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**State of the art on the recovery of refractory metals from secondary resources**

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## Summary

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

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# STATE OF THE ART ON THE RECOVERY OF REFRACTORY METALS FROM SECONDARY RESOURCES

**MSP-REFRAM D3.2**

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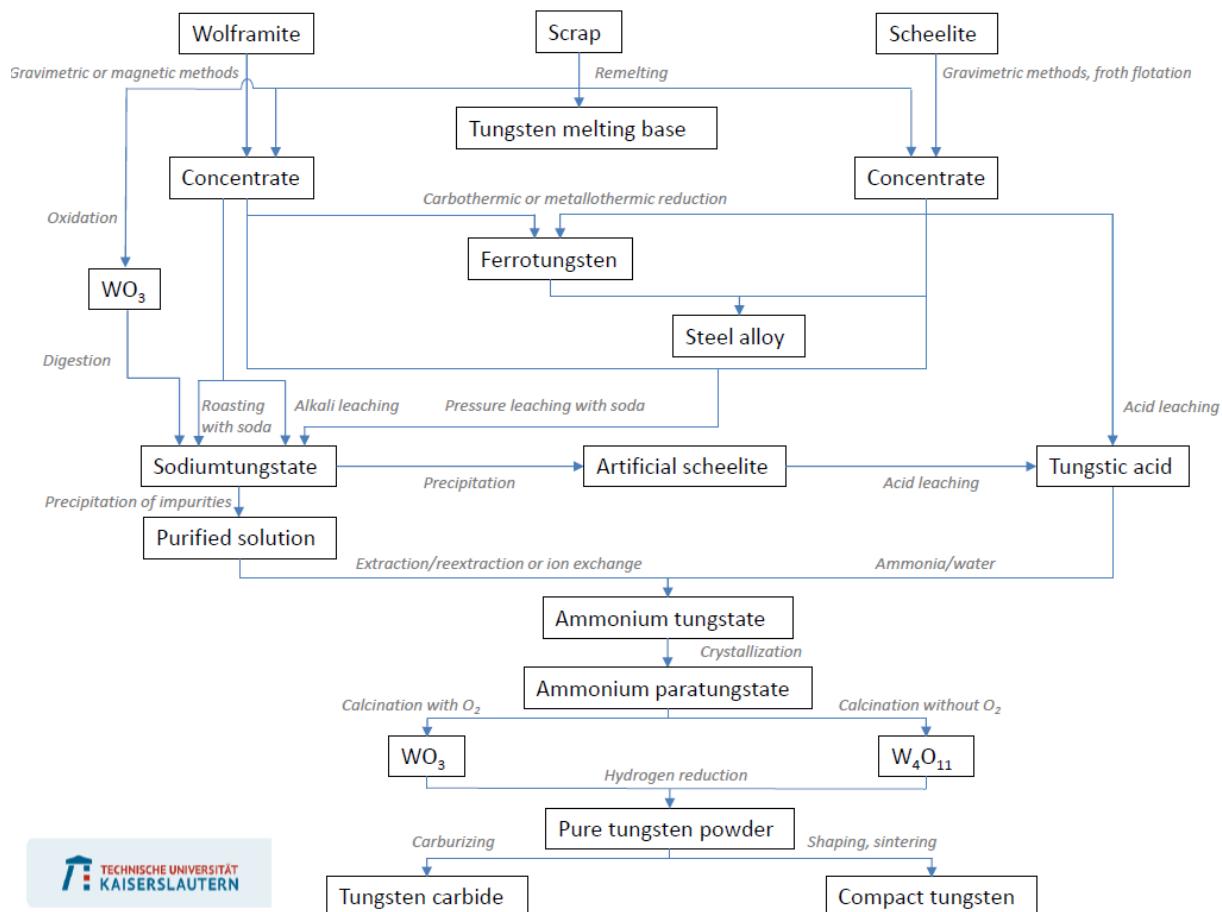
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## CHAPTER 1 TUNGSTEN



**Figure 1-1** General flow chart for tungsten processing/production from primary and secondary resources

### 1 MAPPING OF SECONDARY RESOURCES OF TUNGSTEN

A list of tungsten resources in Europe or possibly available for European production is shown in **Table 1-1**. The W-containing wastes or residues can be possibly found in the places as indicated in **Table 1-1**.

**Table 1-1** List of tungsten mines in Europe.

Mine	Location	Owner	Resource type, reserve and grade	Situation
Wolf Minerals mine	10 km northeast of Plymouth, in Devon Devon, England	Wolf Minerals	Hemerdon ore, wolframite as tungsten mineral. Reserve of 35.7 MT @ 0.18% tungsten and 0.03% tin	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% WO <sub>3</sub> along with 460 t/y tin concentrate. Expected to begin introducing ore into the plant in June 2015.
Los Santos mine	Northern Spain	Almonty Industries		
Barreycopardo tungsten project	Western Spain	Ormonde Mining	27.39 Mt @ 0.26 % WO <sub>3</sub> .	Expected to produce 227 000 tonnes of tungsten per year
La Parilla project	Extremadura region of Southwest Spain	W Resources		Expected to begin production in mid-2016, a production rate of 1200 to 1300 t/y @ grade 66 % WO <sub>3</sub> . Full mine developed in 2017/2018, and target production 5 000 t/y of tungsten.
Panasqueira mine	Covilhã, Castelo Branco, Portugal		Mineralisation includes an oxide-silicate stage consisting of wolframite, cassiterite, arsenopyrite, topaz, muscovite and tourmaline.	An underground mine. 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.
Borralha,	Portugal	Blackheath Resources	0.29 % WO <sub>3</sub>	
Tabuaço	Norte Region, Portugal		2.75 Mt ore @0.57% W	

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As the secondary resources of tungsten are largely generated in the mineral processing process, therefore a general description on the mineral processing wastes is given as the follows.

Mineral processing wastes are referred to in the Resource Conservation and Recovery Act (RCRA) as wastes that are generated during the extraction and beneficiation of ores and minerals. These wastes can be subdivided into a number of categories: waste rock, mill tailings, coal refuse, wash slimes, and spent oil shale.[1] Waste rock and mill tailings from mineral processing could be major secondary sources of metals including tungsten. Large amounts of waste rock are produced from surface mining operations, such as open-pit copper, phosphate, uranium, iron, and taconite mines. Small amounts are generated from underground mining.

Waste rock generally consists of coarse, crushed, or blocky material covering a range of sizes, from very large boulders or blocks to fine sand-size particles and dust. Waste rock is typically removed during mining operations along with overburden and often has little or no practical mineral value. Types of rock included are igneous (granite, rhyolite, quartz, etc.), metamorphic (taconite, schist, hornblende, etc.) and sedimentary (dolomite, limestone, sandstone, oil shale, etc.). It is estimated that approximately 0.9 billion metric tons (1 billion tons) of waste rock are generated each year in the United States.[2]

Mill tailings consist predominantly of extremely fine particles that are rejected from the grinding, screening, or processing of the raw material. Typically, mill tailings range from sand to silt-clay in particle size, depending on the degree of processing needed to recover the ore. The basic mineral processing techniques involved in the milling or concentrating of ore are crushing, then separation by any one or more of the following methods including heavy media separation, gravity separation, froth flotation, or magnetic separation. About 450 million metric tons per year of mill tailings are generated from copper, iron, taconite, lead, and zinc ore concentration processes and uranium refining, as well as other ores, such as barite, feldspar, gold, molybdenum, nickel, and silver which may contain tungsten.[2]

The global mass flow of tungsten in 2010 was reported in the paper.[3] In 2010 in total 102.5 kt tungsten mass was contained in the mined ore, from which 76.9 kt was produced in the tungsten concentrate. In total 30.3 kt  $\text{WO}_3$  was lost in the waste streams, of which 25.6 kt  $\text{WO}_3$  was lost in the mine tailings and 4.7 kt  $\text{WO}_3$  in the processing residues. In 2010 about 24% of the total tungsten production was from the End-of-life scrap. However, the recovery of lost tungsten in the mine tailings and the processing residues has not been statistically reported.

Historical tungsten mine tailings contain slimes (ultrafine grain size), in which tungsten minerals are difficult to be recovered such as in Panasqueira mine (a large tungsten mine) in Portugal. Currently, Panasqueira mining generates almost 100 tonnes of waste-rock per day.

Mineral extraction and processing produce, primarily, two main types of mine tailings, accordingly to its grain size: coarse waste-rock tailings (sterile material) derived from rock blasting and waste-mud tailings from crushing and milling conveyed by pipelines into lagoons (mud dams), amounting to several million tons. In the 1980's Panasqueira mining was generating about 300 tons of waste-rock tailings per day; currently, it is still generating almost 100 tons per day. [4]

In Luanchuan mine in China the tailings of the Molybdenum flotation contain scheelite with 0.143% WO<sub>3</sub>.[5][6] The chemical compositions of the Molybdenum flotation tailings and the particle size distribution and tungsten distributions in the size fractions are shown in **Table 1-2** and **Table 1-3**.

The processing tungsten-bearing dumps and tailings produced from the Barruecopardo tungsten mine in Spain have the data in **Table 1-4**.[7] The material in the western part in this mine has higher tungsten grades of 0.1% WO<sub>3</sub> and with a higher proportion of fine material amenable to direct spiral concentration.

**Table 1-2** The chemical compositions of the molybdenum flotation tailings in Luanchuan mine (wt.%).

	Mo	WO <sub>3</sub>	S	P	As	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>
Ore	0.224	0.148	1.87	0.24	0.059	6.97	43.64	3.95
	CaO	CaCO <sub>3</sub>	MgO	CaF <sub>2</sub>	Cu	Pb	Au (g/t)	Ag (g/t)
	27.06	6.73	1.77	4.76	0.038	0.035	0.96	20.33
Tailings	Mo	WO <sub>3</sub>	S	P	As	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>
	0.02	0.143	0.64	0.18	0.049	6.67	46.88	3.4
	CaO	CaCO <sub>3</sub>	MgO	CaF <sub>2</sub>	Cu	Pb	Au (g/t)	Ag (g/t)
	25.36	5.24	1.46	5.02	0.02	0.024	0.56	6.03

**Table 1-3** Particle size distribution and tungsten distributions in the size fractions.

Size fraction, mm	Weight, %	WO <sub>3</sub> grade, %	WO <sub>3</sub> distribution, %
+0.2	3.96	0.028	0.78
-0.2+0.154	18.35	0.042	5.39
-0.154+0.105	12.55	0.081	7.11
-0.105+0.074	16.47	0.134	15.43
-0.074+0.037	10.07	0.242	17.04
-0.037+0.019	11.87	0.228	18.93
-0.019+0.010	17.58	0.189	23.29
-0.010	9.15	0.188	12.03
<b>Total</b>	100	0.143	100

**Table 1-4** Contents of tungsten in the processing tungsten-bearing dumps and tailings produced from the Barruecopardo tungsten mine.

	Average WO <sub>3</sub> %		Average distribution	
	-1 mm	+1 mm	-1 mm	+1 mm
Tailings	0.093	0.088	73%	27%
Dumps	0.044	0.022	38%	62%

The Bom-Gorhon tungsten ore deposits are located in the Petrovsky-Trans-Baikal area of Chita region in Russia. The Vein deposit contains tungsten mainly in the form of hubnerite (74-95%), the rest is scheelite. From the explored reserves 13.4 thousand tons have relatively high grade (WO<sub>3</sub> 0.917%). The enrichment of Bom-Gorkhon ore by a gravity method resulted in hundred thousand tons of the tailings with WO<sub>3</sub> content from 0.1% to 0.35% were accumulated. Besides the main element (tungsten), there are associated components – bismuth and tin.[8]

Tin tailings in Bolivia contains tungsten (grade of 0.64% WO<sub>3</sub>), and also Cu (grade of 0.84%) and Sn (grade of 0.84%), Tungsten is predominately present in wolframite and tin in cassiterite.[9] In order to effectively utilize industrial wastes, ceramic substrates was successfully prepared by conventional ceramic sintering process using tungsten mine tailings from different production regions in China as the main raw material.[10]

Tailings from Cantung Mine in Canada was reported by North American Tungsten Corporation Ltd.[11] The amount of the material accumulated from 1971-2007 reached 3.7 to 4.1 Mt (short tons) with the grade of 0.29-0.35% WO<sub>3</sub> and 0.24-0.28% Cu.

In La Parrilla mine (a tungsten mine) in Spain[12] 7 Mt of ore was processed, from which some 2 Mm<sup>3</sup> of coarse tailings and 1.2 Mm<sup>3</sup> of slimes were produced during the period 1968-1986 with a grade of 0.28% WO<sub>3</sub> (the assay result with a 1000 kg composite sample collected in 1980-1982). In Los Santos mine (another tungsten mine in Spain) two different kinds of tailings are produced:[13] the coarse rejects from the thickening cyclones and dewatering screens and the fine rejects from the filter press.

In Kolar and Hutt gold fields in India,[14] scheelite is associated with gold mineralization. The old tailing dumps of Kolar including Walker dump and Balaghat dump were tested for recovery of scheelite in 1986. The Walker dumps amounted to 17 tons at 0.18% WO<sub>3</sub>, and the Balaghat dumps to 81 tons at 0.04%.

The tungsten containing waste rock and mill tailings from different sources are listed in **Table 1-5**.

**Table 1-5** The tungsten containing waste rock and mill tailings from different sources.

Source	Company	Location	Grade of WO <sub>3</sub>	Reserve, Mineralogy & Characterization	Ref.
Waste-rock	Almonty Industries	Panasqueira mine, Portugal		Producing 100 t/d Derived from rock blasting, coarse grain size, high content of arsenic in arsenopyrite contained	[4]
waste-mud tailings (slimes)	Almonty Industries	Panasqueira mine, Portugal		Amounting to several million tons; Derived from crushing and milling processes, high content of arsenic; wolframite most below 25 microns in size and associated with a complex mixture	[4]
Mo flotation tailings	China Molybdenum Company Limited	Luanchuan mine in China	0.143%	Scheelite, grain size -0.074 mm 48.7%, over 71% WO <sub>3</sub> distribution in fraction of -0.074 mm	[5-6]
tungsten-bearing dumps	Ormonde Mining	Barruecopardo tungsten mine, Spain	-1 mm: 0.044; +1 mm: 0.022	Grain size distribution: -1 mm 38%, +1 mm 62%	[7]
tungsten-bearing tailings	Ormonde Mining	Barruecopardo tungsten mine, Spain	-1 mm: 0.093%; +1 mm: 0.088%	Grain size distribution: -1 mm 73%, +1 mm 27%	[7]
Milling tailings		Bom-Gorhon tungsten ore deposits, Russia	>0.1%	hundred thousand tons accumulated; hubnerite and scheelite associated components – bismuth and tin	[8]

Tin milling tailings		Bolivia	$\text{WO}_3$ 0.64% (Cu 0.84%, Sn 0.84%)	Wolframite, cassiterite	[9]
Mine Tailings	North American Tungsten Corporation Ltd	Cantung Mine, Western Northwest Territories, Canada	0.29-0.35% $\text{WO}_3$ 0.24-0.28% Cu	accumulated material from 1971-2007: 3.7 to 4.1 Mt	[11]
Coarse tailings and slimes	Tungsten Resources	La Parrila mine, Extremadura region of Southwest Spain	0.28% $\text{WO}_3$	In the period 1968-1986 the 7 Mt of ore processed produced some 2 Mm <sup>3</sup> of coarse tailings and 1.2 Mm <sup>3</sup> of slimes	[12]
Old tailing dumps of Kolar (Walker dump and Balaghat dump)		Kolar and Hutt gold fields in India	scheelite is associated with gold	0.01% - 0.53% $\text{WO}_3$ ; Walker dumps amounting to 17 tons at 0.18% $\text{WO}_3$ , and Balaghat dumps with 81 tons at 0.04% $\text{WO}_3$	[14]
Tailings of coarse rejects (thickening cyclones and dewatering screens)	Almonty Industries	Los Santos mine, Spain	scheelite	2010-2012: 705 kt, 0.14% $\text{WO}_3$ 2012-2013: 216 kt, 0.10% $\text{WO}_3$ 2013-2015: 643 kt, 0.14% $\text{WO}_3$	[13]
Tailings of fine rejects (filter press)	Almonty Industries	Los Santos mine, Spain	scheelite	2010-2012: 309 kt, 0.24% $\text{WO}_3$ 2012-2013: 114 kt, 0.20% $\text{WO}_3$ 2013-2015: 76 kt, 0.14% $\text{WO}_3$	[13]

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## 2 SECONDARY MINING OF TUNGSTEN

### 2.1 MINING OF TUNGSTEN FROM WASTE ROCK AND TAILINGS

Mineral processing wastes including waste rock and mill tailings are referred to major secondary resources of tungsten. Waste rock generally consists of coarse, crushed, or blocky material covering a range of sizes, from very large boulders or blocks to fine sand-size particles and dust. Over billion tons waste rock are generated each year.[1] Mill tailings consist predominantly of extremely fine particles that are rejected from the grinding, screening, or processing of the raw material. Typically, mill tailings range from sand to silt-clay in particle size, depending on the degree of processing needed to recover the ore. About 450 million metric tons per year of mill tailings are generated from various ores concentration processes. [1]

A sonic drill program throughout the summer of 2011 and spring of 2012 at Cantung Mine Site in Canada was conducted by North American Tungsten Corporation Ltd. to explore the possibility of reprocessing unrecovered  $\text{WO}_3$ , Cu and Au from the tailings (Tailings Pond 3).[2] The program was designed to establish the approximate tonnage and grade of the available tailings which were then compared to historical production statistics.

- A total of 25 holes were drilled with a spacing of approximately 200 feet depending on ground conditions.
- Tailings samples were acquired at 5 foot intervals over the entire length of each hole and assayed. In-house assay work along with preliminary metallurgical work was also conducted on site.
- A preliminary block model was constructed using Mine sight software.

The next phase of the tailings reprocessing plant at the Cantung Mine Site in Canada is ready to begin now that the 2011 and 2012 drilling and modeling program have been completed.[2] The tailings reprocessing plant will include baseline flotation test work plus locked cycle flotation tests to determine the feasibility of recovering a marketable concentrate. Magnetic separation, presently used in the production plant flowsheet, will also be evaluated. The program is expected to conclude with off-site testing of a bulk sample, providing necessary scale-up information for commercial processing. In history from 1971 until February 2007, Tailings Pond 3 was the primary storage facility for all underground and surface production. During this period of operation, mill feed graded considerably higher than current feed, leading to significant amounts of  $\text{WO}_3$  being

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discarded as tailings, despite good plant recoveries at the time. The tailings pond has a maximum height of 41 meters, a footprint area of approximately 102 000 square meters and a volume of approximately 2.24 million cubic meters, providing a substantial readily available prospective source of material for reprocessing and resource recovery.[2]

In La Parrilla mine in Spain in late 2009, the coarse tailings dumps were sampled by digging 21 trenches with variable depths between 1 and 5.5 meters. The 20 kg samples were collected at each site and sent for preparation and analysis. In 2010, a detailed survey of the coarse tailings dumps showed a total volume of 1.2 million cubic meters equivalent to 2.5 million tons.[3]

A pilot plant testing is currently being undertaken by ERAL (a Spanish gravity concentration consulting firm) to assess the concentration on the fraction -2 mm tailings existing in the dumps of La Parrilla Mine. The test is carried out at Rio Arimosan facilities where the original La Parrilla material was sieved at -2mm. The testing plant basically consists of the main hopper equipped with belt feeder of variable speed to regulate the dosage, the conveyor belt to feed the spiral plant and the concentration pilot plant with pumping group, hydrocyclone and spiral.

The preliminary test undertaken on some 100 metric tons of tailings sieved to -2 mm showed excellent recovery of the scheelite with a good concentration rate. A second spiral concentration was performed on concentrate from a first spiral passage giving a very good concentrate. A second batch of test was carried out on 500 metric tons of tailings at Rio Arimosan facilities. The material was wet sieved to +4, 4-2 and -2mm and the -60 $\mu$  fraction removed by cycloning. The +4, 4-2 and -60 $\mu$  fractions were sampled for WO<sub>3</sub> and Sn assays before being discarded for metallurgical balance and the fraction of +60 $\mu$ -2mm was treated in the ERAL spiral plant. The tailings dump at La Parrilla Mine is shown in **Figure 1-2**.



**Figure 1-2** Tailings dump at La Parrilla Mine.

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The development of a new process route for ultrafine wolframite recovery was described in [4] to enable the efficient reprocessing of historical mine railings as well as current plant slimes tailings from the Beraltnatut Wolfram operations at Panasqueira mine in Portugal.

In Kolar and Hutt gold fields in India,[5] scheelite is associated with gold mineralization. The old tailing dumps of Kolar including Walker dumps amounting to 17 tons at 0.18% WO<sub>3</sub> and Balaghat dumps with 81 tons at 0.04% WO<sub>3</sub> were processed for recovery of tungsten (scheelite) in 1986. The amenability of these dumps has been tested at Pilot Plant on site to produce scheelite concentrate. It was ascertained that tabling, flotation and magnetic separation processes combine to yield a concentrate of 65% WO<sub>3</sub> from a feed of 0.2% WO<sub>3</sub>. Process programme included: the Rajasthan State Tungsten Development Corporation planed in 1986 to have a concentrator of 100 tpd with gravity, flotation and magnetic separation processes and the Atomic Minerals Division installed a 20 tpd gravity concentrator at Degana.

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## 2.2 MINING OF TUNGSTEN FROM OTHER RESIDUES

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### W-CONTAINING GRINDING SLUDGE/SWARFE

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Grinding processes are commonly used in the forming of metal objects, such as high speed steel and cemented tungsten carbide, to the desired shape, size and sharpness. During these processes extremely fine metal fragments are cut off from the objects being ground. These fragments are called grinding sludge/swarf since the grinding normally is done in a wet way with a liquid water or oil for cooling, for lubrication and/or for corrosion prevention. The grinding sludge/swarf is often a mixture of microscopic fragments of the metal, the grinding media (such as silicon carbide, aluminum oxide, etc.), the solid contaminants and, more often, the cutting oil.[6-7] The sludge/swarf can be reclaimed by a centralized collection and filtration system to get rid of the oil; however, the sludge can still contain approximately 20 wt.% of the oil.[6] Besides the undesired components, the grinding sludge, for example, from high speed steel and cemented tungsten carbide, contains considerable amounts of tungsten, which can be recycled.

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### MILL SCALE

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Mill scale is generated during the continuous casting and rolling mill processes, where steel is subjected to hot working in the oxidant atmosphere. Mill scale has the similar chemical composition of the steel except its oxygen content, and it represents 2% of the amount of the steel produced. In the integrated plants, mill scale is recycled internally as raw materials, for example, at the sintering plant; however in the mini-mills which operate with EAF and where there are no reduction reactors, the mill scale is often sent to landfills.[8] The W-containing mill scale is generated from W-containing steel production. In Brazilian mini-mill

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plant it was reported that the mill scale contained 0.83% tungsten.[8] In Erasteel, Sweden ASP® high speed steels are produced by powder metallurgy through a 3-step process: gas-atomization, hot isostatic pressing and post processing operations such as forging/rolling/drawing.[9] The latter step generates considerable amount of mill scale, and it is estimated that the mill scale contains 1-5% tungsten, which is dependent on the types of the steels.

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### Other residues

The other residues that contain tungsten include steelmaking dust, grinding dust, floor sweeps, etc. The main obstacles for recycling tungsten from these residues lie in that either the tungsten content is too low to be effectively extracted or the residues are too hard to be efficiently and/or economically collected.

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### 3 MINERAL/WASTE PROCESSING OF SECONDARY TUNGSTEN RESOURCES

#### 3.1 MINERAL/WASTE PROCESSING OF TUNGSTEN FROM WASTE ROCK AND TAILINGS

At Panasqueira Mine in Portugal flotation,[1] magnetic separation and gravity concentration testwork, was undertaken at both laboratory and pilot scale on the historical mine tailings and on the current slimes tailings of the plant. In both tailings much of the wolframite is below 25 microns in size and is associated with a complex mixture of other minerals including zinc, copper and other sulphides, tourmaline, siderite, ferromagnetic and other strongly magnetic material. Froth flotation of the Panasqueira wolframite has been investigated over a number of years with very inconsistent results that the current tailings were floated well but the old dam tailings were not floated. High intensity magnetic separation (at low to moderate fields) could not recover the finest wolframite and could not separate the wolframite from siderite and the other strong magnetic minerals present. At higher fields, there was a substantial recovery of the magnetic silicates and consequently poor weight rejection. Gravity separation testwork results indicated that a three stage process with intermediate sulphide flotation could potentially produce a wolframite concentrate of 50% to 55%  $\text{WO}_3$  at a reasonable recovery. Computer simulation also played an integral part in developing the overall process flowsheet and in optimising this flowsheet to maximize recoveries. [1]

The fines recovery process has historically been inefficient and consequently has produced slimes containing an average of 0.3 %  $\text{WO}_3$ . This complex and difficult tailings material, historically untreatable, is now thought more amenable to processing because of recent advances in process technology (e.g., high efficiency slimes gravity separators, new flotation reagents etc.). The problem is that many of the other minerals in the tailings are also of high specific gravity or are strongly paramagnetic with little relative differential between them and the wolframite. The main focus of the development reported here was to find an efficient route to achieve the differential separations needed for the fine sizes that are present. [1]

The containing scheelite tailings of Molybdenum flotation from Luanchuan mine in China was re-concentrated to recover scheelite by flotation in the flowsheet of one rougher (reagents  $\text{Na}_2\text{SiO}_3$ , P-1, T-1 and cyanide added), two scavengers (P-1, T-1 added) and two cleaners flotation. Rough concentrate with grade 1.5%  $\text{WO}_3$ , after thickening and dereagent treatment by heating to 85°C, agitating for 30 min and being diluted, was treated by five-stage high temperature cleaners. The final concentrate with the grade 25-35%  $\text{WO}_3$  and recovery 63% was obtained. [2-3]

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A low-cost operation processing tungsten-bearing dumps and tailings produced from the Barruecopardo tungsten mine has been evaluated. [4] The characterizations of the materials (dumps and tailings) are shown that the percentages of -1 mm and +1 mm fractions are 73% and 23% in the tailings and 38% and 62% in the dumps. For the finer grained tailings with a higher overall grade and importantly a higher proportion of -1mm direct processing through a gravity separation spiral would reduce operating costs (no crushing required) and thereby improve the operating margin.

