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Outlook for Tungsten

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Abstract

Tungsten is a very unusual metal element that is useful in many applications. Its material properties make it ideal as an alloy component, which makes tungsten a technology industrial metal.

Tungsten has been classified as a Critical Raw Material by the European Commission.

Scheelite and wolframite are the only tungsten minerals mined commercially and are mainly found in five types of deposits: skarn, vein/sheeted vein/stockwork, porphyry, disseminated and stratabound.

Tungsten ore can be complex, which can result in challenging beneficiation results. Due to the brittle character of both scheelite and wolframite, comminution is carefully designed to avoid overgrinding, that is, to minimize formation of fines. Rod milling of scheelite has some advantages to ball milling in this context. Gravity concentration and flotation are the beneficiation techniques most commonly applied to scheelite ore, and gravity and/or magnetic separation for wolframite ore. Magnetic separation of tungsten minerals can be viable in some ore specific circumstances. Hydrometallurgy can be used to extract tungsten, depending on the ore texture and mineral content. X-ray sorting and gravitational methods can be used for pre-concentration. Optical sorting and/or hand-picking methods are also used for pre-concentration of wolframite ore.

Tungsten concentrates are subject to further processes to output a number of saleable tungsten products. Recycling can be done technically but is usually not economically viable. There are some options for substitution of tungsten in manufacture but not for all applications. This implies the best source of tungsten at this time would come from the mining of mineralized resources.

Keywords

tungsten, scheelite, wolframite, CRM, beneficiation, recycling, products

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1 INTRODUCTION

This report is a general introduction to tungsten. Issues covered are what tungsten is, what it is used for, market demand, substitution options, tungsten minerals, tungsten ore and deposit classes, global reserves and resources, tungsten global production, mineral processing beneficiation, tungsten product manufacture and recycling. As with all useful metals/minerals, there are specific issues around the tungsten value chain that need to be understood for its effective use.

2 PROPERTIES OF TUNGSTEN METAL

Tungsten, also known as wolfram, with symbol W and atomic number 74, has the highest melting point of all metals (3422 ± 15 °C). With its density of 19.25 g/cm^3, tungsten is also among the heaviest metals. Tungsten (W) is a lustrous greyish-white metal, which is a solid at room temperature. It has the highest melting point and lowest vapor pressure of all metals, and at temperatures over 1650 °C has the highest tensile strength. It has excellent corrosion resistance and is attacked only slightly by most mineral acids. Tungsten has been listed as one of critical raw materials in Europe due to its high economic importance and the fact that its supply is at risk. Table 1 and 2 shows the material properties of tungsten.

Table 1. Material properties of Tungsten (Source: Haynes *et al* 2016)

Material Property	Value	Units
Atomic Number	74	
Atomic Weight	183.86	
Group Number	6	
Electron Configuration	1s2 2s2 2p6 3s2 3p6 4s2 3d10 4p6 5s2 4d10 5p6 6s2 4f14 5d4	
CAS Registry Number	7440-33-7	
Atomic Volume	9.53	
Lattice Type	Body Centered Cube	
Lattice Constant at 20 ºC,	3.1585	Angstroms
Natural Isotopes	180, 182, 183, 184, 186	
Density @ 20 ºC	19.3	(gm/cc)
Density @ 20 ºC	0.697	(lb./cu. in.)
Melting Point	3410	^{0}C
Boiling Point	5530	^{0}C
Linear Coefficient of Expansion per ºC	4.3 x 10E-6	
Thermal Conductivity @ 20 ºC	0.40	(cal/cm/ºC/sec)
Specific Heat @ 20 ºC	0.032	(cal/gram/ºC)

Table 2. Material properties of Tungsten (Source: Haynes *et al* 2016)

Material Property	Value	Units
Electronegativity (eV) Pauling	2.36	eV
Electronegativity (eV) Sanderson	0.98	eV
Electronegativity (eV) Allred Rochow	1.40	eV
Electrical Conductivity, % IACS	31	
Electrical Resistivity @ 20 ºC	5.5	(microhm-cm)
Electrical Resistivity @ 227 ºC	10.5	(microhm-cm)
Electrical Resistivity @ 727 ºC	24.3	(microhm-cm)
Electrical Resistivity @ 1727 ºC	55.7	(microhm-cm)
Electrical Resistivity @ 2727 ºC	90.4	(microhm-cm)
Electrical Resistivity @ 3227 ºC	108.5	(microhm-cm)
Temperature Coefficient of Electrical Resistivity	0.0046	Per ºC (0 – 100 ºC)
Tensile Strength @ Room Temp.	100,000 – 500,000	psi
Tensile Strength @ 500 ^{0}C	75,000 – 200,000	psi
Tensile Strength @ 1000 ^{0}C	50,000 – 75,000	psi
Poisson's Ratio	0.284	
Hardness (Mineral)	7.5	
Hardness (Vickers)	343	
Hardness (Brinell)	2570	
Reflectivity	62%	
Total Emissivity @ 1500 ^{0}C	0.23	
Total Emissivity @ 2000 ^{0}C	0.28	
Working Temperature	<1700	^{0}C
Recrystallization Temperature	1300 – 1500	^{0}C

3 USE AND APPLICATIONS OF TUNGSTEN

Tungsten is another relatively rare metal, with highly specialized applications, particularly within old-style incandescent lamp manufacture, special alloys and hard materials, as well as catalysts and military applications. Because tungsten oxides have two unique properties—intercalation and polycondensation—there is a great opportunity for tungsten to be used in fuel cell or energy-saving technologies in the future.

Table 3 shows an overview of estimated use of tungsten in Europe in 2012. Table 4 shows some tungsten compounds. Figure 1 shows an estimation of historical use of tungsten in Europe.

Table 3. Overview of estimated use of tungsten in Europe in 2012 (Source: SCRREEN 2.3)

Group	Application	tungsten [kt]	fraction [-]
Steel and super alloy	Aeronautics & Energy applications	1.10	0.05
	High speed steel	1.32	0.06
	High temp. Steel	0.44	0.02
Cemented carbide	Mill and cutting tools	6.82	0.31
	Mining & construction tools	4.62	0.21
	Other wear tools	3.74	0.17
Tungsten products	Lighting & electronic uses	1.32	0.06
Chemicals and others	Catalysts & pigments	1.54	0.07
	Other (e.g. nuclear fusion)	1.10	0.05
Total	Total	22	1

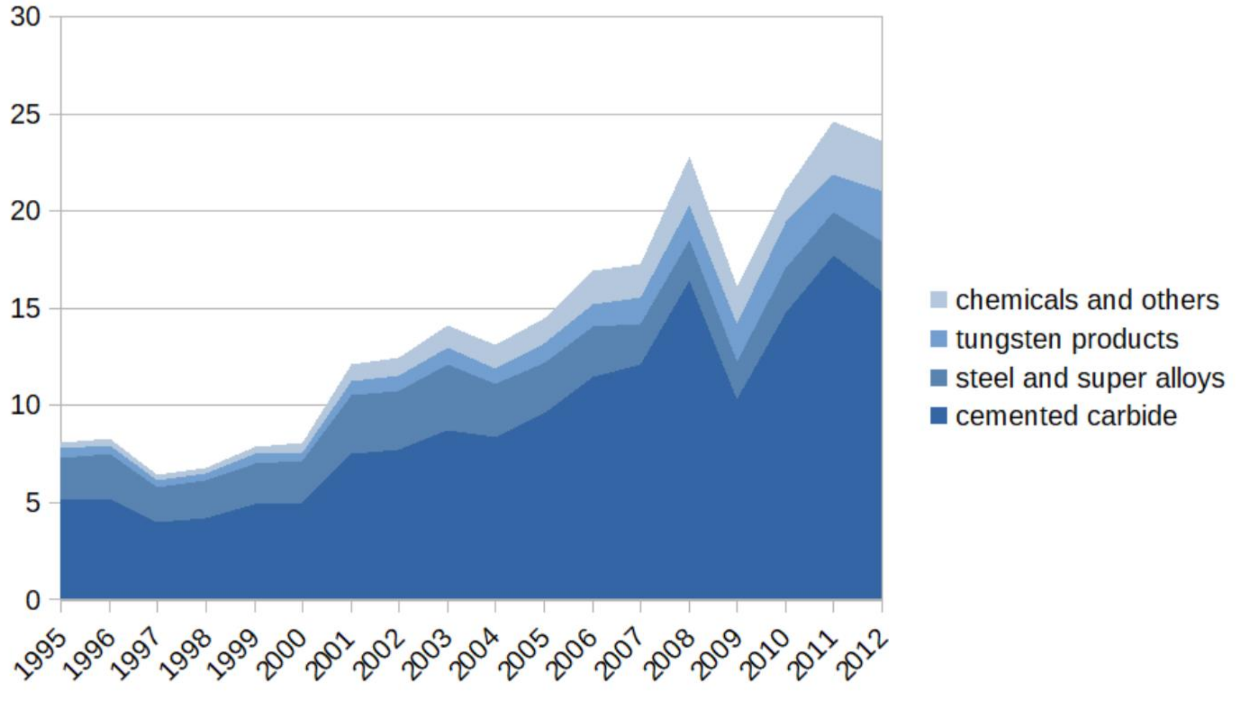

Figure 1. Estimation of historical use of tungsten in Europe from 1995 to 2012
(Source: SCRREEN 3.2, Data from Mesman 2016)

Table 4. List of some important tungsten compounds (Source: International Tungsten Industry Association).

Compound Names	Applications
Tungsten Silicide	Microelectronics
Calcium Tungstate	Phosphors
Heterpolytungstates	Lackers and toners Catalysts Passivation of steel
Na-12 Tungstophosphate	Manufacture of organic pigments Carroting (surface treating of furs) Antistatic agent for treatment of acryl-based fibres Leather tanning Water proofing Additive to chrome-plating bath, in cements and adhesives to impart water resistivity
Tungsten Disulfide	Lubricant
Tungsten Diselenide	Lubricant
Tungsten Hexaflouride	For metallisation in the semiconductor industry
Tungsten Hexachloride	Metallization
Tungsten Hexacarbonyl	Catalyst and organometallic compounds production

3.1 Cemented Carbides

Cemented carbides, or hardmetals as they are often called, are materials made by "cementing" very hard tungsten monocarbide (WC) grains in a binder matrix of a tough cobalt or nickel alloy by liquid phase sintering. This accounts for approximately 60% of tungsten use. Cemented carbides combine the high hardness and strength of metallic carbides (WC, TiC, TaC) or carbonitrides (eg TiCN) with the toughness and plasticity of a metallic alloy binder (Co, Ni, Fe), in which the hard particles are evenly distributed to form a metallic composite. Tungsten carbide is the most metallic of the carbides, and by far the most important hard phase. The more hard carbide particles are within the material, the harder it is but the less tough it behaves during loading; and, vice versa, significant increases in toughness are achieved by a higher amount of metallic binder at the expense of hardness.

Within the field of engineering materials, cemented carbides play a crucial role as they combine high hardness and strength with good toughness within a wide property range, and thus constitute the most versatile hard materials group for engineering and tooling applications.

3.2 Tungsten in Steel as an Alloy

Tungsten is used in high speed steel, which can contain as much as 18% tungsten. Due to its properties, tungsten is used in aerospace and automotive industries and radiation shielding. Tungsten was among the first alloying elements systematically studied and used to improve steel properties, for example hardness, cutting efficiency and cutting speed of tool steels. Different tungsten containing steels were developed in Austria, Germany, France and England, followed by high speed steels in the USA.

The addition of tungsten to construction steels has decreased since 1940 because alloying with Mo and Cr, as well as with V and Ni, yielded better performance at a lower price. From 1927, when cemented carbides (hardmetals) were developed, the production of total tungsten consumed in steelmaking declined constantly to a current figure of about 20%, but nevertheless steel is today the second biggest consumer. Figure 2 shows how tungsten alloys are used in the aeronautics industry.

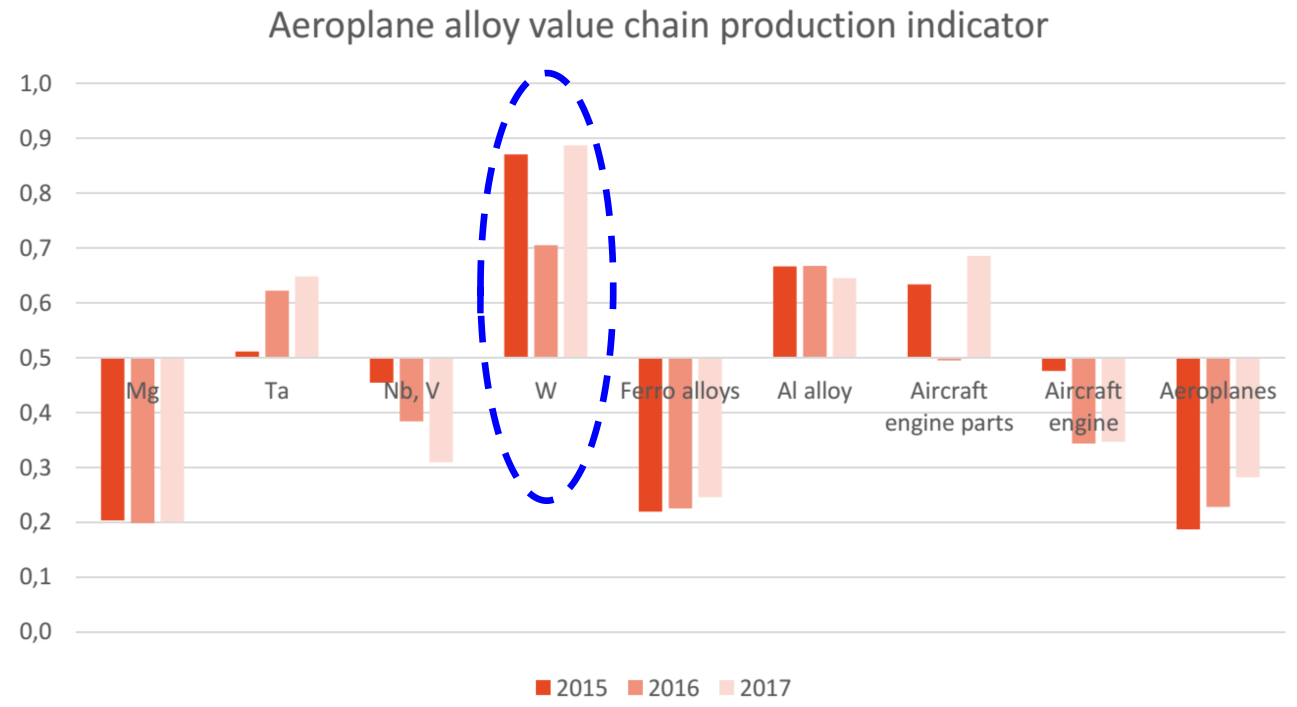

Figure 2. Production indicator (prod/imp+prod) for aeroplane alloy value chain in 2015, 2016 and 2017 (Source: SCRREEN 5.3)

3.3 Lamp Industry

The use of tungsten filaments in light bulbs has become a matter of course, in particular in domestic lighting. Tungsten is used in this application because of its extremely high melting temperature (~3,695 K), low vapour pressure, high stiffness and excellent creep resistance at elevated temperatures.

About 4% of the annual tungsten production is consumed by the lighting industry, which uses about 15% of the global electric power produced worldwide.

3.4 Chemical Applications

Tungsten sulphide is a high temperature lubricant and is a component of catalysts for hydrodesulfurization (Spivey 2002). Tungsten oxides are used in ceramic glazes and calcium/magnesium tungstates are used widely in fluorescent lighting. They are also used in selective catalytic reduction (SCR) catalysts found in coal-fired power plants. Crystal tungstates are used as scintillation detectors in nuclear physics and nuclear medicine. There are a number of Tungsten chemicals that have been used in the medical and dental fields for X-ray shielding and conversely, X-ray opacity. Other salts that contain tungsten are used in the chemical and tanning industries.

3.5 Electronics and Electrical Industry

Elemental Tungsten is used in many high-temperature applications, such as light bulb, cathode-ray tube, and vacuum tube filaments, heating elements, and rocket engine nozzles. Thanks to its conductive properties it is also used in electrodes and in the emitter tips in electron-beam instruments that use field emission guns, such as electron microscopes.

Tungsten is practically the only material used for electron emitters. Although other, more electropositive, metals would yield higher emission rates, the advantage of tungsten is its extremely low vapor pressure even at high temperatures.

This property is also important for electrical contact materials. While more conductive metals like copper or silver evaporate (erode) under the conditions of an electric arc, tungsten withstands these.

Tungsten is one of the most important components in modern integrated circuitry and tungsten-copper heat sinks are used to remove the heat of microelectronic devices.

3.6 Military use and Application of Tungsten

Tungsten is used by the military to produce bullets, due to its hardness and high density. Where tungsten is most effective is to produce armor penetrating bullets. Thus, it is required to use military weapons made with tungsten in them, to maintain a tactical edge in a military conflict. Tungsten metal is used in many applications from bullets, grenades to even rockets. The combination of tungsten and carbon the Tungsten Carbide is also used because it has, even more, strength and it is more durable than the pure tungsten. Tungsten can also be used for nuclear weapon material shell protection.

While this application accounts for a very small proportion of total global demand, it does create a geopolitical sensitivity.

Ammunition

Tungsten is almost an indispensable part of armor-piercer. The kinetic armor-piercer made from tungsten alloy can compete directly with the depleted uranium bomb (depleted uranium has become an environmental problem, where the Gulf War battlefields of Kuwait have become a case study) (Source: U.S. Department of Defense 2004).

Compared to lead and depleted uranium, the combination of tungsten and carbon is proving to be less environmentally hazardous, where the presence of spent ammunition in large volumes has led to problems in the past.

- The GNU-44 Viper Strike missile, carried by armed drones, has a tungsten sleeve to produce antipersonnel shrapnel.
- The 130-round-per-second Phalanx anti-missile Gatling gun, deployed on U.S. and Royal Navy ships, originally used DU rounds. They were replaced with tungsten, for environmental reasons.
- 120mm anti-tank rounds, use tungsten as an alternative to DU in training. So do the 25mm anti-tank rounds, on board the M2/M3 Bradley fighting vehicle.
- Armor-piercing .308 M993 rifle rounds.

- The 120mm M1028 anti-personnel round, fired by the Abrams tank. This round is essentially a large shotgun shell loaded with 1100 tungsten balls, each 3/8th of an inch in size.
- Dense Inert Metal Explosives, the "focused lethality" munition used by the U.S. and Israel. It contains micro-shrapnel made of tungsten powder.
- Some 70mm rockets fired by Apache helicopters release tungsten flechettes.

Vehicle use

Another very common use of this metal is in military vehicles, usually, helicopters and aircraft and sometimes for armored vehicles. Tungsten is used in helicopters to even out the weight of the rotors, skids or the craft nose. This metal is used because it has a great size to weight ratio, where a small volume has a comparatively high mass. Sometimes it is also used for protection of some vehicles because of its material strength.

