloresces in dry air and loses its water at 100°C. As an aqueous solution, it is slightly alkaline (pH, 8-9). When heated to decomposition, it emits toxic fumes of sodium oxide [5]. Tungsten trioxide reacts violently with chlorofluorine, lithium and chlorine. With chlorine trifluoride, incandescence occurs.

PRODUCTION OF TUNGSTEN

Tungsten is produced commercially by the reduction of tungsten trioxide with hydrogen or carbon. It can also be prepared by the aluminothermic reduction of tungsten.
trioxide, the hydrogen reduction of tungstic acid or its anhydride, or by the hydrogenation of tungsten trioxide or ammonium paratungstate [5]. Large single crystals are grown by the fusion process and granules are obtained by the reduction of tungsten hexafluoride. Through the recycling of cemented carbide scrap, tungsten can be converted to the intermediate product ammonium paratungstate, which is then used to produce tungsten carbide powder, tungsten chemicals or metal powder [6].

Sodium tungstate is prepared by the reaction of a mixture of soft and hard tungsten carbide with a mixture of sodium nitrate and sodium hydroxide in a fusion process. The dihydrate can be obtained by dissolving tungsten trioxide or the ground ore in sodium hydroxide. Tungsten trioxide can also be prepared from sodium tungstate. It can also be produced by the treatment of scheelite ore with hydrochloric acid, yielding ammonium tungstate, which is then ignited to obtain the desired compound. The reaction of tungsten ore concentrates with sodium carbonate gives ammonium paratungstate which is used to produce tungsten trioxide [6].

CHEMICAL ANALYSIS OF TUNGSTEN

In air, tungsten can be determined by flame atomic Absorption (FAA), inductively coupled plasma atomic emission spectrometry (ICP – AES) and Atomic Absorption spectroscopy (AAS). In water and air, trace concentrations of tungsten can be estimated by instrumental neutron activation analysis (NAA), using automatic r – ray spectroscopy [5]. In biological samples, trace amounts of tungsten in the presence of molybdenum can quantitatively be determined using a spectrophotometric method. In urine, tungsten has been determined using inductively coupled plasma – mass spectrometry (ICP – MS).

Tungsten is available commercially in technical powder, single crystal and ultrapure granule grades. Current U.S suppliers include; Alfa Aesar/ Johnson matthey; Atlantic Equipment Engineers, Division micron metals inc; Atomergic Chemetals Corporation [5], etc.

USES OF TUNGSTEN

Tungsten is used to increase the hardness, toughness, elasticity and tensile strength of steel. It is used in the manufacture of alloys, in light filaments, in x-ray and electron tubes, in phonograph needles and in contact points for vehicles, telegraph, radio and television equipments [7]. Other applications include its use in glass to metal seals, metal evaporative work, windings and heating elements, ferrous and non ferrous alloys (example, high speed tool steel), molding electrodes, rocket nozzles and other aerospace applications, shell steel, chemical apparatuses, high speed rotor (example, gyroscopes), solar energy devices and plating material. Tungsten in also used to prepare green and blue pigments and to make cellulose non flammable. A more recent use for tungsten [6], is as a substitute for lead in military and recreational ammunition and in products of the sporting goods industry such as golf clubs.

Sodium tungstate is used for fire and water proofing fabrics, in the preparation of complex compounds (example phosphotungstate and silicon tungstate), as a reagent for biological products and as a precipitant for alkaloids. It is also used as a catalyst in the oxidation of maleic acid [7]. Tungsten trioxide is used as pigments in ceramics and as colour resistant mordents for textiles and fireproofing fabrics. It is used to form metals by reduction in alloys and in x-ray screens. With iron (iron: tungsten ratio 1:0.005-0.8), it can reduce nitrogen oxides in exhausts or industrial waste gases [7].

Tungsten carbide is of great importance to the metal working, mining and petroleum industries. Calcium and magnesium tungstate are widely used in fluorescent lighting. Other salts of tungsten are used in the chemical and tanning industries. Tungsten disulphide is a dry, high temperature lubricant, stable to 500°C. Tungsten bronzes and other tungsten compound are used in paints; its powder is very expensive [4].

