1. INTRODUCTION

Tungsten is a metal of superlative properties. The melting point of 3410 °C is the highest of all metals. The density of tungsten is 19.25 g/cm³, which is almost as high as the density of gold. Tungsten has the lowest vapour pressure and the lowest expansion coefficient of all metals. The total consumption of tungsten metal is 40,000 t/year. Best known is the usage of tungsten wire in various lamps. Wires for filaments of household lamps have a diameter of 17 to 45 µm. 3 kg of sintered tungsten will yield 365,000 m of a 24-µm filament corresponding to 500,000 coils for a 40–W lamp. 60 – 70 % of the tungsten metal is further processed to tungsten monocarbide, which is the main constituent of hardmetals. The latter materials are used in a wide range of applications in the industry. Well known are drill bits which are inserted in tools, used in the mining-, oil- and gas industry and in mechanical engineering. Figure 1 shows examples for different high end tungsten carbide tools.

2. MINING AND ORE BENEFICIATION

Tungsten occurs in the ore as tungstates. The minerals of importance are:
- Scheelite, (CaWO₄)
- Wolframite, (Fe,Mn)WO₄
- Ferberite, FeWO₄
- Hünbnerite, MnWO₄

The total mineable reserves are estimated at 4,000,000 t W of which China holds about 40 %. The world’s largest tungsten deposits are summarized in Table 1. Due to low tungsten prices in the mid-eighties, a number of mines throughout the world had to cease production. Among these were Cantung mine, Canada, Pine Creek, USA, Strawberry, USA, Mt. Carabine, Australia, King Island, Australia, Sangdong, South Korea and the mines in Bolivia and Peru. At the end of 2000, the prices for tungsten concentrates rose from 35 US$/mtu to 67 US$/mtu due to a lack of supply of tungsten products from China. During this time, companies saw a possibility, to reopen operations which had been on reserve and maintenance or on reduced production levels. In the forth quarter of 2001, the prices for tungsten products dropped dramatically which led to a sudden stop in reopening of mines or investing into an increased production.

During the past decade China converted from a net exporter of tungsten concentrates and intermediate products to a net importer. This led to a significant increase in tungsten concentrate prices during the past years which despite the critical economic situation remained at a level around 100 US$ /metric ton unit and higher.

Today, Mittersill, Austria; Panasqueira, Portugal; Cantung, Canda; Chojlla, Bolivia; Vostok-2 and Lermontovsky, Russia are the major producing mines outside of China. There is also some small scale mining in South America, Asia and Africa.

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Table 1: Summary of the most important tungsten deposits

<table>
<thead>
<tr>
<th>Deposit (Province)</th>
<th>Region</th>
<th>Tungsten Mineral</th>
<th>W-Content, 1,000t</th>
</tr>
</thead>
<tbody>
<tr>
<td>Verkhne-Kayrakty (Dzhezkazgan Oblast)</td>
<td>CIS</td>
<td>Wolframite / Scheelite</td>
<td>872</td>
</tr>
<tr>
<td>Mactung (Yukon &amp; Northwest Territories)</td>
<td>Canada</td>
<td>Scheelite</td>
<td>617</td>
</tr>
<tr>
<td>Shi-zhu-yuan (Hunan)</td>
<td>China</td>
<td>Scheelite</td>
<td>502</td>
</tr>
<tr>
<td>Tynauz (Kabardino-Balkarien)</td>
<td>CIS</td>
<td>Scheelite</td>
<td>244</td>
</tr>
<tr>
<td>Logtung (Yukon Territory)</td>
<td>Canada</td>
<td>Scheelite</td>
<td>168</td>
</tr>
<tr>
<td>Yangchuling (Jiangxi)</td>
<td>China</td>
<td>Scheelite</td>
<td>160</td>
</tr>
<tr>
<td>Xingluokeng (Fujian)</td>
<td>China</td>
<td>Wolframite / Scheelite</td>
<td>144</td>
</tr>
<tr>
<td>Damingshan (Gaungxi)</td>
<td>China</td>
<td>Wolframite / Scheelite</td>
<td>116</td>
</tr>
<tr>
<td>Vostok-2 (Primorskye)</td>
<td>CIS</td>
<td>Scheelite</td>
<td>102</td>
</tr>
<tr>
<td>Taérgou (Gansu)</td>
<td>China</td>
<td>Scheelite</td>
<td>100</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td><strong>3,025</strong></td>
</tr>
</tbody>
</table>