Tungsten toxicity

The use of tungsten as an alternative to depleted uranium to manufacture armor piecing ammunition may not be as environmentally 'clean' as previously thought. Which means all sorts of rockets, missiles, and anti-tank rounds may present an environmental hazard and a health risk.

The British Army looked into the tungsten problem in (Doust *et al* 2007). A study of possible implications found that there was tungsten in the ground water of at least one UK tank firing range, and recommended that further studies be carried out. The literature review in this study identified the relative lack of knowledge regarding the behavior and toxicity of tungsten in the environment and that there are few legislative standards or guidance for tungsten in the environment.

Meanwhile, the United States Army seems to still trying to establish a consistent approach. On one hand, the US military has recommended the stopping production of tungsten-based training ammunition, while simultaneously looking into using tungsten as a DU-replacement in a wider scope of application.

This issue may make the future use of tungsten in military applications more difficult.

4 TUNGSTEN DEMAND CONSUMPTION

Cemented carbides, steel and alloys, mill products, and chemicals and specialists are the main applications of tungsten. The consumption of W continues to increase as the amount of carbide tool production increases with the expansion of markets in developing countries.

China was the world's leading tungsten consumer. Analysts forecast global tungsten demand in 2019 to be less than that in 2018, as a result of destocking by consumers and reduced consumption owing to reported slowing global economic growth. Proportions of demand in Europe are shown in Figure 3.

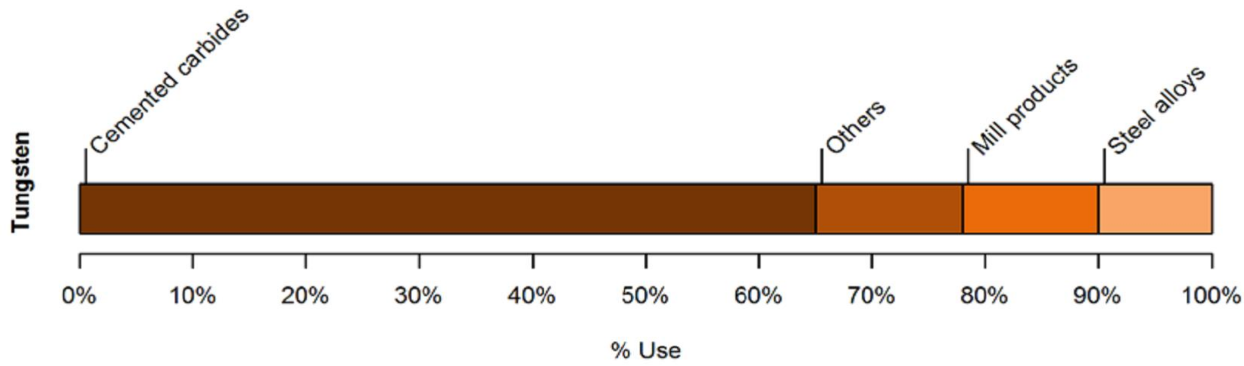

Figure 3. Distribution of recent tungsten demand in the EU
(Source: Tercero Espinoza *et al* 2018, data from Argus Media 2016)

This section firstly describes what 'apparent consumption' and 'import reliance' are and how they can be measured. The levels of apparent consumption for each CRM are presented, where possible, followed by an assessment of the import reliance position in 2015. Data relating to 'true' consumption are not generally collected from mineral processors and manufacturers. The 'apparent' consumption can be calculated (at either a national or EU level) using the formula:

Apparent Consumption = Production + Imports – Exports +/– Stock Changes

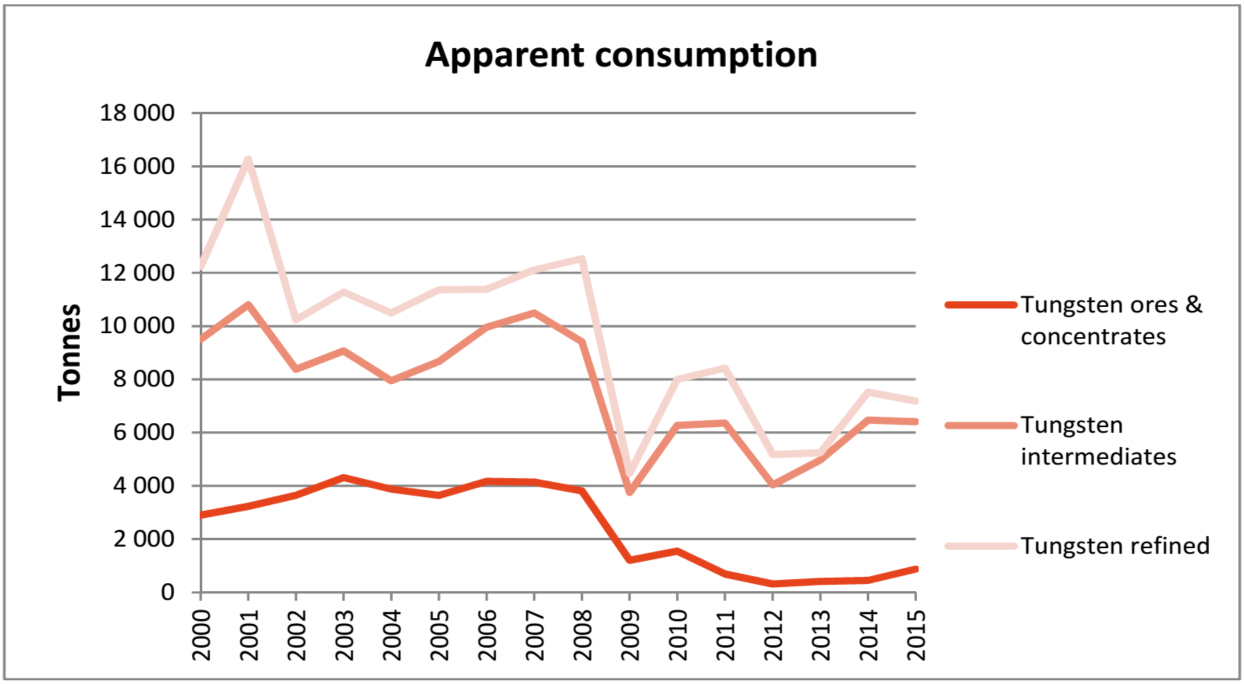

Figure 4. Apparent consumption of tungsten in Europe 2000 to 2015
(Source: Brown *et al* 2018)

4.1 European Import Reliance for Tungsten

Import reliance is defined as the proportion of a nation state's consumption of a mineral commodity that is imported from elsewhere. In precise terms, it is 'net import reliance' because exports also have to be taken into account in case part of the import quantity is immediately re-exported. Import reliance can be calculated using the following formula, which assumes 'consumption' is apparent consumption, and is expressed as a percentage:

Import Reliance = (Imports – Exports) / Apparent Consumption x 100

Trends in import reliance are presented in the following charts (where data are available) is shown in Figures 5 to 7.

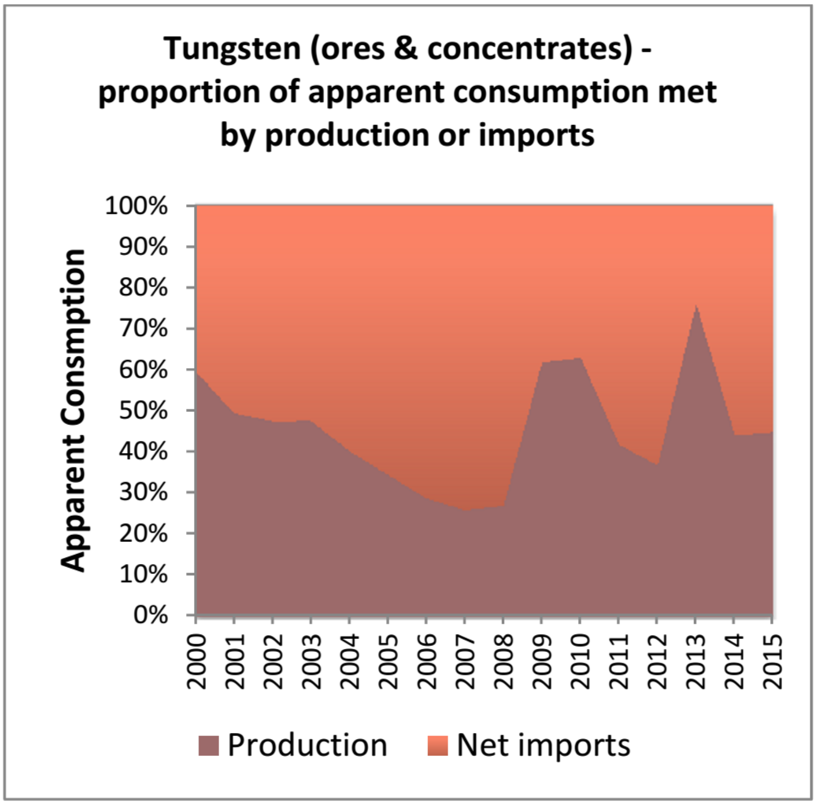

Figure 5. Tungsten ore & concentrates European import reliance
(Source: Brown *et al* 2018)

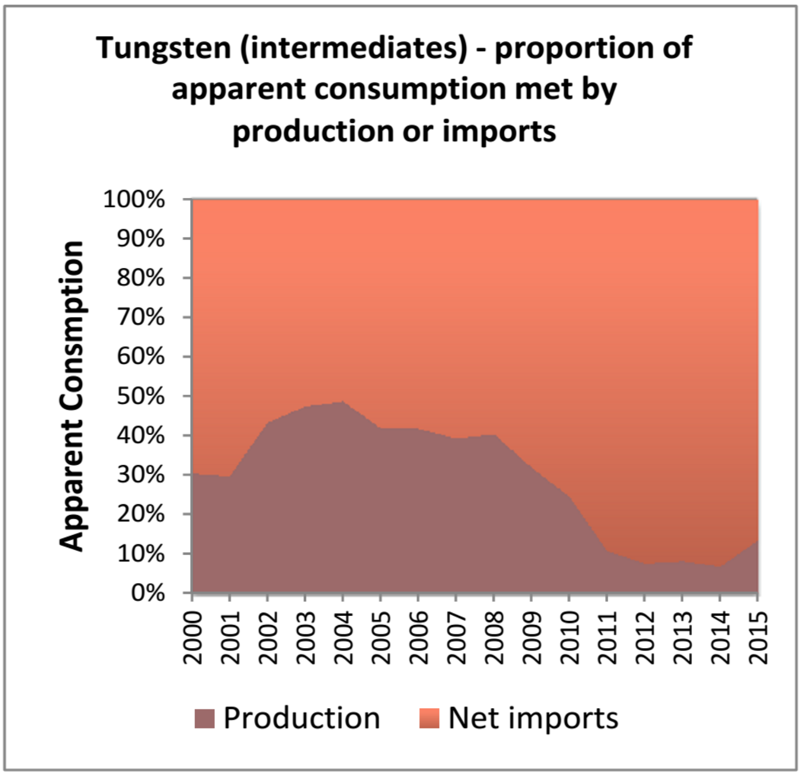

Figure 6. Tungsten intermediates European import reliance
(Source: Brown *et al* 2018)

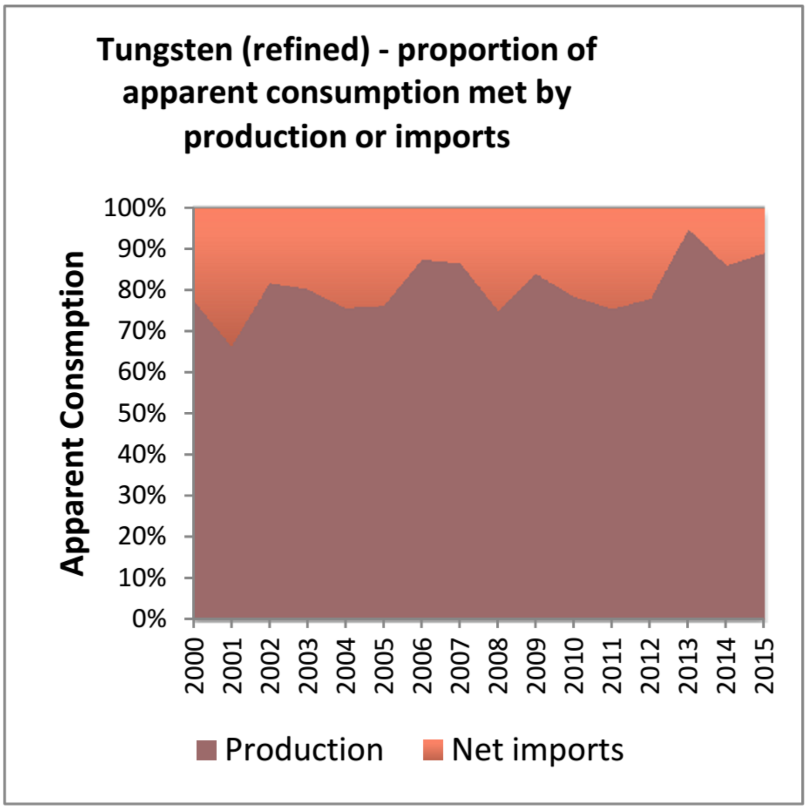

Figure 7. Tungsten refined products European import reliance
(Source: Brown *et al* 2018)

5 TUNGSTEN CRM PROFILE WITHIN THE EUROPEAN UNION

Due to its economic importance, and high supply risk, tungsten has been listed as a critical raw material for the EU since the original criticality assessment in 2010 (European Commission 2010, 2014b, 2017b). The British Geological Survey's risk list ranked tungsten in the top ten materials facing potential supply disruptions (BGS 2011b, 2012, 2015). Figure 8 and Table 5 shows the current CRM map (European Commission 2017). Figure 9 shows the global critical mineral supply to Europe. Europe has mines of tungsten in its territory but the mine production still does not meet the demand of the European industries.

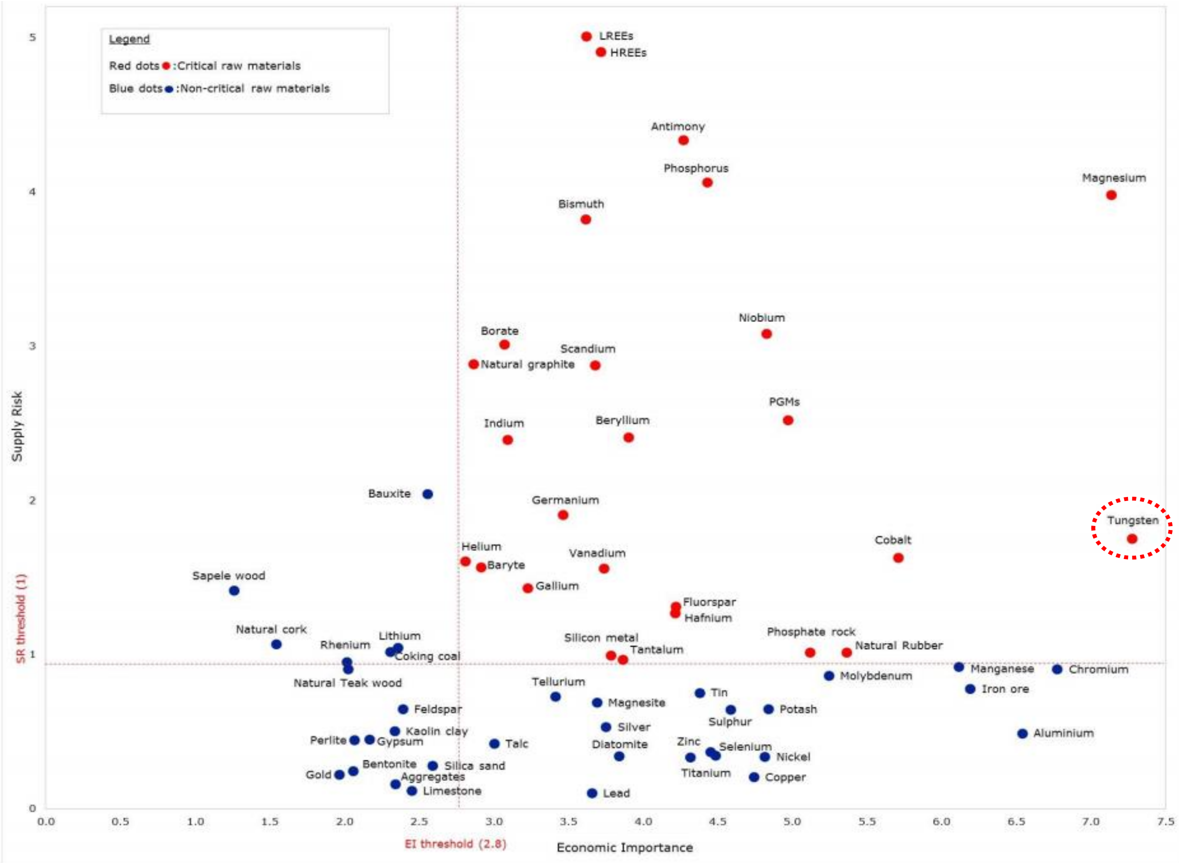

Figure 8. Economic importance and supply risk results of 2017 criticality assessment (Source: European Commission 2017)

Table 5. The list of Critical raw Materials (excluding natural rubber) (Source: European Commission 2017)

2017 Critical Raw Materials				
Antimony	Cobalt	Hafnium	Magnesium	Phosphorus
Baryte	Coking coal	Helium	Natural graphite	Scandium
Beryllium	Fluorspar	HREEs	Niobium	Silicon metal
Bismuth	Gallium	Indium	PGMs	Tantalum
Borate	Germanium	LREEs	Phosphate rock	Tungsten
				Vanadium

