State of the art on the recovery of refractory metals from primary resources

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Summary

State of the art on the recovery of refractory metals from primary resources The mining and mines of refractory metals, tungsten, tantalum, molybdenum, niobium and rhenium in Europe and the world are described and the existing technologies of mining, mineral processing and extractive metallurgy (hydrometallurgy and pyrometallurgy) are reviewed on recovery of refractory metals from primary resources. Based on metal type the document is assigned into five chapters : Chapter 1 Tungsten, Chapter 2 Tantalum, Chapter 3 Molybdenum, Chapter 4 Niobium and Chapter 5 Rhenium. The mining and mineral processing technologies of niobium and tantalum are jointly introduced in Chapter 2 Tantalum because of the co-occurrence of two metals.

Approval

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STATE OF THE ART ON THE RECOVERY OF REFRACTORY METALS FROM PRIMARY RESOURCES

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CONTENT

INTRODUCTION

In this report the mining and mines of refractory metals, tungsten, tantalum, molybdenum, niobium and rhenium in Europe and the world are describedthe and the technologies of mining, mineral processing and extractive metallurgy (hydrometallurgy and pyrometallurgy) are reviewed on recovery of refractory metals from primary resources. Based on metal type the document is assigned into five chapters : Chapter 1 Tungsten, Chapter 2 Tantalum, Chaper 3 Molybdenum, Chapter 4 Niobium and Chapter 5 Rhenium.

Because niobium and tantalum usually co-occur in the same minerals or the same mineral deposits the mining and mineral processing technologies of two metals are jointly introduced in Chapter 2 Tantalum. In addition, rhenium is produced as by-product in Mo and Cu processing, or in other words, rhenium is mainly recovered from the secondary resources. The technologies of the pyro and hydrometallurgical processing of rhenium are covered in the work package 3 for secondary resources.

CHAPTER 1 TUNGSTEN

GENERAL FLOWSHEET OF PRODUCTION

The general flowsheet of tungsten production including mining, mineral processing and extractive metallurgy is shown in the Figure 1-1 [2].
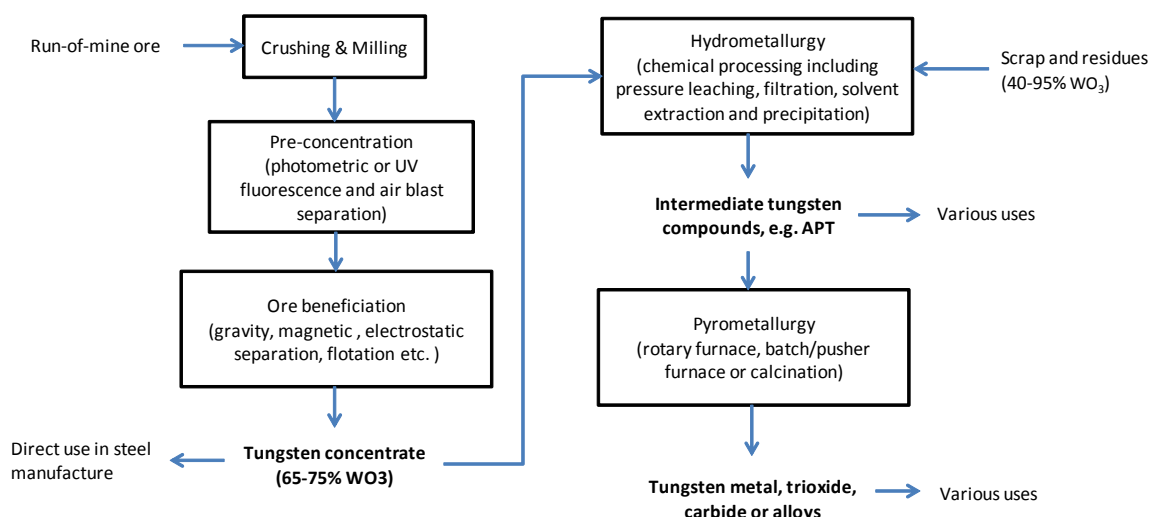

Figure 1-1 The general flowsheet of tungsten production

MINING

ORE DEPOSIT TYPES

Three types of tungsten deposits are: Classical vein deposits, Skarn deposits and Bulk mineable deposits (greisen, porphyry, stockwork) [10].
Classical vein deposits contain more or less continuous veins of decimetres to metres in thickness, mainly comprising quartz in granite itself or in surrounding host rock. Most deposits have ferberite or hübnerite mineralisation, but scheelite vein deposits do also occur. Typical tonnages are from few 10s to few 100,000s of tonnes of ore with typical grades of 0.5 – 5% WO_3. Sn typically co-occurs as by-product. Object of mining is the individual quartz vein with its content of tungsten mineralisation. Examples of active mines are: Panasqueira in Portugal; San Fix in Spain; Pasta Bueno in Peru and Chollja in Bolivia.
Skarn deposits are formed by replacement of carbonate rock (e.g. limestone) by calc-silicate minerals (garnet, epidote, amphiboles and others) near to the contact of a granitic / felsic intrusion. Mineralisation might be mono-metallic tungsten (almost exclusively as scheelite) or polymetallic (often with Mo or base metals: Pb, Zn, Cu), also together with gold, fluorite or magnetite. In some cases, tungsten is only by-product. Typical tonnages are few million tonnes, but much larger deposits are found. Typical grades are 0.3 – 1% WO_3. Examples of

active mines are Cantung in Canada; Shizhuyuan in China; Vostok-2 in Russia; Los Santos in Spain; Bonfim and Brejui in Brazil.

Bulk mineable deposits are either W-Sn or W-Mo deposits. Both scheelite and wolframite occur in bulk mineable deposits, and some deposits contain both minerals together, which leads to problems with beneficiation as mixed concentrates are more difficult to market. Typical tonnages are dozens or hundreds of million tones with typical grades of 0.1 – 0.3% WO_3. Object of mining is not the individual mineralised vein but the entire rock mass including the quartz or greisen veins. Examples of mines include Lianhuashan in China and Mittersill in Austria.

TUNGSTEN MINES IN EUROPE AND THE WORLD

According to the most recent US Geological Survey (USGS) report [16] on the metal, world tungsten production reached 87,000 metric tons in 2015, an increase over 2014's 86,800 metric tons. Top 10 production countries in 2015 are China (71,000 metric tons), Vietnam (5,000 metric tons), Russia (2,500 metric tons), Canada, Bolivia (1,200 metric tons), Rwanda (1,000 metric tons), Austria (870 metric tons), Spain (730 metric tons), Portugal (630 metric tons) and UK (600 metric tons)[12].

China is the largest producer of tungsten. Its mine production in 2015 was 71,000 metric tons. The top 10 tungsten mines in China are listed in Table 1-1. Their annual output are from 1,350 to 5,750 tons of WO_3. Xianglushan mine is the largest mine in Jiangxi China with the reserves of 217,000 tons of WO_3.

Table 1-1 Top 10 tungsten mines in China

Deposit Name	Company	Location and Country	Status	Reserves Mt and grade WO_3 %
Xianglushan	Jiangxi Xiushui Xianglushan Tungsten Ind.Co.	Xiushui, Jiangxi, China	Annual output 5,750 t WO3	217,000 t WO_3
Shizhuyuan[*]	Hunan Shizhuyuan Non-ferrous Metal	Chenzhou Hunan, China	Annual output 5,498t	705,000 t
Yaogangxian	Hunan Yaogangxian Mining Ind.Co	Yizhang Hunan, China	Annual output 4,500 t	200,000 t
Dajishan[**]	Jiangxi Dajishan Tungsten Ind. CO	Quannan Jiangxi, China	Annual output 2,800 t	173,900 t
Taoxikeng	Chongyi Zhangyuan Tungsten Ind.Co	Chongyi Jiangxi, China	Annual output 2,500 t	74,066 t
Maoping	Jiangxi Yaosheng Tungsten Ind. Co	Chongyi Jiangxi, China	Annual output 2,500 t	41,594 t
Tieshanlong	Jiangxi Tieshanlong Tungsten Ind. Co	Yudu Jiangxi, China	Annual output 1,900 t	-
Piaotang	Jiangxi Piaotang Tungsten Ind. Co	Dadu Jiangxi, China	Annual output 1,500 t	47,775 t
Xialong	Jiangxi Xialong Tungsten Ind. Co	Dayu Jiangxi, China	Annual output 1,450 t	-
Xihuashan[***]	Jiangxi Xialong Tungsten Ind. Co	Dayu Jiangxi, China	Annual output 1,350 t	81,300 t

*Ore type skarn deposits

**Mineralogy: tungstates, Niobates, Oxides, Sulfides, Manganoniobite, Tantalite, Wolframite, Scheelite, Beryl, Cassiterite, Bismuhinite, Galeba, Sphalerite, Stannite

***Mineralogy: wolframite, Bismtutite, Cassiterite, Chalcopyrite, Scheelite, Pyrrhotite, Beryl, Bornite, Shalerite, Arsenopyrite and REE minerals

Vietnam jumped two spots on the list to become the world's second-largest tungsten producer for 2015. The country produced 5,000 metric tons in 2015 compared to 4,000 mtric tons in 2014. The Vietnam-based Nui Phao mine owned by Masan Resources is the largest tungsten mine outside of China with mining reserve of 66million tonnes of ore with average grade 0.21% WO_3. Since Masan acquired the mine in 2010, it has seen consistent growth. It is an unique polymetallic mine with significant deposits of tungsten, fluorspar, bismuth, copper and among the largest producers of acid-grade fluorspar and bismuth in the world. With open-pit mining and low strip ratio, it is one of the lowest-cost producers of tungsten in the world[20].

Russia produced tungsten 2,500 metric tons in 2015. Vostok_2 is Russia's largest skarn deposit of high grade sulfide–scheelite ore with substantial Base metal and gold mineralization. It has been mined since 1969 by the Primorsky Mining and Concentrating Combine first in open pit, and subsequently by means of underground mining operations (until now) [17]. The initial tungsten reserves and resources exceeded (with allowance for follow up exploration) 180 kt WO_3.

Canada's tungsten production was 1,700 metric tons in 2015 to, down from 2,340 metric tons a year earlier. Owned by North American Tungsten Corporation Ltd. Cantung mine is located in western Northwest Territories of Canada and one of the largest tungsten mines outside of China [14]. It is a skarn type of deposit with the reserves of 1,818,000 tons at the grade 0.81 % WO_3. It is continuously operating underground and seasonally operating in open pit.

Austria, Spain, Portugal and UK are major tungsten production countries in Europe. They ranked 7th to 10th in the list of the world's top tungsten-producing countries.

Austria produced 870 metric tons of tungsten in 2015, the same amount it produced in 2014. Much of that production can be attributed to the Mittersill mine located in Salzburg province and operated by Wolfram Bergbau and Hutten which is owned by Metallgesellschaft Frankfurt, W. Germany (47,5%), Vbest-Alpine Corporation, Austria (47,5%) and Teledyne Corporation, USA (5%). The Mittersill mine hosts the largest tungsten deposit in Europe. The deposit was discovered in 1967. By 1973, the orebody had been explored by two exploration adits. Mining activities commenced in 1975, the ore dressing plant started operations in 1976. Scheelite concentrates are further processed in the Bergla tungsten smelter, Styria [18-19]. The deposit consists of two parts, the Ostfeld open pit and the Westfeld underground mine. In the Ostfeld up to 90% of the ore in these orebodies can therefore be recovered by opencast methods. Medium WO_3-contents average 0.75%, in pure ore quartzites and may increase to 3.5% WOs. The Westfeld deposit outcrops over 500 m. Within a mineralized thickness of 300 m, six economic horizons have been established so far. Within these horizons mineralization occurs in 60—200 m long and 3—20 m thick orebodies, the compositional axis of which dips towards the northwest. Intercalated "barren" rocks frequently carry 0.15—0.25% WO_3 over thicknesses of tens of meters. The Westfeld has an average content of 0.45% WO3 which is not as rich as in the Ostfeld. However, the total

potential reserves of the Westfeld are expected to be significantly larger than those of the topographically limited Ostfeld. Underground mining in the Westfeld commenced in October 1978 by opening up various adits and inclines; the official opening ceremony took place in September 1979. Production of the Mittersill mine in 1978 was 291.140 tons of ore with an average grade of 0.65% WO_3, yielding a WOs-content of 1.954 tons [19].

Spain produced 730 metric tons of tungsten that marks a drop from 800 metric tons of output in 2014. There are a number of companies engaged in the exploration, development and mining of tungsten assets in Spain including Almonty Industries, Ormonde Mining, Plymouth Minerals and W Resources. The Los Santos Mine was acquired by Almonty in September 2011. The mine was originally opened in 2008 and commissioned in July 2010 by its former owner. The Los Santos Mine is an open pit scheelite skarn deposit located approximately 50 kilometres from Salamanca in western Spain and produces tungsten concentrate [21]. Total reserves 3,582,000 tonnes at average grade 0.23% WO_3. Potential high grade underground resource from bottom of main Los Santos pit: 15 m crown pillar to remain between open pit and underground development and underground potential from 985 to 880 m delineated at 0.4% cut-off grade. Based on the current underground resource a 15,000 tpm operation has been evaluated by management: Additional 4 year mine life; Exploration drilling results demonstrate that substantial potential exists below delineated resources; and Underground development has the potential to materially extend mine life [21][22]. Barruecopardo Tungsten Project [11] situated in the Castilla y Leon region of Spain. It is 100% owned and operated by Ormonde Mining and has a life of nine years. The mine is planned to be an open pit operation. It will be one of the biggest tungsten projects in Europe. A definitive feasibility study (DFS) for the mine was completed in February 2012. The mine is expected to produce 1.1 million ton (mt) annually, according to the DFS report. First production is expected in the fourth quarter of 2013. Tungsten mineralisation is found in quartz veins mostly in the form of coarse grained scheelites less than 10cm in thickness. Intense veining at the deposit is nearly 40m wide. Minor traces of wolframite are also part of the deposit.

Portugal's tungsten production fell to an estimated 630 metric tons in 2015 from 671 metric tons in 2014. The Panasqueira mine is Portugal's largest tungsten-producing mine. The largest past-producing mine in the country, the Borralha mine, is currently owned by Blackheath Resources. UK had 600 metric tons of tungsten production in 2015. In the fall of 2015, Wolf Minerals opened its Hemerdon tungsten mine in Devon. According to the BBC, Hemerdon was the first tungsten mine to open in Britain in over 40 years.
The mines in Europe and the world out of China are listed in Table 1-2.

Table 1-2 The mines in Europe and the world out of China

Deposit Name	Company	Location and Country	Status	Type of Ore	Mining method	Mineralogy	Reserves Mt and grade WO3 %
Wolf Minerals mine	Wolf Minerals	10 km northeast of Plymouth, in Devon Devon, England	Feasibility Study completed in May 2011. Construction began in February 2014. Production estimated at 350,000 t/y of a tungsten concentrate with a grade of 65% WO3 along with 460 t/y tin concentrate. Expected to begin introducing ore into the plant in June 2015.	Hemerdon ore, wolframite as tungsten mineral.	open pit methods		35.7 MT@0.18% tungsten and 0.03% tin
Los Santos mine[21-22]	Almonty Industries	approximately 50 kilometres from Salamanca in western Spain	mine was originally opened in 2008 and commissioned in July 2010 by its former owner and produces tungsten concentrate [21].	open pit scheelite skarn deposit	open pit methods	Pyrite, arsenopyrite (and/or lollingite), pyrrhotite and chalcopyrite Scheelite, pseudo galena, bismuth, bismuthinite, and marcasite	Total reserves 3,582,000 tonnes at average grade 0.23% WO3 [21]
Barruecopar	Ormonde	Western Spain	Ormonde planned to	In quartz veins	conventional	Scheelite,	27.39 Mt @

do tungsten project [11]	Mining		produce scheelite concentrates containing an average of 1,800 t/yr of tungsten during the initial 9 years of operation [9][11]	mostly in the form of coarse grained scheelites less than 10cm in thickness, minor traces of wolframite	open pit methods	minor traces of wolframite	0.26 % WO3;
La Parilla project	Tungsten Resources	Extremadura region of Southwest Spain	Expected to begin production in mid-2016, a production rate of 1,200 to 1,300 t/y @ grade 66 % WO3. Full mine developed in 2017/2018, and target production 5,000 t/y of tungsten.				
Panasqueira mine	Almonty Industries	Covihã, Castelo Branco, Portugal	Tungsten and tin have been mined since the 1890s. During the period 1947 to 2001, over 27 million tonnes of rock were mined, from which approximately 92,800 t of tungsten concentrate, 4,800 t of tin concentrate, and 28,600 t of copper concentrate were produced.	Mineralisation includes an oxide-silicate stage consisting of wolframite, cassiterite, arsenopyrite, topaz, muscovite and tourmaline	An underground mine	wolframite, cassiterite, arsenopyrite, topaz, muscovite and tourmaline	4.91 Mt @ 0.22 %.
Borralha,	Blackheath Resources	Portugal					0.29 % WO3
Tabuaço		Norte Region, Portugal					2.75 Mt ore @0.57% W

Valtreixal project	Almonty Industries	Spain	In exploration				2.5 Mt @ 0.34 % WO3
San Fix	Spain			Classical vein deposit			
Pasta Bueno	Peru			Classical vein deposit			
Mittersill scheelite mine[18-19]	Metallgesellschaft Frankfurt, W. Germany (47,5%), Vbest-Alpine Corporation, Austria (47,5%) and Teledyne Corporation, USA (5°/o).	Salzburg province, Austria	The deposit was discovered in 1967. By 1973, the orebody had been explored by two exploration adits. Mining activities commenced in 1975, the ore dressing plant started operations in 1976. Scheelite concentrates are further processed in the Bergla tungsten smelter, Styria.	Bulk mineable deposits	The deposit consists of two parts, the Ostfeld open pit and the Westfeld underground mine.	scheelite	Production in 1978 was 291.140 tons of ore with an average grade of 0,65°/o W03 , yielding a WOs-content of 1.954 tons.
Chollja		Bolivia		Classical vein deposit			
Cantung[14]	North American Tungsten Corporation Ltd.	western Northwest Territories, Canada	The mine currently produces ore at a rate of 1,350 dry short tons per day. Mineral Reserves support a mine life to at least 2017. Processing by gravity and flotation circuits. Final products include a premium gravity	Skarn deposits	continuously operating underground and seasonally operated open pit	scheelite	1,818,000 tons @0.81% WO3

			concentrate (G1), containing on average, 65% WO3; a flotation concentrate containing, on average, 35% WO3 and a copper concentrate averaging 28% Cu.				
Vostok-2	Primorsky Mining and Concentrating Combine	East Russia	The Vostok 2 deposit was discovered in 1961 and has been mined since 1969 by the Primorsky Mining and Concentrating Combine first in open pit, and subsequently by means of underground mining operations (until now).	Skarn deposits		High grade sulfide–scheelite ore with substantial Base metal and gold mineralization	initial tungsten reserves 180 kt WO3, grade 1.7% WO3
Nui Phao mine[20]	Masan Resources	the Dai Tu District of the Thai Nguyen Province, Vietnam	the largest tungsten mine outside of China. Since Masan acquired the mine in 2010, it has seen consistent growth. With open-pit mining and low strip ratio, is be one of the lowest-cost producers of tungsten in the world.		open-pit mining	unique tungsten-polymetallic mine, Tungsten, Fluorspar, Bismuth and Copper	reserve of 66million tonnes of ore with average WO$_3$ grade of 0.21%[20].

MINING TECHNOLOGY

There are numerous tungsten minerals, but only scheelite ($CaWO_4$) and wolframite ($(Fe,Mn)WO_4$) are mined commercially [3][27]. Wolframite accounts for about 70% of the total tungsten resources and scheelite accounts for about 30%. Wolframite mainly occurs in quartz veins and pegmatites associated with granitic intrusive rock. Scheelite occurs in contact metamorphic skarns, in high-temperature hydrothermal veins and greisens, and less commonly in granite pegmatites.

Scheelite and/or wolframite are frequently located in narrow veins which are slightly inclined and often widen with the depth. So underground mining is more commonly used. The selection of a suitable mining method open pit or underground mining depends on numerous governing factors, including ground conditions (physical properties of the ore and the encasing rock mass - e.g. massive or broken); size of the deposit and proposed annual production; ore value (high grade versus low-grade deposits - this governs the money that can be spent to extract the ore); and economic, environmental, legal and regulatory considerations [3].

Open pit mining

Most active tungsten mines are of moderate scale (WO_3 production of a few 100,000t of ore per year), and thus the few operations that use open pit mining techniques are of a much smaller scale than for example copper or iron ore mines [3].

Currently, open pitting is used for example at Los Santos (skarn, Spain), at Kara (skarn, tungsten is by-product, Australia), for part of the production at Cantung (skarn, Canada) and in various Chinese operations. Most of the currently promoted tungsten mining projects would also be using open pitting. Some proposed tungsten mining projects call for mining rates of some 20,000t per day of low-grade ore and would be using large-scale loading and hauling equipment[3].

Underground mining

Underground mining methods commonly used include[3]:

Best suited for steeply dipping veins or narrow well-delineated skarn orebodies
- Narrow-vein open stoping, e.g. Chollja mine, Bolivia
- Shrinkage Stoping, e.g. Pasta Bueno mine, Peru
- Cut & fill with resuing fill
- Cut & fill, e.g. historic Springer, USA

Best suited for flatly dipping veins or flat tabular skarn orebodies
- Room & pillar mining, e.g. Panasqueira, Portugal
- Best suited for thicker tabular or lense-shaped orebodies with medium to steep dip (or very thick flat orebodies)
- Cut & fill
- Post pillar mining, e.g. historic Dolphin, Australia
- Sublevel stoping with delayed fill, e.g. Mittersill, Austria

- Sublevel stoping with cemented fill and secondary pillar recovery, e.g. Cantung, Canada
- Vertical Crater Retreat
- Sublevel caving, e.g. Mittersill, Austria

There are two fundamentally different techniques in underground mining:

- **-** "conventional" / track-bound (electric drives for haulage, pneumatic (compressed air) for semi-stationary tasks): pneumatic drills (often hand-held), pneumatic over-head loaders, haulage with locos and mine carts.
- **-** Rubber-tyre equipment (diesel-powered plus electric for semi-stationary tasks): drill jumbos, diesel-driven scooptrams (LHD – load/haul/dump), underground trucks.

Mining at Barruecopardo mine [11] was operational until the 1980s, when mining activities ceased due to unsafe and uneconomic conditions. These mining activities were carried out in southern part of the mine in open pits that are 800m x 100m in size. The steeply dipping structure of the mine facilitates easy extraction of ore. Ormonde plans to use largely mechanised mining techniques including drilling and blasting, and shovel and truck operations. Open pit mining will be carried out during the first five years. After five years, underground mining using conventional mechanised bulk and open stoping mining methods will be carried out. The open pits drilled for the current mining operations will be an extension of those drilled previously.

The Los Santos deposit has been divided into a number of zones, six of which form the basis of the current project. From west to east these are known as Las Cortinas, Sector Central, Capa East and Los Santos Sur. The strike length varies for each zone and zone dips are fairly uniform across the deposit varying between 60o to 90o. Within each zone, the skarn mineralisation is located within a number of individual beds, separated by barren lithologies. The major skarn beds vary between 2m and 20m in width; there are, however, numerous thinner bands measuring tens of centimetres.

The open pit operations at Los Santos mine in Spain [22] are conventional drill and blast operations, using mining contractors MOVITEX (Movimientos de Tierra y Excavaciones Nieto S.L.U.) for initial drillin blasting, loading and transport, and Perforaciones Noroeste S.A. --- All other drilling.

Mining operations are based on mining 10m benches in waste, and 5m benches in ore, with 0.5m of sub-drilling. Tamrock CHA1100 rigs are used for blasthole drilling. The blastholes are 3.5 in. in diameter, and drilled on a 3m x 2.5m pattern in Los Santos Sur, and a 3m x 2.5m pattern in the other pits. Pre-split lines are drilled along the edges of final walls. These pre-split holes are 3 in. in diameter, and are 0.8m apart. When water is present, water-resistant emulsion explosives (Riogel) are used. Mucking operations are completed using Hitachi 210W and Komatsu PC1250 excavators, loading Komatsu HD465 55 tonnes loaders. Short-term grade control starts with sampling of blasthole drilling cuttings. These average grades of these each blasthole are used to delineate ore and waste boundaries, as well as ore grade categories, at the time of mining [22]. The night following every blasting containing ore, a team of geologists checks with ultra-violet (UV) lighting the real position of the ore after blasting displacement, in order to reduce dilution to the minimum. They also pass the UV

lamp by the waste dumps and stockpiles, to check for any kind of error on ore/waste selection. These practices were introduced during 2012, and have demonstrated improvements. During all ore mucking operations, a grade control geologist is always present, to check and check for any other variations that can be seen in the pit with the blasted skarn material.

MINERAL PROCESSING

BENEFICIATION OF TUNGSTEN ORES

The beneficiation process generally consists of a pre-concentration step after crushing and grinding of the run-of-mine ore, followed by processing the pre-concentrate, concentrate cleaning or up-gradation step, and a final purification stage to meet the market specifications [24]. Only scheelite is readily amenable to flotation. Wolframite, in contrast to scheelite, is paramagnetic. Thus beneficiation techniques focus on gravity concentration and flotation for scheelite ore, and gravity and/or magnetic separation for wolframite. In addition, pre-concentration methods are usually used to discard a portion of the run-of-mine ore and increase the head grade prior to traditional beneficiation methods [3]. The beneficiation methods for scheelite ore and wolframite ore are listed in Table 1-3.

Table 1-3 Beneficiation methods for scheelite ore and wolframite ore

Beneficiation methods	Scheelite ore	Wolframite ore
Comminution (crushing and grinding)	Due to the brittle character of both scheelite and wolframite, comminution is carefully designed to avoid overgrinding, that is, at every stage of comminution, appropriate sizing techniques (screening, hydro-classifications by using hydrocyclones or classifiers), are used to minimise formation of fines, and rod milling is more commonly used than ball milling.	
Pre-concentration	**X-ray sorting**: the most advanced approach, looking "inside" the individual rock fragments. **Gravitational methods**: sluicing and Dense-media separation	**Hand-picking**: large grade contrasts or good visual distinction, e.g. in several tungsten deposits in China; **Optical sorting**: a strong brightness contrast exists between higher-grade portions of the overall run-of-mine ore (wolframite-quartz), e.g. at historic Mt Carbine operation in 1970s and 80s, and Dajishan mine in China. **X-ray sorting** **Gravitational methods**
Gravity concentration	The high density of both scheelite and wolframite facilitates their separation from the gangue materials by gravity techniques. Examples of gravity techniques that can be used are described below: **Jigging**: repeated jigging action leads to a separation of the higher and lower-density particles on the jig bed, suitable for coarse particles. There	

	is a large variety of different jig types, from the basic Pan-African jig with bicycle drive to highly sophisticated circular jigs such as the Knelson, Kelsey and Falcon concentrators. **Spiralling**: a very economic method, by the combined effect of centrifugal force and differential settling rates, suitable for fine particles separation. **Shaking tabling:** most efficient means of density separation, and they are commonly used to produce final concentrates from pre-concentrates obtained by jigging and spiraling concentrations; Various types and brands have been developed, such as Wilfley, Deister and Holman tables, and special flotation tables, usually used to remove sulphides from density concentrates.	
Flotation	**Two flowsheets:** Whole ore flotation after preconcentration (such as by x-ray sorting) Gravity concentration -flotation Gravity concentration is to remove the low-density fraction (e.g. calcite or fluorite) before flotation of scheelite. **Reagents:** using fatty acids as the collector, in the case of the Petrov process, flotation with fatty acids is undertaken at elevated temperatures which increase selectivity; in China, higher temperatures are only used in the cleaner flotation, together with using depressants including sodium silicate for effective depression of Ca-bearing minerals other than scheelite. The high-grade concentrate from skarn ores is obtained.	Wolframite flotation is performed similarly to the scheelite flotation, but is not pH sensitive and can therefore be undertaken in both acidic and alkaline solutions. However, flotation is rarely applied to wolframite since it occurs mainly in much coarser mineralization with then a preference to gravity and magnetic methods [23].
Magnetic separation	No application cases	**Low-intensity magnetic separation (LIMS):** used to remove magnetite and other ferromagnetic materials, "magnetising roast" might also be used for transforming hematite into magnetite prior to LIMS, and **High intensity magnetic separation (HIMS)**: used to separate wolframite from diamagnetic minerals such as cassiterite.

Several processes are implemented in order to produce a concentrate with 65-75% WO_3 fulfilling the requirements of international trading from a deposit containing generally some tenths of a percent of WO_3 [23]. The beneficiation flowsheet largely depends on the nature of the mineralization in the ore body and on the liberation size of the tungsten minerals. In particular, the liberation can be found in a wide range of size from several mm to 10-20 µm. Weathering and other alteration processes lead to secondary tungsten minerals such as hydrotungstite ($H_2WO_4 \cdot H_2O$), anthoinite ($AlWO_3(OH)_3$) and cerotungstite ($CeW_2O_6(OH)_3$). Presence of these minerals might lead to lower process recovery and/or lower concentrate grade and thus, could have an important negative economic impact [27].

Scheelite flotation is performed in alkaline medium, with sodium carbonate or sodium hydroxide to adjust the pH to about 9 - 10.5. Collectors commonly used are sodium oleate, tall oil or oxidized paraffin soap [26]. Scheelite ore has good floatability but it is often associated with other Ca-bearing minerals in the gangue (such as calcite, fluorite and apatite) which make the flotation difficult due to similar surface properties of calcium minerals and high reactivity with their conventional reagents [25]. In order to improve the selectivity of flotation of scheelite and calcic gangue minerals, metal salts such as ferrous sulfate are used in combination to sodium silicate in order to improve the effect of scheelite flotation [26].

Electrodynamic or electrostatic separators are used only for scheelite-cassiterite mixtures[23]. Scheelite is non-conducting whereas cassiterite is a conducting material. Acid leaching can be performed to removed apatite (P, Ca) and calcite (Ca). For example, the process implemented at the Salau mine (France, closed in 1986) used HNO_3- to remove the apatite and carbonates contained in the scheelite after flotation.

