

Review on Tungsten Recovery and Sustainable Practices

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ABSTRACT: Tungsten, a versatile transition metal located in Group VI of the Periodic Table, is prized for its strength and eco-friendly attributes, finding essential roles in numerous industries. Its applications range from light bulb filaments, X-ray tubes, to military technology, thanks to its outstanding hardness and density. In the chemical sector, tungsten compounds act as catalysts, sourced from minerals like wolframite and scheelite via flotation methods. Tungsten's unique capability to form diverse complexes in different oxidation states is notable, with primary minerals being wolframite and scheelite, and secondary ones influenced by geological processes. Recovery of tungsten has advanced from historical empirical methods to more efficient and eco-conscious practices, involving digestion with soda or caustic soda, crystallization, and the use of solvent extraction or ion exchange to eliminate impurities. Commercial APT production employs an evaporation crystallization process and pyrometallurgical methods, such as roasting, carbothermic reduction, and electric arc melting, to reduce tungsten oxide to its metal form. These processes, combined with novel approaches and recycling methods, contribute to the versatile and sustainable use of this valuable metal. The provided information summarizes the recovery of tungsten from complex sources, including the removal of arsenic from tungsten residues. Key points encompass tungsten recovery methods, hydrometallurgy for tungsten recovery, arsenic removal from tungsten residues, and innovative processes and recycling.

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I. INTRODUCTION

Tungsten, situated in Group VI of the Periodic Table, is a transition metal renowned for its eco-friendly characteristics. Its uniqueness stems from its robust, refractory nature and relative rarity. Tungsten alloys hold pivotal roles across various industries, serving as crucial components in the production of incandescent light bulb filaments, X-ray tubes, welding electrodes, radiation shielding materials, and superalloys. Furthermore, owing to its exceptional strength, hardness, and density, tungsten is highly prized for military applications, particularly in penetrating projectiles.

Within the chemical industry, tungsten compounds serve as catalysts in an extensive array of industrial processes. These processes encompass dehydrogenation, isomerization, polymerization, hydrocracking, hydrosulfurization, hydrodenitrification of mineral oil products, and the selective catalytic reduction of nitrogen oxides emitted from combustion power plant stack gases.

Tungsten is naturally present in the Earth's crust, primarily occurring in minerals chemically bound with other elements. The principal ore minerals housing tungsten, namely wolframite ((Fe,Mn)WO₄) and scheelite (CaWO₄), are abundant and hold significant commercial value. Various physical beneficiation techniques, including gravity separation, flotation, magnetic separation, and electrostatic separation, are conventionally employed for tungsten ore processing. For minerals with particle sizes smaller than 10-20 microns, flotation methods utilizing fine air bubbles are often favored for efficient tungsten extraction. Flotation is a surface-chemistry-based process that leverages differences in mineral particle surface wettability.

Over the last two decades, substantial progress has been made in the study of floatability and the development of specialized reagents. As high-quality tungsten deposits are being depleted, the demand for extracting tungsten from low-grade and complex ores is increasing. Extracting tungsten from low-grade deposits is challenging due to their fine dispersion and complex composition, which includes high calcium gangue minerals and numerous valuable minerals. [Yin, et al., 2014; Sunet al., 2011; Gao, et al.,2015a; Gao, et al.,2015b; Deng, et al.,2015; Deng, et al., 2016; Bo, et al., 2015; Gao et al.,2018]

I.1. Tungsten Characteristics and Mineralogy

Properties, both Physical and Chemical Transition metal tungsten has two to six oxidation states and five to nine coordination numbers (Dori, 1981). Tungsten's ability to form soluble complexes with a wide variety of inorganic and organic ligands is due to its high coordination number. Tungsten is typically complexable with aqueous, oxo, halide, organo, and even mixed ligands. Only at pH 6.2 and in the absence of complexing agents does tungstate (WO₄²⁻) exist as a monomer (Koutsospyros et al,2006). Meanwhile, tungsten can exist in several different oxidation states in nature, but nothing is known about its speciation (Lassner et al.,1999).

I.1.1. Minerals

Tungsten is relatively scarce in the Earth's crust, with an average abundance of approximately 1.5 parts per million (ppm). This scarcity places it in a category even rarer than most rare earth elements (REEs). Naturally occurring primary tungsten minerals can be categorized, with one group being the wolframite group, which includes minerals like wolframite. [(Fe,Mn)WO₄], hübnerite (MnWO₄), ferberite (FeWO₄), and sanmartinite [(Zn,Fe)WO₄] (White, 1983), and scheelite group, including scheelite (CaWO₄), and stolzite and raspite (PbWO₄) (Klopprogge et al.,2004).

Nonetheless, it's important to note that among the primary tungsten minerals, only wolframite and scheelite are both abundant and economically significant. The other primary tungsten minerals are quite rare and typically occur in minuscule quantities. On the other hand, secondary tungsten minerals are generally believed to result from hydrothermal or supergene alteration processes acting upon primary tungsten minerals, rather than being formed through atmospheric weathering. (Sahama, 1981).

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], jixian ite [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 [$CaFe_3H(WO_4)_6 \cdot 10H_2O$]

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 (Steffen ,2012). Weathered tungsten mineral ores can undergo substantial alterations in their mineral composition and properties. These changes often render them unsuitable for flotation and gravity beneficiation processes (Tarassov and Tarassova, 2018) . Additionally, the presence of secondary tungsten minerals can lead to reduced tungsten recovery during the processing of these ores. (International Tungsten Industry Association,1981).

Tungsten mineralization is known to form under a broad range of geological conditions, spanning from magmatic to hydrothermal systems. Various geological deposit types associated with tungsten include skarn, porphyry, vein/stockwork, strata-bound, breccia ,pegmatite, brine/evaporite, placer, and disseminated deposits (Werner et al.,1998). Figure (1) provides an illustration of the different types of tungsten deposits found worldwide.

Globally, the majority of tungsten mineralizations are closely linked to granitic intrusions, particularly those featuring quartz vein systems containing wolframite. These systems are typically located at depths of less than 5 km. For example, tungsten-tin vein-stockwork deposits are often situated within granitic intrusions that were emplaced at depths ranging from 1 to 4 km. These deposits are commonly found near the contact zones of these intrusions and may occur within the granitic rocks themselves or in association with sedimentary, volcanic, metamorphic, or older intrusive rocks(Sinclair et al., 1996) . Tungsten mineralization exhibits distinctive characteristics, primarily in the form of either wolframite [$(Fe,Mn)WO_4$] or scheelite ($CaWO_4$), and this choice of mineral often depends on the specific origin of the deposit. Wolframite mineralization is consistently found alongside greisen formations, while scheelite mineralization is typically associated with skarnization processes (Zhang et al., 2018)Wolframite is primarily found within veins, commonly in conjunction with cassiterite, and within quartz and pegmatite veins of hydrothermal origin that are linked to granitic intrusive rocks (White, 1983), Scheelite crystals exhibit a tetragonal crystal system and possess two distinct cation sites. The tetrahedral [WO_4]²⁻ sites typically accommodate highly charged and smaller cations, such as W^{6+} , Mo^{6+} , As^{5+} , and Nb^{5+} ,while the dodecahedral [CaO_8] sites tend to house alkaline earths and alkali cations(Li et al.,2019).