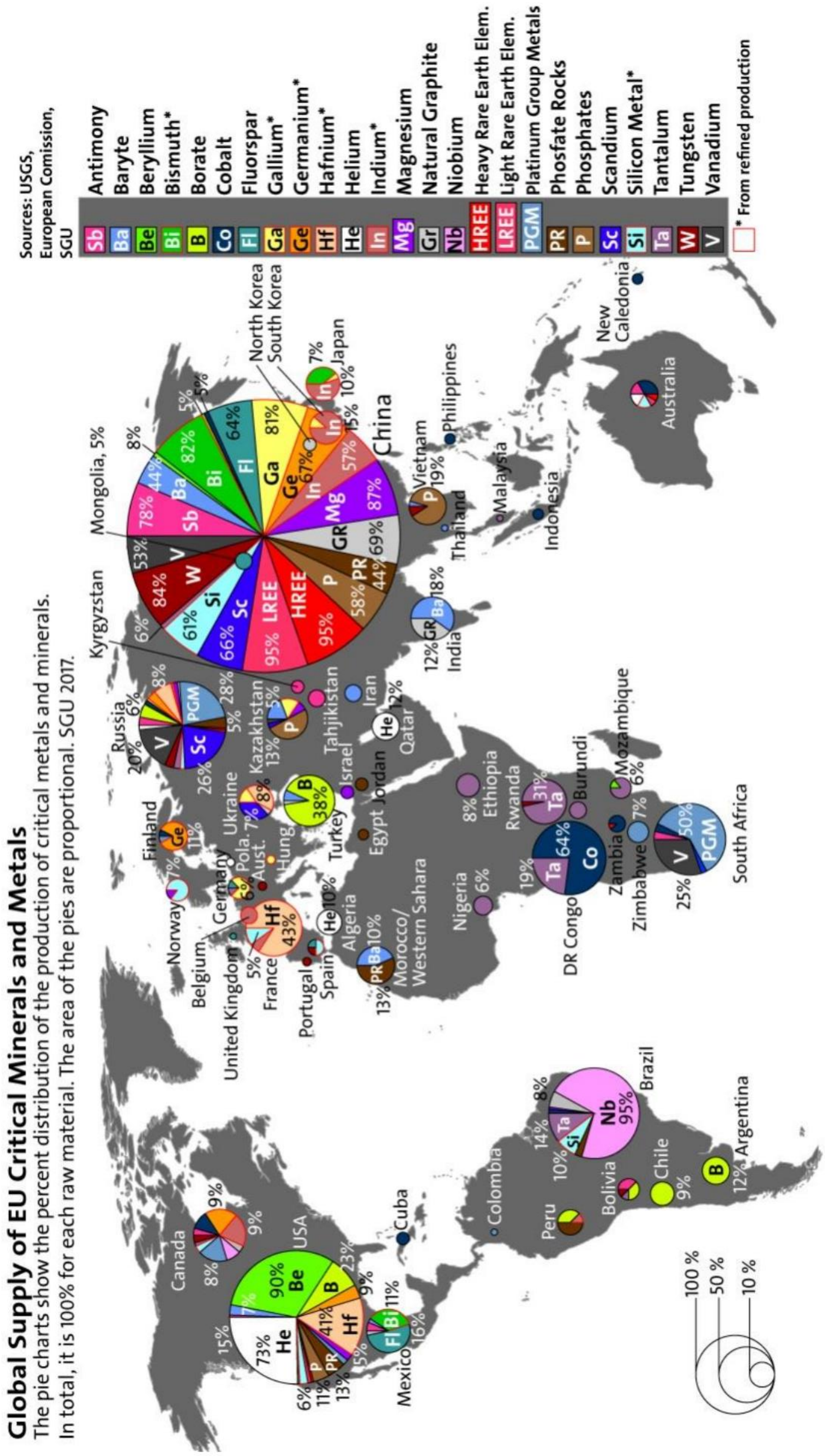

Figure 9. Countries accounting for largest share of global supply of CRMs (Source: SGU 2016)

Many CRM, particularly the critical metals, are produced in very small quantities globally and the total production value of many of them is relatively low. For this reason some critical metals are also classified as 'minor metals'. The mining and processing of the ores of the minor metals is generally less economically attractive to major mining companies than that of the major industrial metals, such as iron ore and bauxite, where the production level is orders of magnitude larger, where the markets are well established and relatively stable, and where the risks are lower and profits potentially greater. Accordingly both the mining and processing of minor metals tends to be carried out by a relatively small number of companies operating at only a few locations where the resources are located and/or the appropriate processing technology is in place. Figure 10 shows the comparative production volumes between different technology minerals and CRM minerals compared to bauxite in 2015. Note W at the top right hand side of the figure.

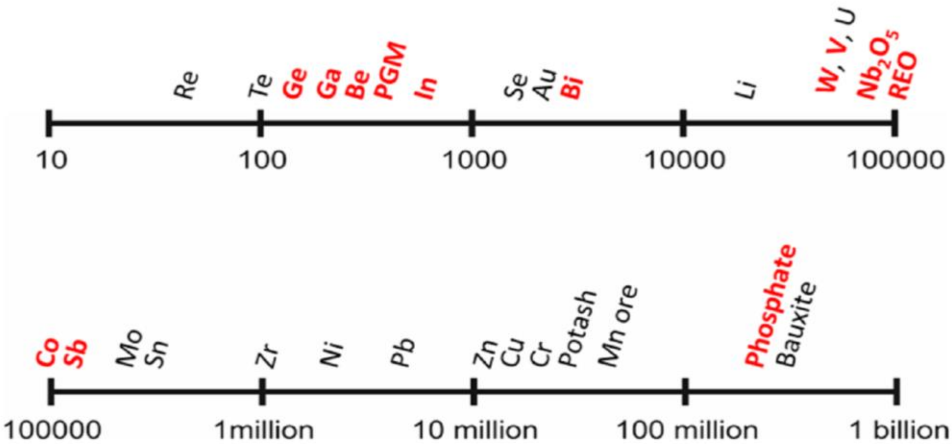

Figure 10. Indicative global annual production (metric tonnes, log scale) of selected metals and ores in 2015. Elements highlighted in red are CRM minerals. (Source: Brown *et al* 2018, data from BGS, 2017 and USGS Mineral Commodity Summaries). Those metals and ores in red are currently classified as critical the EU (EC, 2017a).

6 TUNGSTEN AS A CONFLICT METAL/MINERAL

Conflict minerals are minerals mined in politically unstable areas, where armed groups often use forced labor to mine minerals, or minerals are mined in conditions of armed conflict and human rights abuses. Also, minerals that are sold or traded by armed groups to fund their activities, for example to buy weapons. The European Commission has passed regulations (European Commission trade policy regulations: https://ec.europa.eu/trade/policy/in-focus/conflict-minerals-regulation/) to address:

- Conflict minerals and metals from being exported to the EU;
- Global and EU smelters and refiners from using conflict minerals, and;
- Mine workers from being abused.

The law (starts to apply on 1 January 2021) also supports the development of local communities. It requires EU companies to ensure they import these minerals and metals from responsible sources only.

Tungsten is used to make armor piercing ammunition and is used in many military applications that are required to maintain a technological competitive edge, has resulted in tungsten to be considered a conflict metal. This combination makes tungsten a geopolitically sensitive metal. Table 6 shows the conflict mineral list according to the United Kingdom guidance.

Table 6. Conflict minerals according to United Kingdom government guidance
(Source: United Kingdom Government conflict minerals Guidance: https://www.gov.uk/guidance/conflict-minerals)

Mineral	Mineral Source	Major Applications
Cassiterite	Ore from which tin is extracted	Plating and solders for joining pipes and electronic circuits
Columbite-tantalite	Ore from which tantalum is extracted	Electrical components (including those used in mobile phones, computers, videogame consoles), aircraft and surgical components
Gold	Rare metal found in a native (pure) form and obtained as a by-product of other mining operations	Jewellery, electronic, communications and aerospace equipment
Wolframite	Ore from which tungsten is extracted	Metal wires, electrodes and contacts in lighting, electronic, electrical, heating and welding applications

Mining is an intensive process involving potential social and environmental risks that, if not properly managed, can cause lasting negative impacts. A growing perception supports that these risks are associated with a variety of metals and minerals that extend beyond tin, tungsten, tantalum and gold (3TG). NGO groups like Responsible Minerals Initiative and Minerals Due Diligence seek to raise awareness of this (Source: http://www.responsiblemineralsinitiative.org/).

"Conflict minerals," as defined by the US legislation, currently include the metals tantalum, tin, tungsten and gold, which are the derivatives of the minerals cassiterite, columbite-tantalite and wolframite, respectively. Downstream companies often refer to the derivatives of these minerals as 3TG.

Some of the mining of minerals in the Democratic Republic of Congo (DRC) has been classified in the conflict minerals spectrum. Conflict minerals in the eastern DRC are generally defined (including in US legislation and the OECD due diligence guidance for responsible mineral supply chains) as cassiterite (tin), coltan (tantalum), wolframite (tungsten) and gold, or derivatives of these minerals. Sometimes these minerals are referred to as the 'three Ts' - tin, tantalum and tungsten.

This has an outcome that any tungsten producer in the world has to comply with conflict mineral classification legislation from the United States, United Kingdom, Europe EU-28 and the OECD.

7 SUBSTITUTION OPTIONS FOR TUNGSTEN

The "Substitutability Index" is a measure of the difficulty in substituting the material, scored and weighted across all applications. Values are between 0 and 100, with 100 being the least substitutable (Bouyer 2019). Figure 11 shows all elements on the periodic table in context of the Sustainability Index.

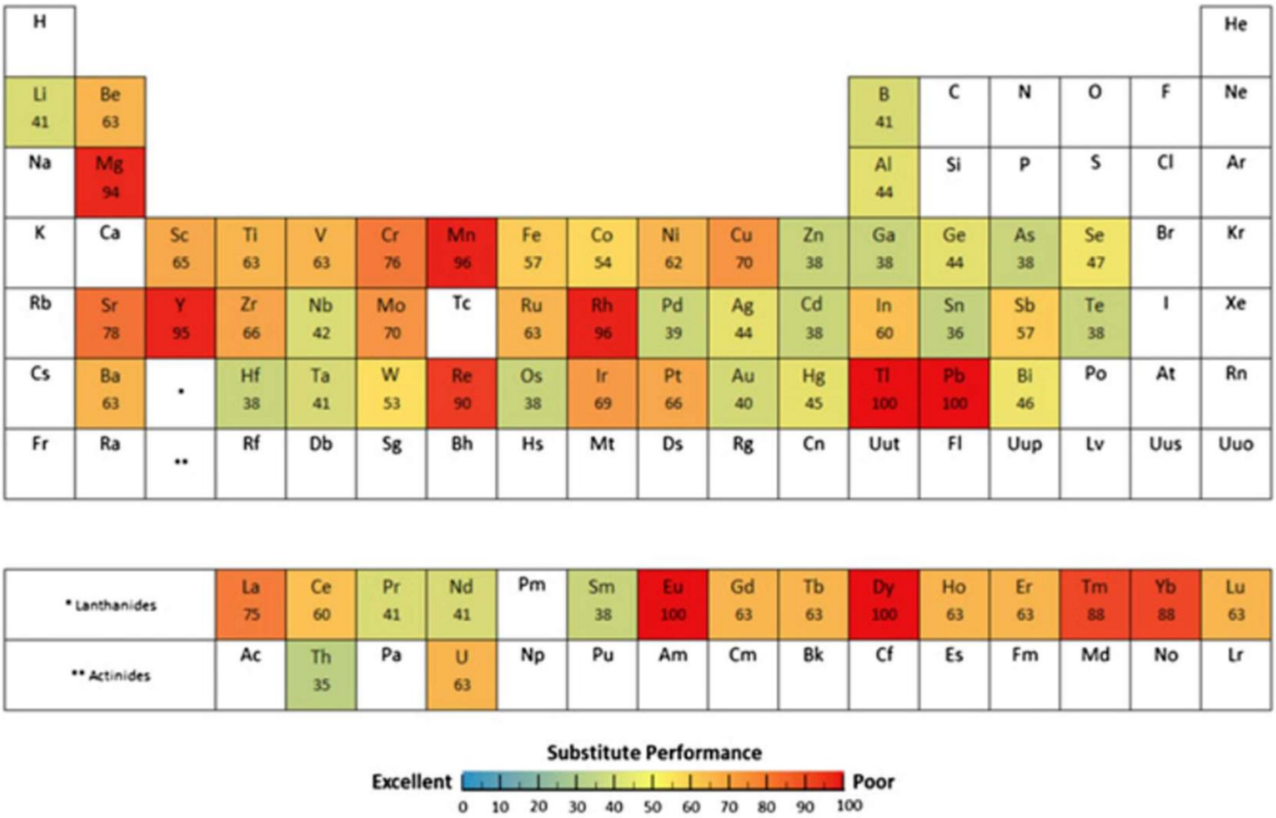

Figure 11. The periodic table of substitute performance (Source: Bouyer 2019)

Potential substitutes for cemented tungsten carbides include cemented carbides based on molybdenum carbide, niobium carbide, or titanium carbide; ceramics; ceramic-metallic composites (cermets); and tool steels. Most of these options reduce, rather than replace, the amount of tungsten used.

Potential substitutes for other applications are as follows: molybdenum for certain tungsten mill products; molybdenum steels for tungsten steels, although most molybdenum steels still contain tungsten; lighting based on carbon nanotube filaments, induction technology, and light-emitting diodes for lighting based on tungsten electrodes or filaments; depleted uranium or lead for tungsten or tungsten alloys in applications requiring high-density or the ability to shield radiation; and depleted uranium alloys or hardened steel for cemented tungsten carbides or tungsten alloys in armor-piercing projectiles. In some applications, substitution would result in increased cost or a loss in product performance.

For tungsten's main application, WC-based cemented carbides, substitution is appears technically possible but implies higher costs and, in some cases, a decrease in performance. Titanium carbides (Ti-C) and nitride (Ti-N) are potential substitute but the technology is not competitive at the moment. Tungsten can be replaced by other refractory metals such as niobium (CRM) or molybdenum in ste el products. In other application areas, possible substitution of tungsten is affordable, as super-alloys substituted by Ceramic Matrix Composites (CMCs) made from a silicon carbide/nitride matrix for gas turbine engines (Tercero Espinoza *et al* 2018). Also, substitution with nanostructured n-alloys such as Fe-Ta, is could be possible in 10 year since current TRLs are very low (TRL 3-4).

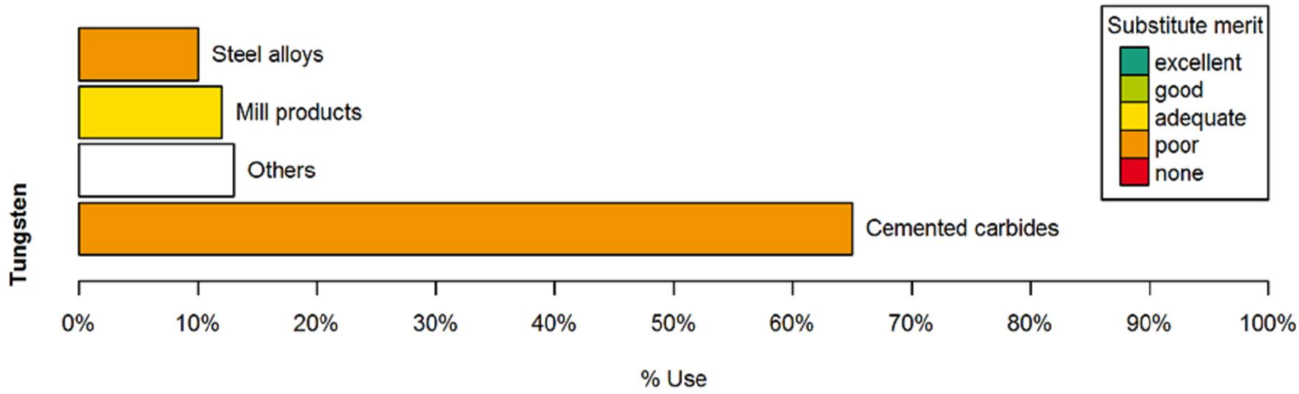

Figure 12. Summary substitutability assessment for tungsten
(Source: Tercero Espinoza *et al* 2018)

8 FUTURE USE OF TUNGSTEN

The predicted future use of tungsten is not thought to be that different in proportion of application or volumes for the foreseeable future.

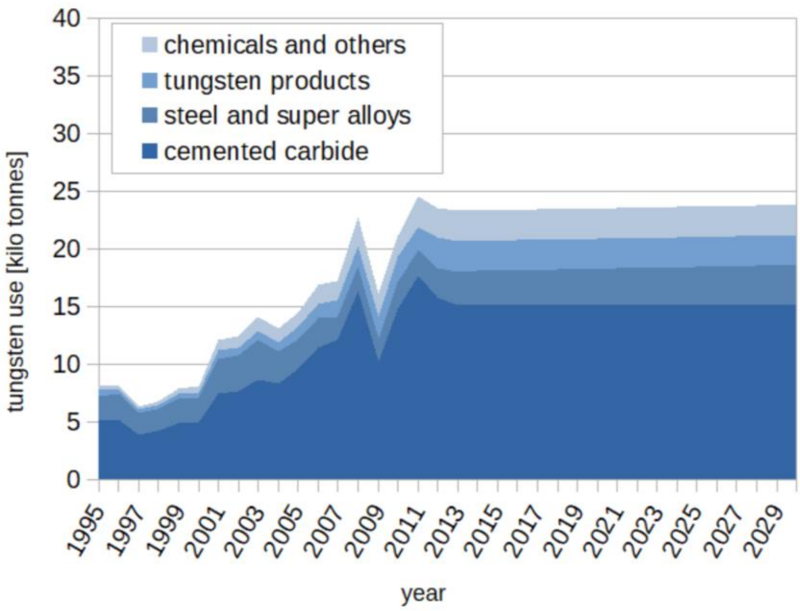

Figure 13. Scenario for the future use of tungsten in Europe. Future use is determined by the assumption of a constant volume of construction work and manufacturing work in Europe for the coming decade.
(Source: SCRREEN 3.2)

9 ORE CHARACTERISTICS OF TUNGSTEN

The average abundance of tungsten in the earth's crust is estimated to be 1.25–1.5 ppm, about the same as that of tin and molybdenum. It is more abundant in granite (about 2 ppm) than basaltic (1 ppm) and ultra-mafic rocks (0.5 ppm). Table 6 shows the basic properties and W content of the most common tungsten bearing minerals.

Table 7. Properties of the most common tungsten minerals (Reproduced from BGS Tungsten Mineral Profile 2011)

Mineral Name	Chemical Formula	Tungsten Content (WO_3 %)	Specific Gravity (g/cm^3)	Appearance (colour and lustre)	Crystal Structure
Feberite	$FeWO_4$	76.3	7.5	Black, sub-metallic to metallic	Monoclinic
Wolframite	$(Fe,Mn)WO_4$	76.5	7.1-7.5	Dark grey to black, sub-metallic to metallic	Monoclinic
Hubnerite	$MnWO_4$	76.6	7.2-7.3	Re-brown to black, sub-metallic to adamantine	Monoclinic
Scheelite	$CaWO_4$	80.6	5.4-6.1	Pale yellow to orange, green to dark brown, pinkish-tan, dark blue to black, white or colourless, vitreous or resinous	Tetragonal
Stolzite	$PbWO_4$	50.9	8.28	Reddish-brown to yellow-green, sub-adamantine to resinous	Tetragonal

There are numerous tungsten minerals, but only scheelite ($CaWO_4$) and wolframite ($(Fe, Mn)WO_4$) are of economic importance (Schmidt 2012a & 2012b; BGS, 2011). However, wolframite is not a mineral species but a series between ferberite ($FeWO_4$) and hubnerite ($MnWO_4$). The domination of either iron or manganese would result in forming one of two minerals. The iron dominated one will result in forming ferberite while the manganese dominated one will result in forming hübnerite (Errandonea and Segura, 2010).

There are three broad types of Tungsten deposits:

- Classical vein deposits: these are more or less continuous veins of varying thickness, ranging from several decimetres to several metres, mainly comprised of quartz contained in the granite itself or in the surrounding host rock. Most deposits exhibit ferberite or hübnerite mineralization characteristics, but scheelite vein deposits occur as well. Typical grades of Tungsten are of 0.5-5% WO_3. Sn typically occurs as a by-product. In the EU, there is one active mines of this type where Tungsten is extracted: the Panasqueira Mine in Portugal. The San Fix Mine in Spain was recently operational but has temporarily suspended production.