Tungsten beneficiation plants normally operate with a recovery of 60-85%. The beneficiation recovery rate for the Mittersill tungsten mine in Austria has been estimated at 75–85%, whereas that of the Los Santos project in Spain has been reported at 57–65% and that of the Cantung mine in Canada is around 75–79% [29].

Most of the losses of tungsten occur in slimes, which are difficult to treat with conventional beneficiation techniques. Generation of tungsten mineral slimes occurs due to [24]:

- The brittleness of the tungsten minerals, leading to their preferential grinding during the comminution steps.
- The high density of the tungsten minerals, they tend then to go into over-size fraction during classification by cyclones or hydraulic type of classifiers used in the grinding circuit, and get recycled to the grinding mill, leading to their over-grinding.

Impact of the specifications of the concentrate on the beneficiation process

As described before, tungsten ore can contain a wide range of minerals associated with scheelite and/or wolframite. Some of the elements contained in these associated minerals have an influence on the beneficiation flowsheet, in order to reach the international

specification for the use of the produced WO₃ concentrate. These specifications are presented in the Table 1-4.

Two examples of the modifications needed to reach these composition requirements are the following [27]:

- As: in unoxidised status, As (in the form of arsenopyrite) can be removed by sulphide flotation. In the case of weathered or oxidised ore, for example near the surface, oxide arsenic mineral might pose a far bigger challenge.
- Mo: if Mo is in the form of molybdenite then it can be removed through a flotation stage. However, if Mo occurs as powellite, separation during beneficiation is very difficult.

Table 1-4 International specifications for the chemical composition (in %) of scheelite and wolframite concentrates (from BGR, 2010)

	Wolframite			Scheelite		
	General	Grade I	Grade II	General	Grade I	Grade II
WO3	65.00-70.00	>=65	60-64.99	60.00-70.00	>=70	65-69.99[1)]
Sn	1.00-1.50	0.20-1.00	<=2.5	<=0.1		
As	0.10-0.25	<=0.20	<=0.40	<=0.10	<=0.3	
Cu	<=0.10	0.08-0.40	<=1.0	<=0.10	-	
Mo	0.04-0.40	<=0.40	<=1.0	0.05-0.40	<=2.0	<=4.0
P	0.05-0.10	0.03-0.08	<=0.25	0.05-0.10	<=0.1	
S	0.10-0.50	0.20-0.75	<=2.0	<=0.5		
Bi	<=1.00			0.05-1.00		
Sb	<=0.50	-		<=0.05	<=0.2	
Mn	0.00			<=1.00		

[1)]Lower grade scheelite ores are usually converted into artificial scheelite direct at the mine or later into ammonium paratungstate, an important intermediate product of the synthesis of tungsten.

CASE STUDIES

Two types of wolframite deposits are being worked at Degana, Rajasthan, India. One of them is quartz lode where wolframite is mineralised in quartz veins. The other type is finely disseminated tungsten mineralised in granite body itself. Pre-concentrate was studied with the sample of quartz lode at -12 mm. In upgrading lean tungsten ore, gravity concentration by jigging of vein quartz produced a pre-concentrate containing 4.5% WO3. For further upgrading the pre-concentrate, beneficiation studies were conducted with an objective of obtaining a product of 65% WO3 with less than 1% impurities of SiO2 and S each. Desired product could be obtained by pre-concentration of the jig pre-concentrate by tabling followed by flotation.

In Panasqueira, the ore treatment process begins with heavy media separation for the coarse fractions of material. In a second phase, cyclones are used to produce ore concentrates with high metal content, and tables are used to treat the sands. Froth flotation of the Panasqueira wolframite has been investigated over a number of years. Many different collectors have been tested on both the current slimes tailings and on the historical dam deposits (slimes -25 µm), however the results have always proved to be inconsistent. In the paper [7], some collectors were investigated:

Procol CA 540 (Na phosphonate), Briphos S2D (phosphate ester) + kerosene, Briphos S3D (phosphate ester) + kerosene, Flotinor SM-15 (Mixture of Phosphoric acid and esters), Briquest 2N81 25S (methylene phosphonate) and Briquest 281 25S (methylene phosphonate). The experimental flowsheet: desliming, bulk sulphide rougher flotation, wolframite flotation with rougher and one cleaner stage. Flotation was carried out at pH 2.5. The feed grade was approximately 0.3 % WO3. Only two of the above collectors showed any potential with the tailings material, and this potential was itself limited to the current tailings. Much lower WO3 grades and recoveries were obtained from the dam deposited material than for the fresh tailings, under the same reagent conditions.

Processing of tungsten ores in general [9]: gravity separation, where lighter gangue is discarded; magnetic separation, in which iron and iron bearing minerals are removed; flotation, in which the sulphide minerals are removed; and, finally electrostatic separation, in which less conducting minerals are removed to yield a richer concentrate of tungsten mineral.

Ore processing at Barruecopardo mine [11] the project does not require a primary grinding circuit because of its coarse mineralisation. Tailings dam is also not required, resulting in low capital and operational costs. A gravity processing plant designed by Jacobs Engineering Group will be built to process the ore. The design of the processing circuit is similar to that used during the mining operations in the 1980s. Test work carried out at the mine indicated that the processing plant can achieve tungsten recovery of nearly 78%. The processing will begin with a four stage 1.1mtpa crushing circuit which will crush the feed to a size of less than 5mm. The crushed ore will be screened before sending for gravity pre-concentration, in which heavy tungsten minerals will be recovered by jigs and spirals. The next step includes a clean-up and tabling circuit which will remove any sulphides present in the concentrate.

At Cantung mine in Canada [15] although the mill was designed to process 1,000 dry short tons per day, it has achieved continuous processing rates of up to 1,300 tons per day. The Life of Mine Plan (LOMP) details an average processing tonnage of 1,160 tons per day at a recovery rate of 79.5% of WO3. Final products will be approximately 377 tons per month of gravity concentrate (G1), containing 60% to 70 % WO3 at 58.3% recovery and approximately 185 tons per month of flotation concentrate containing 45% to 50% WO3 at 21.2% recovery. These target numbers appear to be obtainable based on projected ore metallurgical characteristics and past performance attained by the operation. Ore is handled from the stockpile by a loader or directly dumped from haulage truck into a 30 ton receiving bin equipped with 42 in x 10 ft apron feeder, which, in turn, feeds a 42 in x 48 in jaw crusher. The jaw crusher is set to produce a nominal five inch crushed product. A conveyor transports crushed ore into a 1,000 ton capacity coarse ore bin. This bin acts as a surge bin for the secondary crushing circuit;

The flowsheet of ore dressing includes primary, secondary & tertiary crushing, grinding, classification and talc flotation, sulphide flotation, gravity and scheelite flotation.

The process plant in Los Santos mine is primarily based on gravimetric separation, aimed at recovering a high grade scheelite concentrate [22]. An average feed grade was 0.32% WO3 and the average plant recovery was 60%. The primary crushing circuit employs a jaw crusher, with a nominal 100tph capacity, followed by two cone crushers, generating a minus 12 mm size material in a conical open stockpile ahead of the main process plant. A conveyor feeds this material at 65 tph rate into a rod mill which produces a ground product. This ground ore is then wet-screened at 1000 µm, with the oversize being reground in a regrind ball mill and

the minus 1000 μm undersize product being the raw feed to the gravity circuits. Two banks of hydrocyclones then split the gravity circuit feed material into 1000/150 μm and 150/30 μm size fractions. Both size fractions go through low intensity magnetic separation to remove mill steel and pyrrhotite ahead of gravity separation. The non-magnetics streams from the two size fractions then go to their respective banks of rougher spirals. Middlings are recycled via middlings-cleaners spirals, and the rough spiral tails exit as waste. In both circuits, rougher concentrates are cleaned in a bank of cleaner spirals before going forward to shaking tables. Concentrates from the coarse and fines spirals are fed to a hydrosizer which feeds four separate tabling circuits. Tailings from the cleaner step of all tabling circuits are recycled back to the hydrosizer, The coarse tailings are dewatered by thickening cyclones and a high frequency screen. Fine tailings are dewatered in a thickener and filter press. In both cases, the final tailings product is dry enough to be trucked and disposed of on the mine waste dump. The thickener overflow is recycled as process water and the plant operates with a zero discharge. The combined gravity concentrates are batch-processed through two 3m^3 flotation cells to float off sulphides. The non-floating material, principally scheelite, is discharged into a dewatering cone, and then goes through a rotary kiln dryer, followed by three-stage high intensity magnetic separation, to remove any remaining mill steel and pyrrhotite and any paramagnetics (mainly pyroxene). A final high grade scheelite concentrate constitutes the final saleable product, and typically has a grade of approximately 65% WO_3.

EXTRACTIVE METALLURGY

HYDRO-METALLURGY

The hydrometallurgical recovery of tungsten from various sources (e.g. minerals, tailings, scrap) follows several process steps. After digestion and purification of the raw material, the concentrated leachates enter the solvent extraction cycle. Here, the state-of-the-art processes are pointed out in order to produce high-purity ammonium paratungstate (APT), which is the most important intermediate for pure tungsten production.

Digestion

Tungsten is economically extractable from the two minerals wolframite ((Fe, Mn)WO_4) and scheelite (CaWO$_4$) and from tungsten containing scrap (e.g. catalysts). There are three hydrometallurgical routes for processing the tungsten bearing raw materials:

Alkali leaching

$$(Fe, Mn)WO_4 + 2\ NaOH \rightarrow Na_2WO_4 + (Fe, Mn)(OH)_2$$
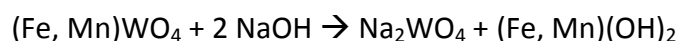
The wolframite or oxidized soft scrap is dissolved in concentrated NaOH (40 – 50 %) at 100 – 150 °C or by high-pressure digestion with dilute NaOH. Fe and Mn build low soluble hydroxides.

Pressure leaching with soda

$$(Fe, Mn)WO_4 + Na_2CO_3 \rightarrow Na_2WO_4 + (Fe, Mn)CO_3$$
$$CaWO_4 + Na_2CO_3 \rightarrow Na_2WO_4 + CaCO_3$$
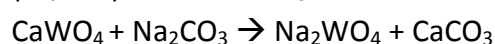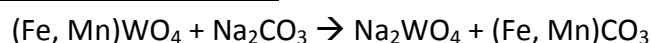
The wolframite or scheelite is leached with Na_2CO_3 (10 – 18 %) under pressure (10 – 25 bar) in steel autoclaves at 200 °C. A large excess of reagent is necessary.

<u>Acid leaching</u>

$$CaWO_4 + 2\ HCl \rightarrow CaCl_2 + H_2WO_4$$
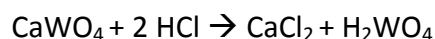
The scheelite is leached with concentrated HCl, but other acids are also possible. The precipitated tungstic acid is filtrated from the aqueous $CaCl_2$ solution and treated with ammonia and water to produce APT.

Purification

The obtained sodium tungstate solutions from alkali and soda leaching need to be purified by filtration and precipitation, because they may contain several dissolved impurity elements. If the concentration of those impurities is too high, the subsequent processing is disturbed.

Silicates are common impurities, which can be precipitated by aluminium sulfate or magnesium sulfate solution (or a mixture) at pH 8 – 11. Phosphates and fluorides are co-precipitated.

Molybdenum as a common accompanying element in tungsten bearing material is precipitated by sodium sulfide in neutral or slightly alkaline environment forming thiomolybdate. By adding sulfuric acid to pH 2.5 – 3 the molybdenum is precipitated as trisulfide. This precipitation step is also selective for other insoluble sulfides as As, Sb, Bi, Pb, and Co.

The sodium ion concentration must be reduced from 70 g/l to < 10 mg/l as otherwise problems occur with the reduction to metal powder. This purification step is accompanied by a concentration step of tungsten, which is either done by solvent extraction or ion exchange resins.

Solvent extraction

The purified acidic sodium tungstate solution (pH 2 – 3) is contacted with the organic phase. Tertiary or secondary aliphatic amines (e.g. trioctylamine, tricaprylamine) are the most important extractants, unless in literature, various other extractants have been tested. The extractants are dissolved in kerosene or other aliphatic solvents. Phase modifiers like isodecanol can be added. The anionic exchange mechanism writes as follows:

$$\left[W_xO_yH_z\right]^{n-} + \overline{nX\,HY} \rightleftarrows \overline{(X\,H)_nW_xO_yH_z} + nY^-$$
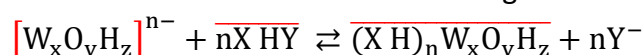
Here X represents the extractant (amine) and Y the anionic leaving group, where the overbars indicate the organic species. The tungsten ionic species is pH-dependent. The predominant aqueous species are $\left[W_6O_{21}H_3\right]^{3-}$, $\left[W_{12}O_{42}H_6\right]^{6-}$ and $\left[W_{12}O_{40}H_2\right]^{6-}$ at pH 2, $\left[WO_4\right]^{2-}$ at pH 7 and $\left[WO_6H_2\right]^{4-}$ at pH 12. The distribution coefficient at pH 2 is between 30 – 50. Therefore a two-stage countercurrent extraction is sufficient for an extraction of 99.9 %.

The extract is washed with deionized water and reextracted by a dilute ammonia solution into the aqueous phase:

$$\overline{(X\,H)_n W_x O_y H_z} + nOH^- \rightleftarrows \left[W_x O_y H_z\right]^{n-} + \overline{n(XH)(OH)}$$
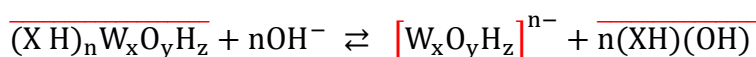
The solvent is regenerated and recycled.

Ion exchange

Here the sodium tungstate solution is contacted with a strongly alkaline ion exchange resin in the chloride from, where the tungstate is adsorbed. Desorption is carried out with ammonium chloride solution. Elements that form heteropolytungstates like Si, P, As and Mo can additionally be removed.

Crystallization

The isopolytungstate solution is evaporated and water and ammonia is distilled, which is recycled to the solvent extraction step. The solubility becomes lower and APT crystallizes in recirculating batch crystallizers. Additionally, this is a further purification step, where soluble impurities remain in the mother liquid.

PYRO-METALLURGY

As shown in Figure 1-2[38], tungsten concentrates (wolframite or scheelite), obtained after mineral processing of tungsten ore, can be directly used to produce ferrotungsten, steel and tungsten chemicals, or indirectly used to produce tungsten metal powder and tungsten carbide.
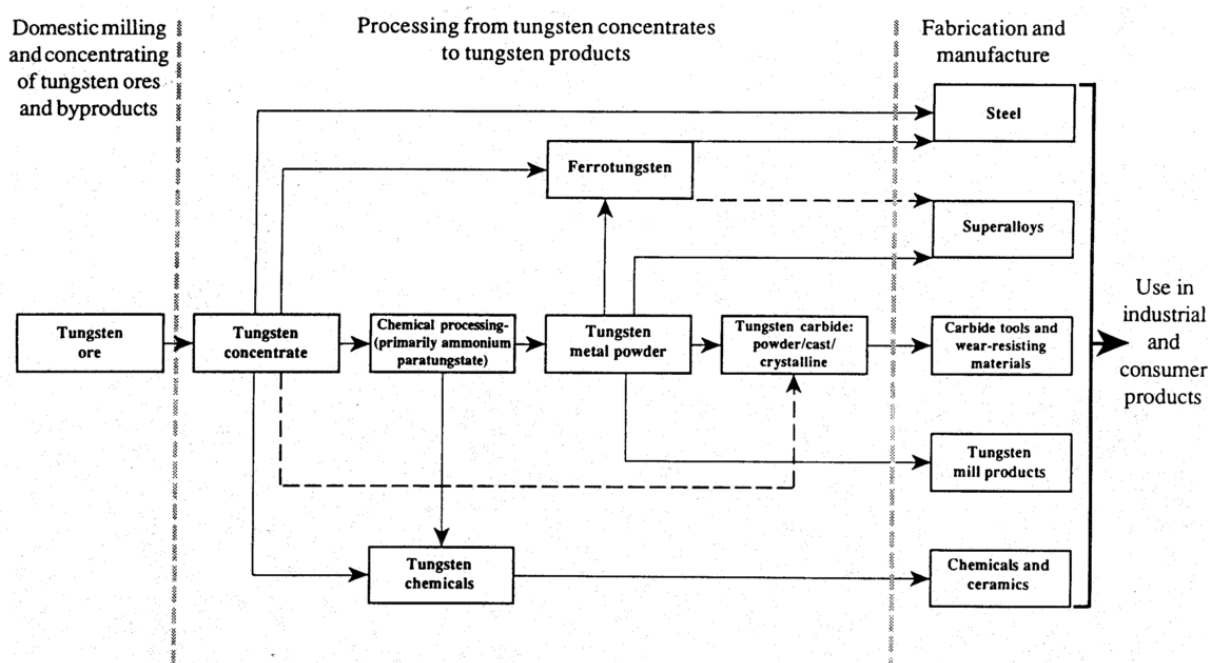

Figure 1-2 General tungsten flow diagram from primary resources

Using tungsten concentrate to produce ferrotungsten

Ferrotungsten, contains ~ 75-85% W, is a master alloy for the production of tungsten-containing steels[39]. Ferrotungsten is normally produced in the electric arc furnace by either carbo-thermic reduction, carbo-/silico-thermic reduction or alumino-thermic reduction of tungsten concentrates, among which the carbo-thermic reduction and carbo-/silico-thermic reduction are preferred processes due to the cost reasons and the high tolerance level for impurities, such as As and Sn, in the raw materials[39][40].

Carbothermic reduction process. The carbo-thermic reduction process of tungsten concentrates can be well illustrated by Figure 1-3[39]. It is seen that this process is operated in two stages: the refining stage and the reduction stage. In the refining stage an ingot of high-grade ferrotungsten (80% W) and a WO_3-rich slag (25% W) are produced. The ferrotungsten ingot is removed from the furnace and cleaned after the electric arc furnace is switched off, as tapping of the melt is not possible due to a high melting temperature of the ferrotungsten. In the reduction stage the WO_3-rich slag is processed to ferrotungsten of 50% W and a slag with less than 1% WO_3. The 50% W together with the outer parts of the cleaned, high-grade ingot are recycled and be processed to high-grade ferrotungsten in the refining stage. If several furnaces are used in parallel, the production can then take place as a quasi-continuous process.
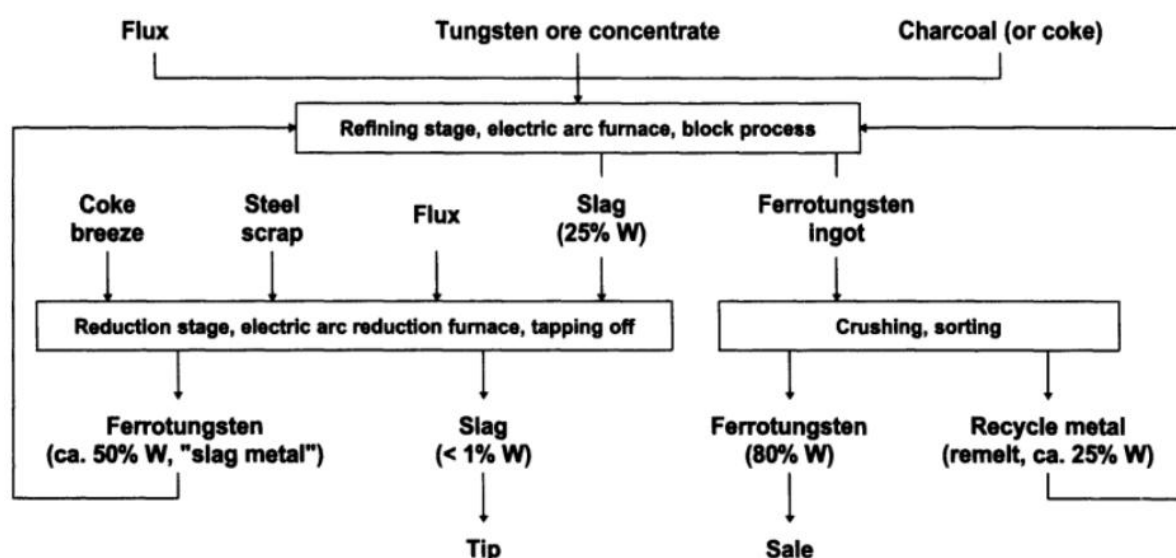

Figure 1-3 Scheme of ferrotungsten production by carbothermic reduction process

Carbo- and silico-thermic reduction process. This process is carried out in three successive stages in the electric arc furnace. In the first stage tungsten concentrates are reduced by carbon under WO_3 rich slag (10-16% W) and the resulting ferrotungsten (75% W) is scooped out. In the second stage iron scrap is added into the furnace and the WO_3-rich slag from the first stage is reduced by silicon (in the form of ferrosilicon with 75% Si), which will result in a metal phase with 50-70% W and a slag phase with < 1% WO_3 being tapped off. In the third stage the metal phase in the second stage is refined by adding tungsten concentrates, resulting in a WO_3-rich slag (18-25% W) and the W in the metal phase being increased.

Carbo-/silico-thermic reduction process is a continuous operation process, which therefore saves electric energy and prolongs the service time of the lining. However, it necessitates the laborious scooping operation; moreover, ferrotungsten tends to accumulate on the furnace wall, and this can only be removed until next furnace relining.

Alumino-thermic reduction process. In this process aluminum is used instead of carbon and/or silicon to reduce the tungsten concentrates, which are mainly scheelite. Due to the chemical properties of aluminum the reduction proceeds rather rapidly and the impurities, such as As and Sn, can also be reduced. Therefore, the tungsten concentrates with fewer impurities are required for this process. The resulting product is low carbon ferrotungsten. Due to the economic reason, this process is mainly used to meet special customer needs.

Using tungsten concentrates to produce W-bearing steels

Besides using ferrotungsten for W-bearing steel production, tungsten concentrates (normally scheelite) can be directly, for example, charged into the EAF, to produce W-bearing steel.[38][41][42] In this process tungsten oxides in the concentrates is reduced to tungsten by carbonaceous materials in the furnace and the steel is alloyed with tungsten.

Using tungsten concentrates to produce ammonium paratungstate (APT) and its downstream products (mainly tungsten metal powder and tungsten carbide)

APT production. Besides a part of tungsten concentrates are used to produce ferroalloys and steels, tungsten concentrates (~ 90% in amount[43]) are largely used to produce APT, a most common intermediate product used for tungsten metal powder and tungsten carbide production. APT is produced by the modern hydrometallurgical process,[42][44][45] which can be well described by Figure 1-4. In this process tungsten concentrates after roasting or calcination are digested by either soda or concentrated NaOH solution, which will result in the formation of sodium tungstate solution. The sodium tungstate solution is purified by precipitation and filtration, and thereafter it is converted into an ammonium tungstate solution, exclusively by solvent extraction or ion exchange resins. Finally, high purity APT is obtained by crystallization, with the formula $(NH_4)_{10}(H_2W_{12}O_{42}) \cdot 4H_2O$.
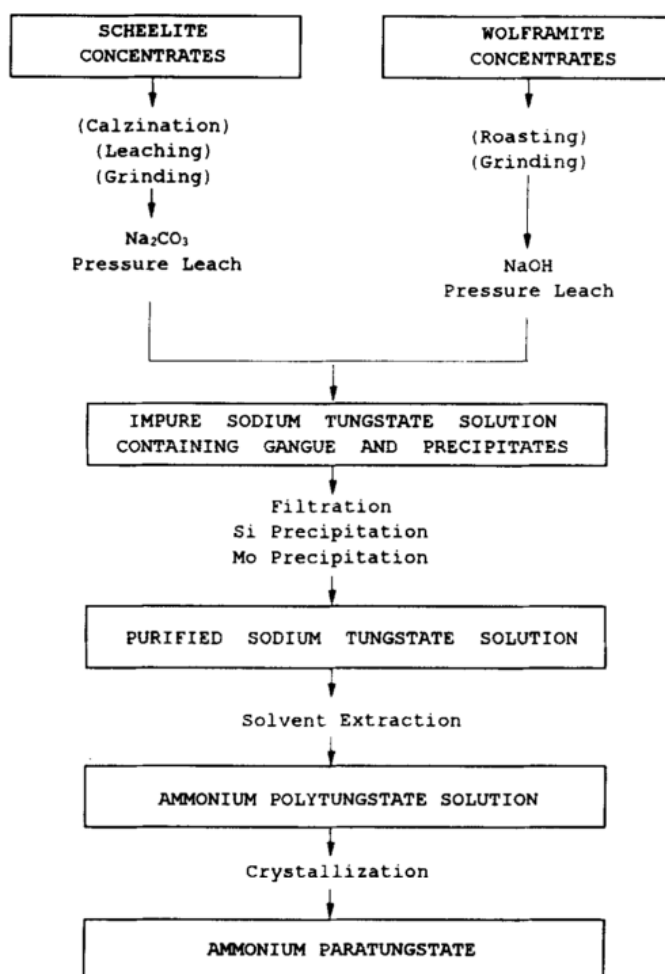
Figure 1-4 Scheme of APT and WO₃ production by modern hydro-metallurgical process

Tungsten powder production. Although it is possible to produce tungsten metal powder by direct hydrogen reduction of APT, metal powder is more commonly produced by the hydrogen reduction of tungsten oxide at 600-1000 ^{o}C, which is produced by the thermal decomposition of the APT, as shown in Figure 1-4. By changing reduction conditions this process offers the possibility to produce tungsten powder with various particle sizes (within the range of 0.1-100 μm)[45-47]. The other innovative tungsten powder production processes include solid carbon reduction process, gas phase precipitation process, plasma process, amalgam process, carbonyl process, electrochemical reduction process,[47-49] etc.

Tungsten carbide powder production. Conventionally, tungsten carbide is produced by two steps: the step of producing high purity tungsten powder with desired properties and the step of tungsten powder carbonization by high purity carbon black, soot or graphite. The carbonization step is implemented by (i) mixing the tungsten powder with carbon black, soot or graphite by ball milling and (ii) carbonizing tungsten powder at temperatures of 1400 - 1600°C in hydrogen atmosphere for 2-10 hours. By far a large percentage of WC is

manufactured by this direct carburization of tungsten powder process and it covers the widest range of powder qualities in regard to average particle size (0.15–12μm).[50][51] The other innovative tungsten powder production processes include direct carbothermic reduction of WO_3, scheelite or wolframite,[52]–[54] direct carbonization of WO_3 by CH_4-H_2 mixtures[55], direct carbothermic reduction of carbon coated WO_3[51], etc.

 An assessment of the extractive technologies for tungsten

Due to the extreme high melting temperature of tungsten, hydrometallurgical process will continue to the prevalent one for extracting tungsten from the tungsten ore concentrates. However, the new emerging technologies, such as electrochemical reduction of the tungsten ore,[48][49] should be appraised by considering both the economic aspect of the process and the properties of the tungsten powder that produced. For WC production, direct reduction of tungsten oxide or tungsten ore concentrate will be the trend for the future, since this will on one hand tailor the present cumbersome and costly two-step (tungsten powder production and carbonization) production process into a single one, and on the hand, this has the advantageous of producing WC powder with finer crystal structure of nanometer and with improved mechanical properties[56]. For the production of W-bearing steels, the direct use of tungsten ore should be appreciated, as the use of ferrotungsten can be avoided, which implies both fewer materials loss from the production chain and higher economy/energy efficiency.

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CHAPTER 2 TANTALUM

MINING

NIOBIUM-TANTALUM MINERAL DEPOSITS

Niobium and tantalum usually occur together in the same type of mineral deposits and in minerals of similar characteristics. Very often, these metals are found in solid solutions (Černý & Ercit, 1989; Atencio et al., 2010), as it is the case of columbite – tantalite (columbite series, also known as coltan), with the formula $(Fe, Mg, Mn)(Nb, Ta)_2O_6$, or the minerals from the pyrochlore group.

The mineral deposits sourcing niobium and tantalum are associated to some very specific types of igneous rocks. There are three main types of rocks that can contain profitable contents of these metals (BGS, 2011): Carbonatites and associated rocks, alkaline to peralkaline granites and syenites, and pegmatites. The weathering of these deposit types can result in other types of Nb – Ta mineral deposits, as laterites and alluvial deposits (placers). Carbonatite-associated deposits contain disseminated pyrochlore minerals, being the main source of niobium. These deposits rarely contain profitable concentrations of tantalum, neither as by-product. In some cases, due to magmatic crystallization process, pyrochlore minerals accumulate in preferential parts of the rock leading to enriched zones. The weathering of these deposits, specially in tropical regions, result in the formation of pyrochlore concentrated laterites, e.g. the Araxá deposit operated by CBMM (Companhia Brasileira de Metalurgia e Mineração), the major Nb-producing mine in the world.

Alkaline granite and syenites, can contain profitable concentrations of REE, tin and niobium and, in some cases tantalum that can be obtained as a by-product. Also in this case, ore minerals may be concentrated due to magmatic crystallization or hydrothermal processes. The main Nb and Ta minerals in these deposit types are those from the pyrochlore group or minerals from the columbite – tantalite series. Other minerals can occur, but they are less frequent. Also the weathering of these deposits in tropical regions favours the re-concentration of these metals in supergene deposits.

Deposits associated to pegmatites are more widespread in the world. In some cases they can accumulate in specific areas, as it occurs in central Africa, where a large zone with tantalum – bearing pegmatites occurs. Niobium and tantalum occur together with other metals, as lithium, caesium, beryllium or tin, among other metals. Although some of the deposits can be operated exclusively for niobium and tantalum. Main niobium and tantalum minerals in this type of deposits are columbite – tantalite series.

NIOBIUM-TANTALUM MINING IN THE WORLD

Niobium is almost completely produced by 3 mines in the world (Table 1), two of them in Brazil (Araxá and Catalão), accounting for the 90% of the total production, and one in Canada (Niobec). Although other countries can produce niobium, the world reserves of this metal are in these two countries.

Regarding tantalum, the largest reserves are located in Brazil and Australia. However, the combination between demand, lack of control on the production and commerce and the small-scale mining (and the association of both Nb and Ta to conflict minerals), lead to countries in the Great Lakes Region of Africa to dominate the tantalum production in the last years.

