総 說

REVIEW

텅스텐 抽出工程에 關한 考察*

M. Shamsuddin** · 孫 洪 鏞

유타대학교 공과대학 금속 및 금속공학과

A Review of Tungsten Extraction Processes

M. Shamsuddin and H.Y. Sohn

Department of Metallurgy and Metallurgical Engineering,
University of Utah, Salt Lake City, Utah 84112

요 약

여러가지 高溫用 金屬中에서 텅스텐은 1370°C 以上에서 重量當 强度가 特出히 높아서 高溫에서의 應用度가 크다. 지난 30년 동안에 텅스텐 抽出方法의 向上과 또 鑛石에서 金屬까지 거치는 工程數를 감소하기 위한 새로운 方法의 發明에 관한 硏究가 進行되어 왔다. 이 總說에서는 텅스텐 鑛物의 分布와 選鑛法을 간단히 소개한 후에 wolframlte와 scheelite로 부터의 抽出法과 酸化 텅스텐의 還元方法을 考察하였다. 이어서 廢金屬物에서부터의 回收方法과 現在의 硏究動向을 요약했다.

ABSTRACT

Amongst various refractory metals, tungsten has the greatest potentiality for high temperature applications due to its exceptional strength to weight ratio at temperatures above 1370°C (2500°F). During the past three decades significant research efforts have been directed towards the improvement of the conventional metholds of tungsten extraction and to devop new processes to reduce the number of steps from ore to metallic tungsten. In this paper geological occurrence of tungsten minerals and principles of benefication methods are outlined. The commercial processes of extraction from wolframite and scheelite and different approaches to the reduction of tungstic oxide are discussed. Methods of recovery from scrap and the current research efforts are also reviewed.

---

* This Paper is a revision of the paper "Extractive Metallurgy of Tungsten," pp. 205～230 in *Extractive Metallurgy of Refractory Metals*, edited by H.Y. Sohn, O.N Carlson, and J.T. Smith; c 1980, The Metallurgical Society of AIME, Warrendale, Pennsylvania 15086, U.S.A.

** M.Shamsuddin, formerly Visiting Scientist, is a Reader at the Department of Metallurgical Engineering, Banaras Hindu University, Varanasi-221005, India.

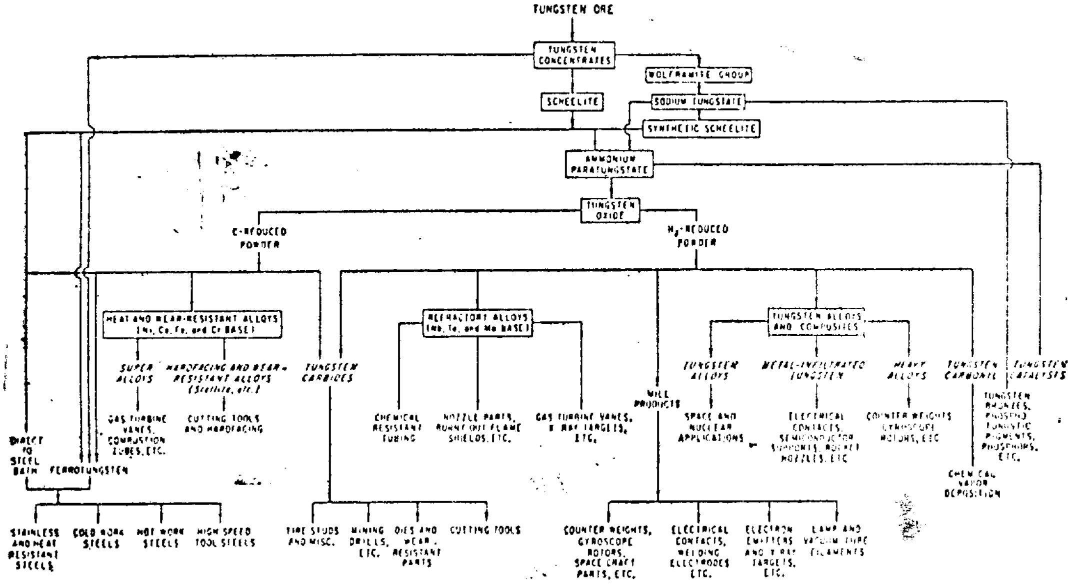


Fig. 1. Tungsten production processes and product applications (Ref. 4, p. 428)

I. Introduction

Tungsten belongs to the VI Group of the Periodic Table. It has a melting point of 3410°C and boiling point of 5927°C. Its specific gravity is 19.3. Tungsten is the most important member of the refractory group metals. Amonst the pure refractory metals it has the highest potentiality for structural purposes in high temperature applications due to its exceptional strength to weight ratio at temperatures above 1370°C (2500°F). The most important usage of tungsen in unalloyed form is for incandescent lamp filaments due to its unique combination of high melting point, favorable radiation range, low vapor pressure, and high shock resistance. In addition, tungsten wires and rods are used as heating elements for high temperature furnaces and fluorescent lamps, electronic heaters and emitters, x-ray and transmission tubes, lamp filament supports, glass-to-metal seals, electrical contacts, electrodes for arc lamp, and in welding and electric discharge machining.

Alloying tungsten with niobium, tantalum, molybdenum, rhenium improves ductility and high temperature strength. In recent years these alloys have found applications in space vehicles and tubings in nuclear reactors, and as x-ray targets. Addition of tungsten in niobium and tantalum increases tensile and creep strength at elevated temperatures. These alloys are used in high temperature gas turbine vanes, rocket nozzles, flame shields, space vehicle parts, and containers in very corrosive environments. Tungsten is an important alloying element in tool steels. Cemented tungsten carbide has its importance in cutting tool applications.

Tungsten was isolated from its mineral, wolframite in 1753 by Spanish Scientists J.J. Elhujar and F.deElhujar[1] In 1847, Oxland[2] patented a process to obtain sodium tungstate which can be used to produce high purity tungsten. In 1910, Johnson[3] developed a method to decompose scheelite with hydrochloric acid. The recent book on tungsten by Yih and Wang[4] has revived as the occurrence, geology, mining and beneficiation of tungsten ores as well as extraction of tungsten.

It the present review geological occurence, and principles of beneficiation of tungsten ores will be briefly mentioned. The commercial methods of extraction will be discussed with the aid of flow sheets. In tungsten extraction hydrometallurgy plays an imporant role. *Figure 1* out lines the methods of production of tungsten from ores and applications of products. The current research trends viz. chlorination and electrolysis as alternative routes for tungsten extraction and recovery of tungsten from brines will also be reviewed.

Ⅱ. Occurrence

Tungsten does not occur in elemental form. In the earth crust its concentration ranges from 1 to 1.3 ppm[5] and ranks about 18 th among the metals and 26 th among the elements of relative abundance. The principal ores of tungsten are categorized in two groups viz. wolframite (Fe. • MnWO) and scheelite ($CaWO_4$). Noncommercial minerals are anthionite $Al(WO_4)(OH)$. H_2O; cuprotungstite, $Cu_2(WO_4)(OH)_2$; ferritungstite, $Ca_2Fe_2^{2+}Fe_2^{3+}(WO_4)^4$. $9H_2O$; raspite, $PbWO_4$ etc. The minerals ferberite, wolframite, and huebnerite belong to wolframite group. Scheelite, $CaWO_4$ is the only mineral of importance in scheelite group.

Tungsten deposits are distributed throughout the world, but major reserves are concentrated only in a few countries viz. China, Soviet Union, United States, Korea and Bolivia. Major U.S. producers of concentrates and tungsten processors can be found in Ref. 5. China is the largest producer of tungsten concentrate[6] *Table 1* summarizes the estimated world tungsten reserves, approximate annual production with consumption in different countries. The high grade wolframite deposits of China are mined in Nanling and Kiangi. In the Soviet Union, mines are located in North Caucasus, Transbaykal Far East, Central Asia, and Kazakhstan. In South Korea about 90% of the total tungsten of the country is obtained from the Sang Dong Mine. The Chojla Mine of Bolivia is the largest producer in South America. Canada has large reserves of Tungsten ore but relatively low annual production.

