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Innovation potential in the recovery of refractory metals from secondary resources

Authors : Mrs. Lena SUNDQVIST OEQVIST (Swerea)

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Summary

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Date	By
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INNOVATION POTENTIAL IN THE RECOVERY OF REFRACTORY METALS FROM SECONDARY RESOURCES

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Lena Sundqvist Ökvist, Guozhu Ye and Xianfeng Hu (Swerea MEFOS)

Contributors:

W: Stefan Willersinn (UNIKL) and Jiasen Yang (GTK)

Mo: Xianfeng Hu, Lena Sundqvist Ökvist, Guozhu Ye (Swerea MEFOS), Tuomo Sainio (LUT)
and Jiasen Yang (GTK)

Nb and **Ta:** Marta Macias Aragonés (IDENER) and Eugen ANDREIADIS (CEA), **Ta** Nourredine
MENAD and Kathy BRU (BRGM)

Re: Tuomo Sainio (LUT), Witold Kurylak (IMN), Marta Macias Aragonés (IDENER) and Eugen Andreiadis (CEA)

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CHAPTER 1 TUNGSTEN

1.1 INTRODUCTION

The state-of-the-art technologies for the recovery and recycling of tungsten were described in detail in the deliverables D2.2, D3.2 and D4.2. Mining and ore beneficiation often needs high amounts of energy (depending on the grade) and generates high amounts of harmful waste water and rock (tailings, etc.). On the other side, secondary resources might have higher tungsten contents, but its recovery is still in many cases economically unfavorable. Due to the high dependence from Chinese exports, innovative concepts are necessary to guarantee a sustainable supply of tungsten, especially for resource-poor countries like in the European Union. In the following, the future challenges for the hydrometallurgical recovery and processing of tungsten are described. Afterwards, some innovative concepts and studies are presented, which are not (yet) state-of-the-art processes, but have a high potential to be focused on for further research activities and industrial implementation. After that, the economic and ecological impact is evaluated and barriers, as well as possible solutions for increasing the recycling rates are identified and discussed.

The future challenges for recycling tungsten from the secondary resources include the following aspects:

Beneficiation & leaching

A challenge in concentrating scheelite and wolframite ores (or secondary resources) is a further increase of the yield, which is accompanied by a reduction of the W content in the residue. Tungsten's beneficiation process leads to considerable losses of about 10 – 40 % of the tungsten content of the ore [1].

The leaching step is usually performed with a large excess of NaOH or NaCO₃ at an elevated temperature and high pressure in steel autoclaves. In terms of resource efficiency, a future challenge is to save those reagents by reduction or substitution or to improve the operational conditions in order to increase the yield and produce lower amounts of waste streams. Additionally, the treatment in autoclaves consumes large amounts of energy. The energy balance and a heat integration approach should be included in an overall economical and ecological evaluation [2].

Purification

As already pointed out in deliverable D3.2, the obtained sodium tungstate solutions are purified by precipitation in order to remove the main impurities like Si, Mo, As, Sb, Bi, Pb and Co. Here, the main focus lies again on the reduction of tungsten losses into the precipitation

sludge. Maybe these sludges can internally be recycled or used for other low-grade products [2].

Solvent extraction

For the final conversion of tungsten into APT (Ammonium paratungstate), solvent extraction or ion exchange resins methods are applied. A central question is, when and for which kind of feed stream is one of them preferred [2]. As state-of-the-art process, solvent extraction is performed from acidic media (pH 2-3), but the leachates are alkaline, which means, that large amounts of acid are necessary and large amounts of useless salts have to be removed from process.

Ion exchange

On the other hand, the sodium tungstate solutions may be contacted with strongly alkaline ion exchange resins, where the tungstate is adsorbed. The central question is, how the treatment of the raffinate (digestion, waste reduction, energy saving) and stripping (stripping agent, ionic strength) can be improved [2].

Recycling

As pointed out in deliverable D3.2 tungsten-bearing scrap is often treated in the zinc process or coldstream process. Sometimes direct physical re-using (for example for high-grade scrap like cemented carbide) seems to be more efficient than feeding into the recycling process. Additionally, for example tungsten carbide made from scrap may not always have the same properties as freshly produced tungsten carbide and might only be used for some applications as low grade products [2].

At the moment, most of tungsten-bearing metal scrap is withdrawn from the European value chain and exported to China, where scrap recyclers and tungsten producers offer better prices. Especially at the beginning, political regulatory procedures might be a useful tool to prevent the export of valuable scrap and support local recycling initiatives [2].

1.2 MINING AND RE-PROCESSING OF TUNGSTEN CONTAINING TAILINGS

1.2.1 MINING AND ENRICHMENT TECHNIQUE INNOVATIONS

It was reported (North American Tungsten Corporation Ltd.) that drilling and conceptual modeling program was completed at Cantung Mine in March 2013 to explore the possibility of reprocessing unrecovered WO_3 , Cu and Au from Tailings Pond 3. A preliminary block model was constructed using Minesight software. The potential tonnage and grade determined by the drilling and modeling program are comparable with available historical mill production statistics from 1974 to 2006 [3].

The analysis on the stale tailings of Bom-Gorhon deposit has confirmed that the maximum tungsten content is contained in the fine fractions < 0.1 mm [4]. High intensity magnetic separation of tungsten ore slime samples from Rajasthan, India, assaying 5.30% and 2.87% WO_3 , was studied with the application of polymeric dispersant [4]. The grade of the concentrate was improved compared to when no dispersant was used. Enhanced magnetic separation using dispersant is by virtue of reducing hetero-coagulation amongst the particles. The recovery grade relationship shows a field intensity of 1 Tesla, which was just sufficient to attract wolframite; this resulted in better grade of concentrate as compared to higher field intensity, however, at the cost of a decrease in recovery by 3%.

