A Review of Tungsten Resources and Potential Extraction from Mine Waste

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Abstract: Tungsten is recognized as a critical metal due to its unique properties, economic importance, and limited sources of supply. It has wide applications where hardness, high density, high wear, and high-temperature resistance are required, such as in mining, construction, energy generation, electronics, aerospace, and defense sectors. The two primary tungsten minerals, and the only minerals of economic importance, are wolframite and scheelite. Secondary tungsten minerals are rare and generated by hydrothermal or supergene alteration rather than by atmospheric weathering. There are no reported concerns for tungsten toxicity. However, tungsten tailings and other residues may represent severe risks to human health and the environment. Tungsten metal scrap is the only secondary source for this metal but reprocessing of tungsten tailings may also become important in the future. Enhanced gravity separation, wet high-intensity magnetic separation, and flotation have been reported to be successful in reprocessing tungsten tailings, while bioleaching can assist with removing some toxic elements. In 2020, the world's tungsten mine production was estimated at 84 kt of tungsten (106 kt WO_3), with known tungsten reserves of 3400 kt. In addition, old tungsten tailings deposits may have great potential for exploration. The incomplete statistics indicate about 96 kt of tungsten content in those deposits, with an average grade of 0.1% WO_3 (versus typical grades of 0.3–1% in primary deposits). This paper aims to provide an overview of tungsten minerals, tungsten primary and secondary resources, and tungsten mine waste, including its environmental risks and potential for reprocessing.

Keywords: tungsten resources; mine waste; recycling; wolframite; scheelite

1. Introduction

Tungsten is an important raw material and has numerous applications in different industrial sectors, such as energy, materials, information technology, and consumer staples. Specifically, tungsten has been widely used in metalworking, mining and stone-cutting tools, high-temperature technologies, lighting, catalyst and pigment, petroleum, armaments, and aerospace industries [1]. Tungsten carbide—a dense, metal-like substance—is the major end-use material application for tungsten, widely used in automotive and aircraft production, construction, electronics manufacturing, oil and gas drilling, and defense [2]. Recent studies have shown tungsten alloys could be the most promising materials as plasma-facing first walls in future commercial nuclear fusion devices [3].

The special properties, wide application in different sectors, a lack of potential substitutes, and geographically concentrated production make tungsten a critical element and strategic resource in the global economy [4]. In May 2018, the United States Department of Interior published the Final List of Critical Minerals 2018 (83 FR 23295); tungsten was included in the 35 minerals (or mineral material groups) deemed critical [5]. The European Union also listed tungsten as one of the critical raw materials since 2011 [6]. Besides the US and EU, tungsten is considered a critical element in every region except Australia [7].

China started to dominate the world tungsten market in 1949 and has been the primary tungsten producer for over 70 years. China produced more than 40% of tungsten

concentrates between 1949 and 1985 and more than 66% between 1986 and 2008 [8]. In 2020, China held 82% of the world's tungsten mine production and 56% of the world's tungsten reserves [9]. Meanwhile, China has adopted stricter pollution control and safety regulations on tungsten production and shut down numerous tungsten mining facilities since 2017, which resulted in a reduced supply of tungsten to the world market and high volatility in prices for tungsten commodities [10]. Consequently, to balance the global tungsten demand and supply, markets would need to rely on exploring new primary deposits around the world and utilizing secondary tungsten resources [11].

Currently, tungsten waste contamination to the environment has also been a concern. For example, the Panasqueira mine, the largest Sn–W deposit in Western Europe, had stored a significant amount of tungsten tailings in tailing dams. These tailings generate low pH (~3) and are enriched in toxic elements acid mine drainage (AMD), leaking into the nearby river [12]. At the Lianhuashan mine, one of the largest tungsten mines in China, it was found that surface water, soil, and plants around the tailing dam were severely contaminated by heavy metals and arsenic [13]. Further study in the same area showed that tungsten tailings have potential health risks to the surrounding residents [14]. Consequently, appropriate treatment for tungsten tailings to prevent potential contamination may be required. Meanwhile, tungsten tailings may contain numerous valuable elements and minerals and could be used as a secondary resource for metal recovery.

This paper focuses on a comprehensive literature review of tungsten properties and mineralogy, potential risks of tungsten to the environment and humans, tungsten primary and secondary resources, and potential reprocessing approaches for tungsten tailings.

2. Tungsten Characteristics and Mineralogy

2.1. Physical and Chemical Characteristics

Tungsten is a transition metal element with -2 to $+6$ oxidation states and 5 to 9 coordination numbers [15]. Because tungsten has a wide range of coordination numbers, it can form a host of soluble complexes with numerous inorganic and organic ligands. Usually, aqua-, oxo-, halide-, organo-, or mixed ligands can complex with tungsten. The monomeric state of tungstate (WO_4^{2-}) is only stable in solutions at pH $\geq$ 6.2 and free of complexing agents [16]. The tungstate polymerization process under different pH and time scales is shown in Figure 1. Meanwhile, tungsten can exist in multiple oxidation states naturally, but speciation is poorly known [17].

2.2. Occurrence

The average abundance of tungsten in the earth's crust is around 1.5 ppm—much rarer than most rare earth elements (REEs). Naturally occurring primary tungsten minerals could be divided into wolframite group, including wolframite [(Fe,Mn)WO_4], hübnerite (MnWO_4), ferberite (FeWO_4), and sanmartinite [(Zn,Fe)WO_4] [18], and scheelite group, including scheelite (CaWO_4), and stolzite and raspite (PbWO_4) [19]. However, only wolframite and scheelite have great abundance and are of economic importance. The remaining minerals are rare and usually present in trace amounts.

Secondary tungsten minerals are usually thought to be generated by hydrothermal or supergene alteration of primary tungsten minerals rather than by atmospheric weathering [20]. Grey et al. (2006) reported that hydrothermal alteration effects on primary tungstate minerals, such as ferberite and scheelite, could generate several secondary tungsten minerals, including ferritungstite [(W,Fe)(O,OH)$_3$], aluminotungstite [(W,Al)(O,OH)$_3$], jixianite [Pb(W,Fe)$_2$(O,OH)$_7$], elsmoreite [$WO_3 \cdot 0.5H_2O$], hydrotungstite [$WO_3 \cdot 2H_2O$], tungstate [$WO_3 \cdot H_2O$], anthoinite [AlWO_3(OH)$_3$], and phyllotungstite [CaFe$_3$H(WO_4)$_6 \cdot 10H_2O$] [21]. Typical secondary tungsten minerals include hydrotungstite ($WO_3 \cdot 2H_2O$), anthoinite [AlWO_3(OH)$_3$], and cerotungstite [CeW_2O_6(OH)$_3$]; these substances together can form whitish to yellowish earthy masses [22]. The weathered tungsten minerals ores may experience a significant change in the mineral composition and properties, which make them no longer suitable for flotation and gravity beneficiation [23]. The presence of secondary tungsten minerals can