Despite the proliferation of small-scale mines in Africa, Nb and Ta are produced by a limited number of mines in the world (Table 2-1).

MINING TECHNOLOGY

Mining methods for tantalum and niobium are similar to other metals of similar occurrence. The main factors taken into account for the type of mining, open pit versus underground mine are the ore size and grade, the depth of the ore, the distribution of the ore minerals (disseminated into a large rock body or concentrated in zones or veins), and the geotechnical properties of the rocks. In some cases a combination of open pit and underground mining can coexist, open pit mining in the near-surface weathered zone of the deposit and underground mining of the deeper primary ore.

An special case of surface mining is that used in artisanal and small-scale mining (ASM), as in most cases these mines do not use heavy machinery for the extraction, as earthmovers, excavators or trucks; instead the main tools are picks, shovels and buckets. Comparison of mining methods in highly industrialized mines (left) and artisanal small-scale mines is shown in Figure 2-1.

Open pit mining

At present almost all mines in carbonatites and other steeply-dipping intrusive rock structures are mined in open pits. Moreover, most of the mines located in tropical regions mining starts in the most surficial weathered part of the deposit (Araxá mine, CBMM), and only in some cases mining operation can shift to the primary ore either by continuing surface mining or through underground facilities. The only underground mine in this type of deposits is Niobec mine. In the case of pegmatite-type deposits, most mines also operate through surface mining.

Underground mining

Underground mining is restricted to deep deposits, Tanco in Canada operated the mine fully through underground works and Greenbushes in Australia have some underground facilities

Figure 2-1 Comparison of mining methods in highly industrialized mines (left) and artisanal small-scale mines (right, picture taken by Philip Schütte, BGR, 2012, used with permission)

for the deepest part of the deposit, whereas the upper part of the deposit was mined from open pit.

Although there are no examples, deep-seated pegmatite deposits could be mined by underground facilities, this option should be evaluated depending on capital and operating costs and metal prices.

NIOBIUM-TANTALUM MINING IN EUROPE

At present there are no mines obtaining niobium or tantalum in Europe. There are some exploration projects (Table 2-2), but none of them passed from the exploration status. These projects are mainly associated to the carbonatites and syenites from Finland and Greenland and the pegmatite deposits from Spain and Portugal.

Another potential source of Ta and Nb could be associated to tin deposits, which are also under investigation in Europe.

Table 2-1 Operating Nb – Ta mines in the world

Deposit Name	Company	Country	Status	Type of Ore	Mining method	Commodity	Nb-Ta Mineralogy	Reserves Mt	% Nb$_2$O$_5$	% Ta$_2$O$_5$
Araxá	CBMM	Brazil	Operation	Weathered Carbonatite	Open pit	Nb	Pyrochlore	462	2,48	
Catalao - Boa Vista	Anglo American	Brazil	Operation	Weathered Carbonatite	Open pit	Nb	Pyrochlore	42	1,2	
Niobec mine	Magris Resources Inc.	Canada	Operation	Mineralized Carbonatite	Underground	Nb	Pyrochlore	630	0,42	
Aley	Tasako Mines Ltd. Corp.	Canada	EIA process	Mineralized Carbonatite	Open pit	Nb	Pyrochlore	84	0,5	
Greenbushes mine	Global Advanced Metals	Australia	Operation	Pegmatite	Open pit + Underground	Ta ± Nb, Sn	Wodginite, Ixiolite, Tantalite, Tapiolite, Microlite	68	0,023	0,026
Wodgina mine	Global Advanced Metals	Australia	Operation (discontinuous)	Pegmatite	Open pit	Ta ± Be, Sn	Tantalite ± Columbite, Wodginite	28		0,042

Deposit Name	Company	Country	Status	Type of Ore	Mining method	Commodity	Nb-Ta Mineralogy	Reserves Mt	% Nb$_2$O$_5$	% Ta$_2$O$_5$
Mibra / Volta Grande mine	Advanced Metallurgical Group	Brazil	Operation	Pegmatite	Open pit	Ta, Nb, Sn Li, Feldspar, Albite, Kaolin	Tantalite, Columbite	6	0,009	0,038
Mt Cattlin	Galaxy Resources Ltd.	Australia	Operation	Pegmatite	Open pit	Li, Ta	Tantalite	10		0,015
Tanco	Cabot Corporation	Canada	Operation	Pegmatite	Underground	Ta, Cs, Li	14 different Ta minerals	2		0,22
Toongi / Dubbo Zirconia	Alkane Resources Ltd.	Australia	Development	Trachyte	Open pit	Zr, Hf, Nb, Y, Ta, REE	Natroniobite	73	0,46	0,03
Pitinga Mine	Minsur / Mineração Taboca	Brazil	Operation	Weathered and Fresh albite-rich peralkaline granite	Open pit	Sn, Nb, Ta	Columbite	267	0,22	0,027
Kenticha mine	Elenilto Mining	Ethiopia	Operation	Pegmatite	Open pit	Ta, Nb	Tantalite, Columbite	116		0,02
Tabba Tabba	Pilabara Minerals Ltd.	Australia	Operation	Pegmatite	Open pit	Ta	Tantalite, Wodginite, Microlite	0.318		0.095

Deposit Name	Company	Country	Status	Type of Ore	Mining method	Commodity	Nb-Ta Mineralogy	Reserves Mt	% Nb$_2$O$_5$	% Ta$_2$O$_5$
Kanyika	Globe Metals & Mining Africa (Pty) Ltd.	Malawi	Bankable Feasibility	Mineralized Nepheline Syenite	Open pit	Nb, Ta, U, Zr	Pyrochlore	21	0,33	0,015
Abu Dabbab	Gippsland Ltd.	Egypt	Bankable Feasibility	Granite	Open pit	Ta, Sn, Feldspar	Tantalite	32		0,027
Several artisanal small-scale mines		Central Africa	Operation	Weathered Pegmatites	Open pit	Ta, Nb	Tantalite, Columbite			

Table 2-2 Nb and Ta Projects in Europe

Deposit Name	Company	Country	Type of ore	Status	Reserves
Penouta mine	Strategic Minerals Spain	Spain	Alkaline granite	Exploration	95.6 Mt @ 0.0094% Ta$_2$O$_5$, 0.0090% Nb$_2$O$_5$, 0.044% Sn
Alberta II	Strategic Minerals Spain	Spain	Pegmatites	Exploration	12.3 Mt @ 0.0121% Ta$_2$O$_5$, 0.044% Sn, 0.204% Li
Motzfeldt	Regency Mines	Greenland	Syenite	Exploration	340 Mt @ 0.19% Nb$_2$O$_5$, 0.012% Ta$_2$O$_5$, 0.46 ZrO$_2$
Sokli	Yara International ASA	Finland	Carbonatite	Exploration stopped	110 @ 0.1% Nb$_2$O$_5$, 16.5% P$_2$O$_5$

MINERAL PROCESSING

Despite discrepancies from source to source, about 50% of Ta production is from primary resources, 30% from scrap recycling and 20% from Sn slags. The contribution of scrap recycling and Sn slags is increasing continuously. With EU producing 1% of the world's Ta production at the most, Ta supply is an important and critical issue for the European industry.

Mineral processing produces a Ta-Nb concentrate that is eventually treated by extractive metallurgy, generally using acid dissolution followed by separation of Ta by solvent extraction.

Ta is known to occur in a variety of geological horizons. The variety of occurrences of Ta in nature explains that there is not a single processing method for beneficiation of Ta-bearing ores. The 5 principal types are listed hereafter:

- Deposits associated with granitic pegmatites. Mineralisation of Ta occurs as quartz veins associated with Sn and rare earth elements. Deposits associated with granitic pegmatites have been the largest Ta producers in the world. This explains why Ta-Nb concentrate is generally recovered as a byproduct of tin (Cassiterite SnO_2) mining (Davis).

- Deposits associated with granits. In general, Ta mineralisation associated with granitic intrusions have large volumes and low grade. Other metallic elements that are associated with Ta include Li, Nb or Sn.

- Deposits associated with carbonatite complexes. Carbonatite complexes often bear Nb, Ta and rare earths elements.

- Deposits associated with hyperalkaline intrusive complexes. These complexes are economically mined for extraction of rare earth elements, however they can also exhibit significant grades is Ta and Nb.

- Deposits associated with alluvial placers. These deposits have high Ta grades. The Ta ore can be easily concentrated using simple gravity separation techniques. These deposits are found in Central Africa (DRC, Rwanda, Burundi).

Notwithstanding the great variety of mineral textures, it can be read that mineral Tantalum minerals have been identified with over 70 different chemical compositions. Table 2-3 (Zhu and Cheng, 2011) gives the main economical ores for Ta production, of which the first 3 are of greatest economic importance.

Table 2-3 The main economical ores for Ta production

Mineral	Formula	Ta_2O_5 Content	Nb_2O_5 Content
Tantalite	$(Fe,Mn)(Ta,Nb)_2O_6$	40-80% Ta_2O_5	2-30% Nb_2O_5
Wodginite	$(Ta,Nb,Sn,Mn,Fe,Ti)_{16}O_{32}$	45-75% Ta_2O_5	1-15% Nb_2O_5
Microlite	$(Ca,Na)_2(Ta,Nb)_2(O,OH,F)_7$	50-79% Ta_2O_5	1-10% Nb_2O_5
Columbite	$(Fe,Mn)(Ta,Nb)_2O_6$	1-40% Ta_2O_5	30-75% Nb_2O_5
Stueverite	$(Fe,Mn)(Ta,Nb,Ti)_2O_6$	5-26% Ta_2O_5	7-17% Nb_2O_5
Euxenite	$(Y,Ca,Ce,U,Th)(Ta,Nb,Ti)_2O_6$	2-12% Ta_2O_5	22-30% Nb_2O_5
Samarskite	$(Fe,Ca,U,Y,Ce)_2(Ta,Nb)_2O_6$	15-30% Ta_2O_5	40-55% Nb_2O_5

The natural co-occurrence of Ta and Nb in Ta-bearing ores explains their co-production from primary resources. Tantalite is the primary mineral for industrial production of Ta; it is referred to as ferrotantalite and manganotantalite depending on the presence of Fe or Mn. It is worth noting however that Nb can be found without Ta in the mineral pyrochlore $(NaCaNb_2O_6F)$.

With modern processing techniques, it appears that 90% of the Ta present in the ore can be recovered (eg. Tanco mine in Manitoba, Canada).

Notwithstanding artisanal mining from placer deposits in Central Africa, where Ta is either hand-picked or concentrated using rudimentary gravity separation, industrial beneficiation of tantalite-bearing ores at the industrial scale relies upon the combination of:

- crushing (jaw, cone or impact crusher) to say < 15-20 mm
- grinding (ball or rod milling) and classification (screens and hydrocyclones) in closed circuit to <1 mm
- conventional (jig, shaking table), centrifugal (spiral) and enhanced gravity separation (MGS, Falcon concentrator), depending on the size of the liberated particles. The gravity separation takes advantage of the high density of the Ta-bearing phases, with specific density in the range 6 to 8 depending on the associated phases.
- selective reverse flotation to concentrate the finest material
- regular and high magnetic separation to remove companion magnetic phases.
- Thickening circuit to recycle the process water.

The combination and nature of the above-mentioned processes is more or less complex depending on the mineralization of the Ta-bearing ores (liberation grain size, textural associations and minerals present).

With coarse particles (e.g. ores with coarse mineralization and a liberation size of a few hundred micrometers), a sequence of spirals and shaking tables are used to produce Ta-Nb concentrates.

As the mineralization of tantalite gets finer, the grinding circuit, in particular the classification step becomes more critical in order to reduce the production of irrecoverable ultrafine Ta. Fine particle recovery is a major issue in most situations, leading to flotation and enhanced gravity separation.

The flotation process is generally conducted at controlled pH, thereby requiring pH regulators and appropriate collectors (eg. alkyl sulfonated succinate, PVPA). The high consumption of additives is a significant cost factor for the flotation processing of Ta-Nb fines, as well as a pollution issue.

Selective reverse flotation is used to concentrating Ta-fines that are liberated by milling, with a recovery of the order of 90%. As the flotation concentrate is highly diluted (4-7% solids), subsequent gravity separation for concentration of fine particles requires efficient gravity concentration.

For fines recovery, continuous enhanced gravity separators such as the continuous Falcon separator can be used due to their ability to scavenge the majority of the plant's conventional gravity equipment rejects (Deveau and Young, 2005). As an illustration, the following figure shows the evolution of the post-flotation process used by Cabbott Corp. at the now closed Tanco mine to improve the recovery of Ta fines from dilute flotation product stream.
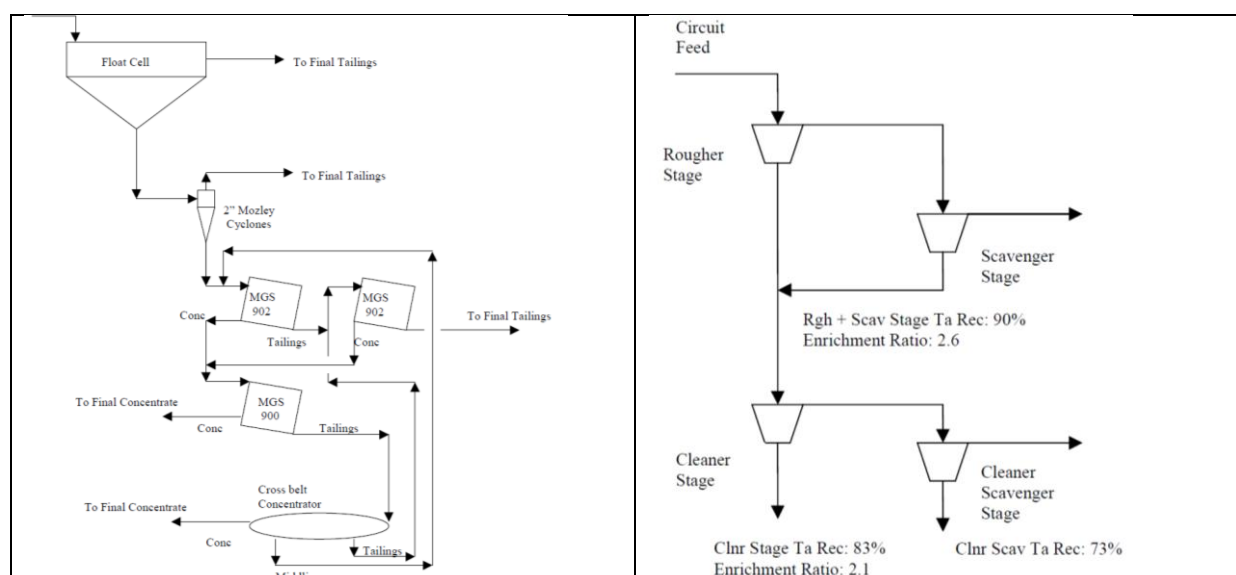

Figure 2-2 Example of gravity circuit process design for improved recovery of Ta-fines (Deveau and Young, 2005). The combination of 2" cyclones, MGS and cross-belt separators is replaced with enhanced gravity Falcon separators, allowing a higher recovery of Ta-fines.

Separation from strong magnetic minerals (as well as iron scraps in recycling) are disposed of using low-intensity magnetic separation during final up-grading of Ta and Nb minerals. Removal of quartz-calcite is achieved in this manner.

The ore is typically dried and divided into three size grades +200µm, +100µm, -100µm) and then processed through a dry high-intensity magnetic separator to remove the magnetic constituents and produce a high grade Ta-Nb concentrate.

The Ta-Nb concentrate is then processed by hydrometallurgy to separate out the metals.

EXTRACTIVE METALLURGY

HYDRO-METALLURGY

High purity tantalum is mainly applied in electronic industry for manufacturing capacitors, which represents 60 % of its consumption. Tantalum is always links in minerals with niobium and hydrometallurgy process is so often used for the separation and purification of tantalum from niobium and others impurities.

Leaching

The first step in the industrial hydrometallurgical process is the extraction of Nb and Ta from high grade Nb and Ta concentrates, after ore and/or pyrometallurgical processing. This extraction was carried out by acid digestion in a mixture of hydrofluoric acid HF with other mineral acids, generally sulfuric acid H_2SO_4. Sulfuric acid lowers the partial pressure of hydrofluoric acid, thereby reducing volatilisation losses and acid consumption. The mineral acid improves also the dissolution process, increasing the Ta and Nb leaching yields. Such mixture is indeed a rare medium, in which Ta and Nb are soluble in high concentrations (several tens g/L). The following reactions are involved:

$$Ta_2O_5, nH_2O_{(s)} + 14\,HF \rightleftarrows 2[TaF_7]^{2-} + 4H^+ + (5+n)H_2O$$
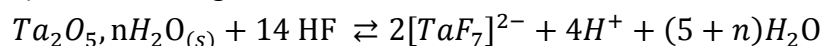
Fractional Crystallization

Until recently, the separation process based on fractional crystallization of double fluorides was used on an industrial scale for the separation of similar elements, such as hafnium from zirconium and niobium from tantalum. The process for separation of tantalum from niobium utilizes the differences in solubility of chemical species of one element as compared to that of another in an aqueous phase in a certain set of conditions. The separation should be carried preferably at an acid concentration of about 1 to 7% HF, where the solubility of niobium complex is nearly 10 to 12 times more than that of tantalum. Apart from acidity, many other factors, such as temperature and the presence of other ionic species, affect the solubility of the complex species.

The separation of niobium and tantalum by fractional crystallization is accomplished from their double fluoride complexes with potassium. Since the solubility of potassium fluotantalate (K_2TaF_7) is low, it crystallizes out. The crystalline solid is redissolved and recrystallized. The process is conducted in several stages. The process works quite satisfactorily and relatively easily as far as the preparation of pure tantalum complex K_2TaF_7 is concerned.

Silicon, if present, is in the form of K_2SiF_6. It crystallizes out along with tantalum and, therefore, remains as an impurity in the tantalum complex. Titanium is invariably present as $K_2TiF_6 \cdot H_2O$ It is partitioned equally between the crystalline and the aqueous phases. The addition of hydrochloric acid to the aqueous phase favors the retention of titanium in

solution, thus reducing its transfer to the crystalline phase. The presence of HCl also improves tantalum recovery, because it facilitates the dissolution of tantalum oxyfluoride, if formed during the process.

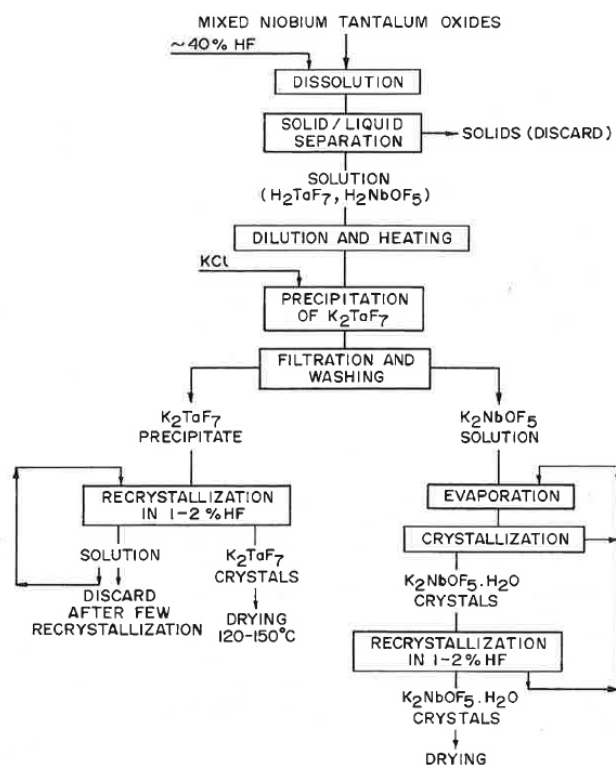The process as applied to the separation of tantalum from niobium is illustrated below.
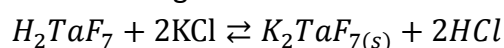

Figure 2-3 Separation of niobium and tantalum by fractional crystallization (Gupta, 1994)

Mixed niobium tantalum oxides are dissolved in concentrated hydrofluoric acid (35 to 40% HF) using a slight excess of acid over the stoichiometric requirement for the formation of fluoroniobic and fluorotantalic acids. The dissolution is carried out in rubber-lined or lead-lined vessels at a temperature of 70 to 80°C. After dissolution, solids are separated out and KCl is added to the solution to form potassium salts. The concentration is adjusted so that the K_2NbOF_5 content of the liquor is about 3 to 4%, which is below the solubility limit, and free HF is less than 1%. The tantalum salt separates out as insoluble needle-shaped crystals which are separated by filtration after cooling. Silicon in the form of K_2SiF_6, nearly half of the titanium and about one sixteenth to one twentieth of the niobium also precipitate. Additional purification is accomplished by recrystallization of K_2TaF_7 from 1 to 2% HF. The mother liquor containg niobium and some other impurities is evaporated allowing the niobium complex ($KrNbOF_5$) to crystallize. This is further purified by recrystallization, whereas the mother liquor is recirculated. By adopting this processing scheme, it is possible to produce a pure tantalum salt but the niobium complex obtained is not very pure.

For many years, the commercial technology for separating Ta from Nb involved the selective crystallization of potassium heptafluorotantalate K_2TaF_7 away from potassium

oxypentafluoroniobate monohydrate K$_2$NbOF$_5$,H$_2$O, discovered by Marignac in 1866. Indeed, the differences in the chemical and physical properties of newly formed fluoride complexes after dissolution allow the separation of the two elements by addition of KCl, as K$_2$TaF$_7$ is ten times less soluble in hydrofluoric acid than K$_2$NbOF$_5$,H$_2$O. After several cycles of crystallisation, this method is excellent for the production of a relatively pure Ta compound. The following reaction is involved:

$$H_2TaF_7 + 2\text{KCl} \rightleftarrows K_2TaF_{7(s)} + 2HCl$$

The next figure describes the flowsheet used for the separation of niobium and tantalum by crystallisation. After dissolution of the niobium and tantalum oxides in hydrofluoric acid with a slight excess over the stoichiometric requirement to form the fluoro compounds and precipitation of tantalum by addition of KCl and cooling. Further recrystallisation in HF solution could be involved to purify the tantalum salts.
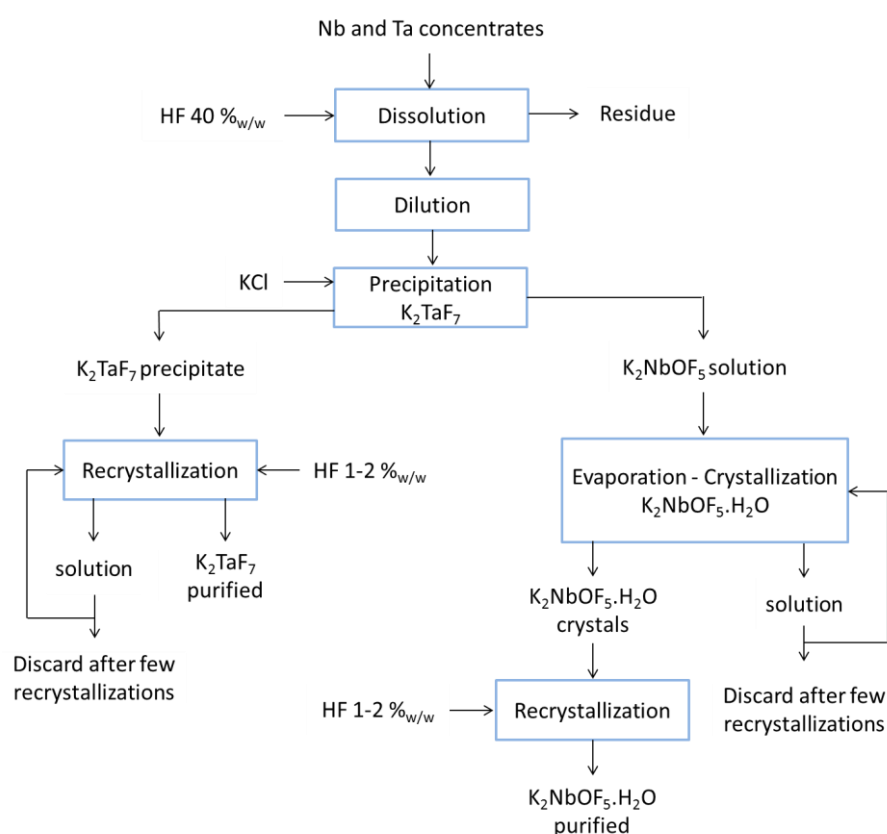

Figure 2-4 Flowsheet of the Marignac process for the Nb and Ta separation by crystallization

Solvent extraction

Most of the solvent extraction processes developed for niobium are equally employed for tantalum, as the two elements occur together in different minerals and have very similar chemical properties. Therefore, the main information is provided in the chapter dealing with Nb extraction. Herein are included only a few additions concerning particularly tantalum.

The previous method was progressively replaced by a solvent extraction process from fluoride containing solution, which was popularized by the company CBMM in the 80's years. All commercialised solvent extraction process are indeed exclusively operated in the presence of fluoride ions, because of the speciation differences between Nb and Ta in a such medium.

MIBK extractant

Although a lot of extractants have been studied for separating and purifying Nb and Ta , methyl iso-butyl ketone (MIBK) was widely used industrially, despite of several disadvantages, such as its relatively high solubility in water ($\sim$2 %$_{v/v}$), its low flash point (14 °C) and its high volatility. However, MIBK is also a not expensive product, has a low density and viscosity and can be purified by steam distillation and recycled through the system.

The key parameter of the solvent extraction by MIBK is the H$^+$ concentration, which controls the degree of separation as well as the recovery of the two metals. Indeed, niobium forms the fluoride complexes $NbOF_5^{2-}$ at low acidity and NbF_6^- at high acidity, whereas tantalum forms TaF_7^{2-} at low acidity and TaF_6^- at high acidity. As the species $NbOF_5^{2-}$ are very few extracted by MIBK, it is possible to separate these two elements. On the other hand, the impurities such as iron, aluminium copper, manganese, calcium and silicon are not extracted and left in the raffinate. Very pure tantalum and niobium products can be obtained with impurity in the range of 1-10 à mg/L. The chemical mechanism is the following:

Ta extraction: $TaF_7^{2-} + 2H^+ + \overline{MIBK} \rightleftarrows \overline{H_2TaF_7MIBK}$

Ta stripping: $\overline{H_2TaF_7MIBK} + H_2O \rightleftarrows TaF_7^{2-} + 2H_3O^+ + \overline{MIBK}$

Acidification: $NbOF_5^{2-} + HF + H^+ \rightleftarrows NbF_6^-$

Nb extraction: $NbF_6^- + H^+ + \overline{MIBK} \rightleftarrows \overline{HNbF_6MIBK}$

Nb stripping: $\overline{HNbF_6MIBK} + H_2O \rightleftarrows NbOF_5^{2-} + HF + 2H^+ + \overline{MIBK}$

An another strategy, which was developed by the Ames Laboratory is to dissolve the Nb/Ta containing metals in a binary acid system, hydrofluoric acid and high concentrated sulfuric acid. The two fluoro Ta and Nb complexes are subsequently extracted, leaving the impurities in the aqueous layer. Niobium is then separated from tantalum by reducing the acidity and is stripped into the aqueous phase. Finally, the Ta fluoride complex is stripped from the organic phase with water.

The final purified products are then recovered by precipitation either with NH$_4$OH or KCl in the case of tantalum (as the Marignac process). The different chemical reactions involved are the following:

$2H_2TaF_7 + 14NH_4\text{OH} + \text{n}H_2O \rightleftarrows Ta_2O_5, nH_2O_{(s)} + 14NH_4F + 9H_2O$

$or\ H_2TaF_7 + 2\text{KCl} \rightleftarrows K_2TaF_{7(s)} + 2HCl$

The hydrated Ta oxides can be then dried and calcinated to obtain Ta_2O_5. The potassium heptafluorotantalate K$_2$TaF$_7$ is used to produce Ta^0 by reduction with metal sodium.

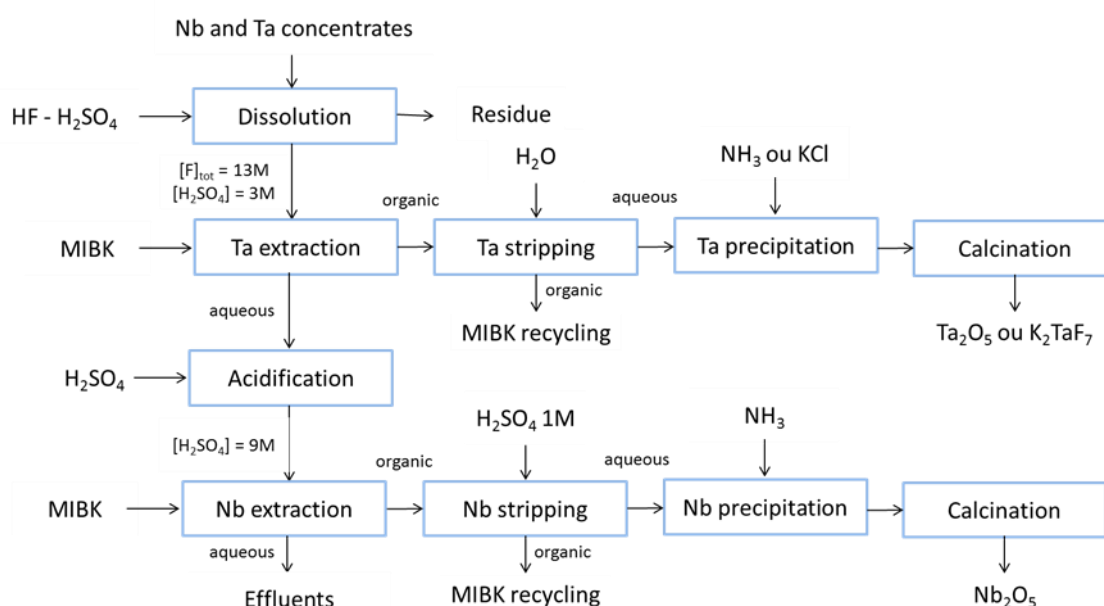The following simplified flowsheet presents the different steps.