Table 1. World Reserves, Annual Consumption, and Production of Tungsten Ores and Concentrates[1] (unites: 10^6kg contained tungsten)

Country	Estimated[2] Reserves	Annual[2] Consumption	Annual Production[2] 1973	1974	1975
World	1881.8	(34.5)	(37.600)[4]	(37.200)[4]	(37.800)
Africa			(0.830)[4]	(0.659)[4]	(0.835)
Namibia	na	na	0.22	—	0.007
Nigeria			(0.001)	(0.001)	—
Southern Rhodesia			0.154	0.191	0.038
Rwanda	2.3	na	0.302	(0.260)	0.425
South Africa	na	0.27	0.001	—	—
Uganda			(0.109)	(0.109)	(0.109)

United Republic of Tanzania			0.001	—	0.001
Zaire			0.240[4]	0.198[4]	0.225[4]
North and Central America			(5.262)[4]	(5.149)[4]	3.848
Canada	216.4	(0.23)	1.669	1.280	1.075
Guatemala			0.043	0.006	0.001
Mexico	0.9	na	0.348	0.309	0.277
United States	108.2	6.59	3.202	3.554	2.495
South America			3.878	3.724	4.464
Argentina	na	0.05	0.082	0.087	(0.056)
Bolivia	39.5	na	2.075	2.044	2.693
Brazil	18.2	0.18	0.926	0.911	1.133
Peru	na	na	0.795	0.682	0.582
Asia			(16.145)[4]	(16.294)[4]	(16.792)
Burma	31.8	na	0.50	(0.340)	0.244
China	955.0	(0.64)	(8.000)	(8.500)	(8.980)
Democratic People's Republic of Korea	114.0	(1.59)	(2.150)[4]	(2.150)[4]	(2.150)
Hong Kong			(0.005)	(0.005)	(0.005)
India	na	0.14	0.017	0.015	0.025
Japan	2.3	3.18	0.831	0.769	0.913
Malayasia	14.5	na	0.125	0.013	0.106
Republic of Korea	45.9	na	1.915	2.180	2.533
Thailand	18.2	na	2.602	2.204	1.773
Europe			(10.236)[4]	(10.280)	(10.726)
Austria	na	1.68	—	—	—
Czechoslovakia	na	(1.36)	(0.075)	(0.080)	(0.080)
East Germany	na	0.36	na	na	na
France	na	1.32	0.695	0.593	0.867
Poland	na	1.68	na	na	na
Portugal	10.0	0.32	1.502	1.478	1.467[3]
Spain	na	0.14	0.312	0.347	0.351[4]
Sweden	na	1.50	0.234	0.166	0.151
United Kingdom	na	3.18	0.013[4]	0.016	0.010
U.S.S.R.	159.1	(6.55)	(7.400)	(7.600)	(7.800)
West Germany	na	3.23	na	na	na
Netherlands (excluded from totals)	na	0.23	0.289	0.485	0.646
Oceania			1.240	1.129	1.158
Australia	34.5	0.05	1.239	1.125	1.533
New Zealand			0.001	0.004	(0.005)

1) Ref. 4
2) symbols: parentheses indicates estimated value; dash indicates nil or negligible; na not available
3) preliminary or provisional
4) revised

III. Beneficiation

As the amount of tungsten in the ore hardly exceeds 3%, upgrading by physical beneficiation methods are necessary to raise the concentration of WO_3 at least to 60%. In general, tungsten minerals are first liberated by cruhshing grinding, and sizing. The resulting fines are concentrated by heavy media, magnetic or electrostatic separation, tabling, and flotation. Occasionally, leaching and/or roasting may be employed to remove arsenic, sulfur and organic matter. It is beyond the scope of this article to go into details of each method. However, it would be appropriate to mention briefly the principles of beneficiation. Mineral characteristics such as specific gravity, friability, hardness, cleavage and magnetic properties are important variables for designing concentrators. Ores containing powellite are subjected to chemical treatment to remove molybdenum. Throughout the world, tungsten minerals occur in quartz veins. These can be easily curshed and concentrated by heavy media or sink-float process. *Table 2* lists the separation characteristics of different minerals whereas common approaches to separation of different types of tungsten ores have been summarized in *Table 3*.

Table 2. Mineral Separation Characteristics[1] (Ref 4, p. 56)

Specific gravity	Minerals floating with scheelite			Minerals that do not float		
	Magnetic	Slightly magnetic	Nonmagnetic	Magnetic	Slightly magnetic	nonmagnetic
7.5		Wolframite				
	Ferberite		Cassiterite			
7.0						
6.5						
6.0			Scheelite			
5.5						
	Magnetite					
5.0			Pyrite			
	Ilmente					
	Pyrrhotite[2]		Molybdenite			
4.5			Powellite			
			Chalcoyrite			
				Garnet		
3.5			Kyanite			
					Epidote	
					Olivine	
	Apatite		Sillimanite			
			Fluorite			
3.0						
					Biotite	
						Muscovite
						Beryl
						Felspars
						Calcite[3]
						Quartz
2.5						

1) typical conditions using oleic acid, sodium silicate, and quebracho (tannin); pH 10
2) depressed by cyanide
3) flotation separation not complete

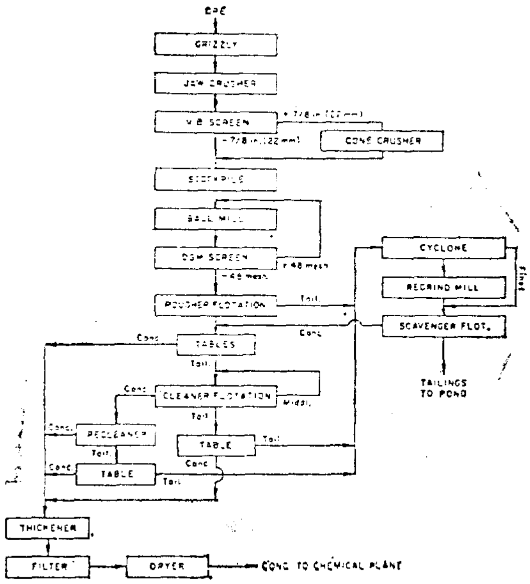


Fig. 2. Glen Mill, Montana flowsheet for sheelite concentration(Ref. 4, p. 68)

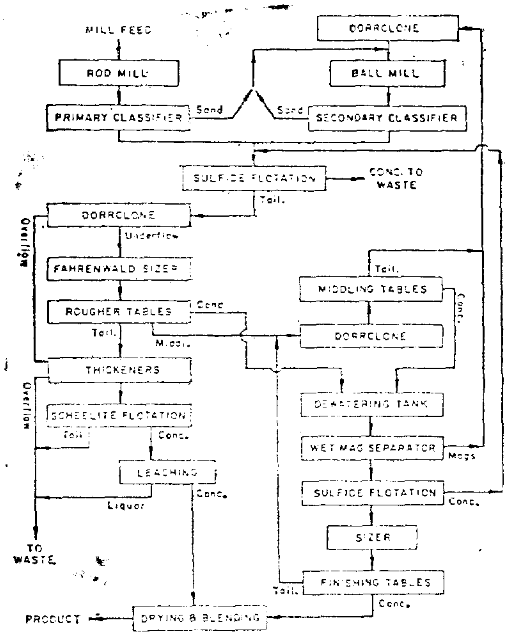


Fig. 3. Candadian Exploration, Ltd. tungsten mill flowsheet(Ref. 4, p. 74)

Table 3. Common Approaches to Mineral Separation (Ref. 4, p. 56)

Ore	Process
Scheelite, simple ore	Gravity, flotation, magnetic
Scheelite, sulfides	Gravity, sulfide flotation, roating, magnetic
Scheelite-cassiterite. concentrete	Electrostatic
Scheelite-calcite-apatite	Flotation, gravity, leaching
Scheelite-powellite concentrate	Chemical processing
Wolframite, simple ore	Gravity, flotation, magnetic
Wolframite-cassiterite ore	Gravity flotation, magnetic
Wolframite-scheelite concentrate	Magnetic
Wolframite-sulfides	Sulfide flotation, gravity, magnetic

Figure 2 presents the flowsheet practiced by the Pine Creek mill near Bishop, Califonia, and the Sang Dong mill in Korea. In the recent past, the Glen mill in Montana followed this flowsheet. A typical flowsheet for concentration of scheelite with high sulfide content practiced by Canadian Exloration, Ltd. Salmo, British Columbia is shown in *Figure 3.* Recently developed Swedish flotation process[7] on pilot plant scale provides 80% recovery of WO_3 in the presence of fluorspar, calcite, and apatite. Development of new collectors may improve the overall recovery of scheelite. In this regard, use of dodecylammonium chloride[8] and lipids of the fungus Blakeslea tripora[9] have been evaluated recently.