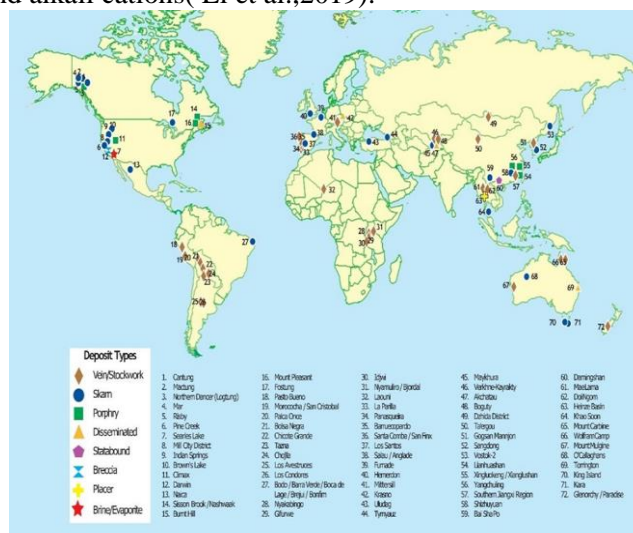


Figure 1. Location and type of major tungsten deposits and district

I.1.2. Recovery of tungsten via hydrometallurgy

I.1.2.1. Leaching process

The history of tungsten extraction technology spans over 150 years, with significant developments occurring since Oxiland patented a method for producing sodium tungstate, tungsten oxide, and metallic tungsten in 1847. Up until the 1950s, tungsten metallurgy relied heavily on empirical methods and was primarily guided by patents (Li and Wang, 1955).

As industrial technologies advanced, the tungsten industry witnessed the adoption of solvent extraction (SX) in 1959 and the introduction of ion exchange (IX) processes in the 1970s. These innovations greatly accelerated the commercial progress of the tungsten industry. More recently, several innovative laboratory processes have been proposed to enhance tungsten recovery and meet stringent environmental standards. These include inorganic acid leaching with phosphor, roasting transformation followed by $(\text{NH}_4)_2\text{CO}_3$ leaching, and H_2SO_4 conversion-ammoniacal $(\text{NH}_4)_2\text{CO}_3$ leaching. A timeline illustrating the evolution of tungsten extractive metallurgy is depicted in Figure 2.

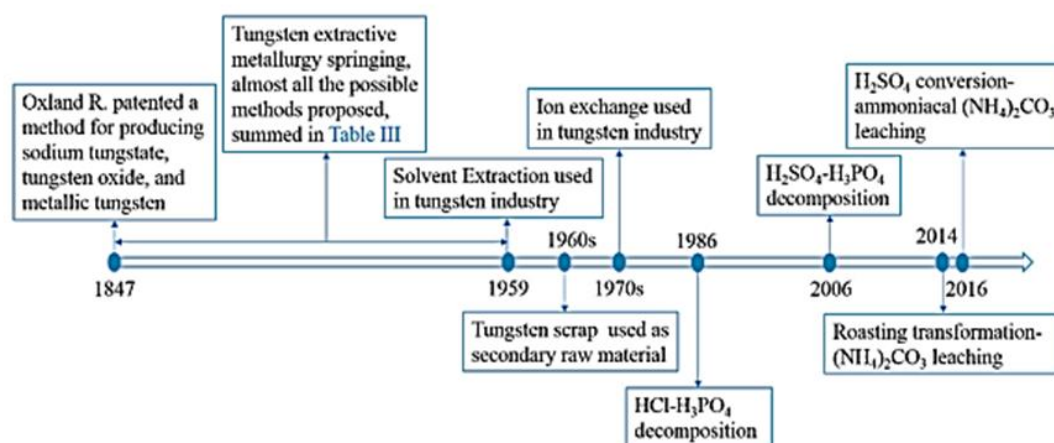


Figure 2. The history and development of tungsten extractive metallurgy

Notably, nearly all the methods for treating tungsten ores that are currently available were proposed prior to the 1950s. Li and Wang's comprehensive summary of tungsten metallurgy in 1955 (Li and Wang, 1955) and Qian's work in 1964 (Qian, 1964) provide valuable insights into the development of tungsten metallurgy. They compile information on the various methods employed before the 1950s, including roasting with substances like Na_2CO_3 , NaOH , NaNO_3 , or neutral salts, leaching with Na_2CO_3 and/or NaOH , and decomposition with H_2SO_4 , HCl , or HNO_3 , among others. These historical methods laid the groundwork for the industrial production of tungsten as we know it today.

The hydrochloric acid process for treating tungsten ores, which has its roots in methods established before the 1950s, has been a significant technique employed in industrial production, primarily using hydrochloric acid as the reagent, as depicted in Figure (3). This process is primarily applied to scheelite ores with relatively low impurity levels. During the decomposition process, impurities are purified and separated from solid H_2WO_4 . The resulting H_2WO_4 can then be directly calcined to produce WO_3 or re-dissolved in aqueous ammonia to obtain an ammonium tungstate solution, especially when dealing with ores that have a high content of impurities in the obtained H_2WO_4 . (Yih and Wang, 1979; Zhang and Zhao, 2005).

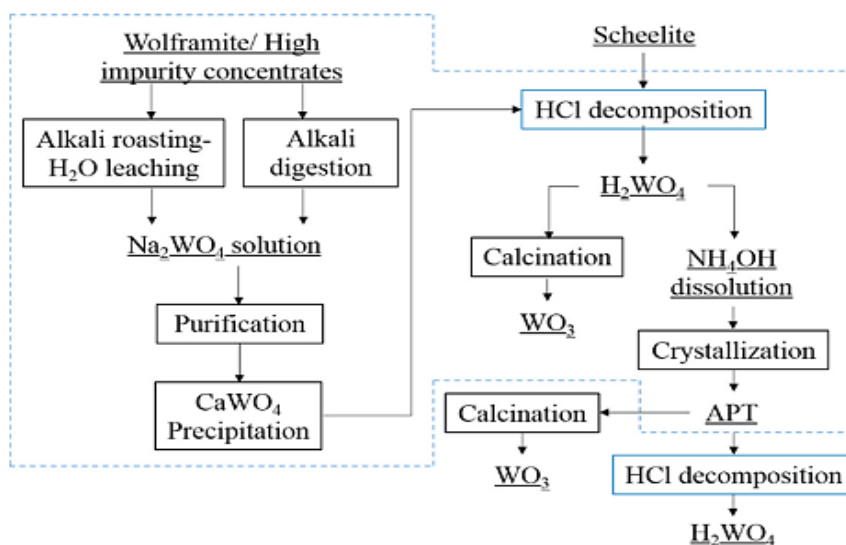


Figure 3. Hydrochloric acid process for APT production (Trasorras et al., 2016; Zhang and Zhao, 2005).

However, when treating wolframite ores or tungsten ores with a substantial impurity content, the process becomes considerably more intricate. It typically involves first producing synthetic scheelite through alkali roasting or alkali digesting, followed by chemical purification steps prior to the actual decomposition in hydrochloric acid.

Even today, the hydrochloric acid tungsten extractive metallurgy decomposition process continues to be employed in certain industries for the production of pure tungstic acid and metatungstic acid. A typical operation of this process involves treating scheelite with an excess of 1.5–3 moles of HCl relative to the stoichiometric amount, at temperatures ranging from 85 to 100 °C (Martins, 2014).

In contrast to the hydrochloric acid process, the current commercial production method offers significant advantages in terms of energy efficiency and reduced labor requirements. This approach utilizes a variety of raw materials to achieve higher WO_3 yields and produce a consistent, high-quality product (Trasorras et al., 2016).

In modern industrial practices, tungsten compounds undergo a digestion process using soda and/or caustic soda. This process leads to the formation of soluble Na_2WO_4 and insoluble carbonates or hydroxides. Following this, the impure Na_2WO_4 solution is subjected to purification and conversion processes to obtain a pure ammonium tungstate solution. This solution is then further processed through crystallization to produce Ammonium Paratungstate (APT). (Gaur, 2006; Lassner, 1995).

The primary processes involved in alkali digestion, followed by either solvent extraction (SX) or ion exchange (IX) steps to transform sodium tungstate into ammonium tungstate, are illustrated in Figure 4 and Figure 5, respectively. Detailed description of the digestion and purification processes is provided, as they are essential components of APT production.