Figure 2-5 Example of flowsheet for the Nb and Ta separation by solvent extraction MIBK

Extraction tantalum in TBP goes, as for niobium, through the formation of solvated complexes. The extraction is usually accomplished from the fluoride media. At very low concentrations of HF, tantalum is extracted through the solvation mechanism as $Ta(OH)F_4 \cdot nTBP$ and $TaF_5 \cdot nTBP$. At intermediate HF concentration, the extracted species is as $HTaF_6 \cdot 3TBP$, and at an acid concentration of more than 10 M HF, tantalum is extracted as $H_2TaF_7 \cdot 3TBP$.

The extraction of tantalum by anion exchangers is relatively less sensitive than Nb to the concentration of hydrofluoric acid; e.g., the distribution coefficient of the tantalum remains constant at about 200 in the acidity range of 1 to 5 M HF. The distribution coefficient of niobium, on the other hand, decreases very sharply when the HF concentration is increased to 2 M. The separation factor $FS_{Ta/Nb}$ in a TOA fluoride system under optimum conditions is of the order of 400. Liquid ion extractant can be used to extract both niobium and tantalum collectively into the organic phase in the first instance. Subsequently, the re-extraction or back-extraction is carried out selectively to effect the separation. In the case of HF medium, the re-extraction of tantalum can be carried out with concentrated HNO3 (9.5 to 12.5 M HNO_3) or 25% NH_4OH. Generally, the extraction of tantalum is favored from fluoride media; the extraction of niobium, on the other hand, is favored from HCl acid solutions with acidity of over 4 to 6 M or from solutions containing a high concentration of chloride ions. Extraction of tantalum from HCl acid media can be improved to an almost quantitative level by the addition of about 0.25 M HF. Niobium and tantalum have also been extracted as tartarate and oxalate complexesin tri-n-octyl amine and as citrate complex in Aliquat 336. The extraction of tantalum as fluoride complex is also possible by using Amberlite LA-2 as anion exchanger.

Alkali fusion

In the case of high grade concentrates of columbite-tantalite, alkali fusion coupled with acid leaching was used on an industrial scale in the 30's and 40's years. Either sodium alkalies as $NaOH/Na_2CO_3$ or potassium alkalies as KOH fusion were performed. In the first case, the fused mass was leached with water and afterwards with hydrochloric acid to obtain Nb and Ta oxides. The purer oxides were then separated and purified by the Marignac's process. In the second case, the fusion of the columbite-tantalite at high temperature (800 – 1000 °C) with caustic potash was followed by a leaching with water to solubilize the potassium niobate and tantalite with some impurities. Nb and Ta were then precipitated by NaCl addition and leached with hydrochloric acid to remove the remaining impurities and convert the sodium complexes into oxides. The next figure resumes this process.
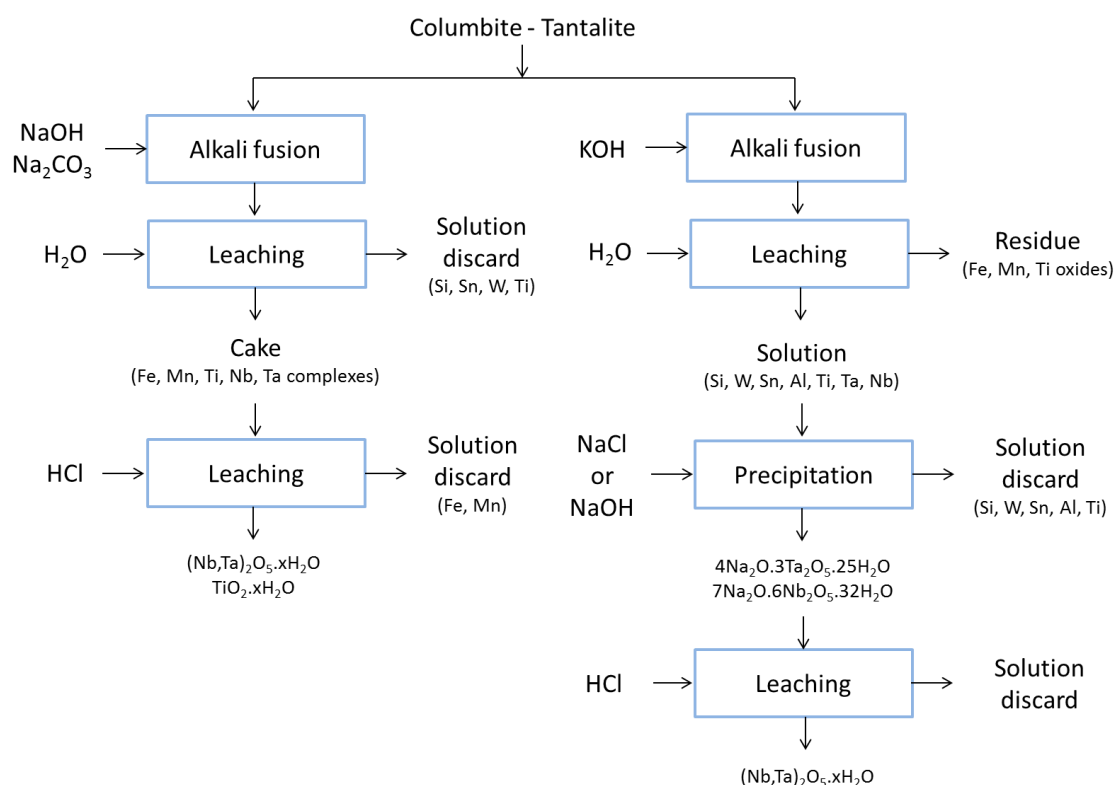

Figure 2-6 Alkali fusion process from columbite - tantalite

PYRO-METALLURGY

Theoretical introduction to pyrometallurgical extraction of Tantalum
Niobium and Tantalum are sister elements that have very close chemical behaviour and properties in terms of extraction, theoretical aspects of Tantalum from primary sources can be inferred in Chapter 4 on Niobium extraction. That is why it has been decided to focus on this part on the separation of these two elements that is needed to produce Tantalum.

Separation of Tantalum and Niobium by Chloride Rectification process

Rectification may be successfully employed in the separation of the mixture of Niobium and Tantalum pentachlorides, as the boiling points of the chlorides differ by 14.3°C (the boiling point of $TaCl_5$ and $NbCl_5$ are 234.0 and 248.3°C respectively). The use of the rectification process for the separation of Tantalum and Niobium is expedient when the ore concentrates are processed by the chlorination method, yielding a condensate of Tantalum and Niobium Chlorides for example in the processing of loparites concentrates. The chlorination of the concentrate usually yields a condensate in which a large fraction of the Niobium is present as the oxychloride $NbOCl_3$. Thus, additional chlorination is required in order to convert the oxychloride to the chloride. The rectification process is characterized by a high output and a high degree of separation. It may be carried out in continuous operations column.

Separation of Tantalum and Niobium by selective reduction of the chlorides

As compared with Tantalum pentachloride, Niobium pentachloride is more readily reduced by hydrogen (or by metals such as aluminium) to the lower chlorides. This is used as the basis of a process for the separation of Tantalum and Niobium. $NbCl_5$ is reduced by Hydrogen at 450-550°C to the non-volatile trichloride according to the following reaction:

$NbCl_5 + H_2 \rightarrow NbCl_3 + 2HCl$
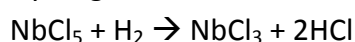
TaCl5 is not reduced under those conditions. In one variations of the method, Tantalum and Niobium are separated by volatilizing the $NbCl_5 + TaCl_5$ mixture at 180-200°C and passing the gaseous chlorides together with hydrogen through a long tube heated to 500-550°C. The $NbCl_3$ formed condenses on the walls of the tube, while the $TaCl_5$ remains in the gaseous phase and is collected in the condenser. The yield of pure $NbCl_3$ from the pentachloride has been reported about 70%.

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CHAPTER 3 MOLBDENUM

MINING

1.1 MOLYBDENUM MINES IN THE WORLD

Molybdenum is mined as a principal ore and is also recovered as a byproduct of copper and tungsten mining. Molybdenum is contained in various minerals, but only molybdenite (MoS_2) is suitable for the industrial production of marketable molybdenum products. Molybdenite can occur as the sole mineralization in an ore body, but is often associated with the sulphide minerals of other metals, notably copper. The Mo content of viable ore bodies ranges between 0.01 and 0.25% [12].

Depending upon the minerals contained in the ore body and their quality, molybdenum mines are grouped in three classes: 1) Primary mines, where the recovery of molybdenite is the sole objective; 2) By-product mines, where the recovery of copper-bearing ores is the primary objective, and molybdenite recovery provides additional economic value; Approximately 50% of the world's molybdenum production comes from Cu–Mo ore as a by-product [6]; and 3) Co-product mines, where the commercial viability of the mine requires that both molybdenite and copper-bearing minerals be recovered [12].

According to the International Molybdenum Association (IMOA), molybdenum production reached a new high of 539.2 million pounds (or about 245 million kilos) in 2013 [17]. The ten largest molybdenum producers accounted for over 60 percent of this total. While most producers extract molybdenum as a by-product from copper mines, four of the ten companies listed are considered primary molybdenum producers. The biggest ten molybdenum producers are:

- Freeport McMoran accounted for 47,000 metric tons of molybdenum production in 2013, or nearly 20 percent of global production. The company's centrepiece molybdenum asset is the Climax Mine, located in Climax Colorado, which first opened in 1918 and is the world's largest, highest grade and lowest cost producing molybdenum mine. Freeport-McMoran also operates the Henderson molybdenum mine in Colorado and extracts moly as a by-product from other sites in North and South America. Company website: www.fcx.com
- Chilean state-owned copper miner Codelco, was the world's second largest molybdenum producer in 2013, refining roughly 23,000 metric tonnes. Based solely in Chile, key molybdenum mines include Salvador, Andina and El Teniente. Molybdenum sales accounted for US$ 493 million in sales for the year. Company website: www.codelco.com

- Grupo Mexico is the largest Mexican mining corporation in Mexico, operating 13 mines in the US, Mexico and Peru. The company's most important molybdenum assets include the Cuajone and Toquepala mines in Peru and the La Caridad mine and processing plant in Mexico. Company website: www.gmexico.com
- China Molybdenum is China's largest molybdenum producer, accounting for about 20 percent of national production and roughly 6 percent of global production. Based in Luoyang, Henan Province, China, the company's molybdenum assets include the Shangfanggou, Sandaozhuang and Xinjiang mines.
- Thompson Creek Metals is a molybdenum-focussed Canadian mining company with operations in Canada and the USA. In 2013, its molybdenum production accounted for over 13,000MT. Molybdenum was mined from the Endako (British Columbia, Canada) and Thompson Creek (Idaho, USA) mines and processed at the Langeloth Metallurgical Facility in Pensylvania. Company Website: www.thompsoncreekmetals.com
- Jinduicheng Molybdenum (or 'JDC Moly') is China's second largest molybdenum producer, accounting for an estimated 13,300MT in 2013. The Jinduicheng open-pit mine is one of the six biggest primary open-pit moly mines in the world and has proven molybdenum reserves of 1 billion tons. Employing over 5000 staff, the company has registered capital of over 3 billion renminbi and employs more than 5000 staff. Company website: http://www.jdcchina.com/
- Chilean copper producer Antofagasta produced 9,000MT of molybdenum as by-product from its Los Pelambres mine in 2013. This represented a 35 percent decrease over 2012. The company has a 60 percent ownership stake in the Las Pelambres mine, which is located in Chile's Coquimbo Region, 240 km north of Santiago. Company website: http://www.antofagasta.co.uk/
- In 2013, Rio Tinto produced 5,700MT of molybdenum from it's Bingham Canyon mine, located southwest of Salt Lake City, Utah. Operated by Kennecott Utah Copper Corporation, the Bingham Canyon mine is one of the largest open pit mines in the world. Production declined 40 percent from 2012 due to a massive landslide closed the mine in April of 2013. Company website: www.riotinto.com
- Anglo American has interests in two molybdenum-producing copper mines in Chile, which accounted for roughly 4,700MT of the metal, in concentrate, in 2013. Anglo American own's a 50.1 percent stake in the 150 year-old Los Bronces copper-molybdenum mine northeast of Santiago, which received a US$ 2.8 billion upgrade in 2011, as well as 100 percent of the Collahuasi open pit mine. Molybdenum production from Collahuasi declined 70% over 2012, reducing Anglo's total molybdenum production by roughly 4.5MT from the previous year. Company website: www.angloamerican.com/
- Teck (Canada) produced 3,780MT of molybdenum in concentrate in 2013, a 35 percent decline from 2012. Three quarters of this total came from the company's 97.5 percent in the Highland Valley Copper Mine, located in south central British Columbia, Canada. The remaining production was accounted for by Teck's 22.5 percent stake in the Antamina mine in Peru. Company website: http://teck.com/

In Europe only small number of molybdenum mines or projects were found. Munka mine owned by Beowulf Mining is located Rappen geological district of the Arjeplog Municipality

in northern Sweden with the reserves of 1.7 Mt ore at 0.156% Mo. All exploration work at the mine has been carried out by the Geological Survey of Sweden (SGU)[38]. In Turkey North Aegean Copper Enterprises owned by Özdoğu Construction Trade Co. produced Cu concentrate 55,000 mt/y at 25-30% Cu and Mo concentrate 2,500 mt/y at 55-57% Mo in 2007 and Özdoğu Construction Trade Co. started Havran Tepeoba molybdenum project in 2010 in Balikesir Turkey [36-37].

Erdenet Mining Corporationa is one of the biggest ore mining and ore processing factory in Asia and a Mongolian-Russian joint venture, 51% of shares is owned by the State Property Committee of Mongolian Government and 49% of shares is owned by the Russian Government. At present it is a fairly large complex processing 25 million tons of ore per year and producing over 530.0 thousand tons of copper concentrate and 3.0 thousand tons of molybdenum concentrates annually [15]. It started its operation in 1978. The main mineral deposit, extracted by the Corporation was the Erdenetiin-Ovoo area which locates 400 kilometers northwest from Ulaanbaatar, 180 kilometers east from Darkhan city, 60 kilometers northern from Center of Bulgan aimag and 140 kilometers from Russian border. The Erdenet is connected with East-Siberian railway network via Naushki station and to the Chinese railway network through Erlyan (Chinese border).

As a subsidiary of Freeport-McMoRan, Henderson is the largest primary producer of molybdenum in the world. The Henderson Mine is located in Clear Creek County on the east side of the Continental Divide, in the beautiful Rocky Mountains fifty miles west of Denver, Colorado [21]. The Henderson Mill is located on the west side of the Continental Divide, fifteen miles from the mine in Grand County. The Mine and the Mill are connected by the world's longest conveyor of its kind; a fifteen-mile elevated belt that passes underneath the Continental Divide through an old train tunnel and then above ground to the Mill [21]. The Climax mine began commercial operations in May 2012. FCX intends to operate the Climax and Henderson molybdenum mines in a flexible manner to meet market requirements [22]. The Climax Mine is located approximately 13 miles northeast of Leadville, Colorado and a porphyry molybdenum deposit with molybdenite as the primary sulfide mineral. This mine was commissioned in mid-2012, and includes a 25,000 metric ton-per-day mill facility.

The major molybdenum mines in the world are listed in Table 3-1[2].

Table 3-1 The major molybdenum mines in the world

Deposit Name	Company	Location and Country	Geology, Mineralogy and Mining
Los Pelambres mine[18][31]	Antofagasta Minerals SA	Coquimbo Region, the central-northern of Chile	An open pit mine, sized 2.5km x 2.2km at surface, an altitude of 3,100m above sea level (asl); chalcopyrite, chalcocite, bornite, covellite and molybdenite; 831Mt ore grading 0.68% Cu, 0.019% Mo, 0.034g/t Au and 1.2g/t Ag; copper, gold, silver and molybdenum
Centinela [31]	Antofagasta Minerals SA	Antofagasta region, Chile	Copper, gold, silver and molybdenum
Los Bronces[33]	Anglo American (50.1%); Mitsubishi (20.4%); Codelco and Mitsui (29.5%)	65km north-east of Santiago, Chile	Mined for more than 150 years, the current life of the mine extendable beyond 30 years with significant exploration potential. Molybdenum production expected to increase up to 5,400tpa during next ten years Open pit mining Chalcopyrite, bornite, chalcocite 2.17 billion tons (bt) grading 0.62% Cu Cu-Mo
Collahuasi [34]	-owned by Xstrata plc (44%) Anglo American (44%)	Northern Chile	low-grade copper porphyry Open-pit mining chalcocite, chalcopyrite and bornite Cu-Mo
Munka mine[38-39]	Beowulf Mining	Rappen geological district of the Arjeplog Municipality in northern Sweden	All exploration work at the mine carried out by the Geological Survey of Sweden (SGU) 1.7 Mt ore at 0.156% Mo
Havran Tepeoba project [36][37]	Özdoğu Construction and Trade Co.	Balikesir, Turkey	Project started November 2010 17,5 million m^3 Molybdenum-Copper ore present Cu-Mo

North Aegean Copper Enterprises[36]	Özdoğu Construction and Trade Co.	Turkey	In 2007 Cu concentrate 55,000 mt/y at 25-30% Cu and Mo concentrate 2,500 mt/y at 55-57% Mo. Cu-Mo
MAX Molybdenum project [25]	FortyTwo Metals Inc. (Roca Mines Inc.)	Trout Lake, B.C., Canada	To produce molybdenite ore from the underground workings to support mill operations at a rate of approximately 72,000 tonnes per year. The mill process consists of a conventional crushing, grinding and flotation circuit to produce a high-grade molybdenum sulphide concentrate with head grade 0.8 to 2.0 % MoS$_2$.
Kitsault [23]	Avanti Mining Inc.	140 km northeast of Prince Rupert, B.C., Canada	Aims to begin production in 2017, an anticipated mine life of 14 years, with an average annual production of 11,300 tonnes of molybdenum and over 1 million ounces of silver. Had operated from 1968 to 1972 and from 1981 until 1982.
Highland Valley[3]	Teck Cominco Limited	Logan Lake, B.C., Canada	Total copper production for 2007 was 136,000 tons, compared to 167,000 tons for 2006. Molybdenem was just under 4 million pounds compared with just over 4 million for 2006. Total ore mined fell also to 42.6Mt. 318Mt grading 0.43% Cu and 0.008% Mo
Endako [28]	Thompson Creek Mining Limited (75%); Sojitz Corporation (25%)	Fraser Lake, B.C., Canada	Began operations in 1965. It includes a concentrator that processes ore through crushing, grinding, and flotation circuits into molybdenum disulfide concentrate, and a multiple-hearth roasting facility that converts the concentrate into technical grade molybdenum oxide. surface molybdenum mine reserves amounting to 448.4 million tonnes of molybdenum ore grading 0.033%[29]
Brenda Mines		British Columbia, Canada	an open pit copper-molybdenum mine which closed in 1990 after 20 years of operation[14]
Climax [22]	Climax Molybdenum Company (Freeport-McMoRan)	Leadville, Colorado USA	Began commercial operations in May 2012. A porphyry molybdenum deposit with molybdenite as the primary sulfide mineral. This mine was commissioned in mid-2012, and includes a 25,000 metric ton-per-day mill facility.

Henderson [21][35]	Climax Molybdenum Company (Freeport-McMoRan)	Clear Creek, Colorado USA	The largest producer of primary Mo in North America. In 2007 the production was around 18,000 t Mo[35]. In operation since 1976, Henderson has produced more than 160 million tons of ore and 770 million pounds of molybdenum; A porphyry-type deposit consisting of a stock of small veins of molybdenite in rhyolite porphyrises of Tertiary age that intrude into Precambrian Silver Plume granite. A large underground mine ; Molybdenite associated with pyrite and quartz; Remaining ore reserves 500 million pounds (0.23 Mt) of Mo in 2006; Ore average 0.2% Mo.
Bingham Canyon[32][13]	Rio Tinto Group, Operated by Kennecott Utah Copper Corp.	Salt Lake, Utah USA	In 2004, ore from the mine yielded 15.4 Mt of copper, 715 t of gold, 5,900 t of silver, and 386, 000 t of molybdenum; a large porphyry copper deposit; open-pit mining, the largest man-made excavation in the world; molybdenite and chalcopyrite; 524Mt ore grading 0.47% copper, 0.044% molybdenum, 0.25g/t gold and 2.08g/t silver[13]
Luanchuan	China Molybdenum Company Limited	Henan province, China	Produced 4,717 tons of molybdenum concentrates, 1,096 tons of ferro-molybdenum, 89 tons of molybdenum powder and 23 tons of molybdenum bars in 1996; Molybdenum 96.74% exists in sulphides and 3.26% in Mo oxide; Out of mine ore grade 0.224% Mo and 0.148 WO_3
Dexing Copper (Moly) mine		Jiangxi Province in China	Porphyry copper–molybdenum ore grading 0.008% Mo; Main sulphide minerals: molybdenite, chalcopyrite, chalcocite, pyrite
Jinduicheng[17]	Jinduicheng Molybdenum Group Mining Corporation	Huaxian County, Shaanxi province, China	The largest molybdenum mining, dressing and smelting complex in China; Annual capacity of producing 12,000 tons of molybdenum concentrates, 10,000 tons of molybdenum oxide, 350,000 tons of sulfur concentrates, 1,000 tons of ammonium molybdate, 1,500 tons of ferro-molybdenum and nearly 1,000 tons of copper concentrates; An open-pit mine [30]; Mo reserve of 1,475,600 tonnes
Yangjiazhangzi	Yangjiazhangzi Molybdenum Mine	Jinxi, Liaoning province, China	In 1996, it produced 2,689 tons of molybdenum concentrate. 22.8 Mt of ore grading 0.15% Mo Mo
Sarcheshmeh mine		Kerman Province, Iran	Porphyry copper –moly deposit with 450 Mt ore, averaging 1.13% Cu and 0.03% Mo

Erdenet Copper/Molybdenum Mine[15-16][24]	Erdenet Mining Corporation	Erdenet Orhon, Mongolia	At present 25 million tons of ore per year and producing over 530.0 thousand tons of copper concentrate and 3.0 thousand tons of molybdenum concentrates annually.
Toquepala mine[26]	Grupo Mexico	in the Tacna Province, Tacna Department, Peru	a large porphyry copper open-pit mine producing copper, molybdenum, rhenium and silver with minor gold and zinc.
Shangfanggou molybdenum and iron mine	China Molybdenum	East Gobi, Hami, Xinjiang, China	Molybdenum reserve of approximately 191,300 tonnes A molybdenum-iron mine
Sandaozhuang mine[27]	China Molybdenum	East Gobi, Hami, Xinjiang, China	An molybdenum-tungsten mine with open-pit mining; Molybdenum reserve of approximately 595,200 tonnes and tungsten reserve of approximately 407,200 tonnes of scheelite.

Other mines also include Gibraltar (Taseko Mines Limited) and Huckleberry mines (Imperial Metals Corporation) in B.C. Canada; Bagdad, Morenci and Sierrita mines (Freeport-McMoRan Copper & Gold Inc.), and Mineral Park mines (Mercator Minerals Ltd.) in Arizona USA; Thompson Creek mine (Thompson Creek Metals Co. Inc.) in Idaho USA; Continental Pit mine (Montana Resources LLP) in Montana USA; Ashdown mine (Win-Eldrich Mines Ltd.) and Robinson mine (Quadra FNX Mining Ltd.) in Nevada USA; Chino (McMoRan Copper & Gold Inc.) and Questa (Chevron Mining Taos) mines in New Mexico USA; and Anduramba (D'Aguilar Gold), Kalkaroo (Havilah Resources NL), Kingsgate (Auzex Resources), Molyhil (Thor Mining PLC) and Spinifex Ridge (Moly Mines Ltd.) mines in Australia.

MINING TECHNOLOGY

If the ore lies close to the surface, open cast pit technology is employed. The overburden is excavated to reveal the ore body for easy extraction. If the ore lies deep underground, the underground block caving technique is employed. Large blocks of ore are undercut and allowed to collapse under their own weight. The resulting rock is removed to the surface for processing [12].

In the Highland Valley Copper-Molybdenum mine [3] in Canada open-pit mining is used in both the Lornex and Valley pits, with around 90% of the ore coming from the Valley pit. Three computerise Bucyrus 49R drills prepare blast hole patterns while nine P&H 4100A 37 yd³ electric shovels load ore into a fleet of Komatsu haul trucks for transport to in-pit crushers. In 2001, eight of the 170t-capacity trucks were replaced by six new 215t haulers. Further support is given by three water trucks, eight road graders, eight tracked bulldozers, three rubber-tyred bulldozers and one front-end loader.

The mine uses two semi-mobile in-pit crushers to minimise haul distances. Several kilometres of conveyors carry up to 12,000t/h of crushed ore to three stockpiles at the Highland mill. Pit operations are monitored and controlled by a Modular Mining Systems computerised dispatch system designed to maximise mine production. In addition minute-by-minute mapping is achieved by combining GPS navigation and survey with GIS mapping techniques.

Bingham Canyon mine located south-west of Salt Lake City, Utah, US, is the deepest open pit mine in the world. The Bingham Canyon pit is more than 1.2km deep and approximately four kilometres wide. The mine, which is owned and operated by Rio Tinto Kennecott, has been in production since 1906. Also known as the Kennecott Copper Mine, Bingham Canyon produced about 179,317t of copper, 279,200 ounces of gold, 2.4 million ounces (Moz) of silver and 20 million pounds (Mlbs) of molybdenum in 2012. The recoverable reserves at the open-pit

exceeded 2.9Mt of copper, 2.8Moz of gold, 31Moz of silver and 240,000t of molybdenum as of December 2012 [11].

Bingham Canyon pit is now 2.5 miles wide and very deep. Mining uses a rotary drilling/blasting – shovel/truck – in-pit crushing system, with two to four blasts per day. To contain costs, management has been quick to utilise the most cost-effective drilling, loading and haulage equipment and management tools available[13]. One of the first of the recent series of major investments was an in-pit, semi-mobile gyratory crushing unit linked to the Copperton Concentrator by an 8km conveyor system. This reduced haulage distances from the working faces substantially but even so the mine needs a large fleet of Caterpillar mechanical drive and Komatsu electric-drive trucks, mostly of 218t-capacity, to service ten P&H electric rope shovels. Dispatching is by the Modular Mining computerised system and Bingham also utilises Thunderbird Pacific's drill monitoring and logging systems. Both GPS and Glonass are used for precise drill positioning. Germany's MAN Takraf has upgraded and relocated the semi-mobile in-pit crushing plant and conveyor system to keep trucking distances down[13].

In Bingham Canyon mine 410,000 t of material are removed from the mine daily. Electric shovels can carry up to 56 cubic yards (43 m^3) or 98 short tons (89 t) of ore in a single scoop. Ore is loaded into a fleet of 64 large dump trucks which each carry 255 short tons (231 t) of ore at a time; the trucks themselves cost about $3 millions each. There is a five-mile (8 km) series of conveyors that take ore to the Copperton concentrator and flotation plant. The longest conveyor is 3 miles (4.8 km) long[32].

Los Pelambres mine [18] is an open pit sized 2.5km x 2.2km at surface, which is at an altitude of 3,100m above sea level (asl). Three Ingersoll-Rand electric rotary rigs drill blastholes, the initial two P&H 4100AS mining shovels and a LeTourneau L-1800 wheel loader, plus a 4100XPB shovel added later, work with a haulage fleet of five 329t-capacity Caterpillar 797 haul trucks to shift waste and ore in equal proportions. The mine works two 12-hour shifts.

In April 2004, the Chilean government approved an Environmental Impact Statement covering a second tailings disposal site, Mauro. Construction would allow Los Pelambres to mine an additional 2,000Mt over the life of mine and extend that life from 22 to 47 years at the current processing rate of 114,000t/d. Alternatively, the concentrator capacity could be increased to 175,000t/d, possibly in stages. Construction of the Mauro tailings dam was completed in December 2008 at a cost of $600 millions.

In its first full year, 2000, Los Pelambres processed 34Mt of ore to produce 298,900t of copper-in-concentrate and 5,450t of molybdenum. In 2003, the plant treated an average of 113,300t/d of ore grading 0.91% copper, with average recovery 89.9%, to produce a total of 826,500t of concentrate grading 40.9% copper. Payable copper-in-concentrate totalled 326,700t and payable molybdenum, 8,700t. In 2004 it was saw a 7.3% increase in output to 350,600t payable copper-in-concentrate despite a lower average ore grade of 0.88% Cu, mainly because of the pebble crusher added to the grinding circuit during 2003. However, the payable molybdenum tonnage fell to 7,900t. In 2005, the copper ore grade fell again to 0.80% and payable copper-in-concentrate output dropped to 322,800t as the mine focused on maximising molybdenum

production, which rose to the 2003 level of 8,700t. A $192m expansion project that was completed in 2007, boosting production capacity of the mine to 130,000t/d. By the end of 2008, the mine produced 136,000t of ore per day, graded at 0.76% ore. A plan for further plant expansion was approved in July 2008. The expansion will boost copper production to 90,000t a year from early 2010. By June 2009, the project was 47% complete and within the allotted $1bn budget [18].

The drilling/blasting technology is used in Jinduicheng Molybdenum surfaces mine [30]. Open pit mining is carried out at Los Bronces mine through drilling and blasting. The ore is extracted with the use of loaders and wheel dozers [33]. The low grade ore undergoes the process of leaching, solvent extraction (SX) and electrowinning (EW) for the production of cathodes. Higher grade ore is sent to the crushers near the mine where the ore is reduced to 1.5inch pieces. The crushed ore is sent by the 4.4km conveyer to the grinding plant, which houses one 40ft SAG mill and two 26ft ball mills. The ore slurry prepared from the milled ore is sent to the Las Tórtolas flotation plant through a 52km pipeline. The slurry undergoes froth flotation for separating the copper and molybdenum concentrates. The concentrate is dried by thickening and filter press till the water content is reduced to 9%. The concentrates are either directly sold in the market or transported to the Charges smelter for the production of copper anodes.