Ⅳ. Extraction

On account of its extremely high melting point, tnngsten is extracted by hydrometallurgical processes. The main objective of the extraction process is to convert tungsten contained in the ore concentrate to an intermediate compound viz tungetic acid or ammonium paratungstate (APT) $5(NH_4)_2$ 0.12 WO_3 which can be reduced to yield metallic tungsten in the subsequent reduction process. Such a conversion needs steps such as pretreatment, chemical ore breakdown and purificaiton of the leach liquors. Although a number of routes have been suggested only a few have come up to the commercial scale. In this section, we shall briefly discuss three commercial proecsses for extraction of tungsten from wolframite and scheelite concentrates.

Often wolframite and scheelite are associated with arsenides and sulfides which are not completely removed during mineral beneficiation operations. In addition, scheelite occurs with apatite minerals. Presence of these impurities causes problems in the purification of tungsten metals. From scheelite these impurities are removed by hydrochloric acid leaching(4). In general, sulfur, arsenic and organic matters from tungsten concentrates are removed by roasting the concentrate at 600° to 800°C for 2 to 4 hrs.

1. Caustic Leaching Process

Sodium hydroxide solution can decompose wolframite according to the following reaction:

$$Fe(Mn)WO_4 + 2NaOH \rightarrow Fe(Mn)(OH)_2 + Na_2WO_4 \qquad (1)$$

However, this method is not much used in

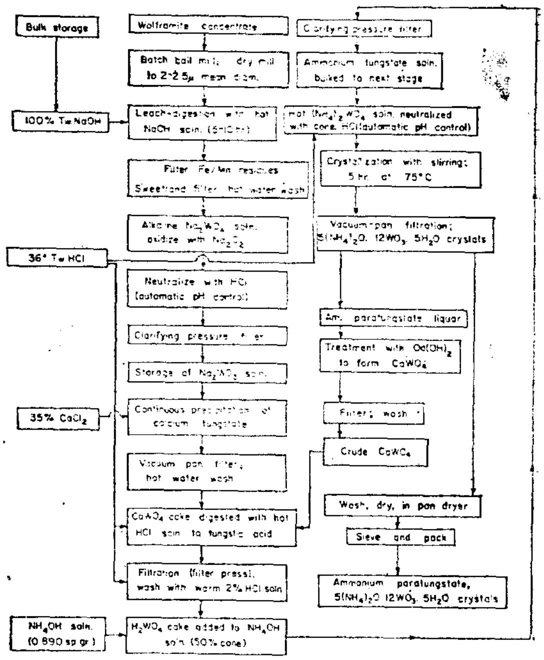


Fig. 4. Ammonium paratungstate process for wolframite(Ref. 4, p. 199)

practice as low grade wolframite produces highly contaminated solution. Further, caustic solution is incapable of attacking more abundant mineral, scheelite. The process further suffers from the additional problem of fitration due to the formation of sodium silicate. A flowsheet[10] shown in *Figure 4* based on caustic leaching of wolframite to produce ammonium paratungstate is practed by Wickman Wimet Limited of the United Kingdom. For efficient digestion the ore is ground to -300 mesh and leached with 40% to 50% sodium hydroxide sclution at 100° to 105°C. The process is carried out in a mild steel tank using 50% excess alkali. The vessel is steam jacketed and fitted with a turbine which agitates the suspended solid and accelerate the formation of sodium tungstate. Recovery of tungsten amounts to 98%.

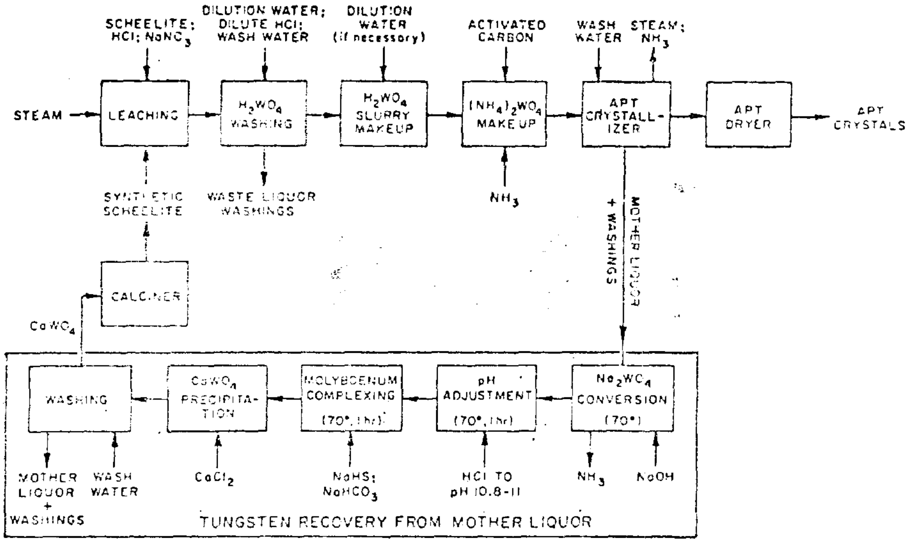


Fig. 5. Scheelite acid leaching-APT process flowsheet, Wah Chang Co., Glen Cove(Ref. 4, p. 116)

The liquoor is diluted at 80°C, filtered to remove solid residues and treated with sodium peroxide to oxidize tungsten. The highly concentrated solution containing about 250g/*l* of sodium tungstate is neutralized with hydrochloric acid and the final pH of the solution is adjusted to 10.5-11.5. Silica, alumina and iron oxide are removed by filtration through pressure filters. The clarified sodium tungstate solution is pumped to a rubberlined mild steel tank. Calcium tungstate is precipitated by the addition of 35% calcium chloride solution. The precipitate is then treated with 50% hydrochloric acid at 40°C to obtain tungstic acid which is filtered and washed with hot hydrochloric acid to remove calcium.

Tungstic acid cake is further purified by treating with 50% ammonium hydroxide(sp. gr. 0.880). One liter of concentrated NH_4OH is required to dissolve 1kg of WO_3. The turbid solution is filtered to remove silica, alumina and calcium oxide. The ammonium paratungstate solution is neutralized with concentrated HCl to a pH of 7.0 to 7.5 and heated to 75°C. APT is crystallized in 6 hours. The crystals are washed and dried. The mother liquor is further treated for the recovery of dissolved tungsten.

2. Acid Leaching Process

Scheelite concentrate can be decomposed to form solid tungstic acid by hydrochloric acid according to the following reaction:

$$CaWO_4 + 2HCl \rightarrow CaCl_2 + H_2WO_4 \qquad (2)$$

Tunstic acid is separated by filtration and washing. The process flowsheet practiced by Wah Chang Corporation at Glen Cove, New York is shown in *Figure 5.* Ten tons of concentrate(60% to 75% WO_3) ground to-200 mesh is leached with commercial hydrochloric acid. In general 100% excess acid is used in the presence of sodium nitrate as an oxidizing agent. The entire charge is agitated by steam spraying and maintained at 70°C for 12 hours. The slurry is diluted and allowed to settle and washed by settling and decantation.