Mining Operations can be characterised by the mineral type and the production capacity:

**Wolframite Mines:**

The mineral Wolframite is concentrated mainly in vein/stockwork deposits, which occur in China, Bolivia, Peru and the CIS. It is generally associated with sulphides (Pyrite, Pyrrhotite, Arsenopyrite, Chalcopyrite, etc.) and Quartz as main gangue minerals. The occurrence is characterised by aggregates of a few mm to some cm size. Due to the relatively coarse intergrowth of Wolframite with the gangue, density separation is the main concentrating method. Attempts to float Wolframite from the gangue minerals is reported in the literature, but no operation is known, which uses flotation as main concentrating method.

**Small Scale Mining in South America:**

Mining in the Andes of South America is performed by collectives. The main processing steps are crushing and grinding, jigging, optical sorting, tabling and sluicing. The bulk concentrate which consists of Wolframite, Cassiterite, Pyrite and Arsenopyrite is sold to bigger companies where it is upgraded by means of roasting and magnetic separation. At some Bolivian small scale mines, the Bolivian buddle is used for fine particle separation.

**Minera Chollja:**

A significant Bolivian mining site is situated 50 km East of the city of La Paz. It is one of the biggest mines in Bolivia, which still operates on a low level production rate. The Tungsten mineral, which is concentrated in Chollja is Wolframite. Wolframite occurs in quartz veins and is associated with Cassiterite, Arsenopyrite, Pyrrhotite, Pyrite, Fluorite and Chalcopyrite. The maximum capacity of Chollja has been 400,000 t per year. The feed grade reached 0.72 % WO₃. The mine employed 600 workers, with 420 workers working underground and 180 working in the mineral processing plant, mechanical and electrical workshops, supervision, laboratory and administration. With the decline of prices for tungsten concentrates, the mine
reduced the production rate to 15,000 t per year. Machines were sold and the complete fine particles processing plant was dismantled. Today the capacity of the mineral processing plant reaches 8 t/h, the recovery is assumed to reach 64%. The run of mine ore is crushed in a two stage crushing system, consisting of a jaw crusher of the type Kue-Ken 20” x 36” and a short head cone crusher of the type short head 36”. The cone crusher discharge is fed to a triple deck screen with screen openings of 15.8 mm, 9.5 mm and 3 mm. The oversize product is recycled to the cone crusher, the fractions 9.5/15.8 and 3/9.5 are fed to two Bendelary jigs of the size 36” x 36” with three chambers each. The concentrate of the Bendelary jigs is regrind in a 10” x 12” roll crusher. The discharge of the roll crusher is upgraded in a Denver Jig of the size 12”x24”. The final concentrate of the Denver jig reaches a grade of 63% WO₃ and Sn. The middlings of the Bendelary jigs and the rejects from the Denver Jig are regrind in a rod mill. The rod mill discharge is classified with a trommel screen with a screen opening of 3 mm. The coarse fraction is recycled to the mill, the fines of the rod mill and the fines from the crushing stage report to a hydro-classifier, where 4 fractions are produced. To reduce the grade of sulphides in the table concentrate, thin film flotation is performed by adding xanthate and mineral oil to the hydro-classifier. The hydroclassifier discharge is pumped to 4 Deister tables. The hydrophobic sulphides float and are washed with the water to the table middlings and to the tailings. The concentrate of the tables reaches 63 % WO₃ and Sn. The concentrate is dried and stored for further upgrading. The middlings of the tables are pumped to 4 additional Deister tables for recleaning. The concentrate of the recleaner tables is dried for further upgrading, the middlings and the light fraction are rejected to the tailings stream. The dry concentrate is screened into 3 fractions. wolframite, cassiterite, siderite and sulfides are separated by using crossbelt magnetic separators. The wolframite and cassiterite concentrate is transported to La Paz, where the arsenic grade of the concentrate is reduced by roasting.