Open-pit mining is carried in Collahuasi mine [34]. The Ujina and Huinquintipa zones were mined first, with a transition to the Rosario orebody completed during 2004. Stripping at Rosario began in 2002. The stripping ratio at Ujina averages 4.4:1 (waste: ore) with a 15m bench height. Huinquintipa is somewhat smaller. The design mining rate of 360,000t/d of rock was achieved in Year 1, involving the blasting of 750,000t of material every two days. Equipment used at Collahuasi includes five Bucyrus-Erie 49R III electric drills and a Drilltech T60KL diesel drill, 40 Komatsu 830E haul trucks and five Bucyrus-Erie 495BI electric rope shovels. Two Krupp Fördertechnik 6,000t/hr semi-mobile crushing plants, one used in each pit initially, provide substantial in-pit haulage cost savings. In 2008, Xstrata Copper announced a 28% increase in the total estimated mineral resource at the mine, representing the equivalent of an additional 11 million tons of contained copper metal from 2007 resources.

Mining is done by block caving in Henderson mine. In 1980 the cavity produced by the panel caving broke through to the surface, producing a large glory hole on the side of Red Mountain. The ore is carried by a 15-mile conveyor belt system through a tunnel beneath the Continental Divide to the ore processing mill near Parshall, Colorado[35]. The ore is treated by froth flotation to obtain molybdenite concentrate, which is shipped to a plant in Fort Madison, Iowa for further processing[35].

The Henderson mine produces molybdenum ore by an underground mining method known as panel caving [40]. The mine site is within Clear Creek County and is surrounded by the Arapaho National Forest. The approximately 11.7 km2 (2900 acre) of land containing the Henderson orebody, located underneath Red Mountain, as well as the proposed UNO site, located underneath Harrison Mountain is entirely privately owned by Climax Molybdenum Company.

Additionally, the 52- km^2 (12,800 acre) mill site located near Kremmling Colorado is also entirely owned by the company. The mine is currently producing about 21,000 tons of raw ore per day. It is estimated that the mine has adequate reserves for about twenty more years of production[40]. The ore bodies are entirely within a Tertiary rhyolite porphyry intrusive complex that has intruded the Precambrian Silver Plume granite. The deposit
is elliptical in plan, with overall dimensions of 670 m by 910 m, with an average thickness of 185 m. The top of the deposit is at an elevation of 2610 m, while the lower limits range from 2,340 m on the west to 2,100 m on the east. The mineralization is relatively continuous in the ore bodies and consists of molybdenite and quartz in random intersecting closely spaced veinlets. The general nature of the orebody and the surrounding host rock is that of very competent (high strength) granite with compressive strengths ranging from 100 to 275 Mpa (14,500 to 40,000 psi). Host rock areas that have very little molybdenite have been found to behave appropriately for medium-strength granite.

From the beginning, the mine was designed as a high capacity operation, and the mine infrastructure is engineered to support production in excess of 30,000 tons per day, which equates to about 10 million tons per year, easily making the Henderson Mine one of the 10 largest underground mines in the world today[40]. The mine is accessed from the surface by an 8.53 m diameter men and material shaft that extends down to the 7500 level. The shaft cages can transport up to 200 people at a time, and the trip from the surface to the 7500 level takes about 5 minutes. The cage can accommodate loads with maximum dimensions 2.6 m wide, 7.1 m long, and 3.9 m high weighing up to 30 tons. Taller items up to 5 m in height (16' 4") can fit on the cage if they are small enough to fit in one corner. Loads of up to 50 tons can be carried if a crosshead is substituted for the cage and counterweights used. An inter-level ramp with a grade of about 7% extends from the 7500 level down to the 7065 truck level. From the 7700 production level, ore is transported with large capacity Load Haul Dump units (LHDs) with capacities of about 10 tons per scoop, to bored 2.5 m diameter ore passes that extend vertically down to the 7065 truck level. On the 7065 truck level, ore is loaded from large ore chutes at the bottom of the ore passes into 80 ton side dump underground haul trucks, (the largest underground trucks manufactured), which haul the ore to the underground crusher. The crusher reduces the size of the ore to pieces 8 inches or less, and has a capacity of 2300 tons per hour.

From the bottom of the crusher below the 7065 level, the ore is loaded on to the first of three conveyor belts, PC1, which transports the ore 1.6 km (1 mi) to the PC1/ PC2 transfer station located at the 7500 level. At the transfer station, the ore is then loaded onto the PC2 underground conveyor, and is transported 16.1 km under the continental divide to the PC2/PC3 transfer station. PC2 is the longest single flight conveyor in the world. Ventilation to the production level is supplied by a multi horizon level 15 to 20 m below. Both intake and exhaust air are transported on two horizons to provide a general north-tosouth fresh air-to-exhaust airflow. Each production ore pass is connected to exhaust air and has an associated intake raise from the intake drifts. Large mining equipments used at the Henderson mine include 10 ton

capacity Load Haul Dump unit (LHD) and 80 ton capacity side dump underground haul truck [40].

MINERAL PROCESSING

Generally, the ores are crushed and ground to fine particles and reported to flotation to separate the metallic minerals including molybdenite from the gangues, and in the case of copper/ molybdenum ores molybdenite is further separated by flotation from copper sulphide. The resulting concentrate contains between 85% and 92% MoS_2. Further treatment by acid leaching can be used to dissolve impurities like copper and lead if necessary[12]. Roasting in air at temperatures between 500 and 650°C converts MoS_2 concentrate into roasted molybdenite (MoO_3) concentrate. The resulting roasted molybdenite concentrate typically contains a minimum of 57% molybdenum, and less than 0.1% sulfur. Some of the by-product molybdenite concentrates from copper mines contain small quantities (<0.10%) of rhenium. Molybdenum roasters equipped to recover rhenium are one of the principal commercial sources for this rare metal [12].

PROCESSING OF PRIMARY MOLYBDENUM ORES

Primary molybdenite recovery is concerned with separation of molybdenum from molybdenum porphyries in which it is the only valuable component. The typical flowsheet for processing of primary molybdenum ore is shown in Figure 3-1[47]. Typically, a final concentrate of 48 to 56% Mo (80 to 93% MoS_2) is produced and overall recovery of molybdenite at primary-ore concentrating plants ranges from 75 to 90% of the in-place ore content [47].
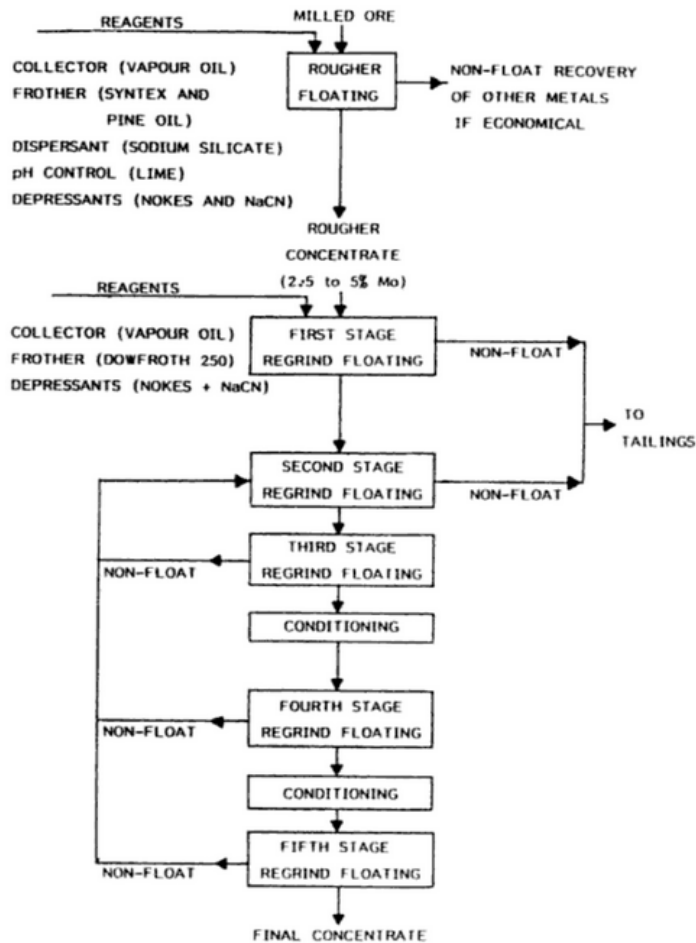
```
                              MILLED ORE
         REAGENTS

COLLECTOR (VAPOUR OIL)       ROUGHER      → NON-FLOAT RECOVERY
FROTHER (SYNTEX AND          FLOATING        OF OTHER METALS
         PINE OIL)                           IF ECONOMICAL
DISPERSANT (SODIUM SILICATE)
pH CONTROL (LIME)
DEPRESSANTS (NOKES AND NaCN)

                             ROUGHER
                             CONCENTRATE
         REAGENTS           (2.5 to 5% Mo)

COLLECTOR (VAPOUR OIL)       FIRST STAGE
FROTHER (DOWFROTH 250)       REGRIND FLOATING    NON-FLOAT
DEPRESSANTS (NOKES + NaCN)
                                                           TO
                                                           TAILINGS
                             SECOND STAGE
                             REGRIND FLOATING    NON-FLOAT

                             THIRD STAGE
              NON-FLOAT      REGRIND FLOATING

                             CONDITIONING

                             FOURTH STAGE
              NON-FLOAT      REGRIND FLOATING

                             CONDITIONING

                             FIFTH STAGE
              NON-FLOAT      REGRIND FLOATING

                             FINAL CONCENTRATE
```

Figure 3-1 Mineral processing flowsheet for primary molybdenum ore

PROCESSING OF SECONDARY MOLYBDENUM ORES

Secondary molybdenum recovery involves copper byproduct from porphyry copper, copper coproduct from copper/molybdenum ores and by-product of complex molybdenite ores (for example the molybdenum-tungsten ores or molybdenum bismuth ores).

Porphyry coppers contain molybdenum as a by-product. In this route of molybdenum recovery, the general practice followed today is to float first a bulk concentrate (Cu-Mo concentrate), and then to proceed with a selective flotation to separate the desired components.

A basic by-product Mo recovery flowsheet from porphyry coppers is shown in Figure 3-2 [48]. Crushed copper ore (containing, for example, 0.75% Cu and 0.015% Mo) is fed to the grinding circuit where water is added and the ore is ground to a proper size. Lime and oil for collecting molybdenum are usually added in the grinding circuit. A copper collector may also be added at this point; The pulp progresses to the flotation cells. Frother and copper collector are usually

added to the pulp just before the roughers. Additional copper collector is often added to the scavenger flotation cells and may be added at several other points. The froth, enriched in copper and molybdenum, is removed from the flotation roughers and scavengers. Enriched material is now called the rougher concentrate or cleaner feed. The combined rougher-scavenger concentrate may be 5% Cu and 0.06% Mo (a concentration factor of 3 to 10 times is typical); The scavenger or combined rougher/scavenger concentrate may go to regrind where it is ground to further liberation of the minerals. The rougher and scavenger concentrates ultimately reach the copper molybdenum cleaners. The cleaners, which represent another cycle of froth flotation, provide additional cleaning and upgrading of the rougher scavenger concentrate; The concentrate, which is now approximately 30% Cu and 0.35% Mo, is pumped to the molybdenum plant where the molybdenum disulfide is separated from the copper sulfide. Chemicals referred to as depressants are added to the pulp to reduce the flotation of the copper minerals while allowing the molybdenum minerals to float. The tailings from the molybdenum plant are the final copper concentrate (typically greater than 30% copper). Following molybdenum rougher flotation and several stages of cleaning, a final molybdenum concentrate is produced. The final molybdenum concentrate is typically greater than 55%.
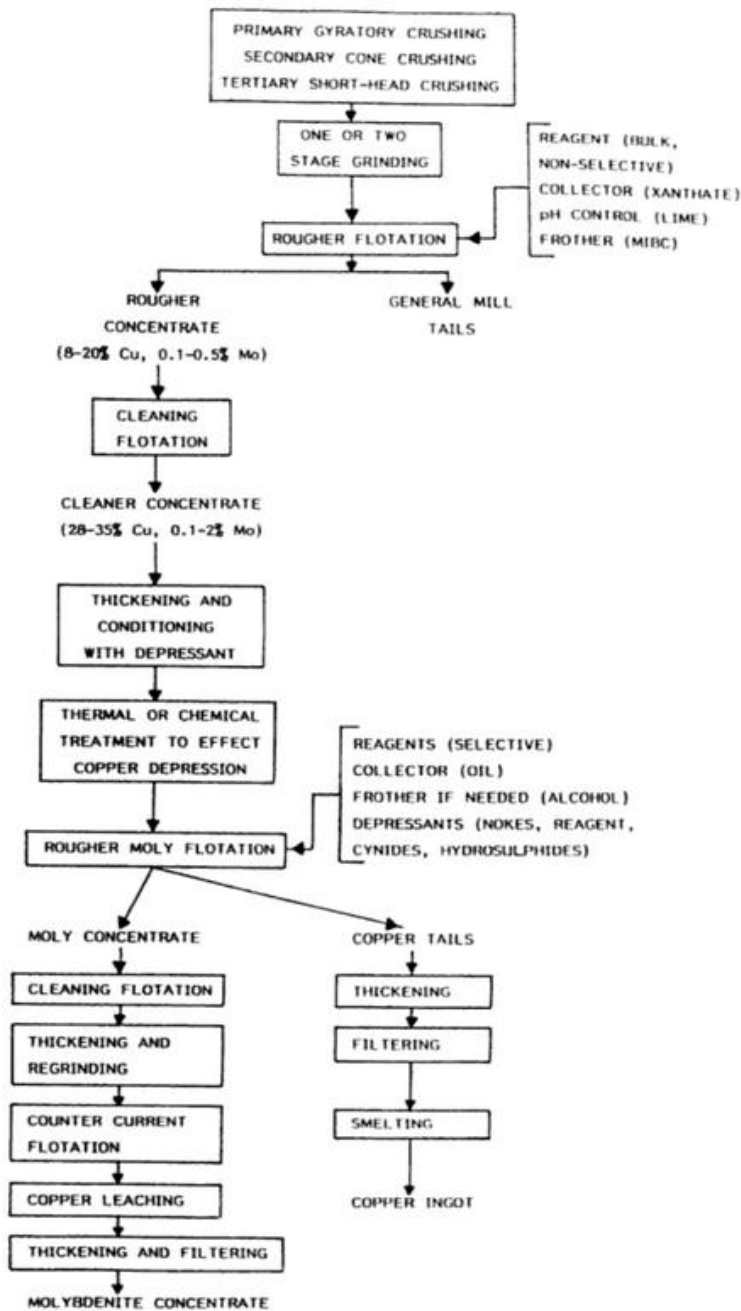
Figure 3-2 A basic by-product Mo recovery flowsheet from porphyry coppers

CASE STUDIES

In the Highland Valley mine the crushed ore enters two grinding stages in five parallel grinding lines incorporating two fully-autogenous mills, and three semi-autogenous (SAG) mills grinding a total of 5,400t/h. The second stage consists of eight ball mills reducing ore to sand-sized particles which feed the flotation circuits. The primary flotation stage extracts copper and molybdenum from the slurry to get Cu-Mo bulk concentrate and then copper and molybdenum are separated. The molybdenum concentrate is mixed with a leaching brine in sealed, pressurised, heated vessels where residual copper is dissolved, leaving a high-grade molybdenum concentrate. Lastly, the copper and molybdenum concentrates are filtered and dried in gas-fired driers for shipping. Three 1m diameter pipelines take the tailings 7km overland from the mill to the Valley tailings pond[3].

In Luanchuan mine in China the mineral processing flowsheet of Mo sulphides:

the ore was crushed to -20 mm by three stage crushing (two open and one closed), then ground to P65=0.074mm (one closed stage) followed by rougher, two scavengers and two cleaners flotation to get bulk Mo sulphides-pyrite concentrate, and the Mo sulphides and pyrite are separated through rougher (butyl xanthate as the collector, pH10.5 using lime), two scavengers and six cleaners flotation (Na_2S and sodium cyanide added at cleaner 3 and 5) to get separate Mo and pyrite concentrates. In the separation circuit, in rougher butyl xanthate is used as the Mo collector at pH10.5 using lime for depressing pyrite, and in cleaner stage Na_2S and sodium cyanide are added (at cleaner 3 and 5).

Combined flotation and biohydrometallurgy method for processing the bulk flotation middlings (Mo-Cu bulk cleaner tail and scavenger concentrate) in Erdenet Mining Corporation plant was investigated[5].

The Kennecott Utah Copperton concentrator consists of a grinding circuit (four SAG mills followed by eight ball mills and an integral pebble crusher)) reducing 150,000 tons per day of run of mine ore to a nominal P80 of 240 μm and two flotation circuits: a bulk copper flotation circuit, where copper/molybdenum concentrate is produced, and molybdenite in the bulk concentrate is separated from the copper minerals. The copper circuit consisted of 5 parallel rows of rougher/scavenger cells. The rougher concentrate was treated in rougher cleaners (2 parallel rows of cells) without regrinding. The scavenger concentrate reported to regrinding (ball milling) along with the rougher cleaner tailing. The regrind circuit product was upgraded in three scavenger cleaner stages, the final concentrate from which, combined with the rougher cleaner concentrate, produced the bulk copper/molybdenum concentrate. The target d80 of the flotation feed was 200 μm, and the pH in the rougher/scavengers was controlled between 9.5 and 10. A bulk concentrate assaying about 25–30% Cu and 2–4% Mo was produced, depending on the ore blend processed [8].

Cyclone overflow is processed through the bulk flotation circuit, consisting of five rows of rougher scavengers with scavenger concentrate regrind and cleaner circuit to produce a 25% copper concentrate containing approximately 2% molybdenum. This bulk concentrate is then

processed through a separate molybdenum flotation plant where the copper is depressed and a high grade molybdenum concentrate is produced. The copper concentrate is pumped to Kennecott's Garfield smelter for further treatment [10].

In the Sarcheshmeh concentrator plant (Iran), after three stages of crushing, the ore is fed to ball mills in closed circuit with cyclones to produce 70% of the product finer than 75 μm. The concentrate of the rougher flotation is reground, and the tailings are discarded to the final tails. The cleaning and re-cleaning stages produce copper concentrate. The reagents used in the flotation circuit are the collectors of Nascol 1451 (dithiophosphate + mercaptobenzothiazol) and Z11 (sodium isopropyl xanthate), frothers of Dow 250 (polypropylene glycol methyl ether), and MIBC (methyl isobutyl carbonyl). To separate and recover the molybdenite mineral from the copper concentrate, copper sulfide and iron sulfide minerals are depressed and the molybdenite floats. The molybdenite concentrate with the grade between 53% and 55% Mo and the copper sulfide concentrate with the grade of 31% Cu (chalcopyrite, chalcocite, and covellite) are recovered as final concentrates with an efficiency of 83-87%, depending on the ore type and the operating conditions. It is known that aluminosilicate minerals adversely affect the flotation of copper sulfides in the Sarcheshmeh flotation plant [9].

In Bingham Canyon mine the Copperton concentrator was expanded in 1992 and fitted with some of the world's largest SAG and ball mills, and large flotation cells. There are four grinding and flotation lines, sequentially yielding a copper and molybdenum concentrate. The copper concentrate is piped about 27km to the smelter. Until its closure in mid-2001, the older North plant supplied about 20% of the copper concentrate for smelting [13].

At the present time, the Erdenet processing plant operates the two-phase Cu–Mo ore dressing flow chart. The flow chart includes three sequential process stages: bulk concentration with production of bulk Cu–Mo concentrate with the Cu content of 15–17% and Mo content of 0.4–0.5%; final concentration (copper–molybdenum flotation by the PP terminology) with production of Cu–Mo concentrate with the content of copper not less than 23.5%; molybdenum concentration with production of quality molybdenum concentrate (not less than 47% content of Mo); copper concentrate is the middlings of the rougher molybdenum flotation[16].

In Los Pelambres mine [18] trucks feed an FFE Minerals 60in x 110in primary gyratory crusher and a sophisticated overland conveyor system engineered by ThyssenKrupp takes the ore 13km to the stockpile at the concentrator, which is down at 1,620m asl. Two 17,000hp FFE Minerals 36ft x 19ft SAG mills work with four 9,500hp FFE Minerals 21ft x 33.5ft ball mills, giving a throughput of about 85,000t/d. In 2001 Los Pelambres decided to install pebble crushing to improve the SAG mill performance, and Bechtel designed an upgrade programme to raise the throughput to 114,000t/d. FFE supplied a redesigned SAG discharge system for this project. The pebble crusher was installed in August 2003 and had an immediate positive effect. Concentration and separation involves two steps, carried out in a bulk flotation plant and a molybdenum plant. Bulk flotation involves rougher, scavenger and cleaner flotation with associated concentrate regrind stages and is optimised by the Metso Minerals VisioFroth

system. Bulk copper-moly concentrate goes to a thickener prior to treatment in the molybdenum plant. Flotation tails go to tailing thickeners. About 70% of process water is recycled.

The concentrate slurry is piped via Salamanca and Illapel to the purpose-built port of Los Vilos (Punta Chungo) where it is dewatered for shipment. Los Pelambres treats the water extracted for use in irrigating a nearby eucalyptus plantation.

In MAX Molybdenum project [25] the mill process will consist of a conventional crushing, grinding and flotation circuit to produce a high-grade molybdenum sulphide concentrate with tailings sent to the proposed tailings storage facility. Run of mine (ROM) mill feed will typically be stored in the stopes, and will be transported to the crushing plant by rail from the underground adit only during processing campaigns in order to minimize double handling. A ROM ore stockpile will be located adjacent to the crushing plant in order to handle ore developed from the levels (i.e. tops and bottoms of stopes) and campaign ore. The metallurgical flowsheet will consist of primary grinding, rougher and scavenger flotation, regrind of rougher concentrate, up to five stages of flotation cleaners, and dewatering to produce a high-grade molybdenum sulphide concentrate that will be marketed to molybdenum buyers and traders. Head grade has been estimated in the order of 0.8 to 2.0 % MoS_2. The thickened tailings discharged to the tailings storage facility. A flocculant addition system will be installed to assist solids settlement.

In Collahuasi mine [34] sulphide ore is crushed, ground and treated by flotation. Run-of-mine sulphide ore enters the primary gyratory crusher prior to transport to two parallel grinding circuits, each consisting of a SAG mill and a ball mill. Secondary closed circuit grinding includes cyclone classifiers, from which the overflow feeds the flotation circuit. Flotation concentrate is thickened to 50% solids for slurry transport in a 200km-long pipeline to Punta Patache, 65km south of Iquique, where it is thickened and filtered before shipment worldwide. An expansion to the concentrator was completed during 2004.

EXTRACTIVE METALLURGY

Molybdenum ore after mineral processing will produce the molybdenite concentrate (mainly MoS_2). As shown in Figure 3-3 [49], besides a small part of molybdenite concentrate is directly used to produce pure molybdenite chemicals, molybdenite in large amount is transformed into molybdenum oxide, an important starting compound for producing molybdenum powder, ferromolybdenum, etc.
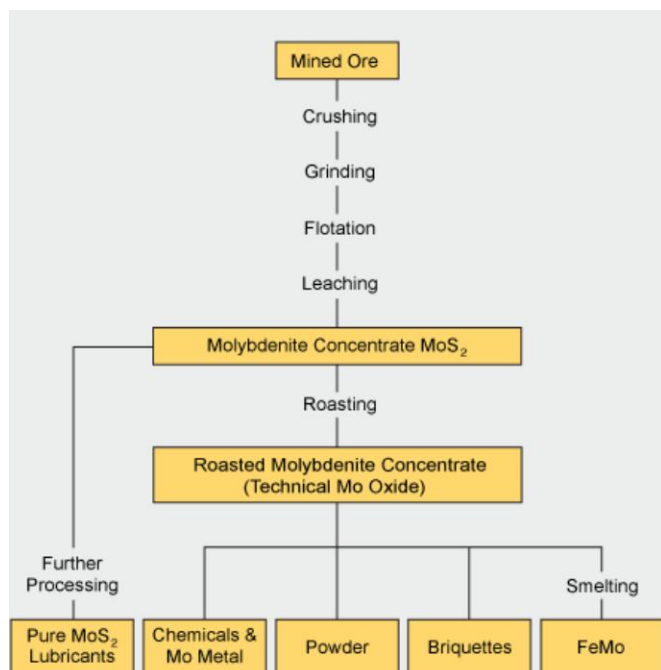
Figure 3-3 General molybdenum flow diagram from primary resources

About ¾ of the molybdenite concentrate is pyrometallurgically roasted to a technical grade and afterwards used directly in steel and iron industry and the rest is further processed to produce a high-grade molybdenum oxide suitable for use in catalysis, pharmaceuticals, fertilizers, pigments, etc.

HYDRO-METALLURGY

Hydrometallurgical methods are applied industrially both to convert molybdenite to techical grade oxide (e.g., sulfuric acid treatment, chlorination, pressure oxidative or nitric acid leaching) and to produce high purity molybdenum oxide (e.g. ammoniacal leaching, solvent extraction, ion exchange, precipitation/crystallization).

Pretreatment processes

In many cases in order to reduce the amount of impurities, a pretreatment stage is performed to reduce the amount of impurities such as copper, gold, lead, calcium and bismuth. The method which is applied mostly depends on the nature of impurities and may include sodium cyanide to remove copper and gold; ferric chloride to remove copper, lead and calcium and hydrochloric acid to remove lead and bismuth (Dorfler and Laferty 1981).

Kennecott Copper Co. also has commercialized sulfuric acid fusion technique to sulfate the insoluble sulfide minerals, like PbS, $CuFeS_2$, CuS, FeS_2 and Cu_2S, which coexist with molybdenite. In order to decrease the sulfation of molybdenite, the temperature must be kept around 290 °C and special care must be taken to use dilute sulfuric acid and short residence times. It has been shown in a pilot test that an off-grade molybdenite concentrate (~38%) has been upgraded to 84% molybdenite concentrate, pure enough for further processing to technical grade oxide (Spedden et al. 1971).

Another approach to remove the impurities before roasting is the chlorination purification. This process has been applied industrially in 1970s by a Swedish company (Bjerkerud et al. 1964). It has been claimed that the process can remove copper, bismuth and lead while just a portion of iron is removed. Chlorine gas is used in a rotary kiln at temperatures below 400 °C (150-300 °C) and molybdenum loss in following leaching process is less than 0.1%.

Beside the purification of molybdenum sulfide and production of high-grade molybdenite for further processing, another approach can be dissolution of molybdenum as a leach liquor and further precipitation of molybdenum. To dissolve the sparingly soluble molybdenum species, usually alkaline fusion (sodium/potassium carbonate) method is applied. At a molar excess of 15-70% of that required based on stoichiometry, in the absence of air and at temperature of 700-950 °C, the molybdenite is heated, followed by cooling, crushing and water leaching. At such conditions, 95% of the molybdenum is leached and the insoluble part can be oxidized using oxygen or other oxidizing agents to recovery the rest of the insoluble molybdenum. (Martin et al. 1973)

Pressure oxidative leaching or autoclave oxidation process of molybdenum was initially investigated in 1950s as an alternative to roasting. This method is mostly used for low-grade molybdenite resources, mostly for copper mines (Jiang et al. 2012). In a typical pressure oxidation process, a mixture of molybdenite concentrate with or without a catalytic agent (e.g. mineral acid or base) is introduced into an autoclave under oxygen pressure. The temperature is increased above 200 °C and the vessel is pressurized to 300-400 psi. (Dorfler and Laferty 1981)

One of the most commonly used catalysts in the oxidative conversion of molybdenite is nitric acid (Kholmogorov et al. 2002). In presence of nitric acid the main solid species that is produced is molybdic acid and in order to keep these species in solid form it is necessary to keep the pH below 0.7 (Kerfoot and Stanley 1976).

According to Smirnov et al. (2010), a POX unit at Molymet Company, Chile, works at 240 °C and 4.4 MPa pressure. It has been mentioned that pressure leaching is quite an efficient process in

removing impurities except when the raw material includes lead. In the presence of lead reductive leaching of impurities is applied (Cochilco 2011).

Nitric acid is a strong oxidation agent and it can act as an oxidative leaching agent without presence of oxygen. During nitric acid leaching, some of the molybdenum precipitates as molybdenum oxide. (Lasheen et al. 2015) According to Prasad et al. (1997) such a process has the advantage of versatility in processing low/high grade molybdenum, no SO_2 off-gas, high purity molybdenum oxide and easy regeneration of acid. Despite, this process is effective in removal of copper, calcium and sodium salts but, its safety and environmental issues accompanied by its low conversion factor (~80%) has prevented this process from being commonly used worldwide (Cochilco 2011).

Hydrometallurgical purification of molybdenum oxide

In order to remove the impurities and produce a high purity product (≥99.95%) suitable for manufacturing of catalysts, molybdenum metal, super-alloys and chemicals, usually two approaches are used, namely, sublimation or chemical methods. Here only the chemical methods are discussed as the sublimation is seen as a pyrometallurgical method.

Ammoniacal leaching

In this method technical grade molybdenum oxide is leached using ammonium hydroxide. Impurities such as $CaMoO_4$, MoO_2 and MoS_2 are not soluble in ammoniacal solution and they end up in tailings. Iron is almost totally precipitated at pH 9.0 (Jha 1999). However, other impurities such as copper, nickel and zinc molybdates, and sulfates, are soluble. In order to avoid introduction of such impurities into the leach liquor, a prewashing stage with water is done for solid feed prior to the leaching. The water removes copper, alkali metals and some of the molybdenum. The solubility of molybdenum oxide may reach 3-5 g/L leading to 4-5% of molybdenum losses. After prewashing of solid particles, the ammoniacal leaching is performed with 8-10% ammonium hydroxide solution at prevailing conditions or 70 °C. Depending on the grade of technical molybdenum oxide, leaching efficiency of molybdenum is typically 80-95% and the remaining molybdenum content in the tailings is 5-25%, which may be further leached. After 3-4 stages of leaching, the tailings are washed with hot water and sent for further processing using soda ash or acidification. (Zelikman et al. 1966)

Acidic digestion

For processing calcine leaching residue, according to Zelikman et al. (1966), in case of molybdenum oxides with high tungsten content (3-5%), the soda ash method fails since most of

the tungsten is also leached as sodium tungstate. In this situation, the calcines are digested using hot 20-30% HCl. At such condition, molybdenum remains dissolved as molybdic acid while just a portion of tungsten containing minerals decompose. Neutralization of solution with ammonium hydroxide (pH 2.5-3.0) precipitates the iron molybdate. The remaining tailing is filtered, roasted and leached using ammonium hydroxide. Up to 85% of molybdenum is extracted by using this method.