Tin tailings in Bolivia contain tungsten (grade of 0.64% WO<sub>3</sub>) and also Cu and Sn. The copper mineral is separated from tungsten and tin minerals by chlorination segregation method. After the chlorination segregation flotation, high intensity magnetic separation, gravity separation, were applied and the optimal technological parameters are obtained as follows: the segregation temperature 950 °C, segregation time 45 min, calcium chloride dosage 3%, coke dosage 3%, primary grinding fineness P95 <74 μm, magnetic field intensity of high intensity magnetic separation H=1.0 Tesla, and secondary grinding fineness P95<38 μm. Under the optimal conditions, the copper concentrate with Cu grade of 25.04% at recovery of 83.19%, tungsten concentrate with WO<sub>3</sub> grade of 60.22% at recovery of 64.26%, tin concentrate with Sn grade of 40.11% at recovery of 65.59% were obtained, respectively.[5]The tailings reprocessing plant at the Cantung Mine Site in Canada included baseline flotation test work plus locked cycle flotation tests to determine the feasibility of recovering tungsten to get a marketable concentrate. Magnetic separation, presently used in the production plant flowsheet, was evaluated. The program was expected to conclude with off-site testing of a bulk sample, providing necessary scale up information for commercial processing. [6]

At La Parrilla mine in Spain, [7] the -3mm tailings was processed in 1986 from the current operation consisting in cyclones, spirals, and shaking tables. Tungsten recovery was reported to be of some 70% and Sn some 60%.

In Kolar and Hutti gold fields in India scheelite is associated with gold mineralization. [8] The amenability of the old tailing dumps of Kolar (Walker dump and Balaghat dump) tested at laboratory and Pilot Plant on site to produce scheelite concentrate. Combination of gravity concentration by tabling, flotation and magnetic separation processes was verified to yield a concentrate of 65% WO<sub>3</sub> from a feed of 0.2% WO<sub>3</sub>.

Magnetic separation tests using a Boxmag-Rapid Model LHW laboratory wet high-intensity magnetic separator were carried out on the old dam tailings and the current tailings configured to simulate a plant-scale carousel operation. [9] The feed to these tests was deslimed at 10 microns (quartz equivalent) and scalped at 850 microns. The feed assayed 0.3% WO<sub>3</sub> and 0.21% WO<sub>3</sub> for the old dam and current tailings respectively. The results showed a peak in wolframite grade at around 0.7 Tesla applied field for both tailings

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samples. Wolframite recoveries of around 80 % for the current tailings and around 65 % for the old tailings were possible at applied field strengths of 0.9 Tesla. These recoveries were increased to 90% and 80% respectively by increasing the applied field to 1.6 Tesla. This was accompanied, however, by a significant decrease in product grade, from 1.2% to 0.6%  $\text{WO}_3$  for the current tailing and from 2% to 1.2% for the old tailing as a substantial portion of the magnetic silicates (eg. tourmaline) begins to be recovered as well. The major wolframite loss was in the ultrafines (< 15 micron particles) which are poorly recovered even at the highest field strengths. A clean wolframite/ siderite separation was not possible at any field strength, due to the close and partially overlapping magnetic susceptibility ranges of these materials.

In Tyrnyauz processing plant in Russia [10] minerals (molybdenite, scheelite, fluorite, calcite) of old molybdenum tailings and ore have uniform properties, which allows application of the current technologies of tungsten–molybdenum ore processing. Flotation of old tailings yielded rough molybdenum concentrate with the content of 49.55% Mo at the recovery of 60.2% Mo; Scheelite concentrate produced from tailings of molybdenum circuit contained 54–55%  $\text{WO}_3$  at the recovery of 61.91–62.08%  $\text{WO}_3$ . It is recommended to use jet flotation system for old tailings: initial slurry is separated into 3 flows, for example, rough concentrate of flow 1 is mixed with initial feed of flow 2, rough concentrate of flow 2 is mixed with initial feed of flow 3, rough concentrate of flow 3 is fed for scavenging. It is efficient to use flotation with heat saturated water steam and air mix.

Patented techniques on tungsten containing tailings are:

- A method [11] using tungsten containing material including scheelite concentrate, high-calcium wolframite and its tailings, tungsten slime and refractory low-grade tungsten ore as material in producing tungsten compound. The addition of certain amount of aluminium oxide or aluminium salt and phosphate or oxides of phosphorus, 4-5 times leaching of ammonium paratungstate crystal obtained after the evaporation and crystallization of ammonium tungstate solution with 2-4% ammonium nitrate or ammonium chloride solution, and the precipitation of artificial white calcium tungstate from the ammonium paratungstate mother liquor and leaching liquor by adding ammonia water and sodium sulfide to regulate its basicity and then adding calcium chloride.
- A method [12] relates to a process for recovering tungsten from low grade tungsten-containing tailing (0.04 to 0.08%  $\text{WO}_3$ ). This wet process includes a buffer pool classification, flannel chute roughing, roughing shaker, yurts selection and shaker sweep the election process.
- A method [13] for the processing of tungsten-bearing ores containing sulphides and precious metals. The gold-containing sulphide and tungsten are separated by magnetic

separation. Rough tungsten concentrate is subject to flotation so that high-grade tungsten concentrate is obtained.

Tungsten scrap [14] is a very valuable raw material due to its high tungsten content in comparison to ore. Contaminated cemented carbide scrap, turnings, grindings and powder scrap are oxidized and chemically processed in a way similar to that used for the processing of tungsten ores. In present, cobalt, tantalum and niobium are recovered in separate processing lines. Other tungsten containing scraps and residues might require a modified process.

The sources of various mine tailings and the reprocessing techniques are listed in **Table 1-6**.

**Table 1-6** The sources of various mine tailings and the reprocessing techniques

Source	Mine & location	Mineralogy & Grade	Reprocessing techniques	Ref.
a) Historical mine tailings b) Current plant slimes tailings	Panasqueira Mine Portugal	Most wolframite -25 microns in size and associated with a complex mixture of other minerals including zinc, copper and other sulphides, tourmaline, siderite, ferromagnetic and other strongly magnetic material.	Flotation, magnetic separation and gravity concentration testwork, at both laboratory and pilot scale; Three stage process of gravity separation with intermediate sulphide flotation could potentially produce a wolframite concentrate of 50% to 55% $\text{WO}_3$ , at a reasonable recovery.	[1]
Scheelite containing tailings from Molybdenum flotation	Luanchuan mine, China	Scheelite	Flotation flowsheet: rougher, two scavengers (P-1, T-1 added) and two cleaners. Rough concentrate grade 1.5% $\text{WO}_3$ ;	[2-3]

			The final concentrate grade 25-35% WO <sub>3</sub> , recovery 63%	
Dumps	Barruecopardo tungsten mine, Spain	Scheelite, -1 mm: 0.044; +1 mm: 0.022	Direct processing through a spiral would reduce operating costs (no crushing required) and thereby improve the operating margin.	[4]
Tailings		Scheelite, -1 mm: 0.093%; +1 mm: 0.088%		
Tungsten containing tailings of tin mine	Tin mine in Bolivia	WO <sub>3</sub> grade of 0.64%	Comprehensive process by chlorination segregation (copper mineral separated), flotation, high intensity magnetic separation, and gravity separation. Copper concentrate Cu 25.04% at recovery 83.19%, tungsten concentrate WO <sub>3</sub> 60.22% at recovery 64.26%, tin concentrate Sn 40.11% at recovery 65.59%	[5]
Milling tailings	Cantung Mine Site in Canada	scheelite 0.29-0.35% WO <sub>3</sub> 0.24-0.28% Cu	Magnetic separation, presently used in the production plant flowsheet to be evaluated.	[6]
-3mm tailings from the current operation consisting	La Parrilla mine in Spain		Tungsten recovery was reported to be of some 70% and	[7]

in cyclones, spirals, and shaking tables			Sn some 60%.	
Old tailing dumps	Kolar and Hutt gold fields in India	scheelite is associated with gold mineralization Scheelite content from 0.01% to 0.53% WO <sub>3</sub> . Walker dumps amounting to 17 tons at 0.18% WO <sub>3</sub> , and Balaghat dumps with 81 tons at 0.04% WO <sub>3</sub>	Two dumps were processed for recovery of scheelite. Tabling, flotation and magnetic separation processes combine ascertained to yield a concentrate of 65% WO <sub>3</sub> from a feed of 0.2% WO <sub>3</sub> .	[8]
Old molybdenum mine tailings	Tyrnyauz processing plant, Russia	molybdenite, fluorite, calcite, scheelite	Flotation of old tailings, scheelite concentrate produced from tailings of molybdenum circuit contained 54–55% WO <sub>3</sub> at the recovery of 61.91–62.08% WO <sub>3</sub> .	[10]

### 3.2 MINERAL/WASTE PROCESSING OF TUNGSTEN FROM OTHER RESIDUALS

#### W-CONTAINING GRINDING SLUDGE/SWARF

Oil contained in the grinding sludge/swarf is a major problem for direct use of the grinding sludge/swarf to extract valuable metals, as oil can be explosively burnt and generate undesirable pollutant compounds, for example, in the secondary smelt foundry. Therefore the oil in the sludge/swarf needs to be removed, for example, by the high pressure filter;[14] it is reported that the tolerant oil content from recycling high speed steel grinding swarf is 1-3%. [15-16] Besides the oil content, the non-metallic and phosphorous in the sludge/swarf also needs to be reduced to no more than 5% and 0.03%, respectively, if the sludge/swarf is to be sent for smelting recycling. The removal of the phosphorous may be done by controlling the oil contents and by the water washing process.[16] While, the remove of the non-metallic may be done by gravity concentration and magnetic separation.[15] The cleaned residues can be used in the smelting furnaces, but they have to be briquetted to

make reuse possible. A systematic description of the sludge processing and recycling in general is shown in **Figure 1-3**.



**Figure 1-3** Grinding sludge recycling system.[17]

#### MILL SCALE

The W-containing mill scale normally needs to be crushed or even ground into fines and made into briquettes before it can be charged into the reduction reactor to extract the W. For some oily mill scale, the oil in the mill scale, in some cases, needs to removed, for example, by the vacuum distillation method before it can be used, as the direct use of oily mill scale can result in the emission of volatile organic compounds, including dioxins. [18]

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## 4 Extractive metallurgy for Tungsten from secondary resources

### 4.1 HYDROMETALLURGICAL EXTRACTION OF TUNGSTEN

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

The recycling of tungsten from secondary resources is becoming increasingly important. Additionally, tungsten recycling is less energy intensive than virgin production. The resources

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are manifold and divided into soft scrap (fine particles, powder, dust, timings, sludges, etc.) and hard scrap (scrap pieces from hard metal, heavy metal, WCu etc.). [1-2] The following methods are applied: the oxidized soft scrap is dissolved in concentrated NaOH (40 – 50 %) at 100 – 150 °C or by high-pressure digestion with dilute NaOH.[3-4] Fe and Mn build low soluble hydroxides. Hard metal scrap is treated in the zinc process. [2,5] Additionally, for hard metal scrap, the alkaline melt digestion with a NaNO<sub>2</sub>, NaNO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> salt mixture and air in autoclaves is an interesting and economic method. This melt digestion can also be performed with mixtures of NaOH and NaNO<sub>3</sub> or NaNO<sub>3</sub>, NaNO<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> or NaOH and Na<sub>2</sub>SO<sub>4</sub> and air without autoclaves at atmospheric pressure. After that, the cooled and mechanically crushed molten salt is leached in water, resulting in sodium tungstate solutions, which need to be further purified.

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### 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. The filter residue, especially from scrap material, may contain other valuable metals like Co, Ta, Ni, Cu and Ag. If the concentration of those impurities is too high, the subsequent processing is disturbed. [4]

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 coprecipitated. [3]

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.[3]

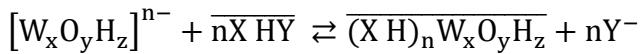
The sodium ion concentration must be reduced from 70 g/l to < 10 mg/l as otherwise problems occur with the reduction to metal powder.[3] This purification step is accompanied by a concentration step of tungsten, which is either done by solvent extraction or ion exchange resins.

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### SOLVENT EXTRACTION

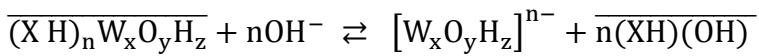
The purified acidic sodium tungstate solution (pH 2 – 3) is contacted with the organic phase.[3] Tertiary or secondary aliphatic amines (e.g. trioctylamine, tricaprylamine) are the most important extractants, although in literature, various other extractants have been tested. [7-9] The extractants are dissolved in kerosene or other aliphatic solvents. Phase

modifiers like isodecanol can be added. The anionic exchange mechanism writes as follows: [9, 10]



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  $[W_6O_{21}H_3]^{3-}$ ,  $[W_{12}O_{42}H_6]^{6-}$  and  $[W_{12}O_{40}H_2]^{6-}$  at pH 2,  $[WO_4]^{2-}$  at pH 7 and  $[WO_6H_2]^{4-}$  at pH 12.<sup>[7]</sup> An extraction efficiency of 99.9 % is reported for the quaternary ammonium salt Aliquat 336 in one stage.<sup>[11]</sup>

The extract is washed with deionized water and reextracted by a dilute ammonia solution into the aqueous phase: [6]



The solvent is regenerated and recycled.

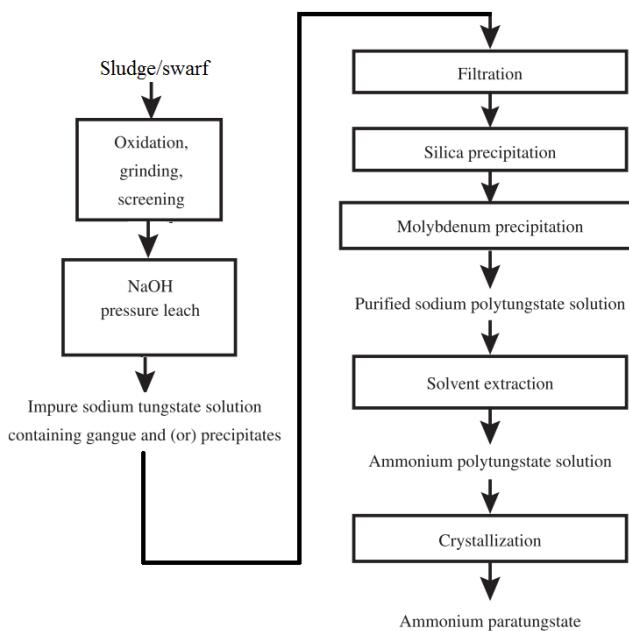
### ION EXCHANGE

Another possibility is an ion exchange resin. [3, 6, 12] Here the sodium tungstate solution is contacted with a strongly alkaline ion exchange resin in the chloride form, 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.

## 4.2 EXTRACTION OF TUNGSTEN FROM OTHER RESIDUALS

### W-CONTAINING GRINDING SLUDGE/SWARF

As shown in **Figure 1-3**, the W-containing grinding sludge/swarf briquette after proper processing can be made into briquettes and be charged into the smelting furnace to produce ferrotungsten or tungsten alloy, in which the tungsten in the scrap is recovered indirectly in the steel in the end. Alternatively, it can be also possible to use a hydrometallurgical process, NaOH pressure leach process, to extract tungsten, since the grinding sludge/swarf is classified as soft tungsten scrap. In this process, the sludge/swarf is dissolved into the NaOH solution and the tungsten is recovered as ammonium paratungstate (APT), which is an important intermediate product for tungsten metal powder and carbide production. The suggested NaOH pressure leach process for tungsten recycling from grinding sludge/swarf is shown in **Figure 1-4**.



**Figure 1-4** Flow sheet for the recovery of tungsten from sludge/swarf by the hydrometallurgical process (revised from [13])

#### MILL SCALE

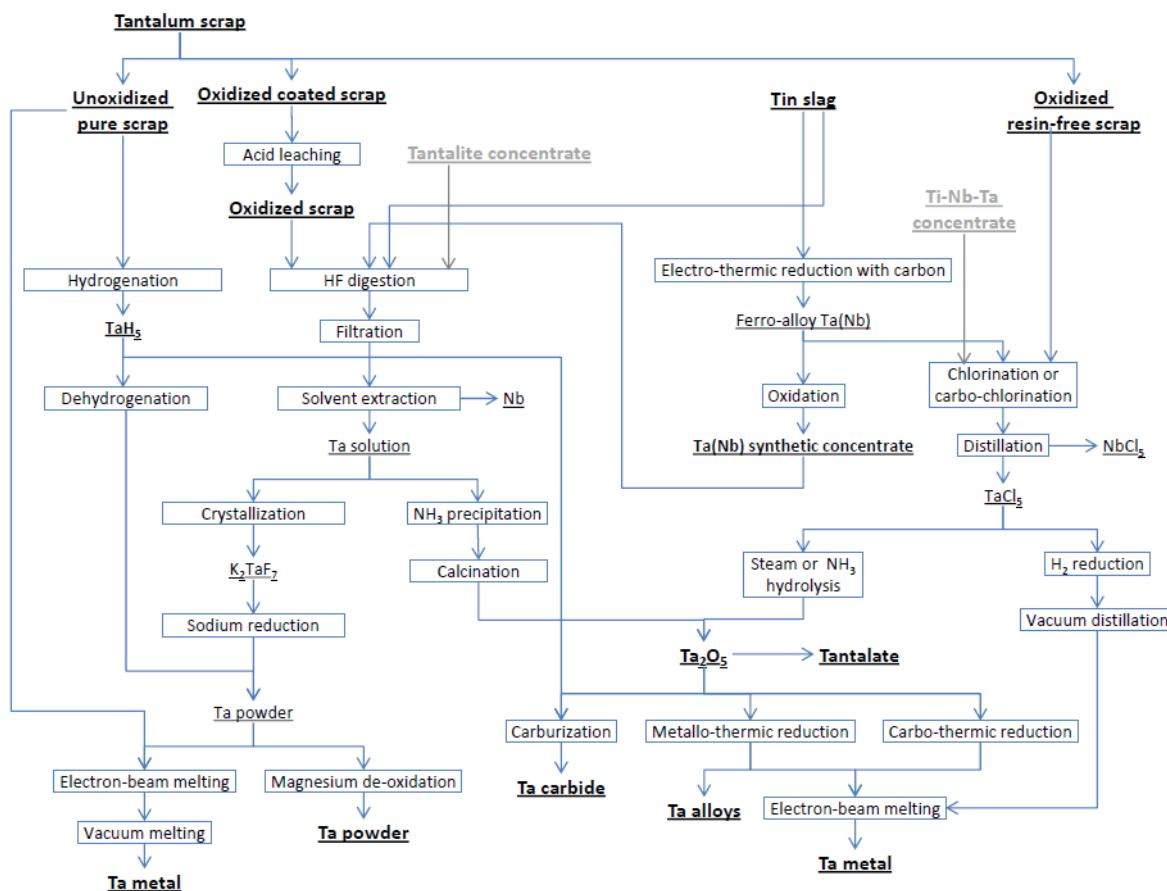
The tungsten in the mill scale can be recovered by reduction and in this case the tungsten content is used directly in the steel. This can be implemented by charging mill scale, for example, into the EAF. Alternatively, the tungsten or tungsten carbide in the mill scale may be recovered by a similar method as shown in **Figure 1-4**, in which the tungsten is recovered as pure material.

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## CHAPTER 2 TANTALUM



**Figure 2-1** General flow chart for tantalum processing/production from primary and secondary resources.

### 1 MAPPING OF SECONDARY RESOURCES OF TANTALUM

Globally, it has been estimated that 10-20 % of the global tantalum supply is produced from tin slags and 20-30% from different types of manufacturing and End-of-Life scrap; according to TIC the production from secondary resources has grown considerably between 2008 and 2012.[1] The best quality slags have been found in Brazil, Thailand and Malaysia, which are most important producers of slag based Ta. Due to reduction of tin mining, the most interesting sources are old slag dumps.

The potential of old tin slags and other waste areas has also been studied in Europe. **Table 2-1** lists some of the identified sources. Based on the available information, potential tailings and slags can be found in Spain, Portugal, France and UK (Tin belt reaching through these countries), but also in Germany and Czech Republic. Tantalum can also be found in waste from uranium mining, which usually contains radioactive thorium. Very little public data

could be found available about the characteristics and Ta potential of the European mine waste areas.

In addition to mine waste areas, Ta can be found also from municipal waste landfills, industrial landfills (such as landfills of WEEE recycling companies) and from incineration slags. It has been estimated that about 5% of WEEE ends up to municipal landfills or incineration plants. Because Ta containing components are mainly used in high-tech electronics, such as portable electronics, it is likely, that the Ta concentrations in MSW landfills and slags are very low.

Other potential sources are scrap from manufacturing of Ta powders and ingots as well as manufacturing of Ta containing products as well as End-of-Life scrap containing Ta. The most important applications of Ta are capacitors and other electronic components, different Ta containing alloys and hard metal, where small percentage of Ta can be used in addition of W. Although for example the largest capacitor manufacturers are situated in USA and Asia, based on Eurostat Prodom statistics there is still considerable manufacture of Ta containing products in Europe. These means that both manufacturing and end-of-life scrap is available in Europe.

A list of secondary resources of tantalum and properties of secondary resources of tantalum are shown in **Table 2-1** and **Table 2-2**, respectively.