Pure ammonium paratungstate from crude

tungstic acid is produced by digesting the acid with aqueous ammonia at 60°C for 2 hrs under stirring. One kg of 28% ammonia is required for one kg of WO_3. Calcium from the resulting solution is precipitated as calcium oxalate. Colloidal iron hydroxide and silica are removed by treating the solution with activated carbon. The solution is clarified through pressure filters and evaporated to obtain APT crystals. The extent of crystallization of APT depends upon the impurity level in ammonium paratungstate solution, desired purity and recovery. Phosphorusand arsenic can be reduced to below 10 ppm by treating tunstic acid with MgO. APT crystals are washed after separation from the mother liquor.

The mother liquor and wash water are combined and treated with sodium hydroxide to obtain sodium tungstate. Ammonia from the solution is removed by heating to 70°C. The pH of the solution is adjusted to 10.5-11.5 by adding hydrochloric acid and molybdenum is complexed by the addition of sodium bicarbonate and sodium hydrogen sulfide. The filtered solution is treated with calcium chloride at 70°C for 1 hr. under stirring to precipitate calcium tungstate, known as synthetic scheelite.

3. Autoclave-Soda Process

Wolframite and scheelite can be decomposed by roasting (4) the ore with sodium carbonate in a rotary kiln at 800° to 900°C in the presence of oxidizing agents viz. $NaNO_3$ or MnO_2. The process was not developed to industrial scale due to the high maintenance requirement of the kiln and large amount of soda loss. Further, the complete conversion of impurities like P, As and Si to soluble salts presents problem in the purification of the leach liquor.

In 1939, Maslenitskii[11] reported the decomposition of scheelite with sodium carbonate solution under pressure according to the reaction:

$$CaWO_4 + Na_2CO_3 \rightarrow Na_2WO_4 + CaCO_3 \quad (3)$$

Following this pioneering work Malsenitskii and Perlov,[12] Zelikman ank Rakova[13] carried further investigations. A decade ago Queneau and Cooke[14] studied in detail the kinetics of dissolution of scheelite in alkaline aqueous solutions. They concluded that the diffusion of Ca^{++} or CO_3^{--} through the calcite layer formed during leaching may be the rate controlling step. However, according to Zelikman and Meerson[15] the rate of leaching is controlled by the rate of chemical reaction. As the process is more applicable, it has received the attention of a number of researchers and thus has undergone some important improvements.

A commercial plant based on the sodium carbonate leaching of scheelite is under operation at Bishop Mine, California for the last 20 years. *Figure 6* shows a flowsheet of the autoclave-soda process practiced by Teledyne Wah Chang, Huntsville, Alabama.

In industrial practicies, scheelite concentrate ground to-150 to +325 mesh is leached with 10% to 18% sodium carbonate solution at 190° to 325°C for 1.5 to 4 hrs in autoclave at a pressure of 150-350psi. Low manganese wolframite can also be leached by this process. The maintenance cost of the process is low but a large amount of excess sodium carbonate is reqired to achieve a recovery of 98%. Actual amount varies from 150% to 300% excess over the stoichiometric requirement depending upon the grade of the ore being processed. The leach liquor contains some of the impurities in the ore. These must

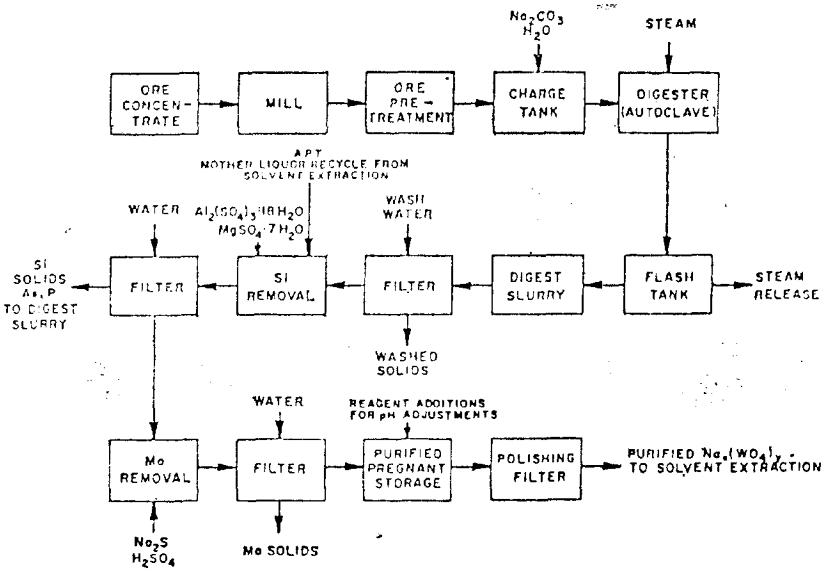


Fig. 6. Flowsheet of autoelave-soda process, Teledyene Wah Chang, Huntsville, Alabama (Ref. 4, p. 120)

be reduced to acceptable levels before the intermediate compound is prepared. The most deleterious impurities are silica, phosphorus, arsenic and molybdenum which are removed by chemical treatment. Prior to the removal of unreacted gangue by filtration, aluminum and magnesium sulfates are added at 70° to 80°C and the solution with pH of 9-9.5 is stirred for 1 hr. Two stage treatment brings silica content in the range of 0.03 to 0.06g/*l*. Phorphorus and arsenic are removed as magnesium phosphate and arsenate, respectively. Residues are separated by filtration.

Molybdenum is removed as molybdenum trisulfide. The solution is first treated with sodium sulfide or sodium hydrogen sulfide at 80° to 85°C for 1 hr at a pH of 10 to form thiomolybdate complex as follows:

$$MoO_4^{2-} + 4S^{2-} + 4H_2O \rightarrow MoS_4^{2-} + 8OH^- \quad (4)$$

Finally molybdenum trisuilfde is precipitated by acidifying the solution (pH = 2.5-3.0) under stirring for 7-9 hrs.

$$MoS_4^{2-} + 2H_3O^+ \rightarrow MoS_3 + H_2S + 2H_2O \quad (5)$$

The purified sodium tungstate solution after filtration is stored in a tank for pH and temperature adjustments. The plant at Huntsville uses continuous LIX(liquid Ion Exchange) process for APT production. As shown in *Figur 6*, the process has separate impurity removal step and a wide variety of ores can be treated. Further, the labor requirement of the process is low and uniform quality of product and a yield over 98% is achieved.

In LIX process sodium tungstate solution (pH 1-7) is allowed to contact with an extractant comprising of 7% amine-336, 7% decanol, and 86% kerosene by volume. During countercurrent flow of two phases tungstate ions are transferred from the aqueous phase to the organic phase according to the reaction:

$$\left[\frac{n}{2}(R_3NH\cdot HSO_4)_2\right]_{(org)} + \left[(W_xO_yH_z)^{n-}\right]_{(aq)} \rightleftarrows \left[(R_3NH)_3\cdot W_xO_yH_z\right]_{(org)} + \left[n(HSO_{4^-})\right]_{(aq)} \quad (6)$$

The extraction is pH dependent and sufficiently high in the range of 1-3. In this pH range, according to Kim et al.[16] tungsten may be present as $W_{12}O_{40}H_2^{6-}$, $W_6O_{21}H^{5-}$ and $W_{12}O_4^{8-}$. The organic phase leaving the extraction section is scrubbed with deionized water to remove contaminated sodium ions.

Tungsten from the loaded organic phase is stripped into aqueous phase of ammonia solution containing ammonium tungstate. The presence of free ammonia in the aqueous phase at 60°C prevents the precipitation of APT in the stripping circuit. Chiola and Liedtke[17] have studied in detail, the concurrent stripping system. The organic phase after stripping of the tungsten value is recirculated for extraction and the ammonium paratungs tate solution is sent to the evaporator for the crytallization of APT.