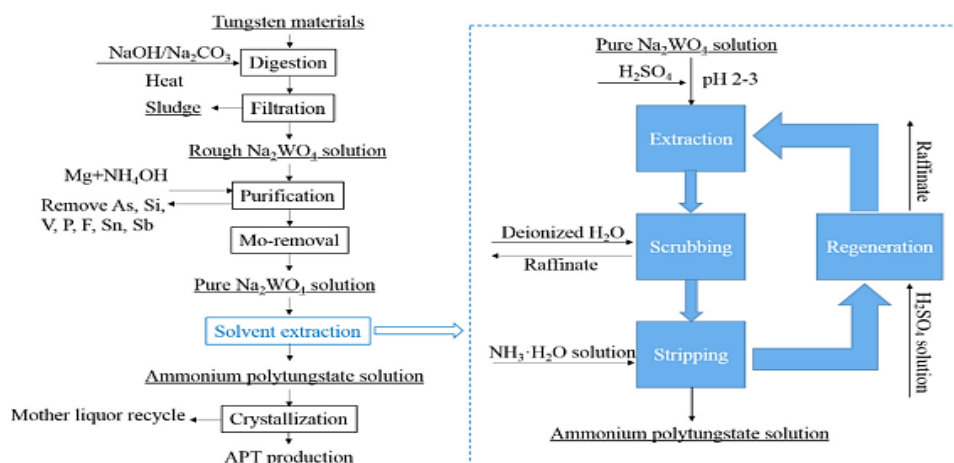


Figure 4. Current APT process with solvent extraction (Trasorras et al., 2016; Zhang and Zhao, 2005).

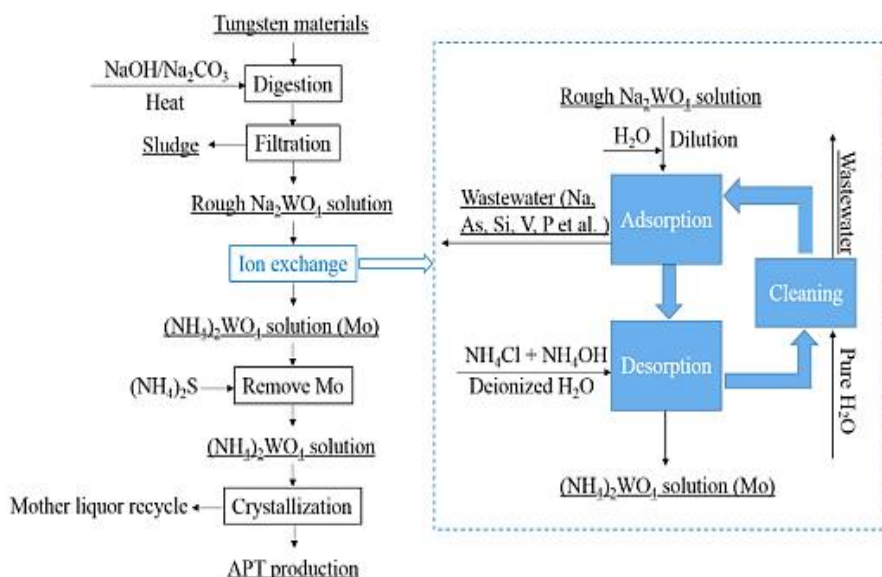


Figure 5. Current APT process with ion exchange (Trasorras et al., 2016; Zhang and Zhao, 2005).

The caustic soda digestion method is commonly employed for treating wolframite, especially when the particle size is less than 44 μm . This process involves the use of concentrated NaOH solutions under atmospheric pressure or, alternatively, dilute NaOH solutions with pressure digestion. Under atmospheric pressure conditions, a caustic soda solution containing 40–50 wt% or 15 mol/L NaOH is utilized at temperatures ranging from 100 to 145 $^{\circ}\text{C}$ to digest wolframite. The duration of the reaction varies from 0.5 to 4 hours, depending on the type of wolframite concentrate. Once the reaction is complete, the slurry is cooled to 90 $^{\circ}\text{C}$ and diluted with water, reducing the NaOH concentration to approximately 5 mol/L. This step facilitates the dissolution of solid Na_2WO_4 , resulting in a WO_3 leaching yield of 97–99% (Yih and Wang, 1979; Quatrini et al., 1982a; Quatrini and Martin, 1982; Quatrini et al., 1982b; Quatrini, 1982).

In the case of pressure digestion, the operation takes place at elevated temperatures, typically ranging from 160 to 195 $^{\circ}\text{C}$. The solid-to-liquid ratio is maintained at 4–5, in a solution containing an excess of $\geq 50\%$ NaOH. The reaction time is typically set at 4 hours, and the total pressure falls within the range of 8 to 12 bar. (Lassner, 1995).

Caustic soda can also be utilized for digesting scheelite, although it requires a higher consumption of NaOH. Achieving a high recovery of WO_3 in scheelite digestion often necessitates simultaneous mechanical activation using a thermo-milling process or a vibratory ball mill, followed by autoclave treatment. This technology is predominantly employed in China (Li et al., 1995; Sun et al., 2003; Zhao et al., 2011a, 2011b, 2011c).

To enhance tungsten extraction from scheelite, Gong et al. (2019) developed a method where CaWO_4 is converted to MgWO_4 by roasting scheelite with MgCl_2 before leaching the roasted product in a NaOH solution at 90°C . Soda digestion is a commonly used method for leaching scheelite concentrate under pressure, especially in Western World plants. This process involves the use of a substantial excess of reagent, but it results in less gangue dissolving in the solution. Soda digestion can be carried out in mild steel autoclaves, while NaOH treatment necessitates Inconel cladding (Maslennitsky, 1939; Cho, 1988; Martins, 1996).

Typical digestion conditions for soda digestion include temperatures in the range of $190\text{--}225^\circ\text{C}$, total pressures ranging from 12 to 26 bar, and the use of a 10–18% Na_2CO_3 solution. The reaction time generally falls between 1.5 to 4 hours. The stoichiometric ratio of Na_2O to WO_3 varies between 2.5 and 4.5 (Yih and Wang, 1979; Lassner, 1995). However, this ratio can increase to as much as 5 when the scheelite concentration is low (Blair, 1966). The excess Na_2CO_3 can sometimes hinder scheelite decomposition by forming insoluble double carbonates ($\text{Na}_2\text{CO}_3\cdot\text{CaCO}_3$ or $\text{Na}_2\text{CO}_3\cdot\text{CaCO}_3$) on the surfaces of scheelite particles (Martins and Martins, 1997; Yang et al., 2018). Wolframite concentrates can also be digested by soda under pressure, following a similar process to that used for scheelite (Lassner, 1995).

Due to the often complex mineralogy of tungsten ores, tungsten concentrate typically consists of a mixture of scheelite and wolframite. In industrial operations, combinations of soda and caustic soda are employed, with the ratio depending on the specific process and the assay of the concentrate. Additionally, there are alternative methods for decomposing tungsten concentrates, such as the soda/caustic soda sintering-water leaching method (Paulino et al., 2012; Srinivas et al., 2000) and NaF digestion (Zhang and Zhao, 2005). These methods are similar to caustic soda and soda digestion in that they produce a Na_2WO_4 solution. However, they do not meet the strict environmental requirements of modern industry due to their high energy consumption, corrosiveness, and pollution caused by the presence of F^- ions.

During the digestion process, certain impurity elements that are initially present as gangue in the tungsten concentrate may dissolve in the solution. Therefore, it becomes necessary to incorporate a purification step to maintain the chemical quality required for APT production. Additionally, the separation of sodium ions (Na^+) is accomplished through solvent extraction (SX) or ion exchange (IX) steps, coupled with the conversion of Na_2WO_4 to $(\text{NH}_4)_2\text{WO}_4$. To ensure the production of high-quality Ammonium Paratungstate (APT) and prevent complications during the manufacturing of metallic tungsten powder, it is essential to reduce the Na^+ concentration to less than 10 mg/L.