decrease tungsten recovery during processing [24]. The primary and secondary tungsten minerals summarized by ITIA are listed in Table 1.
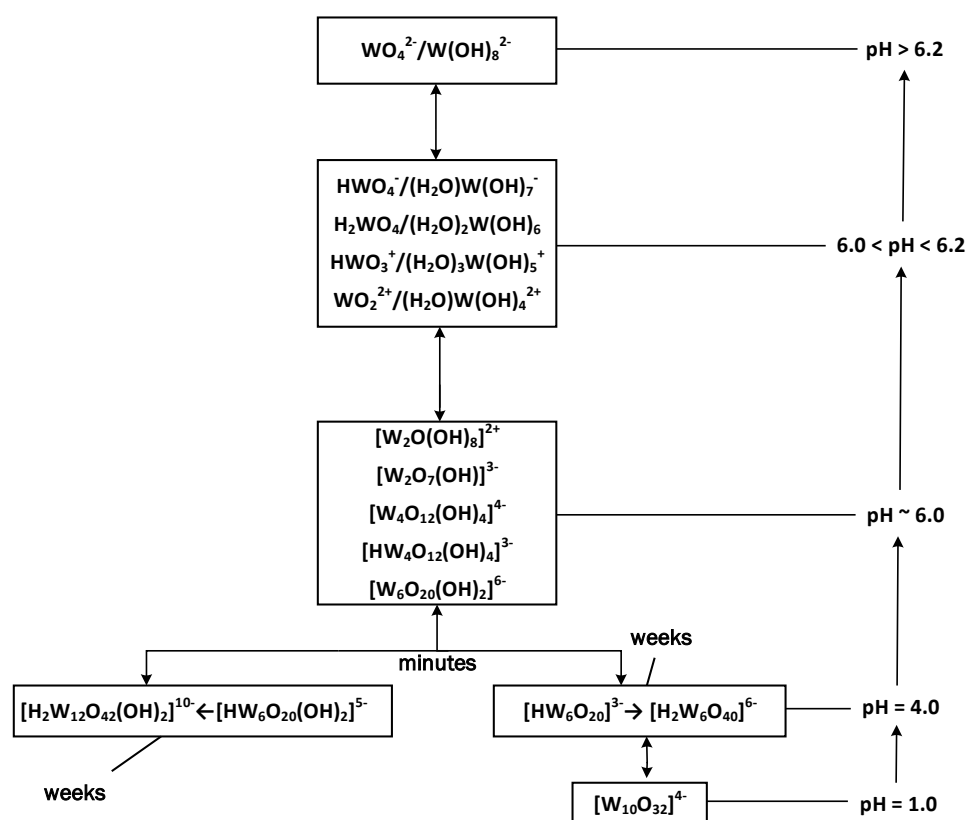

Figure 1. Tungsten speciation as a function of pH [16].

Table 1. Chemistry of tungsten minerals. Based on: [24].

Name	Formula	Name	Formula
Primary Tungsten Minerals			
Ferberite	$FeWO_4$	Scheelite	$CaWO_4$
Hübnerite	$MnWO_4$	Stolzite and Raspite	$PbWO_4$
Sanmartinite	$(Zn,Fe)WO_4$	Wolframite	$(Fe,Mn)WO_4$
Secondary Tungsten Minerals			
Alumotungstite	$(W,Al)(O,OH)_3$	Ovamboite	$Cu_{20}(Fe,Cu,Zn)_6W_2Ge_6S_{32}$
Anthoinite	$AlWO_3(OH)_3$	Paraniite-(Y)	$Ca_2Y(AsO_4)(WO_4)_2$
Catamarcaite	Cu_6GeWS_8	Phyllotungstite	$CaFe_3H[WO_4]_6 \cdot 10H_2O$
Cuprotungstite	$Cu_2[(OH)_2 \mid WO_4]$	Pinalite	$Pb_3WO_5Cl_2$
Elsmoreite	$WO_3 \cdot 0.5H_2O$	Qitianlingite	$(Fe,Mn)_2(Nb,Ta)_2WO_{10}$
Farallonite	$Mg_2W_2SiO_9 \cdot nH_2O$	Rankachite	$(V^{4+},V^{5+})(W,Fe)_2O_8(OH) \cdot (Ca_xH_2O_y)$
Ferritungstite	$(W,Fe)(O,OH)_3$	Mporoite	$AlWO_3(OH)_3 \cdot 2H_2O$
Hydrotungstite	$WO_3 \cdot 2H_2O$	Russellite	$(BiO)_2WO_4$
Jixianite	$Pb(W,Fe)_2(O,OH)_7$	Sanmartinite	$(Zn,Fe)WO_4$
Johnsenite-(Ce)	$Na_{12}(Ce,REE,Sr)_3Ca_6Mn_3Zr_3W(Si_{25}O_{73})(OH)_3(CO_3) \cdot H_2O$	Tungstenite	WS_2
Khomyakovite	$Na_{12}Sr_3Ca_6Fe_3Zr_3W(Si_{25}O_{73})(O,OH,H_2O)_3(OH,Cl)_2$	Tungstite	$WO_3 \cdot H_2O$
Kiddcreekite	Cu_6SnWS_8	Uranotungstite	$(Fe,Ba,Pb)(UO_2)_2[(OH)_2 \mid WO_4] \cdot 12H_2O$
Koragoite	$(Mn,Fe)_3(Nb,Ta,Ti)_{62}(Nb,Mn)_2(W,Ta)_2O_{20}$	Welinite	$Mn_6(W,Mg)_{0.7}[(O,OH)_3 \mid SiO_4]$
Mn-Khomyakovite	$Na_{12}Sr_3Ca_6Mn_3Zr_3W[Si_{25}O_{73}](O,OH,H_2O)_3(OH,Cl)_2$	Yttrotungstite-(Ce)	$(Ce,Nd,Y)W_2O_6(OH)_3$
Meymacite	$WO_3 \cdot 2H_2O$	Yttrotungstite-(Y)	$YW_2O_6(OH)_3$