**Table 2-1** Secondary resources of tantalum.

Material type	Size of source	Location	Owner	Comments	Ref.
Municipal landfills MSW containing WEEE	Estimated Ta concentration in MSW about 1 mg/kg (12) which is lower than the average concentration of Ta (2.4 mg/kg) in earths crust.	In countries where the share of landfilling has been significant in 2000's	Municipalities	Low concentrations mixed into large amounts of MSW. Very little information and no data about Ta concentrations found.	[2-4]
Disposal areas of incineration slags. MSW incineration slags	~61 000 t/d slags produced in EU, most of the Ta in the incinerator feed ends up to bottom ash	EU countries	Municipalities, energy producers, etc.	Low concentrations, contains other metals, very little information from Europe	[3-5]
Industrial landfills containing waste from WEEE processing	n.a	In several EU countries	Recycling companies		[6]

Tin mining residues tantalite Albite- Amblygonite- Arsenopyrite-Beryl- Blende (Sphalerite)- Cassiterite- Columbite- Covellite-Goethite (limonite)- Muscovite-Pyrite- Quartz-Scorodite- Tantalite- Metatorbernite	Not known, Surface storage areas	Vieiros, Canadelo, Porto Region, Portugal		Closed tin mining area,	[7]
Tailings and waste from tin mining	Tailings 5 Mt and waste dump 6.8 Mt.	Penouta, Spain	Aprovecha miento Mineiro; Strategic Minerals Spain, Planning commerziali zation	Closed tin mining area, tailings and waste studied for recovery of Ta.	[8- 11]
Tin slag	Not known	Golbejas, Salamanca Spain		Tin and Ta mine closed in early 1980s, potential to start mining again has been studied (Goldtech) Waste areas have been at least partly reprocessed in 1980's	[8]
Tailings of china clay extraction	Ta, Nb, Ti and Sn Columbite- tantalite, cassiterite, Nb-Ta-rutile No info on concentration	St Austell, Cornwall		Gravity separation can be used for enrichment of Ta concentrate from fine grained waste	[12]
Mine waste and tailings	Not known Cassiterite- Columbite- Feldspar-Quartz- Tantalite- Wolframite	Bessa, Portugal			[7]
Slag	About 1 000 t of	Söve, Norway		Small quantity, due to	[7][1]

	radioactive slag from Nb production In addition, larger amounts of light waste Apatite-Calcite-Mica, deposited to the sea			radioactivity will be either transported to a waste area or contained	3]
Mine waste	Not available	Echassieres France			[7]
Mine waste	Closed pegmatite mine	Hagendorf, Germany			[7]
Waste from uranium mining	n.a	Straz, Czech republic	n.a		[7]
Mine tailings, pegmatite-granite	Closed Be-Ta mine	Rosendal, Finland			[7]
Scrap from Ta powder and castings manufacturing			Manufacturing industries		[14]
Waste from manufacturing of Ta capacitors, super alloys and alloy products, hardmetal products		Several EU countries	Manufacturing industries	More information about applications in D4.1	[14]
End-of-life waste (capacitors, industrial applications of Ta alloys and superalloys, hard metal products, etc.)		All European countries	Consumers, several industrial sectors, medical sector	More information about applications and EoL-waste in D4.1	

**Table 2-2** Properties of secondary resources of Tantalum.

	Physical Properties		Chemical properties			
Material type	Particle size	Moisture	Main components	Content of W	Impurities and other valuable elements	Ref. No.
Municipal landfills; MSW containing WEEE	Soiled small electronic devices or their components		Capacitors and other electronic components mixed in large amounts of MSW and materials used for daily cover		Mainly organic waste, plastics, fine particles. 3-4 % metals, mainly Al and Fe, smaller amounts of several other metals	[2-4]
MSW incineration slags at disposal areas and earth constructions	Mostly in >2mm particles		Estimated 3-5 mg Ta/kg	Estimate 13->100 mg/kg (12, 13)	Minerals, molten slag, grit, unburnt organics; Fe, Al, Zn, Cu, Ni, minor metals	[3-5]
Industrial landfills containing waste from WEEE processing	Mostly crushed materials, particle sizes from very fine to over 10 cm, may contain also specimens that are not crushed	n.a	n.a	n.a	Plastics, mineral material, base (mainly Fe, Cu, Al, Zn), precious and critical metals	[6]
Vieiros, Canadelo, Porto Region, Portugal: Tin mining residues tantalite	n.a	n.a	Ta concentrations not available	n.a		[7]
Penouta, Spain: Tailings and waste from tin mining	n.a		Tailings 48 g/t; Waste dump 27 g/t	n.a	Tailings 390g Sn/t; Waste dump 29 g Nb/t, 460 g Sn/t	[8-11]
Golbejas, Salamanca Spain: Tin slag	n.a	n.a	n.a	n.a	n.a	[8]
St Austell, Cornwall	Fine particles		Several locations		Nb, Ti, Sn	[12]

Tailings of china clay extraction						
Bessa, Portugal: Mine waste and tailings	n.a	n.a	n.a	n.a	n.a	[7]
Söve, Norway: Slag	n.a	n.a	Containing Ta (1.34 % Ta <sub>2</sub> O <sub>5</sub> ), Th, Zircon;		Radioactive containing Th and Zircon	[7] [13]
Echassieres France: Mine waste	n.a	n.a	n.a	n.a		[7]
Hagendorf, Germany: Mine waste	n.a	n.a	n.a	n.a	n.a	[7]
Straz, Czech republic: Waste from Uranium mining	n.a	n.a	n.a	n.a	Radioactive	[7]
Rosendal, Finland; Mine-tailings, pegmatite-granite				Li-Nb-Ta	REE, Sn, Zr	[7]
Scrap from Ta powder and castings manufacturing			More information D4.1			[14]
Waste from manufacturing of Ta capacitors, super alloys and alloy products, hardmetal products			More information D4.1			[14]
End-of-life waste (capacitors, industrial applications of Ta alloys and superalloys, hardmetal products, etc.)			More information D4.1			D4.1

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## 2 SECONDARY MINING OF TANTALUM

Potential secondary sources of Ta include tin slags and tailings from production uranium, china clays, lithium, beryllium, etc. In addition, Ta can be found from industrial landfills, incineration bottom and fly ashes, however mostly the concentrations may be too low for economic beneficiation. Recovery of Ta from End-of-life waste and manufacturing residues is discussed in Deliverable 4.

For most of these sources the treatment sequences do not differ considerably from treatment of primary ores.

### 3.1 MUNICIPAL AND INDUSTRIAL LANDFILL WASTE

The knowledge about recovery potential of scarce and precious metals from landfills is still quite limited. Based on the references found, it can be estimated that the concentrations at MSW landfills are usually so low that recovery of Ta alone is not feasible. The concentrations may be higher in countries where the collection of electronics has not been well organised and particularly on some industrial landfills containing waste from electronics separation processes. [1] It is also possible that if other metals and materials are beneficiated, the recovery of components containing Ta is also feasible.

Landfill mining is planned through investigation and characterisation of the waste material, which is as important as the case of mining of natural resources. The composition of the materials may vary significantly even at the same landfill. In addition of conventional sampling methods (boring and excavation) the suitability of non-destructive geophysical methods has been studied. They can be used as a first investigation stage giving more information about the structure and properties of the landfill. Based on them the sampling can be directed to the most potential areas inside the landfill.

The next stages are excavation and mechanical treatment of the waste material for separation and concentration of different types of materials. The high concentration of fines and moisture of the material are challenges at municipal landfills. In many cases it may be feasible to perform at least the first separation steps at the landfill and transport the materials to different locations for further treatment. The first stages include crushing and separation of fines from larger particle using e.g. rotary screen. The valuable materials in the coarser fraction will be further separated and concentrated. Typical methods include magnetic, density and ballistic separation methods, in some cases also eddy current.

### 3.2 INCINERATION BOTTOM ASH

Processing and recovery of metals from incineration bottom ash resembles in many aspects processing of ores. Typically the bottom ash includes both different sizes of metal pieces and particles as well metals that are chemically bonded. Because of better economic feasibility the target is usually to separate only metallic particles.

Usually the slag is treated at the incineration plant. The treatment plants may be mobile and serve several incinerators. Before treatment slag needs to be stored at least one day for integration of CO<sub>2</sub> and to make it less wet and sticky. Metal pieces and particles are separated by several mechanical processing stages.[2] The basic processes are sieving (bar-sizer and/or trammel sieve for coarse classification, vibrating screen, star screens), crushing and mechanical separation (magnetic, eddy current). Sensor separators can also be used for identification of specific metals. If the target is also separate recovery of specific valuable metals, hand picking of e.g. capacitors from the metal flow may be a viable alternative, although in many cases not cost-effective.

### 3.3 TIN SLAGS AND SILT-LIKE TAILINGS

No information about in-situ treatment of tin slags and silt-like tailings for recovery of Ta was found. Due to the stability of Ta strong chemical digestion or electro-thermic reduction is usually needed. Due to this also in-situ leaching of Ta could be risky for environment.

Same kind of methods can be used for treatment of virgin materials and tailings. For silt-like tailings pre-concentration using gravity separation technologies is also possible.

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## 3 MINERAL/WASTE PROCESSING OF SECONDARY RESOURCES OF TANTALUM

Secondary recovery of columbite (containing Ta) from tailing dump in Nigerian Jos Mines field was presented.[1] Millions of tons of tailing dump at Rayfield mine in Jos in North Central Plateau state of Nigeria have been found to contain large quantity of columbite. The sample of the Rayfield tailings dump was collected from the site using grab sampling method. The grain size distributions of Nb and Ta in the sample are presented in **Table 2-3**.

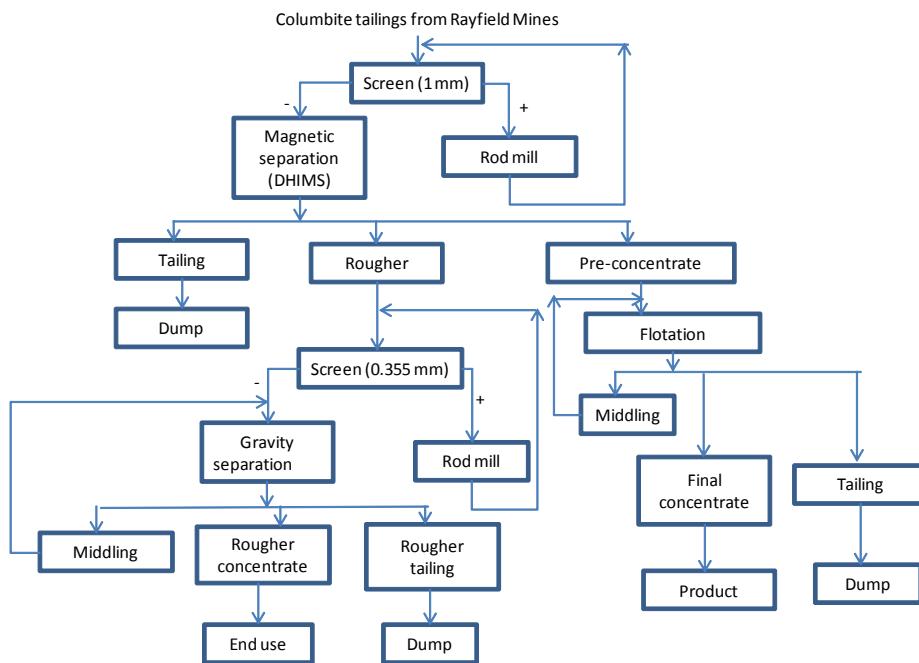
**Table 2-3** Grain size distributions of Nb and Ta.

Size (mm)	%	Nb <sub>2</sub> O <sub>5</sub> %	Ta <sub>2</sub> O <sub>5</sub> %
+1.0	1.2	0.3	0.0
-1.0+0.85	4.8	2.5	0.4
-0.85+0.71	14.8	3.8	0.7
-0.71+0.5	29.9	8.2	1.1
-0.5+0.355	50.2	11.4	1.5
-0.355+0.25	77.7	16.8	1.9
-0.25+0.18	93.4	17.2	2.1
-0.18+0.125	98.1	16.1	2.1
-0.125+0.09	99.6	8.4	1.7
-0.09	100		

**Figure 2-2** shows the processing flowsheet. Fifty kilograms of the columbite tailing was screened using the 1 mm sieve. The oversize portion was fed into rod milling machine to reduce the size and the mill product was recycled to the 1 mm sieve. The undersize of 1 mm was thereafter fed into an optimum efficiency calibrated Dry High-intensity Magnetic Separator (Rapid) Model 4-3-15 OG, operating at a feed rate of 250 kg/hr and 0.5, 0.2 and 1.0 A for magnetite, hematite and columbite; respectively. For maximum recovery, the rougher was processed further by sieving using 0.355 mm sieve size. The oversize particles of 0.355 mm was crushed using the rod mill until all passed through the sieve. The undersize was recycled to the Rapid for further separation. The undersize of the 0.335 mm sieve was further reprocessed using pneumatic (air) floating table, Kipp Kelly model MY. The products of the air floating table were rougher concentrate, middling, and tailings. The middling was recycled to the table while the tailing made up the final tailing. The products of the air flotation were final concentrate (columbite), middling and tailing. The air floatation procedure was repeated for the middling and tailing while the resulting tailing was added to the tailing of the rougher process to form the final tailing of the process. The processing results are shown in **Table 2-4**.

**Table 2-4** Results of Rayfield tailings processing.

Element	Rayfield tailing, %	Concentrate, %	Final tailing, %
Nb <sub>2</sub> O <sub>5</sub>	12.50	69.60	2.91
Ta <sub>2</sub> O <sub>5</sub>	1.90	4.88	0.31



**Figure 2-2** Rayfield tailings processing flowsheet.

Tantalum-containing tin slags are an important source of tantalum supply.[5-7] Depending on circumstances, tin slags may be used directly for extraction of tantalum or they may be first upgraded which is typically performed by means of an electric furnace process that yields a synthetic concentrate. In the extraction of tantalum from these materials, technology makes use mainly of digestion with hydrofluoric acid followed by liquid-liquid extraction with MIBK. This procedure efficiently recovers both tantalum and niobium in the form of separate streams that then can be further processed individually into salts, oxides, and metal. The two streams are produced by a series of counter-current extractions that also remove impurities. The tantalum product stream is a fluotantalic acid solution from which either potassium fluotantalate (K-salt), by addition of potassium chloride or fluoride, or tantalum pentoxide, by addition of ammonia, can be precipitated. Reducing K-salt by sodium is the standard commercial method for making tantalum metal. The product of sodium reduction is a powder that is consolidated by a pressing, vacuum sintering, and melting sequence.[7]

The upgrading of tin slag containing 3.4%  $\text{Nb}_2\text{O}_5$  and 3.0%  $\text{Ta}_2\text{O}_5$  by a combination of chemical treatments was reported in a paper [8]. In the process, unwanted associations in the slag viz. alumina, silica, calcia, iron oxide etc., are selectively solubilized by a sequential treatment with alkali and acid leaching leaving a residue containing 10.6%  $\text{Nb}_2\text{O}_5$  and 10.4%  $\text{Ta}_2\text{O}_5$  with a recovery of 86.5 and 95.5% respectively. The product represents an enrichment of about 3.24 times and was found to be suitable for the extraction of niobium and tantalum by  $\text{HF-H}_2\text{SO}_4$  dissolution.[8]

Tin mineral cassiterite ( $\text{SnO}_2$ ) may contain up to 4%  $\text{Ta}_2\text{O}_5$  either in solid solution or as fine to ultrafine tapiroite exsolutions. These values are concentrated during smelting in the final slags, which may contain as much as 30%  $\text{Ta}_2\text{O}_5$ .[2] Usually tantalum grades of such slag are

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8 to 10% Ta<sub>2</sub>O<sub>5</sub>. The slags are upgrades by an electrothermic reduction process followed by a partial oxidation, which yields the so-called synthetic concentrates containing 50% Ta<sub>2</sub>O<sub>5</sub>+Nb<sub>2</sub>O<sub>5</sub> depending on feed grade.[2] For low grade slags containing less than 2% Ta<sub>2</sub>O<sub>5</sub> the processing is, however, not economic.

An US patent [4] reported a method of beneficiating tantalum- and niobium-containing tin slags. The beneficiation comprises heating the slag in the presence of sufficient carbon to convert the tantalum and niobium oxides to a hearth product containing the tantalum and niobium as carbides in admixture with a carbon-containing iron alloy; separating oxidic gangue constituents from the hearth product; reacting the hearth products with an amount of sodium nitrate such as to insure oxidation of all metallic constituents of the hearth product to their respective highest-valence heat-stable oxidic form of sodium salt, together with a source of additional sodium oxide in amount of at least 25% by weight of sodium nitrate; leaching the resulting reaction product with hot water; subjecting the hot-water insoluble constituents of the reaction product to reaction with an aqueous mineral acid to convert the tantalum and niobium constituents to their hydrated oxides and to dissolve the sodium and iron constituents, and separating the resulting aqueous phase from hydrated oxides to leave as a residue a beneficiated mass of the tantalum and niobium oxide constituents of the starting tin slag.

Chlorination and carbochlorination of tantalum and niobium low and high grade concentrates obtained by leaching of tin slag, were studied using Cl<sub>2</sub> + N<sub>2</sub> and Cl<sub>2</sub> + CO + N<sub>2</sub> gas mixtures.[3]

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## 4 EXTRACTIVE METALLURGY

The secondary raw materials used to produce tantalum are scrap consisting of unoxidised tantalum and oxidised tantalum related with other oxidised metals. The unoxidised tantalum scrap e.g. sintered parts, can be re-melted in an electron beam furnace or treated by dehydrogenation in a vacuum furnace in order to re-produce tantalum powder. The second type of scrap represents the oxidised tantalum, for instance oxidised tantalum anodes coated with manganese dioxide or with conductive silver.[1] This scrap can be treated with nitric or hydrochloric acid and results in a residue containing of oxidised tantalum. Alternatively the scrap that contains manganese dioxide can be melted directly by reducing the oxides in argon-hydrogen plasma to tantalum metal.

### 4.1 HYDRO-METALLURGICAL EXTRACTION OF TANTALUM FROM SECONDARY RESOURCES

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. A literature review was carried out on the solvent extraction of tantalum and niobium with various reagents by Bhattacharyya and Ganguly.[2] 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 et al.[3] reviewed SX technologies applied to the separation and purification of tantalum and niobium to obtain their pure products by focusing on present industrial practice and recent research.

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), octanol, 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. More detail about the general solvent extraction processes employed for the separation of tantalum is presented in the WP2 report.

The extraction and refining of tantalum, including the separation from niobium in these various tantalum-containing mineral concentrates, is generally accomplished by treating the ores with a mixture of hydrofluoric and sulfuric acids at elevated temperatures. This causes the tantalum and niobium values to dissolve as complex fluorides, and numerous impurities

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that were present also dissolve. Other elements such as silicon, iron, manganese, titanium, zirconium, uranium, thorium, rare earths, etc. are generally present. The filtration of the digestion slurry, and further processing via solvent extraction using methyl isobutyl ketone (MIBK) or liquid ion exchange using an amine extractant in kerosene, produces highly purified solutions of tantalum and niobium. Generally, the tantalum values in solution are converted into potassium tantalum fluoride ( $K_2TaF_7$ ) or tantalum oxide ( $Ta_2O_5$ ).

Historically, tantalum-containing tin slags represented an important source of tantalum. In 1980, ca. 50% of world demand was recovered from tin slags.[1] The current fraction of world tantalum demand represented by  $Ta_2O_5$  in tin slag is ca. 5–8%. Tin production has been shifted to areas where cassiterite ores do not contain economically viable tantalum percentages.

When processing tantalum-containing scrap materials, physical and chemical processes are used as much as possible, avoiding processes typically used in ore treatment, i.e., dissolution in hydrofluoric acid and solvent extraction. The tantalum scrap is divided into two categories which differ in difficulty of recycling.[1]

Scrap material of the first type can consist of pure unoxidized metallic tantalum, e.g., sintered tantalum powder pellets (anodes) from the manufacture of tantalum electrolytic capacitors, scrap foil, sheet, and wire, or of anodically oxidized sintered tantalum pellets containing 1.5–3% oxygen from capacitor manufacture and oxidized wire scrap arising from this process. The following processing methods are commonly used for these scrap materials: ingot melting in an electron beam furnace, or conversion to brittle tantalum hydride, grinding, and dehydrogenation at  $> 600\text{ }^{\circ}\text{C}$  in *vacuo* or under a protective gas to form metallic tantalum powder. Alternatively, the ground tantalum hydride can be carburized with carbon black to form tantalum carbide. The oxygen content of oxidized tantalum anodes can be reduced by deoxidation with magnesium or calcium to give high-grade scrap.

Scrap of the second type consists of oxidized tantalum anodes coated with manganese dioxide or with conductive silver, or sometimes welded to nickel conductor wires. This category also includes faulty capacitors, in which the coated and welded tantalum anodes also have an encapsulation of synthetic resin or tinned brass. Pure oxidized tantalum anodes can be recovered from coated anodes and brass-encapsulated capacitors by successive treatments with nitric and hydrochloric acid. Resin-encapsulated capacitors require complex treatment. These can be coarsely size-reduced in grinding mills, the tantalum being recovered by density separation. Foreign metals are removed by treatment with nitric and hydrochloric acid, leaving a residue of oxidized tantalum anodes in granular form. Another method has been described for the treatment of tantalum anode scrap containing manganese dioxide. This can be directly reduced in argon–hydrogen plasma and melted to

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pure tantalum. If the scrap capacitor materials are resin free, the tantalum can be recovered as its pentachloride by chlorination.

Some types of tantalum scrap which contain other impurities are roasted to form the oxide, and treated like ore concentrates. These include condensates formed during the melting of tantalum ingots, scrapped alloy materials, impure sawings and turnings, flue dust, and sediments from the wash liquors from the sodium reduction of potassium heptafluorotantalate.

Hard metals that contain tantalum carbide can be attacked by roasting and treating with caustic soda solution, anodic oxidation, or melting with sodium nitrate, converting the tantalum to its oxide for further recovery treatment.

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## 4.2 CASE STUDIES FOR HYDROMETALLURGICAL EXTRACTION OF TANTALUM

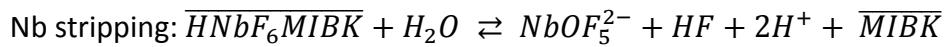
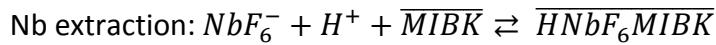
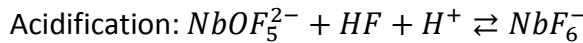
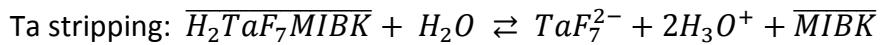
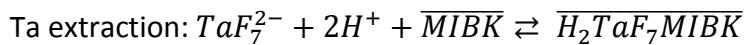
### SOLVENT EXTRACTION BY MIBK

All commercialised solvent extraction processes are exclusively operated in the presence of fluoride ions, because of the speciation differences between Nb and Ta in such medium, from a Nb/Ta concentrate by ore and/or pyrometallurgical processing.

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 ( $\sim 2\text{ \%v/v}$ ), 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.

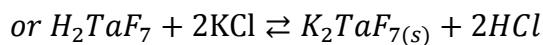
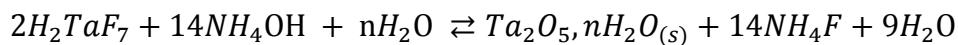
The key parameter of the solvent extraction by MIBK is the  $\text{H}^+$  concentration, which controls the degree of separation as well as the recovery of the two metals. Indeed, niobium forms the fluoride complexes  $\text{NbOF}_5^{2-}$  at low acidity and  $\text{NbF}_6^-$  at high acidity, whereas tantalum forms  $\text{TaF}_7^{2-}$  at low acidity and  $\text{TaF}_6^-$  at high acidity. As the species  $\text{NbOF}_5^{2-}$  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 content in the range of 1-10 mg/L. The chemical mechanism is the following:



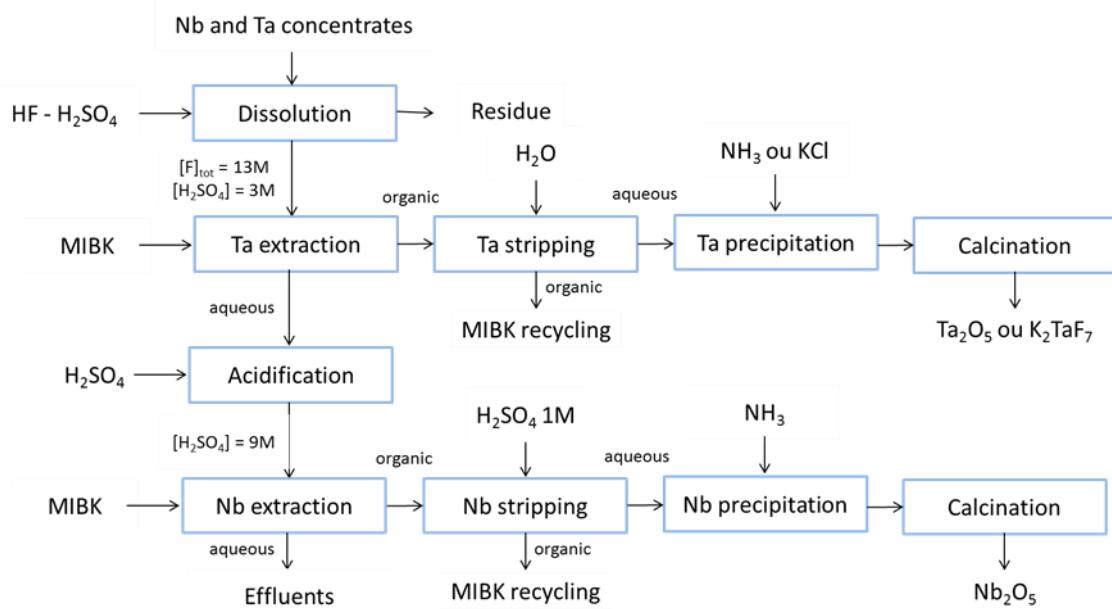
An another strategy, which was developed by the Ames Laboratory is to dissolve the Nb/Ta containing metals in a binary acid system, hydrofluoric acid and high concentrated sulfuric acid. The two fluoro Ta and Nb complexes are subsequently extracted, leaving the impurities in the aqueous layer. Niobium 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<sub>4</sub>OH or KCl in the case of tantalum (as the Marignac process). The different chemical reactions involved are the following:



The hydrated Ta oxides can be then dried and calcinated to obtain Ta<sub>2</sub>O<sub>5</sub>. The potassium heptafluorotantalate K<sub>2</sub>TaF<sub>7</sub> is used to produce Ta<sup>0</sup> by reduction with metal sodium.

**Figure 2-3** presents a simplified flowsheet for the different steps.



**Figure 2-3** Example of flowsheet for the Nb and Ta separation by solvent extraction MIBK.

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#### 4.3 PYRO-METALLURGICAL EXTRACTION OF TANTALUM FROM SECONDARY RESOURCES

Tantalum can be recovered from by-products and scrap, which represent about 20% of total supply. Tantalum is recovered from several items including cemented carbides and alloys. Tantalum can also be recovered from spent sputtering targets, edge trimmings and shavings from metallurgical processes.