- Skarn deposits: formed by replacement of carbonate rock with calc-silicate minerals in close contact with a granitic/felsic intrusion. Mineralization characteristics can be mono-metallic Tungsten or polymetallic (often with Mo or Pb,Zn,Cu), as well as gold, fluorite or magnetite. Typical grades are 0.3-1% WO_3. As for the EU, one active mine of this type is found in the Los Santos mine in Spain.

- Bulk mineable deposits (greisen, porphyry, stockwork and sheeted vein): are either W-Sn, or W-Mo deposits. Both scheelite and wolframite occur in bulk mineable deposits, and some deposits contain both mineral together, which leads to problems with beneficiation as mixed concentrates are more difficult to market. Typical grades are 0.1-0.3% WO_3. In EU there is a mine of this type in Austria, Mittersill.

Table 8 shows the key features of the rock texture of tungsten bearing mineralized ore. Table 9 and 10 shows the approximate size and grade of the different tungsten deposit forms. Table 11 lists the world's largest tungsten deposits as understood in 2011.

Table 8. Key features and examples of tungsten deposit classes (pale grey shading and black text indicate bedrock deposits; no shading and blue text indicate superficial deposits). **(Reproduced from BGS Tungsten Mineral Profile 2011),** Information partly sourcing from descriptive models compiled by the US Geological Survey (Cox and Singer, 1986) and Geological Survey Branch of the British Columbia Ministry of Energy, Mines and Mineral Resources (Lefebure and Ray, 1995).

Deposit Type	Brief Description	Features	Examples
Skarn	Tabular or lenticular scheelite-dominated orebodies in calc-silicate rocks formed by replacement of carbonate rocks and more rarely carbonaceous rocks at contacts with S- and I- type granitoid intrusions	Commonly within extensive thremal aureoles; local greisens. May be associated with porphyry W+/-Mo and stockwork Sn deposits	Vostok-2 (E. Siberia), Uludag (Turkey), Mactung and Cantung (Canada), Sang Dong (S. Korea), King Island (Tasmania, Australia)
Vein	Single and multiple systems of simple or complex fissure filling and replacement veins of quartz + wolframite at margins of flesic plutonic rocks in clastic (meta-) sedimentary country rocks	Greisen-bordered veins that locally pass into stockworks minor breccia zones. Multiple stages of veining +/- ore zoning with Sn, Cu, etc.	Panasqueira (Portugal), Xihuashan (China), Bolsa Negra (Bolivia), Erzgebirge (Czech Rp.), Hemerdon, Redmoor (south-west England)
Sheeted Vein	Felsic-hosted sheeted vein - comprising a complex multi-episodal system, making it somewhat unique, both in mineralisation style and scale (Hemerdon type deposit).	Tungsten dominated, thin (cm scale) veins displaying multiple espisodes.	Hemerdon (United Kingdom) (Reference Shail et al 2017)
Breccia	Near-vertical bodies of fragmented rock formed either by hydraulic fracturing or steam-dominated volcanic explosions marginal to I- or A- type granitic intrusions	Associated with vein / stockwork & porphyry deposits. Commonly zoned. Co- or by-product with Cu, Mo, Ag, Sb, Sn	Wolfram Camp (Queensland, Australia), Doi Ngom & Khao Soon (Thailand), Washington (Mexico)
Porphyry	Medium to large, low-grade stockwork of quartz veinlets and disseminations in subvolcanic felsic intrusive rocks +/- country rocks	Concentrically zoned metals and alteration; characterized by pervasive greisenisation. Co-product with Mo, Sn, Ag	Xingluokeng, Fujian and Yangchulin, Jiangxi, (China), Northern Dancer (Canada), Climax (USA)
Disseminated	Low-grade greisen deposits formed by pervasive metasomatic (endoskarn) alteration in the cupolas of granitic stocks	Locally merge with tungsten beraing greisen-bordered veins and stockworks. Co- or by-product of Sn or Mo	Shizhuyuan, Xihuashan, & Dangping (China), Akchatau, Kara-Oba & Lultin (CIS)
Stratabound	Concordant lenses of stratiform scheelite in submarine volcanosedimentary sequences. Volcanogenic exhalative origin	May include eruption breccias. Metamorphic remoblization into shears and veins	Mittersill (Austria), Damingshan, Guangxi Zhuang (China)
Pegmatite	Dyke-like masses around granitic bodies. Simple unzoned to complex strongly zoned types with more varied mineralogy	May be transitional with greisens and be hosted by skarns. Co- or by-product with Li, Be, Nb, Ta, REE and Sn	Okbang (S. korea), Kular & Priskatel (CIS), Wodgina (W. Australia)
Hot Spring	Siliceous or ferro-maganiferous precipitates deposited by hot groundwater and hot springs. Associated with bedrock tungsten deposits	Relatively high grade but small tonnage. May be associated with Au-Ag	Golconda (Nevada, USA), Uncia (Bolivia), Rotorua-Taupo area (New Zealand)
Placer	Heavy mineral concentrations in alluvial, eluvial or marine sediments derived from proximal bedrock sources of tungsten	Co- or by-product of Sn. Mostly small and only amenable to artisanal exploitation	Heinze Basin (Burma), Dzhida district (E. Siberia), Bodmin Moor (south-west England)
Brine	Tungsten-bearing brines in recent lakes and / or the slaine deposits of palaeo-lakes in arid continental regions	Also tungsten-rich bottom muds of brine-charged lakes & sabkha / playa basins.	Searles Lake (California, USA), other examples in the CIS and western USA

Table 9. Tungsten minerals and accompanying metals (Source: Yang 2018)

Deposit Type	Tungsten Mineral	Accompanying Metals
Skarn	Sheelite	Cu, Mo, Zn and Bi
Vein/Breccia/Stockwork	Wolframite	Sn, Cu, Mo, Bi and Au
Porphyry	Wolframite and/or sheelite	Mo, Bi and Sn
Disseminated	Wolframite and sheelite	Sn, Bi and Mo
Stratabound	Sheelite	

Table 10. Size and grade of major tungsten deposit types
(Reproduced from BGS Tungsten Mineral Profile 2011, Sourced from Schubert et al 2006, ITIA 2020 and Werner et al 1998)

Deposit Type	Deposit Size Range (metric tonnes)	Typical Grade of Tungsten Trioxide Content (WO_3 %)	Estimated Tungsten Metal Content of Known Deposits (thousand tonnes)	(%) of Total
Skarn	$<10^4$ - $5x10^7$	0.3 - 1.4	1764	41
Vein/Breccia/Stockwork	$<10^5$ - 10^8	Variable	1475	35
Porphyry	$<10^7$ - 10^8	0.1 - 0.4	679	16
Disseminated	$<10^7$ - 10^8	0.1 - 0.5	217	5
Stratabound	$<10^6$ - 10^7	0.2 - 1.0	118	3
Total			**4253**	**100**

Table 11. World's largest tungsten deposits
(Reproduced from BGS Tungsten Mineral Profile 2011, partially adapted from Werner *et al* 1998)

Deposit Name (Province)	Country	Type of Deposit	Estimated Contained Tungsten Metal ('000 tonnes)
Verkhne-Kayrakty (Dzhezkazgan Oblast)	Kazakhstan	Vein/stockwork	872
Mactung (Yukon & North West Territories)	Canada	Skarn	617
Shizhuyuan (Hunan)	China	Porphyry	502
Hemerdon (SW England)	UK	Sheeted Vein/Stockwork	309
Tyrnyauz (Kabardino-Balkaria)	Russia	Skarn	244
Northern Dancer (Yukon Territory)	Canada	Porphyry	168
Yangchuling (Jiangxi)	China	Porphyry	160
Xingluokeng/Xianglushan (Fujian)	China	Porphyry	144
O'Callaghan's (Western Australia)	Australia	Skarn	135
Damingshan (Guangxi)	China	Stratabound	116
Vostok-2 (Primorskye)	Russia	Skarn	102
Ta'ergou (Gansu)	China	Vein/stockwork	100
Total			3469

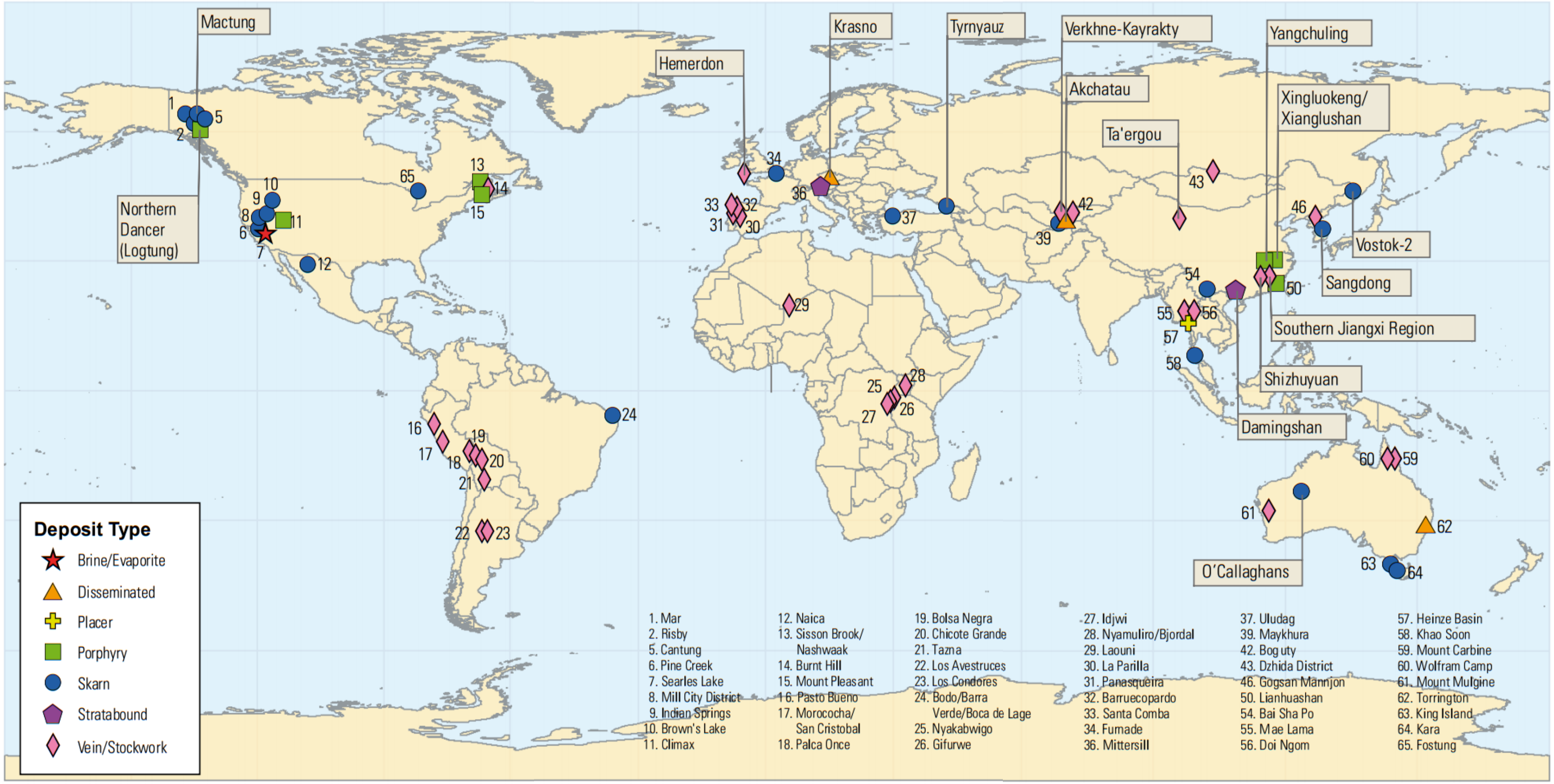

Figure 14. Location and type of major tungsten deposits and districts in the world (**Reproduced from BGS Tungsten Mineral Profile 2011**) (modified after Werner et al 1998). The largest deposits are named; the smaller deposits are numbered according to the key at bottom right

10 GLOBAL TUNGSTEN RESERVES & RESOURCES

The global reserves of tungsten are shown in Figure 15, 16 and Table 11.

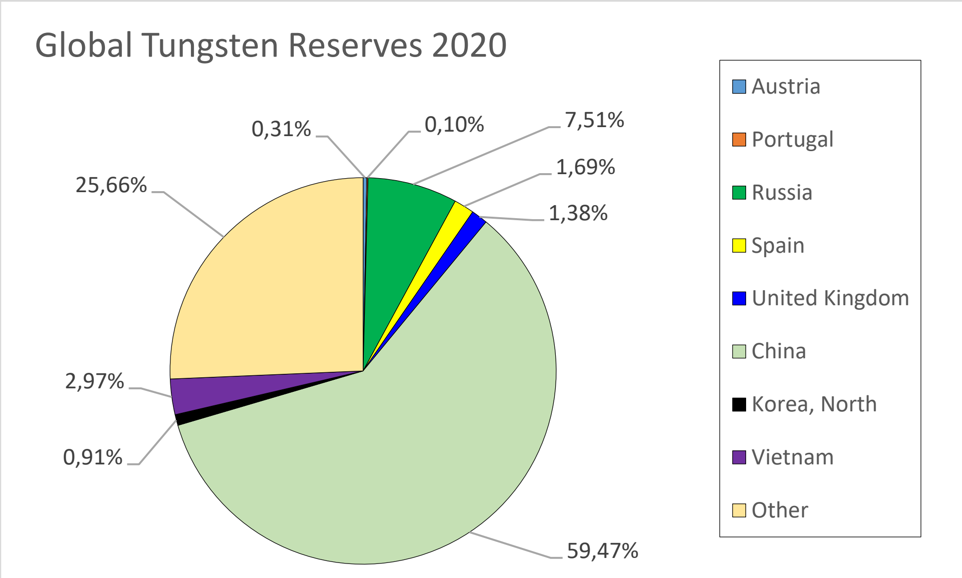

Figure 15. Global tungsten reserves in 2020
(Source: United States Geological Survey Mineral Statistics)

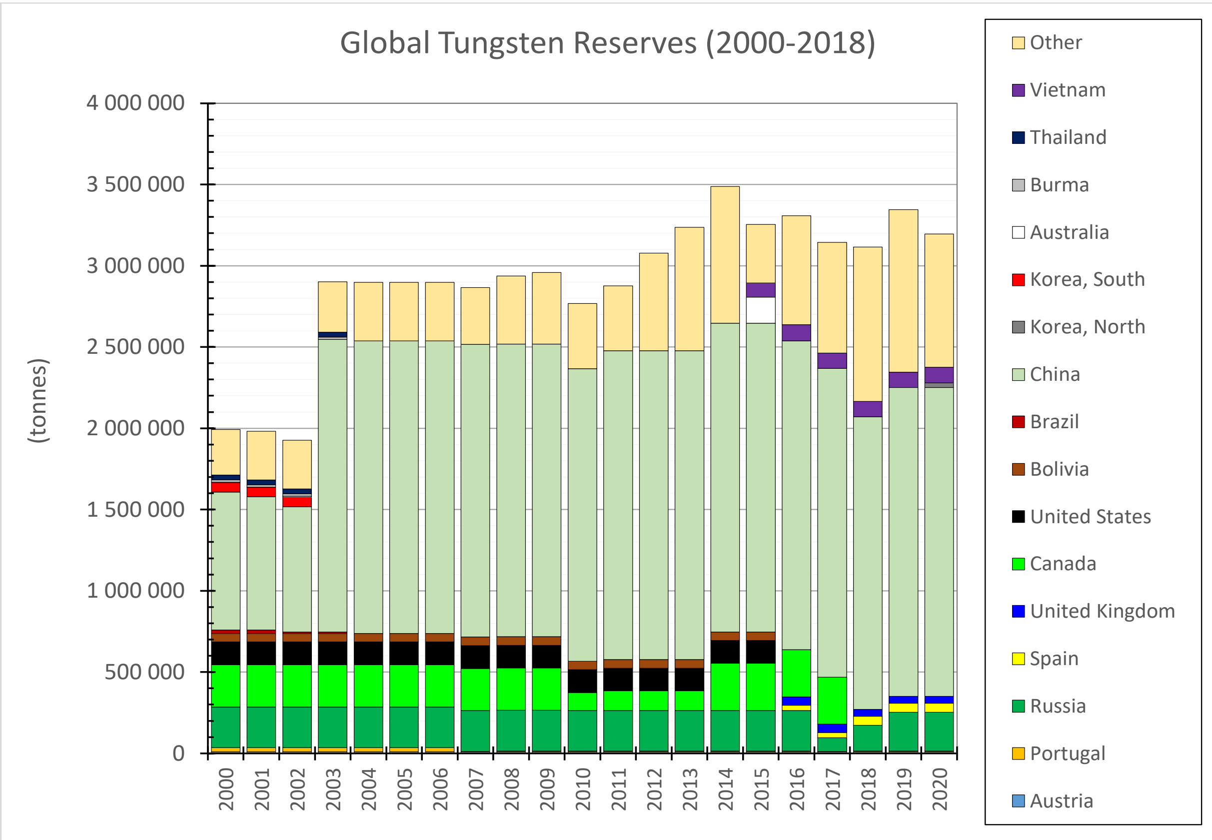

Figure 16. Global tungsten reserves as quoted by USGS 2000 to 2020
(Source: United States Geological Survey Mineral Statistics)

Table 12. Global tungsten reserves as quoted by USGS 2000 to 2020 (Source: USGS Mineral Statistics)

Country	2000 (tonnes)	2001 (tonnes)	2002 (tonnes)	2003 (tonnes)	2004 (tonnes)	2005 (tonnes)	2006 (tonnes)	2007 (tonnes)	2008 (tonnes)	2009 (tonnes)	2010 (tonnes)
Austria	10 000	10 000	10 000	10 000	10 000	10 000	10 000	10 000	10 000	10 000	10 000
Portugal	25 000	25 000	25 000	25 000	25 000	25 000	25 000	2 600	4 700	4 700	4 200
Russia	250 000	250 000	250 000	250 000	250 000	250 000	250 000	250 000	250 000	250 000	250 000
Spain											
United Kingdom											
Canada	260 000	260 000	260 000	260 000	260 000	260 000	260 000	260 000	260 000	260 000	110 000
United States	140 000	140 000	140 000	140 000	140 000	140 000	140 000	140 000	140 000	140 000	140 000
Bolivia	53 000	53 000	53 000	53 000	53 000	53 000	53 000	53 000	53 000	53 000	53 000
Brazil	20 000	20 000	8 500	8 500							
China	850 000	820 000	770 000	1 800 000	1 800 000	1 800 000	1 800 000	1 800 000	1 800 000	1 800 000	1 800 000
Korea, North											
Korea, South	58 000	58 000	58 000								
Australia	1 000	1 000	7 000								
Burma	15 000	15 000	15 000	15 000							
Thailand	30 000	30 000	30 000	30 000							
Vietnam											
Other	280 000	300 000	300 000	310 000	360 000	360 000	360 000	350 000	420 000	440 000	400 000
Global Reserves	1 992 000	1 982 000	1 926 500	2 901 500	2 898 000	2 898 000	2 898 000	2 865 600	2 937 700	2 957 700	2 767 200

Country	2011 (tonnes)	2012 (tonnes)	2013 (tonnes)	2014 (tonnes)	2015 (tonnes)	2016 (tonnes)	2017 (tonnes)	2018 (tonnes)	2019 (tonnes)	2020 (tonnes)
Austria	10 000	10 000	10 000	10 000	10 000	10 000	10 000	10 000	10 000	10 000
Portugal	4 200	4 200	4 200	4 200	4 200	4 200	2 700	3 100	3 100	3 100
Russia	250 000	250 000	250 000	250 000	250 000	250 000	83 000	160 000	240 000	240 000
Spain						32 000	32 000	54 000	54 000	54 000
United Kingdom						51 000	51 000	43 000	43 000	44 000
Canada	120 000	120 000	120 000	290 000	290 000	290 000	290 000			
United States	140 000	140 000	140 000	140 000	140 000					
Bolivia	53 000	53 000	53 000	53 000	53 000					
Brazil										
China	1 900 000	1 900 000	1 900 000	1 900 000	1 900 000	1 900 000	1 900 000	1 800 000	1 900 000	1 900 000
Korea, North										29 000
Korea, South										
Australia					160 000					
Burma										
Thailand										
Vietnam					87 000	100 000	95 000	95 000	95 000	95 000
Other	400 000	600 000	760 000	840 000	360 000	670 000	680 000	950 000	1 000 000	820 000
Global Reserves	2 877 200	3 077 200	3 237 200	3 487 200	3 254 200	3 307 200	3 143 700	3 115 100	3 345 100	3 195 100

Country	**2018** (tonnes)	**2020** (tonnes)
Austria	10 000	10 000
Portugal	3 100	3 100
Russia	160 000	240 000
Spain	54 000	54 000
United Kingdom	43 000	44 000
China	1 800 000	1 900 000
Korea, North		29 000
Vietnam	95 000	95 000
Other	950 000	820 000
Global Reserves	3 115 100	3 195 100

World tungsten resources are geographically widespread. China ranks first in the world in terms of tungsten resources and reserves and has some of the largest deposits. Canada, Kazakhstan, Russia, and the United Kingdom also have significant tungsten resources.

