Modern Hydrometallurgical Production Methods for Tungsten

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Tungsten is one of the most important refractory metals. It is used in the production of numerous end-use items such as incandescent lamps and hard materials. From its ore concentrates and oxidized scrap, tungsten is processed via a hydrometallurgical route. In the last 100 years there has been a significant change in its processing. This paper reviews the methods employed in the hydrometallurgical production of ammonium paratungstate (APT), the main tungsten compound used in the manufacturing of tungsten metal powder. In addition to discussing tungsten feeds, the paper will review all hydrometallurgical steps typically used in the modern methods of APT production.

INTRODUCTION

Tungsten is used in the production of numerous end use items. ^{1,2} It is one of the most important refractory metals used in

Table	I. Composition of Ore	
	Concentrates	

Elements	Wt. (%)
Wolframite Ore	
WO_3	66.2
Al	0.19
Ca	0.84
Fe	12.0
Mn	2.4
Na	1.0
Si	3.9
W	52.0
High-Grade Scheelite Ore	
Al	0.4
Bi	0.4
Ca	13.0
Fe	1.8
K	0.05
Mg	0.5
Mn	0.2
Mo	0.04
0	25.0
P	0.14
S	2.0
Si	2.0
Ti	0.05
W	56.0

the manufacturing of crucial components of light sources.3 Tungsten is also used in the manufacturing of superalloys, hard metals (cemented carbide), and catalysts (hydrodesulphurization and hydrodenitrogenation).1 Other applications of tungsten are in the manufacturing of tungsten-copper and tungsten-silver composites.4 These composites are used in mechanical and electrical engineering; their typical applications include high-, medium-, and low-voltage circuit breakers, resistance welding electrodes, electrode materials for electrical discharge machining, and heat sink materials for microelectronic packaging. In military applications tungsten is employed in the manufacturing of high-kinetic-energy penetrators.

Until 1930, the largest consumption of tungsten was in the steel industry and only a small percentage was used in lamps and cemented carbides. Today, cemented carbides/metal cutting tools use more than 50 percent of the produced tungsten. Since 1910, tungsten production has been continuously growing to more than 30,000 tonnes per year in recent years.

TUNGSTEN FEEDS

Ores

Tungsten minerals that occur in sufficient abundance to be of economic significance can be divided into the wolframite and scheelite groups.

The wolframite group consists of three minerals: ferberite, wolframite, and huebnerite. The iron-rich tungstate (FeWO₄, WO₃ content 76.3%) is ferberite, the manganese-rich tungstate $(MnWO_4, WO_3 content = 76.6\%)$ is huebnerite, and the iron-manganese mixed tungstate ((Fe,Mn)WO₄, WO₃ content = 76.5%) is wolframite. Wolframite contains between 20% and 80% each of FeWO₄ and MnWO₄ in their pure form. Table I presents the composition of a wolframite ore concentrate as well as analytical data of a high-grade scheelite ore concentrate, while Figure 1 depicts the woframite ore concentrate's x-ray-diffraction (XRD) spectrum. Concentration of wolframite from its ores is typically carried out by gravity and magnetic methods, as wolframite occurs mainly in vein-type deposits whose mineralization is much coarser

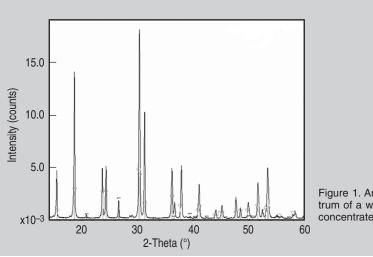


Figure 1. An XRD spectrum of a wolframite ore concentrate.

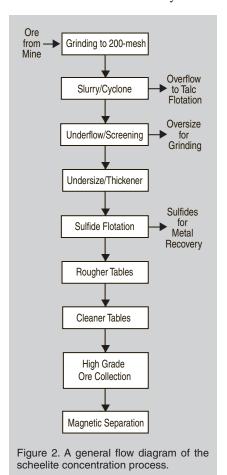
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than most scheelite ores.1

The mineral scheelite (calcium tungstate, CaWO₄) is normally found in quartz veins and in contact with scarn ores of complex mineralogical composition.^{5–10} These scarn minerals include garnets, pyroxene, and amphibole, and other minerals such as calcite, apatite, and quartz.