V. Production of Metallic Tungsten

Ammonium paratungstate can be directly reduced to tungsten or first converted to tunstic oxide. However, the reduction of oxide is generally preferred over APT.

The direct reduction of APT produces large volumes of ammonia and water vapor which cause problems in recovery of hydrogen. Thus conversion of APT to tungstic oxide happens to be the first step towards metal production. Tunsten has various oxides which are distinguished by colors for example, tungstic oxide(WO_3) — yellow; tungsten dioxide (WO_2) — brown; and intermediate oxide(W_4O_{11}) — purple blue.

1. Decomposition of APT

APT is decomposed to yellow oxide at above 250°C in a furnace under the flow of air. A strongly reducing atmosphere is needed to produce blue oxide at 490°C. Both stationary as well as rotary furnaces electrically heated or gas fired are employed for decomposition (4). Inconel boats loaded with APT powder are moved through the hot zone for 4.5-5 hrs. A slight pressure of hydrogen is maintained at the discharge end of the furnace. The flue gas after reduction is scrubbed for ammonia and hydrogen recovery. Rotary furnaces are divided into three zones maintained at three different temperatures of 850°C, 875°C, and 900°C. Material passes from one zone to the other through central holes at the partition. For yellow oxide production, a stream of filtered air is introduced into the furnace whereas for blue oxide, a reduced pressure(38.1mm Hg) is maintained.

2. Reduction of Tungstic Oxide

Tungstic oxide can be reduced by means of a suitable reducing agent R according to the reaction:

$$2R + WO_3 \rightarrow W + R_2O_3 \qquad (7)$$

where R stands for a trivalent metal. In order for this reaction to proceed in the forward direction, the free energy change should be negative, i.e. metal oxide should be more stable compared to WO_3 at the temperature of reduction. For convenience, reductant should have high boiling point and should be easily available at a reasonable price. The reaction should be exothermic so that only a small amount of heat is required at the beginning to start the reaction. For example, reduction reactions with calcium, magnesium and aluminum are sufficiently exothermic but silicon, carbon and hydrogen require external heat. On commercial scale, hydrogen reduction is preferred due to the high purity of the reduced powder.

Prior to the development of hydrogen reduction method, tungsten powder was prepared by carbothermic reduction of tungstic oxide at above 1050°C. The method yields powder with about 0.15% C which has limited applications in alloy steels where purity requirement is not rigid. During the process of reduction, resulting powder reacts with carbon to form carbides(W_2C and WC). The purity varies from 98% to 99.6% with common impurities of Si, Fe, S and P.

During the past seven decades, a number of attempts have been made to produce tungsten powder by metallothermic reduction using sodium, magnesium, calcium, aluminum, silicon and zinc.

According to a British patent[18] tungsten oxide has been reduced with aluminum at 1700°C. Cupta and Jena[19] have reported a process for the preparation of massive metal by aluminothermic reduction of tungstic oxide in a closed-magnesia line reactor in the presence of sulfur at the initiation temperature of about 450°C. Addition of sulfur and exess of aluminum to the charge facilitates the formation of low-melting Al_2O_3-Al_2S_3 slag during the reduction process. This helps the separation and consolidation of the metal and provides better yield. The reaction initially is triggered by small amount of calcium and sulfur in the charge.

Suanstrom and Ramqvist[20] have obtained tungsten alloy by smelting tungsten ore with aluminum and/or silicon in an electric furnace in the temperature range 1800° to 2000° C. The alloy is crushed and chlorinated with HCl gas. The use of calcium has been reported to a limited extent due to its high cost. Good et al[21] have reduced WO_3 with calcium in a closed vessel in the presence of sulfur. Okage[22] has been successful in reducing WO_3 with zinc in the temperature range 750° to 850°C in hydrogen, nitrogen, coal gas and nonoxidizing atmosphere. The product was leached with hydrochloric acid to remove zinc oxide. In a French patent[23] tungsten carbonyl has been produced by reacting mineral oxide with CO under pressure in the presence of iron carbonyl. The resulting carbonyls are fractionally distilled.

On industrial scale, tungstic oxide is reduced with hydrogen. The reduction takes place in stages and the corresponding reactions are represented as follows:

$$4WO_3 + H_2 \rightarrow W_4O_{11} + H_2O \quad (8)$$

$$1/3\ W_4O_{11} + H_2 \rightarrow 4/3WO_2 + H_2O \quad (9)$$

$$1/2\ WO_2 + H_2 \rightarrow 1/2W + H_2O \quad (10)$$

Furnces used for reduction are similar to those used for the decomposition of APT. Yellow oxide is loaded in boats which are passed into the furnace countercurrent to the movement of hydrogen gas. During reduction hydrogen molecules are dissociated and adsorbed on the surface of tungsten metal and exhibit catalytic effect. The effect is inhibited to a large extent by the presence of water vapor.

Particle size of the reduced powder is controlled by the H_2O content of the gas which is affected by temperature. To obtain fine powder a high rate of hydrogen flow to remove water vapor generated during reduction should be used. The depth of oxide in the boat affects the H_2O content in the gas phase. Coarsening of powder can be avoided by adjusting the temperature in different zones separately so as to have gradual reduction from lower to higher temperature.

Ⅵ. Ptoduction of Ferrotungsten

A major amount of tungsten in the form of ferrotungsten is used in the steel industry. Ferrotungsten can be made by metallothermic reduction of ore concentrate in a crucible furnace. Carbon, silicon or aluminum are commonly used as the reductants. On industrial scale, it is manufactured by the direct reduction of tungsten ore with carbon in an electric furnace. The resulting product is refined and decarburized to obtain ferrotungsten of required specification. Ferberite concentrate (4) in general can be reduced with 25% excess carbon in an electric furnace as per the reaction:

$$FeWO_4 + 4C \rightarrow (Fe - W) + 4CO \quad (11)$$

Silica in the ore is fluxed with lime and fluorspar.

Ⅶ. Tungsten Recovery from Scrap

Tungsten carbide tool bits, spent catalysts, grinding sludge, metal scale and machine chips constitute a major part of tungsten scrap. Method of recovery varies with the type of scrap.

Metallic scrap is oxidized in a stream of air or reacted with sodium nitrate at higher temperature under constant agitation (1). The agitation breaks oxide layer and thus fresh metallic tungsten is oxidized. Kalashnik et al.[24] modified the above process for the treatment of Mo-W alloy scrap. In this method about 98% of Mo is volatilized from the scrap by conducting oxidation below 800°C. In a recent report, scrap is roasted with a mixture of $NaNO_3$ or $NaNO_2$ and Na_2CO_3 at 800°C for 1 hr. Oxidizing agent and sodium carbonate in a proportion of 3 : 1 is used for treatment of tungsten steel[25] and 1 : 3 for tungsten chips and grinding dust.[26] In this oxidizing roast process tungsten is converted to WO_3 if air is used as the oxidizing agent and to Na_2WO_4 if $NaNO_3$ is used. Sodium tungstate is leached with hot water and filtered to remove insoluble gangue. Tungstic oxide is leached with sodium hydroxide solution and further treated by the established methods of tungsten recovery.

Carbide scrap can be treated by a variety of methods. In the cold stream process, massive stationary carbide target is shattered by impinging with a high velocity stream. The resulting particles are then air classified and the oversize particles are recycled for further imingement. The fines are resintered. In the zinc process[27,28], tungsten carbide is treated with molten zinc to alloy cobalt, the cementing agent. Zinc is removed by distillation and thus mixture of carbide and the cementing agent can be recovered for reuse. In another process known as leach-milling (4) cemented carbide is treated with mineral acids to dissolve binder metal in a rotating rubber-lined mill.

A number of investigators have sugggested chlorination as a means to recover tungsten from carbide scrap. However, difficulties may be due to carbon buildup on the carbide grains. The problem can be overcome by periodic circulation of CO_2 to form CO[29]. Chlorination forms a step in the treatment of catalysts containing 10% W, Mo or V in alumina or silica as the base material. Erikson et al.[30] have suggested a method in which material is treated with hydrogen sulfide or carbon disulfide and then chlorinated with chlorine or carbontetrachloride at 290° to 370°C. The resulting chloride mixture is separated by distillation.