10.1 European Resources

Tungsten resources found in Europe are listed below (Source: Lauri 2018).

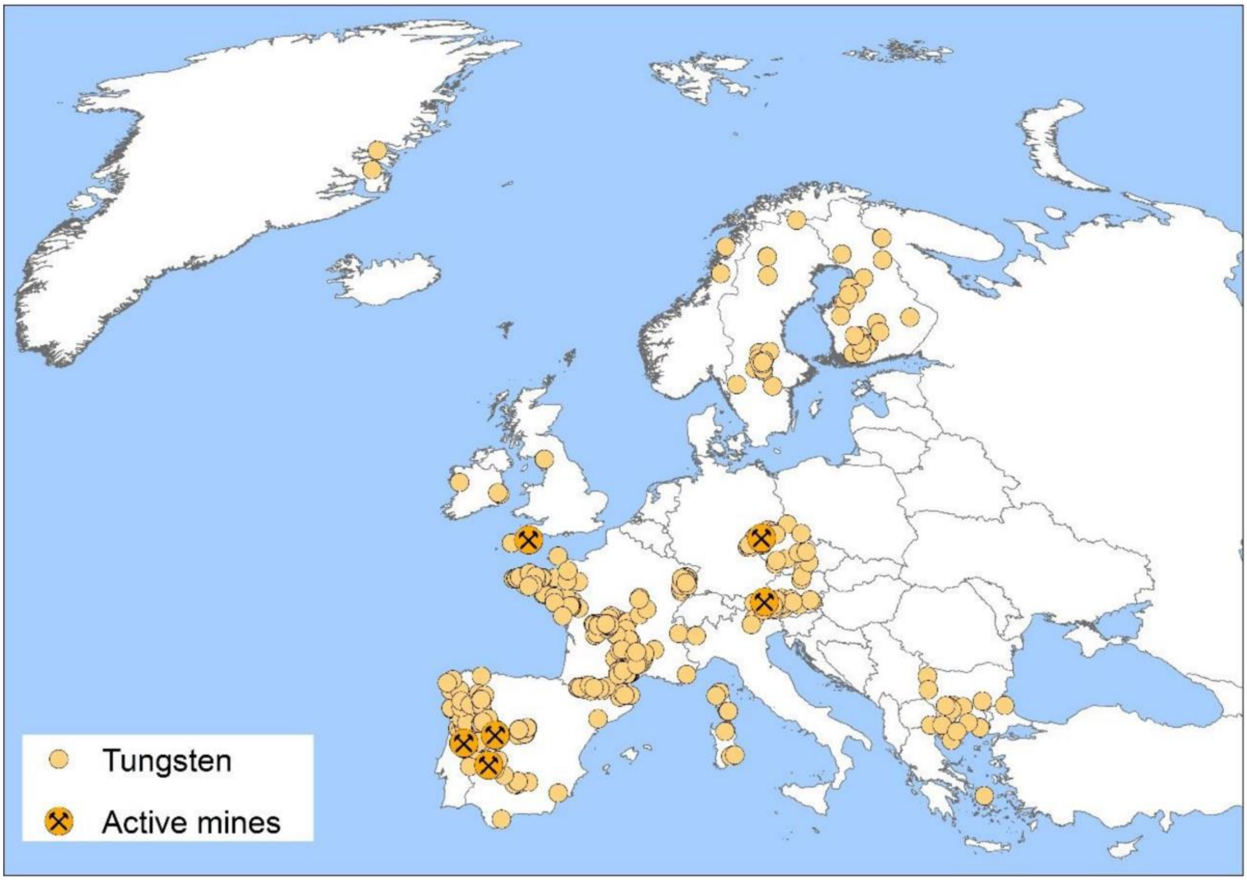

Figure 17. Tungsten occurrence in the EU according to databases (FODD, Promine, M4EU) (Source: Lauri 2018)

Austria: The resources at the Mittersill (Felbertal) mine are about 24,000 t W (Cassard *et al.* 2013). The ProMine database lists also 24 other W occurrences for Austria but does not give any resource data on them.

Bulgaria: Three occurrences with W as the main metal and a number with W as a companion metal are listed in the ProMine database, but none with resource data.

Czech Republic: The Cinovec (Zinnwald) tin granite system has a resource of about 24,000 t W (Cassard *et al.* 2013). In addition, the ProMine database lists six occurrences with W as the main metal, all without any resource figures.

Finland: Finland has 17 occurrences in the FODD database that have tungsten as the main commodity and additional six occurrences in which it is mentioned as a minor commodity (FODD 2017). Five occurrences have associated resource information and in the case of the Ylöjärvi Cu-W mine the data is for the ore mined. Altogether the four other deposits (Ahvenlammi, Apajalahti, Hieronmäki and Kuskoiva) have a non-compliant resource estimate of 2,333 t of tungsten metal, which may be considered as a minimum figure for tungsten resources in Finland.

France: The ProMine database lists 15 W deposits with resource figures and about 100 occurrences without resource data in France. In total, the 15 have a resource of 66,000 t W. There is ongoing exploration to re-open the Salau Au-Cu-W mine (Couflens Project;

http://apollominerals.com.au/projects/couflens-project-france/), in the Pyrenees, where there may be a >5 km long zone of similar orebodies to occur. The ProMine database gives 2,700 t W for the remaining ore at Salau, whereas the largest single resource in France would in the closed Montredon-Labessonnie, with 16,700 t W (Cassard *et al*. 2013).

Germany: Tungsten is listed as a minor metal in several mineral occurrences in Germany, which are mostly granite-related. There is no resource information available for the deposits. The Pöhla deposit in Saxony is currently under investigations (SMEAG 2017).

Greece: There is one medium-sized W deposit with a resource estimated in Greece: the Kimmeria polymetallic skarn. It has a non-compliant resource of 6,000 t W (Cassard *et al*. 2013).

Greenland: Greenland comprises geological environments that are highly prospective for tungsten mineralization. However, only very limited exploration has been undertaken.

East Greenland is considered to have the highest potential for vein- and skarn-type tungsten deposits (Stendal & Frei 2008). Twelve outcropping scheelite occurrences are found in a 350 km long belt in central East Greenland, encompassing the skarn-type occurrences Kalkdal, Knivbjergdal, and Trekantgletscher, and the vein type occurrences Scheelitdal, Galenadal, and Ymer Ø (drilling from three sites revealed approx. 200,000 t @ 0.7-2.5% WO3; Sørensen *et al*. 2014). Several tungsten anomalies associated with gold and arsenic anomalies are present within the Paleoproterozoic Ketilidian Mobile Belt in South Greenland. This tract is considered to hold a moderate potential for tungsten vein deposits. Stratabound, skarn-type scheelite occurrences are known in the Nuuk area (at Ivisaartoq), but unlikely to be of economic interest due to their intermittency.

Ireland: Tungsten occurs in two separate localities in Ireland. In southeast Ireland, tungsten occurs as scheelite in veins and greisened microtonalite sheet complexes close to Ballinglen and in nearby quartz veins or segregations in the country rocks of the Ballinacor area (Gallagher, 1989). In western Ireland, tungsten occurs primarily in skarns and veins associated with granite in Connemara (Kennan *et al*. 1987). Neither location is currently considered to be an economic resource.

Italy: One W occurrence, without a resource, is included into the ProMine database.

Norway: Norway has two tungsten occurrences according to the FODD database (2017). The Laksådal Mo-W deposit contains scheelite and molybdenite, which are present in diopside skarn as veins, lenses and dissemination. The Laksådal deposit was mined in the first half of 20th century. The Målvika tungsten occurrence comprises scheelite mineralisation with some Au+As+Bi anomalies. No resource information is available for the Norwegian deposits.

Portugal: At the end of 2016, the resources (including reserves) at Panasqueira were 10 Mt @ 0.23 % WO3 plus inferred 5.16 Mt @ 0.22 % WO3 (Wheeler 2016). With all the tonnages and tungsten grades calculated into one (no more NI-compliant), the resource is about 27,240 t W metal for Panasqueira. At S. Pedro da Águias (Tabuaço), there is an indicated resource of 0.76 Mt @ 0.58 % WO3 and inferred 1.33 Mt @ 0.57 WO3 (= total 9,500 t W) (Martins 2012). The ProMine database (Cassard et al. 2013) lists eight closed tungsten mines for Portugal; jointly these are reported to contain resources of nearly 40,000 t W. In addition, there are six W occurrences without resource data in the ProMine database.

Spain: At Los Santos, there is a Ni-compliant resource (inclusive reserves) 2.2 Mt @ 0.29 % WO3 plus inferred resources of 1.88 Mt @ 0.25 % WO3 ; this, together with W-rich tailings (2.062 Mt @ 0.15 % WO3) and minor stockpile made a total resource of 15,334 t W metal (2015 data,

http://www.almonty.com/projects/los_santos/). The Valtreixal project in NW Spain has a Ni-compliant W resource of 2.828 Mt @ 0.25 % WO3 , 0.13 % Sn in the indicated and 15.419 Mt @ 0.08 % WO3, 0.12 % Sn (Wheeler 2015). With all the tungsten values calculated into one (no more NI-compliant), the W resource is about 15,400 t for Valtreixal. Three additional W deposits with resource data are listed for Spain in the ProMine database. Jointly these contain 21,800 t W in resources (Cassard *et al*. 2013). In addition, there are 15 closed mines and other W occurrences without a resource in the ProMine database.

Sweden: Sweden has abundant historical tungsten production with at least fourteen small deposits having been in production in 19th and 20th century (FODD 2017). The largest of these deposits is Yxsjöbergsfältet, from which slightly over 5 Mt of ore was produced during the 92 years' time when the mining took place. Noncompliant resource estimates are available for three W occurrences that have not been exploited. Two of these give information on the tungsten content of the ore, with a total of 2.1 Mt of tungsten-bearing ore at 0.2 % of W. This may be considered as a minimum figure for tungsten resources in Sweden.

United Kingdom: Although historic tungsten production has taken place at a number of other mines in south-west and north-west England, any remaining resources associated with these mines have not been quantified. The Hemerdon Mine is the UK's largest tungsten resource and is operated by Tungsten West Ltd. According to the current (September 2019) mineral resource estimate, completed to the JORC (2012) code, the deposit contains 225.9 million tonnes of ore grading 0.12 % WO_3 and 0.02 % Sn. A study to define updated JORC (2012) Reserves of the deposit is in progress at the time of writing this report (Previously quoted by Wolf Minerals in March 2015 as 35.7Mt at 0.18% WO_3 and 0.03% Sn). The Strategic Minerals company have an inferred JORC resource for their Redmoor project which includes a W contribution. Redmoor is a sheeted vein deposit. This deposit, of size 11.7Mt (JORC 2012 resource) at 0.56% WO_3, 0.16% Sn and 0.50% Cu (Strategic Minerals public RNS announcement dated 14/02/2019).

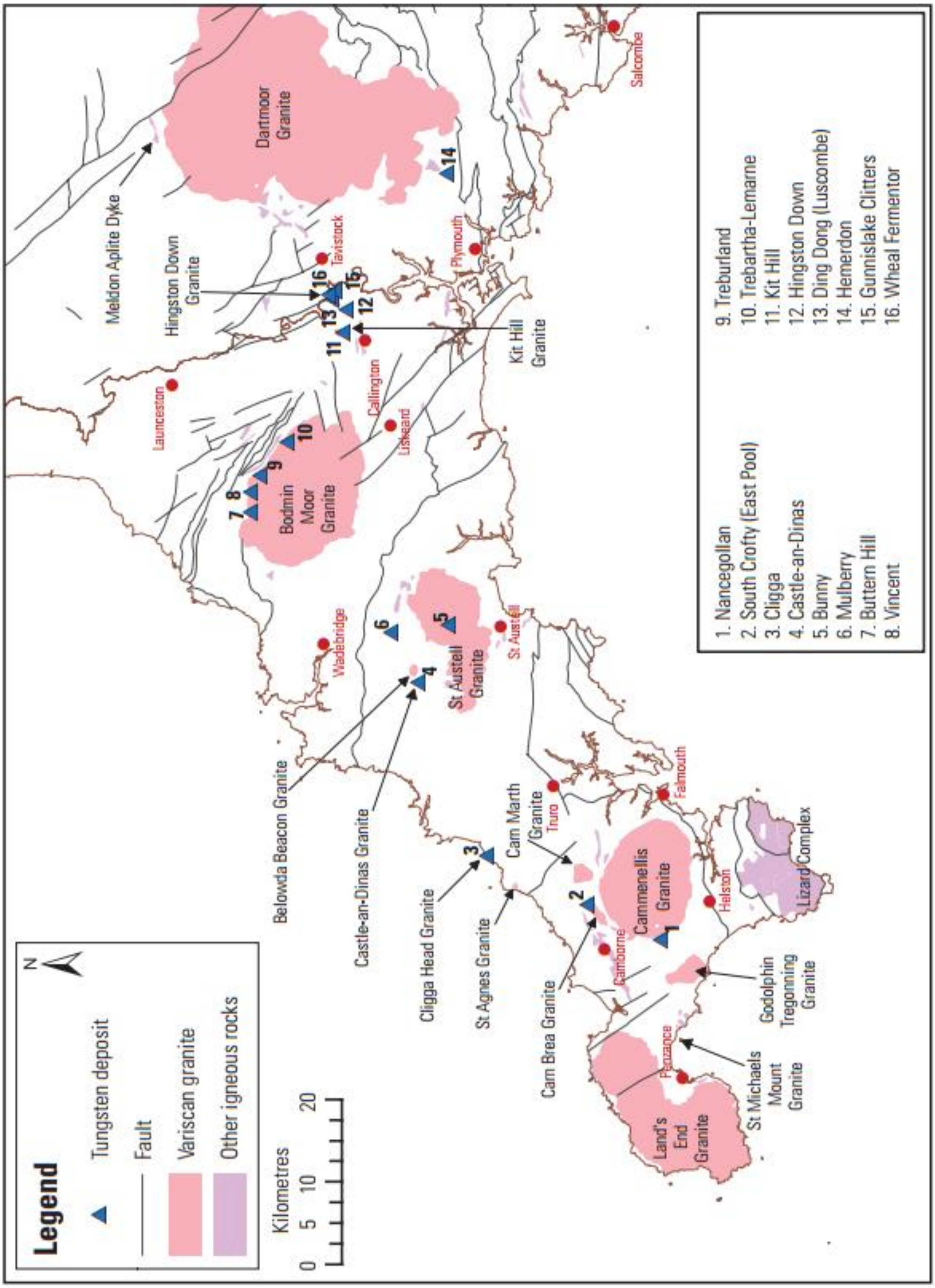

Figure 18. Location of deposits with recorded tungsten production in the Cornubian ore field of south-west England. BGS © NERC. OS topography © Crown Copyright. All rights reserved. BGS 100017897/2011.

11 GLOBAL MINING PRODUCTION OF TUNGSTEN

Figure 19 shows the global production of tungsten in 2018. Figure 20 shows global production by geographical region. Figure 21 and Table 11 show global production data by country between the years 2000 and 2018. Figure 22 shows non-Chinese global production.