In order to purify technical grade molybdenum oxide from low grade resources, one approach is to leach the impurities using sulfuric acid at 80 °C. In this case copper and iron oxide are converted to dissolved sulfate salts while solid molybdenum oxide can be filtered and roasted in rotary kilns at 450 °C to 0.2% of moisture (Cochilco 2011).

Precipitation/crystallization

Precipitation method to purify the molybdenum is applied in removal of impurities and also precipitation of pure molybdenum. Especially in case of ammoniacal solutions, the most common impurities, namely, copper and iron, are removed as sulfides using ammonium sulfide. Since addition of excess ammonium sulfide may lead to formation of thiomolybdates, special care must be taken. In a process for recovery of molybdenum from wulfenite ($PbMoO_4$) alkaline leach liquor, sodium sulfide is used to precipitate lead and later, arsenic, phosphorus and silicon are precipitated by a magnesium salt (Jiang et al. 2012).

Molybdenum solutions which have no heavy metals may be taken to evaporation stage, and after that the hot solution is filtered and send to crystallize fine crystal structured para-molybdate. On the other hand neutralization of ammoniacal solution with HCl after evaporation of solution, leads to precipitation of tetramolybdate dihydrate (55-65 °C, pH 2-3). (Zelikman et al. 1966). In carbonate systems, such as in uranium mining industry, in which molybdenum recovery is economical, after extraction of molybdenum using proper method, the final aqueous solution that contains mostly sodium molybdate is treated by pH adjustment (ca. 6-8) and calcium chloride to precipitate $CaMoO_4$ (Ritcey 2006).

In China the main process for precipitation of commercial ammonium polymolybdate (APM) and ammonium molybdate is neutralization of ammoniacal solution with nitric acid. In the process the extract phase of ammoniacal leaching process is treated in two stages; first impurities are removed using sulfuric precipitation, and after that by adjustment of pH to 2.0-2.5 using nitric acid, ammonium molybdate is precipitated (Jiang et al. 2012).

Ion exchange and adsorption

Ion exchange can be used as an alternative for production of pure molybdenum products in numerous stages during processing of molybdenite or technical grade molybdenum oxide. Industrial application of ion exchange in recovery of molybdenum has been pioneered in Russia since 1950s. According to industrial experiences, it has been shown that polymolybdates, such as $Mo_8O_{26}^{4-}$ and $[MoO_2(SO_4)_2]^{2-}$, are the adsorbed species in recovery of molybdenum from sulfuric acid and nitric acid leachates of molybdenite. On the other hand, chloride species such as $[MoO_2Cl_3]^-$ and $[MoO_2Cl_4]^{2-}$ are the dominant in hydrochloric acid media (Kholmogorov et al. 2004).

According to Jiang et al. (2012), a plant with capacity of 2000 ton per year for recovery of molybdenum from wulfenite has been working since 2009 in China. A schematic of this process is shown in Fig. 3-4. Activated charcoal has been used to adsorb molybdenum from pregnant solution before uranium precipitation in the Pathfinder Mines Corporation Gas Hills mill in Wyoming and at the McClean Lake mill, USA (Edwards and Oliver 2000).

Kholmogorov et al. (2004) have mentioned that for selective recovery of molybdenum, amino-polymers, and for purification of molybdenum solutions, amino-carboxylic and amino-phosphoric amphoteric ion-exchangers, are suitable candidates. Besides, since in the pH range of 1-6 (weak acidic medium), polymeric ions are formed, application of high permeability anion exchangers for selective recovery of molybdenum is the most advantageous method. An important feature of anion exchangers for selective recovery of molybdenum is the nature of polymer backbone. The capacity of styrene based resins, is about 5.1-5.3 mmol/g while the molybdenum adsorption capacity for acrylic based resins reaches up to 10.8-11.1 mmol/g.
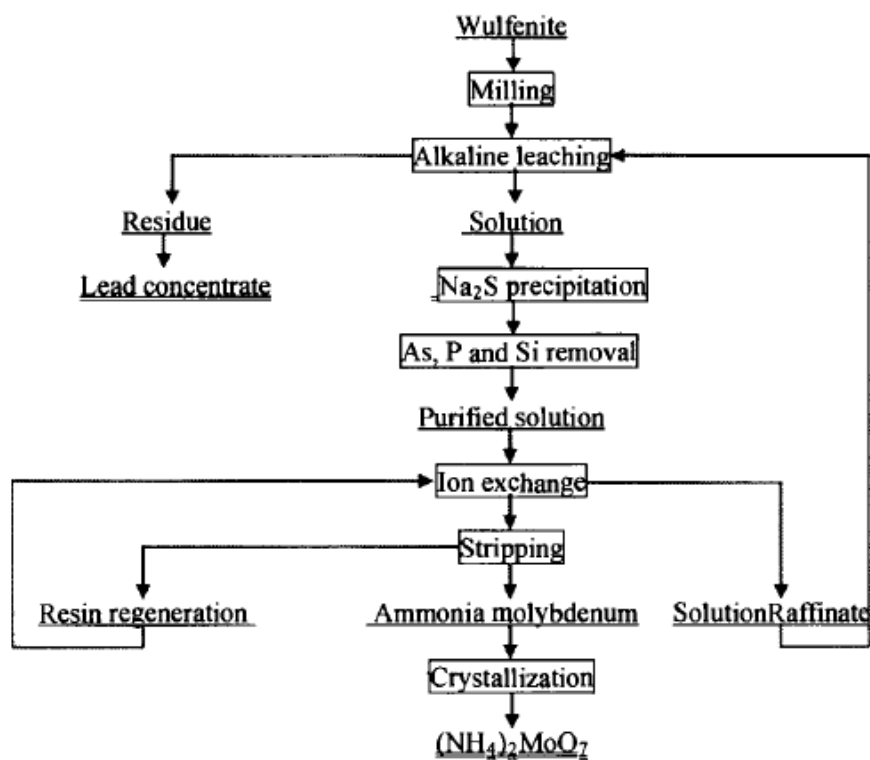
Figure 3-4 Alkaline processing of wulfenite in China containing ion exchange as separation method for molybdenum (Jiang et al. 2012)

In industrial leaching of molybdenite, the aqueous system consists typically of HNO_3, H_2SO_4, H_2O, and molybdenum complexes, e.g. $[Mo_8O_{26}]^{4-}$, $[HMo_8O_{26}]^{3-}$, $[MoO_2(SO_4)_2]^{2-}$ and $[MoO_2]^{2+}$. For example in case of an industrial solution (HNO_3 ~1.7 mol/L, H_2SO_4 ~0.5 mol/L, Mo (VI) ~0.1 mol/L, Fe ~0.3 mol/L) using AN-80P ion exchanger (methyl-acrylate based resin with 7% di-vinyl-benzene as cross linking agent and ethylene-di-amine as functional group), it was found that the molybdenum is adsorbed as $[Mo_8O_{26}]^{4-}$ polymeric oxyanion. By washing the resin with water at pH 3.0-2.5 iron and sulfate are removed and pure molybdenum can be eluted using ammonium hydroxide. (Kholmogorov et al. 2004)

Solvent extraction

Increasing application of POX method in the world and acidic digestion of low-grade molybdenite has increased interest in solvent extraction of molybdenum from sulfate media. Solvent extraction is especially important for the selective separation from tungsten in

multicomponent feed streams. Since molybdenum forms various molybdate ions in the aqueous solutions, secondary and tertiary amines (tri-octyl/decyl-amine, diisododecylamine) are predominately used. One of the commercial reagents used is TOA (commercially known as Alamine 336 or N235), which is diluted in aromatic or aliphatic solvents with alcohols or ketones as phase modifiers. In a process proposed by MacInnis and Kim (1983), the organic phase contained 15% v/v of TOA, the pH of aqueous feed was 4.5 and it contained 100 g/L MoO_3. It has been shown by MacInnis et al. (1974) that the mechanism of extraction is a function of pH. At high pH values the mechanism is anion exchange

$$\left[Mo_xO_yH_z\right]^{n-} + \overline{\frac{n}{2}(X\,HY)_2} \rightleftarrows \overline{(X\,H)_nMo_xO_yH_z} + nY^-$$
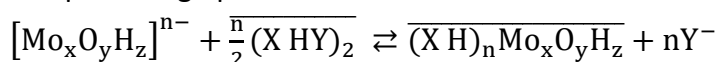
Here X represents the extractant and Y the anionic leaving group, where the overbars indicate the organic phase species. Also tungsten is extracted at high pH with the anionic exchange mechanism. The molybdenum species tend to polymerize as the pH decreases ($\left[Mo\,O_4\right]^{2-}$, $\left[H\,Mo\,O_4\right]^-$, $\left[Mo_7\,O_{24}\right]^{6-}$ etc.). When the pH is less than 3, the cationic forms are predominant ($\left[Mo\,O_2\right]^{2+}$, $\left[Mo_2O_5\right]^{2+}$, $\left[Mo_3O_8\right]^{2+}$) and the extraction switches to a cationic exchange mechanism:

$$\left[Mo_xO_y\right]^{n+} + \overline{n(X\,H)} \rightleftarrows \overline{(X)_nMo_xO_y} + nH^+$$
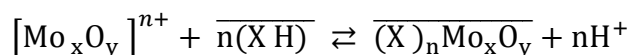
As extractant di-(2-ethylhexyl)phosphoric acid (D2EHPA) is mainly used dissolved in the same solvents and phase modifiers mentioned above. The equilibrium indicates, that the extraction should be favored at high pH. However, the extractant only extracts molybdenum in its cationic form (mainly $\left[Mo\,O_2\right]^{2+}$) at relatively low pH. A maximum distribution ratio is achieved for pH $2 - 2.5$. In this acidic environment, it is possible to selectively separate molybdenum from tungsten, as tungsten remains in the anionic form and is not extracted by D2EHPA. According to MacInnis and Kim (1983), two stages of extraction at pH 4.5 is effective for extraction of molybdenum, and a concentrated ammonium hydroxide solution can strip almost 100% of molybdenum in one stage.

During 1970s, Outotec (then Outokumpu), Finland, had developed a process for recovery of molybdenum from copper shaft residues. In this process the copper residues were digested using sulfuric acid and after dissolution of Fe, Cu, Co, and Ni, the solid residue was leached using alkaline solution. On next stage D2EHPA was used to extract the molybdenum with cation exchange mechanism selectively over rhenium at low pH (Paatero and Virolainen 2014). A

flowsheet example of process utilizing anion exchange reagent TOA for selective molybdenum recovery is given in Fig. 3-5.
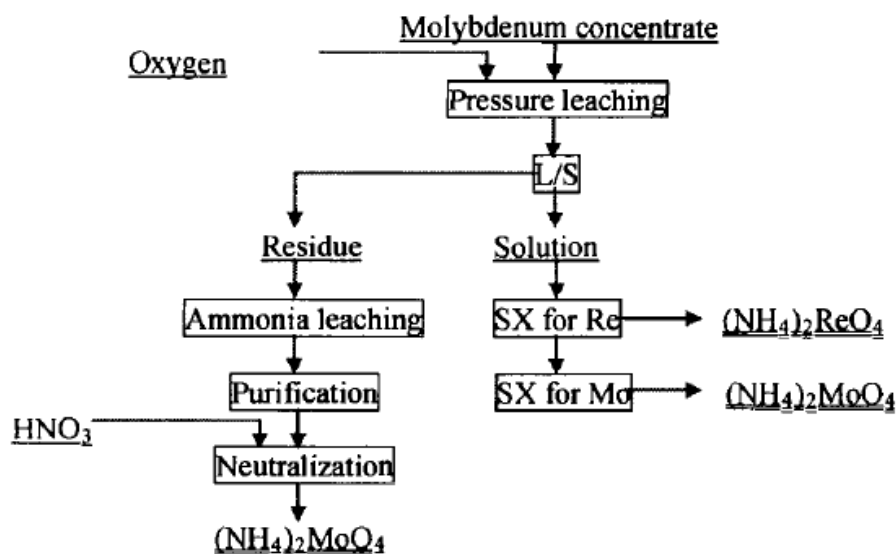

Figure 3-5 Processing of high-grade molybdenite containing solvent extraction as separation method for Mo and Re (Jiang et al. 2012)

CYTEC (2013) has recently commercialized a phosphinic acid based extractant called CYANEX 600 to selectively extract molybdenum from sulfate solutions e.g. from copper SX raffinates, smelter dusts and slags.
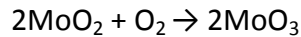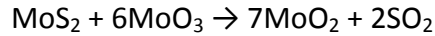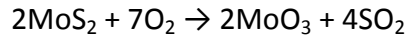

PYRO-METALLURGY

A pyrometallurgical process for Mo production from molybdenite concentrate is to remove sulphur and other impurities from the mineral, at high temperatures (>500 ^{o}C). The Mo grade ranges usually from 40~50 wt.% or higher (e.g. >75 wt.%) after mineral flotation. The typical processes are oxidative roasting, direct reduction, and chlorination.

Oxidative roasting
Roasting is carried out in the multi-level hearth furnaces, in which molybdenite concentrates move from top to bottom against a current of heated air and gases blown from the bottom. In this process, molybdenite concentrate is firstly subjected to oxidation in air at temperatures of

500-650°C and technical grade molybdic oxide can be obtained. The reactions of Mo-S-O system are rather complex (e.g. MoO_2 or MoO_3)[49-50] :

$2MoS_2 + 7O_2 \rightarrow 2MoO_3 + 4SO_2$

$MoS_2 + 6MoO_3 \rightarrow 7MoO_2 + 2SO_2$

$2MoO_2 + O_2 \rightarrow 2MoO_3$

The roasting temperature needs to be below 650 °C otherwise MoO_3 may be lost due to its high volatility. Molybdic oxide starts to sublime at around 593 °C and melt at 795 °C, while it becomes very volatile above 650 °C [51]. During roasting, various stages of oxidation were found that in the early stages MoO_2 is formed and further partially to MoO_3, and only after a certain roasting time, the conversion to MoO_3 can be completed (as given in Figure 3-6).
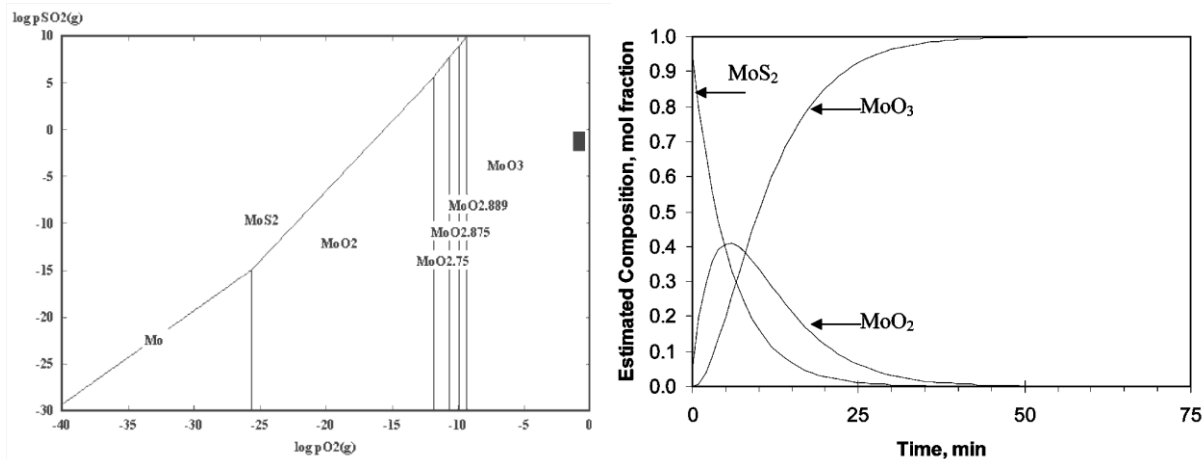
Figure 3-6 Stability diagram at 600 °C for the system Mo-S-O and the predicted composition during oxidative roasting based on the kinetic model. The black box indicates range of partial pressures of oxygen and SO_2 between 0.01 and 0.21 atm

The characteristics for the oxidative roasting are summarised as follows [52]:

- Roasting temperature should not exceed 650 °C, otherwise the MoO_3 formed may soften, volatilize or melt due to local overheating and its high volatility
- The reaction behavior was found to be very complex due to several gas–solid and solid–solid reactions that take place simultaneously
- The heat generated by the rapid combustion of MoS_2 in a fluidized bed may be sufficient to maintain the required temperature for the process
- The resulting roasted molybdenite concentrate typically contains a minimum of 57% molybdenum, and less than 0.1% sulfur.

After oxidative roasting, the calcine is either subsequently leached using acidic or ammonia-based solutions [52]. The recovery rate for Mo is usually above 90%. This process can also treat low-grade molybdenum ores (Figure 3-7).
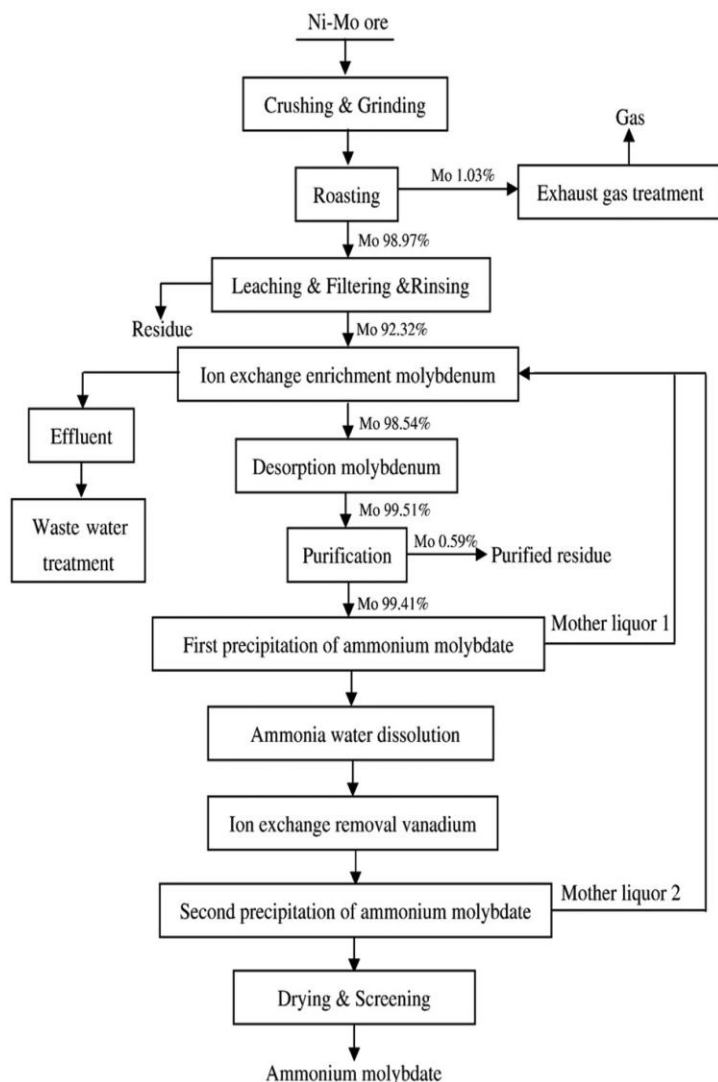

Figure 3-7 A represent flow-sheet for Mo recovery from a low grade Mo mineral (Ni-Mo ore)

Technical MoO_3 is a major commercial product directly used in steelmaking as for alloying. In commercial production, molybdenite is converted to technical-grade MoO_3 by roasting it in air in a multiple-hearth furnace of the Nichols – Herreshoff or Lurgi design [8] (Fig. 3-8). The roasted MoO_3 product typically contains < 0.1% sulfur. The multiple-hearth furnace is used because the hearths can be segmented to accomplish specific and different conversion operations within a single unit. Figure 3-9 shows the hearth-by-hearth composition of the

molybdenum during roasting [53]. The upper hearths of the furnace are mainly used to burn off flotation oils and evaporate water. This part of the process is usually augmented by burning fossil fuels to ensure consistent temperature control and uniform roasting throughout the remainder of the unit. Upper hearth temperatures range between 600 and 700°C.

The produced molybdenum trioxide is the raw materials for Mo metal and other commercial compounds. Technical-grade MoO_3 typically contains 85 – 90% MoO_3, the balance being silica with some Fe_2O_3 and Al_2O_3. In many cases chemical leaching of the concentrate is required prior to roasting to preferentially remove nonferrous impurities detrimental to steel production. Three leaching processes are practiced: (1) sodium cyanide leachate is used for copper and gold removal; (2) iron(III) chloride for copper, lead, and calcium removal; and (3) hydrochloric acid for lead and bismuth removal. This has been described in the previous section for hydrometallurgical processing.

Sulfur dioxide and sulfur trioxide leave the roaster in the flue-gas stream. This gas stream is handled by methods which comply with emission regulations. The most common are contacting the off-gas with lime to produce disposable $CaSO_4 \cdot 2H_2O$ and the production of sulfuric acid. Sulfuric acid is produced by catalytically oxidizing the sulfur dioxide to sulfur trioxide which is absorbed by a H_2SO_4 solution.
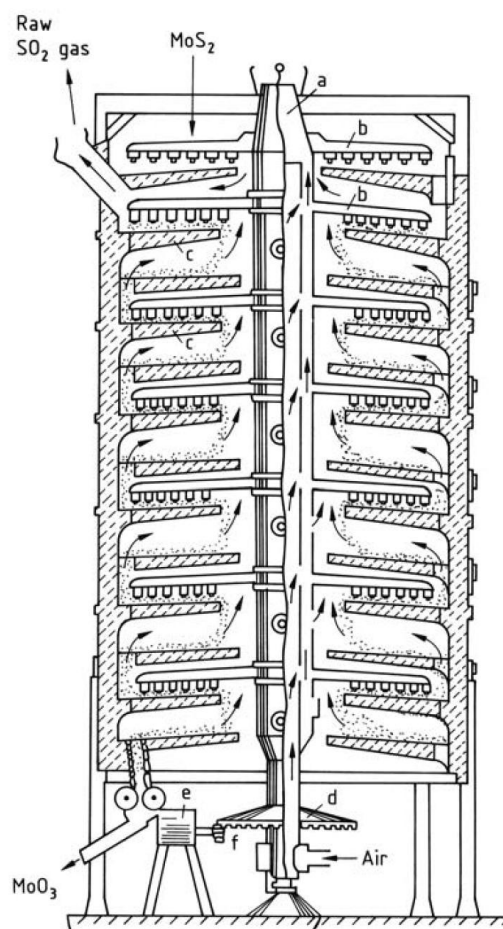
Figure 3-8 Multiple-hearth roasting furnace of the Nichols – Herreshoff type a) Rotating hollow shaft for passage of air to hearth; b) Rabble arms connected to shaft; c) Multilevel hearths; d) Beveled gear; e) Motor; f) Drive gear
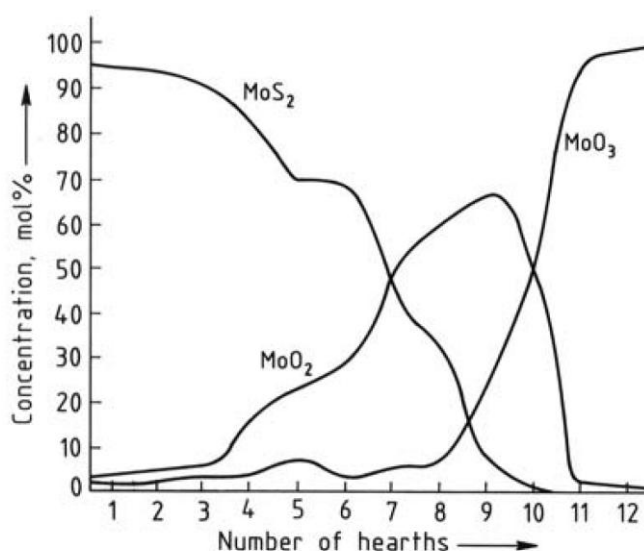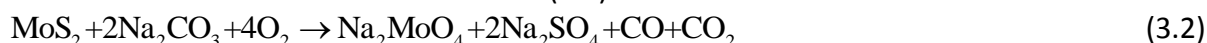
Figure 3-9 Composition of molybdenum sulfide and oxide in multiple-hearth roasting

In order to improve the oxidation efficiency, alkaline additives are possibly used, e.g. sodium carbonate. The main reaction is shown in (3.2):

$$MoS_2 + 2Na_2CO_3 + 4O_2 \rightarrow Na_2MoO_4 + 2Na_2SO_4 + CO + CO_2 \qquad (3.2)$$

In this process, Mo is selectively converted into soluble salt while the emission of SO_2 can be simultaneously eliminated. Usually, higher temperatures than oxidative roasting is used, for instance in the range of 950~1150 ^{o}C during the alkaline assisted roasting [54].

Direct reduction of Molybdenite to metal

In order to reduce MoS_2 into Mo, sulphur acceptors are required and it enables compact-processing for extraction of Mo and at the same time, SO_2 emission can be prevented. The principle reaction is given below:

$$MoS_2 + CaO + (H_2, CO, C) \rightarrow Mo + CaS + (H_2O, CO, CO_2) \qquad (3.3)$$

The reaction temperature is usually between 800~1000 ^{o}C, while the reduction efficiency can be very low with only 40% at 800°C if lime is not used [55]. During the reduction, a number of parallel reactions can be observed with MoO_2 and $CaMoO_4$ as the intermediate products. Additionally carburisation of the metallic product may happen when carbon is used as the reductant (Figure 3-10).
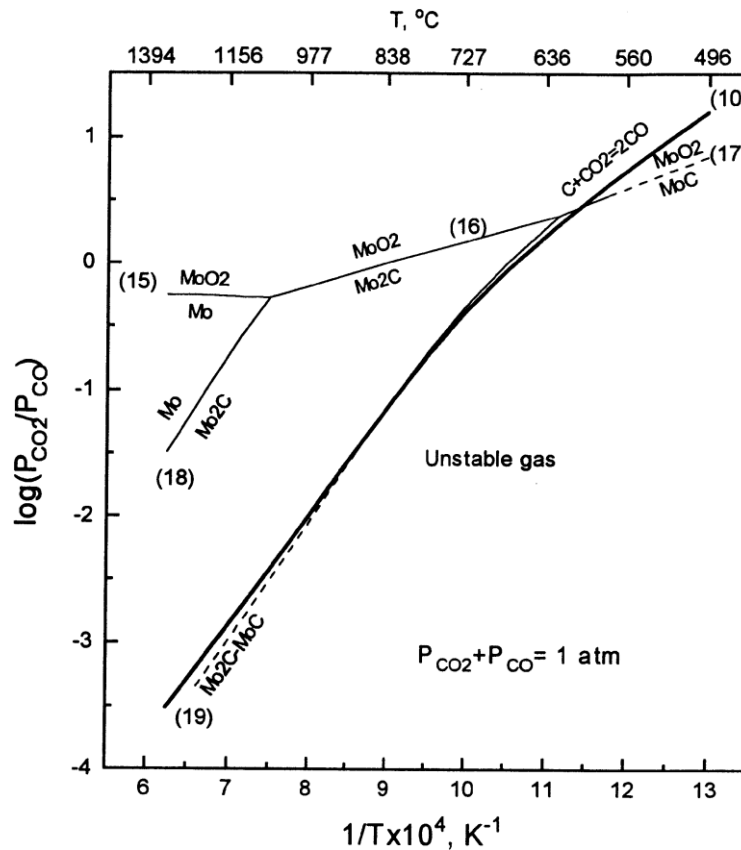
Figure 3-10 Equilibrium gas ratio for the reduction of MoO_2 with carbon

Plasma assisted direct reduction was also investigated. The principle is using a high temperature plasma arc furnace at temperatures above 2000 ^{o}C and ferro-molybdemum alloy could be prepared [56]. However, the large energy consumption and operational difficulties constrain the application of this technology.

Using MoO3 to produce Mo-bearing steels
Adding MoO_3 to steel accounts for the major use of roasted molybdenite concentrate. This is implemented by adding MoO_3 to the charge or the molten bath in the electric arc furnace, to the argon oxygen decarburization (AOD) converter or to the basic oxygen furnace (BOF) in the case of that sufficient C or other reducing agents are present at the time of its addition [57-58]. MoO_3 can be relative easily to be reduced; however, the Mo recovery is sensitive to ways how MoO_3 is to be charged into the furnace/converter[57-58]. This is due to the volatile characteristic of MoO_3 under high temperature condition[59]; the volatilization of MoO_3 will result in the loss of MoO_3 into the dust and lead to a low Mo recovery into the steel. The innovative techniques involve the design of new alloying precursor, by using which the volatilization of MoO_3 can be repressed. One of these techniques is to use "mill scale + MoO_3 +

carbon" as the alloying precursor, and the Mo recovery in this case can reach as high as 98%[60].

Production of Molybdenum Metal Powder

Molybdenum metal powder is produced industrially by reducing high-purity molybdenum compounds (pure molybdic oxide or ammonium molybdate[49-50]) with hydrogen (Figure 3-11). The following compounds are used:

    (1) Molybdenum trioxide, MoO_3 (grey – green powder).
    (2) Ammonium hexamolybdate, $(NH_4)_2Mo_6O_{19}$ (yellow powder).
    (3) Ammonium dimolybdate, $(NH_4)_2Mo_2O_7$ (white powder).