Scheelite ores can be classified into five different categories: simple scheelite, scheelite-sulfides, scheelite-cassiterite, scheelite-calcite-apatite, and scheelite-powellite. From an ore, scheelite is typically concentrated via a flotation process.^{11–13}

In a typical scheelite ore concentration process (Figure 2), the ore (containing 0.4% to 0.6% tungsten) from the mine is brought to the plant and is fed to the grinders to grind below 200 mesh. Ground ore is slurried in water and slurried ore is cycloned. Overflow from the cyclone goes to talc flotation; concentrates from talc flotation cells go to tailings; tail from the cell is screened, with oversized tail going to tailings and undersized going to thickeners for reclamation as flot-grade ore. The under-flow from the cyclone is



screened and oversized tail is returned to regrinding, while undersized tail goes to high-grade ore feed to the thickener. The ground material goes back to the cyclone, and the thickened mud is conditioned for sulfide flotation. Concentrate from the flotation cell, mainly sulfides, goes to the tailings. The tailing of sulfide-flotation cells goes to rougher and cleaner tables for high-grade ore concentrate separation. The ore portion collected in the corners of the high-grade-ore separation tables is flot-grade-ore feed and goes to thickeners.

High-grade-ore concentrate, collected from tables, is roasted at about 540°C to remove organics. The roasted high-grade ore goes to a magnetic separator for final sulfide cleaning. Clean ore is bagged and shipped, while the magnetically separated material goes for another magnetic separation. Rejects from this separator go back to cleaner tables.

In high-grade-ore separation tables, rougher tables pull scheelite concentrate, which then goes to the cleaner tables. Tailings from the rougher go for scheelite scavenging, and scavenged scheelite goes back to the rougher tables. Scheelite from cleaner tables goes to high-gradeore collection. All the tailings from the rougher and cleaner tables are the feed for flot-grade ore and go to flot-gradeore thickeners. Coarser material from the high-grade rougher tables goes for cyclone separation. Underflow from the cyclone goes for ball milling and secondary sulfide flotation and back to high-grade-ore tables; overflow goes to thickener for flot-grade-ore feed.

The mineralogical compositions of a high-grade ore and flot-grade scheelite ore concentrate are shown in Table II.

Scraps

The two types of tungsten carbide (WC) scrap available in the market¹⁴ are typically known as hard scrap and soft scrap.

Hard scrap is normally made of worn tools such as cutting and drilling tool bits of tungsten carbide hard metals. Although the major component of hard scrap is tungsten carbide, it can best be represented by (W,Ti,Ta,Nb)C-Co. In such tungsten carbides, cobalt is used as a binder and TiC, TaC, and/or (Ta,Nb)C are used to modify the properties of the hard metals. Tool bits are normally coated

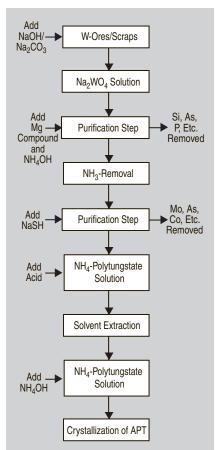


Figure 3. A general flow diagram of the tungsten hydrometallurgical process.

to resist wear and to have high hardness, good chemical stability, resistance to oxidation, and a smooth surface to reduce friction. Characterization of many different tool bits indicated that the most common coating materials were TiC, TiN and/or Ti(C,N), alumina (Al₂O₃), brass (Cu/Zn/Ni alloy), and silver.

Soft scrap pertains to all tungsten-containing scrap that does not have a defined shape. Typically, this scrap contains the rejects of the manufacturing of tungsten products such as wires, coils, powders, and turnings, and contains more metallic impurities than hard scrap. X-ray diffraction analysis of a soft WC-scrap composite sample indicated the presence of WC as the major phase. It also contained small concentrations of TiC, TaC, W₂C, and cobalt metal.