1.1.2.2. Solvent extraction

The solvent extraction process plays a pivotal role in the tungsten industry, particularly in Western countries (Trasorras et al., 2016; Yih and Wang, 1979). As illustrated in Figure 5, the initial step involves the removal of impurities. Impurities such as silicon (Si), phosphorus (P), tin (Sn), arsenic (As), and iron (Fe) are eliminated from the Na_2WO_4 solution through the addition of magnesium salts and ammonium hydroxide, leading to the formation of precipitates. Subsequently, molybdenum removal is carried out by introducing an excess of sulfide to precipitate molybdenum trisulfide in an acidified solution with a pH of 2.5–3.0 (Huggins et al., 1982; Pastukhov and Skripchenko, 2015). To enhance the efficiency of the subsequent solvent extraction step, the Na_2WO_4 solution is acidified to a pH of 2.5–3.0 using an inorganic acid, typically H_2SO_4 .

In the solvent extraction (SX) step, the organic phase consists of a mixture of tertiary or secondary aliphatic amines, along with isodecanol and kerosene (Cica et al., 1990; Moris et al., 1999; Zhang et al., 2016). The extraction process is depicted in Figure 5. Initially, tungsten is extracted as isopolytungstate ions into the organic phase, while sodium is separated and forms a Na_2SO_4 solution. Subsequently, the isopolytungstate is stripped from the organic phase using ammonia solution, resulting in an aqueous phase containing an ammonium isopolytungstate solution after being washed with deionized water. The organic solvent is regenerated through washing with a dilute H_2SO_4 .

solution (Trasorras et al., 2016; Yih and Wang, 1979). Additionally, molybdenum can be removed from ammonium tungstate solutions using solvent extraction with a quaternary ammonium salt extractant (Wu et al., 2019).

I.1.2.3. Ion exchange

The ion exchange (IX) process is predominantly employed in Chinese plants. In industrial facilities, a strongly alkaline ion exchange resin in the chloride form is used, including types such as 201 × 7, WA, and D201 (He, 1989; Zhao et al., 2010). The IX step serves a dual purpose: it can convert Na_2WO_4 to $(\text{NH}_4)_2\text{WO}_4$ and simultaneously remove impurities such as arsenic (As), silicon (Si), vanadium (V), and phosphorus (P) from the tungstate solution. Unlike the SX step, the IX step simplifies the process of impurity removal, and the only additional step required is the removal of molybdenum, achieved by adding ammonium sulfide and a copper compound to form copper thiomolybdate precipitate (Li et al., 1995; Huang et al., 1995).

As depicted in Figure (5), the impure Na_2WO_4 solution must be diluted with softened or deionized water to create a solution containing 15–25 g/L WO_3 , 4–8 g/L NaOH, and less than 0.7 g/L Cl^- . When this solution comes into contact with the IX resin, tungstate is adsorbed, generating substantial quantities of high salinity wastewater. Subsequently, the tungstate is desorbed by washing the resin with an ammonium chloride solution, followed by ammonium hydroxide and deionized water, resulting in the production of an ammonium tungstate solution. The resin can be recycled and reused after the stripping and cleaning steps

I.1.2.4. Crystallization

In the commercial production of Ammonium Paratungstate (APT), the purified ammonium tungstate solution undergoes crystallization through an evaporation crystallization process (Gaur, 2006; Trasorras et al., 2016). During crystallization, the purity of the ammonium tungstate solution and the parameters of crystallization play a critical role in producing high-quality APT. These factors influence the size and morphology of APT crystals. After crystallization, a further separation of impurities from the APT product is carried out, with the mother liquor being recycled back into the process.

The thermal decomposition of APT results in the production of three major intermediate compounds: ammonium metatungstate, yellow oxide, and tungsten blue oxide (Gaur, 2006; Kalpakli et al., 2013). Tungsten powder can be produced by reducing tungsten trioxide using hydrogen (Jiang et al., 2019), ethanol (Cetinkaya and Eroglu, 2017), or methane (Cetinkaya and Eroglu, 2015; Wu et al., 2018).

Since the crystallization and subsequent operations are nearly identical in commercial production, we did not provide detailed information on these steps

I.1.3. Recovery of tungsten via pyrometallurgy

The processing of tungsten concentrates heavily relies on hydrometallurgical processes. However, these approaches face significant challenges due to the decreasing tungsten grade and increasing impurities in tungsten minerals. These challenges include high consumption of chemical reagents, substantial industrial process water usage, environmental concerns related to generated pollutants, and increased wear and tear on equipment due to high pressures and acidic or alkaline conditions.

Considering these challenges in traditional hydrometallurgy, pyrometallurgy technology could be a viable alternative to overcome the difficulties associated with declining tungsten grades. To consolidate the current state of knowledge, identify research gaps, and stimulate new research in the field of pyrometallurgical processing of tungsten concentrates, this chapter examines published research related to the pyrometallurgical processes involved in extracting tungsten and the phase diagrams relevant to tungsten systems.

I.1.3.1. Roasting and Smelting:

Roasting and smelting is a commonly used pyrometallurgical technique for extracting tungsten from its ores. In this process, tungsten ore, often in the form of scheelite or wolframite, is subjected to high temperatures in the presence of oxygen. This thermal treatment converts the tungsten minerals into tungsten trioxide (WO_3). Subsequently, in the smelting step, the tungsten trioxide is reduced using carbon or hydrogen in a specialized furnace. This reduction reaction results in the production of pure tungsten metal (W), which can then be further processed and refined for various applications (He, & Chen, 2019).

I.1.3.2. Carbothermic Reduction:

Carbothermic reduction is another key method for extracting tungsten from its ores. In this process, tungsten ore is intimately mixed with carbon, typically in the form of graphite. The mixture is then subjected to high-temperature conditions in an electric furnace. During this process, the carbon reacts with the tungsten oxide present in the ore. The result is the reduction of tungsten oxide to tungsten metal and the liberation of carbon monoxide gas. Carbothermic reduction is favored for its efficiency and ability to yield high-purity tungsten metal. (Wang et al.,2023)

I.1.3.3. Aluminothermic Reduction

Aluminothermic reduction is an exothermic pyrometallurgical process used to extract tungsten from its oxide forms. This technique involves the use of aluminum powder as a reducing agent. When aluminum reacts with tungsten oxide, it generates extremely high temperatures due to the exothermic nature of the reaction. This heat drives the reduction of tungsten oxide to tungsten metal. Aluminothermic reduction is known for its effectiveness in producing high-purity tungsten metal. (Sheybani, et al. 2019).

I.1.3.4. Electric Arc Melting

Electric arc melting is a specialized pyrometallurgical technique for the production of tungsten metal. In this method, tungsten concentrates, often containing impurities, are loaded into an electric arc furnace. Fluxes are added to aid in the removal of impurities. The process relies on the high temperature generated by an electric arc, which causes the reduction of tungsten oxide to tungsten metal. This method is valued for its ability to produce ultrafine tungsten powders with precise control over composition(He,& Feng2013).

I.1.3.5. Plasma Arc Melting

Plasma arc melting is an advanced pyrometallurgical technique used for the extraction of tungsten from its ore. In this method, a high-temperature plasma arc is created through an electric discharge. Tungsten ore is introduced into the intense heat of the plasma, causing it to vaporize. The vaporized tungsten is then condensed, resulting in the production of tungsten metal. This process offers advantages in terms of purity and precision in tungsten powder production. (Mukherjee et al. 2015).

I.1.4. Noval processes

I.1.4.1. Acid leaching with phosphor

In the quest for efficient extraction methods of tungsten from scheelite ore, researchers have explored various acid leaching approaches. One notable method involves the use of hydrochloric acid in conjunction with phosphoric acid as a complexing agent (Xu et al., 1986). This innovative combination mitigates the hindrance posed by the formation of the H_2WO_4 product layer during the hydrochloric acid process, resulting in the generation of soluble compounds, such as $H_3PW_{12}O_{40}$ and $CaCl_2$ (Xu et al., 1986).