ENVIRONMENTAL OCCURRENCE AND PERSISTENCE OF TUNGSTEN

Tungsten is one of the rare metals, comprising only about 1.5 ppm of the earths crust. It occurs naturally as tungstate (WO$_4^{2-}$). The production and use of tungsten compounds (example, as catalyst and dyes) may result in the release of tungsten to the environment through waste streams. Very small amounts of tungsten (<1.5 ng/m$^3$ [0.20 ppt]), primarily as tungsten trioxide have been released into the atmosphere from industrial emission and nuclear fallout [8]. If released to the air, most tungsten compounds will exist exclusively in the particulate phase in the ambient atmosphere because of their low vapour pressures and can be removed by wet and dry deposition. In urban and sub-urban areas, the measured air concentrations of tungsten were, (<1.5 µg/m$^3$ [0.20ppb]). If released to soil, its compounds will have moderate to low mobility based upon sorption coefficients ranging
from 10 to 50,000 at pH 5 to 6.5 [7]. Expected to exist as ions or insoluble solids in the environment, volatilization from moist soil surfaces is not an important fate process. Further more, the compounds are not expected to volatilize from dry soil surfaces because of their ionic character and low vapour pressures [7]. In surface soils, tungsten concentrations ranged from 0.68 to 2.7 mg/kg [3.7 to 15 mmol/kg]. In plant, levels ranging from, 0.001 to 100 mg/kg [5.4 to 544 nmol/kg] dry weight were reported [8]. If released into water, tungsten compounds will adsorb to suspended solids and sediments. As in soil, volatilization from water surfaces is not an important fate process.

Certain regulatory standards have been set for tungsten and tungsten compounds. The American Conference of Governmental industrial Hygienists (ACGH) threshold limit values are 5mg/m³ [0.7 ppm] as an eight hour time weighted average (TWA) and 10 mg/m³ [1.3 ppm] as a 15 minute short term exposure limit (STEL) for tungsten metal and for insoluble compounds as tungsten. For soluble compounds, as tungsten, the values are 1 and 3 mg/m³ [0.1 and 0.4 ppm], respectively. The National Institute for Occupational safety and Health (NIOSH) recommended exposure limit (REL) (reported as ten-hour TWAS) 5 mg/m³ [0.7ppm] for tungsten and 1 mg/m³ [0.1ppm] for soluble compounds as tungsten. The 15-minute STEL is 3 mg/m³ [0.4 ppm] for soluble compounds as tungsten.

**HUMAN EXPOSURE TO TUNGSTEN**

Occupational exposure to tungsten and its compounds is possible through inhalation of dusts and dermal contact during production and use of tungsten containing compounds. In the manufacture of the metal, harmful exposures to related metals in the ore have been mainly due to arsenic, antimony, bismuth, copper, lead, manganese, molybdenum and tin [8]. Although tungsten electrodes are widely used in welding, tungsten is generally not considered in the workers exposure to heavy metals [7].

For the general population, exposure to tungsten is possible from ingestion of products containing tungsten or its compounds. For examples, beverages such as wine, mineral water, beer, brewed tea and instant coffee were found to significantly contribute to the total dietary intake of tungsten [9]. In healthy subjects, serum tungsten concentration were 6.0 µg/L in 14 unexposed persons [9], the mean tungsten level in urine was 0.21 µg/L. The geometric mean of urine concentrations for the United States population (in 2338 persons > 6 years old), was 0.085 µg/l (95% confidence interval: 0.077-0.093) [9].

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**HEALTH EFFECTS OF TUNGSTEN**

Tungsten has been shown to act by antagonizing the action of the essential trace element molybdenum. Tungsten metal powder administered to animals has been shown in several studies as not altogether inert. It was found that guinea pigs treated orally or intravenously with tungsten suffered from anorexia, colic incoordination of movement, trembling, dyspnea and weight loss [8, 9].

Tungsten is irritating to the skin and eyes on contact. Its inhalation will cause irritation to the lungs and mucus membrane. Irritation to the eyes will cause watering and redness. Reddening, scaling and itching are characteristics of skin inflammation. All these are acute health effects. Safe industrial hygiene practices and wearing protective equipment are advised when handling this element and its compounds. Apparently, there is no chronic effects on exposure to tungsten. Prolonged exposure to this compound is not known to aggravate medical conditions [9]. All tungsten compounds should be regarded as highly toxic [4]. The metal dust presents a fire and explosion hazard.

**CHEMICAL DEPOSITION, METABOLISM AND TOXICOKINETICS**

**Absorption:** When rats were orally administered diets containing tungsten as finely ground metal, sodium tungstate, tungsten trioxide, or ammonium paratungstate, for 100 days, tungsten mainly accumulated in bone and in spleen; trace quantities (<1.0 mg/L) were found in the kidney, liver, blood lung, muscle and testes. When beagle dogs were exposed to radioactive tungsten trioxide (181W) mist (98 mci/ml, specific activity for six hours) by inhalation, 60% of the inhaled activity was rapidly deposited in the respiratory tract. During the first ten days, about 33% of the deposited activity entered the systemic circulation [9]. The remaining activity was cleared from the lungs via the ciliary escalatory system.
In the lungs, 69% of the activity was lost with a biological half life (BHL) of 4 hours. When given a weak acidic aqueous solution of tungsten trioxide absorption was 25% in the animals.