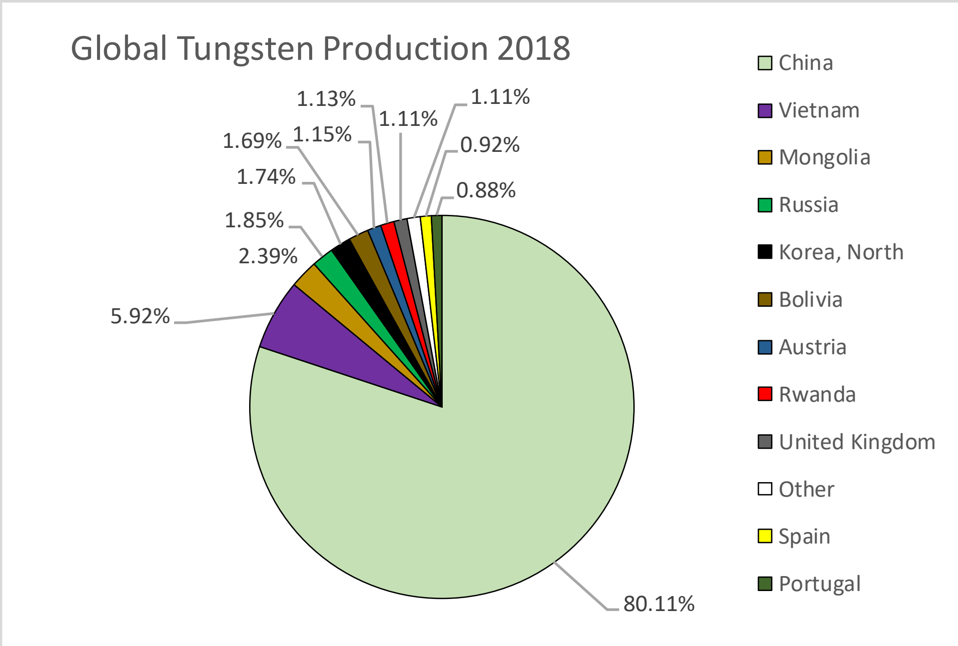

Figure 19. Global tungsten production in 2018 (Source: USGS)

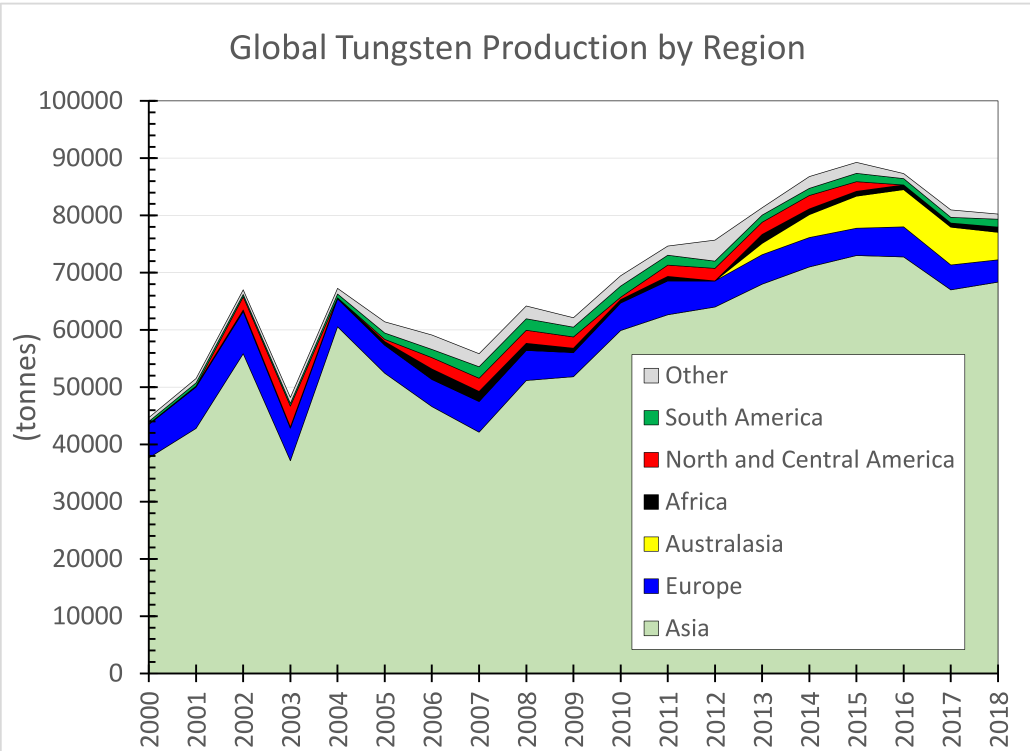

Figure 20. Global tungsten production by geographical region 2000 to 2018 (Source: USGS)

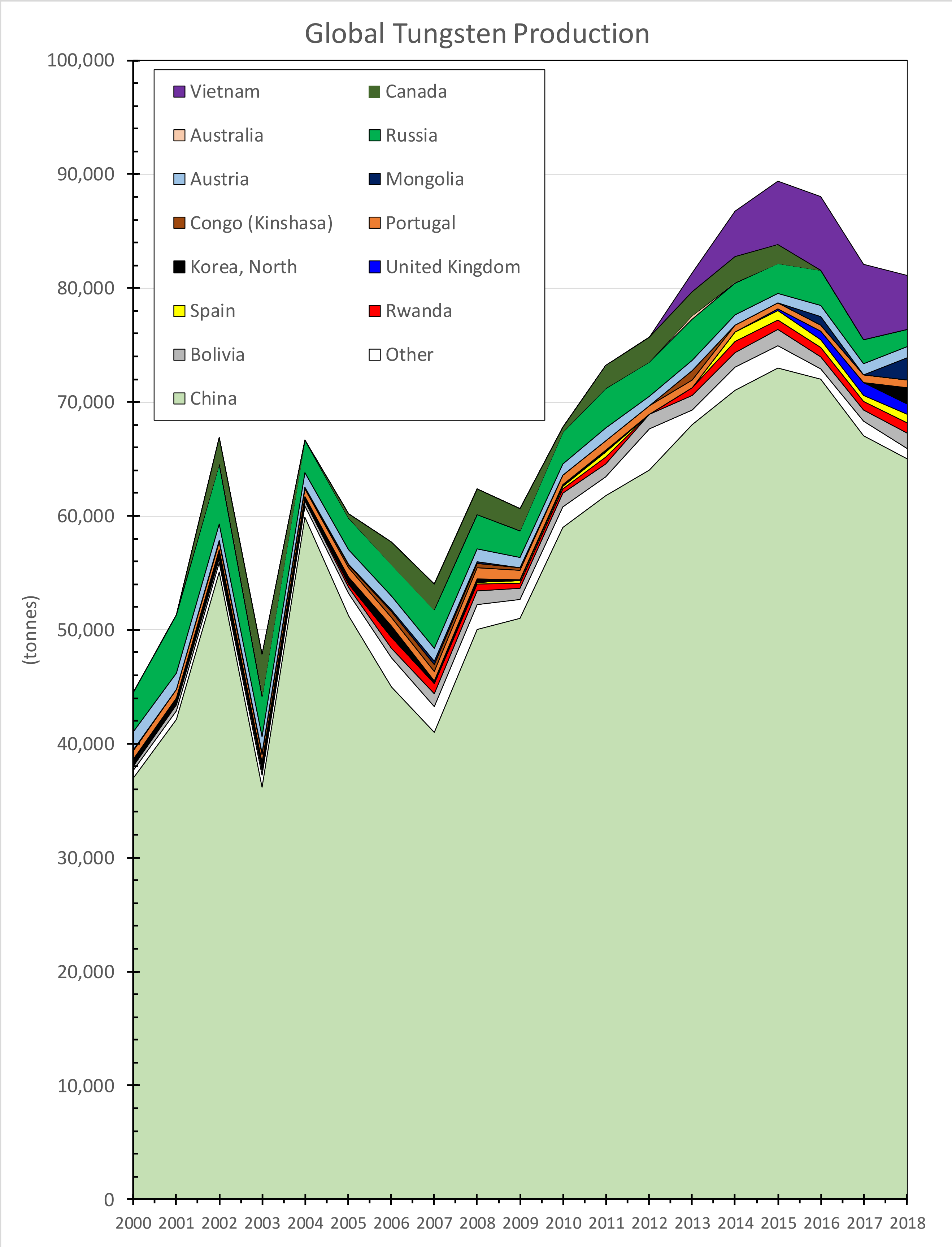

Figure 21. Global production of tungsten 2000 to 2018 (Source: United States Geological Survey Mineral Statistics)

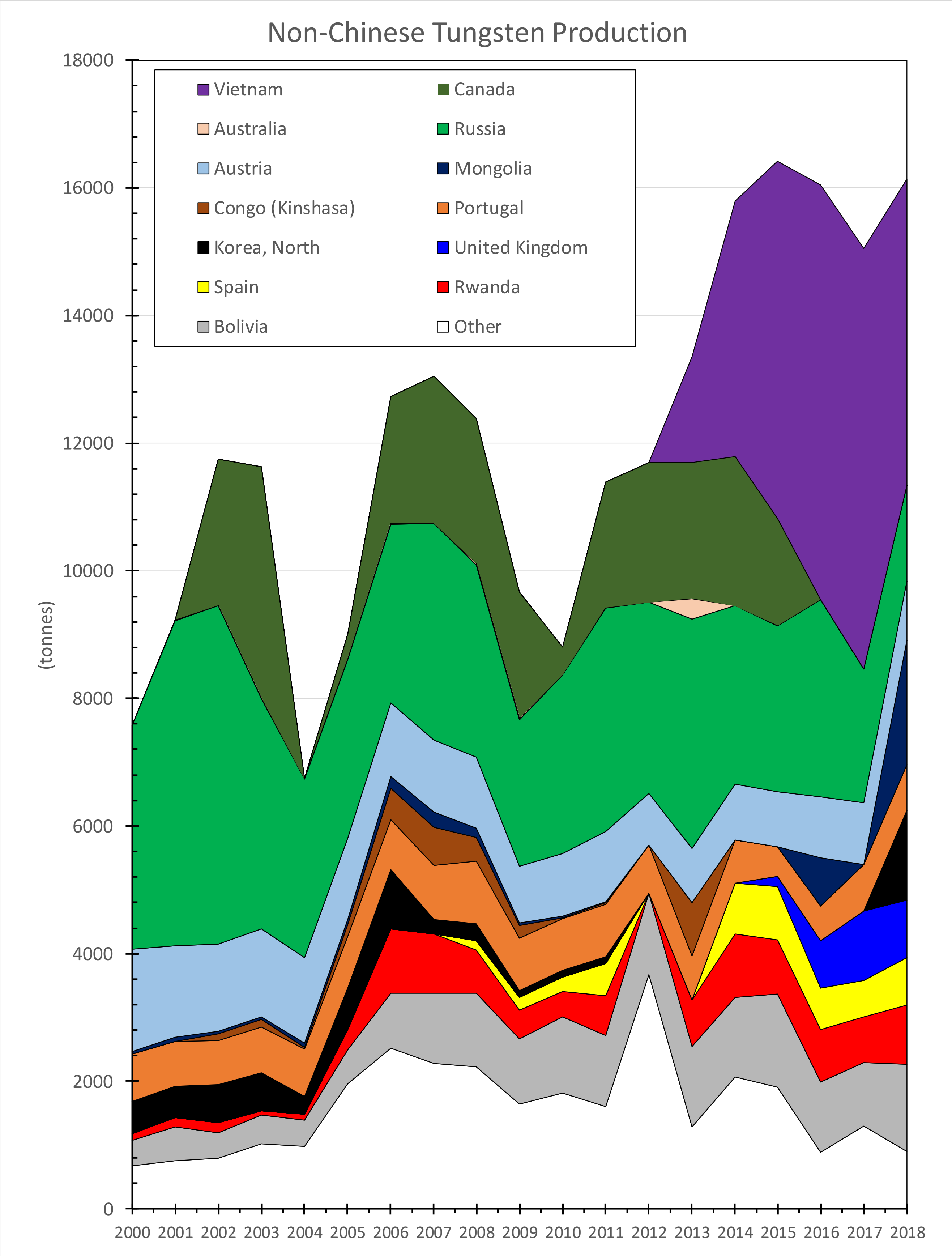

Figure 22. Non-Chinese production of tungsten 2000 to 2018 (Source: United States Geological Survey Mineral Statistics)

Table 13. Global production of tungsten 2000 to 2018 (Source: United States Geological Survey Mineral Statistics)

Country	2000 (tonne)	2001 (tonne)	2002 (tonne)	2003 (tonne)	2004 (tonne)	2005 (tonne)	2006 (tonne)	2007 (tonne)	2008 (tonne)	2009 (tonne)	2010 (tonne)	2011 (tonne)	2012 (tonne)	2013 (tonne)	2014 (tonne)	2015 (tonne)	2016 (tonne)	2017 (tonne)	2018 (tonne)
Austria	1,600	1,429	1,377	1,381	1,335	1,280	1,153	1,117	1,122	887	977	1,100	800	850	870	861	954	975	936
Portugal	743	698	693	715	746	816	780	846	982	823	799	819	763	692	671	474	549	724	715
Russia	3,500	5,100	5,300	3,600	2,800	2,800	2,800	3,400	3,000	2,300	2,800	3,500	3,000	3,600	2,800	2,600	3,100	2,090	1,500
Spain									150	200	229	497			800	835	650	564	750
United Kingdom																150	736	1,090	900
Europe	**5,843**	**7,227**	**7,370**	**5,696**	**4,881**	**4,896**	**4,733**	**5,363**	**5,254**	**4,210**	**4,805**	**5,916**	**4,563**	**5,142**	**5,141**	**4,770**	**5,253**	**4,353**	**3,901**
Burundi				13	8	94	238	144	125	79	107	110							
Congo (Kinshasa)			100	120	20	180	500	600	370	200	25	30		830					
Rwanda	108	142	153	69	90	318	1,000	920	670	450	390	620		730	1,000	850	820	720	920
Uganda		17	16	1	52	36	75	86	50	9	55	10							
Africa	**108**	**159**	**269**	**203**	**170**	**628**	**1,813**	**1,750**	**1,215**	**738**	**577**	**770**		**1,560**	**1,000**	**850**	**820**	**720**	**920**
Canada			2,295	3,636		384	1,983	2,305	2,277	1,964	420	1,967	2,190	2,130	2,340	1,680			
United States	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
North and Central America			**2,295**	**3,636**		**384**	**1,983**	**2,305**	**2,277**	**1,964**	**420**	**1,967**	**2,190**	**2,130**	**2,340**	**1,680**			
Bolivia	393	532	399	441	403	531	868	1,107	1,148	1,023	1,204	1,124	1,270	1,250	1,250	1,460	1,110	994	1,370
Brazil	18	22	24	30	262	577	525	537	408	192	166	170							
Peru				20			50	366	456	502	571	439							
South America	**411**	**554**	**423**	**491**	**665**	**1,108**	**1,443**	**2,010**	**2,012**	**1,717**	**1,941**	**1,733**	**1,270**	**1,250**	**1,250**	**1,460**	**1,110**	**994**	**1,370**
Burma	74	85	83	96	107	168	197	183	136	87	163	130							
China	37,000	42,100	55,100	36,200	59,900	51,200	45,000	41,000	50,000	51,000	59,000	61,800	64,000	68,000	71,000	73,000	72,000	67,000	65,000
Korea, North	500	500	600	600	280	650	930	230	270	100	110	110							1,410
Mongolia	52	63	35	40	77	78	182	245	142	39	20	13					753		1,940
Thailand	30	50	31	216	187	345	303	477	617	600	600	600							
Asia	**37,656**	**42,798**	**55,849**	**37,152**	**60,551**	**52,441**	**46,612**	**42,135**	**51,165**	**51,826**	**59,893**	**62,653**	**64,000**	**68,000**	**71,000**	**73,000**	**72,753**	**67,000**	**68,350**
Australia		15	7	7	12	7	15	7	28	33	16	15		320					
Vietnam														1,660	4,000	5,600	6,500	6,600	4,800
Australasia		**15**	**7**	**7**	**12**	**7**	**15**	**7**	**28**	**33**	**16**	**15**		**1,980**	**4,000**	**5,600**	**6,500**	**6,600**	**4,800**
Other	**674**	**752**	**796**	**1023**	**985**	**1955**	**2515**	**2275**	**2232**	**1641**	**1808**	**1597**	**3670.0**	**1290**	**2060**	**1910**	**880**	**1300**	**900**
World Production	**44,692**	**51,505**	**69,304**	**51,844**	**67,264**	**61,803**	**61,097**	**58,150**	**66,460**	**64,093**	**69,880**	**76,618**	**77,883**	**83,482**	**89,131**	**91,100**	**88,052**	**82,057**	**81,141**

11.1 Chinese Production of Tungsten

The largest international producer of tungsten is China, which has more than ten major tungsten mines with an annual output over 1300 tonnes of WO_3. Most of these mines are located in Jiangxi and Hunan, in the south of China (Yang 2018).

The Xianglushan deposit located in Jiangxi is the largest tungsten mine in China with an annual output of over 5700 tonnes of WO_3. The Shizhuyuan in Hunan is a large polymetallic tungsten mine with an annual output of 5500 tonnes of WO_3. It is a W-Sn-Mo-Bi polymetallic deposit and characterized by low grade and complicated composition (Han et al., 2017). The ore contains scheelite, wolframite, molybdenite, cassiterite, bismuthinite, andfluorite.

11.2 Vietnamese Production of Tungsten

The Nui Phao mine in Vietnam is the largest tungsten mine outside of China and a unique polymetallic mine with significant amounts of tungsten, fluorspar, bismuth and copper. The mining reserves are 66 million tonnes of ore with an average grade 0.21% WO_3 (Masan Resources, 2012).

11.3 European Production of Tungsten

Europe is only partially self-sufficient in the production of tungsten. In 2018, EU28 countries produced 3,901 tonnes of tungsten (contained metal) with production coming Austria, Portugal, Spain, and the United Kingdom. The EU's production has remained relatively constant over the past 20 years, with declines in Austria and Portugal being offset by new production in Spain from 2008 onwards and now also from the UK (Figure 20 and 23).

Table 14. Global and EU supply of tungsten in 2015 (Source: Brown *et al* 2018)

Tungsten sub-commodity or form	Largest three global producers in 2015	Origin of largest three importer to EU-28 from non-EU countries in 2015
Ores & Concentrates	China (89%), Vietnam (6%), Russia (3%)	Mongolia (42%), Bolivia (18%), Brazil (11%)
Oxides & Hydroxides	no data available	Russia (33%), China (30%), USA (25%)
Tungstates	no data available	Vietnam (67%), China (26%), USA (5%)
Carbide	no data available	USA (35%), South Korea (26%), China (15%)
Powders	no data available	China (43%), USA (25%), Canada (25%)
Unwrought metal	no data available	China (45%), Russia (21%), USA (12%)

Globally, production of tungsten in 2018 amounted to 92,132 tonnes, with 80.11% of this being produced by China. The EU's output therefore represents just 4.2% of the global total, or 14.4% of the non-Chinese production.