Another promising technique involves a mixture of hydrochloric acid and phosphoric acid, which serves to decompose scheelite ore. This process leads to the precipitation of a hetero-polytungstate salt known as $(NH_4)_3 \cdot PW_{12}O_{40} \cdot 9H_2O$ (Gürmen et al., 1999; Gürmen et al., 2002). Subsequent calcination of this precipitated salt yields WO_3 powder, which can be further reduced to produce metallic tungsten powder (Gürmen et al., 1999; Gürmen et al., 2002). Additionally, the acid solution utilized in this method can be efficiently recycled for leaching purposes by treating it with H_2SO_4 to form gypsum (Gürmen et al., 1999; Gürmen et al., 2002).

A novel approach introduced by Razavizadeh and Ershad (2006) avoids the treatment of $CaCl_2$ solution and focuses on leaching both low-grade and high-grade scheelite ores using H_2SO_4 in the presence of H_3PO_4 and $NaCl$ at atmospheric pressure. This innovative technique yields a soluble tungstic acid solution and solid $CaSO_4 \cdot 2H_2O$ (Razavizadeh & Ershad, 2006). The addition of NH_4Cl to the leaching solution facilitates the precipitation of $(NH_4)_3P_2O_4 \cdot 4WO_3 \cdot 9H_2O$, which can be subsequently dissolved using ammonium hydroxide. Further purification and evaporation steps are employed to obtain ammonium paratungstate (APT), which can undergo subsequent processing to produce WO_3 and metallic tungsten powder (Razavizadeh & Ershad, 2006).

Additionally, Li and Zhao (2016) employed a mixed solution of H_2SO_4 and H_3PO_4 to digest scheelite concentrate (Li & Zhao, 2016). Their patented method involves the initial formation of phosphotungstic acid crystals, followed by dissolution and transformation through various routes such as the addition of an ammonia solution or the utilization of ion exchange (IX) or solvent extraction (SX) steps (Li & Zhao, 2016).

These diverse acid leaching techniques underscore the versatility and adaptability of the approach in scheelite ore processing, aiming to maximize tungsten extraction efficiency while minimizing environmental impact and resource consumption (Xu et al., 1986; Gürmen et al., 1999; Gürmen et al., 2002; Razavizadeh & Ershad, 2006; Li & Zhao, 2016).

I.1.4.2. Roasting transformation-(NH₄)₂CO₃ leaching

Li et al. (2014a, 2014b) introduced an innovative tungsten extraction method known as the "roasting transformation-(NH₄)₂CO₃ leaching" process, aimed at recycling raw materials and minimizing wastewater discharge. The schematic representation of this technology is illustrated in Fig. 6. This approach involves the initial roasting of a well-mixed combination of tungsten concentrate and calcium carbonate at temperatures ranging from 800 to 850 °C. This roasting step serves to convert tungsten minerals into Ca₃WO₆ (Li et al., 2015) and/or Ca_{3-x}(Fe, Mn)_xWO₆ (0 < x ≤ 1) (Li et al., 2016). Subsequently, the roasted product is subjected to leaching in an ammonium carbonate solution maintained at temperatures between 30 and 80 °C, resulting in the production of (NH₄)₂WO₄ solution (Xu et al., 2019). The leaching residue primarily comprises calcium carbonate, which can be efficiently recycled. The purified leaching solution undergoes evaporation and crystallization processes to yield ammonium paratungstate (APT). The mother liquor, along with additional ammonium carbonate, is recycled back into the leaching process.

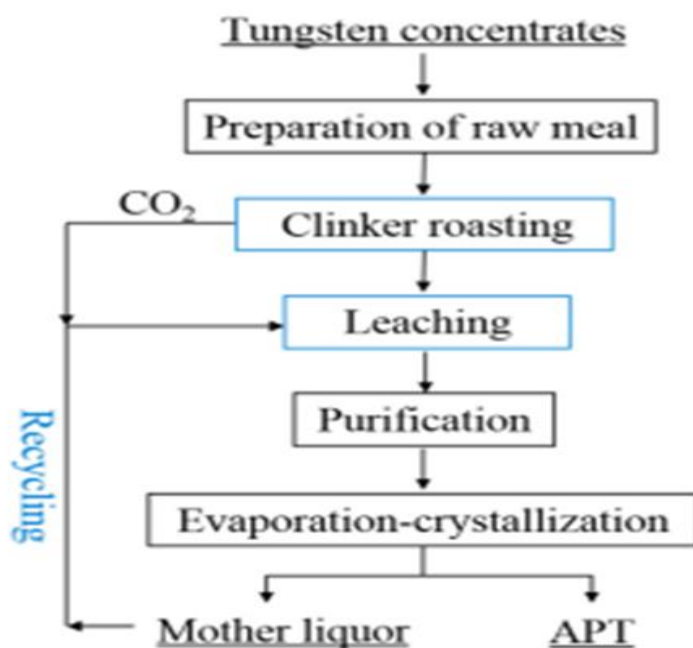


Figure 6. The flow sheet of roasting transformation-(NH₄)₂CO₃ leaching process

I.1.4.3. H₂SO₄ conversion-ammoniacal (NH₄)₂CO₃ leaching

In an effort to enhance efficiency, cost-effectiveness, and environmental sustainability, a novel approach has been proposed, denoted as the "H₂SO₄ conversion-ammoniacal (NH₄)₂CO₃ leaching" route. This approach leverages the advantageous characteristics of sulfuric acid, known for its low volatility and cost-effectiveness, as well as the recyclability of ammoniacal ammonium carbonate solution. The corresponding process flowchart is outlined in Fig. 7. This method enables complete conversion of tungsten concentrates within H₂SO₄ solutions under atmospheric pressure, typically achieved at temperatures ranging from 70 to 90 °C, while controlling H₂SO₄ concentration and oxidizing Fe²⁺/Mn²⁺ in the solution (Li et al., 2017; Shen et al., 2018b,c). The resulting converted solution, containing only minor amounts of metal ions, can be recycled for treating subsequent batches of tungsten concentrate by supplementing it with H₂SO₄. The converted product, a mixture of H₂WO₄ and CaSO₄, is then subjected to leaching at approximately 30 °C under atmospheric pressure within an ammoniacal (NH₄)₂CO₃ solution. This step directly yields (NH₄)₂WO₄ solution and solid CaCO₃ in the leaching residue (Shen et al., 2018d). APT production is subsequently achieved through the evaporation-crystallization of the purified (NH₄)₂WO₄ solution. Following APT crystallization, any residual WO₃ present in the mother liquor is precipitated as solid H₂WO₄ by the addition of

H₂SO₄, thus enabling recycling back to the leaching step. Additionally, the leaching system can be regenerated by capturing gaseous NH₃ and CO₂ from the evaporation-crystallization and recovery process steps. This process represents an efficient, economical, and environmentally friendly pathway for ammonium paratungstate production (Li et al., 2017; Shen et al., 2018b,c,d).