**Operation Minas de Panasqueira of Beralt Tin and Wolfram S.A.**

This site is situated in Portugal near the city of Fundao. Wolframite occurs in horizontal quartz veins. Wolframite is associated with cassiterite, arsenopyrite, Pyrrhotite, Pyrite, Chalcopyrite. The production rate of the mine reaches 400,000 t of crude ore with an average WO3-Grade of 0.30%. Wolframite occurs in quartz veins which are horizontally oriented. As mining method room and pillar is performed. The run of mine ore is crushed to minus 25 mm. The fraction 25/0.5 mm is treated by means of heavy media separation using a heavy media cyclone. The density of the heavy medium is set to 2.7 g/cm³. The capacity of this separation plant is 120 t/h. The floats are rejected and transported to the coarse tailings dump. The sinks of the heavy media separation plant and the fines of the crushing system are pumped to a 10” Mozley cyclone. Cyclone overflow reports to the slime circuit, the cyclone underflow is classified and dewatered in a rake classifier. The underflow of the rake classifier is further split in a hydro-sizer, whereas the rake classifier underflow is pumped to a 4” Warman cyclone and further treated in the slimes circuit. The fractions of the hydro-sizer report to the pre-concentration stage, which consists of 4 Hercules and 6 Plat-O Tables. The Middlings of the rougher tables are recirculated to the crushing, screening and washing process, the concentrate of the Plat-O tables is upgraded in the slimes circuit. The concentrate of the Hercules tables reports to the final concentrating step, where it is split in the fractions, -1.25 mm and +1.25 mm. The two streams are dewatered in rake classifiers and conditioned in drum conditioners under addition of water, sulphuric acid, diesel and naphtha. The conditioner discharge is fed to James flotation tables. The hydrophobic sulphides float on top of the water film and report to the middlings or tailings. The middlings are recirculated, the tailings report to the copper circuit. The concentrate is re-cleaned on re-flotation tables, dried and upgraded by means of magnetic separation, using crossbelt magnetic separators. The fines of the crushing, screening
and washing process as well as the concentrate of the Plat-O tables is pumped to a 5” Mozley cyclone. The cyclone overflow is thickened. The water is recirculated to the process, the solids are pumped to the tailings pond. The cyclone underflow is concentrated on Bartles-Mozley tables. The rejects of the Bartles-Mozley tables are discharged to the tailings pond, the concentrate is re-cleaned on Plat-O tables. The tailings of the Plat-O tables are pumped to the tailings pond and the middlings are upgraded on Duplex Tables. The concentrate of the Plat-O tables and Duplex tables is pumped to a flotation stage, where sulfides are floated. The rejects of the first cell reports to the copper circuit, the floats of the cells 2 – 4 are pumped to the tailings pond. The rejects from the sulphide flotation stage are further upgraded by means of a second Duplex table. The concentrate of the duplex table is re-cleaned by flotation. The floats are pumped to the tailings pond, the rejects which represent a low grade concentrate of 60 % WO₃ are filtered and dried.