General Electric has been awarded patents[31,32] for developing a process to recover tungsten from heavy alloys, thoriated tungsten and tungsten carbide by electrolytic methods. In this procss, scrap is oxidized anodically in an electrolytic cell having mixture of hydroxides of sodium, potassium and ammonium as electrolyte. The resulting tungsten solution is purified by LIX process. Balikhin et al[33] have studied electrolytic dissolution of thoriated tungsten. Zueva et al.[34] have attempted separation of molybdenum and tungsten by the anodic dissolution of alloys in acid media.

Ⅷ. Current Research Efforts

Increasing demand of tungsten in various froms and depletion of the ore quality have encouraged researchers towards the development of new processes as well as improvement of the conventional ones. The present commercial methods based on hydrometallurgical principles have been developed for a particular type of ore. They cannot be employed to treat complex minerals or mixed scheelite and wolframite concentrates. During the past two decades the U.S. Bereau of Mines directed a number of research programs to develop new methods of extraction. The research projects on chlorination as a means of decomposing tungsten ores, electrolytic production of tungsten and recovery of tungsten from brines are worthy of attention. These will be briefly discussed in this Section. In addition, investigations to improve methods of beneficiation, leaching and solvent extraction will be reviewed.

A number of investigations(7-9) have been reported on the development of new collectors to improve recovery of tungsten by flotation. Meerson and Mikhailova[35,36] have investigated two stage leaching of scheelite concentrate with nitric acid at 120°C in a heated ball mill. They have obtained 99% decomposition of scheelite in 8 hrs using 20% excess acid over the stoichiometrically required amount. Simultaneous milling exposes fresh scheelite grains which increases the leaching rate. No work on the recovery of tungsten from nitric acid media has been reported. However, it would be interesting to carry out research investigations in this area to assess economic feasibility of nitric acid leaching. Zelikman et al.[37] have reported the use of sodium fluoride to break scheelite concentrate. Attempts have been made to use sulfuric acid for the decomposition of wolframite concentrate.[38] Born et al.[39] investigated leaching of wolframite containing cassiterite and barnnerite. Sulfuric acid with sodium chlorate or MnO_2 dissolves away barnnerite. Zelikman et al.[40] have considered intensification of the autoclave-soda process of opening scheelite concentrate by mechanical agitation which helps in reducing soda consumption. Vezina and Gow[41] have investigated a continuous process to convert sodium tungstate to ammonium tungstate by ion exchange technique using a cation resin. In order to improve the economics of tungsten extraction and for a better tungsten-molybdenum separation, a number of organic solvents viz. TBP, MIBK,[42] tertiary aliphatic amines,[43] tri-n-octylamine, tri-n-octylbenzylammonium chloride[44] and quarternary ammonium compounds[45] have been employed. Recently, tungsten recovery from hot spring ores[46] have been reported. The ore is calcined at 800°C and then quenched in sodium hydroxide or sodium carbonate solution and the resulting mass is leached in an autoclave at 180° to 300°C 200-300 psi. By this method, 95% tungsten is recovered in the leach liquor.

1. Chlorination

The treatment of scheelite and wolframite with chloine in the presence of carbon produces oxychloride vapors along with other volatile chloride impurities. After the removal of impurities, tungsten oxychloride can be dissolved in water to obtain tungstic acid or subjected to second stage chlorination to produce tungsten hexachloride. Prior to reduction, tungsten hexachloride is fractionally distilled to remove molybdenum and other metal chlorides. In principle, the process appears simple and attractive but presents several problems for operation on commercial scale. Henderson et al.[47] have carried out detailed investigation on the prossibilities of extraction of tungsten from scheelite and concentrate containing mixture of wolframite and scheelite by chlorination on laboratory scale. Chlorination reactions are represented as follows:

$$2CaWO_4 + 3C + 6Cl_2 \xrightarrow{600°C} 2\,CaCl_2 + 2\,WOCl_4 + 3CO_2 \quad (12)$$

$$2Fe(Mn)WO_4 + 3\,C + 7\,Cl_2 \xrightarrow{300°C} 2\,Fe(Mn)Cl_3 + 2\,WOCl_4 + 3\,CO_2 \quad (13)$$

Addition of calcium fluoride to the charge improves tungsten recovery. This is more pronounced in materials containing silica whi ch forms silicon tetrafluoride and thus other metals get converted to chloride. The effect of carbon and calcium fluoride content of the charge and temperature on tungsten recovery have been studied. At 700°C, 90% tungsten has been extracted in 2 hrs with carbon to scheelite ratio of 0.075.[47]

At the temperature of operation, calcium chloride is liquid and hence causes problem in the reactor design. In the case of wolframite, the formation of ferrous chloride presents similar difficulties. The problem may be avoided by the formation of solid calcium sulfate when chlorination is conducted with a gaseous mixtre of sulfur dioxide and chlorine[47] as per the reaction:

$$CaWO_4 + Cl_2 + SO_2 \rightarrow CaSO_4 + WO_2Cl_2 \quad (14)$$

At 550°C, 95% tungsten is converted to volatile oxychlore. Above 550°C, recovery decreases due to the instability of WO_2Cl_2 and shifts in equilibrium between chloride, sulfate and oxide. The oxychloride has to be converted to hexachloride as it forms water vapor during hydrogen reducion or oxide by metallothermic reduction. Its instability also causes problem in handling during purification and reduction. The conversion of $WOCl_4$ to WCl_6 has been studied by Henderson et al.[48] The reaction is temperature dependent and influencen by the form of carbon and the type of chlorinating agent.

Since the preparation of high purity tungsten requires pure WCl_6 purification step is of utmost importance. Skirvin et al.[49] have studied various methods viz. distillation, fused salt scrubbing, activated carbon and zone refining for purifying tungsten hexachloride. In distillation, advantage is taken of the difference in boiling point of various chlorides. WCl_6 and $MoCl_5$ are first evaporated in the initial fraction whereas chlorides of iron, nickel, copper, maganese as residues. The resulting WCl_6 contains less than 10 ppm of metallic impurities. Scrubbing of WCl_6 in a fused salt mixture comprising of LiCl-KCl eutectic produces the same quality. In the temperature range 600° to 850°C, molybdenum chloride can be absorbed in activated carbon and iron chloride in sodium chloride at 300° to 600°C, but the absorption technique is not as effective as distillation and scrubbing. Method of zone refining appers to be more complicated due to the vapor pressure of WCl_6 at the temperature of operation.

Tress et al.[50] have studied hydrogen reduction of WCl_6 and developed an apparatus to produce tungsten powder of required specification. As the reduction is carried in vapor phase particle size can be controlled by gas composition. Argon is used as carrier gas and to control the rate of WC_6. The furnace is divided in two zones. The first part is used for preheating and second for reduction.

Particle size of the resulting powder can be controlled by varying the feed rate of WCl_6, the rate of hydrogen flow and temperature in two zones of the furnace.

Recently Hojo et al.[51] have prepared tungsten carbide(WC and W_2C) powder by the vapor phase reduction of WCl_6-CH_4-H_2 system at 1000° to 1400°C. Carbon content of the product increases with increase in temperature and CH_4 concentration in the gas phase. At 1400°C only WC is obtained. The formation of WC takes place in two steps; tungsten formation followed by carburization.