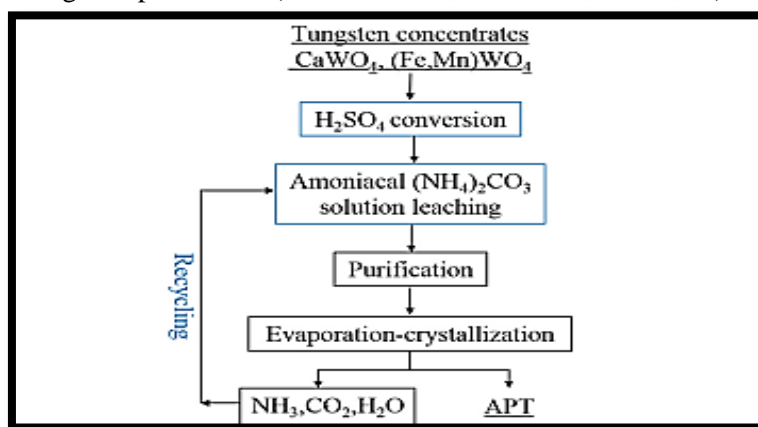


Figure 7. The flow sheet of H₂SO₄ conversion-ammoniacal (NH₄)₂CO₃ leaching process

I.1.5. Recycling tungsten from scrap

The recycling of tungsten from scrap materials has gained increasing importance in the tungsten industry due to the complexity of tungsten minerals and the limited availability of natural resources. Recent years have witnessed extensive research efforts aimed at improving tungsten recycling methods to enhance recovery rates. As illustrated in Figure 8 and outlined in various studies (Trasorras et al., 2016; BGS, 2011a; Shemi et al., 2018), recycling methods can be categorized into three main approaches: direct recycling, semi-direct recycling, and indirect recycling.

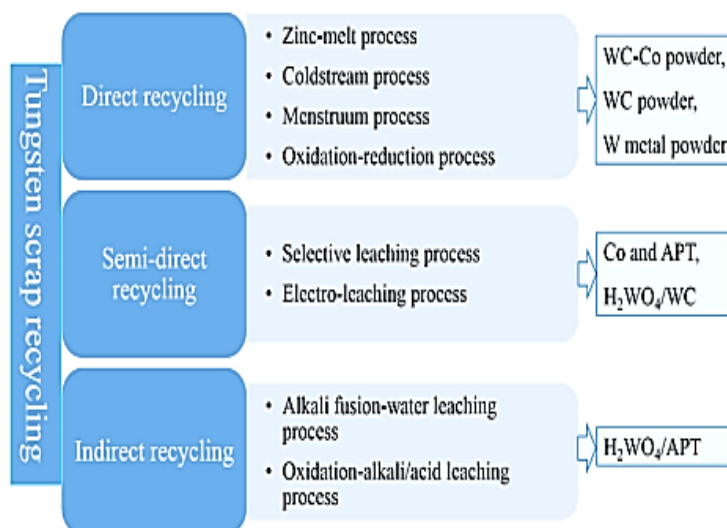


Figure 8. Tungsten recycling methods from the tungsten scraps (Srivastava et al., 2019; Shemi et al., 2018; Trasorras et al., 2016; BGS, 2011a).

Direct recycling involves the conversion of tungsten scrap into powder using environmentally and economically advantageous methods. One common technique is the Zinc-melt process, which is used to recycle cemented carbide scrap and recover WC-Co without the consumption of chemicals. This approach significantly reduces both atmospheric and chemical waste pollution (Freemantle and Sacks, 2015). However, it should be noted that only certain types of scrap can be directly recycled using this method.

Semi-direct recycling is suitable for low-grade scrap that contains other metals. A typical method involves selective acid leaching, where the tungsten scrap is initially leached in a mineral or organic acid to dissolve the binder metal. Subsequently, the remaining materials are leached in another

solution to recover tungsten and other metals (Chio et al., 2018; Edtmaier et al., 2005; Song et al., 2018; Zhang et al., 2018). The resulting powder composition is closely related to the type of scrap and the specific recycling method employed.

Indirect recycling, sometimes referred to as hydrometallurgical recycling, entails the treatment of fused or oxidized tungsten scrap through modern tungsten extraction metallurgical processes to obtain ammonium paratungstate (APT) or H_2WO_4 production (Bhosale et al., 1990). While this method is capable of treating most types of tungsten scrap, it is associated with higher costs, substantial chemical consumption, and the generation of waste during the procedures.

I.2. Tungsten industrial role

Tungsten, a versatile and indispensable element in modern industry, plays a pivotal role across a broad spectrum of applications due to its exceptional properties. With a melting point of 3,422 degrees Celsius, tungsten boasts the highest melting point of any metal, making it a fundamental component in industries that require extreme heat resistance and durability.

In the manufacturing sector, tungsten is a vital player, primarily in the production of cutting tools and alloys. Its unmatched strength and wear resistance ensure that cutting tools maintain their sharpness and longevity even under the most demanding conditions. This characteristic has revolutionized the machining and construction industries, leading to more efficient and cost-effective processes.

Tungsten's electrical conductivity is another key feature that drives its use in the electronics and electrical engineering sectors. It is commonly employed in electrical filaments, particularly in the production of incandescent light bulbs and specialized high-temperature applications. This property ensures efficient energy conversion and enables the creation of high-performance electrical components.

The medical field benefits significantly from tungsten's radiation shielding properties. Tungsten is used in X-ray shielding materials, ensuring the safety of patients and healthcare professionals during medical imaging procedures. Its ability to absorb and block harmful radiation has revolutionized the healthcare industry, contributing to better patient care and diagnosis.

Moreover, tungsten's robustness finds applications in aerospace and aviation industries, where it is used in engine components and structural materials, contributing to the safety and efficiency of air travel.

In conclusion, tungsten's unique properties make it an essential element in various industrial sectors, from manufacturing and construction to electronics, healthcare, and aerospace. Its remarkable strength, heat resistance, and electrical conductivity continue to drive innovation and technological advancements, underlining its pivotal role in shaping the modern industrial landscape. <https://www.britannica.com/science/tungsten>

Tungsten leaching residues are currently designated as hazardous solid waste, requiring proper treatment before disposal, as outlined in reference (Liu et al., 2020). The intricate compositions and mineralogy of these tungsten residues have presented significant challenges, resulting in limited reports regarding their treatment, and no commercially viable process has been established to date. Consequently, these residues have been accumulating near production sites, leading to severe environmental pollution and harm to ecosystems due to the presence of toxic elements, as cited in references (Leal-Ayala et al., 2015)

Typically, tungsten residues contain approximately 1 – 3 wt% of WO_3 , along with a mixture of other materials, including iron, aluminum, calcium, sodium, manganese, arsenic, and lead. The crux of the matter lies in the necessity to remove toxic elements like arsenic and lead while simultaneously recovering valuable metals. This is crucial to maximize the utilization of tungsten resources efficiently. Therefore, the design of a process for the removal of hazardous metals from these residues, without excessive reliance on external additives and energy input, is of paramount importance

The extraction of valuable materials from tungsten residues presents a complex challenge due to their intricate mineralogy and the presence of various mineral phases. A review paper authored by (Liu et al., 2020), as referenced provides an overview of current developments in the tungsten industry and summarizes the existing treatment processes.

Several methods have been explored to recover valuable metals, including tungsten (W), scandium (Sc), tantalum (Ta), and niobium (Nb), from these residues. These methods include pressure leaching

with soda, acid extraction, selective leaching using HF-H₂SO₄, and alkaline fusion, as referenced in (DAI et al.,2008; XIANG et al., 2012) However, hydrometallurgy processes, which are commonly used for this purpose, often require substantial amounts of chemical reagents and high-pressure conditions. A major concern with these processes is that a significant portion of toxic elements remains in the second slag, posing environmental challenges.