Moreover, Ta can be extracted as by-product of tin slag which contains up to 10% of tantalum oxide. Indeed, Ta is a refractory metal, oxidizes easily and moves into the slag produced in pyro-metallurgical processes. By using electrothermic reduction process, the slag is upgraded with up to 50% of tantalum oxides.

Regarding tantalum metal extraction, various metal extraction technologies are available such as carbothermic reduction, metallocermic reduction (Al, Na, Mg), hydrogen reduction, and molten salt electrolysis. The obtained tantalum metal could be refined through using molten salt electro-refining, vacuum sintering, electron beam or plasma refining. Alternatively, if the pyro- or hydro-metallurgical step could generate commercial grade Tantalum oxide or halides, they could also be sold to tantalum smelters as raw materials for metal extraction and refining.

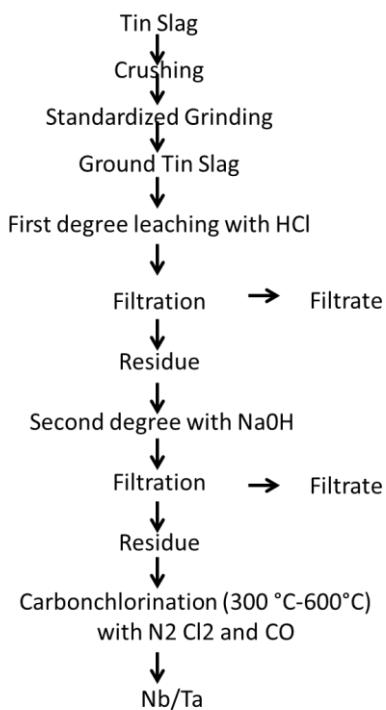
#### **EXTRACTION OF TA FROM TIN SLAG**

The process for treating high grade tin slag ( $> 10\% \text{ TaO}_2 + \text{Nb}_2\text{O}_5$ ) obtained from pyrometallurgy of cassiterite ( $\text{SnO}_2$ ) was developed by Thaisarco (Thailand) and Talison Minerals. After classical treatment of tin, by using electrical furnace, the molten tin is obtained and tin slag is recovered by water granulation. This process allows attending about 15%-18% of  $\text{Ta}_2\text{O}_5$  in the slag of Thaisarco and 30% for Talison, which are similar to ore minerals. Gaballag et al. 1997, reported that the chlorination of high grade tin slag at 1000 °C allowed the extraction of about 84% and 65% of the niobium and tantalum compounds, respectively. However, the carbochlorination at 500 °C allowed complete extraction and recovery of pure tantalum and niobium compounds. The chlorination mechanism, between 700 °C and 850 °C, was likely controlled by the chemical reaction. Between 925 °C and 1000 °C, activation energy  $E_a$  for  $\text{Ta}_2\text{O}_5$  chlorination was 246 kJ/mole. Below 600°C,  $E_a$  for carbochlorination was 74 kJ/mol for  $\text{Nb}_2\text{O}_5$  and 110 kJ/mol for  $\text{Ta}_2\text{O}_5$ .

In the case of low grade tin slag ( $< 10\% \text{ TaO}_2 + \text{Nb}_2\text{O}_5$ ), a hybrid treatment (pyrometallurgy and hydrometallurgy) is used to obtain a synthetic concentrate. Odo et al. have investigated the extraction of valuable metals (Nb/Ta) present in tin slag using leaching and electrothermal method. The suggested process consists of double leaching of tin slag with particle size of 0.15 mm. Then after filtration, the residue is subjected to chlorination or carbochlorination at 300 °C. This process may produce metal oxides with high purity (about 95%).

Tantalum oxide powder ( $\text{Ta}_2\text{O}_5$ ) with high purity can also be recovered by reducing the  $\text{Ta}_2\text{O}_5$  obtained through magnesiothermic reduction.

A flow-sheet for recovery of Nb/Ta from tin slag is shown in **Figure 2-4**.



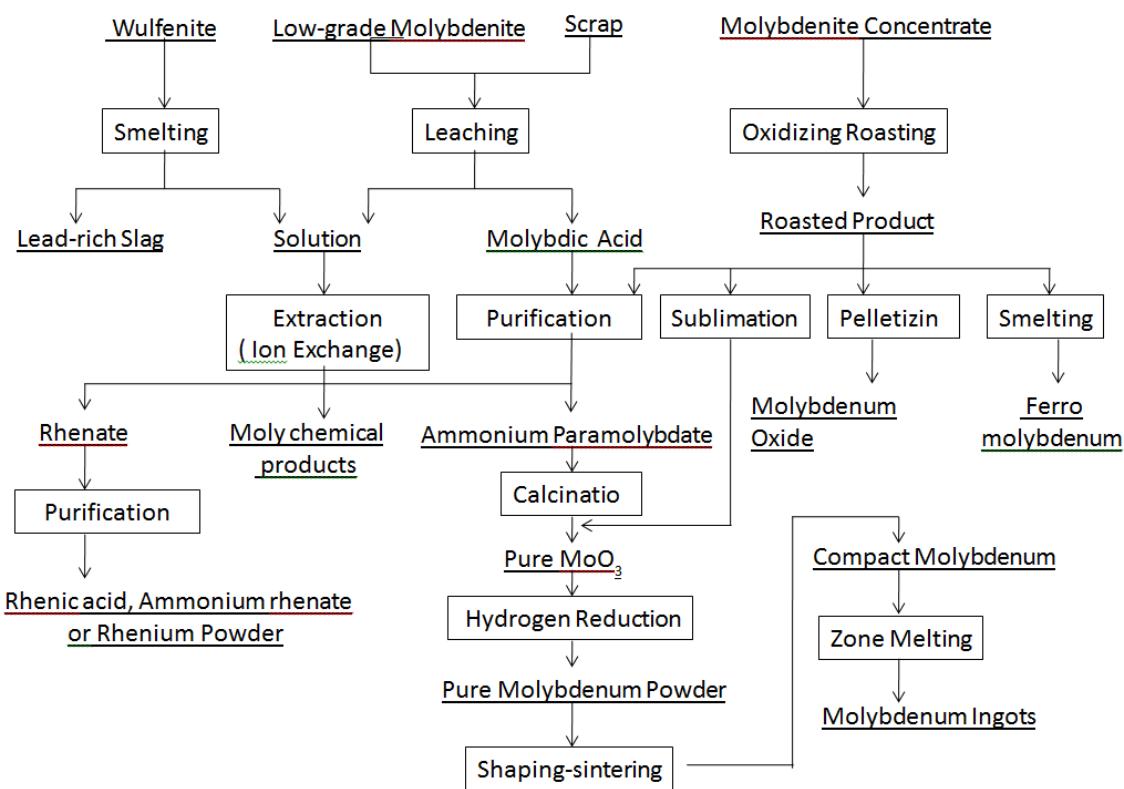
**Figure 2-4.** Flow-sheet of Nb/Ta recovery from tin slag

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## CHAPTER 3 MOLYBDENUM



**Figure 3-1** General flow chart for molybdenum processing/production from primary and secondary resources.

### 1 MAPPING OF SECONDARY RESOURCES OF MOLYBDENUM

Extracting of particular metal from the original resource depends on the economic benefit of the process. If the extraction of a component from the initial raw materials is technically beside the purpose or not economically viable due to the excessively large amount of material, transportation and other costs, then it usually turns out to end up in the waste fraction of the process. Such waste is stored in certain places (next to the production or outside) and for an uncertain time to minimize their environmental impact.

Due to the continuous depletion of the initial mineral resources of useful metals, the economic situation of the world is changing. It is often so that the extraction of useful component of the waste is becoming valuable and companies begin to implement the schemes for waste recycling and recovery. As a rule, such schemes are much more complicated than primary treatment schemes due to the low content of desired components in wastes. All this is fully applicable to strategic refractory metals and, in particular, to molybdenum. A list of molybdenum resources in Europe, or possibly available for European

production, are shown in **Table 3-1**. And the Mo-containing wastes or residues can be possibly found in the places as indicated in **Table 3-1**.

**Table 3-1** List of Molybdenum resources in Europe or possibly available for European production

Country	Mine	Operator	Location
Norway	Knaben Molybdenum Mines	A/S Knaben Molybdængruber	Knaben
Sweden	Munka Mine	Beowulf Mining	Rappen geological district of the Arjeplog Municipality in northern Sweden

## 2 SECONDARY MINING OF MOLYBDENUM

### 2.1 SECONDARY MINING OF MOLYBDENUM FROM WASTE ROCK AND TAILINGS

Flotation tailings from a copper-molybdenum mine contain large contents of slimes and kaolinite. The fine particle sizes and poor locked particles of most of valuable minerals disseminated in the gangue minerals.[1] Mine tailings from Erdenet copper-molybdenum mine in Mongolia were sampled at the outfall of the mine tailings pond.[2] Chromium (Cr) 6.9 to 13.1 mg/kg, arsenic (As) 9.3 to 10.7 mg/kg, lead (Pb) 0.2 to 2.3 mg/kg and copper (Cu) 61.4 to 96.1 mg/kg were detected in tailings by AA and XRF.

The uranium (U) mill tailings in northern Saskatchewan, Canada contain elevated concentrations of molybdenum (Mo).[3] X-ray absorption spectroscopy was used to define the chemical (redox and molecular) speciation of Mo in tailings samples from the Deilmann Tailings Management Facility (DTMF) at the Key Lake operations of Cameco Corporation and Mo exists mainly as molybdate (+6 oxidation state). Principal component analysis of tailings samples spectra followed by linear combination fitting using spectra of reference compounds indicates that various proportions of NiMoO<sub>4</sub> and CaMoO<sub>4</sub> complexes, as well as molybdate adsorbed onto ferrihydrite, are the Mo species present in the U mine tailings. Tailings samples with low Fe/Mo (<708) and high Ni/Mo (>113) molar ratios are dominated by NiMoO<sub>4</sub>, whereas those with high Fe/Mo (>708) and low Ni/Mo (<113) molar ratios are dominated by molybdate adsorbed onto ferrihydrite.

The obsolete molybdenite tailings reservoir since 1950s exceeded 4 million tons with Mo 1.04% in Zhejiang province, China. Main components of the tailings are silicate, calcium-bearing minerals (mainly is calcite), iron-bearing minerals, alumina magnesia minerals and some sulfide minerals like pyrite. The phase analysis of the tailings indicates that molybdenum mineral mainly occurs as sulfides (98.08%) and only 1.92% amount as molybdenum oxide. Particle size analysis was conducted using standard laboratory wet and

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dry screening methods. Over 90% of Mo in the material was distributed in the fraction of -38 µm.[4]

The Kitsault molybdenum deposit in northwest British Columbia will be mined. The company plans to dump some 10 000 tons of waste tailings into the ocean each day. With the life of the mine estimated at 26 years, there will be a total of about 100 million tons of tailings. This waste will contain mercury, cadmium, lead, arsenic, zinc and traces of other toxic elements such as radium 226, uranium and thorium.[5]

Consequently, Erdenet processing plant tailings in Mongolia are composed of three process products: recleaner bulk flotation tailings (tailings I); middling cycle tailings (tailings II); Cu-Mo flotation tailings (tailings III).[6] The final concentration tailings have the copper content of 0.2–0.5% and molybdenum content of 0.1–0.2%.

At the Questa mine in New Mexico, U.S. ore is mined underground then crushed and processed using froth flotation at the mill. Open pit mining took place from 1965 to 1983. Mining operations placed over 328 million tons of acid-generating waste rock into nine piles surrounding the open pit and disposed of over 100 million tons of tailings in the tailing ponds.[7] The Molycorp tailings facility is located west of Questa, nine miles west of the Questa mine and mill.[8] About two-thirds of the tailings can be considered coarse tailings, which are defined as less than 50% fines. Fines are silt and clay sized particles smaller than 0.075 mm. Fine tailings (silt size, less than 30% clay) comprise less than 12% of the tailings. Mineralogically, the tailings consist predominantly of quartz, plagioclase, feldspar, potassium feldspar, and biotite with lesser amounts of chlorite, amphibole, calcite, and sulfide minerals (minor pyrite and molybdenite with trace amounts of chalcopyrite, galena, and pyrrhotite).

It was reported in 2014 that Chevron Mining has permanently closed its Questa molybdenum mine, a nearly 100 year old mine, citing low market prices and increasing operational costs.[9]

In High Atlas Mountains of Marrakesh (Morocco) Cu-Mo-W Azegour Mine is one of the most important mines. In the past about 850,000 tonne of waste rocks and tailings were produced and deposited on the surface and have been exposed to weathering for 40 years. Concentrations of Mo are as high as 17,800-29,700 ppm in the tailings and in the waste rocks being 2,140-92,400 ppm. Therefore, there is a significant potential for reprocessing these wastes.[10]

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## 2.2 SECONDARY MINING OF MOLYBDENUM FROM OTHER RESIDUALS

The selection of the treatment scheme and preparation method for molybdenum recovery from particular industrial residual depends primarily on the physical and chemical form in which the residual exists. **Table 3-2** presents a list of possible industrial residual that contain molybdenum, and consequently can be recovered.

The following describes in details the industrial residuals that are listed in **Table 3-2**.

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### MOLYBDENUM-CONTAINING SPENT ACID

In the lamp making tungsten filament needs to be made into a single coil or coiled coil to make incandescent lamps. To make the coil tungsten wire is wound around a mandrel wire by the machine. In order to set the tungsten coil in a permanent coil configuration, the coil-mandrel assembly is subjected to an annealing treatment at 1000-1600 °C. To withstand such high temperatures, molybdenum wire is normally used as the mandrel. After the

annealing process, a mixture of acid is used to dissolve out the molybdenum from within the tungsten. This acid after several times' use is to be discarded due to its poor capacity of dissolving molybdenum. At this point, the used acid is referred to as spent acid. This spent acid contains 40-70 g/L of molybdenum, which can be recycled.[1-4] The volume of spent acid in coil manufacturing averages 300 to 800 liter per day in a typical lamp factory and this amounts to 20 to 50 kg of molybdenum per day.[2]

**Table 3-2** Industrial residuals for possible Mo recovery

Name of residual	Main industry	Estimated content of Mo	Related research
Spent acid	Lamp industry	40-70 g/L	[1]-[4]
Fly ash	Heavy oil-fired power station	~ 0.35%	[5]
Flue dusts from steelmaking	Steel industry	0.02 – 1.2% (depends on dust)	[6-8]
Mill scale	Steel industry	Similar as the steel products except its oxygen content	[9]
Copper slag	Copper production industry	0.3%	[10]
Aqueous waste waters	Copper, molybdenum and uranium flotation mills	Cu mine in Arizona (1 – 30 mg/L); Uranium mill in Colorado (900 mg/L); Mo mills in Colorado (25 mg/L)	[11]
Radioactive wastes	Production of <sup>99</sup> Mo/ <sup>99m</sup> Tc generators	-	[12]
Molybdenite Roasting Dust	Roasting of Mo concentrate	-	[13-14]

### FLY ASH

Molybdenum is present as trace element in the coal. After combustion of the coal, for example, at the power station, the molybdenum as well as other metal elements, such as Fe, Ni and V, will end up in the residuals, which are largely collected as fly ash. It is reported that the global generation of fly ash from the coal-based power stations is as high as 750 Mt per year.[15] The molybdenum contents in the fly ash vary with the types of the coal that was used, and it can be in the range of several tens of ppm to several thousands of ppm. Considering the amount of fly ash annually generated, fly ash can be regarded as potential secondary mine of molybdenum. Among the others fly ash generated from heavy oil fired power station can be of great interest, as it can contain higher contents of vanadium (~ 5.0%), nickel (~1.54%) and molybdenum (~0.35%).[5]

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### STEELMAKING DUSTS

Globally 29% of the steel is produced by the EAF.[16] During the EAF steelmaking 15-20 kg dust is generated per tonne of steel.[17] The EAF dust contains metal elements, some of which are toxic and soluble in the water, therefore there are high restrictions for landfilling the dust. Considering its metal contents, the metals, such as Mo, Ni, Cr, Fe, etc., in the dust can be recovered.[8] Besides EAF dust, the dust from AOD process also contains valuable metals, such as Mo and Zn, that can be recovered.[7]

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### MILL SCALE

Mill scale is generated during the continuous casting and rolling mill processes, where steel is subjected to hot working in the oxidant atmosphere. Mill scale has the similar chemical composition of the steel except its oxygen content, and it represents 2% of the amount of the steel produced. In the integrated plants, mill scale is recycled internally as raw materials, for example, at the sintering plant; however in the mini-mills which operate with EAF and where there are no reduction reactors, the mill scale is often sent to landfills.[9] In this sense, mill scale from the Mo-containing steel production can be considered as potential secondary mine of molybdenum.

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### COPPER SLAG

Most of the copper in the world is produced by the pyro-metallurgical processing of sulfide ores, during which large quantities of slag are generated as the by product. Frequently the copper slag contains Fe, Zn, Mo, Ag, Au, Cu, etc., which can be recovered.[10], [18], [19] For example, typical Chilean copper slag contains about 0.3 wt.% Mo, which is the grade of primary mine of molybdenite.[10]

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### AQUEOUS WASTE WATERS FROM FLOTATION MILLS

Molybdenum is the principal dissolved metal in the aqueous effluent from many copper, molybdenum and uranium flotation mills. This probably occurs because of high solubility of molybdenum as anionic  $\text{MoO}_4^{2-}$  at the high pH used in flotation. The researchers have showed how it could be possible to remove dissolved Mo from waste water with ferric oxyhydroxide at low pH.[11] The removal efficiency as high as 95% was achieved. After precipitation, residue is obtained; it includes a mixture of iron compounds (natrojarosite, goethite) and amorphous material enriched in molybdenum. The residue can be separated from waste water with filtration. After that, it could be possible to recover molybdenum from amorphous material.

## RADIOACTIVE WASTES FROM MO/TC GENERATORS PRODUCTION

$^{99m}\text{Tc}$  is ready available in the form of convenient  $^{99}\text{Mo}/^{99m}\text{Tc}$  generator systems and used for labelling different pharmaceuticals, which is the most important radionuclide in nuclear medicine practice, and probably will continue to play this important role also in the near future.

During the production of generator systems many radioactive wastes are produced in different forms. Management of this waste is an integral and very important part of  $^{99}\text{Mo}$  production, especially for fission  $^{99}\text{Mo}$ , and should be given high priority during production process development and operation.

These wastes are generated as solids, liquids and gases. They include materials in the low, intermediate and even highly radioactive categories. Initial treatment of waste streams is usually required at the production site, prior to short or long term storage. The treatment required is dictated by both the form of the waste and its activity level. This technology is established and generally available in countries with an existing nuclear industry. Waste processing can be on-site (refers to treatment carried out in the production facilities) and off-site (treatment performed outside the facilities).

The research of International Atomic Energy Agency listed different schemes of treatment of solid, liquid and gas wastes in different countries.[20] The molybdenum could be extracted from liquid radioactive waste as it was shown in research work.[12] They conclude that a separation of molybdenum, zirconium and niobium from the long-lived fission products  $^{90}\text{Sr}$ ,  $^{99}\text{Tc}$ ,  $^{106}\text{Ru}$ ,  $^{137}\text{Cs}$ ,  $^{144}\text{Ce}$  and  $^{147}\text{Pm}$ , containing in aqueous nitric acid, is possible with alkyl phosphoric acids. Separation of molybdenum from zirconium and niobium can be achieved by back-extraction into an aqueous mixture of ammonium fluoride and nitric acid.

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### 3 MINERAL/WASTE PROCESSING OF MOLYBDENUM

#### 3.1 MINERAL/WASTE PROCESSING OF MOLYBDENUM FROM WASTE ROCK AND TAILINGS

For flotation tailings from a copper-molybdenum mine[1] a combined process was studied to recover copper, molybdenum, sulfur and iron minerals which contains pre-desliming, bulk

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flotation of copper and molybdenum of the coarse fraction, separation of Cu-Mo, separating sulfur from bulk flotation tailings and low-intensity magnetic separation of iron from sulfur flotation tailings. The results of the closed circuit test show that it can be obtained copper concentrate with a Cu grade of 20.61% and a recovery rate of 28.52%, molybdenum concentrate with a Mo grade of 36.00% (containing 20% C) and a recovery rate of 43.35%, sulfur concentrate with a S grade of 35.66% and a recovery rate of 42.58%, and iron concentrate with a Fe grade of 68.40% and a recovery rate of 6.85% (75% of phase recovery of magnetite).

Recovering molybdenite from ultrafine waste tailings by oil agglomerate flotation was studied with the obsolete molybdenite tailings.[2] Neutral oils like kerosene, diesel, transformer and rapeseed oil were used as collectors or bridging reagents in conventional flotation and oil agglomeration flotation (OAF) process, and a promising OAF process has been developed for the recycling of ultrafine molybdenite resources from the waste tailings.

Development of the technology for production of marketable copper and molybdenum concentrates from tailings III (bulk cleaner tailings) was researched in Erdenet processing plant.[3] The chemical composition of the test material: 0.2–0.5 % Cu, 0.1–0.2% Mo, 25–35% Fe total, 28–35% S total, 31.9 % S, 20–30% SiO<sub>2</sub>, 5–8% Al<sub>2</sub>O<sub>3</sub>, 1.5% K<sub>2</sub>O, 0.4–0.8% Na<sub>2</sub>O. Over 80% Mo was distributed in the fraction of -71 µm. Mineral composition: molybdenite 0.4%, chalcopyrite 1.4%, secondary copper sulfides (chalcosite and bornite) 0.1%, pyrite 54.4% and other 39.3%. Copper and molybdenum mainly occur in aggregates with non-metals (silicates) and, partly, with pyrite; molybdenite is almost in full dissociated; its loss in tailings is connected with the high content of CaO in process stages.

The process flowsheet was as following. Mo-Cu is separated by flotation; the rougher Mo concentrate goes to Mo recleaner flotation to get final Mo concentrate. The rougher Cu concentrate through washing and regrinding goes to Cu-Py separation to get the final Cu concentrate, Py concentrate and secondary tailings (Cu 0.13%, Mo 0.09%). The molybdenum concentrate was obtained with Mo 45.04% at the recovery of 66.25%, copper concentrate (Cu 15.4% at the recovery of 53.24%), pyrite concentrate (Fe 45.12%, S 52.1%, iron recovery of 89.16%) and secondary tailings (Cu 0.13%, Mo 0.09%) were obtained.

In Tyrnyauz processing plant in Russia[4] minerals (molybdenite, fluorite and calcite) of old tailings and ore have uniform properties, which allows application of the current technologies of tungsten–molybdenum ore processing. Flotation of old tailings yielded rough molybdenum concentrate with the content of 49.55% Mo at the recovery of 60.2% Mo; scheelite concentrate produced from tailings of molybdenum circuit contained 54–55% WO<sub>3</sub> at the recovery of 61.91–62.08% WO<sub>3</sub>. It is recommended to use jet flotation system for old tailings: initial slurry is separated into 3 flows, for example (flotation jets), rough concentrate of flow 1 is mixed with initial feed of flow 2, rough concentrate of flow 2 is mixed with initial

feed of flow 3, rough concentrate of flow 3 is fed for scavenging. It is efficient to use flotation with heat saturated water steam and air mix.

One of the longest-running tailings reprocessing efforts is run by Canadian junior copper and molybdenum producer Amerigo Resources at its facility near Chile's El Teniente, the world's largest underground copper mine. Tailings reprocessing started at El Teniente in 1992, after a group of former executives from state-owned mining company Corporación Nacional del Cobre de Chile (Codelco), El Teniente's owner, founded Minera Valle Central S.A. and signed a 20-year contract to reprocess tailings at the site. Codelco, a Chilean state-owned mining company, is the world's largest copper producer, and the second-biggest producer of molybdenum.[5] In addition to the fresh tailings from El Teniente, Amerigo acquired the rights to process 10 000 tonnes of older tailings per day from the Colihues tailings pond, which is adjacent to the facility and should contain enough material to keep the plant running for 20 years. That was a big plus for Amerigo because these tailings were initially processed using older extraction methods, so they contain more copper and molybdenum than the fresh tailings. In 2004, Amerigo negotiated a new deal with Codelco that lets it process 45 000 tonnes of tailings per day from Colihues. The plant's production continues to rise: in the first quarter of 2012, it produced 6 294 tonnes of copper and 98.11 tonnes of molybdenum. These figures – both records – are up from 5 051 tonnes of copper and 96.22 tonnes of molybdenum a year ago. For all of 2012, the company expects to produce 50 million pounds of copper and close to a million pounds of molybdenum. The Molycorp tailings facility is located the Questa mine and mill where ore is mined underground then crushed and processed using froth flotation.[6]

The sources of various mine molybdenum tailings and the reprocessing techniques are listed in **Table 3-3**.