Supergene alteration of tungsten minerals was studied through a case study in the Grantcharitsa scheelite deposit in Bulgaria [23]. The mineralogy of this deposit is dominated by scheelite and pyrite. The secondary minerals of scheelite were reported to be very complex under different overall pH of supergene solutions in the oxidation zone of the deposit. These minerals under different pH conditions are summarized in Figure 2.
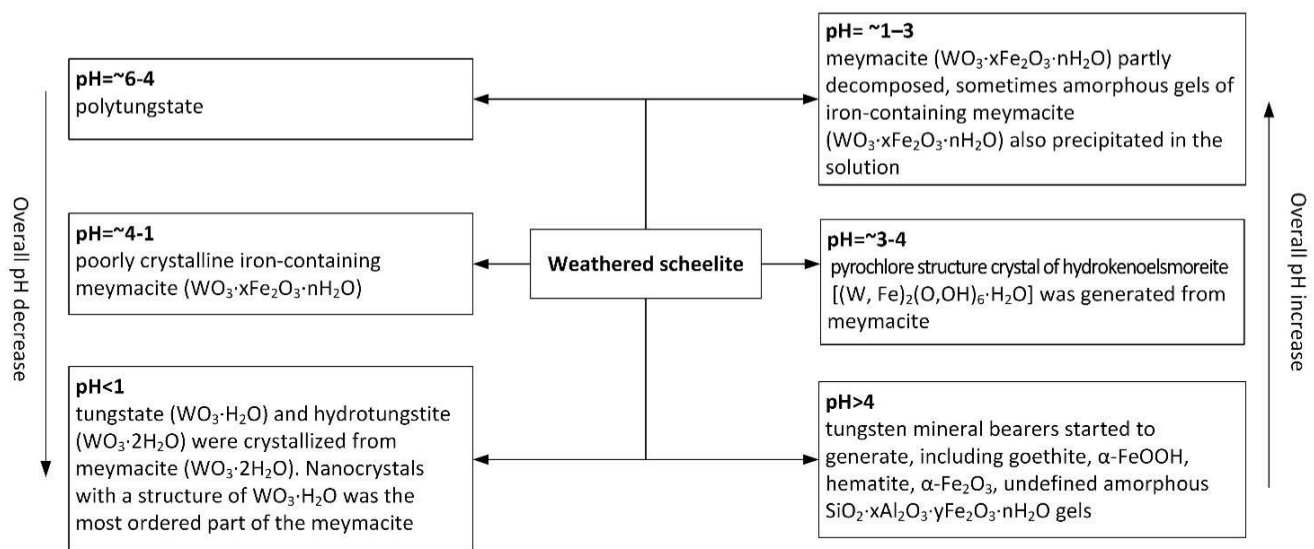
Figure 2. Secondary minerals of scheelite under different overall pH of supergene solutions in the oxidation zone of the Grantcharitsa scheelite deposit in Bulgaria. Based on: [23].

With an increase in pH from <1 to 4, the study found successive changes in the secondary tungsten mineral structure types from ReO_3-type layers in the structures of tungstite and hydrotungstite to hexagonal tungsten bronze type layers in the structure of meymacite, and finally to pyrochlore type layers in the structure of hydrokenoelsmoreite [23].

2.3. Mineralization

Tungsten mineralization forms a variety of tungsten ore deposits under very wide formation conditions from magmatic to hydrothermal systems. Typical tungsten geological deposit types include skarn, vein/stockwork, porphyry, strata-bound, pegmatite, breccia, brine/evaporite, placer, and disseminated [25]. Figure 3 presents different types of tungsten deposits around the world. Almost all tungsten mineralizations in the world are associated with granitic intrusions, especially wolframite-bearing quartz vein systems with <5 km depth granitic intrusions. For example, tungsten-tin vein-stockwork deposits are associated with granitic intrusions emplaced at 1–4 km depth. These deposits occur close to the contact zones of the intrusions and are host to various degrees in the granitic rocks themselves or in associated sedimentary, volcanic, metamorphic, or older intrusive rocks [26].

Tungsten mineralization can be characterized by wolframite [$(Fe,Mn)WO_4$] or scheelite ($CaWO_4$) in individual deposits with different origins. Wolframite mineralization invariably accompanies greisen, while scheelite mineralization is mostly associated with skarnization [27]. Wolframite mainly occurs in veins, usually associated with cassiterite, and in quartz and pegmatite veins of hydrothermal origin genetically related to granitic intrusive rocks [18]. Scheelite crystals are in the tetragonal crystal system, with two kinds of special cation sites: tetrahedral $[WO_4]^{2-}$ sites usually accommodate highly charged and smaller cations, such as W^{6+}, Mo^{6+}, As^{5+} and Nb^{5+}; while dodecahedral $[CaO_8]^{14-}$ sites have alkaline earths and alkalis cations, e.g., Ca^{2+} and Na^+. Because rare earth elements (REEs), Sr and Pb, have similar electron configurations and ionic radii as Ca^{2+}, the research found a significant amount of Ca^{2+} being substituted by these elements in the structure of scheelite [28].
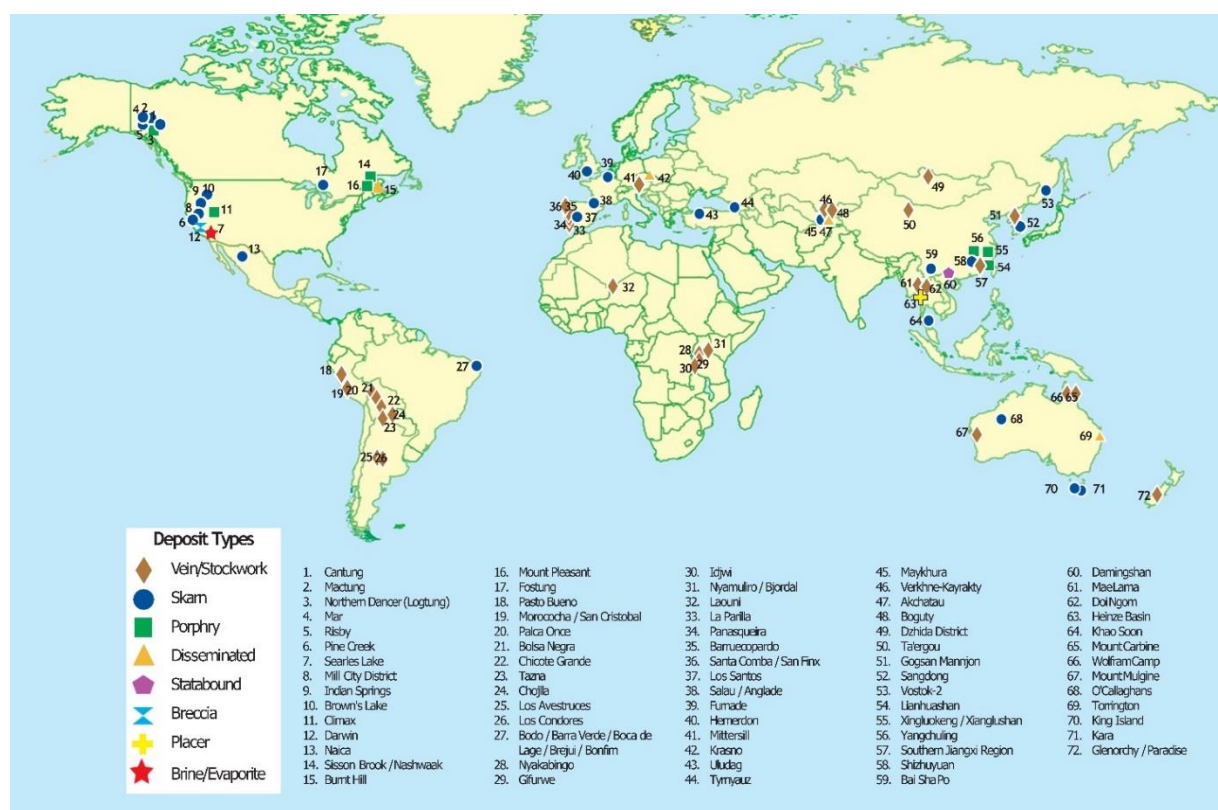
Figure 3. Location and type of major tungsten deposits and districts [22].