An alternative approach investigated is a two-stage carbothermic reduction process through pyrometallurgy, as detailed in (Liu et al.,2020). This process involves the reduction of iron alloys during the procedure, which spontaneously collects other valuable metals. Selective carbothermic reduction has a well-established history in pyrometallurgical industries for extracting valuable metals from resources with complex mineralogy, such as nickeliferous limonitic laterite ores, waste smelter slag, nickel alloy scrap, and polymetallic nodules, as referenced in (Zhiming et al., 1987; Pickles et al.,2014;Banda et al.,2002; Friedmann et al.,2017; Su et al.,2020; Zhao et al.,2019)

Tungsten residues, rich in iron content, are suitable candidates for producing alloyed white cast iron. The recovery of tungsten into white cast iron is desirable as the presence of tungsten enhances its machinability. The selectively carbothermic reduction method is attractive because it allows for the production of high-grade alloy products using a low-cost carbonaceous reductant and operates at relatively low temperatures. However, there is limited literature available on the recovery of tungsten residues through carbothermic reduction. Nevertheless, given the similarities in the general reduction approach, existing reduction technologies can potentially be adapted for processing tungsten residues. An interesting parallel to this approach is the study of selectively carbothermic reduction on polymetallic nodules, as mentioned in (Friedmann et al.,2017 ; Sommerfeld et al., 2018)Polymetallic nodules share a complex mineralogy similar to that of tungsten residues. By controlling the reduction order of metal oxides, it becomes possible to extract valuable metals, such as iron (Fe), nickel (Ni), copper (Cu), and cobalt (Co), as Fe-Ni-Cu-Co alloys. This control is achieved by leveraging the varying Gibbs free energy of different metal oxides. Fluxes are used to adjust the slag's liquidus temperature, optimizing the separation of reduced alloy and slag and reducing energy consumption during the reduction process. Various types of fluxes, including Al₂O₃, SiO₂, CaCO₃, and others, are employed depending on the slag compositions. Thermodynamic simulation software like FactSage aids in calculating the effect of flux on liquidus temperature. This carbothermic reduction approach holds promise for effectively utilizing tungsten residues after systematic evaluation and optimization of reaction conditions. The following equation demonstrates the reactions occurring during carbothermic reduction:



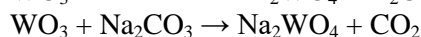
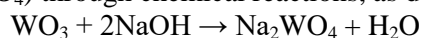
Where Me = W, Bi, Pb, As, Sn, Fe, Mn

After the separation of valuable metals from the residues, the treated residues often contain a significant amount of SiO₂, CaO, and Al₂O₃, which can potentially be used to produce glass ceramics or glass, as explored in (Alfonso et al.,2016; Peng et al., 2014) Researchers have investigated methods for utilizing these residues in glass and glass-ceramic production, with potential applications in building materials.

In addition to carbothermic reduction, research has also focused on tungsten recovery through hydrometallurgy. This involves processes like roasting and leaching with sodium hydroxide, sodium carbonate, and sodium oxide, as reported in the literature (Wan et al.,2009;Xiao et al.,2012 ; Yang et al.,2019;DAI et al., 2003).

Roasting facilitates the conversion of tungsten into soluble sodium tungstate, which can then be separated through leaching. The recycling of dissolved sodium tungstates back into the extraction process minimizes tungsten loss.

Roasting plays a pivotal role in the recovery of tungsten from its alloys, allowing tungsten to form soluble sodium tungstate (Na₂WO₄) through chemical reactions, as described by following Equations:



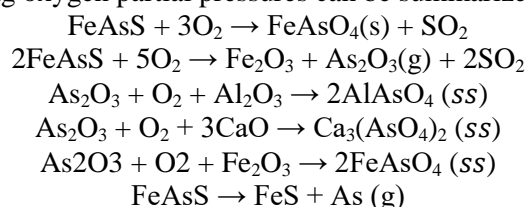
This sodium tungstate is water-soluble and can be effectively separated by leaching. To further enhance tungsten recovery, the dissolved sodium tungstates can be recycled back into the purification

or ion exchange stage of the existing tungsten extraction process, significantly reducing tungsten losses during production.

Research by Du et al., as documented in reference (Du et al., 2014) investigated the impact of roasting conditions on tungsten alloy recovery through leaching. Their findings revealed that tungsten oxidation within the alloy initiated at temperatures equal to or greater than 400 °C, with rapid oxidation occurring as temperatures reached 700 °C. However, the tungsten recovery rate during leaching plateaued when temperatures exceeded 700 °C. The study also delved into the effects of leaching water temperature and time on tungsten recovery. It was determined that a water leaching temperature of 80 °C was optimal to minimize energy consumption and prevent leaching liquor volatilization. The leaching time was found to be most effective at 30 minutes, as tungsten recovery reached its peak during this period.

Another study conducted by Dai et al., as outlined in reference (DAI et al., 2003) focused on recovering tungsten from wolframite residues through soda roasting and subsequent water leaching. The experiments revealed that the actual amount of soda required exceeded theoretical estimations by a factor of six. The optimal roasting temperature range was found to be between 850-950 °C, with a roasting time of 50 minutes. For leaching, the most effective conditions were a leaching time of 90 minutes and a water temperature ranging from 95-100 °C. The research achieved a maximum tungsten recovery rate of 80% during the experiments. However, the presence of CaO or CaCO₃ in the tungsten residues led to the formation of calcium tungstate, which significantly impacted tungsten recovery. Comparatively, the hydrometallurgy route for tungsten recovery demands less energy consumption and generates fewer off-gases compared to the reduction process. Recovered tungsten can be recycled back into the existing tungsten extraction process, minimizing overall tungsten losses.

Arsenic, a toxic element, can be present in various forms, with significant arsenic-containing minerals including orpiment (As₂S₃), realgar (As₂S₂), arsenopyrite (FeAsS), and complex sulfide minerals like proustite (Ag₃AsS₃), enargite (Cu₃AsS₄), and tennantite ((Cu, Fe)₁₂As₄S₁₃) (Du et al., 2014). Arsenic's presence in alloys is undesirable due to its toxicity and its adverse effects on alloy properties. Analytical findings using EPMA indicate that arsenic is primarily present in residues in the form of arsenopyrite (FeAsS). Based on an analysis of existing literature, the reactions of arsenopyrite during roasting under varying oxygen partial pressures can be summarized in following Equations:



Research conducted by Lu et al. focused on arsenic removal from silver-bearing copper ores through roasting under a nitrogen atmosphere (Lu and Yin, 2016). It was observed that FeAsS decomposition occurred at 554 °C under a nitrogen atmosphere. Reducing the oxygen concentration from 20% to 0% significantly increased arsenic removal from 67.0% to 96.9%.

Cheng et al. investigated the mechanism of arsenic removal from arsenopyrite-bearing iron ore through roasting (Cheng et al., 2019). In this study, iron ores were mixed with graphite reductants and arsenopyrites and then roasted under oxygen or nitrogen atmospheres. The results indicated that arsenic removal favored low oxygen partial pressure, particularly within the roasting temperature range of 700 - 1,000 °C (Cheng et al., 2019).

Yin et al. also found support for low oxygen partial pressure in their study on arsenic removal through roasting under vacuum conditions (Yin et al., 2014). Figure (9) illustrates the impact of temperatures and oxygen partial pressures on arsenic-containing products in dust ash generated by reduction roasting (Cheng et al., 2019). The figure demonstrates that excessive oxygen partial pressure is not advantageous for arsenic removal.

Furthermore, thermodynamic calculations under a reduction environment showed that arsenate formation occurs when the roasting temperature is ≤390 °C. When the roasting temperature falls between 390–890 °C, arsenic gases are formed and easily volatilized. However, at temperatures ≥890

°C, arsenates are formed, inhibiting the volatilization of arsenic products and affecting the efficiency of arsenic removal.