**Table 3-3** The sources of various mine molybdenum tailings and the reprocessing techniques.

Source	Mine & location	Mineralogy & Grade	Reprocessing	Ref.
Flotation tailings	copper-molybdenum mine	unknown	Combined process: bulk flotation of copper and molybdenum of the coarse fraction, separation of Cu-Mo, separating sulfur from bulk flotation tailings and low-intensity magnetic separation of iron from sulfur flotation tailings; Copper concentrate Cu 20.61% at recovery 28.52%, molybdenum concentrate Mo 36.00% at recovery 43.35%	[1]
molybdenite tailings	unknown	ultrafine waste	Oil agglomerate flotation was studied with neutral oils (kerosene, diesel,	[2]

			transformer and rapeseed oil) used as collectors or bridging reagents.	
Copper/molybdenum mine tailings	Erdenet processing plant in Mongolia	0.1–0.2% Mo over 80% Mo was distributed in the fraction of -71 µm	Mo-Cu is separated by flotation; the rougher Mo concentrate goes to Mo recleaner flotation to get final Mo concentrate with Mo 45.04% at the recovery of 66.25%. Secondary tailings with Cu 0.13% and Mo 0.09%	[3]
Old mine tailings	Tyrnyauz processing plant, Russia	molybdenite, fluorite, calcite, scheelite	Flotation of old tailings yielded rough molybdenum concentrate with the content of 49.55% Mo at the recovery of 60.2% Mo; scheelite concentrate produced from tailings of molybdenum circuit contained 54–55% WO <sub>3</sub> at the recovery of 61.91–62.08% WO <sub>3</sub> . It is efficient to use flotation with heat saturated water steam and air mix.	[4]
Mill tailings	El Teniente, Amerigo Resources, Chile	unknown	Started in 1992, and a 20-year contract signed to reprocess tailings at the site. In addition to the fresh tailings from El Teniente, Amerigo acquired the rights to process 10 000 tonnes of older tailings per day from the Colihues tailings pond	[5]
Mine tailings	Questa mine, US	Two-thirds is coarse tailings (<50% fines). Fine tailings (silt size, less than 30% clay) comprise less than 12% of the tailings. Mineralogy, sulfide minerals (minor pyrite and molybdenite with trace amounts of chalcopyrite, galena, and pyrrhotite)	Flotation	[6]

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## 3.2 MINERAL/WASTE PROCESSING OF MOLYBDENUM FROM OTHER RESIDUALS

The ways in which the mineral/waste processing of molybdenum from other industrial wastes should be adopted are highly dependent on the properties of the wastes. Here the mineral/wastes processing of selected wastes shown in **Table 3-2** is described.

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### MOLYBDENUM-CONTAINING SPENT ACID

The spent acid has an acidity of approximately 15 N, the common practice of pretreatment of this acid is adding ammonia into the acid followed by mechanical stirring to get a solution with PH between 2 and 3. [1][2]

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### FLY ASH

A grinding process may be needed for the fly ash, if it is to be treated by a hydrometallurgical process to extract Mo.[3]

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### STEELMAKING DUSTS

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The Steelmaking dusts normally need to be made into briquettes before it can be charged into the furnace to recover molybdenum.[4] In a hydrometallurgical process, the dusts may, however, be used directly.[5]

#### MILL SCALE

The Mo-containing mill scale normally needs to be crushed or even ground into fines and made into briquettes before it can be charged into the reduction reactor to extract the Mo. For the oily mill scale, the oil in the mill scale, in some cases, needs to be removed, for example, by the vacuum distillation method before it can be used, as the direct use of oily mill scale can result in the emission of volatile organic compounds, including dioxins.[6]

#### COPPER SLAG

The commercial operation of extracting Mo from copper slag is not yet available; however, it is believed that production of a fine (250 mesh) water granulated slag is a prerequisite.[7]

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## 4 EXTRACTIVE METALLURGY OF MOLYBDENUM

Traditional methods of molybdenum extraction, namely, roasting of molybdenite concentrate by ammonia leach and distillation processes are applicable for high-grade MoS<sub>2</sub> concentrates derived from the primary molybdenum ores. An ever-increasing quantity of complex low-grade molybdenite concentrates is being produced from secondary sources as by-products of copper and uranium mining. Such secondary low-grade MoS<sub>2</sub> concentrates require extensive modifications in the already complex conventional routes. Being essentially environment friendly lime-scavenged reduction, pyro-chlorination and hypochlorite leaching routes are expected to enjoy cost benefits.

### 4.1 EXTRACTION OF MOLYBDENUM FROM WASTE ROCK AND TAILINGS

Secondary sources of molybdenum in the world are mostly by-product of copper mines, by-product of tungsten mines and by-product of uranium mines in the USA/South America;[1] and by-product of copper mines, graphite shale containing Ni-Mo and wulfenite in China.[2] For the time being, Armenia is the only producer of molybdenum in Europe (6.7 kt in 2014), but the corresponding technology is roasting of molybdenite concentrate (pyro-metallurgy) in and outside of Armenia.[3] Existing industrial hydrometallurgical routes to recover molybdenum from such sources consists of: (a) pressure oxidative leaching (POX) or acidic/alkaline leaching and (b) precipitation/crystallization, ion-exchange and solvent extraction.[1]

- 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.[2]
- Precipitation/crystallization is the most common method for recovery of ammonium/sodium molybdates.[1] Ion-exchange method (using aminated acrylonitrile ion-exchangers) has been industrially used to recover molybdenum from wulfenite in China, and from molybdenite in Russia.[4] Solvent extraction also has been applied industrially using common extractants such as amines, hydroxy-oximes and organophosphorus compounds.[1][2]

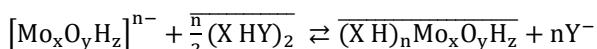
Hydrometallurgical processes have advantages of low energy consumption and no emission of SO<sub>2</sub> and they are attractive especially for low-grade molybdenum sources. The general steps for hydrometallurgical processes are described as follows.

## LEACHING

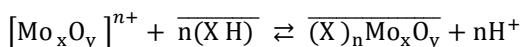
The leaching of molybdenum-bearing scrap is often conducted with nitric acid (8 – 9 M) or a mixture of nitric and sulfuric acid, which results in acidic MoO<sub>3</sub> solutions. Ammonia is added for precipitation (ammonium molybdate). For precipitation as molybdic acid, the leach liquor is boiled slightly. For purification and concentration reasons, the leach liquor can be treated by solvent extraction or ion exchange.

## SOLVENT EXTRACTION

Basically, there are two different mechanisms for solvent extraction of molybdenum from aqueous solutions, which is especially important for the selective separation from tungsten in multicomponent feed streams. First, the same anionic exchange mechanism as for tungsten prevails at high pH:



Here X represents the extractant and Y the anionic leaving group, where the overbars indicate the organic species. As extractant, secondary and tertiary amines (tri-octyl/decylamine, diisododecylamine) are predominately used, dissolved in kerosene or other aliphatic solvents, with alcohols or ketones as phase modifiers. The molybdenum species tend to polymerize as the pH decreases ([MoO<sub>4</sub>]<sup>2-</sup>, [HMoO<sub>4</sub>]<sup>-</sup>, [Mo<sub>7</sub>O<sub>24</sub>]<sup>6-</sup> etc.). When the pH is less than 3, the cationic forms are predominant ([MoO<sub>2</sub>]<sup>2+</sup>, [Mo<sub>2</sub>O<sub>5</sub>]<sup>2+</sup>, [Mo<sub>3</sub>O<sub>8</sub>]<sup>2+</sup>) and the extraction switches to a cationic exchange mechanism:



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 [MoO<sub>2</sub>]<sup>2+</sup> 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.

## ION EXCHANGE

Here the alkali leaching solution is contacted with a weak alkali acrylic type anion exchange resin with –NH<sub>2</sub> (D314) or a quaternary ammonium (D201) as functional group, where the molybdenum is adsorbed. Desorption is carried out with 10 % ammonia solution.

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## CRYSTALLIZATION

The filtered ammonium molybdate solution is fed into an evaporative crystallizer at atmospheric pressure to produce ammonium dimolybdate. This is also an important purification step in order to remove sodium, calcium, magnesium and aluminum. Calcining ammonium dimolybdate produces pure MoO<sub>3</sub>.

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## 4.2 CASE STUDIES FOR HYDROMETALLURGICAL EXTRACTION OF MOYBDENUM

Chinese have proposed a process[1] for recovery of molybdenum from leach liquor of pressure oxidative leaching. The concentrate feed contains, 45% of Mo, 0.07% of Re, 2.3% of Cu, 37% of S, 3% Fe, 5.1% SiO<sub>2</sub>, 4.6% Al<sub>2</sub>O<sub>3</sub>. In this method 15-20% of molybdenum is dissolved at 230-250 °C. The pressure oxidative leachate contains 6-8 g/L of Mo, 0.165 g/L of

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Re, 5.7% g/L of Cu, 2.1% g/L of Fe, and 210-230 g/L sulfuric acid. The filtered solid molybdenum oxide residue was leached (99.2%) using ammonium hydroxide. The ammonium leachate was treated by sulfuric precipitation of impurities followed by precipitation of ammonium molybdate using nitric acid at pH 2.0-2.5. After solvent extraction of dissolved rhenium, the dissolved molybdenum content of oxidative leaching was extracted (98%) using 25% tri-octyl-amine+5% isoctanol+75% sulfonated kerosene, O/A: ½ and in two stages with no crud formation. Stripping is done using ammonium hydroxide solution.

In Russian industrial experience, [2] an industrial sample containing  $\text{HNO}_3 \sim 1.7 \text{ M}$ ,  $\text{H}_2\text{SO}_4 0.5 \text{ M}$ , Mo (VI)  $\sim 0.1 \text{ M}$  and Fe  $\sim 0.3 \text{ M}$ , was treated using ion exchange resins (AN-80P: an acrylic resin with ethylene-di-amine as functional group). Complete molybdenum sorption occurred at nitric acid concentrations below 0.3 M and IR spectra showed that molybdenum sorption occurs as  $\text{Mo}_8\text{O}_{26-4}$  polyions. The saturated resin was washed with water (pH  $\sim 3.0-2.5$ ) to remove the impurities followed by elution with ammonium hydroxide to recovery pure ammonium paramolybdate or polymolybdate.

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- [1] Jiang, K., Wang, H., Zou, X., Zhang, L. and Zhang, B. 2012. The Development of China's Molybdenum Metallurgical Technologies, In: S. Wang, J. E. Dutrizac, M. L. Free, J. Y. Hwang & D. Kim (eds.) T.T. Chen Honorary Symposium on Hydrometallurgy, Electrometallurgy and Materials Characterization, John Wiley & Sons, Inc.
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## 4.3 EXTRACTION OF MOLYBDENUM FROM OTHER RESIDUALS

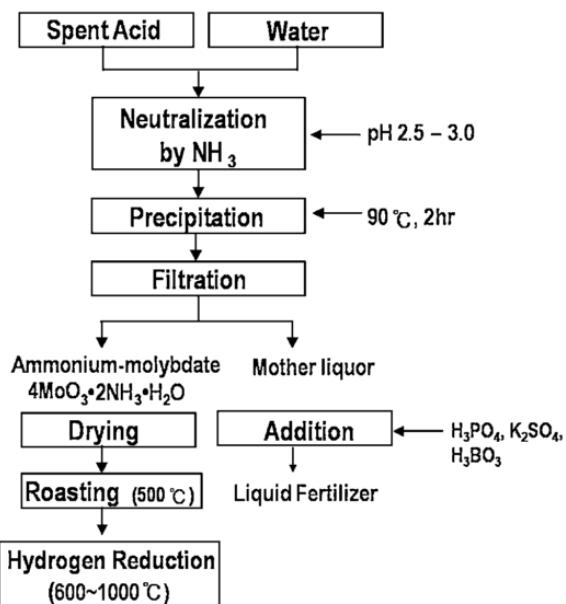
The ways in which the extracting molybdenum from residuals should be adopted are also highly dependent on the properties of the residuals. Here the extraction methods of selected residuals shown in **Table 3-2** are described.

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### MOLYBDENUM-CONTAINING SPENT ACID

Molybdenum is normally extracted from the spent acid by ammonia precipitation method, which includes both hydrometallurgical and pyrometallurgical steps;[1]–[3] a general flow sheet for molybdenum recovery by this method is shown in **Figure 3-2**.[2] In this method, the spent acid is mixed with water in certain volume ratio, and the solution is neutralized by ammonia to get a solution with PH in the range of 2.5-3.0. Due to that the neutralization process is highly exothermic the solution temperature will be increased to above 90 °C in the middle of the process. After neutralization the solution temperature was maintained at

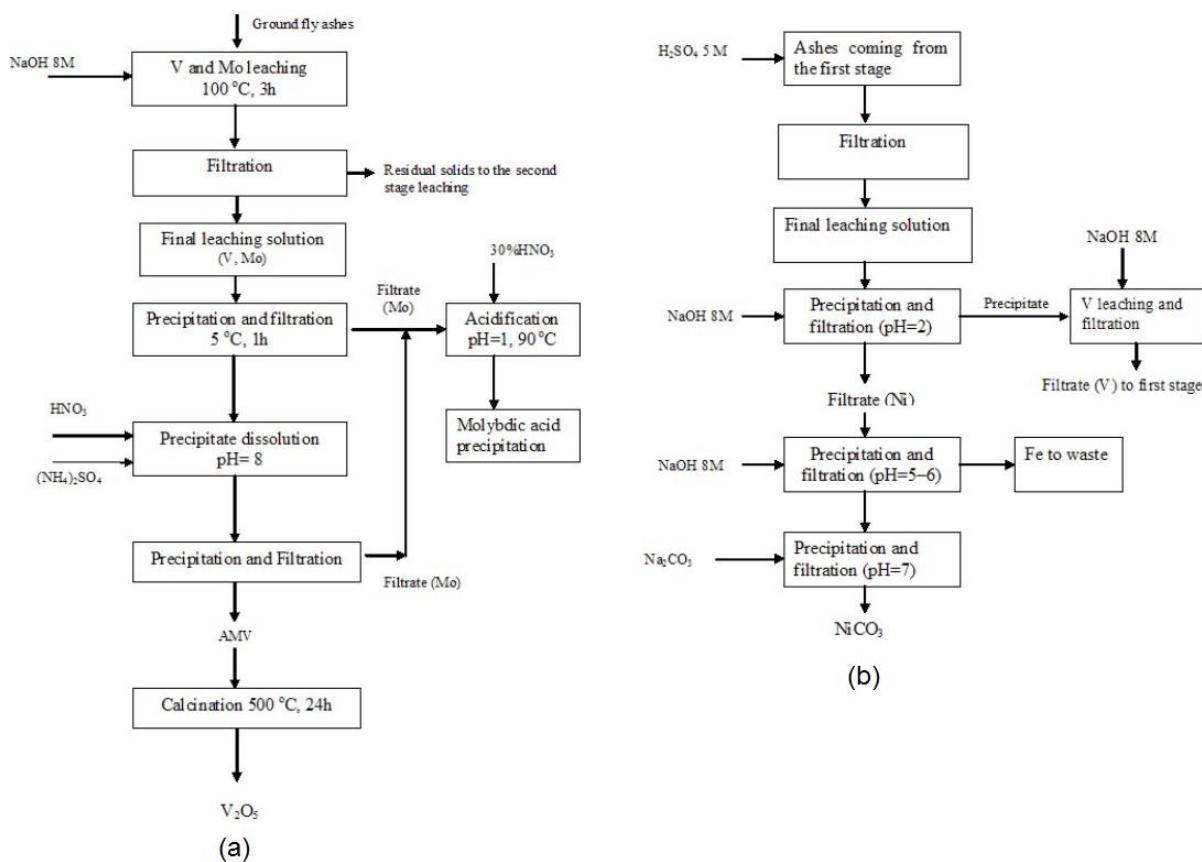
above 90 °C for at least 2 hours. During this period the solution is agitated, and ammonium molybdate will precipitate. Thereafter the ammonium molybdate is collected by filtration. The obtained ammonium molybdate was dried at 120 °C and roasted in the air at 500 °C to obtain MoO<sub>3</sub> powder. The final molybdenum powder is obtained by two-stage hydrogen reduction: first stage for reducing MoO<sub>3</sub> to MoO<sub>2</sub> at 600 °C and second stage for reducing MoO<sub>2</sub> to Mo at 930-1000 °C.



**Figure 3-2** Flowsheet for Mo recovery from spent acid by ammonia precipitation.[2]

#### FLY ASH

The recovery of vanadium, nickel and molybdenum from fly ashes produced from heavy oil-fired electrical power station can be well described by the flow sheet shown in **Figure 3-3**. As it can be seen that the recovery was achieved using two-stage leaching process, which consists of an alkaline leaching to dissolve vanadium and molybdenum followed by sulfuric acid leaching to recover nickel.[4] The molybdenum is extracted in the first stage. In this stage fly ash was leached with 8 M sodium hydroxide to dissolve vanadium and molybdenum at 100 °C. After 3 hours of mixing the slurry was filtered and the residual ashes were sent to the second stage leaching. The final leaching solution containing vanadium and molybdenum was cooled to 5 °C for 1 hour under mild agitation; alkali-precipitate containing vanadium and trace of molybdenum was precipitated. The precipitate was separated from the leach solution by filtration. More than 90% of the leached vanadium was precipitated, while the filtrate containing sodium molybdate was acidified with 30% nitric acid to adjust the pH to 1 and heated to 80-90 °C. Molybdenum was precipitated from the filtrate as molybdic acid (H<sub>2</sub>MoO<sub>4</sub>), which can be further used to produce Mo powder or other products.



**Figure 3-3** Flowsheet for Mo, V and Ni recovery from fly ash produced from heavy oil-fired electrical power station: (a) first stage leaching to recover V and Mo; (b) second stage leaching to recover nickel.[4]

#### MILL SCALE

There is no special extraction of molybdenum from the mill scale, instead it is believed that the molybdenum in the mill scale is recovered by reduction, and the Mo content is used directly. The possible way to reducing the mill scale includes: (i) making the mix of mill scale and carbon into briquettes and charging them into the EAF for smelting reduction;[5] (ii) carbothermic reduction of the mill scale using microwave heating.[6]

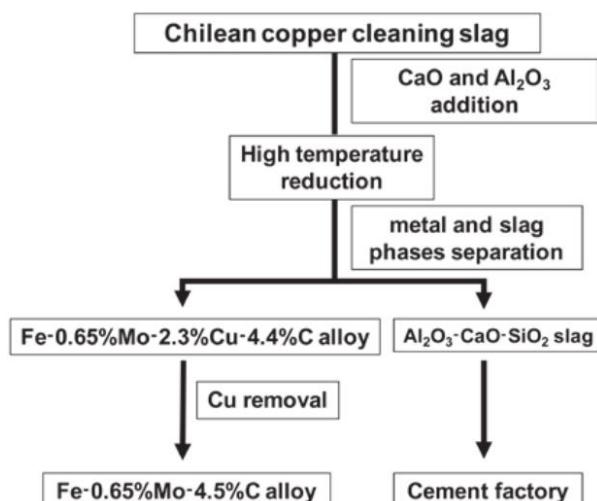
#### STEELMAKING DUST

The metal elements, including Mo, in the fly ash are recovered mainly by the pyrometallurgical processes, among which the commercially implemented ones include:[7] (i) the rotary hearth kiln pre-reduction of pellets followed by submerged arc furnace smelting (Inmetco USA, other plants in Japan Nippon Steel and Taiwan); (ii) the non-transferred plasma arc heated coke-filled shaft kiln with dust injection via tuyeres (Scandust Sweden); (iii) the smelting of briquetted dust in a conventional submerged arc furnace (Metal Europe France);

(iv) the DC transferred open arc furnace (Heckett Multiserv Italy and Mogale Alloys South Africa); (v) DC arc process for the reduction of selected metal oxides at high temperatures by means of carbonaceous reducing agents (Mintek).

### COPPER SLAG

Copper slag under strongly reducing conditions allows recovery of cobalt and molybdenum in an iron alloy for granulation and chemical treatment by chemical dissolution. However, large amounts of iron are dissolved and require expensive processing prior to use or disposal. One proposal is to oxidize the slag to hematite, in which case copper and molybdenum can all be selectively recovered from the hematite calcine using mild acid leaching.[8] Another proposed process for the recovery of molybdenum from Chilean copper slag is shown in **Figure 3-4.**[9] In this process Mo is recovery from the copper slag as Fe-Mo alloy by carbothermic reduction. The recovered Fe-Mo alloy can be used in the special steel industry, while the generated slag can be used as raw material by the cement industry.



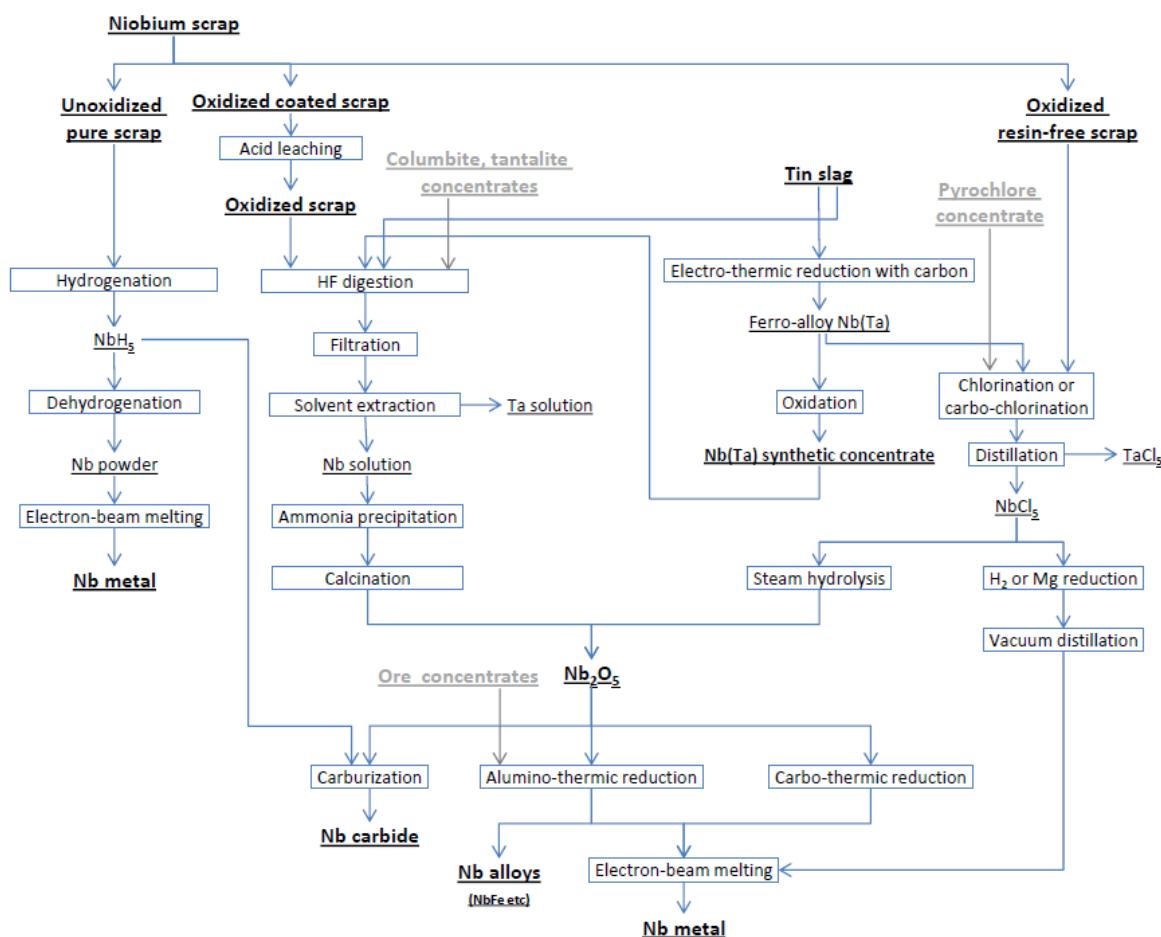
**Figure 3-4** Flow sheet of Mo recovery from Chilean copper slag.[9]

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- [5] Q. Yang, N. Holmberg, and B. Björkman, "EAF Smelting Trials of Waste-Carbon Briquettes at Avesta Works of Outokumpu Stainless AB for Recycling Oily Mill Scale Sludge from Stainless Steel Production," *steel Res. Int.*, vol. 80, no. 6, pp. 422–428, 2009.
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  - [7] G. M. Denton, N. a Barcza, P. D. Scott, and T. Fulton, "EAF Stainless Steel Dust Processing," Spring, pp. 1–9, 2005.
  - [8] M. Sánchez and M. Sudbury, "Reutilisation of primary metallurgical wastes: copper slag as a source of copper, molybdenum, and iron - Brief review of test work and the proposed way forward," pp. 135–146, 2013.
  - [9] T. Van Long, J. Palacios, M. Sanches, T. Miki, Y. Sasaki, and Mitsutaka Hino, "Recovery of Molybdenum from Copper Slag," *Tetsu-to-Hagane*, vol. 98, no. 2, pp. 48–54, 2012

## CHAPTER 4 NIOBIUM



**Figure 4-1** General flow chart for the niobium processing/production from primary and secondary resources.

### 1 MAPPING OF SECONDARY RESOURCES OF NIOBIUM

Niobium does not occur naturally as a free metal; however, niobium occurs in a range of oxide mineral species that are economically important, including columbite (78.72%  $\text{Nb}_2\text{O}_5$ ), euxenite (47.43%  $\text{Nb}_2\text{O}_5$ ), lueshite (81.09%  $\text{Nb}_2\text{O}_5$ ), and pyrochlore (75.12%  $\text{Nb}_2\text{O}_5$ ). Brazil has been the leading niobium producer and Canada the second-ranked producer.[1] The EU does not currently produce any niobium and consequently it is entirely dependent on imports from other countries.[2] Since there has been no significant niobium mining since the late 1950s,[2] recovering niobium from secondary resources is an underestimated component of the niobium supply.