To allow further processing by powder metallurgy, reduction conditions should result in a powder that can be pressed and sintered. Reduction is usually performed in two stages:

    (1) Reduction to MoO_2 (molybdenum red).
    (2) Reduction of MoO_2 to molybdenum metal powder.
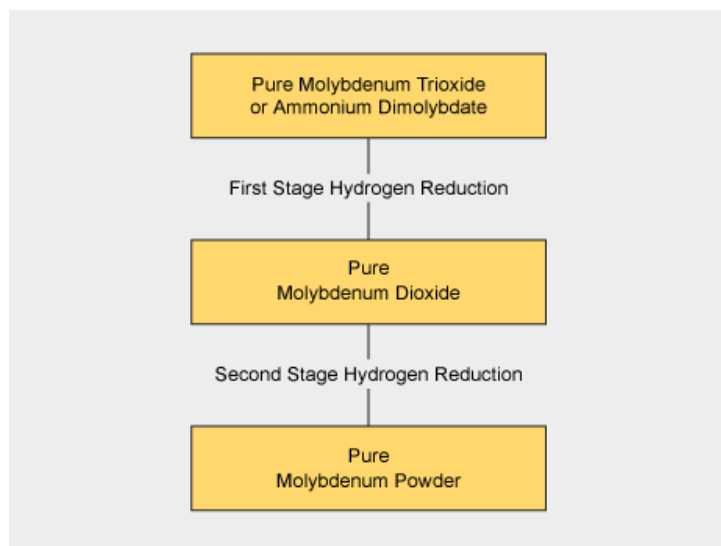

Figure 3-11 Molybdenum metal powder production

This gives satisfactory yields of a completely reduced powder with the desired particle size distribution and a sufficiently high specific surface area in a reasonable length of time. Since reduction to MoO2 is exothermic, this step is performed in the 450-650°C range to prevent caking due to the melting of MoO3 (mp 800 $^{\circ}$C) and to prevent the formation of volatile MoO_3 species. The MoO_2 is reduced to molybdenum powder at ca. 1050 $^{\circ}$C . The powder has a particle size of 2 – 10 mm, a specific surface area of 0.1 – 1 m^2/g, and an oxygen content of 100 – 500 mg/kg (partly adsorbed and partly as oxide).

Reduction is usually performed in an electrically heated continuous furnace (e.g., a pusher furnace, a walking beam furnace, or a rotary kiln) with a counter-flowing stream of hydrogen. Rotary furnaces, where powder is fed continuously through a rotating inclined tube in a flowing hydrogen atmosphere, are becoming common in first stage reduction operations, where they provide increased production efficiencies. Reduction in fluidized-bed reactors is also known. Introduction of impurities should be avoided at all stages. Molybdenum powder 5N5 with an impurity content of ≤ 5 mg/kg can be produced; this figure does not, however, take into consideration gases and refractory metals. Special purification procedures such as multiple recrystallization, ion exchange, solvent extraction and adsorption are used to remove undesirable impurities such as alkali metals, ferrous metals, and radioactive elements from molybdenum to be used in the semiconductor industry. Special mixer linings, furnace linings, and sintering boats prevent contamination with iron and ceramic particles.

Good flow properties and a constant apparent density are critical for satisfactory processing of molybdenum powder in automatic presses. Molybdenum powder is typically mixed with an organic binder, e.g., poly(vinyl alcohol), and a volatile agent, e.g., water. The slurry is sprayed into a heated free-fall chamber where spherical agglomerates are formed due to surface tension. Heating causes vaporization of the volatile agent, giving a hard, densely packed agglomerate (spray-drying process).

Using MoO3 to produce ferromolybdenum (FeMo)

In the steel and foundry industry molybdenum is added to melts, either as technical oxide or in the form of ferromolybdenum. The typical molybdenum content in ferromolybdenum ranges from 55 to 75 %. Compared to pure molybdenum, ferromolybdenum dissolves much more easily in the steel melt and is cheaper to produce. Practical experience has shown that alloys with up to 75% molybdenum do not cause any dissolution problems. Nevertheless there is still a demand for 65% molybdenum alloys which are even less critical as regards dissolution characteristics[53].

Technical-grade molybdenum trioxide is commonly used as the molybdenum raw material. Two principal processes are used for molybdenum oxide reduction: carbothermic reduction in a submerged arc furnace and metallothermic reduction. In the former, the charge materials are a mixture of MoO_3, iron oxide, iron scrap, fluorspar and lime, which needs to be charged in the form of briquettes. This is to minimize the loss of MoO_3 due to its sublimation at the process temperatures. The most commonly applied method is the silicothermic reduction, however, a type of metallothermic reduction[50][61].

Metallothermic reduction in which silicon (or aluminum) is used to reduce the MoO_3 is the commonly used production process for ferromolybdenum. Its advantages are that it is a single-step process which results in a saleable metal and a lowmolybdenum slag and that it requires only basic process equipment. Due to the large difference in the Gibbs free energy for aluminum oxide and silicon dioxide formation compared to molybdenum oxide formation, the

reduction process approaches 100% molybdenum reduction. The resulting FeMo contains ~65-75% molybdenum.

Other innovative FeMo production processes include ferromanganese reduction of molybdenum oxide[50], aluminothermic reduction of calcium molybdate[62], plasma smelting process[64], etc. Recent developments have centered on improving process economics. Automatic handling and weighing of the raw materials as well as finished metal and ferromolybdenum slag is one area of activity. Other activities center around the optimization of ingredient and consumable costs.

SUMMARY OF HYDROMETALLURGICAL PROCESSING

Existing industrial hydrometallurgical routes to recover molybdenum from beneficiation concentrates consists of 1) pressure oxidative leaching (POX) or acidic/alkaline leaching, and 2) precipitation, crystallization, ion exchange or solvent extraction. POX method is becoming more popular due to its environmental friendliness and versatility in treatment of high/low-grade concentrates. Acidic/alkaline leaching methods have been industrially used in India and China for processing low-grade molybdenite and wulfenite concentrates, respectively. Precipitation and crystallization are the most common methods for recovery of ammonium/sodium molybdates. Ion exchange has been industrially used to recover molybdenum from wulfenite in China, and from molybdenite in Russia. Solvent extraction has been applied industrially using common extractants such as amines, hydroxyoximes and organophosphorus derivatives.

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CHAPTER 4 NIOBIUM

MINING AND MINERAL PROCESSING

Niobium and tantalum usually co-occur in the same type of mineral deposits and in minerals of similar characteristics. Mining and mineral Processing of niobium are introduced in Chapter 2 Tantalum.

EXTRACTIVE METALLURGY

Niobium concentrates obtained from naturally occurring sources constitute the primary sources of metal. The metal is also recovered from a variety of other sources, such as tin slags, sludge from the cemented carbide tool industry, mill scrap from alloyed and unalloyed metal fabrication, and scrap from industrial alloys and superalloys. All these latter sources are termed secondary sources and will be dealt with in a separate work package. The primary sources have described adequately in the previous chapter. AII sources, whether primary or secondary, do not find direct usage for any of the industrial applications. Whatever may be the source, the first step for obtaining the metal in any industrially usable form is the chemical processing of the source to extract the metal values and prepare pure compounds such as oxide, fluoride/double fluoride complex, or chloride. These salts then act as the starting materials for producing the metal, its alloys, and compounds. The pyrochlore concentrate obtained after physical beneficiation followed by chemical leaching to remove certain impurities, however, is of the right specification and it can be utilized directly for the production of ferroniobium by aluminothermic reduction process. Ferroniobium thus produced is used as an additive for the steel industry and also as a starting material for producing pure compounds, metal, and its alloys.

Figure 4-1 below shows the flow diagram for the processing of niobium raw materials.
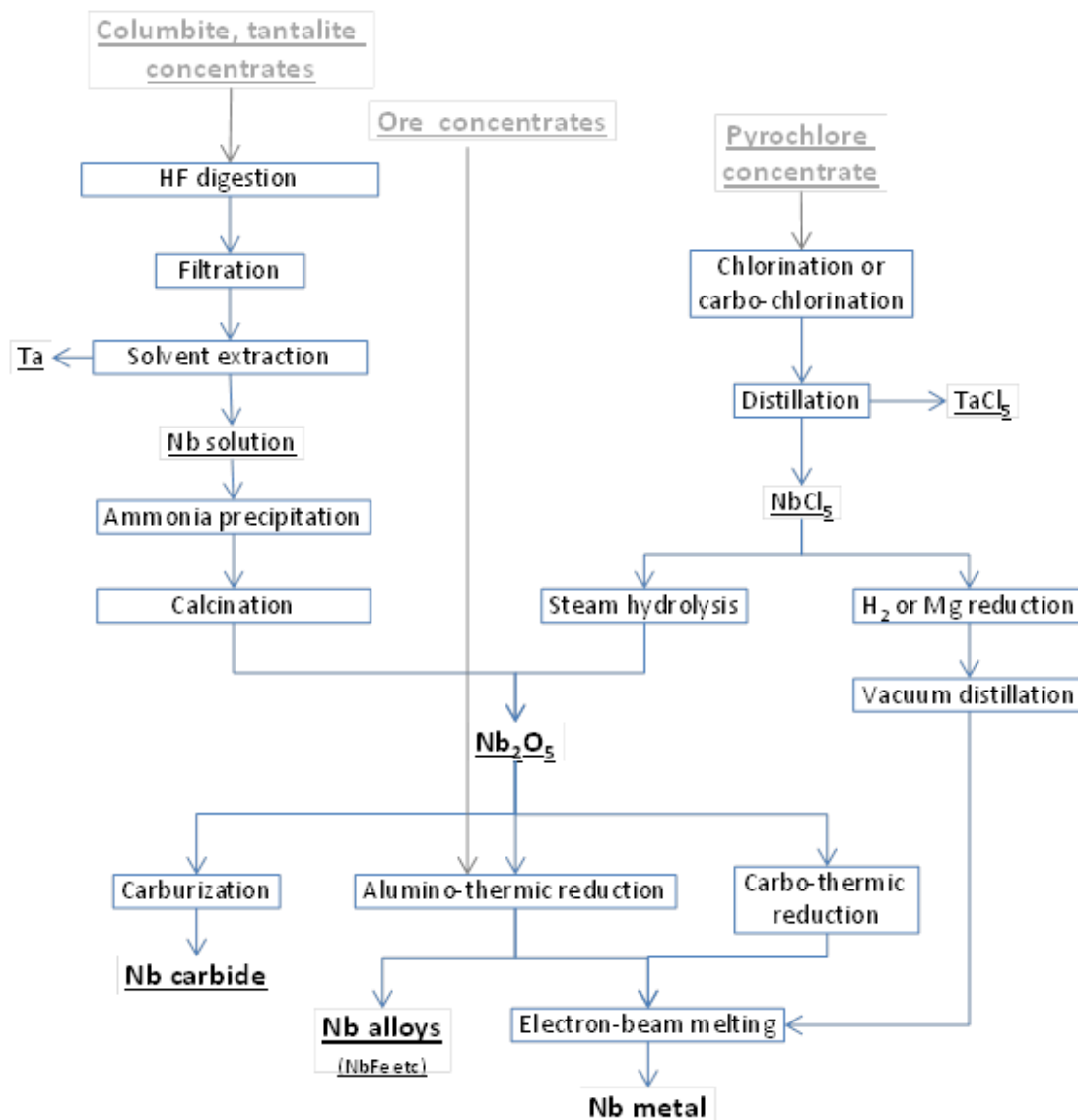
Figure 4-1 Global processing flowsheet for various niobium primary sources

HYDRO-METALLURGY

Niobium and tantalum always occur together in columbites and tantalites and must therefore be separated from each other. A variety of chemical schemes have been suggested and developed for effecting the separation using the differences in physical and/or chemical properties of various species of niobium and tantalum. The industrial separation of tantalum from niobium was historically carried out by the Marignac process of fractional crystallization of potassium heptafluorotantalate and potassium heptafluoroniobate until the 1950s (Ullmann, 2012) but this expensive and environmentally unacceptable process has

been abandoned, together with the long established Fansteel process, in favor of separation processes based on solvent extraction.

A literature review was carried out on the extraction of niobium and tantalum with various reagents by Bhattacharyya and Ganguly (1984). A large number of extractants and their extraction mechanisms are listed with emphasis on the separation of niobium and tantalum from each other. More recently, Zhu (2011) reviewed SX technologies applied to the separation and purification of niobium and tantalum to obtain their pure products by focusing on present industrial practice and recent research.

Tantalite and columbite are digested with a mixture of hydrofluoric and sulfuric acid at elevated temperature to form the complex heptafluorides H_2TaF_7 and H_2NbOF_5 or H_2NbF_7. The accompanying elements (iron, manganese, titanium and various other impurities) are dissolved along with the tantalum and niobium. After filtering off the insoluble fluorides of alkaline earth and rare earth metals, the aqueous solution of Ta–Nb in hydrofluoric acid is extracted with an organic solvent, such as methyl isobutyl ketone (MIBK). A number of alternative extraction media have been reported in the literature, most of which have never been used in industry, except for tributyl phosphate (TBP) and tri-n-octylphosphine oxide (TOPO) (Zhu, 2011). The equipment used consists usually of a series of continuously operated mixer-settlers. The complex fluorides of niobium and tantalum are extracted by the organic phase, whereas most of the impurities and other elements remain in the aqueous phase. The organic phase is washed with concentrated sulfuric acid and then reextracted with water or dilute sulfuric acid to obtain the niobium. Gaseous or aqueous ammonia is added to the aqueous niobium solution to precipitate niobium oxide hydrate. Crystallization of K_2NbF_7 can only be achieved in strong hydrofluoric acid solution; therefore, it is only carried out on a small scale because of the high costs arising from the increased consumption of hydrofluoric acid.
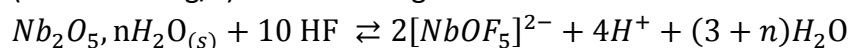
The oxide hydrates are collected by filtration, dried, and calcined at up to 1100°C. Variation of the conditions of precipitation, drying and calcination produces different particle sizes, giving oxides suitable for various applications. Depending on the quality requirements, the calcination is carried out in directly or indirectly heated chamber or rotary furnaces. The nature of the furnace lining has considerable influence on purity.

Sophisticated process control and optimization enable niobium and tantalum to be produced with high yield (> 95%) and purity (> 99.9%).

Ferroniobium as the raw material for high performance steel or super-alloys consumes the most of niobium and is produced industrially from pyrochlore ore, using mainly a pyrometallurgical process. A small portion of niobium with very high purity (% Nb_2O_5 > 99,9 %) is used also in electronics, optics, ceramics and supraconductors and is generally produced as by-product of Ta via an hydrometallurgical process.

Leaching

The first step in the industrial hydrometallurgical process is the extraction of Nb and Ta from high grade Nb and Ta concentrates, after ore and/or pyrometallurgical processing. This extraction was carried out by acid digestion in a mixture of hydrofluoric acid HF with other mineral acids, generally sulfuric acid H_2SO_4. Sulfuric acid lowers the partial pressure of hydrofluoric acid, thereby reducing volatilisation losses and acid consumption. The mineral acid improves also the dissolution process, increasing the Ta and Nb leaching yields. Such mixture is indeed a rare medium, in which Ta and Nb are soluble in high concentrations (several tens g/L). The following reaction is involved:

$$Nb_2O_5, nH_2O_{(s)} + 10\,HF \rightleftarrows 2[NbOF_5]^{2-} + 4H^+ + (3+n)H_2O$$

Crystallisation

The process works quite satisfactorily and relatively easily as far as the preparation of pure tantalum complex K_2TaF_7 is concerned. This is, however, not so for niobium compound preparation in pure form. The mother liquor left after the separation of tantalum not only contains other impurities such as titanium but also some tantalum, which cannot be separated readily. This process is, therefore, not very satisfactory for the preparation of pure niobium complex.

For many years, the commercial technology for separating Ta from Nb involved the selective crystallization of potassium heptafluorotantalate K_2TaF_7 away from potassium oxypentafluoroniobate monohydrate K_2NbOF_5,H_2O, discovered by Marignac in 1866. Indeed, the differences in the chemical and physical properties of newly formed fluoride complexes after dissolution allow the separation of the two elements by addition of KCl, as K_2TaF_7 is ten times less soluble in hydrofluoric acid than K_2NbOF_5,H_2O. After several cycles of crystallisation, this method is excellent for the production of a relatively pure Ta compound. However, the Nb compound obtained was always contaminated by impurities, such as titanium but also tantalum. Therefore, this process is not satisfactory for the synthesis of pure niobium. The following reaction is involved:
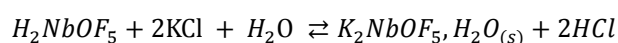
$$H_2NbOF_5 + 2KCl + H_2O \rightleftarrows K_2NbOF_5, H_2O_{(s)} + 2HCl$$

The next figure describes the flowsheet used for the separation of niobium and tantalum by crystallisation. After dissolution of the niobium and tantalum oxides in hydrofluoric acid with a slight excess over the stoichiometric requirement to form the fluoro compounds and precipitation of tantalum by addition of KCl and cooling, the mother liquor, which contains niobium and others impurities, is evaporated and K_2NbOF_5,H_2O is crystallized. Further recrystallisation in HF solution could be involved to purify the niobium salts.
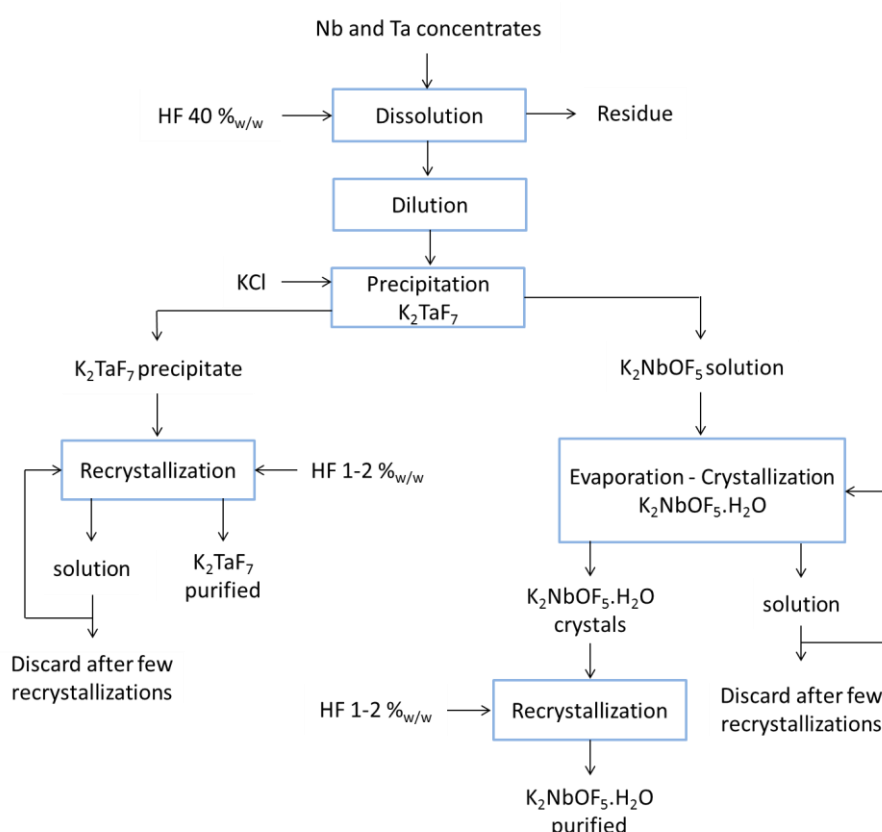
Figure 4-2 Flowsheet of the Marignac process for the Nb and Ta separation by crystallisation

Solvent extraction

The previous method was progressively replaced by a solvent extraction process from fluoride containing solution, which was popularized by the company CBMM in the 80's years. All commercialised solvent extraction process are indeed exclusively operated in the presence of fluoride ions, because of the speciation differences between Nb and Ta in a such medium.

Niobium and tantalum separation by solvent extraction is normally performed in the presence of fluorides, as both metals can form very stable complexes with fluorides, being less prone to form polymeric species in solution. A large number of solvent extraction processes using over 200 combinations of various organic solvents and mineral acids have been investigated for the extraction and separation of niobium and tantalum (Gupta, 1994). These metals are usually present in the aqueous phase as niobates, tantalates, and complex ions, such as fluorides, thiocyanates, and other ions. The stability of these complexes and the tendency to form solvation complexes with the organic extractant depend greatly on the chemistry of the aqueous phase. By varying this, it is entirely feasible to extract selectively either niobium or tantalum or co-extract both niobium and tantalum into the organic phase. The separation of niobium and tantalum in the latter case is then accomplished by selective back extraction/stripping of the desired species. The organic solvents that have shown a

good feasibility for the extraction/separation of niobium and tantalum can be grouped broadly under two categories.
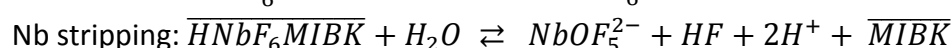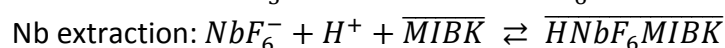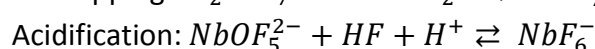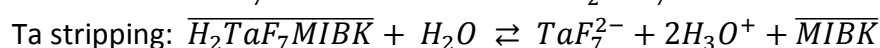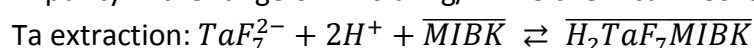
One of the categories includes neutral oxygen-containing extractants, such as ketones, tributyl phosphate (TBP), trioctylphosphine oxide (TOPO), N-oxides, sulfoxides, etc. The anion exchangers, such as trioctylamine (TOA), fall into the other category of extractants. Of all these, only processes based on ketones (MIBK and cyclohexanone), tri-butylphosphate (TBP) and 2-octanol are widely used industrially.

The next few paragraphs briefly provide some characteristics and important features for a few of the organic extractants that have been used for the extraction/separation of niobium and tantalum.

MIBK extractant

Although a lot of extractants have been studied for separating and purifying Nb and Ta , methyl iso-butyl ketone (MIBK) was widely used industrially, despite of several disadvantages, such as its relatively high solubility in water (~2 %$_{v/v}$), its low flash point (14 °C) and its high volatility. However, MIBK is also a not expensive product, has a low density and viscosity and can be purified by steam distillation and recycled through the system.

The key parameter of the solvent extraction by MIBK is the H$^+$ concentration, which controls the degree of separation as well as the recovery of the two metals. Indeed, niobium forms the fluoride complexes $NbOF_5^{2-}$ at low acidity and NbF_6^- at high acidity, whereas tantalum forms TaF_7^{2-} at low acidity and TaF_6^- at high acidity. As the species $NbOF_5^{2-}$ are very few extracted by MIBK, it is possible to separate these two elements. On the other hand, the impurities such as iron, aluminium copper, manganese, calcium and silicon are not extracted and left in the raffinate. Very pure tantalum and niobium products can be obtained with impurity in the range of 1-10 à mg/L. The chemical mechanism is the following:

Ta extraction: $TaF_7^{2-} + 2H^+ + \overline{MIBK} \rightleftarrows \overline{H_2TaF_7MIBK}$

Ta stripping: $\overline{H_2TaF_7MIBK} + H_2O \rightleftarrows TaF_7^{2-} + 2H_3O^+ + \overline{MIBK}$

Acidification: $NbOF_5^{2-} + HF + H^+ \rightleftarrows NbF_6^-$

Nb extraction: $NbF_6^- + H^+ + \overline{MIBK} \rightleftarrows \overline{HNbF_6MIBK}$

Nb stripping: $\overline{HNbF_6MIBK} + H_2O \rightleftarrows NbOF_5^{2-} + HF + 2H^+ + \overline{MIBK}$

An another strategy, which was developed by the Ames Laboratory is to dissolve the Nb/Ta containing metals in a binary acid system, hydrofluoric acid and high concentrated sulfuric acid. The two fluoro Ta and Nb complexes are subsequently extracted, leaving the impurities in the aqueous layer. Niobium is then separated from tantalum by reducing the acidity and is stripped into the aqueous phase. Finally, the Ta fluoride complex is stripped from the organic phase with water.

The final purified products are then recovered by precipitation either with NH$_4$OH in the case of niobium (as the Marignac process). The different chemical reactions involved are the following:

$2H_2NbOF_5 + 10NH_4OH + nH_2O \rightleftarrows Nb_2O_5, nH_2O_{(s)} + 10NH_4F + 7H_2O$
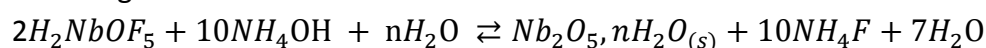
The hydrated Nb oxides can be then dried and calcinated to obtain Nb_2O_5.

The following simplified flowsheet presents the different steps.
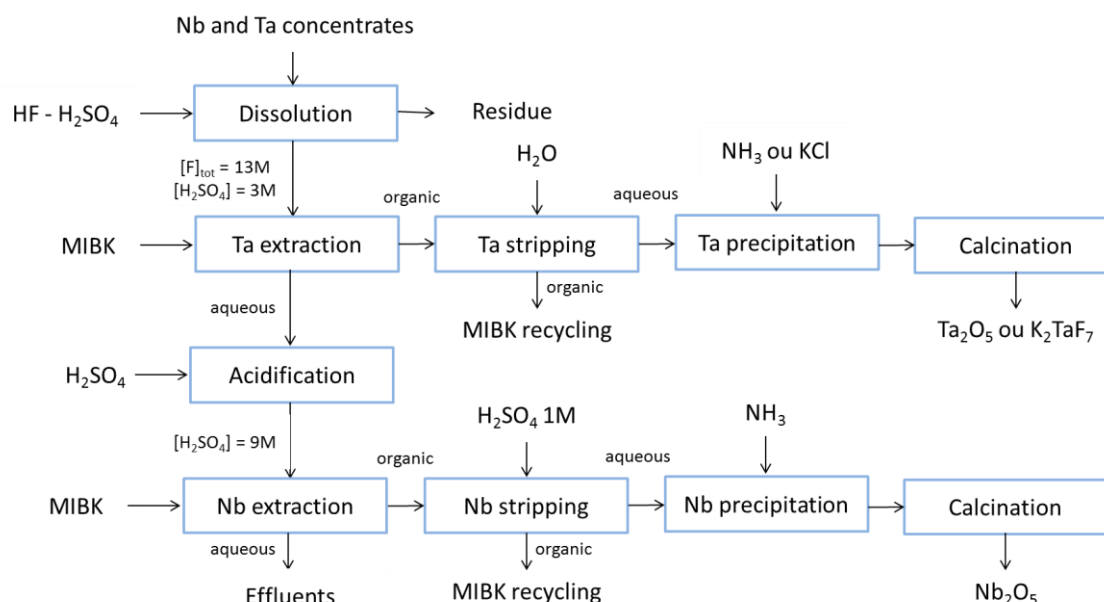

Figure 4-3 Example of flowsheet for the Nb and Ta separation by solvent extraction MIBK

Other extractants

Cyclohexanone (CHO) is rarely reported to be applied for the separation and purification of niobium and tantalum (Gupta, 1994). The extraction of both elements can be achieved in a solution containing 6 M HF and 2.5 M H_2SO_4. Niobium can be stripped with water. Complete selective extraction of tantalum can be achieved from a solution containing approximately 4.75 M H_2SO_4 and 1.5 M ammonium sulphate with the addition of some ammonium fluoride. Co-extracted niobium can be effectively scrubbed with a scrub solution containing 1 M H_2SO_4 and 0.35 M ammonium sulphate. Bulk stripping tantalum can be performed with ammonium fluoride. Separation factors of 10^3–10^4 could be achieved for tantalum over niobium. The advantage of CHO compared with MIBK is the highly efficient extraction of tantalum with low mineral acid concentrations. Most probably because of its very high solubility of approximately 16% in water, CHO is not widely used.

Tri-butyl phosphate (TBP) is another widely used reagent for the separation and purification of niobium and tantalum, particularly in India and Russia (Gupta, 1994; Zhu, 2011). Extraction of niobium and tantalum in TBP goes through the formation of solvated complexes. The extraction is usually accomplished from the fluoride media. Niobium forms several complexes, such as HNbF6·3TBP, H2NbF7·3TBP, HNbOF4·3TBP, and H2NbOF5·3TBP, which depend on the concentration of IIF. The extraction of niobium into the organic phase takes place through the hydration-solvation mechanism. At low acid concentration, there is practically no transfer of niobium into the organic phase, whereas at high acid concentration niobium extraction is highly favored. In fact, the differences in extractabilities of niobium

and tantalum at low concentrations permit efficient separation of niobium and tantalum either at the extraction or at the re-extraction stage, or by combining both. If the aqueous phase contains a considerable amount of tantalum, then tantalum is first extracted into the organic phase, leaving niobium in the aqueous phase, using a low acidity of about 1 M HF and 0.5 M H_2SO_4. The sulfuric acid is added partly to replace HF and also to act as a salting out agent, thereby improving the extraction. If the niobium content is quite high, then the first step is usually the bulk extraction of both niobium and tantalum using a high acidity. Several investigators have suggested various combinations of acid concentrations, such as 6 M HF + 3 M H_2SO_4, 6 M HF + 8 N H_2SO_4, and 12 to 13 M HF + 3 to 4 M H_2SO_4. Niobium is then re-extracted either with water or with dilute HF. After the re-extraction of niobium, tantalum is reextracted with a solution of 5% caustic soda or ammonium fluoride. Alternately, both metals are re-extracted with ammonia to the aqueous phase. Tantalum from the aqueous phase is transferred once again to the organic phase.

