

5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

5.1 PRODUCTION

Mining of tungsten is almost exclusively by underground methods. Since the tungsten content of typical deposits is only 0.3–1.5% WO_3 , all mines have beneficiation facilities that produce a concentrate containing 60–75% WO_3 . During the beneficiation process, the ores are crushed and ground in stages with the fine fractions being removed after each stage and the coarse fraction being recirculated. Because tungsten minerals have a high specific gravity, they can be beneficiated by gravity separation, usually by tabling. The ore concentrate may first be pretreated by acid leaching with hydrochloric acid or roasting with soda ash in an autoclave with a solution of aqueous sodium carbonate at ca. 200 °C and a pressure of >11.9 atm. This is followed by digestion to extract the tungsten as sodium tungstate. This compound is subsequently converted to ammonium tungstate by means of a liquid ion-exchange process. The solvent is then evaporated and tungsten is converted to crystalline ammonium paratungstate (APT, $[\text{NH}_4]_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot 4\text{H}_2\text{O}$). Tungsten metal powder is obtained from ammonium paratungstate by stepwise reduction with carbon or hydrogen. The reduction is carried out in either tube or rotary furnaces. Tungsten carbide is produced by heating tungsten metal powder and carbon black at high temperatures. The presence of hydrogen or a hydrocarbon gas catalyzes the reaction. Tungsten carbide may also be prepared from oxygen containing tungsten compounds. Tungsten hexachloride is prepared by the direct chlorination of pure tungsten metal in a flow system at 1 atmosphere and 600 °C. Tungsten hexafluoride may be prepared by treating hydrogen fluoride, arsenic trifluoride, or antimony pentafluoride or by direct fluorination of tungsten metal powder. Tungsten hexacarbonyl may be prepared by the aluminum reduction of tungsten hexachloride in anhydrous ether under a pressure of ca. 1 atm of carbon monoxide at 70 °C. Tungsten trioxide is usually prepared from tungstic acid or tungstates (Penrice 1997a, 1997b). Ferrotungsten is produced by carbothermic reduction in an electric arc furnace or by metallothermic reduction with silicon and/or aluminum (Lassner et al. 1996).

No tungsten was reported to have been mined in the United States in 2001. World production of tungsten concentrates was 44,200 metric tons in 2001. The primary world producer of tungsten concentrates is China, which produced 37,000 metric tons in 2001. The U.S. supply of raw tungsten is comprised of imports, tungsten-bearing scrap, releases from industrial stocks, and sales of excess materials from the National Defense Stockpile. Major processors of tungsten materials operating in 2001 included (USGS 2001): Allegheny Technologies Inc.'s Metalworking Products business (Huntsville, Alabama); Buffalo

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Tungsten, Inc. (Depew, New York); General Electric Co. (Euclid, Ohio); Kennametal, Inc. (Latrobe, Pennsylvania; Fallon, Nevada); OM Group, Inc. (Midland, Michigan; St. George, Utah); and Osram Sylvania, Inc. (Towanda, Pennsylvania).

Producers of tungsten compounds in the United States in 2002 are as follows (SRI 2002): Tungsten carbide: Alldyne Powder Technologies (Huntsville, Alabama); Dow Chemical U.S.A. (Midland, Michigan; Traverse City, Michigan); Geoliquids, Inc. (Prospect Heights, Illinois); OMG Apex (St. George, Utah); and Osram Sylvania, Inc. (Towanda, Pennsylvania). Tungsten trioxide: Johnson Matthey, Inc. (Ward Hill, Massachusetts); and Osram Sylvania, Inc. (Towanda, Pennsylvania). Tungsten hexafluoride: Air Products and Chemicals (Hometown, Pennsylvania) and Ozark Fluorine Specialties (Tulsa, Oklahoma). Tungsten carbonyl: Strem Chemicals, Inc. (Newburyport, Massachusetts). Tungsten hexachloride: Osram Sylvania, Inc. (Towanda, Pennsylvania).

Since tungsten and tungsten compounds are not covered under Superfund Amendments and Reauthorization Act (SARA), Title III, manufacturers and users are not required to report releases to the EPA's Toxics Release Inventory.