Recycling in direction of niobium is a balancing act between technological and economical feasibilities and sustainable use. Niobium secondary resources include two parts: the part of

niobium occurring in the process of smelting and processing waste and the part of niobium occurring in the scrap components.

Tin slags is very essential for tantalum and niobium. Portugal is the only country in Europe that has a tin mine (39 t in 2011) but no primary production. Belgium has a secondary copper smelter with a production of 10 000 t tin (share of global production  $\sim 3\%$ , 2011).[3] Due to these reasons, the European Economic Area requires raw materials, which are not available from domestic primary sources. Thus the Member States of the European Union are completely dependent on the exporting countries. The market dynamics and the prognosticated global consumption must be considered for the future supply of raw materials. So it is possible to use secondary streams to win niobium. Based on the corresponding infrastructures, scraps are collected and processed with appropriate techniques.[4]

A list of secondary niobium-containing resources that are available for Europe use is shown in **Table 4-1**.

**Table 4-1** Secondary resources of niobium in Europe.

Type of Material	Company	Location	Grade of Nb	Reserve, mineralogy and characterization
(Sme Mine waste dumpling) Slag	Kiprianos Kavodokanos Komobil Ayia Paraskevi Neapoli Panormos Fougara	Greece	2.13 ppm – 6.74 ppm	Surface storage 825 000 m <sup>3</sup>
Mine waste dump	Buchim Mine	Macedonia	2.50 ppm	Active plant Surface storage. 46.410 Mm <sup>3</sup> , Mineralogy: Chalcocite-Chalcopyrite-Covellite-Cuprite-Galena-Hematite-Goethite (limonite)-Magnetite-Pyrite-Sphalerite-Tenorite-Native metal

#### References:

- [1] USGS 2012 Minerals Yearbook: Niobium and tantalum, 2012.
- [2] British Geological Survey: Niobium-tantalum, 2011, pp: 22.
- [3] Brown,J.,et al.(2012):Europe Mineral Statistics 2007-11-British Geological Survey(BGS), Keyworth/GB, <http://www.bgs.ac.uk/downloads/start.cfm?id=2701>.
- [4] Thomas Angerer, Stefan Luidold, Helmut Antrekowitsch. Recycling potentials of the two refractory metals tantalum and niobium[C].Proceedings of EMC 2013, pp, 1069-1084.

## 2 SECONDARY MINING OF NIOBIUM

### 2.1 SECONDARY MINING OF NIOBIUM FROM TAILINGS AND SLAG

It was reported that British miner Anglo American has begun operations at its niobium tailings project in Goiás state, central Brazil.[1] The idea is to recover niobium from phosphate tailings produced at Anglo's Copebrás phosphate plant in the city of Ouvidor. The project received investments of US\$ 30 million which will result in a 30% niobium production increase. The chemical analysis and the granulometric analysis of the phosphate rock tailings sample from the phosphate rock processing plant are shown in **Table 4-2** and **Table 4-3**, respectively. [2]

**Table 4-2** Analysis of phosphate rock tailings given in terms of oxides (wt.%).

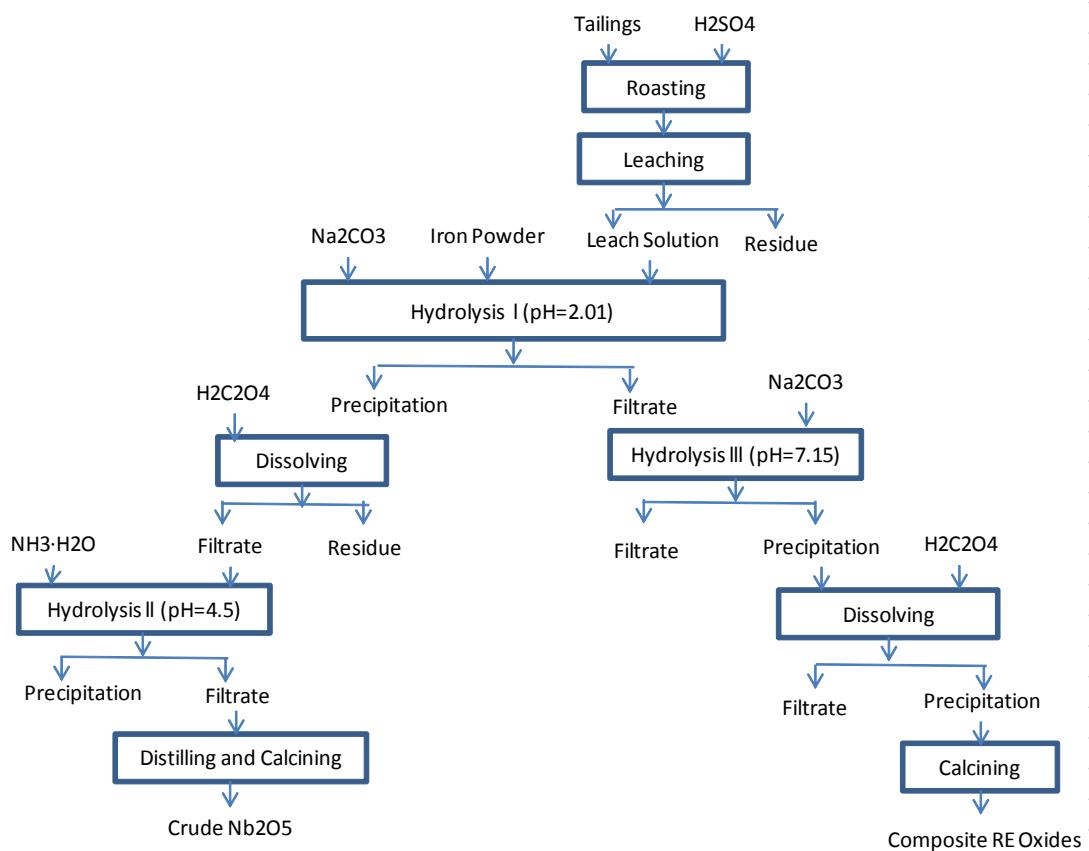
P <sub>2</sub> O <sub>5</sub>	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	BaO	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	N <sub>b</sub> 2O <sub>5</sub>
11.10	31.37	21.45	1.22	3.72	12.91	1.62	0.70

**Table 4-3** Phosphate rock tailings granulometric analysis.

Aperture	μmW	212	149	106	74	53	44	37
	#	65	100	150	200	270	325	400
% accumulated passing		99.3	98.8	98.5	97.6	97.1	96.6	96.2

The technical reconstruction for the tantalum-niobium tailing mine in Yichun China has been investigated. [3]

Bayan Obo is a large REE–Fe–Nb deposit with average grade Nb 0.13% in niobium minerals of columbite, aeschynite, fergusonite, fersmite and pyrochlore etc. Currently, niobium is not specifically recovered in the beneficiation processing circuits in the Bayan Obo mines.[4] Large quantities of tailings containing Nb are produced during the processing of Bayan Obo ore.[5] Many complicated factors such as low grade, fine-grained dissemination and complex mineral composition are the main problems encountered in recovery of RE and Nb. Studies have been conducted on tailings processing with various techniques such as smelting reduction – selective oxidation – dephosphorization –smelting, magnetizing roasting – magnetic separation – plasma smelting, selective prereduction – smelting separation – smelting, briquetting – chlorination – segmented condensation – hydrolysis, hydrochloric acid washing – sulfuric acid decomposition – leaching – N235 extraction – crystallization, selective prereduction – magnetic separation – hydrochloric acid washing, mixing – sulfuric acid roasting – leaching – filtering and washing, grinding ore – sulfuric acid decomposition – leaching – hydrolysis and magnetic separation – neutralization and smelting. A novel approach is presented in **Figure 4-2** for achieving the separation and extraction of Re and Nb from Bayan Obo tailings. [5]



**Figure 4-2** A novel approach for achieving the separation and extraction of RE and Nb from Bayan Obo tailings.

In addition, the recovery of rare earths, niobium, and thorium from Bayan Obo's tailings has been investigated. [6]

Niobium from BOF slag due to the use of Bayan Obo ore can be another secondary mine for niobium. In Baotou Steel China Bayan Obo ore is used as the raw material for hot metal production and the hot metal contains 0.015-0.034% niobium. In the following BOF process most of niobium is oxidized into BOF slag, in which the niobium oxide content is about 0.2-0.3% Nb.[7] The annual amount of the BOF slag is about 1.5 million tons, which currently is stockpiled. Many research projects have been carried out. However, no promising concept has been developed so far.

The main secondary resources of niobium are wastes of the pyrometallurgical processing of tin ores (the resulting slags contain 4% up to even 15% of Ta and Nb oxides).[8] However, such slag contributes less than 2% to the Nb production.[9] These residuals are processed through the primary Nb production route.

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## 2.2 SECONDARY MINING OF NIOBIUM FROM OTHER RESIDUALS

### SLURRIES AND PRESSING WASTES

The manufacturing of hard metals produces residuals like grinding slurries or pressing wastes (pre-consumer scraps). Post-consumer scraps are for example cutting insert or drilling pits. Depending on the infrastructure both scrap types can be processed. Based on the global use of tungsten carbide (54 650 t WC from 51 300 t W in 2010[10]) and an average hard metals composition of 80% WC and an estimated content of about 1% Nb the extrapolation results in a worldwide Nb recycling potential of 700 t. Direct recycling techniques for hard metal scraps recirculate the carbide and binder metals phases, whereas at indirect recycling technologies Nb is either partially dissipated in the solid waste or can be recovered beside others.

### RESIDUES FROM ALLOYS

The global consumption of niobium for superconducting materials ( $\text{Nb}_3\text{Sn}$  and  $\text{NbTi}$ ) is estimated between 60 t and 70 t per year.[11] The actual waste from spent superconductors (e.g. magnetic coils) is not documented. A laboratory scale recycling method for residues of  $\text{NbTi}$  alloys that combines an electrochemical copper winning with a chlorination step has been developed. [12]

### SPENT CATALYSTS

Due to the fact of widespread and various applications of Nb containing catalysts and the lack of data concerning the annual amount of spent catalysts, the calculation of the recycling potential is not feasible. Further, no industrial recycling technologies are known, which process spent catalysts for the extraction of niobium.

### OTHERS

The recycling potential of all other minor applications of niobium and accordingly its chemical compounds cannot be calculated. It is assumed that spent products attain to other recycling streams or end up on landfills.

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[http://www.bnamicas.com/en/news/mining/Anglo\\_American\\_phosphate\\_tailings\\_to\\_yield\\_niobium\\_in\\_Goias](http://www.bnamicas.com/en/news/mining/Anglo_American_phosphate_tailings_to_yield_niobium_in_Goias)
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[http://www.scielo.br/scielo.php?script=sci\\_arttext&pid=S0370-44672015000100103](http://www.scielo.br/scielo.php?script=sci_arttext&pid=S0370-44672015000100103)

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### 3 MINERAL/WASTE PROCESSING OF NIOBIUM

Tin smelting slags are generally upgraded by a pyrometallurgical process, involving the production of ferroalloy called block metal, which acts as a collector for niobium and tantalum.[1] Tin slag contains many important metals such as niobium, tantalum, manganese, iron, aluminum, titanium, etc. Tin slag processing is not practised in the industry.[2] The selective extraction of niobium and tantalum from the slag is somewhat complicated and depends to a large extent on the structure and composition of the slag. The block metal is further upgraded by a simple acid leaching or by a combination of oxidative smelting followed by acid leaching of the slag derived from the second smelting. The upgraded slag is used for the extraction of niobium and tantalum by hydrofluoric acid. A number of hydrometallurgical processing schemes have been developed for treatment of tin slags.[3] From the limited information available in the literature, it appears that

hydrometallurgical processing of low grade (< 10% niobium + tantalum oxide) is not practised in the industry. It is shown that acid leaching on an Indonesian slag containing silicon, iron and aluminium as neighbours in a calcium pseudo-structure, leads to the dissolution of calcium, aluminium and iron thereby resulting in the collapse of the configuration and liberates fine silicon dioxide particles as a colloidal solution. Whereas a slag from Zaire with niobium and tantalum as neighbours surrounding calcium will lead to loss of niobium and tantalum with the dissolution of calcium.

The recovery of niobium and tantalum from the sludge can be accomplished by many processing routes. Direct dissolution of the sludge in HF is somewhat difficult but can be accomplished. Tungsten in solution subsequently interferes with the solvent extraction and therefore direct dissolution is not preferred.

#### References:

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- [3] Ono-Ichiro, Japan Patent No. 7,036,091 dated 17.11.1970.

## 4 EXTRACTIVE METALLURGY OF NIOBIUM

Niobium recovered from such secondary sources as tin slags, residue sludge from the cemented carbide tool industries, and the scrap generated during the fabrication of niobium, niobium alloys, and superalloys is an underestimated component of the niobium supply. While it is necessary to adopt chemical processes for the treatment of tin slag and the residue sludge, well-characterized and relatively uncontaminated scrap from the fabrication and cemented carbide tool industries can be reused for the same application within the same industry by a minimum of processing. For instance, well-classified metal scrap can be reused by pulverizing it after hydriding, acid leaching to remove contamination of iron, if any, and then reusing in the fabrication stream. Similarly, well-classified scrap of cemented carbide tools consisting primarily of alloy carbide (WC-TaC-NbC) cemented with cobalt binder can be reused within the fabrication plant after separating the carbides from the cementing material. This can be achieved by a simple process involving treatment of the scrap with molten zinc. Cobalt and zinc form an alloy which has a higher specific volume. This results in exerting high stresses, thereby disintegrating the cemented carbide shapes. The carbide powder can then be reused as such, and cobalt is recovered by vacuum distillation of zinc. If, however, the scrap is not well classified and is also contaminated it becomes necessary to process it by chemical treatment to recover the individual constituents. The

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sources of scrap generation, and the ways and means of their processing to recover tantalum and associated niobium, are described below.

#### 4.1 HYDROMETALLURGICAL EXTRACTION OF NIOBIUM FROM SECONDARY RESOURCES

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 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. [1]

A literature review was carried out on the extraction of niobium and tantalum with various reagents by Bhattacharyya and Ganguly.[2] 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 et al. [3] 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.

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), octanol, 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. More detail about the general solvent extraction processes employed for the separation of niobium is presented in the WP2 report. A short summary and the main conclusions are listed below:[3]

-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. Sulfuric and hydrochloric acid solutions are characterized by association and polymerization of complexes of these elements, which prevent their selective isolation. The extraction of tantalum is much stronger than that of niobium in low HF concentration solutions with the commercially used extractants. Although the use of fluorides generates serious environmental pollution and increases the operation cost, it is very difficult to recover pure niobium and tantalum products without the presence of fluorides.

- MIBK (the MIBK process is described in Chapter 2) is the most commonly used extractant worldwide due to its lower density, lower water solubility, lower cost, higher chemical and operational stability, compared with other commercially used extractants. The obvious drawbacks of MIBK, such as high volatility and low flash point, lead to high reagent losses and potentially dangerous operation. Other commercially used extractants such as TBP, cyclohexanone and 2-octanol have some advantages over MIBK.
- Tertiary amines such as Alamine® 336 are promising extractants for purifying niobium and tantalum with low HF usage or in oxalic acid systems without the presence of HF. Further investigation is required to develop their practical applications.
- Developing aqueous complexing systems and SX systems are of importance to recover niobium and tantalum without the presence of fluorides in the aqueous solution.

The next few paragraphs briefly provide some characteristics and important features for a few of the processes that have been used for the extraction/separation of niobium from secondary sources.

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## 4.2 CASE STUDIES FOR HYDROMETALLURGICAL EXTRACTION OF NIOBIUM

### TIN SLAG

A large number of processes have been investigated to treat medium- and low-grade slags for the recovery of niobium and tantalum. The processes can be broadly grouped into three categories, with the aims defined as: (i) to upgrade the niobium tantalum content of the slags, (ii) to prepare synthetic concentrate, and (iii) to recover niobium-tantalum directly from medium-grade slags.

Niobium and tantalum content in tin slags can be upgraded by separating some of the constituents either by leaching or by separation. One of the methods involves acid leaching of slag with 2% H<sub>2</sub>SO<sub>4</sub> at 50 °C. This results in dissolution of some acid-soluble constituents and conversion of silica to colloidal form, which can be separated. Li and Baker upgraded the niobium and tantalum content of the slags by adopting a combination of alkali and acid leaching processes. The process involved treatment of a slag containing 10 to 40% SiO<sub>2</sub> with an aqueous solution of 10% NaOH under a pressure of 2.5 kg/cm<sup>2</sup> to open the slag and

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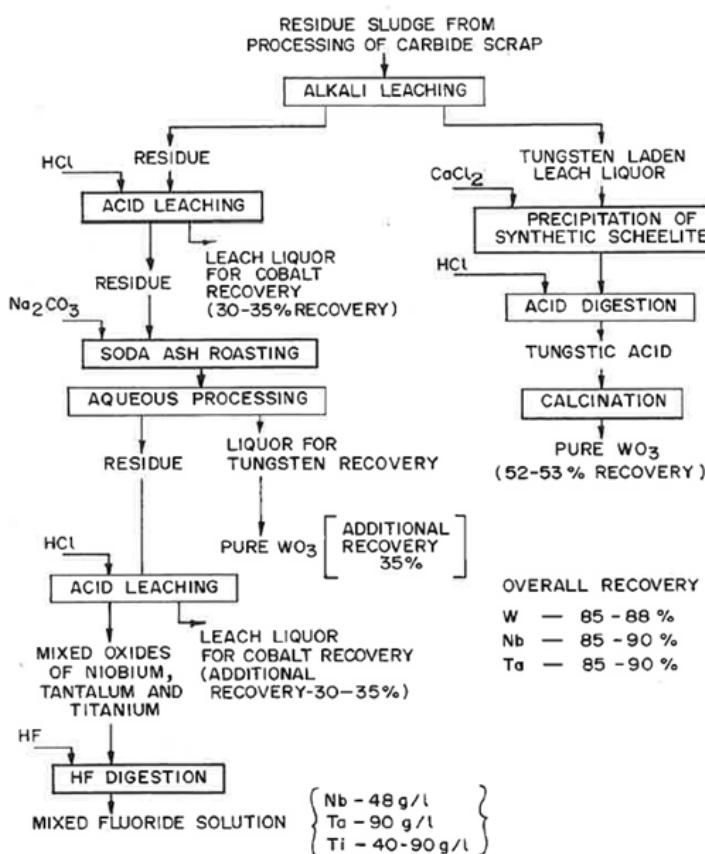
render the impurities more accessible for subsequent dissolution. After the separation of liquid, the residue is treated with hydrochloric acid to solubilize the acid-soluble impurities, such as compounds of calcium, iron, manganese, etc. Another sequence of alkali, followed by acid leaching, results in considerable improvement in the niobium-tantalum content of the upgraded slag. A similar process has been applied by Irio and Taylor to treat tin slags of the South African Iscor's plant containing about 6%  $Ta_2O_5$  and 9%  $Nb_2O_5$ . The process involves magnetic separation of prills of iron-tin alloy followed by successive hydrochloric acid and caustic soda leaching. Adoption of this process removes the bulk of those constituents which would otherwise consume hydrofluoric acid in subsequent processing.

A study by Gaballah and co-workers was conducted on tin slags of Zaire, Thailand, and Indonesia. The proposed process involved a combination of alkali and acid leaching treatment to upgrade the content of niobium and tantalum, followed by further chlorination of the leached residue. The sequence of adoption of acid-alkali or alkali-acid leaching was found to make a difference in the upgrading of metal contents and the difference in behavior was attributed to the nature of the slag. From these studies, it could be inferred that a combination of alkali leaching followed by acid leaching is best suited for Thai and Zairian slags because it would give a residue rich in tantalum and niobium, as compared to a combination involving acid leaching followed by alkali leaching. Similarly, a combination of acid leaching followed by alkali leaching is suited for Indonesian slags. Adopting these processing schemes, it was possible to obtain upgraded oxides containing about 60% of mixed niobium-tantalum oxides. The oxides were then subjected to chlorination, with or without the presence of carbon, to produce almost pure condensates containing niobium and tantalum.

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#### NIOBIUM-TANTALUM-BEARING CARBIDE SLUDGE

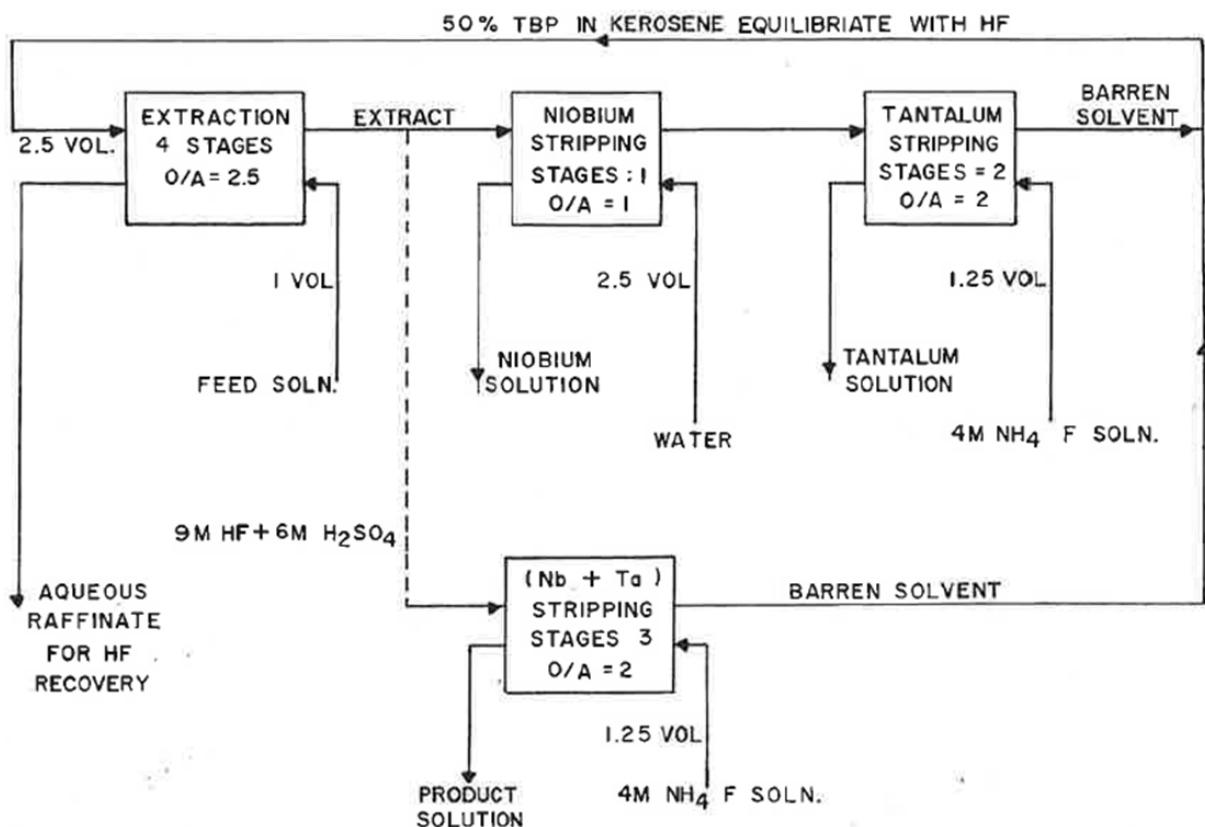
The recovery of niobium and tantalum from the sludge can be accomplished by many processing routes. Direct dissolution of the sludge in HF is somewhat difficult but can be accomplished. Tungsten in solution subsequently interferes with the solvent extraction and therefore direct dissolution is not preferred. A processing scheme has been developed by Gupta to treat the sludge as a polymetallic source to recover tungsten, cobalt, niobium, and tantalum. The flowsheet of the process is shown in **Figure 4-3**.