3. Tungsten Resources

3.1. Primary Resources

Tungsten deposits occur in each continent in the world [29]. The most important and abundant tungsten deposits have been discovered in Southeast China and the Southeast Asian belt. There are also significant resources in the Central Andean belt, East Australian belt, Mesoproterozoic Karagwe-Ankole belt, and European Variscan belt [30]. The prominent reserves of tungsten deposits around the world are listed in Table 2.

Table 2. Prominent reserves of tungsten deposits around the world.

Deposit	Deposit Type	Reserves, Mt	Grade, WO$_3$ %	Reference
Xihuashan (China)	W-Sn	81.3	1.08	[31]
Hemerdon (UK)	W-Sn	26.7	0.19	[32]
Mt Pleasant (Canada)	W-Mo-Bi	14.4	0.26–0.33	[33]
Sangdong (South Korea)	W-Mo	13.3	0.43	[32]
Panasqueira (Portugal)	W-Sn	10.3	0.24	[34]
Barruecopardo (Spain)	W-Mo	8.7	0.30	[32]
Kilba (Australia)	W-Mo	5.0	0.27	[32]
Dzhida (Russia)	W-Mo	1.4	0.15	[35]

According to the 2021 Mineral Commodity Summaries on tungsten by the US Geological Survey (USGS), the major tungsten-producing countries around the world are China, Vietnam, Russia, Mongolia, Bolivia, Austria, and Rwanda [9]. However, compared with a decade ago, one significant change in the global tungsten supply and demand market is that the US completely stopped tungsten production in 2014 and now heavily relies on imports of tungsten.

In 2020, the global tungsten output was about 84 kt. Among major tungsten-producing countries, China remained the largest supplier. The production of tungsten in China

accounts for more than 82% of the world's production, reaching about 69 kt [9]. More than 90% of Chinese tungsten resources are stored in the Nanling Range, which is located in Southeast China. There are more than 10 giant and more than 100 medium to small tungsten deposits in this range [36]. Vietnam was the second-largest producer of tungsten concentrate, with a share of about 5% (4300 t), while Russia ranked third, with about 3% (2200 t), followed by Mongolia, Bolivia, Rwanda, and Austria, which produced over 1% of the world's production (1900 t; 1400 t; 1000 t; and 890 t, respectively) [9].

In 2020, the estimated global tungsten reserves were around 3400 kt. China accounts for about 1900 kt or more than 56% of the global total. Russia and Vietnam have the second (400 kt; 12%) and third (95 kt; 3%) largest tungsten reserves. This is followed by Spain and North Korea, with 54 kt and 29 kt (more than 1% of the global total). Austria and Mongolia represent less than 1% of the global reserves, with 10 kt and 4 kt, respectively [9].

As is shown in Table 3, hard-rock deposits are the major sources of wolframite and scheelite. However, wolframite can also be recovered from placer deposits. At present, there is mass production of tungsten from skarn, vein/stockwork, porphyry, and strata-bound deposits. Only a small amount of tungsten production originates from disseminated, pegmatite, breccia, brine, and placer deposits [37].

Table 3. Typical tungsten mine parameters worldwide [37,38].

Deposit Type	Mining Methods	Processing Methods	Ore Grade, WO$_3$ %	Tungsten Mineral	Accompanying Economic Metals	Typical Mine around the World	Mineralogy and Geology
Skarn (deposit size < 10^4–5 × 10^7 t)	Underground/ Open-pit	Magnetic, gravity, flotation	0.3–1.4	Scheelite	Cu, Mo, Zn, and Bi	Vostok-2 (Russia), Uludag (Turkey), Mactung and Cantung (Canada), Sang Dong (South Korea), King Island (Australia)	Tabular or lenticular scheelite-dominated ore bodies in calc-silicate rocks formed by replacement of carbonate rocks and more rarely carbonaceous rocks at contacts with S- and I-type granitoid intrusions
Vein/stockwork (deposit size < 10^5–10^8 t)	Underground/ Open-pit	Gravity, flotation, magnetic, dense media, chemical leaching	Variable	Wolframite	Sn, Cu, Mo, Bi, and Au	Panasqueira (Portugal), Xihuashan (China), Bolsa Negra (Bolivia), Erzgebirge (Czech Rep.), Hemerdon (UK)	Single and multiple systems of simple or complex fissure filling and replacement veins of quartz + wolframite at margins of felsic plutonic rocks in clastic (meta-) sedimentary country rocks
Porphyry (deposit size < 10^7–10^8 t)	Open-pit	Gravity, flotation	0.1–0.4	Wolframite or/and scheelite	Mo, Bi, and Sn	Xingluokeng (China), Yangchulin (China), Northern Dancer (Canada),Climax (USA)	Medium to large, low-grade stockwork of quartz veinlets and disseminations in subvolcanic felsic intrusive rocks ± country rocks
Disseminated (deposit size < 10^7–10^8 t)	Underground	Magnetic, gravity, flotation	0.1–0.5	Wolframite and scheelite	Sn, Bi, and Mo	Shizhuyuan, Xihuashan, and Dangping (China), Akchatau, Kara-Oba, and Lultin (Russia)	Low-grade greisen deposits formed by pervasive metasomatic (endoskarn) alteration in the cupolas of granitic stocks
Stratabound (deposit size < 10^6–10^7 t)	Underground/ Open-pit	Gravity, flotation	0.2–1.0	Scheelite	Mo	Mittersill (Austria), Damingshan (China), Mount Mulgine (Australia)	Concordant lenses of stratiform scheelite in submarine volcano sedimentary sequences. Volcanogenic exhalative origin
Breccia (small, little production from them)	Open-pit	Magnetic, gravity, flotation	0.14–1.0	Wolframite	Cu, Mo, Ag, Sb, and Sn	Wolfram camp (Australia), Doi Ngom, and Khao Soon (Thailand), Washington (Mexico)	Near-vertical bodies of fragmented rock formed either by hydraulic fracturing or steam-dominated volcanic explosions marginal to I- or A-type granitic intrusions
Pegmatite (deposit size < 10^6–10^7 t)	Underground	Flotation	0.5–0.8	Scheelite or/and Wolframite	Li, Be, Nb, Ta, REEs, and Sn	Okbang mine (South Korea), Mawchi mine (Myanmar)	Dyke-like masses around granitic bodies. Simple unzoned to complex strongly zoned types with more varied mineralogy
Placer (deposit size < 3 × 10^4–10^7 t)	Open-pit	Magnetic, gravity, flotation	0.43	Wolframite and scheelite	Sn	Heinze Basin (Myanmar), Andrew mine (USA), Mergui district (Myanmar), Dzhida district (Russia), Bodmin Moor (UK)	Heavy mineral concentrations in alluvial, eluvial, or marine sediments derived from proximal bedrock sources of tungsten.
Brine/evaporate (deposit size < 10^4–10^5 t)	Salt flats	Chemical, ion-exchange	7 × 10^{-4}	Lake brines	Salts of a complex mixture	Searles Lake (USA), other examples in the CIS and the western USA	Tungsten-bearing brines in lakes and the saline deposits of palaeolakes in arid continental regions