In dogs and rats orally administered a solution of sodium tungstate (25 or 50 mg/kg [0.085 or 0.17 mmol/kg]), absorption of tungsten occurred between one and two hours. In beagle dogs, uptake of tungsten was from 54-74%. As in dogs, absorption in rats was 40 – 92% when tungsten was administered as tungstate and only 1% when administered as tungstic acid.

**Distribution and retention:** *In vivo* experiments using various species, routes of administrations and compounds showed that a majority of the administered tungsten is rapidly removed from blood. Injection, inhalation or ingestion of tungsten generally produced higher tungsten levels in the liver compared to other body tissues, which may be explained by the ability of tungsten to replace molybdenum in certain liver enzymes. The other soft tissues, which accumulates a significant amount of deposited tungsten immediately after entering the blood, eliminate it within a few hours.

When male and female pregnant mice were injected with $^{185}$W – tungstate, an increase in tungsten levels was found in the skeleton, kidneys, liver and spleen; tungsten was then rapidly excreted in urine and feces [10]. Transfer of tungsten from mother to foetus, particularly in late gestation, was also observed. Significant retention of the compound was found in the maternal skeleton, kidneys and spleen and in the visceral yolk sac epithelium and skeleton of the foetus [8].

In guinea pigs, oral administration or injection of sodium tungstate produced anorexia, colic, confusion, tremors and dyspnea. When applied directly to the corneal stroma of rabbits, it produced toxic effects in the pH range of 7 to 9 [10]. When there is intake of the affected food, convulsion, hypermotility and diarrhea in the rabbits results. Injection and oral administration of tungstate is rapidly eliminated through urine or feces; the former appears to be the major excretion pathway. In rats and dogs, 80-98% is excreted within 24 hours after administration [11].

The injection of tungsten in rat causes regional or vascular dilation, liver damage (not otherwise specified) and blood changes. White rats given a single intracheal dose of metallic tungsten (50 mg [0.27 mmol) and sacrificed four, six or eight months later exhibited a proliferative reaction of the lymphoid and mild fibrosis. In guinea pigs receiving an intrarenous suspension of tungsten metal dust (150 mg [0.816 mmol]) as three equal doses and observed for up to one year, focal interstitial pneumonics and bronchiolitis, focal interstitial infiltration, atrophic emphysema, peribronchial and periarterial fibrocellular reaction and endarteritis obliteration were observed. When applied to the skin and eyes of rabbits for 24 hours tungsten (500mg [2.72 mmol] was a mild irritant.

**Short term and subchronic exposure**

**Tungsten:** In weanling rats fed tungsten metal powder at concentrations of 2.5 and 10% of the diet for 70 days, no effect on the growth rate was observed in male rats. In females, however, a 15% reduction in weight gain was reported.

Sodium tungstate (equivalent to 2% tungsten) orally administered to young rats caused the deaths of all animals within ten days. When diets were reduced to contain an equivalent of 0.5% tungsten, death occurred in 75% of rats by the end of the 70 days exposure period. When given by garage or in drinking water to young rats sodium tungstate (15-100 mg/kg 0.051-3.403 mmol/kg per day) for four or 13 weeks produced emesis, anorexia, cachexia pallor and dyspnea. At the high dose, level of urea, creatinin and cholesterol were increased, while erythrocyte count and glucose, (AST/ALT), protein, hematocrit and hemoglobin levels were decreased: all parameters returned to normal after a recovery period of six weeks.

**Synergistic/antagonistic effects:** In mammals, tungsten has been found capable of serving as a substitute for molybdenum in enzymes. In studies with rats, chickens, goats and cows, tungsten was an antagonist toward molybdenum. It decreased sulphite and xanthine oxidase activities and hepatic molybdenum levels. Its ability to activate brain glutaminase and inactivate liver glutaminase shows that it can act at more than one enzyme site. Tungstate, like molybdate, can also replace phosphate in bones. At 5 ppm [0.02 mmol/kg], it can reduce the toxic effects of selenium [11]. Small doses of the metals tungsten, molybdenum, nickel, lead and copper in drinking water can cause nonspecific changes in metabolic processes. When rats were given tungsten in drinking water at an effective dose (ED) for six months, molybdenum and copper decreased in bone tissues and kidneys; at a threshold dose (T.D) both elements increased in bone tissue. With molybdenum at effective dose, tungsten decreased in the liver, kidney and blood [12].
Genotoxicity: In *Saccharomyces cerevisiae*, sodium tungstate (100 mM/L [25.4 mg/ml]) produced gene conversion, mitotic recombination and sex chromosome loss and non-disjunction. In *Escherichia coli*, the compound 5 mmol/L [1 mg/ml] caused phage inhibition capacity. In Syrian hamster embryo cells, sodium tungstate did not induce morphological transformation, sister chromatid exchange (SCE) or chromosomes aberration (CA); the latter two were also not seen in human lymphocytes.