**Figure 4-3** Proposed flowsheet for treatment of niobium-tantalum-bearing carbide sludge.

The solution obtained after leaching invariably contains niobium, tantalum, titanium, tungsten, cobalt, and some amounts of other metallic impurities. While separation with respect to most of the metallic impurities can be accomplished readily, separation with respect to titanium is somewhat more difficult, because titanium generally gets coextracted together with niobium and tantalum in a fluoride medium. The extraction of titanium was suppressed by the addition of 6 N sulfuric acid to the leach liquor so that titanium in the aqueous phase is present as titanium sulfate, whereas niobium and tantalum are retained as fluoride complexes. The extraction of niobium and tantalum from the aqueous phase containing about 75 g/L of total oxide and a free acid of 2 M hydrofluoric acid and 7 M sulfuric acid was accomplished with an organic phase containing 50% TBP in kerosene (pre-equilibrated with hydrofluoric acid) using an organic-to-aqueous O/A ratio of 2.5 in four extraction stages. The loaded extract was then stripped either to yield a solution containing both niobium and tantalum in the same ratio as the starting feed or as solutions predominantly rich in one of the metals. Stripping of both niobium and tantalum was accomplished with 4 M ammonium fluoride using an O/A ratio of 2. For obtaining enriched 90% niobium solution, the stripping is carried out with demineralized water using a phase ratio of 1, and the raffinate is then stripped with 4 M ammonium fluoride to obtain a solution enriched with tantalum containing up to about 10% niobium. Niobium and tantalum

are then recovered as hydroxides from the solution by precipitation with ammonia gas; the hydroxides are then calcined to obtain the respective oxides. Ammonium fluoride is also recovered as a byproduct. Hydrofluoric acid from the raffinate is recovered and recycled. This is carried out by contacting the raffinate with TBP to remove the impurities, followed by stripping with water. Recovered HF is concentrated and used for equilibrating with the solvent. The flow sheet for the recovery of niobium and tantalum from cutting tool scrap sludge solution is shown in **Figure 4-4**.



**Figure 4-4** A solvent extraction flowsheet for recovery of niobium and tantalum from cutting tool scrap sludge solution.

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#### 4.3 PYRO-METALLURGICAL EXTRACTION OF NIOBIUM FROM SECONDARY RESOURCES

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##### EXTRACTION OF NIOBIUM BY CHLORINATION

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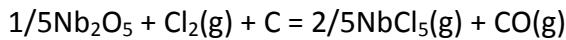
Chlorination as a process for breakdown of ores and concentrates of many of the refractory metals, and even some of the commonly used metal, is very attractive. Important features of chlorination include the high reactivity of chlorine, relative ease in gasifying many of the constituents of the concentrate 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-occurring 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:

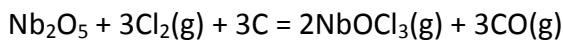


This reaction is thermodynamically feasible for very few oxides, such as CuO, PbO, but not for most of the oxides of refractory metals and especially for Niobium, Tantalum, Titanium and Zirconium.

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:



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:



The chlorination product obtained by chlorinating a charge composed of Niobium oxide and carbon is an equimolar mixture of NbOCl<sub>3</sub> and NbCl<sub>5</sub> at temperatures above 500°C. The

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proportion of  $\text{NbOCl}_3$  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 undesirable, although ferric chloride is a good 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  $\text{NaFeCl}_4$ , or  $\text{CaF}_2$  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 brick-lined 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.

The chlorination of ore/concentrate is usually performed at 750 to 850°C. In many cases chlorination is exothermic and then just needs an initiation by external heating.

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## CHAPTER 5 RHENIUM

### 1 MAPPING OF SECONDARY RESOURCES OF RHENIUM

Extracting of the particular metal from the original resource depends on the economic benefit of the process. If the extraction of a component from the initial raw materials is technically beside the purpose or not economically viable due to the excessively large costs on material, transportation and others, then it usually turns out to be production residue. Such residue is stored in certain places (next to the production or outside) and for an uncertain time to minimize their environmental impact.

Due to the continuous depletion of the initial mineral resources of useful metals, the world economic situation is changing. It is often so that the extraction of useful component from the residue is becoming valuable and companies begin to implement the schemes for waste recycling and recovery. As a rule, such schemes are much more complicated than primary treatment schemes due to the low content of desired components in wastes.

All this is fully applicable to strategic refractory metals and, in particular, to rhenium. The secondary resource of rhenium available for European production is shown in **Table 5-1**.

**Table 5-1** Secondary resource of rhenium available for European production

Type of Material	Company	Location	Grade of Mo	Reserve, Mineralogy and Characterization
Flue dust (pyrometallurgical, electrochemical processes)	Mansfeld (smelter)	Germany	63 g/t	Surface Storage 257 000 m <sup>3</sup> Anglesite-Galena-Quartz- Sphalerite-Wurtzite-Acanthite- Augite-Boléite-Bornite- Chalcopyrite-Digenite-Fayalite- Galena-Hardystonite-Melilite- Sphalerite-Djurleite

### 2 SECONDARY MINING OF RHENIUM

Recently, over 50 % of rhenium global output comes from Chile where a world leader Molibdenosy Metales - Molymet (almost all of production is metallic rhenium that is imported mainly by American aerospace industry) is operating. This company has one of the biggest rhenium recovery plants from molybdenite concentrates. In addition to installation in Chile Molymet owns: roasting plant Molymex in Mexico (based on concentrates from La Caridad mine managed by Grupo Mexico), roasting plants and ferromolybdenum smelters in Belgium (Sadaci) and metallurgical plants Chemiometall in Germany and Luoyang High-tech Molybdenum & Tungsten Material in China. Besides, it is processing copper-molibdenite

concentrates in form of service, coming from other Chilean roasting plants, mainly Codelco and Xstrata companies but also imported from Peru, Canada and USA.[1-5]

USA is the second rhenium producer that acquires rhenium as a by-product of molybdenite concentrate roasting from porphyry-type of Cu-Mo deposits. Sierrita, Freeport McMoRan Copper&Gold in Arizona is the only roasting plant for rhenium recovery in the USA.

In Kazakhstan rhenium raw materials are bought by national Redmet Company from rhenium-bearing wastes during metallurgical processing of copper ores in a Copper Factory Dzhezkazgan managed by Kazachmysi Samsung.

Other important rhenium producers are: Russia (Uralelektromed), Uzbekistan (Navoi — Cu-Mo concentrate processing plant in Metallurgical Factory Almalyk, enables rhenium and osmium recovery), Armenia (Ironworks Yerevan equipped with plant for rhenium and molybdenum production by a German Cronimet Holding) and Poland (KGHM Ecuren).

In Poland rhenium exists in domestic copper concentrates (table). These concentrates are processed by KGHM Polska Miedź S.A. in three smelters, i.e., Huta Miedzi "Głogów I", Huta Miedzi "Głogów II" and Huta Miedzi "Legnica".[5] The rhenium contents in the ore and that in the concentrate from the three smelters is shown in **Table 5-2**.

**Table 5-2** Rhenium contents in the ore and that in the concentrate from the three smelters

Mines	Rhenium content in ore, g/Mg	Rhenium content in concentrate, g/Mg
ZG „Lubin”	1.22	8.26
ZG „Rudna”	1.41	12.1
ZG „Polkowice”	1.68	12.5

In some countries, such as, Iran, Mongolia and Chile, only a part of rhenium from molybdenite concentrates is recovered. This is due to the lack of appropriate plants (roasting plants equipped with wet dust collectors). There are many technologies for rhenium recovery from rhenium-bearing materials worldwide.

In Poland rhenium is recovered as a by-product from copper concentrates. **Table 5-3** presents the concentration of rhenium in selected intermediates generated in copper production cycle. At this moment rhenium is recovered in Poland from the first three materials i.e. washing acids.[6,7]

**Table 5-3** Rhenium in selected intermediates generated in copper production cycle

Materials	Compositions
washing acid I generated in HM "Głogów II"	3-5 % H <sub>2</sub> SO <sub>4</sub> , 0.02-0.06 g/dm <sup>3</sup> Re
washing acid II generated in HM "Głogów I"	6-8 % H <sub>2</sub> SO <sub>4</sub> , 0.02-0.06 g/dm <sup>3</sup> Re
washing acid III generated in HM "Legnica"	38-40 % H <sub>2</sub> SO <sub>4</sub> , 0.01-0.05 g/dm <sup>3</sup> Re
secondary dusts from lead production	100 g Re/Mg
Fe-As alloy	up to 1000 g Re/Mg

Chile, USA, Poland as well as Armenia, Kazakhstan, Russia and Uzbekistan are the main producers of rhenium. **Table 5-4** presents global rhenium production in 2012-2015.

**Table 5-4** Global rhenium production in 2012-2015

Country	Rhenium production, Mg			
	2012	2013	2014	2015
Chile	27	25	25	26
USA	7.9	7.1	8.5	8.5
Poland	6.0	7.5	7.6	7.8
Armenia	0.6	0.3	0.35	0.35
Kazakhstan	3.0	2.5	0.3	0.2
Uzbekistan	5.4	5.5	0.9	1.0
Russia	1.5	-	-	-
Others	1.2	1.0	2.0	2.0
Global production	52.6	48.9	44.65	45.85

Treatment scheme selection and preparation method for rhenium recovery from particular industrial residue materials depends primarily on the physical and chemical form in which the residue exists. **Table 5-5** presents a list of possible industrial residues that contain rhenium, and consequently can be recovered.

**Table 5-5** Industrial residues for possible Re recovery.

Name of residue source	Main industry	Estimated content of Re	Related research
Rhenium containing titania spent catalyst	Hydrogenation reactions (reforming of naphtha). Preparation of hydrocarbons from synthesis gas via the Fischer-Tropsch process	1.20%	[8]
Spent platinum-rhenium reformer catalysts	Petroleum industry	-	[9-11]
Dust from exhaust gas	Mo concentrate roasting process	-	[12]
residue materials	Residue materials from the old sulphur abandoned mine	1.34 – 3.40 ppm	[13]

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[13] M.O. Figueiredo, T.P. da Silva, J.P. Veiga, D. de Oliveira, M.J. Batista. Towards the Recovery of By-Product Metals from Mine Wastes: An X-Ray Absorption Spectroscopy Study on the Binding State of Rhenium in Debris from a Centennial Iberian Pyrite Belt Mine. *Journal of Minerals and Materials Characterization and Engineering*, 2014, 2, 135-143.

### 3 MINERAL/WASTE PROCESSING OF RHENIUM

The current chapter describes in details the industrial residue processing for rhenium recovery processes listed in **Table 5-5**. The main attention is paid to the pre-treatment methods of processing, covered in different research studies.

#### 3.1 RHENIUM CONTAINING TITANIA SPENT CATALYSTS

Catalysts comprising a catalytically active metal on a support such as silica or alumina are known from hydrogenation reactions. For example, catalysts comprising rhenium have been found to be highly effective for such processes as:

- 1) Reforming process of naphtha;
- 2) Preparation of hydrocarbons from synthesis gas via the Fischer-Tropsch process.

In certain chemical reactions, it is believed to be advantageous to deposit a catalytic metal or metals on a titania support. For example, rhenium supported on titania is preferred by some workers for Fischer-Tropsch reactions because it is more active for CO conversion than when supported on alumina or silica. In addition, titania supported catalysts may be preferred for use in hydrothermal environments where alumina supports may show a tendency to degrade to some extent.

During use catalysts tend to become less active and require periodic regeneration. After many times of regeneration, the catalyst will no longer be capable of being restored to a satisfactory activity level. It then becomes necessary to replace the deactivated or spent catalyst with fresh catalyst. The spent catalyst contains expensive metals and need to be recovered.

ExxonMobil Research and Engineering Company developed and patented the method for recovering rhenium from a titania-supported, rhenium-containing catalyst by treating the catalyst in the reduced form with an acid in an amount and for a time sufficient to dissolve the rhenium without dissolving the support. [1]

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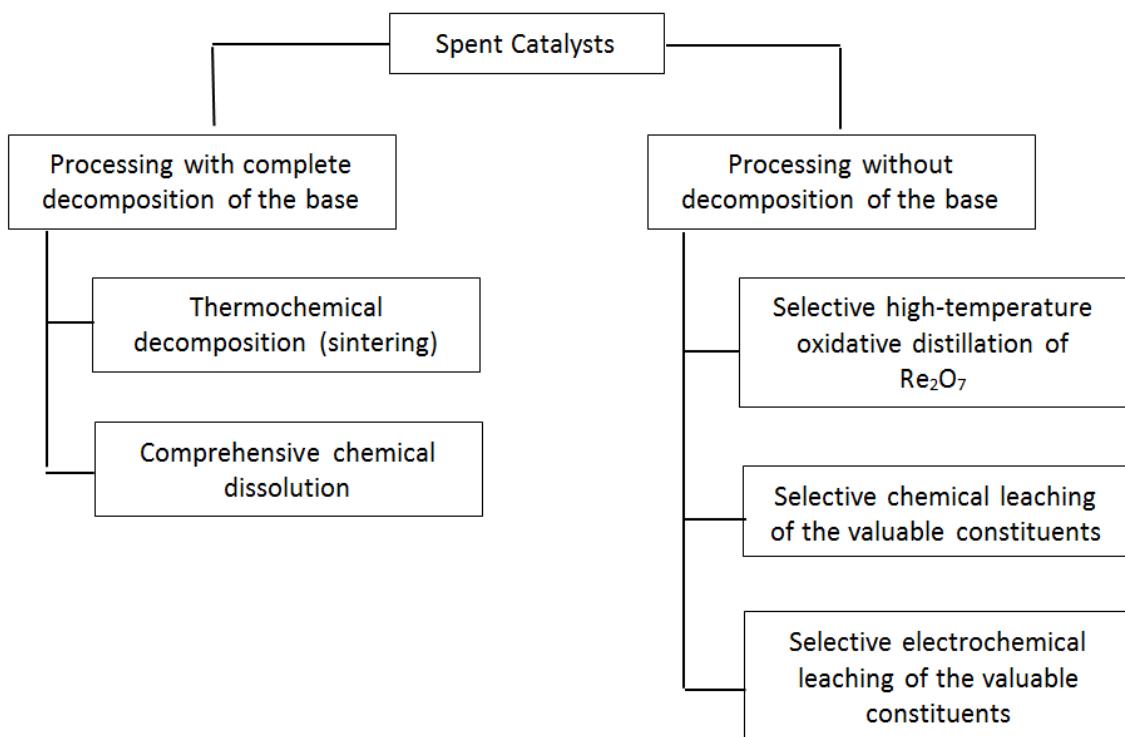
In the method of the present invention, it is necessary that rhenium, and other catalytic metals when present, on the titania-supported catalyst be in the reduced state prior to treatment according to the invention. For example, a slurry of spent, rhenium-containing, titania-supported catalyst in liquid hydrocarbons, such as those produced in a Fischer-Tropsch hydrocarbon synthesis process, is separated from the hydrocarbons in a catalyst separation zone. The separated catalyst then is contacted with hydrogen or a mixture of hydrogen and an inert gas at temperatures in the range of about 250°C to about 550°C (preferably from about 275°C to about 425°C) and pressures ranging from above ambient to about 40 atm for a time sufficient to reduce the rhenium. Typically, about 30 minutes to about 24 hours is sufficient to reduce the rhenium.

Alternatively, a slurry of spent, rhenium-containing, titania-supported catalyst in the liquid hydrocarbons may be reduced in the presence of the liquid hydrocarbons by contacting the slurry with H<sub>2</sub> and CO in the molar ratio of about 1.5 to 4.0 at pressures of 1 to about 100 atm and preferably 10 to 25 atm at temperatures of 175°C to 450°C for a time sufficient to reduce the rhenium. Then the reduced catalyst is separated from the liquid hydrocarbons for future treatment according to the invention.

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### 3.2 SPENT PLATINUM-RHENIUM REFORMER CATALYSTS

Annually, over 5 million lbs. of spent Reformer Catalysts are treated for the recovery of contained platinum and rhenium. The technologies available for recycling of the spent platinum-rhenium catalysts can be roughly divided into two groups (**Figure 5-1**), one incorporating decomposition of catalyst aluminum oxide base, the other – selective extraction of rhenium without the base decomposition. In the former, the catalyst is decomposed by chemical (acid or base leaching) and thermochemical methods (sintering with base), yielding much rhenium but undesirable due to high reagent consumption and sizeable aluminate residue. The other group incorporates selective high-temperature distillation Re<sub>2</sub>O<sub>7</sub>, selective chemical leaching (with weak acid under oxidative conditions) and electrochemical leaching (with acid solutions under direct or alternating current).



**Figure 5-1** Technologies available for recycling of the spent platinum-rhenium catalysts. [2]

In another publication, a summary of available technology and methods employed for the processing of spent Pt-Re Catalyst was discussed by the author [3]. Special emphasis was made on rhenium recovery, purification and production of Catalytic Grade Ammonium Perrhenate. Furthermore, the factors influencing the chemical processing, the residence time and the purity of products in addition to metal accountability was discussed.

### 3.3 DUST FROM EXHAUST GASES

Significant amounts of rhenium compounds evaporate during molybdenum roasting process. The dust in exhaust gases can be collected with scrubbers and then be processed for recovery of rhenium.

A device that was used to recover dust and rhenium from molybdenum concentrate roasting exhaust gas was developed by authors [4]. The device combine the self-swash dust catcher and spherical tray tower technology: the self-swash dust catcher was used to recover dust and rhenium; spherical tray tower was used to further dust and rhenium recovery and its application to engineering in practice. This was the first successful device used to recover dust and rhenium integration from calcination exhaust of molybdenum concentrate which contains rhenium in production practice. Through production practice it is proved that the device is feasible with high efficiency. It has the advantages of simple structure, convenient operation, low cost and low energy consumption.

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### 3.4 RESIDUES FROM OLD ABANDONED SULPHUR MINE

Rhenium can be found in residues resulting from a long-term mining, particularly of sulphide ore deposits. For example the waste materials from the old sulphur factory at the abandoned mine of São Domingos (Iberian Pyrite Belt, Southeast Portugal), exploited since the Roman occupation of Iberia, contains up to 3 ppm of the metal. Aiming at a potential sustainable recovery of rhenium as a by-product, X-ray near-edge absorption spectroscopy (XANES) was applied to clarify the Re-binding and mode of occurrence by comparing Re L<sub>3</sub>-edge XANES spectra obtained from mine residue samples (previously fully characterized by X-ray laboratory techniques) with similar spectra collected from Re-rich molybdenite ( $\text{Mo}_{1-x}\text{Re}_x\text{S}_2$ ) and from Re-O model compounds configuring various valences and coordination environments of rhenium ions. The authors of the research concluded that in the analyzed mine waste materials the bining belonged to Re-O binding other than Re-S binding.[5]

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## 4 EXTRACTIVE METALLURGY OF RHENIUM

### 4.1 HYDROMETALLURGICAL EXTRACTION OF RHENIUM FROM SECONDARY RESOURCES

For the time being, Poland is the major producer of rhenium from mineral resources within Europe with 7.8 tonnes of production in 2015.[1] Armenia is also producing around 300 kg of rhenium in the form of potassium perrhenate per year which is exported to Germany. Armenian's rhenium is produced from molybdenite roasting facilities in and outside of Armenia but no data has been found on the details of the rhenium recovery process. Rhenium can be recovered from off-gas and dusts of molybdenite roasting facilities, off-gas of copper smelting process, leachate of pressure oxidative leaching and pregnant leach solution (PLS) of copper heap leaching.[2] In a typical method used for recovery of rhenium from off-gas of molybdenite roasting, vaporized rhenium heptoxide is dissolved in water as perrhenic acid. The impure solution is either treated with pH adjustment to precipitate some of the impurities (e.g. Kennecott Process, USA) or is directly sent to ion exchange unit (e.g. KGHM's Glogow Process, Poland). If the ion exchange resin is a strong basic anion exchanger (Kennecott Process), the stripping is performed by using a strong mineral acid solution and if a weakly basic anion exchanger is used (KGHM's Glogow Process, Poland), the stripping is performed by ammonia solution. In case of stripping with acid solution, the eluate undergoes pH adjustment, precipitation of rhenium sulfide and dissolution as ammonium perrhenate; while, in case of weakly basic anion exchanger, the eluate is already a solution of ammonium perrhenate. [2-3] KGHM's Glogow Process, Poland[4] is dependent on ion-exchange recovery of the dissolved rhenium content of acid wash produced in sulfuric acid unit of copper smelters. The other alternative for selective separation of rhenium is solvent extraction which has been proposed for application in Kazakhstan, as the owner of one the richest deposits of rhenium in the world. [5] In this method the vaporized rhenium from copper smelting furnaces, is solubilized in aqueous media and later transferred to a system of tri-alkyl-amine+kerosene system followed by stripping with ammonium hydroxide. In case of pressure oxidation of molybdenite, the leachate is usually treated with solvent extraction followed by stripping with ammonium hydroxide. [6] In another process developed for recovery of rhenium from copper heap leachates (Pilot operation in the USA),[7] the rhenium containing leachate of copper ore is sent to activated carbon adsorption circuit, and later the rhenium is eluted using a solution of sodium hydroxide and ammonium hydroxide at neutral pH values. The eluate later is purified using solvent extraction (Alamine 336) or ion exchange (Purolite A170), with ion exchange being preferred since its eluate is compatible with the downstream rhenium production plant. [6] In a Russian Process, [3] in case of molybdenum impurities, desorption of molybdenum from activated carbon is performed by cold sodium carbonate followed by rhenium desorption using hot sodium carbonate. Irrespective to the type of process (ion exchange or solvent extraction), the final stage of

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purification is commonly repetitive crystallization to produce high purity rhenium perrhenate. As an alternative method instead of crystallization, electro-winning can be used, but not as commonplace as crystallization.[2] Approximately the same methods of ion-exchange/solvent extraction have been applied for recovery of rhenium from uranium mining facilities (investigation in the USA and Russia). [2]

In KGHM's Glogow Process, [4] Poland, after condensation of copper smelting facilities' off-gas an acidic solution is created containing 20 ppm of Re with other impurities and suspended solids (40-500 ppm). In KGHM's Glogow process first the acid wash is filtered in a propylene filtration press to remove suspended silicon dioxide and the filtrate is sent to adsorption on weakly basic ion exchanger. There are 4 resin beds in series each holding 5 cubic meters of Ionite. The rhenium is adsorbed in the form of  $\text{ReO}^{4-}$ . The washing of resin bed is performed with water to remove the residual mother liquor followed by rhenium stripping with dilute ammonia solution. After elution a second round of water wash is done. Rhenium containing eluates, are filtered and sent to vacuum evaporation to crystallize ammonium perrhenate. Further purification of ammonium perrhenate is performed by consecutive recrystallization. The typical purity of the final ammonium perrhenate is min. 69.4% Re (0.1% humidity) with other metal concentrations in ppm: Hg < 1; Al, Cu, Fe, Mg, Mn, Mo, Na, Ni, Pb, Zn < 5; Ag, Ba, Ca, Cd, Co, Cr, Pd, Rh, Ru, Sb, Sn, Tl < 10; As, Se, Si, W < 20; V, P, Ir < 50 and Cl<sub>2</sub> < 0.05%. Such purity meets the required minimum purity of 69.2% Re (0.05% humidity) with other metal concentrations in ppm: Al, Cu, Mg, Mn, Mo, Na, Ni, Pb, Zn < 5 ppm; Ca < 10 ppm; S, Si, W < 20 ppm and P < 50 ppm.

In a typical process [2] for recovery of rhenium from electrostatic filter dust of molybdenite roasting, performed in Russia, the dust (containing 0.4-1.5% Re and the rest  $\text{MoO}_3$ ,  $\text{MoS}_2$ ) is leached twice using hot water with addition of pyrolusite as an oxidative agent of rhenium. The leachate mostly contain 0.5-0.6 g/L of Re, 8-10 g/L of Mo and 20-30 g/L of sulfuric acid and some copper and iron sulfate. The solution is treated with lime to pH of 11-12 and heated to 60-70 °C. After filtration of precipitates, the solution is evaporated to rhenium content of 15-20 g/L. Later the rhenium is precipitated by addition of KCl as  $\text{KReO}_4$ .

Chinese have proposed a process [5] for recovery of rhenium from leach liquor of pressure oxidative leaching. In this method 98.5% of rhenium is dissolved at 230 °C. The leachate contains 6-8 g/L of Mo, 0.165 g/L of Re and 210-230 g/L sulfuric acid. Rhenium was extracted about 98.5% using 0.5% tri-octyl-amine+15% isoctanol+84.5% sulfonated kerosene, O/A: ½ and in three stages at low pH values with 0.15% co-extraction of molybdenum. Stripping is done using ammonium hydroxide solution.