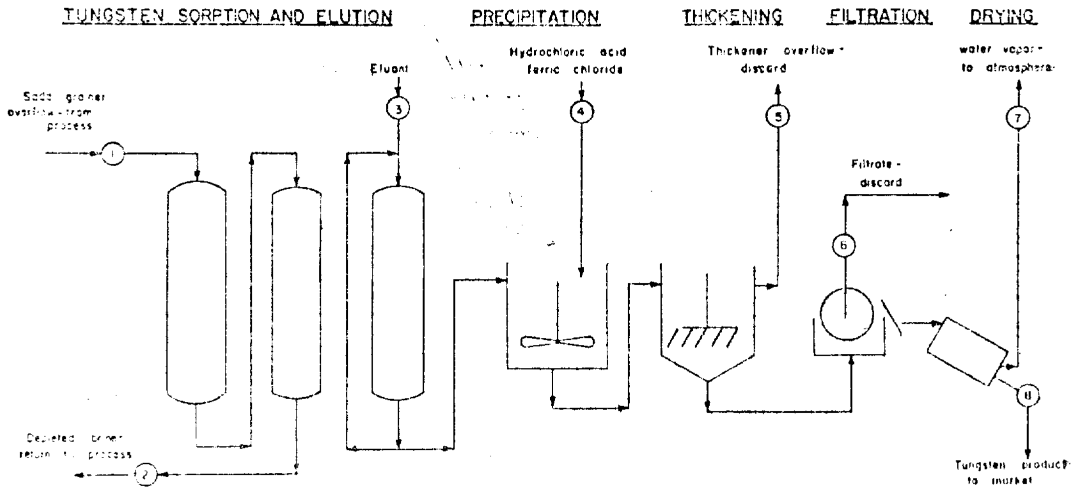
2. Electrolytio Method of Tungsten Production

Zadra and Gomes[52] have prepared tungsten metal by the electrolysis of scheelite using fused salt bath consisting of alkali, phosphate and borate at 900° to 1100°C, Mo and W have been deposited sparately and the purity of tungsten range from 99.7% to 99.4%. Cattoir[53] has evaluated some fused salt electrolytes for refining tungsten. Electrolytes solely composed of chlorides are not useful due to the volatility of tungsten chloride. A temperature of 900°C is necessary to maintain a good dissolution rate at the anode and acceptable cell operation. Gomes et at[54] have deposited 99.9% pure tungsten at 1000°C from an electrolyte comprising 7 parts sodium pryophosphate, 2 parts sodium chloride, and 1 part sodium tetraborate. The feed material was scheelite concentrate containing 25% to 73% WO_3 and varying amounts of iron, lime and silica. Gomes et al.[55] have evaluated two molten salt systems viz. NaCl-NaF-$KAlF_4$ and sodium pyrophosphate-sodium chloride as electrolytes. The former is used at 800°C to obtain 99.8% pure tungsten whereas the latter produces a purity of 99.9%. According to these investigators, electrolyte life is increased by the periodic addition of B_2O_3[56] which reacts with lime liberated during electrolysis of scheelite. Gomes and Wong[57] have propared tungsten carbide by the electrolysis of sodium tungstate using graphite anode. Optimum results are derived from an electrolyte composed of 83 mole percent NaCl, 5.7 mole percent each sodium tungstate, molybdate and hyroxide at the temperature of 1000° to 1025°C. Gomes et al[58] have investigated two methods of electrowinning tungsten from wolframite. The direct electrowinning from the concentrate dissolved in molten salt mixture of sodium phosphate, sodium borate, and sodium halide resulted in impure metal. Electrowinning from a halide-tungstate melt with additions of sodium metaphosphate and boric acid yielded 99.9% pure metal. Tungsten carbide is electrodeposited from the halide-tungstate melt consisting of sodium metaborate, sodium chloride and sodium hydroxide. They have also compared techniques for electrowinning tungsten from scheelite.[59]

Keith et al.[60] have evaluated the properties of electrowon tungsten powder by comparing its characteristics with hydrogen-reduced powder. Electrowon powder had better compressibility and higher flow rates compared to hydrogen-reduced powder. But its large particle size prevents its usage to produce high density products by powder metallurgical methods. Keith, Winston and Iverson[61] have examined electrowon powder for sheet production.

3. Tungsten Recovery from Brines

Some lake brines contain an appreciable amount of tungstic oxide as tn the case of Searles Lake located in the Mojave desert, 170 miles northeast of Los Angeles. The Lake



Stream number	①	②	③	④	⑤	⑥	⑦	⑧
Stream name	Soda grainer overflow	Depleted brine	Eluent	Precipitant	Thickener overflow	Filtrate	Vapor	Tungsten product
Volume, gal	2,592,000	2,591,000	145,152	1,739	127,431	17,455	-	-
Total weight, lb	27,241,920	27,236,300	1,212,553	17,509	1,064,442	145,352	18,434	3,314
WO_3, lb	1,577	32	0	0	77	10	0	1,458
B_4O_7, lb	240,000	238,900	35	0	945	130	0	60
Fe, lb	0	0	0	612	34	6	0	572
HCl, lb	0	0	0	6,053	0	0	0	0
Na_2CO_3, lb	-	-	6,053	0	-	-	0	0
H_2O, lb	-	-	1,201,753	11,764	-	-	18,434	0

Fig. 7. Conceptual flowsheet for recovering tungsten from 2.59 million gallons daily of sodagrainer overflow (Ref. 62, p. 13)

covers about 35 square miles of area and contains on the average 70 ppm of WO_3. The total tungsten in this lake brine amounts to 50% to 60% of the entire U.S. deposit. U.S. Bureau of Mines has been engaged in development of a process to recover tungsten from brine for the last few years. Altringer et al[62] have recently published a report on the feasibility of tungsten recovery from Searles Lake brine. Since the brine is highly alkaline (pH is 9-8) precipitation of tungstic acid by chemical methods will be highly uneconomical due to the large requirements of chemicals. Therefore, methods without changing the chemical character of the brine were attempted. Ion exchange method seems to be quite promising and thus a number of resins were developed. Development work has been summarized by Altringer et al.[62] They have studied in detail various process variables to optimize the recovery on laboratory scale. Based on laboratory data a flowsheet(*Figure 7*) for treatment of 1800 gallons per minute of carbonated soda grainer overflow has been proposed. This overflow is obtained from the chemical plants treating the Searles brine for the production of a number of chemicals.

As shown in *Figure 7*, the unit consists of 15 fixed-bed columns of 9.6 ft diameter. Three columns constitute a group. In each group, two columns are used for sorption and the third on for elution. Resin is loaded at a flow rate of 5 gallons per minute per sq. ft of the column area. The eluant flow is 0.5 gallons per minutte per sq. ft. This enables 98% of tungsten from soda grainer overflow to be sorbed in HERF resin developed by the Bureau chemists.[62] Tungsten-free brine is returned to the process. Tungsten from the resin bed is eluted in sodium carbonate solution without deteriorating the nature of the resin. A number of reagents have been attempted to recover tungsten from the eluate but the best result has been obtained by the use of acidified ferric chloride in the pH range of 3.5 to 4.5. This treatment precipitates tungsten as iron tungstate. The composition of chemicals at various stage of operation has been listed in *Figure 7*.

Ⅸ. Conclusions

Although commercial methods for the production of tungsten from scheelite and wolframite are well established, there is a need for the development of processes involving a fewer number of steps for the treatment of low grade and complex ores or mixed concentrates. If design problems can be overcome, the chlorination mothod has potentiality for further development. The hydrogen redution of tungsten hexachloride is capable of producing tungsten powders of high purity, ultrafine particle size, and narrow particle size distribution.

Successful attempts have been made in laboratories to produce high purity tungsten by the electrolysis of molten salts containing tungsten oxides or halides. The process seems to be economical for the treatment of wolframite and scheelite ores to obtain metallic tungsten and tungsten carbide. But so far no large scale operations have been conducted mainly due to the problem of problem of undesired particle size. Electorolytic methods produce powders of large size and elongated shape which are unsuitable for consolidation by powder metallurgy techniques.

Ion exchange method to recover tunsten from brines has been successfully demonstrated on bench scale. The favorable results have encouraged scientists of the Bureau of Mines to examine economic feasibility of the process on a larger scale. As the economics of the process entirely depends on the performance of the resin, major efforts are needed to improve the chemical as well as physical characteristics of the resin.