Scheelite Mines:

Scheelite occurs in vein/stockwork, skarn or stratiform deposits. Depending of formation of the deposit, the main gangue minerals are quartz, sulphides, calcite, apatite, fluorite, mica, talc, pyroxenes and amphibolites. Scheelite is very often finely disseminated in the ore, so that flotation is the main concentrating process. In some cases, a combination of density separation and flotation is used. The problem in processing alkali earth metal minerals or the so called salt type minerals is to selectively concentrate the mineral and to depress gangue minerals which have a very similar flotation behaviour as the mineral itself. The main collectors used in the flotation of alkali earth minerals are fatty acids. The collector is chemisorbed on the mineral surface and forms very stable soaps with the alkali earth metal ions, present in the lattice of the mineral. Therefore complicated collector - depressants combinations and process lay-outs have to be found, to achieve acceptable concentrates at reasonable costs. Many of the processes described in patents or papers are not applicable to the industry, because of the high amounts of reagents and costs to produce concentrates. Many of the papers describe processes which were tested in laboratories under ideal conditions using artificial mixtures of minerals as feed material to the flotation cell. New, more selective reagents are not available to the industry, because of the high developing costs and the new legislation which complicates the testing and using of not listed substances. Prior to testing or selling of new substances, extensive test work has to be performed to assess the risk potential for the population and the environment resulting from using of these reagents.

The operation Vostok 2 of the Primorsky Group of Mining Enterprises:

Vostok 2 is a skarn deposit with Scheelite as the tungsten mineral. The average grade of the run of mine ore is 1% WO₃. The main gangue minerals are quartz, calcite, fluorite, apatite, pyrite, arsenopyrite and chalcopyrite. The total capacity of the plant is 480 000 t/year. The maximum throughput of the processing plant is 60 – 65 t/h. The run of mine ore is stored on a stockpile, form where it is transported by trucks to the 3 stage crushing system, consisting of one jaw crusher and two cone crushers. The jaw crusher and the first cone crusher are operated in open circuit, the third crushing stage operates in by-pass with a vibrating screen. The crushed ore is stored in ore bins from where the ore is transported to the grinding system. The grinding system consists of to lines each equipped with one rod mill, operating in open circuit. The rod mill discharge reports to a screw classifier which operates in closed circuit with a ball mill. The overflow of the screw classifier is pumped to screens with an opening of 0.33 mm. The screen overflow is fed to a screw classifier which operates in closed circuit with a ball mill. The screen underflow and the classifier overflow of the second ball mill circuit is pumped to the flotation process. The pulp is conditioned with Aerofloat a
The dithiophosphate collector and sodium silicate. The rougher concentrate of the sulphide rougher is cleaned in 2 cleaning stages. Arsenopyrite is depressed by adding sodium hydrophosphate to the copper rougher. The rejects of the sulphide flotation are pumped to the scheelite rougher. The pH-value is adjusted to 9.8 by adding sodium carbonate. As depressant for gangue minerals sodium silicate is added to the pulp. Prior to the scheelite rougher, oleic acid is added. A bulk concentrate is floated consisting of scheelite, calcite, fluorite and apatite. The rougher concentrate is cleaned in a first cleaning stage. The concentrate of the first cleaner is pumped to a thickener. The thickener underflow reports to a four stage conditioning stage. In the first conditioner, the pulp is heated to 90°C. In the second stage, sodium silicate is added as depressant for the gangue minerals. The temperature of the pulp is reduced in stage 3 and 4 to 30°C. The pulp is diluted with water and recleaned in 2 additional cleaning stages. The Scheelite concentrate has an average grade of 53% WO₃. The WO₃-recovery of the process is given with 85%. The concentrate is filtered, dried, homogenized, packed in big bags and transported to the companies stock which is situated just by the Trans Siberian Railway Line which connects Vladivostok with Moscow. The operation is equipped with a well equipped test laboratory. There are 128 workers in the processing plant. The energy consumption of the processing plant is 11 650 000 kWh per year, which corresponds to a specific energy consumption of 46.6 kWh/t.

To heat the pulp and the processing plant 5 900 000 dm³ of oil are needed every year. The specific consumption of Sodium Carbonate reaches 2.3 kg/t, Sodium silicate is added in concentrations of 7 kg/t. The specific consumption of oleic acid is given with 350 g/t.