3.2. Secondary Resources

Currently, the only secondary resource of tungsten used in industry is tungsten scrap. It has already been used as a substitute for tungsten ore concentrates at conversion plants [39]. Tungsten scrap (e.g., metal drill scrap, superalloys, and tungsten carbide products scrap, and powder metallurgical tungsten new scrap) could be divided into three types: new scrap (by-products of tungsten materials or products), old scrap (spent tungsten-bearing materials), and unrecovered scrap (excess reactants) [1]. The W grade of tungsten scrap is in the range of 40–95 wt.% [40]. Since 2000, a wide variety of tungsten scrap recycling methods have been used globally. The methods to process tungsten-bearing scrap for tungsten recovery can be classified into four groups: hydrometallurgy, melting metallurgy, direct recycling, and semidirect recycling [39]. Approximately 30% of world tungsten demand is met through tungsten scrap recycling [41].

Another possible secondary resource of tungsten is tungsten tailings. They are solid waste generated in the process of tungsten ores beneficiation. Because of the relatively low tungsten content in the ore, around 0.4–0.6% on average [42], the production of 1 t of tungsten concentrate (50–65% WO_3) generates 7–10 t of tailings [43]. The major components of tungsten tailings are typically SiO_2, Al_2O_3, CaO, and Fe_2O_3, while W, Cu, S, Sn, Zn, Be, and Bi are the major trace elements [44]. Much of the wolframite in tungsten tailings is below 25 μm [45], and the scheelite is below 74 μm [46]. Essentially, the remaining tungsten minerals in tailings are mainly in the fine and ultrafine fractions, which makes it difficult for reprocessing by conventional methods. Nevertheless, the incomplete statistics of tungsten tailings deposits around the world, presented in Table 4, indicates more than 100 Mt of tailings, containing about 96 kt of WO_3. As a result, there may be a great potential for recovering tungsten from these unexploited secondary resources.

Table 4. Worldwide tungsten tailings deposits and known reuse examples.

Tungsten Tailings Deposit	Type	Tailings, Mt	Grade (WO_3), %	WO_3, kt	Known Reuse Examples	Reference
Dzhidinsky (Russia)	Mo-W	40	0.1	40	Nil	[47]
Luanchuan (China)	W-Mo	20	0.14	28	Reprocessing for tungsten recovery	[48]
Kaitashskoe (Uzbekistan)	W-Mo	12	-	-	Flotation tailings reuse trials for ceramic tile production	[49]
Sangdong (South Korea)	W-Mo	12	0.1	12	Feasibility study for reuse in cement production	[50]
Panasqueira (Portugal)	W-Sn	8	0.12	9.6	Reprocessing trials for tungsten recovery	[45,48,51,52]
Yxsjöberg (Sweden)	W-Cu-F	5.2	0.08	4.2	Nil	[53,54]
Mount Carbine (Australia)	Sn-W	2	0.1	2	Reprocessing for tungsten recovery	[55]
Wolfram Camp (Australia)	W-Mo	1	0.06	0.6	Nil	Authors' estimate
Total		**100.2**		**96.4**		

The total global mass flow of tungsten was estimated at 126.5 kt in 2010, including 102.5 kt of tungsten content in mined ores and 24 kt in the end-of-life tungsten scrap. However, about 30.3 kt of tungsten was lost in the waste streams during processing, including 4.7 kt in different residues (~5% processing loss) and 25.6 kt in tailings (~25% loss on recovery from mined ores) [56]. This also indicates a potential for recycling and further exploiting tungsten tailings as a secondary resource of tungsten.

4. Tungsten Geochemical Mobility, Toxicity and Environmental Risks

4.1. Geochemical Mobility

Koutsospyros et al. (2006) reported tungsten can be released to aquatic systems through a host of natural and anthropogenic routes from terrestrial, atmospheric and biotic environments. The natural processes of tungsten mobility include the weathering of

tungsten-rich rocks and soils, dissolution of tungsten minerals, hydrothermal and volcanic activities, wet and dry atmospheric precipitation, and excretion of metabolites of tungsten enriched plants. They also reported both soluble and particulate forms of tungsten can exist in aquatic environments, but soluble tungsten is of higher environmental concern because of its higher mobility and toxicity [16]. Tungsten and its compounds usually have limited aquatic solubility and mobility. The reactions of tungsten with water play a major role in its mobility. Microbial activities can also promote tungsten mobility in solution. The iron-oxidizing bacteria and manganese-oxidizing bacteria can significantly accelerate the breakdown of tungsten minerals because these bacteria can destroy the crystalline structure of tungsten minerals and release soluble tungsten compounds [57].

Tungsten exists naturally in ocean water and sediments, surface water bodies, and groundwater in areas of hydrothermal activity [16]. Tungsten metal does not occur in nature, but tungstate anion persists and is thermodynamically stable under most environmental conditions. Tungstate anion can polymerize with itself and other oxyanions (e.g., molybdate, phosphate, and silicate) and generate a variety of polymer species. Polymerization of tungstate anion will impact the mobility of tungsten in ground or surface water due to different geochemical properties of the various polytungstates [58].