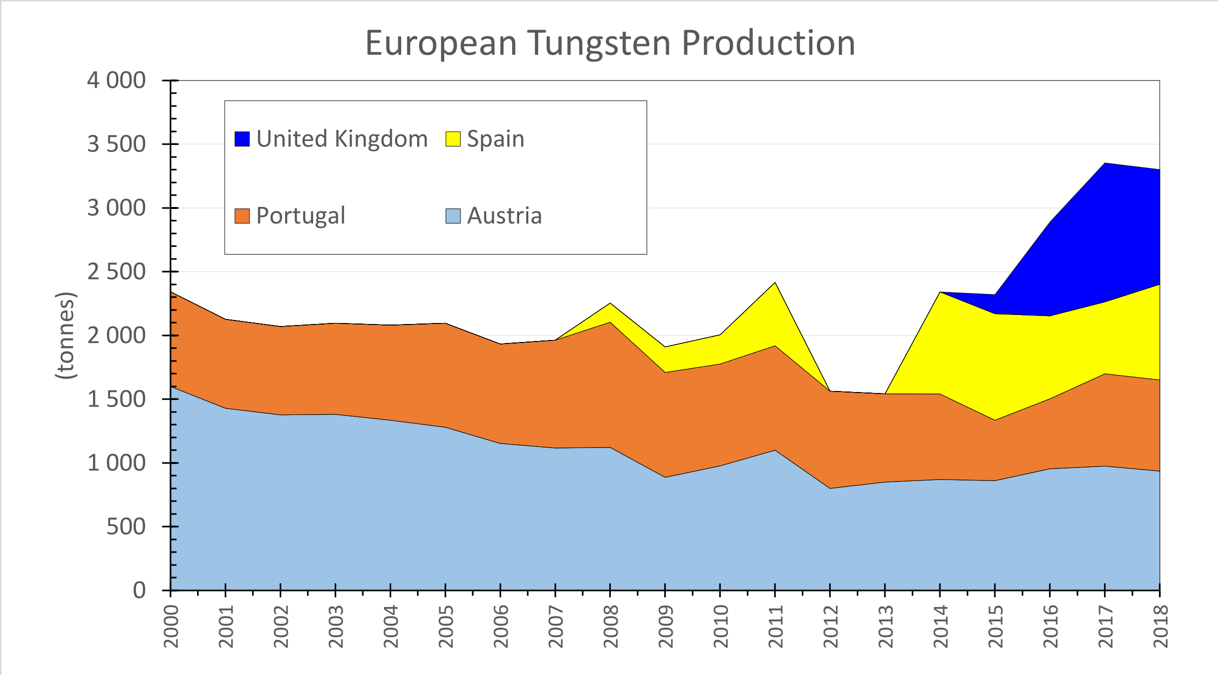

Figure 23. Mine production of tungsten in EU-28 countries between years 1996 to 2015
(Source: Brown *et al* 2018)

Austria: Tungsten is produced from the Mittersill scheelite deposit in Austria by Wolfram Bergbau und Hütten AG. Mittersill is a metamorphosed granite-related stockwork-type tungsten deposit. The scheelite concentrate produced is used by the company for upstream products (tungsten carbide powder, tungsten metal powder and tungsten oxide). Annual capacity of the mine is in the range of 0.4 Mt @ 0.4 % WO 3 (Raith & Schmidt 2010). According to USGS (2018), the mine production of tungsten in 2017 in Austria was estimated at 950 Mt. (Source: Brown et al 2018)

Germany: Saxony Minerals and Exploration AG is working at the Pöhla deposit in Saxony, Germany with the aim of starting tungsten, tin, indium and fluorite production (SMEAG 2017). According to the company, pilot scale production started in late 2017.

Portugal: The Panasqueira tungsten mine in Portugal is operated by Almonty Industries (2018). The production has since 2000 varied at 630–1330 t/a W (Wheeler 2016); in 2017 the production is estimated to be 658 t W (USGS 2018).

Spain: In 2017, tungsten production in Spain is estimated to be about 570 t (USGS 2018). Almonty Industries holds the Los Santos mine, which produces tungsten concentrate. The La Parilla tungsten mine started operation in 2016; it has JORC-compliant resources of 49 Mt @ 0.10 % WO3 and 0.11 % Sn by W Resources (2018). The W metal resource of the mine is, hence, 38,855 t.

United Kingdom: The UK has a history of tungsten production spanning almost 120 years. During this time, the UK has produced approximately 5,000 tonnes of tungsten, primarily from mines in the south-west of England. The majority of this production occurred during the First (1914–1918) and Second (1939–1945) World Wars when demand for high-speed steel and munitions increased dramatically (Pitfield and Brown 2011).

In the UK, primary tungsten production only takes place at one mine, the Hemerdon tungsten-tin mine (Formerly called Drakelands Mine) in Devon. This depoist could be one of world's largest tungsten and tin resources. The Hemerdon Mine is working the Hemerdon deposit which was first discovered in 1867; however, it wasn't until 1917 that it was worked on a commercial scale, which stopped operation in 1944. The Hemerdon Ball mine was renamed as Drakelands Mine in 2007 and operated by Wolf Minerals until 2018. In 2019, Hemerdon was reopened by Tungsten West Limited, with the goal of restarting production.

12 BENEFICIATION OF TUNGSTEN

Scheelite ($CaWO_4$) and wolframite ($(Fe, Mn) WO_4$) are the only tungsten minerals mined commercially and are mainly found in five types of deposits: skarn, vein/stockwork, porphyry, disseminated and stratabound. Gravity concentration and flotation are the beneficiation techniques most commonly applied to scheelite ore, and gravity and/or magnetic separation for wolframite ore.

Beneficiation processes normally involve a pre-concentration step after crushing and grinding the run-of-mine ore, which is followed by processing the pre-concentrate, cleaning the concentrate or subjecting it to an up-gradation process, and lastly, a final purification stage to meet market specifications. The tungsten concentrate has to be 65 to 75% WO_3 to meet the requirements of international trading (Krishna, 1996; Lassner and Schubert, 1998).

The main challenges in tungsten ore beneficiation which may affect process recovery and/or concentrate grade are as follows (Yang 2018):

- Scheelite ore often has good floatability but it is often associated with other calcium containing minerals such as calcite, fluorite and apatite, which have similar surface chemistry properties to scheelite. It is usually difficult to separate scheelite using flotation from these minerals using conventional reagents (Yin and Wang, 2014).

- In the beneficiation process, most of the loss of tungsten occurs in slimes, which are difficult to be treated with conventional beneficiation techniques. The generation of tungsten mineral slimes results from the brittleness of the tungsten minerals, leading to their preferential grinding during the comminution stages; moreover, due to their high density, the tungsten minerals tend to remain in the over-size fraction or underflow during classification by hydrocyclones or hydraulic type of classifiers used in the grinding circuit, and then get recycled to the grinding mill, leading to their over-grinding (Krishna 1996).
- The beneficiation flow sheet largely depends on the ore mineralization and the liberation size of tungsten minerals. Tungsten ores usually have complex mineralogy (complex mineral compositions and ore textures). Other metallic minerals are present and the liberation of tungsten minerals can be found in a wide size range from several mm to 10–20µm. These factors cause beneficiation flow sheets complex.

- Weathering and other alteration processes lead to secondary tungsten minerals such as hydrotungstite ($H_2WO_4 \cdot H_2O$), anthoinite ($AlWO_3(OH)_3$) and cerotungstite ($CeW_2O_6(OH)_3$). The presence of these minerals might cause lower process recovery and/or lower concentrate grade (Schmidt 2012a & 2012b).

12.1 Comminution of Tungsten

Comminution of tungsten ore could be the most economically useful process step to optimize for final recovery. Due to the brittle character of both scheelite and wolframite, comminution is carefully designed to avoid overgrinding, that is, to minimize formation of fines; at every stage of comminution, appropriate sizing techniques (screening, hydro-classifications by using hydrocyclones or classifiers) are used, and rod milling is more commonly used than ball milling. Rod milling of scheelite has another benefit compared to ball milling according a study by Li and Gao (2017), which concluded that the rod milled scheelite particles are deemed to be more hydrophobic and have a higher flotation recovery due to stronger interaction with the collector and easier attachment to air bubbles.

12.2 Sorting of Tungsten

X-ray sorting and gravitational methods are normally used for pre-concentration. Optical sorting and/or hand-picking methods are also used for pre-concentration of wolframite ore (Yang 2018). Tungsten West have shown this to be a particularly effective preconcentration method at Hemerdon.

12.3 Gravity Separation of Tungsten

The high density of both scheelite and wolframite facilitates their separation from the gangue minerals by gravity techniques. Jigs, spirals, shaking tables and centrifugal concentrators (the Knelson, Kelsey and Falcon concentrators) are usually used in operations where there is a wide range of particle size.

Normally, two concentration flowsheets are used for scheelite ore flotation: (1) whole ore flotation after pre-concentration and; (2) gravity-flotation flowsheet. Gravity concentration is to remove the low density fraction (e.g. calcite, fluorite etc.) before flotation of scheelite (Yang 2018).

12.4 Magnetic Separation of Tungsten

Wolframite can be paramagnetic. Ferberite is paramagnetic, specifically when as the Fe end member. Thus, high intensity magnetic separation (HIMS) can be used to separate wolframite and scheelite from diamagnetic minerals such as cassiterite (Angadi 2015). Industrial applications of magnetic separations for scheelite ore concentration are rare but high gradient magnetic separation (HGMS) is used for scheelite - wolframite separation at the Shizhuyuan mine in China (Han et al., 2017).

Low-intensity magnetic separation (LIMS) can be used to remove magnetite and other ferromagnetic materials.

Electrodynamic or electrostatic separators are used for scheelite cassiterite separation as scheelite is non-conducting whereas cassiterite is a conducting material (Lassner and Schubert, 1998) and also used to separate cassiterite from wolframite and scheelite for a wolframite scheelite-cassiterite ore (Angadi 2015).

12.5 Flotation of Tungsten

Flotation is rarely applied to wolframite ore since it occurs mainly in much coarser mineralization for which there is a preference for gravity and magnetic methods (Lassner and Schubert, 1998). Only scheelite is readily amenable to flotation. But for fine grained and complex wolframite ores flotation becomes an effective method for recovery of fine wolframite (Pradip, 1996; Meng et al. 2015a; Ai et al., 2017a). Wolframite flotation is performed similarly to the scheelite flotation, but is not pH sensitive and can therefore be undertaken in both acidic and alkaline solutions.

The beneficiation techniques of gravity concentration and flotation are often applied for scheelite ore, and gravity and/or magnetic separation for wolframite ore. Moreover, pre-concentration methods are usually used to discard a portion of the run-of-mine ore and increase the head grade prior to traditional beneficiation stages. The beneficiation flow-sheet depends on the nature of the mineralization in the ore body and on the chosen liberation particle size, defined by the grain size of the tungsten minerals.

Scheelite flotation is performed in an alkaline medium, with sodium carbonate or sodium hydroxide to adjust the pH to about 9–10.5. The most important collectors are fatty acids such as oleic acid, linoleic acid and palmitic acid (Bernhart, 2015), and sodium oleate, tall oil or oxidized paraffin soap (Han *et al.*, 2017). Figure 24 shows the beneficiation flow sheet of tungsten minerals (scheelite and wolframite) at the Shizhuyuan mine in China.

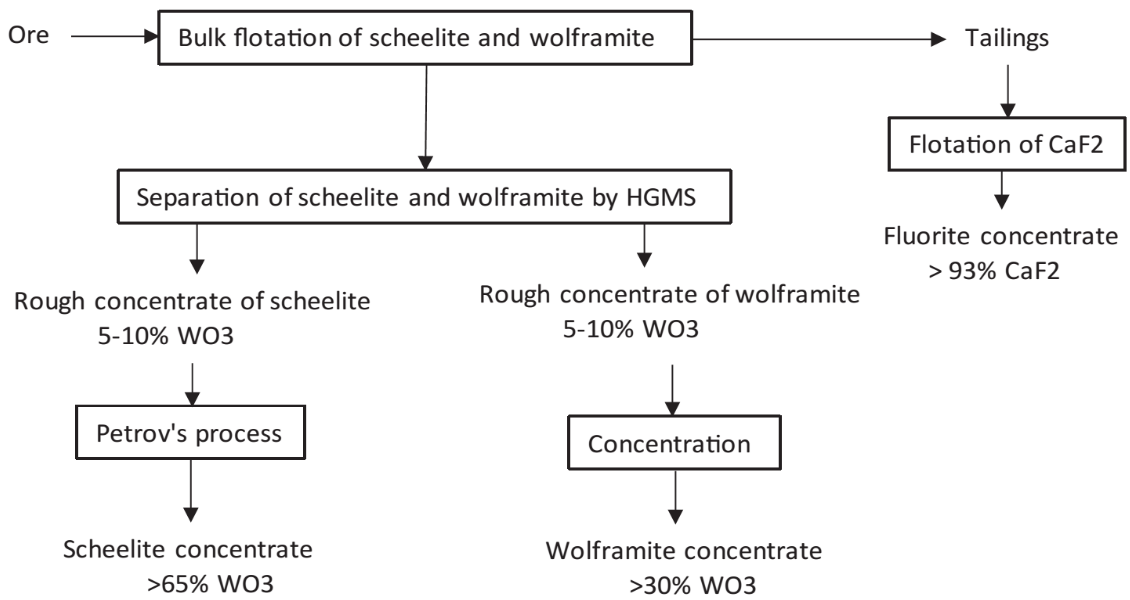

Figure 24. Beneficiation flowsheet of tungsten minerals (scheelite and wolframite) at the Shizhuyuan mine (Source: Yang 2018)

12.6 Hydro-metallurgy of Tungsten

Acid leaching can be performed to remove apatite and calcite (Li and Li, 1983). For example, in the process implemented at the Salau mine (France, closed in 1986) HNO_3 was used to remove the apatite and carbonates present in the scheelite concentrate after flotation.

After digestion and purification of the raw material, the concentrated leachates enter the solvent extraction cycle. There are several processes to produce high-purity ammonium paratungstate (APT), the most important intermediate for pure Tungsten production:

1. **Digestion**: alkali leaching, pressure leaching with soda and acid leaching.

2. **Purification**: filtration and precipitation. Silicates are common impurities, which can be precipitated by aluminum sulphate or magnesium sulphate solution at pH 8-11. Phosphates and fluorides are co-precipitated. Molybdenum is precipitated with sodium sulphide in a neutral or slightly alkaline environment, forming triomolybdate, which is in turn precipitated into trisulfide, by adding sulphuric acid at pH 2.5-3. This is also selected for other sulphides: As, Sb, Bi, Pb and Co.

3. **Solvent extraction**: tertiary or secondary aliphatic amines are the most important extractants. Extractants are dissolved in kerosene or other aliphatic solvents. Phase modifiers such as isodecanol can be added.

4. **Ion exchange**: the sodium tungstate solution is contacted with a strongly alkaline ion exchange resin in the chloride form, where the tungstate is adsorbed. Desorption is carried out with an ammonium chloride solution.

5. **Crystallization**: the isopolytungstate solution is evaporated and the water and ammonia are distilled, which are in turn recycled in the solvent extraction step. The solubility becomes lower and APT crystallizes in recirculating batch crystallizers, which is an additional purification step, in which soluble impurities remain in the mother liquid.

12.7 Pyrometallurgy of Tungsten

Tungsten concentrates that remain after processing the ore may be directly converted into Ferro-Tungsten (aluminothermic and carbothermic reduction process), steel (in an EAF) and Tungsten chemicals, or indirectly into metal powder (hydrogen reduction of tungsten oxide at 600-1000ºC) and carbides (resulting in high purity tungsten powder and tungsten powder carbonization using high-purity carbon black, soot or graphite).

12.8 Fine and very fine scheelite and wolframite recovery

In the operations of tungsten concentration most tungsten loss can be attributed to slimes or very fine particles (Yang 2018). According to an early published paper up to 1/5th of the tungsten mined in the world is lost in the form of fines (Subrahmanyam and Forssberg, 1990).

The terms 'fines' and 'very fines' can be applied to particles less than 100 µm and 20 µm, respectively, according to the size classification proposed by Sivamohan and Forssberg (1985). In order to increase the recovery for low grade and finely disseminated mineral deposits many flotation operations need to improve the liberation of minerals by grinding them to very fine sizes (Miettinen *et al.*, 2010). Due to their brittle nature tungsten minerals (wolframite and scheelite) are easily over-crushed and over-ground in the comminution circuits which causes the formation of fine particles (Yang 2018).

Since the 1990's some experimental studies have been carried out on fine tungsten recovery by gravity separation methods (Traore *et al.* 1995; Wells, 1991). A multi-gravity separator (MGS) was evaluated through testing using a fine scheelite ore with a particle size of −100 µm (Traore et al., 1995). The design and optimization of fine gravity concentration circuits were described using some heavy minerals including scheelite and wolframite (Wells, 1991). However, most investigations on fine scheelite and wolframite beneficiation focused on flotation (Yang 2018).

Wolframite is generally recovered by gravity methods as long as the particle size is sufficiently large, the recovery of fine wolframite by gravity methods being normally below 45% (Ai et al., 2017a). Flotation is therefore applied for recovery of fine wolframite. The studies by Shang et al. (2015) and Yang et al. (2014) indicated that the floatability of wolframite is related to the iron-manganese ratio in wolframite, which affects the reaction mechanism between the wolframite surface and the reagents (Yang 2018).

Flotation of fine wolframite was investigated in recent years mainly with the hydroxamic acid type of reagent as the collector for wolframite, such as sodium hydroxamate, octyl hydroxamic acid and benzohydroxamic acid (Hu *et al* 1997a & 1997b; Meng *et al*. 2015a & 2017; Ai et al. 2017b). The tests (Meng et al., 2015a & 2017) indicated that better floatability of wolframite was obtained at pH 7.0–10.0 using octyl hydroxamic acid as the collector (Yang 2018).

13 TUNGSTEN PRODUCT MANUFACTURE

This section looks at what form do tungsten saleable products take.

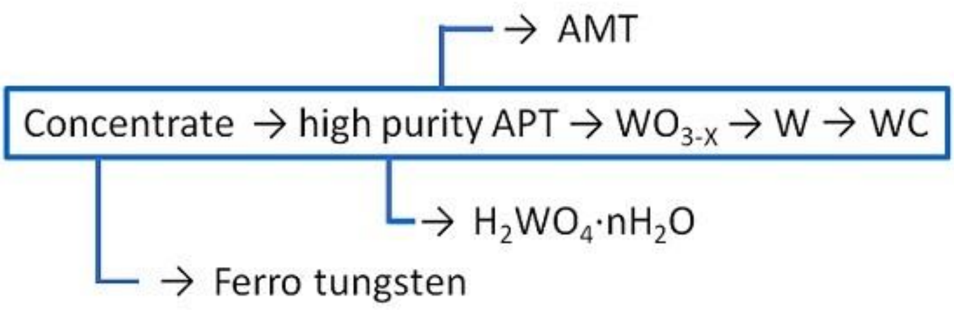

Figure 25. The basic process path of tungsten product manufacture
(Source: 2011 International Tungsten Industry Association)

13.1 Concentrates

Marketable ore concentrates of scheelite and wolframite (hübnerite, ferberite) contain typically 65 – 70 % WO_3. Off-grade concentrates having lower WO_3 concentrations are seldom on the market and if so, only for a lower price. In fully integrated companies lower grades (6-40% WO_3) are often preferred, because upgrading to high concentrations is mostly combined with a lower yield.

Concentrates are packaged either in large polyethylene bags (1 to 2 tons) or, alternatively, in steel drums and individual packaging (40 to 200kg) (Source: International Tungsten Industry Association).

13.2 Ammonium Paratungstate

Ammonium Paratungstate $(NH_4)10[H_2W_{12}O_{42}].4H_2O$ is the most important precursor for the majority of tungsten products (also termed APT). Exceptions are only products of melting metallurgy and Menstrum WC produced directly from ore concentrates.

All other intermediates such as tungsten trioxide, tungsten blue oxide, tungstic acid and ammonium metatungstate can be derived from APT, either by thermal decomposition or chemical conversion.

APT is a white crystallized powder having average crystal size between 30 and 100 µm. Especially crucial for the quality is the purity (Source: International Tungsten Industry Association).

Table 15. Typical levels of today's commercial APT (Source: International Tungsten Industry Association)

Element	Upper Limit of containimation (µg/g)	Element	Upper Limit of containimation (µg/g)
Al	1-7	Mo	5-30
As	5-10	Na	5-10
Bi	0.5-1	Ni	1-7
Ca	1-10	P	5-7
Co	1-10	Pb	1-5
Cr	1-10	S	5-7
Cu	1-3	Si	1-10
Fe	3-10	Sn	1-10
K	2-10	Ti	3-10
Mg	1-7	U	3-10
Mn	1-10		

13.3 Tungsten Oxides & Acid

Intermediates, such as tungsten trioxide, tungsten blue oxide, tungstic acid, and ammonium metatungstate can be derived from APT as shown below, either by partial or complete thermal decomposition or by chemical attack (Source: International Tungsten Industry Association).