PROCESSING

In the old methods of hydrometallurgical processing of tungsten, scheelite was mainly processed by acid digestion. During this digestion reaction, scheelite converted to tungstic acid: $CaWO_4 + 2HC1 \rightarrow CaCl_2 + H_2WO_4$. Tungstic

Table II. Mineralogical Composition of a High-Grade and Flot-Grade Scheelite Ore Concentrate

Component	Dry Ore (wt.%)	
High-Grade		
CaWO ₄ (scheelite)	88	
Phlogopite and Talc	8	
Fe _{1-x} S / CuFeS ₂	2-3	
Calcite (CaCO ₃)	1–2	
Flot-Grade		
CaWO ₄	32	
Phlogopite and Talc	33	
Calcite	14	
Apatite	4	
$Fe_{1-x}S + CuFeS_2$	17	

acid, thus obtained, was dissolved in ammonium hydroxide and the solution after purification was crystallized to ammonium paratungstate (APT) via evaporation. A similar procedure was also used for wolframite, which initially was digested in an alkali solution but the resulting sodium tungstate solution was converted to CaWO₄. The CaWO₄ was processed via acid digestion as described.

However, in the modern hydrometallurgical process, all tungsten feeds are digested in sodium hydroxide or sodium carbonate, and the sodium tungstate that results after purification steps is converted to APT after the separation of sodium via liquid ion exchange (LIX).

Figure 3 depicts a general flow diagram of the APT process. 15 In the modern process, separation of sodium from purified sodium tungstate solution is largely carried out by solvent extraction.16 In some plants (especially in China), ion exchange resins are also employed for the separation of sodium from sodium tungstate solution.1

Digestion

Digestion of tungsten-containing feeds is carried out in alkali solutions such as NaOH and/or Na2CO2 according to Equations 1–6. (All equations are shown in the Equations table.) Much of the tungsten production results from the high-grade tungsten ore concentrates (such as wolframite and scheelite) and synthetic concentrates obtained from tungsten scraps. 1,14

In a basic process of producing soluble sodium tungstate, the ore concentrate is digested in concentrated sodium hydroxide or sodium carbonate¹⁷⁻²² to produce a mixture comprising soluble sodium tungstate and an insoluble sludge, or

residue. The mixture is next diluted to form an aqueous portion containing dissolved sodium tungstate, which is separated from an insoluble sludge portion via filtration.

Purification of Impure Sodium Tungstate Solution

Separation of Si, As, Sn, P, and F

Silicon, As, Sn, P, and F are impurities that are present as anions and are separated by suitable precipitation methods.^{23–26} For example, phosphorous, silicon, and arsenic are precipitated by the addition of a magnesium compound and ammonium hydroxide into impure sodium tungstate solution. To ascertain the maximum separation of impurity elements, a much larger concentration of magnesium compound and ammonium hydroxide than stoichiometrically required amounts are added. Equations 7–9 typically occur in the separation of silicon, phosphorous, and arsenic.

Magnesium compounds in combination with an aluminum compound are also used for the separation of silicon, phosphorous, and fluorine.²⁴ Tin can also be separated using magnesium compound and ammonium hydroxide.26

Separation of Molybdenum

A small concentration of molybdenum from concentrated sodium tungstate solution can be separated by treating alkaline or neutral tungstate solution with NaHS.^{27–31} Under these conditions, molybdate ions are converted to thiomolybdate.

The chemical reactions that describe the preferential precipitation of molybdenum trisulfide in the separation of molybdenum from tungsten are as follows. Sodium hydrogen sulfide at a basic pH reacts with sodium molybdate to form sodium thiomolybdate (see Equation 10). The addition of sulfuric acid to the alkaline thiomolybdate solution neutralizes the sodium hydroxide and excess sodium carbonate coming from the digestion step (see Equation 11 and Equation 12).