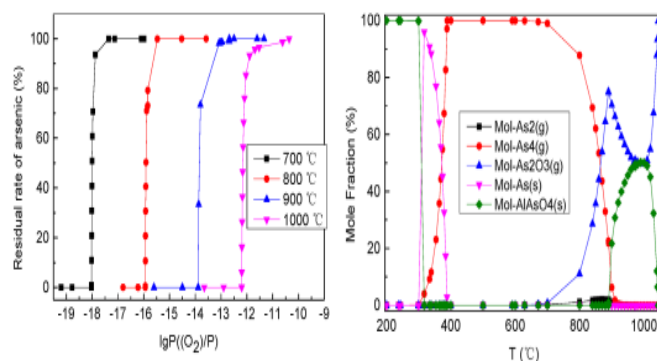


Figure 9. Effect of temperatures and oxygen partial pressures on arsenic-containing products by reduction roasting

The mechanism of arsenic removal from arsenopyrite ore during a sintering process was further explored by (Cheng et al.,2017). Their investigation revealed that arsenic removal occurred in various zones, including the ignition layer, the sintered layer, and the combustion zone. This removal process was driven by the reaction of a portion of FeAsS with excess oxygen, resulting in the formation of FeAsO₄, while the remaining FeAsS reacted with oxygen to produce arsenic trioxide (As₂O₃) and sulfur dioxide (SO₂) gases. During these reactions, some of the arsenic trioxide gases could combine with other metal oxides, such as CaO or Al₂O₃, forming compounds like Ca₃(AsO₄)₂ and AlAsO₄. These arsenate compounds retained arsenic within the sintering products. Importantly, because the formation of arsenic gases during roasting is favored under low oxygen partial pressure conditions, roasting under a nitrogen or argon atmosphere shows promise for efficient arsenic removal from tungsten residues. The roasting process allows arsenic to separate as gases from other solid materials. However, it's worth noting that a disadvantage of this process is the need to collect and treat the off-gases generated during reactions before releasing them into the environment. Therefore, the roasting method is preferable for treating tungsten residues with lower arsenic contents to maintain reasonable off-gas treatment costs.

In addition to roasting, some researchers have explored hydrometallurgical methods for arsenic removal. Yu et al. investigated the extraction of arsenic from arsenic-containing cobalt and nickel slag (Yu et al.,2014) They achieved a maximum arsenic removal rate of 99.1% by leaching the arsenic-containing slag in an alkaline aqueous medium while bubbling oxygen into the solution at 140 °C. The study reported that the crystallization of sodium arsenate (Na₃AsO₄) occurred during the cooling of the hot leachate, and this compound is soluble in water, remaining dissolved in the leachate during the cooling stage.

Guo et al. developed a method for precipitating arsenic as sodium arsenate from alkaline leachate through an oxidation-precipitation process. This method selectively extracted arsenic from arsenic-bearing dust. The extracted sodium arsenic was converted into a calcium-arsenic (Ca-As) compound by adding excess CaO. The resulting Ca-As compound was then dissolved in an H₂SO₄ solution to produce Ca₅(AsO₄)₃OH, which crystallized as octahedral-shaped As₂O₃. This process achieved the extraction of over 90.0% of the arsenic present.

Xu et al. proposed a method to separate arsenic from residues by roasting them with soda or caustic soda and subsequently leaching them with water (Xu et al.,2019). According to the patent, the amount of soda or caustic soda required during the process ranged from 20% to 80% of the treated residues. Roasting needed to be carried out within a temperature range of 300-1100 °C for a duration of 0.05-12 hours. Leaching the roasted residues with water effectively removed arsenic from the solid products, reducing the arsenic concentration in the leached residues to ≤0.1%. Although hydrometallurgical methods for arsenic extraction consume significant quantities of chemical reagents, they do not generate harmful gases. These approaches offer high arsenic recovery rates with lower energy consumption, making them ideal for treating tungsten residues with high arsenic

contents. Furthermore, the arsenic in the leachate can be recycled back to the ion exchange stage, mitigating risks and costs associated with further treatment of arsenic products.

II. Conclusion

Tungsten, a versatile transition metal found in Group VI of the Periodic Table, is renowned for its strength and environmentally friendly characteristics. It plays a pivotal role in numerous industries, from light bulb filaments and X-ray tubes to military applications, thanks to its exceptional hardness and density.

In the chemical sector, tungsten compounds act as catalysts in various industrial processes. Tungsten is naturally sourced from minerals such as wolframite and scheelite, with extraction methods primarily involving flotation. Tungsten exhibits remarkable flexibility in forming complexes with different ligands in various oxidation states. Primary tungsten minerals include wolframite and scheelite, while secondary minerals result from geological processes, influencing the ore composition. Tungsten mineralization occurs under diverse geological conditions, often linked to granitic intrusions, which can lead to deposits manifesting as either wolframite or scheelite.

The recovery of tungsten has seen significant evolution. Historical techniques employed before the 1950s included empirical methods such as roasting, leaching, and decomposition. However, advancements have led to the adoption of more efficient and environmentally friendly processes. Modern practices involve digestion with soda and/or caustic soda to create soluble sodium tungstate and insoluble carbonates or hydroxides, followed by crystallization to produce Ammonium Paratungstate (APT). Incorporating solvent extraction (SX) or ion exchange (IX) steps aids in achieving high-quality tungsten products by eliminating impurities. Ion exchange (IX) processes, particularly prevalent in Chinese plants, simplify impurity removal and effectively convert sodium tungstate to ammonium tungstate, while resins can be recycled after the stripping and cleaning steps.

Commercial APT production entails an evaporation crystallization process to yield APT crystals, with further separation of impurities. The thermal decomposition of APT results in intermediate compounds that can be reduced to tungsten powder. Pyrometallurgical methods include roasting and smelting, carbothermic reduction, aluminothermic reduction, electric arc melting, and plasma arc melting. These techniques are employed to reduce tungsten oxide to tungsten metal, utilizing various reducing agents and high-temperature conditions.

In summary, the recovery of tungsten involves a combination of hydrometallurgical and pyrometallurgical processes, each tailored to specific ore types and purity requirements. These processes contribute to the versatility and widespread applications of this valuable metal. The information provided discusses various methods and approaches for the recovery of tungsten from complex sources, as well as the removal of arsenic from tungsten residues. Here is a concise summary of the key points:

Tungsten Recovery Methods:

- Tungsten residues, rich in iron, can be processed using carbothermic reduction, leading to the production of alloyed white cast iron.
- Carbothermic reduction is an attractive method due to its ability to produce high-grade alloy products using a low-cost carbonaceous reductant at relatively low temperatures.
- Limited literature is available on tungsten residue recovery through carbothermic reduction, but existing reduction technologies can potentially be adapted for this purpose.
- Carbothermic reduction has been studied for polymetallic nodules, which share similarities in mineralogy with tungsten residues. It offers the potential to extract valuable metals as alloys.
- Fluxes are used to optimize the separation of reduced alloy and slag while reducing energy consumption.
- Research suggests the promise of this approach for effective tungsten residue utilization after systematic evaluation and optimization of reaction conditions.

Hydrometallurgy for Tungsten Recovery:

- Hydrometallurgical methods for tungsten recovery have been explored, including roasting and leaching processes.
- Roasting facilitates the conversion of tungsten into soluble sodium tungstate, which can be separated through leaching.

- Recycling of dissolved sodium tungstates back into the extraction process minimizes tungsten loss.
- The hydrometallurgical route for tungsten recovery is known for its lower energy consumption and reduced off-gas emissions compared to the reduction process.
- Research has focused on optimizing parameters such as roasting temperature and leaching conditions to enhance tungsten recovery.

Arsenic Removal from Tungsten Residues:

- Tungsten residues can contain arsenic, a toxic element that needs to be removed during processing.
- Roasting under controlled conditions is an effective method for arsenic removal, leading to the formation of arsenic gases that can be separated.
- Hydrometallurgical methods have been explored for arsenic removal, which consume chemical reagents but do not generate harmful gases.
- The extracted arsenic can be recycled back into the process to mitigate risks and costs associated with further treatment of arsenic products.

Novel Processes and Recycling:

- Researchers have explored novel methods, including acid leaching with phosphoric acid, to efficiently extract tungsten from scheelite ore.
- The "roasting transformation-(NH₄)₂CO₃ leaching" process has been introduced, which aims to recycle raw materials and minimize wastewater discharge.
- Recycling of tungsten from scrap materials is essential to maximize recovery and minimize waste.

These methods aim to efficiently recover tungsten from complex sources while addressing challenges related to mineral composition and the presence of toxic elements like arsenic. The choice of method depends on specific characteristics and desired final products

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