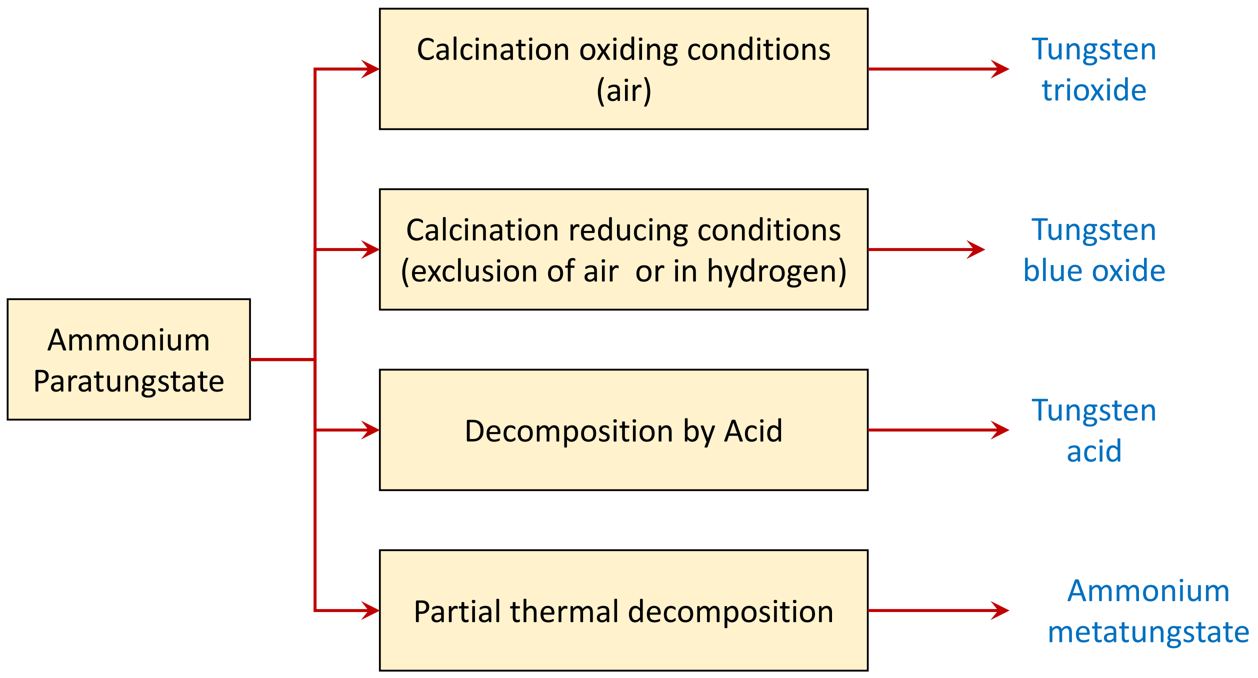

Figure 26. Tungsten Oxides & Acid products (Source: International Tungsten Industry Association)

Tungsten Trioxide (WO_3)
Tungsten trioxide is almost exclusively manufactured by calcination of APT under oxidising conditions (in air). WO_3 is one of the most important, highly pure intermediates for the production of other tungsten compounds including tungsten metal powder. In the latter application, it was substituted to a large extent by tungsten blue oxide. Because of its bright yellow colour it is used as a pigment in oil and water colours. It is employed in a wide variety of catalysts, most recently for the control of air pollution and industrial hygiene (DeNOx) (Source: International Tungsten Industry Association).

Tungsten trioxide particles are pseudomorphous to APT; which means the particles have the same shape and size as the former APT crystals, but consist of very small WO_3 grains. The yellow powder is packaged in sealed polyethylene-lined steel drums and individual packaging (20 to 50kg).

Tungsten Blue Oxide (TBO; WO_3-X)
TBO is manufactured by calcination of APT under more or less reducing conditions which vary from producer to producer. TBO is not a chemically defined compound, but consists of various different constituents, like trioxide, tungsten bronzes and different lower tungsten oxides. The relative amount of these compounds in TBO depends on the calcination parameters, (the parameter x typically varies between 0.01 and 0.10).

TBO is the most important precursor in the line from oxide to W and WC powder. The color varies between deep dark blue to blue, faint blue and green blue. Also the TBO particles are pseudomorphous to the original APT crystals, as described for tungsten trioxide (Source: International Tungsten Industry Association).

Tungstic Acid $H_2WO_4.nH_2O$

Tungstic acid, formally the most important intermediate in tungsten chemistry, is now exclusively manufactured from APT, in order to make use of the high purity APT level. For that purpose an aqueous APT slurry is treated with hydrochloric acid and tungstic acid is precipitated, which is then filtered, washed and dried. Tungstic acid has a very high active surface and is only used in small quantities for special purposes such as the production of ultrafine W and WC powders and tungsten chemicals (Source: International Tungsten Industry Association).

Ammonium Metatungstate $(NH_4)6[H_2W_{12}O_40].3H_2O$

Ammonium Metatungstate $(NH_4)6[H_6W_{12}O_40].3H_2O$ has gained increasing usage for a variety of applications, especially chemicals and catalysts, because of its excellent solubility in water. The usual commercial product contains 3 to 4 molecules of water. On an industrial scale, it is obtained by partial thermal decomposition or partial replacement of ammonium ions by hydrogen ions using selective ion exchange and subsequent evaporation (Source: International Tungsten Industry Association).

AMT is a white crystallized powder. Between 200 and 300°C, it converts to the anhydrous form. Further decomposition leads to WO_3. At 80°C, 2,200 g WO_3/l are dissolved in water.

AMT is used for the preparation of heteropoly acids, which consist of inorganic oxyacids of phosphorous or silicon and that of tungsten. Such compounds are attractive catalysts for many kinds of organic reactions.

13.4 Tungsten Powder

Technical tungsten powder qualities are prepared by hydrogen reduction and are available in average particle sizes from 0.1 (100nm) to 100µm. The reduction process is, in some respects, unique. It offers the possibility to produce tungsten powder of any desired average particle size within the above limits only by changes in reduction conditions (Source: International Tungsten Industry Association).

The whole palette of particle sizes finds applications in cemented carbide production. The main portion of tungsten powder is directed to that manufacture. Starting tungsten powder for ductile tungsten and powder metallurgically produced tungsten alloys covers particle sizes between 2 and 6µm. Extremely coarse powder gained by screening to separate any finer particles has excellent flow characteristics and is used in plasma spraying.

The purity of the tungsten powder is of particular importance in all applications and is mainly influenced by the purity of the original APT. Typical upper limits of foreign element concentrations in are:

- Co, Cu, Mg, Mn, Pb ≤ 2 µg/g
- Al, Fe, Ni, Si, Ca, Cr, Sn ≤10 µg/g
- Mo ≤ 20 µg/g

The crucial physical properties are average particle size, particle size distribution, apparent, tap and compact or green density, specific surface area, degree of agglomeration and morphology. They are to a certain extent related to each other and can be influenced between limits by the oxide properties and the reduction conditions (Source: International Tungsten Industry Association).

13.5 Tungsten Carbide Powder

Tungsten carbide powder is the intermediate in the line from W powder to cemented carbides. It can be produced from different raw materials and by different processes. By far the biggest percentage is manufactured by the conventional method - carburization of tungsten powder - and covers the widest range of powder qualities in regard to average particle size (0.15–12µm). All other methods in use yield very fine or very coarse powder grades.

The conventional process of carburization comprises mixing of the respective tungsten powder of desired particle size with high purity carbon (lamp black or graphite) and reacting at temperatures between 1,300 to 1,600°C in hydrogen atmosphere. The average particle size and particle size distribution of the original tungsten powder determine size and distribution of the WC powder.

The final carbon content of the WC Powder depends on the production mode of the hard metal producer and is one item of the rigid specification and varies from slightly sub-stoichiometric to stoichiometric (6.13% C) to slightly over-stoichiometric. But not only is the carbon content specified but also a series of physical properties including average particle size, particle size distribution, apparent (bulk) density and homogeneity (Source: International Tungsten Industry Association).

High temperature carburized WC powders (1,700–2,200 °C) are usually coarse 10 to 50µm, but sometimes also 5 to 10µm grades are treated that way. The percentage of high temperature WC is small.

13.6 Ferro-Tungsten & Melting Base

Ferro-Tungsten

Ferro-tungsten is a master alloy for the production of tungsten-containing steels. The raw materials for ferro-tungsten production are rich ore or ore concentrates of wolframite or scheelite. Also, artificial scheelite or soft scrap can be used. The tungsten trioxide in these compounds can be reduced either carbothermically in electric arc furnaces or metallothermically by silicon and/or aluminum. A mixed carbothermic-silicothermic production is also in use (Source: International Tungsten Industry Association).

Commercial ferro-tungsten contains between 75 and 85% W. It has a steel grey appearance and a fine-grained structure consisting of FeW and Fe2W. It is supplied in 80–100 mm lumps.

Melting Base

Melting Base is another master alloy in tungsten steel production. It can have various compositions according to the tungsten scrap material in use. The tungsten content varies depending on type between 10 and 38% besides iron and sometimes 5.5% Mo and also 5 to 10% Co.

Different types of scrap materials are mixed to meet the required composition. Reductive melting is done in electric arc furnaces and the melt is finally granulated by casting on a rotating disc and quenching in water (size <10 mm) (Source: International Tungsten Industry Association).

14 RECYCLING OPTIONS FOR TUNGSTEN

Due to its characteristics, specific applications and relatively high value, tungsten is very amenable to recycling. The recycling of tungsten has been done for some decades and it is already technically possible to recycle most types of scrap and turn them directly into new products or convert them to APT. The methods for extracting W from the wastes include direct recycling, semi-direct recycling, pyro-metallurgy and hydro-metallurgy, they are most often used for the recycling of cemented tungsten carbides, which comprises 70% of the tungsten usage in Europe.

Tungsten hard metal products (monocarbides) can be relatively easily recycled with established technologies. In other products like in steel alloys and in other applications, tungsten is diluted throughout the material to trace element quantities. This means that recycling of W alloys can be problematic, and tungsten cannot really be recovered.

Table 16. Recycling rates of tungsten by source (Source: Ladenberger *et al* 2018)

Potential secondary resources	End of life recycling input rate - EoL-RIR	Industrial (new) scrap recycling rates	Challenges/comments
Contaminated cemented carbide scarp, turnings, grindings and powder scrap	42 %		Secondary tungsten is processed to ATP
Clean cemented carbide and compacts			Converted to power
Tungsten containing scrap and residues			
High speed steel		60-70%	
Lamp filaments, welding electrodes and chemical uses	0 %		Concentration is low so not econoimic to recycle

For recycling to be economically viable, a large volume of tungsten bearing waste has to be consistently supplied. Thus to increase tungsten recycling rates, a reliable identification and estimation of available secondary resources is required in a logistically practical fashion. Although large tungsten-bearing tailings in Europe have been identified, various other potential feed streams remain undiscovered, especially various kinds of industrial waste (mill tailings, grinding sludge, dust, sweepings) which are withdrawn from the value chain of recycling. The recovery of tungsten from secondary resources (waste streams), can be classified in the following approximate groups (not an exhaustive list):

(1) Processing waste and historical waste (mining and metallurgical wastes)

- Waste rock
- Mill tailings

(2) Urban mines and manufacturing residues (new scrap and old scrap)

- Cemented carbide
- Heavy metal alloy scrap
- Mill scale
- Grinding sludge
- Drill bits
- E-waste
- Spent Ni-W catalysts

Where:

- New scrap: waste from processing the material containing niobium
- Old scrap: end of life products from urban mines and manufacturing residues

The following process path methods are used to do this:

1. **Direct recycling**. The wastes are transformed into powder with the same chemical composition of the wastes by chemical and/or physical treatment; thereafter the powder is used to produce new products.

2. **Semi-direct recycling**. Heavy metal pieces (such as cemented carbide scrap pieces) are selectively dissolved by chemical method, leaving undissolved tungsten carbide to be recycled.

3. **Pyro-metallurgy**. Scrap is smelted in the furnace and the tungsten in the scrap is used as alloying element and thereby recycled.

4. **Hydro-metallurgy**. Chemical methods are applied to recycle tungsten in the form of compounds, which can be used as a substitute of tungsten ore.

More complex hydrometallurgical routes are being developed that can treat a wider variety of scrap. One of the biggest challenges is making the process profitable as these methods are very energy intensive and require a lot of reagents. Solutions might be to develop processing plants that can recover multiple metals and can turn them into high quality end-products. Another difficult issue is that these plants produce a lot of effluents and waste. New technologies might also be needed to reduce the environmental impact of these type of recycling plants.

Besides methods for the recycling of scrap, new technologies are also being developed to recycling tungsten from other sources such as drill bits, roller collars, catalysts and e-waste. Recycling technologies for these types of waste are still in an early stage of development. The main barriers to post-consumer recycling are dispersion or dilution in the material/structure
(low-grade material); lack of appropriate post-consumer collection systems for open-loop recycling and poor economic viability.

The techniques that are needed for pre-treating of W-bearing scrap depend on the types of wastes and the way in which they are to be recycled. These techniques include the following:

- Physical dismounting/sorting and/or sorting by chemical analysis into different grades. The sorting will lead to a purpose-oriented recycling of various W-bearing waste;

- Crushing, screening, milling and grinding. This will produce a waste being adapted to a specific recycling process;

- Acid cleaning to remove the impurities;

- Roasting, chlorination, alkali fusion, oxidation and electrolytic dissolution, etc. The tungsten is transformed into other compounds (such as APT, ammonium paratungstate) that can be recycled in an easy way.

The biggest barriers regarding tungsten recycling are securing a steady supply of scrap. Additionally, tungsten carbide made from scrap may not always have the same properties as freshly produced tungsten carbide and might only be used for some applications as low-grade products. The purity cannot be controlled, and further treatment is necessary if the quality of the product is important. One of the biggest challenges is making the process profitable as these methods are very energy intensive and require a lot of reagents. Solutions might be to develop processing plants that can recover multiple metals and can turn them into high quality end-products. Another issue is that these plants produce a lot of effluents and waste.

Sometimes direct physical re-using (for example for high-grade scrap like cemented carbide) seems to be more efficient than feeding into the recycling process.

14.1 Waste rock and mill tailings

Mineral processing wastes are generated during the extraction and beneficiation of ores and minerals. Tungsten can be recovered form waste rock and mill tailings contained in these wastes. In the EU, waste-rock and tailings are found at the Panasqueira mine, which produces 100 t/d and several million tons of these materials, respectively. At the Barruecopardo mine in Spain, Tungsten-containing dumps and tailings are found. Coarse tailings and slimes can also be found at La Parilla mine in Spain, with a grade of 0.28% of WO_3. At Los Santos mine in Spain, tailings of coarse particles (643 kt, 0.14% WO_3, 2013-2015) and fine particles (76 kt, 0.14% WO_3, 2013-2015) rejects are also produced. (Source: Ladenberger et al 2018). Historical tailings at Hemerdon (then called Drakelands while operated by Wolf Minerals) consisted of 3.2Mt at 0.19% WO_3 (non-compliant internal estimate).

14.2 Tungsten containing grinding sludge/swarf

The fine metal cuttings that result from grinding processes of high speed steel or cemented Tungsten carbide are collected and referred to as “swarf”, which contains considerable amounts of Tungsten which can be recycled. (Source: International Tungsten Industry Association)

14.3 Mill scale

Mill scale is generated during continuous casting and rolling mill processes, where steel is subjected to hot working in an oxidant atmosphere. It represents 2% of all steel produced. To give an example, there was the case of a mini-mill plant in Brazil where mill scale was reported to contain 0.83% Tungsten.

14.4 Other residues

Steelmaking dust, grinding dust, floor sweeps, etc. (Source: International Tungsten Industry Association)

15 SUMMARY

Tungsten is a very unusual metal element that is useful in many applications. Its material properties make it ideal as an alloy component, which makes tungsten a technology industrial metal. It has excellent corrosion resistance and is attacked only slightly by most mineral acids, the highest melting point of all metals, and at temperatures over 1650 °C has the highest tensile strength of all metals.

Applications include old-style incandescent lamp manufacture, special alloys and hard materials, as well as catalysts and military applications to make armor piecing ammunition in military applications (required for high technology weaponry).

Tungsten has been classified as a Critical Raw Material by the European Commission. This classification was the result of the bulk of global tungsten supply comes from one nation state, China. The Chinese production accounts for 80.1% of global tungsten market. Due to difficulties of mining in the Democratic Republic of Congo, tungsten bearing minerals have been classified as conflict minerals, with associated legislation compliance requirements.

Scheelite and wolframite are the only tungsten minerals mined commercially and are mainly found in five types of deposits: skarn, vein/sheeted vein/stockwork, porphyry, disseminated and stratabound.

Global reserves of tungsten in 2019 was estimated (USGS data) to be 3.19 million tonnes. The largest national reserves of tungsten were in China at 1.9 million tonnes. Global production of tungsten in 2019 was estimated to be 85 000 tonnes, with China supplying 70 000 tonnes of the global total.

Tungsten ore can be complex, which can result in challenging beneficiation results. Due to the brittle character of both scheelite and wolframite, comminution is carefully designed to avoid overgrinding, that is, to minimize formation of fines. Rod milling of scheelite has some advantages to ball milling in this context. Gravity concentration and flotation are the beneficiation techniques most commonly applied to scheelite ore, and gravity and/or magnetic separation for wolframite ore. Magnetic separation of tungsten minerals can be viable in some ore specific circumstances. Hydrometallurgy can be used to extract tungsten, depending on the ore texture and mineral content. X-ray sorting and gravitational methods can be used for pre-concentration. Optical sorting and/or hand-picking methods are also used for pre-concentration of wolframite ore.

Tungsten concentrates are subject to further processes to output a number of saleable tungsten products. Product examples are concentrates, ammonium paratungstate, tungsten oxides, tungsten acids, tungsten powder, tungsten carbide powder, ferro-tungsten and melting base.

Recycling can be done technically but is usually not economically viable. There are some options for substitution of tungsten in manufacture but not for all applications.

Due to its characteristics, specific applications and relatively high value, tungsten is very amenable to recycling. The recycling of tungsten has been done for some decades and it is already technically possible to recycle most types of scrap and turn them directly into new products or convert them to APT. The methods for extracting W from the wastes include direct recycling, semi-direct recycling, pyro-metallurgy and hydro-metallurgy, they are most often used for the recycling of cemented tungsten carbides, which comprises 70% of the tungsten usage in Europe.

For tungsten's main application, WC-based cemented carbides, substitution is technically possible but implies higher costs and, in some cases, a decrease in performance. There are substitution options but they are not economically viable, resulting in a relatively poor substitution index for tungsten.

This implies the best source of tungsten at this time would come from the mining of mineralized resources.

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