4.2. Toxicity

Research has shown that tungsten at very high concentrations and long-term contact (occupational exposure and chronic tungsten poisoning) is harmful to humans. For example, occupational exposure to tungsten may lead to pulmonary fibrosis related to hard metal lung disease, while exposure to tungsten at an environmental level concentration by breathing air, eating food, or drinking water has a low possibility to have harmful effects on humans [59]. A report from the US Center for Disease Control and Prevention (US CDC) investigated the cases of childhood leukemia and compared tungsten exposure in a control community with the community of relatively high exposure through drinking water (~45 times higher). There was no direct evidence showing that tungsten would definitively cause childhood leukemia [60], and the latest follow-up papers also supported this conclusion [61,62].

In the natural environment, tungsten is non-toxic to certain microorganisms but plays an essential role in the biology of microorganisms. Experiments even found tungsten could stimulate the growth of some species of microorganisms [63]. Tungsten also formed a variety of metal enzymes in natural biological systems, and these tungsten-containing enzymes played active roles in the anaerobic aspects of the carbon cycle. For example, tungsten could form tungstoenzymes, which occurred and prevailed in thermophilic and hyperthermophilic in the vicinity of deep-sea hydrothermal vents [64]. For plants, a study found that tungsten can be enriched by several plants [65]. For example, rice can enrich tungsten from the soil, and the enrichment factor of tungsten decreased in the following order: root, leaf, stem, and grain [66].

However, a study also reported that tungsten has potential fetus toxicity and affected the early stages of fish development [67]. In addition, Wistar rats also had a significant rise in the DNA damage and micronuclei, and a difference in biochemical levels and histopathological alterations, after 28 days of repeated oral administration of 1000 mg/kg dose of tungsten trioxide (WO_3) nanoparticles. Tungsten biodistribution was detected in all tissues in different concentrations. The highest concentration of tungsten was found in the liver, and the lowest, in the brain of treated rats. However, the overall conclusion from this experiment was that tungsten trioxide nanoparticles have little toxicity hazard even at the highest dose (1000 mg/kg bw/day dose) after 28 days of repeated oral exposure, according to the Organization for Economic Cooperation and Development (OECD) test guideline 407 (2008) [68].

4.3. Environmental Risks of Tungsten Waste

Though tungsten showed little toxicity to humans, animals, and plants, the tungsten mine wastes pose non-neglectable threats to the environment. It was reported that most of the tungsten (about 93% on average) in the soil is in the residual fraction, with low mobility and bioavailability [66]. As a result, the major pollutants released from tungsten mine waste do not necessarily relate to tungsten due to its low concentration and low mobility, but other contaminants present in tailings, such as-, Zn- and Pb-bearing sulfides, carbonates, and sulfates [69].

Acid mine drainage (AMD) generated from tungsten tailings storage facilities (TSFs) proved to be another environmental and health risk. Lianhuashan tungsten mine, one of the largest tungsten mines in southern China, is rich in polymetallic sulfide ores. The major minerals of this mine are wolframite, scheelite, arsenopyrite, pyrite, magnetite, chalcopyrite, quartz, sericite, chlorite, and feldspar. This mine was closed in 1991 and left a huge amount of untreated tailings in the TSFs. During the rainy season, AMD and weathered slag were released into the ambient environment and resulted in serious contaminations. Pollutants included Cu, Cd, Zn, Pb, Hg, and As, with As being the prominent pollutant. It also demonstrated that tungsten was not a significant contaminant element in tungsten tailings [14].

Currently, there is no environmental guideline on tungsten pollution in the United States or the European Union, neither in Australia, nor published data on the environmental effects of tungsten are inadequate [70]. Only for major tungsten substances, International Tungsten Industry Association (ITIA) published hazard classifications (Table 5) [71].

Table 5. Hazard classifications for the major tungsten substances. Based on: [71].

Substance	Hazard Class (EC1272/2008)	Hazard Warning
Ammonium Metatungstate	Acute oral toxicity 4	Harmful if swallowed
Ammonium Paratungstate	Not classified	None
Sodium Tungstate	Acute oral toxicity 4	Harmful if swallowed
Tungsten Powder (0.6–0.9 μm)	Flammable solid 1; Self-heating 2	Flammable solid; Self-heating in large quantities; may catch fire
Tungsten Powder (<1.0 μm)	Flammable solid 1	Flammable solid
Tungsten Powder (1.0–1.5 μm)	Flammable solid 2	Flammable solid
Tungsten Powder (>1.5 μm)	Not classified	None
Tungsten Blue Oxide	Not classified	None
Tungsten Carbide	Not classified	None
Tungsten Disulfide	Not classified	None
Tungsten Trioxide	Not classified	None

5. Potential Reprocessing Approaches for Tungsten Recovery from Tailings

5.1. A Summary of Previous Reprocessing Trials

The tungsten ores beneficiation process usually consists of pre-concentration, roughing, cleaning and purification after ore crushing and grinding. The final tungsten concentrates usually contain ≥65% WO$_3$ [72]. Wolframite ores are of good quality, high grade, easy mining, easy selection, have convenient subsequent treatment, and less environmental hazard [73]. Gravity and magnetic separation are the most common methods for the enrichment of wolframite because it is a paramagnetic, heavy, and dense mineral. But these methods are not suitable for the recovery of ultra-fine wolframite, especially for particle sizes below 20 μm [74]. In comparison, scheelite is amenable to flotation, which is the conventional approach applied in scheelite beneficiation [75]. To date, tungsten tailings are still mainly treated as a waste rather than a resource, and only limited experiments have been done on tungsten tailings reprocessing.

One reprocessing experiment at the Panasqueira tungsten mine in Portugal was carried out to recover ultrafine wolframite from old and new tailings. Froth flotation, magnetic separation, and gravity separation were compared for reprocessing both old and new tailings. The results indicated that froth flotation was the only feasible approach to reprocess new tailings to recover wolframite, while magnetic separation showed low recovery rates at different magnetic intensity levels. A three-stage gravity separation combined with intermediate sulfide flotation generated 50–55% WO_3 wolframite concentrates at reasonable recovery from tungsten tailings. However, because the reprocessing of 1 t of tungsten tailings delivered only a few kilograms of tungsten concentrate, it was considered to be uneconomic [45]. Table 6 lists a few other reported tailings reprocessing trials for tungsten concentrates recovery.