To neutralize the pulp aluminium sulfate is added to the pulp. The specific consumption of aluminium sulfate reaches 5.5 kg/t.

The Mining Operation Mittersill of Wolfram Bergbau und Hütten GmbH:

Wolfram Bergbau- operates a scheelite mine near Mittersill in the Province of Salzburg and a conversion plant in Bergla in the southern part of Styria. The mine is located 7 km south of Mittersill, just in the neighbourhood of the National Park Hohe Tauern. All facilities are situated within an environmentally protected area. Operating the mine and the plant at 5 days a week, the capacity of the operation is limited to 400 000 t/year. The mine works 1 shift per day, 5 days a week, and the processing plant operates 3 shifts per day, 5 days a week. Maintenance shut down is 2 – 3 weeks during July and August. The total staff of the operation comprises 75 employees, with 50 workers in the mine and 25 workers in the mill, supervisory staff and maintenance crew included.

The deposit is classified as of stratiform type. The scheelite occurs in volcanic sedimentary sequences. The deposit is divided in two ore-bearing zones. The "Ostfeld" in the eastern part of the deposit was centre of the mining activities from 1975 until 1986. The open pit mine was operated at an altitude of 1700 – 2200 m above sea-level.

The development of the western part of the deposit, the “Westfeld”, started in 1977 and was completed in 1984 with the construction of the three stage crusher station, which is located underground for environmental reasons. The methods used for mining the ore are sublevel caving, sublevel stoping and cut and fill. The mine and the mill are connected by a 3 km long conveyor gallery. The ore is hauled to the processing plant by a conveyor belt system.

The Processing Plant:

The ore which is transported to the mill has a top size of 10 mm. With decreasing ore grades, the throughput of the plant had to be increased to 450 000 t/year. Therefore a forth crushing stage was installed in the plant. A cone crusher operates in closed circuit with a screen. A
product with a d99 of 9 mm is produced and stored in two fine ore bins with an overall capacity of 1,200 t each.

To achieve sufficient liberation of the scheelite, the ore has to be ground to 80% passing 180 μm. The fine ore with a top size of 9 mm is fed to a single stage ball mill. The mill discharge is classified with a vibrating screen. Screen oversize is transported to the ball mill, the fines are pumped to a cyclone. Due to the high density of Scheelite, liberated and floatable Scheelite is concentrated in the cyclone underflow. To prevent overgrinding, the cyclone underflow is classified on vibrating screens. The opening of the screens are 600 μm. The screen overflow is recycled to the ball mill, the cyclone overflow and the fines of the screen flow to the rougher flotation stage. With this installation, which was completed in 2000, the circulating load through the rougher flotation was reduced by 24 t/h. In the rougher flotation, a concentrate with an average grade of 4 – 6% WO₃ is floated. The rougher concentrate is cleaned in 4 cleaning stages. A concentrate with an average grade of 32% WO₃ is produced, the recovery is in the range of 88%. The concentrate is ground in a small stirred ball mill to reduce the top size to a d99 of 100 μm. The ground concentrate is thickened and homogenized in an agitator prior to filtering. The filter cake is filled into big bags, which are transported by trucks to the company’s conversion plant in St. Martin in Styria. The rougher tailings are pumped to a cyclone a classifying unit which separates the particles according to particle size and density. The coarse particles as well as the non-floatable scheelite are concentrated in the cyclone underflow, which is returned to the ball mill for further grinding. The cyclone overflow which represents the final tailings is pumped to the tailings pond which is situated near the little village of Stuhlfelden, approximately 10 km away from the processing plant.