Carbon dioxide released in this step slows down the addition of sulfuric acid due to the foam generation (therefore,

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Ea	uations	

$CaWO_4 + 2NaOH \rightarrow Ca(OH)_2 + Na_2WO_4$	(1)
$CaWO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2WO_4$	(2)
$MnWO_4 + 2NaOH \rightarrow Mn(OH)_2 + Na_2WO_4$	(3)
$FeWO_4 + 2NaOH \rightarrow Fe(OH)_2 + Na_2WO_4$	(4)
$WO_3 + 2NaOH \rightarrow H_2O + Na_2WO_4$	(5)
$CoWO_4 + 2NaOH \rightarrow Co(OH)_2 + Na_2WO_4$	(6)
$MgSO_4 + Na_2SiO_3 \rightarrow MgSiO_3 + Na_2SO_4$	(7)
$\mathrm{MgSO_4} + \mathrm{NH_4OH} + \mathrm{Na_3PO_4} \rightarrow \mathrm{MgNH_4PO_4} + \mathrm{NaOH} + \mathrm{Na_2SO_4}$	(8)
$\mathrm{MgSO_4} + \mathrm{NH_4OH} + \mathrm{Na_3AsO_4} \rightarrow \mathrm{MgNH_4AsO_4} + \mathrm{NaOH} + \mathrm{Na_2SO_4}$	(9)
$4 \text{NaHS} + \text{Na}_2 \text{MoO}_4 \rightarrow \text{Na}_2 \text{MoS}_4 + 4 \text{NaOH}$	(10)
$2\mathrm{NaOH} + \mathrm{H_2SO_4} \rightarrow \mathrm{Na_2SO_4} + \mathrm{H_2O}$	(11)
$\text{Na}_2\text{CO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{CO}_2$	(12)
$\mathrm{Na_2MoS_4} + \mathrm{H_2SO_4} \rightarrow \mathrm{MoS_3} + \mathrm{H_2S} + \mathrm{Na_2SO_4}$	(13)
$10(R_{3}NH)^{+} + 5SO_{4}^{2-} + 2HW_{6}O_{21}^{5-} + 10Na^{+} \rightarrow 2(R_{3}NH)_{5}H W_{6}O_{21} + 5Na_{2}SO_{4}$	(14)
$(R_3NH)_5HW_6O_{21} + 5NH_4OH \rightarrow (NH_4)_5HW_6O_{21} + 5(R_3NH)OH$	(15)
$2(NH_4)_5HW_6O_{21} + 14NH_4OH \rightarrow 12(NH_4)_2WO_4 + 8H_2O$	(16)
$12(\mathrm{NH_4})_2\mathrm{WO_4} \rightarrow (\mathrm{NH_4})_{10}\mathrm{H_2W_{12}O_{42}} \ 4\mathrm{H_2O} + 2\mathrm{H_2O} + 14\mathrm{NH_3}$	(17)

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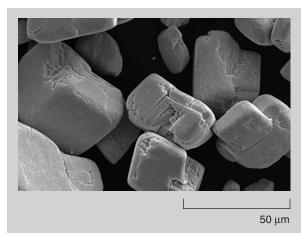


Figure 4. A scanning-electron micrograph of APT crystals.

carbonate should be separated from the solution before this step to prevent the foam generation). The continued addition of sulfuric acid decomposes the thiomolybdate ion to precipitate molybdenum trisulfide and release hydrogen sulfide (see Equation 13).

The minimum quantity of NaSH used in this step is critical for complete removal of molybdenum. Typically 2.0 to 2.5 times the required concentration of NaSH based on the previously stated chemical equations is added, as tungsten and other impurities, such as cobalt and arsenic, also consume sulfide.