Table 6. Worldwide reprocessing trials for tungsten recovery from tailings.

| Tungsten Tailings Type	Deposits	Major Tungsten Minerals	Tailings Grade, WO_3%	Reprocessing Methods	Reprocessing Results	Reference
High-intensity magnetic separation tungsten ore slime	Rajasthan (India)	Wolframite	2.87 and 5.30	Polymeric dispersant with magnetic separation	Wolframite was enriched from tungsten slimes to 5.4–11% WO_3 concentrates. The grade of tungsten concentrates was increased to 10% when dispersant is applied	[76]
Fine tungsten tailings	Dajishan (China)	Wolframite	0.45	Flotation	30.18% WO_3 concentrates with an 80% recovery rate from very fine wolframite slime	[77]
Historical mine tailings and current plant slimes tailings	Panasqueira (Portugal)	Wolframite, most of the particles below 25 μm	0.1	Flotation, magnetic separation, and gravity concentration	A three-stage gravity separation combined with intermediate sulfide flotation produced tungsten concentrates with 50–55% WO_3	[45]
Tin mine tailings	Potosi Mine tin processing plant (Bolivia)	Wolframite	0.64	Chlorination segregation, flotation, high-intensity magnetic separation, and gravity separation	60.22% WO_3 concentrate with 64.26% recovery rate; 25.04% copper concentrate with 83.19% recovery; and 40.11% tin concentrate with 65.59% recovery	[78]
Old tailing dumps	Kolar and Hutti goldfields (India)	Scheelite	0.2	Tabling, flotation, and magnetic separation	65% WO_3 concentrate from a feed of tungsten tailings	[79]
Old molybdenum mine tailings	Tyrnyauz processing plant (Russia)	Scheelite	0.05	Flotation	54–55% WO_3 concentrate with 61.91–62.08% recovery rate from wolframite-molybdenum sand tailings	[80,81]

5.2. Gravity Separation

Gravity separation is an important approach in wolframite beneficiation. Compared with other mineral processing technologies, gravity separation has several advantages, such as high separation efficiency, low investment and operation costs, no additional chemical reagents required, and no potential pollution to the environment [82]. But conventional gravity separation is inefficient for the fine and ultrafine fractions of wolframite: it was reported to be below 45% [74]. Due to wolframite's hard and brittle properties, the generation of over crushed wolframite is inevitable during ore grinding [83]. As a result, a large portion of fine and ultrafine wolframite may be left in tailings after beneficiation by gravity separation. Nevertheless, in the same study, enhanced gravity concentrators were successfully applied for the fine tungsten minerals beneficiation [83]. Hang and vibrate cone concentrator and Falcon concentrator are two very selective separators for fine-sized mineral particles (typically +10–75 μm) and have very high mineral upgrading ratios (typically 20 to 1). An artificial sample consisted of pure and fine minerals of scheelite, wolframite, cassiterite, fluorite, and calcite was prepared to test these two enhanced gravity

concentrators for the fine tungsten minerals recovery. Most of the minerals in this sample were distributed in the -74 μm fraction, with the superfine fraction (−19 μm) accounting for more than 30%. The results showed that these two concentrators could respectively achieve 83.15% and 76.38% tungsten recovery rates. However, it was also found that these separators were still not efficient in the recovery of ultrafine (−10 μm) wolframite particles [82].

5.3. Magnetic Separation

In wolframite beneficiation, magnetic separation is usually operated in a high-intensity magnetic separation system for ideal wolframite recovery. In the conventional magnetic separation process, wolframite particle size plays a prominent role, similarly to gravity separation. With a decrease in the wolframite particle size, magnetic forces acting on the wolframite particle would drop quickly and cannot resist a hydrodynamic drag. As a result, the fine fraction of wolframite is lost to tailings. Furthermore, feeding flow and washing water can also wash away ultrafine wolframite from the separation plates in the magnetic field [84]. Figure 4 shows that the recovery of wolframite through magnetic separation varies under different particle sizes and magnetic intensities. For the particle sizes above 10 μm, the maximum recovery of wolframite could reach approximately 90% with an increase in magnetic intensity to 1.3 Tesla (1.3 T). However, for wolframite particles below 10 μm, the maximum recovery could only achieve approximately 60%, even with the highest 1.5 T magnetic intensity [84].
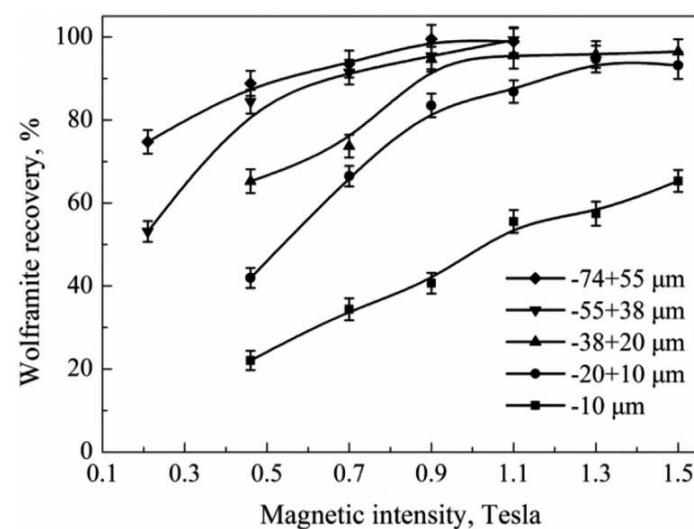
Figure 4. Recovery of different size fractions of wolframite as a function of magnetic intensity [84].

Wet high-intensity magnetic separation (WHIMS) has been used as an effective enhanced approach to separate minerals of low magnetic susceptibility from tailings [85]. A WHIMS modeling on tungsten tailings predicted good wolframite recovery rates: approximately 80% (90%) for new tailings and 65% (80%) for old tailings at 0.9 T (1.6 T) magnetic intensity [86]. Another study also found that WHIMS can successfully recover the fine fraction of wolframite from tungsten ore slimes and reach 90% recovery at 1.15 T magnetic intensity [76].

5.4. Flotation

Flotation is a physicochemical separation process for minerals, which usually utilizes various minerals' surface properties to separate valuable minerals and unwanted gangue minerals. Selective flocculants, dispersants, depressants, and flotation collectors are usually used in flotation. Major influencing factors for flotation are mineral surface wettability, surface lattice ion dissolution, surface electrical properties, and solution chemical properties [87]. For scheelite ores, especially occurring in skarns, fluorite, apatite, and

calcite constitute common gangue minerals, flotation is currently the major processing method [88]. Frequently used scheelite flotation depressants are sodium silicate, phosphates, and fluorosilicates [73].

For wolframite, because of its low floatability, selective flotation was hardly used for its beneficiation at an industrial scale. However, for ultrafine wolframite, due to its poor recovery by conventional gravity separation and magnetic separation, flotation was successfully applied. For example, froth flotation, shear flocculation, and spherical agglomeration with highly selective reagents, such as alkyl hydroxamates, phosphonic acid derivatives, and alkylated nitroso-napthols, can significantly enrich fine and ultrafine wolframite from tungsten ore slimes [89]. It was also reported that benzohydroxamic acid (BHA) and sodium oleate (NaOl) as flotation collectors could efficiently improve the fine wolframite collecting capability [90]. While adding lead ions (Pb^{2+}) into flotation collectors could improve the adsorption of BHA onto the wolframite surface in the pH range from 4 to 10.5, which can significantly increase the recovery of fine wolframite in flotation [91]. More recent studies found that a novel surfactant N-(6-(hydroxyamino)-6-oxohexyl) octanamide (NHOO) is a more efficient collector in wolframite flotation [92].