During the first years of operation, the processing plant was faced with the problem of being supplied with ore varying in a wide range of the mineral composition and humidity. Especially high amounts of clay minerals as well as humus caused extreme frothing in the flotation process, which yielded in losses in concentrate grade and recovery. The mineralogical composition of the ore (Table 2) from the open pit mine changed with continued operation towards higher amounts of talc, a natural hydrophobic mineral and carbonates, mainly calcite. This leads to selectivity problems in the flotation process. Laboratory testwork was performed and a modified reagents regime was developed.

Table 2: mineralogical composition of the ores from the open pit and the underground orebody of the Mittersill deposit

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Percentage of minerals in the run of mine ore</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ostfeld weathered rock</td>
</tr>
<tr>
<td>Scheelite</td>
<td>0.7</td>
</tr>
<tr>
<td>Calcite</td>
<td>0.5</td>
</tr>
<tr>
<td>other carbonates</td>
<td>0.5</td>
</tr>
<tr>
<td>Apatite</td>
<td>0.1</td>
</tr>
<tr>
<td>Fluorspar</td>
<td>0.1</td>
</tr>
<tr>
<td>Sulfides</td>
<td>0.2</td>
</tr>
<tr>
<td>Biotite</td>
<td>5.0 – 10.0</td>
</tr>
<tr>
<td>Muscovite</td>
<td>1.0 – 2.0</td>
</tr>
<tr>
<td>Chlorite</td>
<td>2.0 – 3.0</td>
</tr>
<tr>
<td>Talc</td>
<td>2.0</td>
</tr>
<tr>
<td>Garnet</td>
<td>0.1</td>
</tr>
</tbody>
</table>
The problem in the flotation process of salt type minerals also called sparingly soluble minerals are the collectors which should be selectively attached to the surface of the mineral to be concentrated. This group comprises the minerals summarized in table 3.

### Table 3: sparingly soluble minerals

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>scheelite</td>
<td>CaWO₄</td>
</tr>
<tr>
<td>calcite</td>
<td>CaCO₃</td>
</tr>
<tr>
<td>magnesite</td>
<td>MgCO₃</td>
</tr>
<tr>
<td>dolomite</td>
<td>Ca,Mg(CO₃)₂</td>
</tr>
<tr>
<td>apatite</td>
<td>Ca₅F(PO₄)₃</td>
</tr>
<tr>
<td>fluorspar</td>
<td>CaF₂</td>
</tr>
<tr>
<td>baryte</td>
<td>BaCO₃</td>
</tr>
</tbody>
</table>

A characteristic feature of all of these minerals is that they bear ions of the alkaline earth metals in the mineralogical structure. The main collectors used to float these minerals are called oxhydril collectors. A few examples are shown in Table 4. The most important collectors are fatty acids which contain oleic acid, linoleic acid and palmitic acid.

### Table 4: The main collectors used to float the sparingly soluble minerals

<table>
<thead>
<tr>
<th>Collector</th>
<th>Structural Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>fatty acid (carboxylate)</td>
<td>R—C—OH</td>
</tr>
<tr>
<td>alkyl sulfonate</td>
<td>R—S—O Na</td>
</tr>
<tr>
<td>alkyl sulfate</td>
<td>R—O—S—O Na</td>
</tr>
</tbody>
</table>

The collector ions do not exclusively attach to the positively charged Ca²⁺ of the scheelite but also to the Ca- and Mg-bearing minerals which were mentioned before and which are higher concentrated in the ore than the scheelite itself. The collector is chemisorbed on the mineral surface and forms metallic soaps with the ions of the alkaline earth metals. Therefore, the use of diverse depressants and modifiers is a requirement to achieve acceptable concentrates, when two or more of the above mentioned minerals are present in the ore.

Another problem of floating concentrates of acceptable grades is the presence of naturally hydrophobic minerals like talc and molybdenite. They readily float only with frothers present in the flotation pulp.