In *Saccharomyces cerevisiae* sodium, tungstate dehydrate (dose(s) not provided) induced disomic and diploid meiotic products. In a test for SCE in human lymphocytes, no conclusion could be made regarding its mutagenicity.

Tungsten alloys used in military projectiles were genotoxic in SCE, micronuclei and alkaline filter elution assays. Like depleted uranium (DU) compounds, they are neoplastic transforming agents but at a lower frequency suggesting a possible relationship between long-term exposure and the development of neoplastic disease [12].

Sodium tungstate may be useful in the treatment of diet induced obesity. When diet induced obese wistar rats were given sodium tungstate (2 g/l [7 mM]) in the rinking water for 32 days, body weight gain was significantly decreased, as was triglyceride, free fatty acid and insulin plasma levels. No toxic effects were observed. The animals quickly gained body weight during a recovery period of 35 days.

CHEMICAL DEPOSITION, METABOLISM AND TOXICOGENICITY IN HUMANS

The daily dietary intake of tungsten is about 0.01 mg (0.05 µmol) while the median intake for daily urinary excretion is 0.007 mg (0.40 µmol ). Tungsten (vi) is well absorbed. About 75% of the amount ingested is excreted in the urine. In a limited study with no specific exposure, four healthy young adults eliminated trace quantities of tungsten in urine [13]. In a limited study with no specific exposure, four healthy young adults eliminated trace quantities of tungsten in urine (2.0-13.0 µg [0.01-0.07 µmol]) and feces (1.6-5.7 µg [8.7-31 µmol]) over 24 hours periods [8].

Toxicity: No data on occupational exposure to tungsten compounds implicate them as toxic or hazardous. In a powder metallurgy operations plant using tungsten metal, workers’ chronically exposed to air concentration of 5 mg/m³ [0.7 ppm] tungsten developed to pneumoconiosis. Tungsten poisoning however, has occurred after continued exposure to dusts and vapours during the refining of tungsten. One case of tungsten poisoning has been reported after the accidental ingestion [8] of tungsten. A 19 year old man who drank 250 ml of a mixture of beer and wine that he had rinsed in a hot gun barrel experienced nausea, followed by seizures and then became comatose for 24 hours, showing signs of encephalopathy. Moderate renal failure became an extensive tubular necrosis with anuria by day two. High concentration of tungsten were found in the drink (1540 mg/l [8.376 mM), gastric content content (8 mg/l, [44µµM]), blood (5 mg/l [27 µm]) and urine (101 mg/l [549 µm]). The high levels in blood (>0.005 mg/l [0.03 µm]) were observed until day 13 despite six hemodialyses and in urine until day 33. Hair and nails also contained tungsten. The individual fully recovered after five months [8].

Carcinogenicity: Lung cancer mortality in tungsten metal miners has been associated with silicosis. A more recent study, however, found to the dust-exposed level, while the rate was not in proportion with the stage of silicosis. The result therefore, did not support the etiological relationship between silicosis and lung cancer.

Elemental tungsten is basically insoluble and as a result is considered to be of low toxicity soluble compounds are more toxic than insoluble forms.

CONCLUSIONS

Tungsten in its elemental form have not been implicated in health and risk assessment issues in humans and the environment. Few toxicological studies have been conducted on tungsten and tungsten compounds. While epidemiological surveys and other studies have been conducted on tungsten carbide, which usually contains cobalt in elemental form, the majority of the toxicological data included in this report are studies with tungsten metal powder, sodium tungsten and tungsten trioxide. Limited data for tungsten hexachloride, the ammonium salt of tungsto antimonic acid and anitmono tungstate exists.

Tungsten, especially tungsten vapor and tungsten compounds have been known to cause more acute health effects then chronic health effects. Thus, exposures to tungsten and its compounds to values exceeding the minimum exposure limits should strongly be avoided.
REFERENCES