Separation of Sodium

After the separation of molybdenum, sodium tungstate solution is treated by liquid ion exchange or solid ion exchange resins for the separation of sodium. 1,32-35 In the old process, separation of sodium was carried out via its conversion to calcium tungstate: Na₂WO₄ + Ca(OH)₂ \rightarrow CaWO₄ + 2NaOH, which was processed via acid digestion: CaWO₄ + 2HCl → CaCl₂ + H₂WO₄. Tungstic acid, thus obtained, was dissolved in ammonium hydroxide and the solution was crystallized to produce APT. In a modern solvent-extraction method, tungsten is extracted from slightly acidic sodium tungstate solution by aliphatic amines dissolved in an organic solvent. The solvent extraction of tungstate ionic species from acidic solution occurs in four main, continuous steps: extraction, scrubbing, stripping, and regeneration of amine.

Extracting reagents are long-chained primary, secondary, tertiary, and quaternary ammonium compounds, with chain length C8 to C10, such as trioctylamine and tridecylamine. Commercial

products are: Primene JMC (primary amine), Amberlite LA-1 or Adogen 283 (secondary amine), Tri-octylamine (tertiary amine), and Aliquat 336 (quaternary ammonium compound). Depending upon the process conditions, either secondary or tertiary amines are preferred. Primary amines are advantageous for higher condensed tungstate solutions than those derived from the electrodialytic process.

The concentration of reagent varies between 1% and 22%, as reported in the literature.^{32–35} The organic phase consists of two or three components: reagent (amine), modifier, and solvent. Solvent is either kerosene or mixtures of alkalyl benzenes like tolune or xylene. Modifiers are necessary when kerosene is used as the solvent. A modifier such as isodecanol (5%) or tributyl phosphate (12%) increases the solubility of the isopoly tungstate-amine complex, which is low in kerosene.

Before extraction, the organic amine is converted into its salt by the reaction of acid. For example, the reaction of amine with sulfuric acid will convert it into sulfate salt. The reaction of salted amine with isopoly tungstate, the main tungsten species at low pH, typically occurs as shown in Equation 14.

An organic reagent, or amine, extracts only tungsten species, while sodium, sulfate, and other cations report to the aqueous phase, or raffinate, which is recycled or discarded. The loaded organic after scrubbing is stripped in ammonium hydroxide, leaving tungsten in the aqueous phase as ammonium tungstate (see Equations 15 and 16).

Stripping³⁶ is typically carried out in concentrated, 1-10% ammonia solution (pH = 8-13). For APT crystallization,

highly concentrated ammonium tungstate solution is desired from the stripping step. Stripped amine is regenerated by sulfuric acid into sulfate form for its continuous re-use in the LIX step. Sodium-free ammonium tungstate solution is crystallized to form ammonium paratungstate.

Crystallization of Ammonium Tungstate Solution to APT

Concentrated ammonium tungstate solution is crystallized via evaporation crystallization, ^{37,38} as shown in Equation 17. During crystallization, a further separation of impurities is achieved, when APT separates after crystallization is dried and blended. The size and morphology of APT crystals depend upon the purity of the ammonium tungstate solution and crystallization parameters. Industrially produced APT consists of faceted crystals (Figure 4).

Mother liquor from APT crystallization is recycled back in the process³⁹ or converted into low-purity APT.¹

Synthesis of Tungsten Metal Powder

Thermal decomposition of APT in the 300–800°C temperature range produces several high-purity intermediate tungsten compounds that are used in the synthesis of tungsten chemicals for catalyst applications and tungsten metal powder for wire, alloys, and hard metal applications. The synthesis of a desired decomposition product depends upon the decomposition temperature, time, and atmosphere. Various decomposition reactions of APT at different temperature ranges can be found in the literature. ¹

There are three major intermediate decomposition compounds produced from APT: ammonium metatungstate, yellow oxide, and tungsten blue oxide. Tungsten metal powders are produced via hydrogen reduction of tungsten oxides. Changes in the reduction parameters allow the production of tungsten powders with various characteristics such as different grain size, grain size distribution, and powder density. Although modern lamp wire production uses NS-doped tungsten metal powder40-42 (produced via hydrogen reduction of doped tungsten blue oxide), the basic process still employs the principles established by Coolidge.43

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