### 3. METALLURGICAL PROCESSING

The tungsten concentrates received from the mining operations are refined in a combination of hydrometallurgical and pyrometallurgical processes either to tungsten powders or tungsten carbide powders. Depending on the mineralogical form, the process routes to digest the
tungsten minerals can differ substantially. In particular for the treatment of low grade scheelite concentrates, a pre-treatment by a so called “activating” grinding process is performed. This should increase the digestion rate of the tungsten mineral(s). The metallurgical conversion process from tungsten concentrates can be divided in the following stages: calcination; digestion; refining (solution purification); solvent extraction; crystallisation; transforming calcination; reduction and carburisation. The latter step is used to produce the tungsten carbide for special industrial machining tools (Fig. 1).

Fig. 1 Examples for applications of cemented tungsten carbides

During the calcination stage, the flotation reagents which are adsorbed on the mineral surface have to be removed prior to the digestion process. Calcination of the concentrates is performed in rotating calciners at temperatures between 300 – 400°C. Digestion of the tungsten minerals scheelite and wolframite is performed in rotating drum or stirred type autoclaves at temperatures of 190°C – 250°C and pressures between 12 - 26 bar. In the scheelite concentrate refining process, NaCO₃ is added to the autoclave to act as a solvent for scheelite causing the tungstate ion being transformed to water soluble Na₂WO₄ while the Ca-ion of scheelite is precipitated to CaCO₃. In the wolframite process, NaOH is used as solvent instead. During the digestion process impurities such as Mo, Si, Al, F are dissolved and have to be precipitated in several refining stages from the sodium tungstate solution. The reactions and the processes of digestion and refining are shown in Figs. 2 and 3. The transformation of sodium tungstate to ammonium para tungstate is either performed by solvent extraction (Fig. 4) or using an ion exchange process (Fig. 5). The transformation of crystallized ammonium-para-tungstate ((NH₄)₁₀[H₂W₁₂O₄₇].4H₂O) to blue oxide WO₂.₉ occurs by calcination at temperatures between 450 – 650°C while mostly yellow oxide, WO₃ is formed at temperatures between 560 – 850°C. During the transforming calcination process, ammonia gas is stripped off and captured in a scrubber forming ammonia solution which is recirculated to the solvent extraction process. A high temperature reduction process takes place under hydrogen atmosphere to produce the metal. The reduction of tungsten oxide to tungsten powder is performed at temperatures between 800 – 1,100°C. Tungsten powder serves the basis for a wide variety of industrial applications, for example in the lightning or X-Ray technology. Still a much higher percentage of the tungsten powder is further transformed to tungsten carbide powder, forming the raw material for cemented carbide tools. For the production of tungsten carbide powders tungsten powder is intensively


mixed with carbon black and fed to a high temperature conversion process, the **carburization**. The heat treatment process takes place under hydrogen atmosphere in a temperature range of 1.400 – 1.800°C.

**Stage 1:** calcination  
removal of organic flotation reagents from the mineral surface

**Stage 2:** pressure digestion  
digestion in autoclaves  
CaWO₄ + Na₂CO₃ -> Na₂WO₄ + CaCO₃

**Stage 3:** filtration  
Separation of solids and  
Na₂WO₄ – pregnant solution

**Stage 4:** Si-precipitation  
2Na₂SiO₂ + Al₂(SO₄)₃ + 2Na₂CO₃ ->  
Na₂O·Al₂O₃·2SiO₂ + 2CO₂ + 3Na₂SO₄  
Temp. = 80 - 110°C  
pH = 10 - 11

**Stage 5:** filtration  
separation of residue and Na₂WO₄ – pregnant solution

**Stage 6:** Si-precipitation  
Na₂SiO₂ + 2MgSO₄ + Na₂CO₃ ->  
2MgO·SiO₂ + CO₂ + 2Na₂SO₄  
Temp. = 20 - 60°C  
pH = 7 - 8