In a pilot process[6] by Freeport-McMoran Corporation, USA, copper heap leach solution (PLS) was contacted with four columns in series containing fixed bed activated carbon. The leachate contains 0.65 mg/L of rhenium. Impurities, such as Al, Cd, Ca, Co, Cu, Fe, Mg, Mn,

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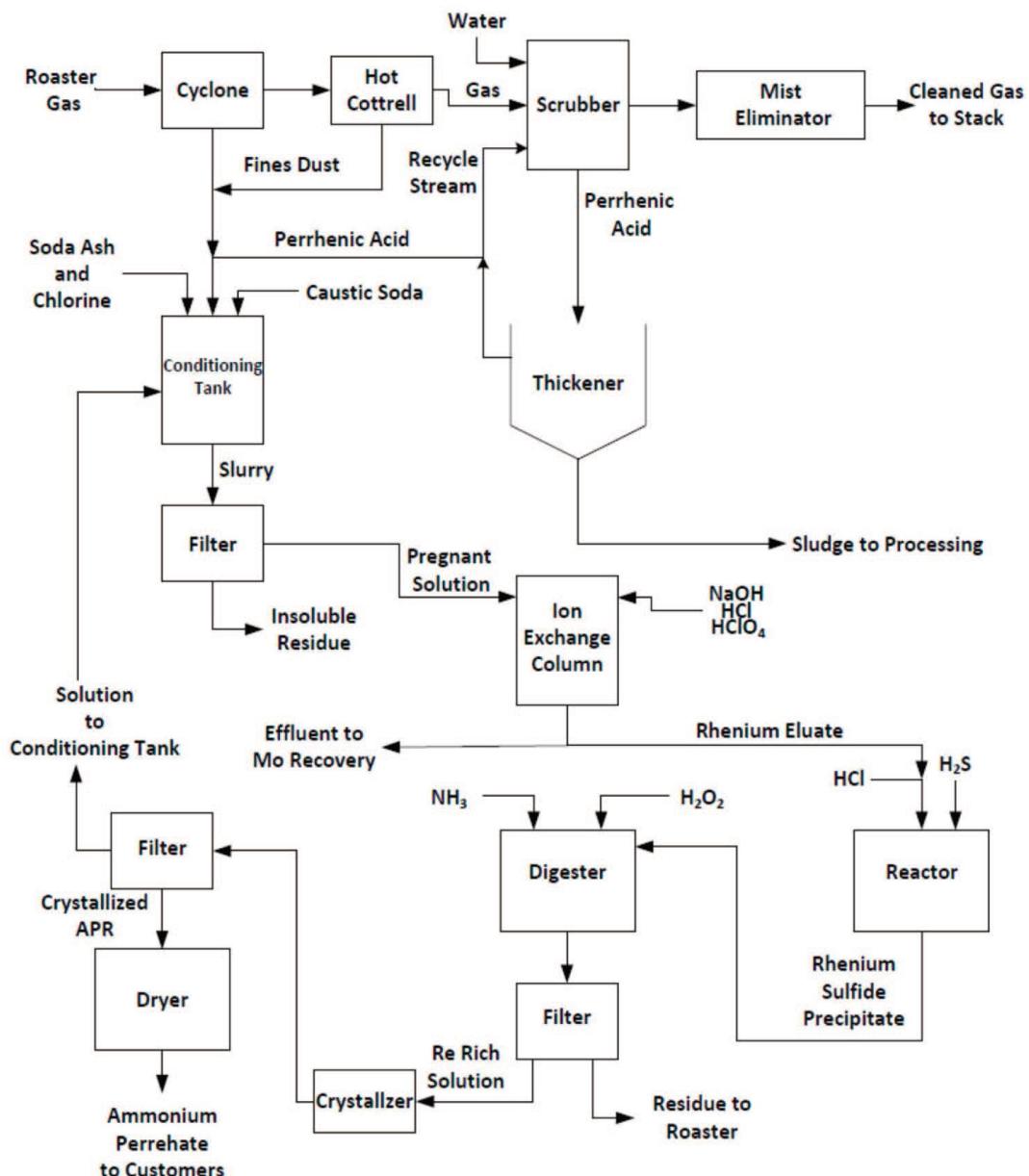
Na, Ni, Si, V, Yt and Z were present in leachate in concentrations greater than the concentration of dissolved rhenium. When the feed rhenium content was 0.57 ppm, highest loading of rhenium on carbon was ~2900 ppm corresponding to a concentration increase of ~5100 times that dwarfs concentration increase of other metal species (e.g. Mo: 64 times, Fe: 1.3 times, Cu: 0.87 times). The average rhenium recovery from the leach solution was 96%. The average rhenium loading onto the carbon in column 1 was greater than 2 g-Re/kg-carbon. Elution was satisfactory using sodium hydroxide (2%) at 110 °C. The elution resulted in a solution with 80-120 ppm rhenium. Ion exchange resin (Purolite A170) and solvent extraction (5% Alamine 304 or Alamine 336) were satisfactory for further purification of solution. In case of solvent extraction, stripping of loaded organic was performed using 18 g/L NaOH and the final product contained 10-24 g/L of rhenium. The compatibility of the stripped solution for further purification within FCX rhenium production plant was tested by rhenium loading on Amberlite resin. The goal was 180 g-Re/L-resin at 98% loading efficiency but when the stripped solution was loaded on Amberlite, loading efficiency was < 40%. Due to such low loading efficiency, solvent extraction was replaced with ion exchange (Purolite A170). The loaded resin was stripped using NaOH and the compatibility test results were 187.6 g-Re/L-resin at 98.3% loading efficiency with no fouling and damage on the resin. According to these pilot scale data, ion exchange has been selected for industrial scale operation.

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## 4.2 CASE STUDIES FOR HYDROMETALLURGICAL EXTRACTION OF RHENIUM

### KENNECOTT PROCESS



**Figure 5-2** Rhenium recovery by Kennecott process.

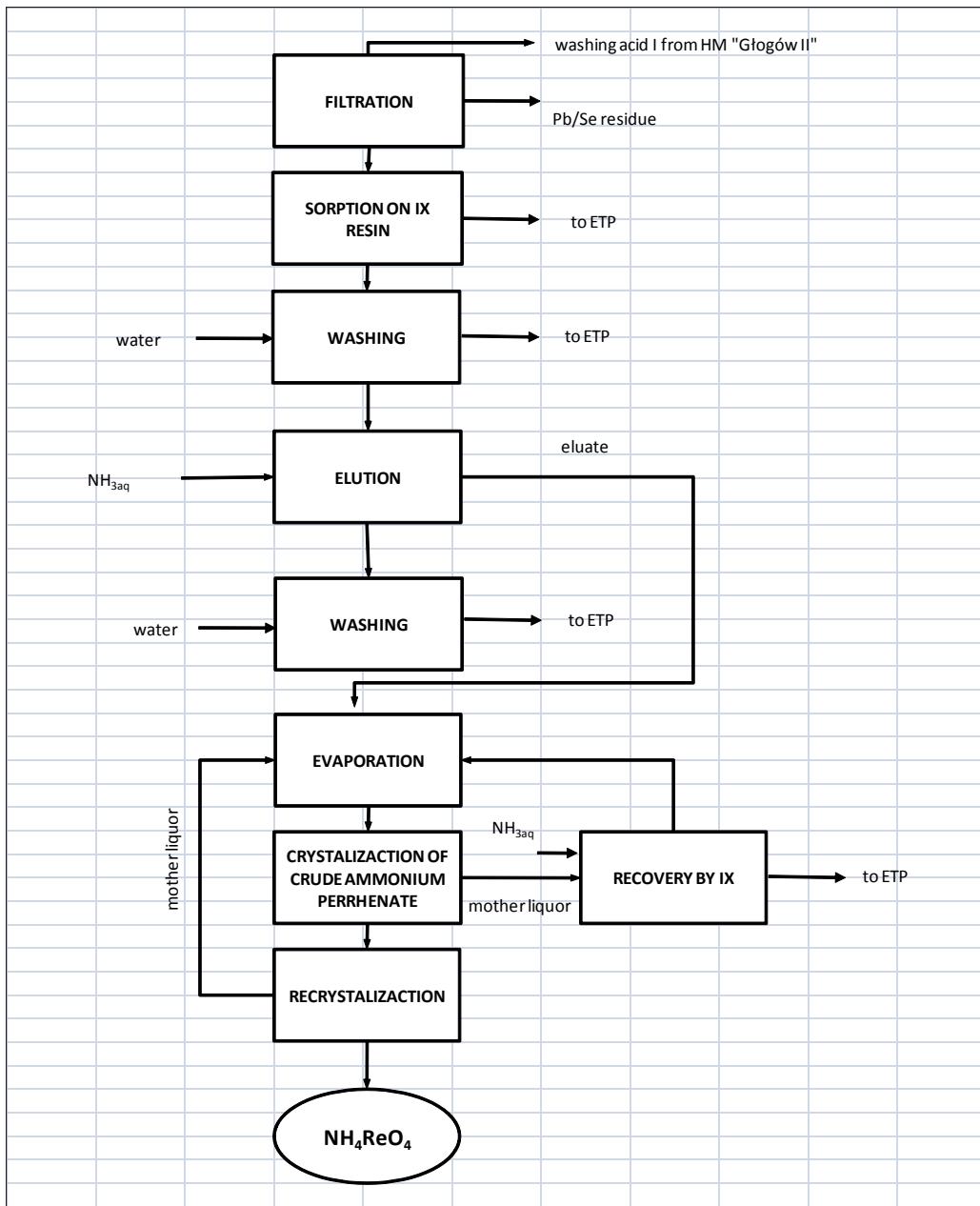
The original Kennecott Process for the recovery of rhenium involves a scrubbing process, in which the exhaust gases of the molybdenum roasting circuit are washed with water to produce perrhenic acid. The pregnant solution is continually recirculated through the scrubber circuit until the rhenium concentration reaches approximately  $100 \text{ mg/dm}^3$ . After this, the solution is conditioned for 24 hours with caustic soda, soda ash and oxidized with calcium hypochlorite. The pH of this solution is brought up to 10 to precipitate any

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contaminants (primarily iron) remaining in the solution and allow them to settle. The solution is filtered and sent to an ion exchange circuit, where the anionic resin preferentially adsorbs the aqueous rhenium from the alkaline solution. After the loading stage is finished, the rhenium is stripped by the addition of hydrochloric acid. A caustic soda solution is then used to remove the remaining adsorbed molybdenum, which is subsequently recovered as calcium molybdate. Perchloric acid and hydrogen sulfide are then added to this solution to precipitate rhenium as rhenium sulfide. This precipitate is then re-dissolved in a solution of ammonia and hydrogen peroxide, from which it crystallizes as ammonium perrhenate.[1,4] The flow sheet of rhenium recovery by Kennecott process is shown in **Figure 5-2**.

### KGHM PROCESS

Research of rhenium recovery in Poland has been carried out since 1960s. Initially main impact was set on rhenium recovery from lead secondary dusts. As a result two leaching technologies of dusts in water or sulfuric acid were developed and the rhenium from these solutions was recovered by ion exchange on highly basic resin. Ammonium perrhenate was a product in this technology. Change of dust collecting technology from dry into wet one in smelter caused unprofitability of this method. Therefore further research was targeted on rhenium recovery from washing acids and it resulted in many new technologies, however, the most important one is the last one i.e. precipitation method of rhenium from washing acid in HM "Legnica". In the first stage rhenium was precipitated by 60 % sulfuric(VI) acid solution with  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ . Rhenium concentrate was filtered and leached with water and hydrogen peroxide. Solution was then neutralized by ammonia solution to pH 7, filtered and sorption was made on a highly basic anion exchanging resin. Rhenium was eluted by 3 %  $\text{NH}_4\text{SCN}$ . Eluted solutions were concentrated and ammonium perrhenate was crystallized. This technology was implemented in industry with a maximum production of the plant at the level 250 kg of ammonium perrhenate. The technology was withdrawn in 1993 because of fall in the rhenium demand. Research was restarted in Poland in April 2002. As a consequence of IMN and KGHM Ecoren S.A. cooperation a new technology of rhenium sorption on a weak basic anion exchanging resin was developed.



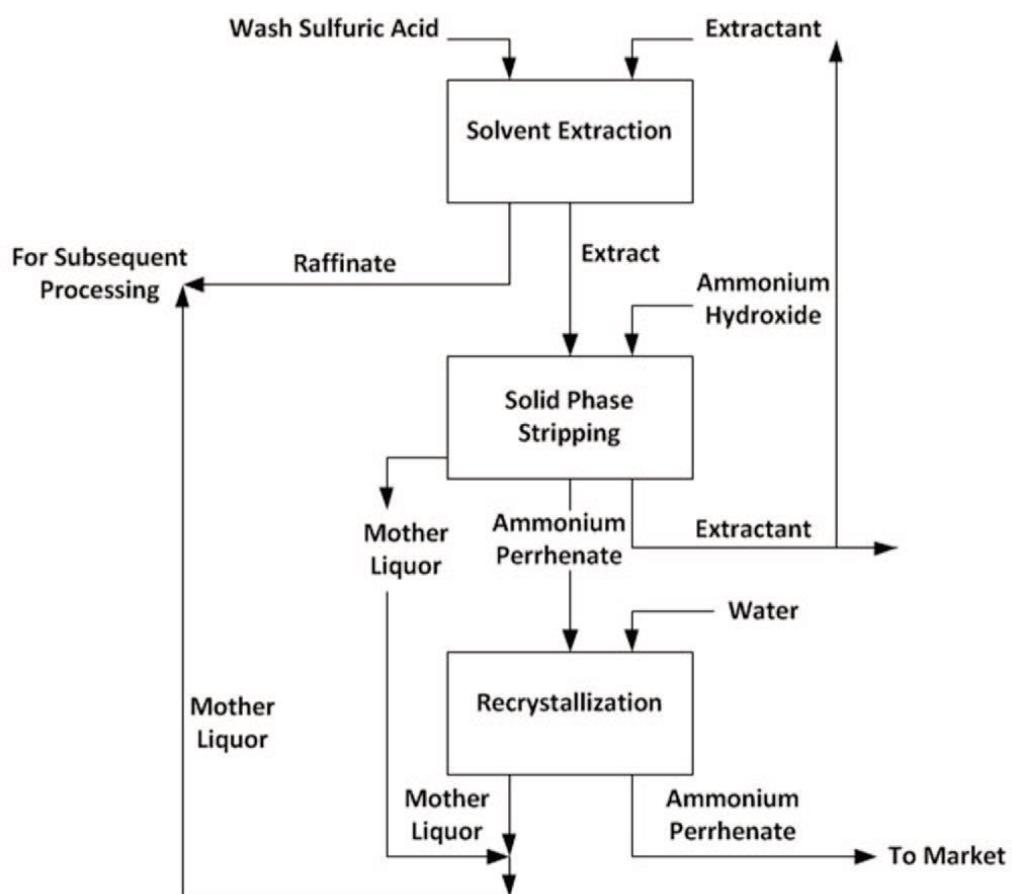
**Figure 5-3** Rhenium recovery by KGHM process.

The technology is composed of two main parts. In the first one automated and computer-controlled ammonia rhenium eluates are produced. In the second one eluates are concentrated and ammonium perrhenate(VII) is extracted. The technology scheme is presented in a **Figure 5-3**. Before sorption acid solution is directed to filtration in a filter press made of polypropylene, to remove  $\text{SiO}_2$  and maximize ion exchanger life. Purified acid is sent to sorption unit on a weak basic resin. The bed is set in four columns connected in series, each of which contains  $5 \text{ m}^3$  of ion exchanger. Acid for sorption is stored and prepared in two storage tanks and is subsequently passed through the bed. Uniform acid flow is controlled by columns equipped with special distributors supplying and discharging

acid and air vent valves for gas removal (i.e. SO<sub>2</sub> and air). As a result rhenium is held in an ion exchanger in form of ReO<sub>4</sub><sup>-</sup> while acid sludge formed (with rhenium content < 1mg/dm<sup>3</sup>) is passed to the installation for washing acid. When sorption is finished acid flow is stopped on the one saturated column and column is washed with water. It aims to remove residual acid and impurities. Rhenium in a column is eluted by weak ammonia solution. After this operation it is once again washed with water. Solution from this washing is directed to washing acid installation. Eluted column is connected as the last one in a series. Rhenium sorption and rhenium eluates production is executed in three installations set in all three smelters. Eluates from these installations are combined together and processed in one. In this installation eluates are processed together with end liquors and eluates produced during primary liquors processing, then these are filtered and concentrated by evaporation. Concentrated solution is a source of ammonium perrhenate obtained by crystallization and product is finally passed to re-crystallization. Primary liquors are sent to rhenium recovery by ion exchanger. Raw ammonium perrhenate purification is made in a set of crystallizers equipped with mechanic stirrers and cooling coils. Pure ammonium perrhenate separated from end liquors is dried to a constant weight. End liquors are connected with eluates and directed to concentration and crystallization step. Total production capacity of these installations allows producing about 8 tons of ammonium perrhenate. Based on this technology KGHM Ecuren S.A. produces and sells ammonium perrhenate: of catalytic purity – fulfilling following requirements: min. 69.4 % Re; moisture content: 0.1 %; Hg < 1ppm; Al, Cu, Fe, Mg, Mn, Mo, Na, Ni, Pb, Zn < 5 ppm; Ag, Ba, Ca, Cd, Co, Cr, Pd, Rh, Ru, Sb, Sn, Tl < 10 ppm; As, Se, Si, W < 20 ppm; V, P, Ir < 50 ppm, Cl<sub>2</sub> < 0,05 % and of basic purity - fulfilling following requirements: min. 69.2 % Re; moisture content: 0,05 %; Al, Cu, Mg, Mn, Na, Ni, Pb, Zn < 5 ppm; Ca, < 10 ppm; S, Si, W < 20 ppm; P < 50 ppm.[1,2,5]

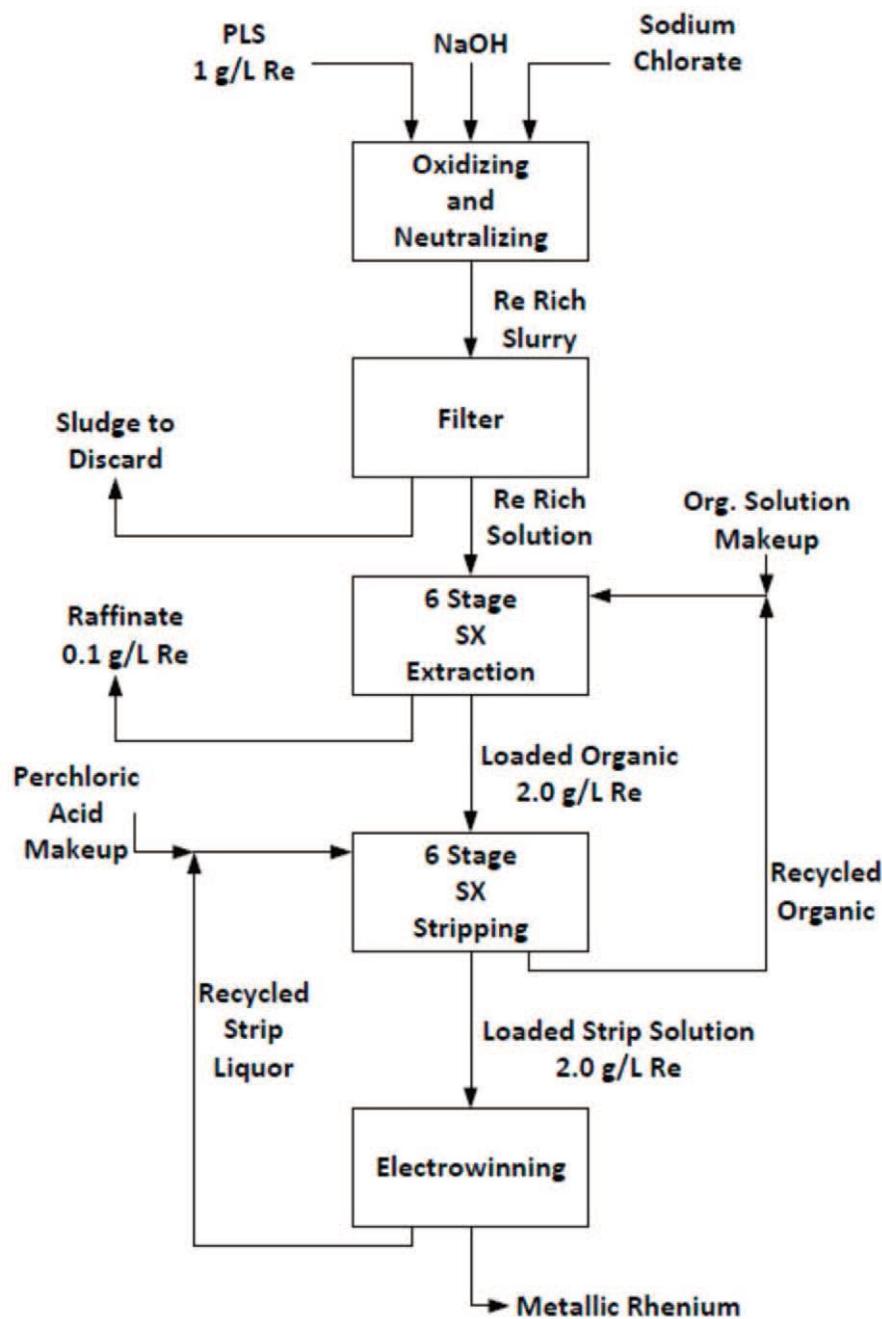
## SOLVENT EXTRACTION PROCESSES

Some of the richest rhenium containing deposits in the world are found in Kazakhstan. In the Zhezkazgan deposit, produced copper concentrates can contain up to 30 g/Mg of rhenium. Abisheva et al. have proposed a process in which the copper concentrate is electro-smelted, and the rhenium present is volatilized, as rhenium heptoxide , and scrubbed with water/dilute sulfuric acid to form perrhenic acid in concentrations of up to 0.25 g/dm<sup>3</sup>. The aqueous rhenium solution is sent to a solvent extraction step for the selective separation of rhenium from the impurity elements present. The extractant used in this technology is trialklamine organic compound (TAA) in a kerosene diluent. The loaded organic phase is stripped using ammonium hydroxide to produce ammonium perrhenate. The barren organic phase is then recycled for further use in solvent extraction, and the impure ammonium perrhenate is continually dissolved and recrystallized to produce a 98.5% pure ammonium perrhenate. [1,6] A flow chart for the process is shown in **Figure 5-4**.



**Figure 5-4** Solvent extraction process for rhenium recovery from copper concentrates.

As an alternative to the conventional method of ammonium perrhenate precipitation, the United States Bureau of Mining developed a solvent-extraction/electro-winning process for rhenium recovery from molybdenite roasting. Once more, rhenium heptoxide present in the flue gas was scrubbed using water. The aqueous rhenium was oxidized using sodium chlorate and the pH of the solution was brought to 12 by caustic soda addition. Prior to the solvent extraction step, the solution was filtered to remove any precipitates that formed during pH adjustment. The pregnant solution was then sent to a six-stage extraction circuit, which used a combination of: 5% aliquat 336, 5% primary decyl alcohol (PDA) and 90% kerosene as the extractant phase. The loaded organic was then stripped using a perchloric acid/ammonium sulfate solution. After stripping, the rhenium-rich electrolyte was sent for electro-winning using a current density of  $360 \text{ A/m}^2$ . Results from the pilot plant experimentation show that rhenium metal can be prepared from dilute impure solutions containing aqueous rhenium and molybdenum.[1,7] A flow chart for the process is shown in **Figure 5-5**.



**Figure 5-5** Solvent extraction process for rhenium recovery from molybdenite roasting.

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#### 4.3 PYRO-METALLURGICAL EXTRACTION OF RHENIUM FROM SECONDARY RESOURCES

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##### RHENIUM RECOVERY FROM PYROMETALLURGICAL EFFLUENT STREAMS

In pyrometallurgical roasting of molybdenum concentrates containing rhenium, rhenium present in the molybdenum concentrate is oxidized to rhenium heptoxide. It should be noted that rhenium heptoxide is extremely volatile thus, at the temperatures used for molybdenum roasting (900-950 K) it is likely that nearly all of the rhenium present is volatilized. This volatile product exits the furnace with the flue gases and is subsequently recovered as perrhenic acid after being scrubbed with water. After scrubbing, the aqueous rhenium is typically recovered using solvent extraction or ion-exchange processes. Generally, the end precursor product produced by these methods is ammonium perrhenate via crystallization. In Poland rhenium is recovered as a by-product from copper concentrates. Because of high volatility of oxidized rhenium compounds during copper concentrate pyrometallurgical processing there is an accumulation of rhenium in dusts and gases. In a classical shaft furnace technology rhenium is partially distilled and as a sulfide is gathered in a sludge. The rest remains in copper matte, and passes to gas phase as a dirhenium heptaoxide after converting process. Then it is eluted from gas phase in a sulfuric acid plant. In the flash furnace technology rhenium is distilled as an oxide and together with gases goes to sulfuric acid plant, where is passed to weak waste sulfuric acid during washing-cooling stage. Shaft furnace dusts, sludge from wet dust collectors, dusts from convertors and dusts from flash furnace are directed to lead smelter. During raw lead smelting in rocking-rotary furnace rhenium in dusts partially passes to gas phase and is recovered from secondary dusts. In lead recovery there is produced also Fe-As alloys called "szpejza" which contains significant quantities of rhenium; because of high arsenic content it is very difficult to process this material. [1-3]

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