An example of the extraction of niobium and tantalum from Indian columbite-tantalite based on the fluoride-TBP system is represented below. The processing scheme utilizes two types of sources, one of which is the concentrate and another a hydrated oxide cake predominantly containing niobium hydroxide (which accumulated during the production of tantalum). About 160 kg of the concentrate or the hydrated oxide cake was leached per day in two batches, each lasting about 6 to 8 h; leaching was carried out with concentrated HF at a temperature of about 80°C. The leach liquor contained 250 g/L of total oxide, with a total acidity of 12 N. The leach liquor was allowed to settle prior to use for solvent extraction using mixer-settlers fabricated out of polymeric material resistant to hydrofluoric acid. The composition of the solution was adjusted to attain a total oxide concentration of about 120 g/L, with a niobium oxide concentration of about 80 g/L and a free acid concentration of 7 N H_2SO_4 and 4 N HF. A three-stage solvent extraction (using an organic to aqueous O/A ratio of 10), followed by a ten-stage scrubbing with a mixture of 7 N H_2SO_4 and 4 N HF was used. Niobium from the organic extract is then stripped with 2 N H_2SO_4 in five stages using an O/A ratio of 5. Niobium from the strip solution is precipitated as hydrated oxide by admitting ammonia gas into the solution. The precipitate is allowed to settle then decanted and centrifuged. It is then washed, filtered, and dried prior to calcination to obtain pure niobium oxide. Analysis shows that less than 0.1 wt% of Ta and other metallic impurities (Ti, Fe, Ni) are present in the final product. The organic extractant, after stripping of niobium, contains practically all the tantalum and some residual niobium. It is then stripped with a 2 N NaOH solution to recover both niobium and tantalum as mixed oxide. The effluents of solvent extraction are treated and disposed of as solid waste.
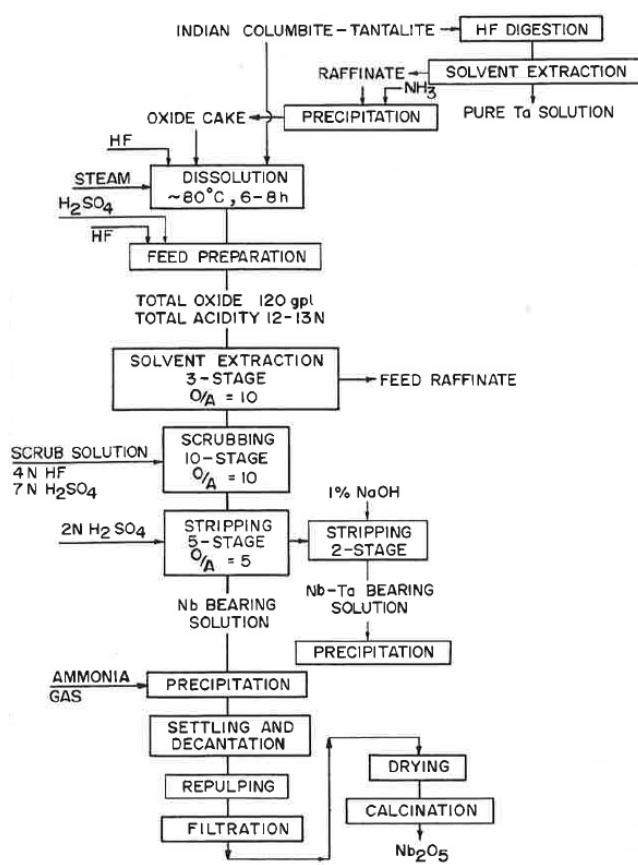
Figure 4-4 Flowsheet for the processing of lndian columbite-tantalite using TBP (Gupta, 1993)

Selective extraction of tantalum with 50% TBP from a feed solution containing a total of 100 g/L Ta_2O_5 and Nb_2O_5 with a Ta_2O_5/Nb_2O_5 ratio of 21:46 (w/w), 0.5 M HF and 1M H_2SO_4 at an A/O of 1:1 was reported (Zhu, 2011). When 90% of tantalum was extracted by the organic phase, only minor niobium was co-extracted. After 2 stages of scrubbing with a scrub solution consisting of 0.5 M HF and 1M H_2SO_4, the niobium concentration was reduced to 250 mg/L in the tantalum-loaded organic solution. Complete niobium extraction from the raffinate containing 5M HF and 4.5M H_2SO_4 was suggested. The extracted niobium and tantalum could be stripped with water or ammonium fluoride solution and pure niobium and tantalum products could be obtained by precipitation.

The separation of niobium and tantalum from impurities such as iron, tin, titanium, manganese and silicon to obtain their pure products was reported to be more efficient with TBP than with MIBK in the HF / H_2SO_4 system and in the pure HF system (Zhu, 2011). In a solution containing 10 M HF and 6 M H_2SO_4, at an A/O of 1:1 with undiluted TBP, the separation factors (SF) of niobium and tantalum over the impurities of concern are very high with a minimum of 6000, suggesting very good separation with this system.

The extraction of niobium from solutions with high concentrations of pure HNO_3, H_2SO_4 and HCl systems using TBP was also investigated (Zhu, 2011). The extraction efficiency was low, which made the industrial application of these systems impossible.

The most important advantages of using TBP as extractant are its very high flash point of 193°C and its low solubility of 0.5% (v/v) in water. However, several drawbacks of TBP confined its wide application. Firstly, TBP is not stable in HF acid system. Secondly, the hydrolysed products of TBP can impair the purity of the final products, and thirdly, the density of TBP of 0.95 is high, resulting in difficulty in phase separation.

Apart from ketones and TBP, other organic solvents that have been used for the separation of niobium and tantalum on a reasonably large scale are listed below (Gupta, 1994):

- A solution containing 3 M $HClO_4$ in the presence of HF, using TOPO as an organic solvent.
- A solution containing 0.01 M HCl, HNO_3, or H_2SO_4 using 4-(5-nonyl)pyridine-N-oxide.
- Petroleum sulfoxides have also been used as extractants from solutions containing about 5 M HF and 5 N H_2SO_4.

Petroleum sulfoxyde extractants are essentially similar to TBP, but with an increased efficiency and charge capacity. These compounds, however, have the disadvantage of high viscosity, which can be circumvented to some extent by dilution with alcohols. Tantalum and niobium from a solution containing about 115 g/L Nb_2O_5, 8.7 g/L Ta_2O_5, 40 g/L HF, and 300 g/L H_2SO_4 have been extracted with petroleum sulfoxide dissolved in C_6-C_8 alcohols. The extracted volume contained 140 g/L Nb_2O_5 and 15 g/L Ta_2O_5. Niobium was recovered by re-extraction with water, whereas tantalum was recovered by re-extraction with 50 g/L of ammonium fluoride.

2-octanol is commercially used for the separation and purification of niobium and tantalum in China (Zhu, 2011). The tantalum and niobium species extracted from the HF/H_2SO_4 binary system with octanol are reported to be $HTaF_6$ and $HNbF_6$, respectively (Agulyansky, 2004). The process consists of the collective extraction of tantalum and niobium (5-7 extraction stages), scrubbing (6-9 stages), niobium stripping (5-7 stages) followed by tantalum stripping (4-6 stages). Sulfuric acid was added to Ta_2O_5 (50-60 g/L) and Nb_2O_5 (30 g/L) solutions in order to obtain the optimal acidity level, which is about 2.5-3.5 M H_2SO_4 for tantalum and 4-5 M for niobium extraction.

As an analogue of 2-octanol, 1-octanol, was also studied extensively for the separation and purification of niobium and tantalum, particularly in Russia (Zhu, 2011). The extraction behavior of 1-OCL is very similar to that of 2-octanol. However, the solubility of 1-octanol is 5% which is much higher than that of 2-octanol of <0.1% (w/w). This is probably the main reason why 2-octanol, instead of 1-octanol, is selected for commercial application.

The extraction of niobium and tantalum by anion exchange type of extractants takes place due to the exchange of complex metal ion in the aqueous phase with that of a correspondingly charged ion in the organic phase. Some of the liquid ion extractants used for

niobium are trioctylamine (TOA), tribenzyl amine (TBA), Amberlite LA-2, and Aliquat 336. Although no commercial application of amines has been found in the niobium and tantalum industry, they have been extensively studied and have the most possible potential for application. Such extractants can be used to extract both niobium and tantalum collectively into the organic phase in the first instance. Subsequently, the re-extraction or back-extraction is carried out selectively to effect the separation. In the case of HF medium, the re-extraction of niobium from organic to aqueous stream can be carried out with 7% HCl, 6 to 10% HNO_3, or l4 % NH_4Cl. Generally, the extraction of tantalum is favored from fluoride media; the extraction of niobium, on the other hand, is favored from HCl acid solutions with acidity of over 4 to 6 M or from solutions containing a high concentration of chloride ions. The extractability also depends on the nature of the diluent used and the chemistry of the aqueous phase. Niobium from chloride media can be extracted into tribenzyl amine TBA phase dissolved in chloroform. Niobium and tantalum have also been extracted as tartarate and oxalate complexesin tri-n-octyl amine and as citrate complex in Aliquat 336.

The main properties of the different commercialized extractants are compared in Table 4-1(Nikolaev and Maiorov, 2007). It should be noted that MIBK is very stable and its cost is much lower than TBP. In terms of operation safety and organic lost in the aqueous phase, TBP and 2-octanol with higher flash point and lower solubility are superior to MIBK. However, in terms of phase separation and stability, TBP with higher density and viscosity and lower stability is inferior to 2-octanol and MIBK. On the basis of physical and chemical properties, 2-octanol should be the best selection for an industrial process and is also reported to be the cost-effective extractant (Zhu, 2011).

Table 4-1 The main properties of the different commercialized extractants

Property	Order
Stability	CHO < TBP < OCL ~ MIBK
Selectivity	MIBK < CHO < OCL < TBP
Extraction properties	OCL ≤ MIBK < CHO < TBP
Water solubility	TBP < OCL < MIBK < CHO
Fire hazard	TBP < OCL < CHO < MIBK
Cost	OCL < CHO < MIBK << TBP

Alkali fusion

In the case of high grade concentrates of columbite-tantalite, alkali fusion coupled with acid leaching was used on an industrial scale in the 30's and 40's years. Either sodium alkalies as $NaOH/Na_2CO_3$ or potassium alkalies as KOH fusion were performed. In the first case, the fused mass was leached with water and afterwards with hydrochloric acid to obtain Nb and Ta oxides. The purer oxides were then separated and purified by the Marignac's process. In the second case, the fusion of the columbite-tantalite at high temperature (800 – 1000 °C) with caustic potash was followed by a leaching with water to solubilize the potassium

niobate and tantalite with some impurities. Nb and Ta were then precipitated by NaCl addition and leached with hydrochloric acid to remove the remaining impurities and convert the sodium complexes into oxides. The next figure resumes this process.
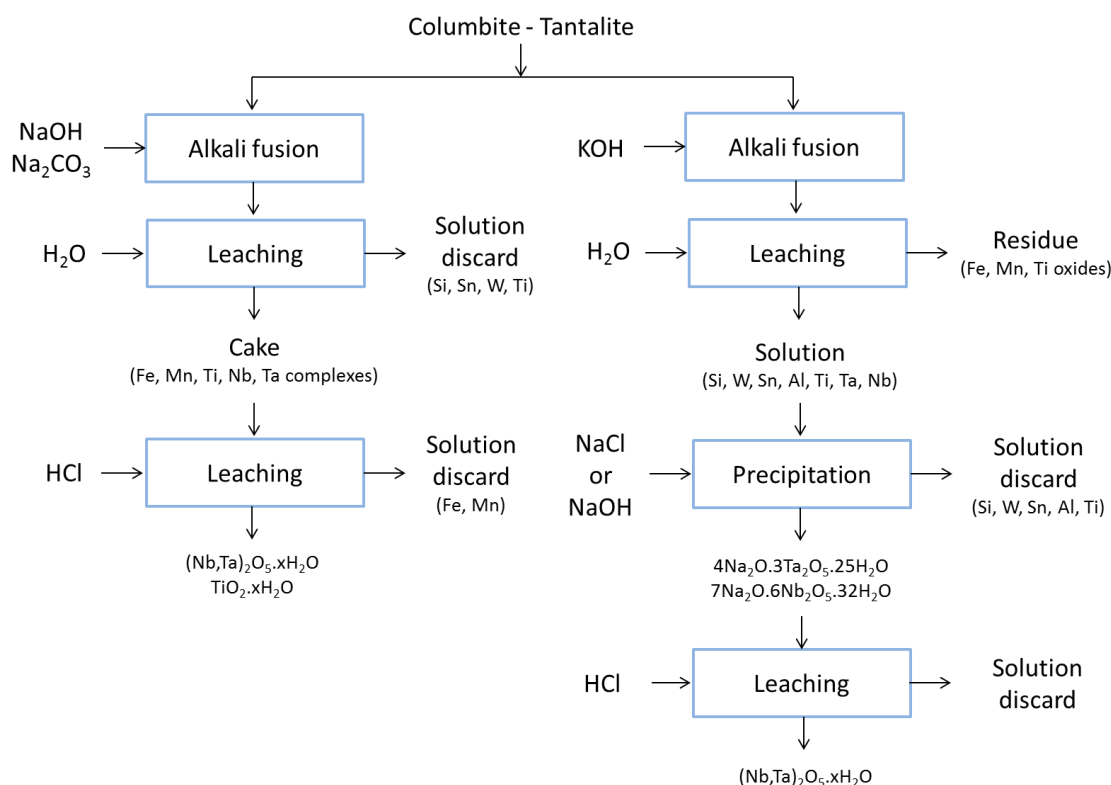

Figure 4-5 Alkali fusion process from columbite - tantalite

PYRO-METALLURGY

Theoretical introduction to pyrometallurgical extraction of Niobium

The two main extraction techniques for Niobium extraction in pyrometallurgy used industrially are reduction and chlorination which main theorical aspects are described here after.

Reduction

One of the simplest methods for breakdown treatment of concentrates of niobium is direct reduction with aluminium and carbon with or without the addition of iron and iron oxides.

Aluminothermy

A reference to the enthalpy and free energy of various compounds indicates that the aluminothermic reduction is highly exothermic and is thermodynamically feasible even at room temperature. During reaction, all the oxides that have free energy of formation less negative than that of alumina are reduced to the metallic state and joins the ferroalloy , whereas others report to the slag phase.

Chemical reactions for Niobium and Iron are described below with their enthalpy:

10 Al° + 3 Nb$_2$O$_5$ = 6 Nb + 5 Al$_2$O$_3$ $\quad$ ΔH°$_{298K}$= -265-269 kJ/mole of aluminium

Fe$_2$O$_3$ + 2 Al° = 2Fe + Al$_2$O$_3$ $\quad\quad$ ΔH°$_{298K}$= -428-438 kJ/mole of aluminium
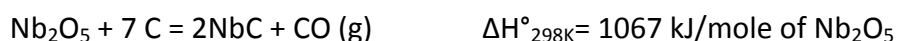
The product from aluminothermy extraction is usually a ferroalloy and especially a ferro-niobium alloy.

These reactions are exothermic as previously said, but the energy produced generally is not enough to supply a good slag-metal separation implying metal losses. That is why an addition of energy can be brought by:

- An addition of hematite Fe$_2$O$_3$ that is reduced by aluminium in the aluminothermic process in converters
- Electric energy in the smelting arc furnace process

Carbothermic reduction

The carbothermic reduction is thermodynamically feasible at high temperatures (generally over 1500°C) and is highly endothermic in nature. Moreover, Niobium reacts with excess carbon and form carbides. Chemical reactions are the following:

Nb$_2$O$_5$ + 7 C = 2NbC + CO (g) $\quad\quad$ ΔH°$_{298K}$= 1067 kJ/mole of Nb$_2$O$_5$

Nb$_2$O$_5$ + 5 C = 2Nb + CO(g) $\quad\quad$ ΔH°$_{298K}$= 1345 kJ/ mole of Nb$_2$O$_5$

Thus the product from carbothermic reduction is an alloy carbide that contains practically all of the niobium and tantalum, together with many other other elements that are present in the starting concentrate.

Carbothermic reduction is usually carried out in smelting electric arc furnace. The reaction product was unvariably a fluid slag and a viscous metal like product. The metallic type of product was allowed to solidify in the furnace after having the slag tapped out. It was finally recovered by scoping out, which then acted as the starting material for the preparation of various pure intermediate compounds.
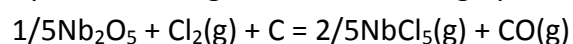
Chlorination

Chlorination as a process for breakdown of ores and concentrates of many of the refractory metals, and even some of the commonly used metal, is very attractive. Important features of chlorination include the high reactivity of chlorine, relative ease in gasifying many of the constituents of the concentrate due to the high volatility of most of the chlorides and high water solubility of most of the chlorides. The chlorides formed can also be separated due to differences of vapor pressures or due to differences in reactivity with oxygen or water vapor and their reducibilities with hydrogen. Thus the chlorination process is suitable not only for the breakdown of the ore concentrate but also for separation/purification of various elements co-occuring in the concentrate and for the reduction to metallic forms.

The general formation of a chloride from an oxide can be represented in a simplified form as:

MO(s) + Cl$_2$(g) = MCl$_2$(g) +1/2O$_2$(g)
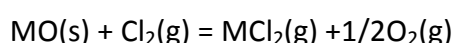
This reaction is thermodynamically feasible for very few oxides, such as CuO, PbO, but not for most of the oxides of refractory metals and especially for Niobium, Tantalum, Titanium, Zirconium.

However, the chlorination reaction, can be readily driven or facilitated in the forward direction by incorporating a reducing agent such as carbon or carbon monoxide as exhibited by the following reaction that is highly feasible at 1000 K thermodynamically:

$1/5Nb_2O_5 + Cl_2(g) + C = 2/5NbCl_5(g) + CO(g)$

There may be a formation of other chlorides or oxichlorides in the chlorination reaction. Some of the possible reactions in the chlorination of Niobium oxide in the presence of carbon can be presented as:

$Nb_2O_5 + 3Cl_2(g) + 3C = 2NbOCl_3(g) + 3CO(g)$
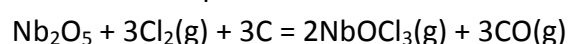
The chlorination product obtained by chlorinating a charge composed of Niobium oxide and carbon is an equimolar mixture of $NbOCl_3$ and $NbCl_5$ at temperatures above 500°C. The proportion of $NbOCl_3$ is high below 500°C. The oxychloride component present in a chlorinated product can be converted to pentachloride by passing it through a porous plug of carbon maintained at a temperature of 400°C.

Many of the associated elements present initially in the treated concentrate also get chlorinated along with Niobium and influence the overall process, they would contaminate the product but also may interfere with the chlorination reaction itself by forming liquid phases or complexes and acting as a trap which adversely influences the desirable results of the chlorination process.

In the case of Niobium the presence of iron is highly indesirable, although ferric chloride is a good chrloridizing agent. It gets reduced by carbon at ferrous state and inhibits further chlorination by forming a coating on the charge material. The issue of iron can be solved by acid leaching of the concentrate before chlorination or with addition of sodium chloride in the charge that form a stable complex $NaFeCl_4$, or CaF_2 that prevent ferric iron to be reduced in ferrous state.

Chlorination that is a solid-gas reaction can be carried out in many types of reactor systems. The most commonly used is fluidized bed types of reactor. The charge for static bed chlorination consists of briquettes of the ore/concentrate and carbon with a binder. The firing/thermal treatment results a porous bonded structure which is readily amenable to chlorination. Briquettes are charged into a bricklined shaft type chlorinator and react with ascending chlorine. Chlorides are then collected in condensers and gas washed in scrubbers. Continuous operations can be carried out in fluid bed reactors where agglomeration is not needed.

In many cases chlorination is exothermic and then just needs an initiation by external heating.

The chlorination of ore/concentrate is usually performed at 750 to 850°C.

Industrial Cases studies in Pyrometallurgy

The three major Fe-Nb producers using pyrometallurgical processes produce it from pyrochlore concentrates and use aluminothermy to reduce Niobium at the metallic state. However, before this step, impurities from pyrochlore concentrate are eliminated by several steps that are detailed in Table 4-2 for the three main Fe-Nb producers.

Table 4-2 Eliminated steps of impurities from pyrochlore concentrate

Company	NIOBEC	CBMM-->1976	CBMM --> 1994	CBMM 2000--> present	CATALAO I	CATALAO II
Production zone	Canada	Brazil	Brazil	Brazil	Brazil	Brazil
Nb2O5 grade in concentrate	51.50%	55-60%			?	
Leaching	HCl	Soda	HCl	None	HCl	Caustic Soda
	P	P,Ca,S			P,Ca,S	
Drying -Roasting	counter current Rotary dryer	rotary kiln at 200°C	rotary kiln at 850°C	agglomeration	Rotary kiln	Rotary kiln
	H2O	H2O	H2O,Pb	S,H2O	H2O	H2O
Dephosophorization	-	-	-	EAF	-	-
Aluminothermic reduction	Converter	Converter	EAF	Converter	Converter	Converter

NIOBEC and CATALAO kept purification processes based on leaching, roasting and aluminothermic reduction in converter. While CBMM made evolve its process in order to eliminate lead by chlorination and finally dephosphorizate it with electrical furnace.

EXTRACTION FROM COLUMBITE-TANTALITE - Carbothermic Reduction-Chlorination

One of the first approach for niobium (and tantalum) from columbite - tantalite was based on breakdown of the concentrate by carbothermic reduction of the concentrate over 1800°C in electric arc furnaces (Figure 4-5).

After this step, impurities such as iron and manganese are generally eliminated by hydrochloric acid leaching, leaving a carbide residue rich in niobium (and tantalum). The residue has been processed in numbers of ways as shows the following flowsheet. It can be treated with HF either directly or after oxidation of the leached product followed by solvent extraction (described in hydrometallurgy part). Or it can be treated by chlorination in order to recover $NbCl_5$ or $TaCl_5$.
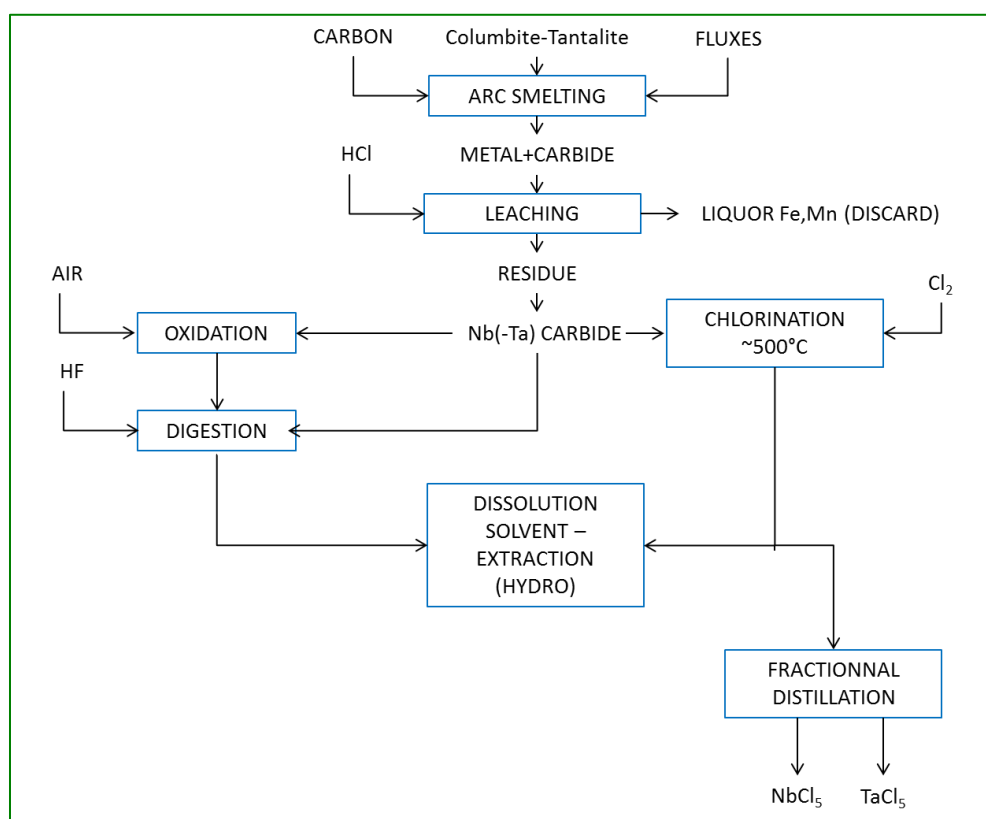
Figure 4-6 Flowhseet of extraction from columbite-tantalite

EXTRACTION FROM OTHER MINERALS: LOPARITE-EUXENITE-Chlorination

In the cases of loparite and euxenite, aqueous processes based on acid leaching result in solutions with complex compositions. The presence of large amounts of titanium in loparite and as well rare earth, uranium and thorium in euxenite makes it rather difficult to accomplish separations. Accordingly, chlorination processes have been developed for the treatment of these two sources.

Loparite

For Loparite from the Commonwealth of Independent states, as showed in the following flowsheet (Figure 4-6), the concentrate is ground, mixed with petroleum coke and a binder and then briquetted, before being coked at 700-800°C to expel volatiles and increase porosity. These briquettes are then chlorinated at 750-850°C in a vertical shaft furnace. This reaction is controlled by the addition of chlorine. Vapors are collected in two condensers: the first one between 160 and 180°C collects niobium, tantalum, iron and aluminium chlorides, and the second titanium and silicon chloride. Vapors coming out the second condenser are scrubbed with lime to fix HCl and chlorines vapors. Rare earths present in the concentrate are recovered as a lquid after chlorination from molten rare earth chlorides, which are non-volatiles at the chlorination.
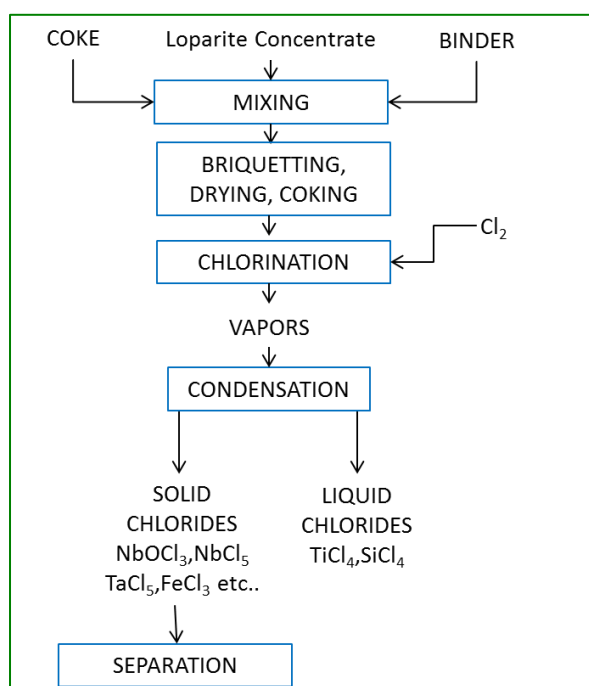
Figure 4-7 Flowhseet of extraction from Loparite

Euxenite

Euxenite concentrate from Bear Valley Idaho contained niobium and tantalum, but also titanium, rare earth, iron, thorium, uranium and impurities such as ZrO_2, CaO,Al_2O_3, SiO_2, MgO,ZrO_2.

The extraction from euxenite implied chlorination with carbon at 500°C with or without addition of sodium chloride, that formed successfully double chloride complex with most of the iron and uranium and also eliminated the adverse effect of ferrous chloride. Uranium and iron can be retained in non volatile fraction, other products are collected: residue of rare earth in the chlorinator, niobium and tantalum chlorides in the first condenser, liquid titanium tetrachloride in second condenser. Gases are finally scrubbed with lime water/caustic soda solution prior to discharge to the atmosphere.

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MINING AND MINERAL PROCESSING

Rhenium is the rarest element in the Earth's crust. Rhenium is probably not found free in nature, but occurs in amounts up to 0.2% in the mineral molybdenite, the major commercial source. Some molybdenum ores contain 0.001% to 0.2% rhenium. Most extracted rhenium is a byproduct of copper mining, with about 80 percent recovered from flue dust during the processing of molybdenite concentrates from porphyry copper deposits [1]. Molybdenite, which commonly contains between 100 and 3,000 parts per million rhenium, is the principal source of rhenium in porphyry copper deposits. Porphyry copper ores typically contain less than 0.5 grams per metric ton rhenium, but rhenium production is feasible because of the large ore tonnage processed (hundreds of millions to billions of metric tons, the presence of sufficient molybdenite to make its recovery economically practical, and the presence of specialized facilities that allow rhenium recovery from molybdenite)[1].

Worldwide mine production of rhenium in 2012 was 52,600 kilograms (kg) and about 27,000 kg were produced from porphyry copper mines in Chile [2]. Molybdenite from porphyry-type deposits of Mo and Cu-Mo ores located in Chile, USA and Peru, where rhenium content is in the range 0.025 to 0.07%, is the most important source of rhenium. Rhenium can be also found as an accompanying element in sedimentary sulfide deposits of copper ores in Kazakhstan, Uzbekistan, Armenia, Russia, Iran, Mongolia, Congo/Kinshasa (Cu-Co ores) and China.

Potential sources of rhenium are:
- volcanic gases in the Kuril Islands,
- oil shale in Russia,
- copper as an accompanying product in nickel production in Russian Norilsk Nickel company,
- uranium ores in the USA and Uzbekistan.
  The highest rhenium content was found in copper ore deposits i.e.:
- in San Manuel, USA (900 ppm),
- on the Copper island, Canada (1000 ppm),
- in Agarak and Kadsharan, Armenia (do 650 ppm).

In a Polish copper concentrates rhenium content is very low and amount to 5 to 20 ppm. It should be pointed out that rhenium is a metal which is not independently produced from primary resources. It is a so called accompanying metal for copper or molybdenum ores and is recovered during their production. Table 5-1 presents main molybdenum mines where rhenium was identified.

Table 5-1 The molybdenum mines where rhenium was identified

Country	Company	Mine	Re in a concentrate ppm
Armenia	Zangezur Copper-Molybdenum Combine	Kadzharan	250
Canada	BHP Billiton	Islan Copper	1000
	Imperial Metals/Japan Group	Huckleberry	500
	Taseko Mines	Gibralatar	50
	Teck Cominco	Highland Valley Copper	300
Chile	Codelco	Chuquicamata	220
		Andina	300
		El Teniente	400
		El Salvador	500
Iran	National Iranian Copper	Sarcheshmeh	650
Kazakhstan	Celtic Resources/Kazatomprom	Shorskoye	320
Mexico	Mexicana de Cobre	La Caridad	400
	Molymex	Maria	300-400
Mongolia	Mongolian/Russian states	Erdenet	500
Peru	SPCC	Toquepala	300-350
		Cuajone	450
Russia	Molibden	Sorsk	250
USA	Asarco	Mission	600
	BHP Billiton	San Manuel	900
	Kennecott	Bingham Canyon	150
	Montana Resources	Butte	150
	Phelps Dodge	Bagdad	250-300
	Phelps Dodge	Sierrita	150-200
	Phelps Dodge	Chino	1000

EXTRACTIVE METALLURGY

Because rhenium is usualy produced as by-product in Mo and Cu processing, or in other words, rhenium is mainly recovered from the secondary resources. The technologies of the pyro and hydrometallurgical processing of rhenium are covered in the work package 3 for secondary resources.

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