**Stage 7:** filtration  
separation of residue and Na₂WO₄ – pregnant solution

**Stage 8:** Mo-precipitation  
step 1:  
Na₂MoO₄ + 4Na₂S + 4H₂O ->  
MoS₂° + 10 Na⁺ +8OH⁻  
step 2:  
MoS₂° + 10 Na⁺ +8OH⁻ + 5H₂SO₄ ->  
Mo₂S₃ + 5Na₂SO₄ + 8H₂O + H₂S  
Step 3:  
Polymerisation of tungsten-atom at low pH-values  
12Na₂WO₄ + 7H₂SO₄ ->  
2Na₂H₂W₁₂O₄ · 7Na₂SO₄ + 6H₂O

**Stage 9:** filtration  
Separation of the residue from the Mo-precipitation stage and the Na-Iso-Polytungstate-solution

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Fig. 2 Digestion and refining process for scheelite concentrates.
stage 1: calcination
removal of organics from the mineral surface

stage 2: size reduction

stage 3: pressure digestion
digestion in autoclaves 
Fe,Mn)WO₄ + 2NaOH -> 
Na₂WO₄ + (Fe, Mn)(OH)₂

stage 4: filtration
separation of solids from 
Na₂WO₄ – pregnant solution

stage 5: Si-precipitation
2Na₂SiO₃ + Al₂(SO₄)₃ + 2Na₂CO₃ -> 
Na₂O·Al₂O₃·2SiO₂ + 2CO₂ + 3Na₂SO₄  
Temp. = 60 - 110°C 
pH = 10 - 11

stage 6: filtration
separation of solids from 
Na₂WO₄ – pregnant solution

stage 7: Si-precipitation
Na₂SO₄ + 2MgSO₄ + Na₂CO₃ ->  
2MgO·SiO₂ + CO₂ + 2Na₂SO₄ 
Temp. = 20 - 60°C 
pH = 7 - 8

stage 8: Filtration
separation of solids from 
Na₂WO₄ – pregnant solution

stage 9: Mo-precipitation
step 1: 
Na₂MoO₄ + 4Na₂S + 4H₂O -> 
MoS₂ + 10 Na⁺ +8OH⁻  
step 2:  
MoS₂ + 10 Na⁺ +8OH⁻ + 5H₂SO₄ -> 
MoS₃ + 5Na₂SO₄ + 8H₂O + H₂S  
step 3: 
Polymerisation of the tungstate ion at low pH-values  
12Na₂WO₄ + 7H₂SO₄ ->  
2Na₂H₂WO₄ + 7Na₂SO₄ + 6H₂O

stage 10: filtration
separation of solids from 
Na₂WO₄ – pregnant solution

Fig. 3 Digestion and refining process for wolframite concentrates.
Fig. 4 Solvent extraction process for the transformation of sodium tungstate to ammonium para tungstate (APT).
Fig. 5 Combined ion exchange process for the transformation of tungsten concentrates to ammonium para tungstate.
4. CONCLUSIONS

Although the availability and quality of tungsten ores are limited and the price of the metal greatly fluctuates, its special physical properties and applications pose a reliable demand for production. As ore reserves still constitute the major sources of this metal, the consideration of sustainable mining operations and efficient beneficiation technologies are imperative for assuring satisfactory production. The quality and the costs of producing the metal greatly depends on the efficiency of the concentrating steps performed at the rather limited number of mining sites. The low tungsten content and the interference of the gangue minerals in the ore makes it complicated and costly to provide a suitable concentrate for the metallurgical processing. In order to provide this special metal as a pure powder or a further transformed compound product, it is necessary to combine various special hydrometallurgical steps, implying high pressure digestion in alkaline media, solvent extraction or ion exchange for conversion and calcination, implying also the regeneration of reagent materials. This offers an outstanding example of how important the raw material preparation and metal extraction operations are for the production of high quality metals, metal compounds and high-tech industrial products indispensable for modern technology and society. The special properties exploited in tungsten products are linked to very special mineral processing and metallurgical technologies.