The application of flotation was demonstrated for the fine slimes from a wolframite processing plant. The process could obtain 36.87% WO_3 tungsten concentrates with 62.90% recovery from 0.26% WO_3 fine wolframite slime [83]. However, though flotation could enrich fine and ultra-fine wolframite and reprocess tungsten tailings, the flotation beneficiation reagents left in the new tailings can result in new contamination to the environment, especially some arsenic (As)-bearing reagents (e.g., arsonic acid).

5.5. Chemical Leaching

Chemical leaching for minerals beneficiation is heap leaching. It is a relatively low-cost processing method, widely used for metal extraction from low-grade ores, including copper (Cu), gold (Au), silver (Ag), and uranium (U) [93]. Furthermore, it was also used in soil remediation, reprocessing agglomerated flotation tailings, and for the treatment of coarse rejects from semi-autogenous grinding circuits [94]. This method usually involves acids, alkalis, and cyanide to mobilize and collect valuable metals in solution. However, the main drawbacks of chemical heap leaching are that it can be slow and inefficient and may result in potential risks to the environment [95].

Although chemical heap leaching could be used to reprocess tailings and residue materials [95], it is unlikely to reprocess tungsten tailings. Scheelite is hard to decompose by acids at normal temperature because the generation of the solid-colloidal layer of tungstic acid (H_2WO_4) on the scheelite surface would stop its further decomposition [96]. While decomposing scheelite with sodium hydroxide (NaOH) or sodium carbonate (Na_2CO_3), digestion would require the reaction temperature above 180 °C in an autoclave [97]. It was also reported that scheelite could not be decomposed by NaOH under commercial conditions [98]. Similarly, scheelite leaching with hydrochloric acid (HCl) for tungstic acid would require a reaction temperature above 125 °C [99]. It was almost the same condition needed for wolframite decomposition. Caustic digestion is a conventional method employed to decompose wolframite to produce soluble tungstate (WO_4^{2-}) in the industry. However, it may require higher temperature, pressure, and some other conditions [100,101]. Therefore, it is not feasible for reprocessing of tungsten tailings through chemical heap leaching under natural conditions.

5.6. Bioleaching

Over the past decades, bioleaching has quickly developed and is used to recover metals from ores in the mining industry. So far, bioleaching has been applied to extract zinc (Zn), cobalt (Co), copper (Cu), nickel (Ni), lead (Pb), gold (Au), and arsenic (As) from minerals in the industry [102,103]. For example, bioleaching of copper can achieve a higher than 90% recovery rate, and each year approximately 20% of global copper is produced

through bioleaching [104]. Compared with conventional mineral processing methods, bioleaching is low-cost, highly safe, simple to operate, and environmentally friendly [105].

Currently, bioleaching is more and more frequently applied to extract, recover and remove heavy metals from solid waste as well, including mine tailings and sediments [106,107]. In most cases, acidophilic chemolithotrophic microorganisms are the major microbes for bioleaching. Biological oxidation and complexation reactions are the ways for bioleaching to mobilize metal cations from insoluble minerals [108]. However, bioleaching is sensitive to several conditions, such as solids concentration, temperature, oxygen, pH, redox potential, bacterial strain, and cell concentration. These factors play important roles in the optimization of the bioleaching process [109]. Besides single strain microbe of metal sulfide bioleaching, mixed microbe cultures can be a more efficient way to decompose minerals [110]. Mixed cultures can use elemental sulfur (S^0) and ferrous ion (Fe^{2+}) as energy sources and can either fix atmospheric carbon dioxide (CO_2) or use organic carbon as a carbon source. Usually, it is a much more stable and effective mineral bioleaching consortium. Different bacterial strains in the consortium can also cooperate to respond better to environmental changes during bioleaching [111]. The feasibility of bioleaching for mine tailing reprocessing can be supported by its successful application in the mining industry worldwide.

The growing demand for metals has already led to the re-assessment of old tailings as a potential resource. A few studies have proved that valuable or toxic elements in tailings can be recovered or removed by bioleaching in appropriate ways. A study has demonstrated a successful application of bioleaching to remove heavy metals from low-grade Zn-Pb mine tailings [112]. The experiments also showed that bioleaching is quite effective in recovering Zn and In from old Zn-Pb tailings, with respective recovery rates of up to 100% and 80% [113]. For tungsten minerals, the latest research demonstrated that some microbes (the extreme thermoacidophile *Metallosphaera sedula*) can grow on and directly extract tungsten from scheelite, which proposed a new approach for tungsten tailings reprocessing [114]. One successful bioleaching experiment on tungsten tailings was to remove As and manganese (Mn) from tungsten tailings. When mixed cultures of *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* were applied, the recovery of As could reach 96.7%, and the recovery of Mn almost 100% [115,116].

6. Conclusions

Tungsten is recognized as a strategic and critical metal globally. China has been dominating the tungsten market for over 70 years and currently accounts for more than 82% in production and 56% in reserves (2020). Currently, primary mining covers most of the demand for this metal, with recycling mainly limited to industrial scrap. The reprocessing of old tungsten tailings has been acknowledged in the literature. However, it is still lacking a comprehensive approach. The value of recovered minerals from tailings is usually insufficient to justify a project on a commercial basis. The benefits of tailings decontamination and rehabilitation of abandoned mine sites should also be taken into account.

Tungsten itself is not a toxic element. Except for occupational exposure to tungsten, the environmental level of exposure to tungsten has found no significant health hazards to humans. However, tungsten tailings often represent a significant risk of contamination to the environment; this is due to other heavy metals and elements (e.g., arsenic) present in tailings rather than tungsten itself.

Except for primary tungsten minerals, scheelite and wolframite, secondary tungsten minerals are not well studied. However, in reprocessing, secondary tungsten minerals may lower the recovery of tungsten. The remaining tungsten in tailings is typically present in the fines or slimes. Enhanced gravity separation, wet high-intensity magnetic separation (WHIMS), flotation with newly developed reagents can effectively recover fine and ultra-fine tungsten minerals. Chemical leaching, however, is not feasible in tungsten tailings reprocessing due to special conditions required for tungsten minerals decomposition. Bioleaching trials on tungsten low-grade ores and tailings have been mainly successful for

decontamination purposes, but the technology is still in the early stages of development and can be considered as a part of tailings comprehensive treatment strategy in the future.

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