REFERENCES

1. C.J. Smithells, *Tungsten*, Chemical Publishing Co., New York, 1953.
2. R. Oxland, British Patent 11848, 1847.
3. C.M. Johson, British Pantent 24501, 1910.
4. S.W.H. Yih and C.T. Wang, *Tungsten Sources, Metallurgy, Properties and Applications*, Plenum, New York, 1979.
5. B.A. Kornhausner, Tungsten in *Minerals Yearbook*, U.S. Bureau Mines, 1976.
6. R.W. Barr, J. Metals, **32** (1980)62.
7. F.M. Grabserg, World Mining, **32** (3) (1979) 54.
8. R. Arnold, E.E. Brownbill ande S.W. Ihle, Intl. J. Miner. Process, 5(12)(1979) 143.
9. P.M. Solozhenkin, M.N. Bekhtereva, L. F.S amokhralova, N.G. Nazaretyan, S.M. Bobneva, R.V. Kazaryan and A.L. Solodukhin; Izv. Adak. Nauk. Tadzh, SSR, Otd. Fiz-Met. Geol. Khim. Nauk, (4) (1979) 47. Chem Abs. 91 : 77210e.

10. W. Ryan, Ed., *Nonferrous Extraction Metallurgy*, London, 1968.
11. I.N. Naslenitski, Tsvetneye Metal, No (4-5) (193i140; Chem Abs. 34 : 3521.
12. N.N. Maslenitskii and P.M. Perlov, Intl. Mineral Processing Congress, Group VII, Paper No 41, London, 1960.
13. A.N. Zelikman and Rakova; Tsventnye Metal, 7 (3) (1966) 64.
14. P.B. Queneau and S.R.B. Cooke, TMS-AIME, 245 (1969) 245 (1969) 2451.
15. A.N. Zelikmanand G.A. Meerson, *Metallurgiya Redkikh Metallov*, Metallurgiya Moscow, 1973.
16. T.K.Kim, R.W. Mooney and V. Chiolia, Separation Sci., 3 (1968) 467.
17. V. Chiola and F.W. Liedtke, South African Patent 68/4892, 1968.
18. B. Felder-Clement, Aktien Gesellschaft, British Patent 187375, 1922.
19. C.K. Cupta and P.K. Jena, J. Less Common Metals, 13 (1967) 269.
20. E.K.A. Svanstrom and L.H. Ramquist, Canadian Patent 887568, 1971.
21. P.C. Good, D.H Yee and F.E. Block, U.S. Bureau Mines RI-5828, 1961.
22. M. Okage, British Patent 932168, July 14, 1963.
23. E. Slatineaner, French Patent 1169052, Dec. 6, 1956.
24. A.N. Kalashnik, A.A. Reznyakov, L.A. Mirkin, N.V. Ogorodnik, and V. Yakol' tesva, Tsvtnye Metal 14(12) (1973) 64.
25. B. Topalov, G. Danev, D. Petrov and A. Todorov; Ruddboiv; Met. (Sofia)21 (10) (1966) 17. Chem. Abs. 67 : 46124e.
26. Societe Electrometallurgique de Saint-Etienne, British Patent 695843, 1953.
27. E.M. Trent, U.S. Patent 2407752, 1946.
28. P.G. Barnard, A.G. Starliper and H. Kenworthy, U.S. Patent 3595484, 1971.
29. K. Johnson, Soth African Patent 68/1504, 1968.
30. H. Erikson, P. Forest, and R.L. Foster; U.S. Patent 3539290, 1970.
31. General Electric Co., British Patent 84862 1960.
32. General Electric Co., British Patent 857969 1961.
33. V.S. Balikhin, V.A. Reznichenko, S.G. Korneeva, I.V. Korchagin and P.N. Krepkov, Tsvetnye Metal., 13(11) (1972) 71.
34. A.F. Zueva, A.D. Styrkas, and V.M. Tarakanov, Zhur. Prikl. Khim (Leningrad) 46 (7) (1973) 1621, Chem. Abs. 79 : 142200v.
35. G.A. Meerson and V.G. Mikhailova, Tsvetnye Metal. 8(4) (1967) 69.
36. V.G. Mikhailova and G.A. Meerson, Tsvetnye Metal. 7 (8) (1967) 77.
37. A.N. Zelikman, T. Sh. Aganokov, and N.N. Rakova, Nauchn. Trudy Moskov. Inst. Stali Stlevov, 75 (1972) 8, Metals 1973, 42-0449.
38. L.A. Anfilogova, Trudy Irktsk Politckhn. Inst. 37 (1967) 59, Metals Abs. 1968, 42 -0551.
39. C.A. Born, P.B. Queneau and R.A. Ronzio, Trans. Soc. Mining Engineers, AIME, 258(3) (1975) 218.
40. A.N. Zelikman, N.N. Rakova, and F.A. Aramisova, Tsvetnye Metal. (7) (1978) 57, Metals Abs. 1979, 42-0478.
41. J.A. Vezina and W.A. Gow, *Symposium on Advances in Extractive Metallurgy*, Inst. Mining Met., London, 1968.
42. K. Ya Shapiro, I.V. Volk-Karachevskaya and V.V. Kulakova, Tsvetnye Metal, 8 (6) (1967) 80.
43. M.A. Petrov, M.N. Maslenitskii and A. D. Davydova, Tsvetnye Metal, (3)(1974) 38. Chem Abs. 83 : 62798p.
44. Yu S. Tseryuta, V.V. Bagreev, N.A. Agrinskaya, N.V. Gushchin, A.S. Basov, and Yu A. Zolotov; Zhur Anal. Khim, 28 (5) (1973) 946. Chem Abs. 79 : 70679h.
45. G.N. Chicagova, I.M. Ivanov, L.M. Grindin, A.S. Basov, and L.S. Chernikova, Izvest. Sibir. Otdel. Akad. Nauk. SSSR, Ser Khim (2) (1972) 65; Chem. Abs. 77 : 131364g.
46. J.M. Gomes, D.A. O'Keefe, and A.E. Ra-

ddatz, U.S. Patent 4467666, September 11, 1979.

47. A.W. Henderson, S.C. Rohoads, and R.R. Brown, U.S. Bureau Mines, RI-6612, 1965.
48. A.W. Henderson, D.H. Yee and F.E. Block, U.S. Bureau Mines, RI-7152, 1968.
49. F.A. Skirvin, T.T. Campbell, and F.E. Block, U.S. Bureau Mines, RI-6984, 1967.
50. J.E. Tress, T.T. Campbell, and F.E. Block, U.S. Bureau Mines, RI-6835, 1966.
51. J. Hojo, T. Oku and A. Koto, J. Less Common Metals, **59** (1978) 85.
52. J.B. Zadra and J.M. Gomes, U.S. Bureau Mines, RI-5554, 1959.
53. F.R. Cattoir, U.S. Bureau Mines, RI-6154, 1963.
54. J.M. Gomes, J.B. Zadra, and D.H. Baker, U.S. Bureau Mines, RI-6512, 1964.
55. J.M. Gomes, K. Uchida, and D.H. Baker, U.S. Bureau Mines, RI-6742, 1966.
56. J.M. Gomes, K. Uchida, and D.H. Baker, U.S. Bureau Mines RI-6805, 1966.
57. J.M. Gomes and M.M. Wong, U.S. Bureau Mines, RI-7247, 1969.
58. J.M. Gomes, K. Uchida, and M.M. Wong, U.S. Bureau Mines, RI-7344, 1970.
59. J.M. Gomes, K. Uchida, and M.M. Wong, U.S. Bureau Mines, RI-7580, 1971.
60. G.H. Keith, B.D. Jonesand E.A. Rowe, U.S. Bureau Mines, RI-6578, 1965.
61. G.H. Keith, J.S. Winston, and H.G. Iverson, U.S. Bureau Mines, RI-7385, 1970.
62. P.B. Altringer, W.N. Marchant, R.O. Dannenberg, and P.F. Brooks, U.S. Bureau Mines, 1978.