5.2 IMPORT/EXPORT

In 2002 approximately 10,900 metric tons of tungsten concentrates and other forms were imported into the United States amounting to approximately 25% of world production. The largest amounts of tungsten-bearing materials imported for consumption into the United States were from China (e.g., 1,965 metric tons in 2001). Tungsten concentrates and other forms imported for consumption were 13,240, 11,100, 10,180, and 10,830 metric tons for the years 1998, 1999, 2000, and 2001, respectively (USGS 2001, 2003).

In 2002, approximately 3,590 metric tons of tungsten concentrates and other forms were exported from the United States. Exports of tungsten concentrates and other forms were 3,650, 2,886, 2,870, and 5,080 metric tons for the years 1998, 1999, 2000, and 2001, respectively (USGS 2003).

5.3 USE

Tungsten is consumed in the form of tungsten carbide (65%), alloy additives (16%), metallic tungsten (16%), and tungsten chemicals (3%). Tungsten carbide, because of its high hardness at high temperature,

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is used as a component of cutting tools, abrasion-resistant surfaces, and forming tools. It is used primarily in the form of cemented carbides, which are used for cutting tools, mining and drilling tools, forming and drawing dies, bearings, valve seats, and several other wear-resistant applications. As an alloy additive, tungsten metal imparts high-temperature strength and wear resistance in steel, nickel, and cobalt-based super-alloys. Metallic tungsten is used as welding electrodes (e.g., thoriated tungsten); in the manufacture of lamp filaments; as an electron emitter; in x-ray and electron tubes; as furnace elements; as heat shields; as vacuum metalizing coils and boats; in glass melting equipment; and as arc-lamp electrodes; in contact points (for vehicle, telegraph, radio, and television equipment), in rocket nozzles and other aerospace applications, and in high-speed rotors (e.g., gyroscopes). It is also used in high-speed impact printers, in glass-to-metal seals, and as a base for silicon semiconductors (O'Neil et al. 2001; Penrice 1997a, 1997b). An increasing use is in military weaponry, in which tungsten alloys are used as an alternate to depleted uranium for armor penetration and tungsten is replacing lead in "green" bullets. Currently, 200 million tungsten bullets are produced annually, using an ounce of tungsten each (>5,500 tons) (ITIA, 2001). Tungsten chemicals, especially the oxides, sulfides, and heteropoly complexes, form stable catalysts for a variety of commercial chemical processes. Tungsten hexachloride is used for preparing tungsten metathesis catalysts and metallic tungsten films. Sodium tungstate is used in the manufacture of heteropolyacid color lakes used in printing inks, plants, waxes, glasses, and textiles and as a fuel-cell electrode material, and in cigarette filters. Other uses of sodium tungstate include the manufacture of tungsten-based catalysts and for fireproofing textiles. Ammonium paratungstate is commercially significant because it is the precursor of high purity tungsten oxides, tungsten, and tungsten carbide powders. Tungsten trioxide is a principal source of tungsten metal and tungsten carbide powders. It is also used as a pigment in oil and water colors, in a wide variety of catalysts, and in the control of air pollution and industrial hygiene (O'Neil et al. 2001; Penrice 1997a, 1997b). Tungsten hexafluoride is used by the electronics industry as a source of tungsten metal that connects the aluminum layers within semiconductor devices (USGS 2001). Ferrotungsten is primarily used as an alloying material in the steel industry (Lassner et al. 1996).

5.4 DISPOSAL

A significant percentage of tungsten is recycled. During the year 2002, the tungsten content of scrap consumed by processors and end-users was estimated at 4,500 metric tons. This represented approximately 35% of apparent U.S. consumption of tungsten in all forms (USGS 2001).

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Most tungsten minerals, tungsten compounds, and tungsten-containing materials do not require special disposal and handling requirements. However, some chemical forms may be classified as hazardous materials if the compound is chemically reactive, flammable, or toxic. Care should be taken to read and understand all of the hazards, precautions, and safety procedures for each specific chemical form. In addition, all federal, state, and local laws and regulations should be investigated and subsequently followed with regard to disposal and handling of the specific chemical form of the tungsten compound or material.