A new process route for ultrafine wolframite recovery was developed [6], to enable the efficient reprocessing of historical mine tailings as well as current plant slimes tailings from Panasqueira mine in Portugal. Much of the wolframite in these tailings 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. Flotation, magnetic separation and gravity concentration testwork, at both laboratory and pilot scale on the historical mine tailings and on the current slimes tailings of the plant were conducted. Froth flotation of the Panasqueira wolframite has been investigated over a number of years with very inconsistent results between the current tailings (which floated) and the old dam tailings. This could be attributed to the surface weathered for the old dam tailings which causes the difficulty for flotation. High intensity magnetic separation (at low to moderate fields) could not recover the finest wolframite and could not achieve the differential needed between the wolframite and siderite and the other strongly magnetic minerals present. At higher fields, there was a substantial recovery of the magnetic silicates and consequently poor weight rejection. Gravity separation testwork with a multi-gravity separator and some work also being carried out using the Kelsey jig and Duplex separators. A three stage process with intermediate sulphide flotation could potentially produce a wolframite concentrate of 50-55% WO_3 , at a reasonable recovery. Because of tungsten minerals being in very fine particles such as wolframite in the tailings from Panasqueira mine is below 25 μm , complex mineralogy and low grade combined enrichment techniques (flotation, magnetic and gravity separations), complicated approaches and strict control of conditions (reagents, intensities, dispersions etc.) are needed for effective recovery of these tungsten minerals. The feasibility in economy could be doubtful.

Flotation-gravity separation process was tested for recovering scheelite from a sulphide tailings containing 0.11% WO_3 in China [7]. A spiral (LP900) was used for rougher concentration of scheelite followed by sulphide flotation, and then scheelite was further enriched by shaking tabling. A tungsten concentrate with the grade 32.16% (WO_3) and recovery 30.29% was obtained. In addition, a sulphide concentrate with the grade 45.89% (S) and recovery 57.28% was obtained. Although this is a simple and cheap process, the grade of tungsten concentrate and the recovery were quite low. The reasons could be the target

minerals were not liberated enough or fine particles of scheelite were not recovered effectively. Process mineralogical studies should be conducted and then more suitable enrichment techniques and flowsheet should be selected.

Recovery of tungsten and tantalum from slimes was experimentally investigated through a process of centrifugal separation and sulphide flotation [8]. The material of slimes from a tungsten mine in Jiangxi China contained 0.041% WO_3 and 0.011% Ta_2O_5 . The process was compared by experiments with other two flowsheets, whole flotation and sulphide flotation-fine shaking tabling. The centrifugal separation process contained one time of roughing and four times of cleaning and the sulphide flotation process contained one time of roughing, one time of scavenging and one time of cleaning. A W-Ta bulk concentrate was obtained with 33.35% WO_3 at recovery 65.6% and 3.36% Ta at recovery 24.3%.

Research on tungsten slimes processing in China was reviewed [9]. Because of fine particles and complex compositions of the slimes, concentration was difficult for traditional techniques of flotation, gravity concentration and magnetic separation. As new types of separation equipment such as centrifugal separators and high gradient magnetic separators were applied into the processing of tungsten slimes, the recovery efficiencies had been increased. Therefore, the authors pointed that the development of higher efficient separators and more selective flotation reagents would be the key for improving tungsten slimes processing [9]. A case study was on the process optimization of a tungsten slimes containing scheelite and wolframite from a tungsten mine in Jiangxi China [10]. A combined gravity separation-flotation-gravity separation flowsheet was used. Rough concentration was conducted by using centrifugal separation and shaking tabling, and then flotation was used to float scheelite and wolframite. In cleaning stage heating flotation and shaking tabling were applied to get bulk scheelite and wolframite concentrate with the grade 50% WO_3 at recovery over 62%.

Tungsten and tin were recovered from a scheelite concentrate tailings by using a patented fine gravity separator called the suspended vibration cone concentrator [11]. Comparing to a shaking table the new separator could improve the efficiency of W and Sn recovery. A bulk W-Sn concentrate with the tungsten grade 25.5% WO_3 at the recovery 44.8% and the tin grade 6.9% Sn at the recovery 52.3% was obtained. In addition, the suspended vibration cone concentrator was used as the gravity concentrator in a gravity concentration-flotation process for processing a wolframite-scheelite tailings in which 95% of tungsten was contained in the fractions of -0.037mm and molybdenum and bismuth are also contained in the tailings [12]. The technical flowsheet was that, after gravity concentration including one rougher and one cleaner, the rougher concentrate was processed by flotation in which Mo, Bi and W (both wolframite and scheelite) were floated in sequence. Final concentrates obtained were: tungsten concentrate 35.5% WO_3 at recovery 48.2%; molybdenum

concentrate 5.1% Mo at recovery 26.6% and bismuth concentrate 15.9% Bi at recovery 57.8%.

Experiments were carried out for recovery tungsten from flotation tailings at a scheelite mine in Gansu, China [13]. A new collector FX-6 was applied. In rougher stage Na_2CO_3 at 1800 g/t, Na_2SiO_3 at 2000 g/t and FX-6 at 1800 g/t were added. A rougher concentrate with the grade 1.3% WO_3 at the recovery 69% was obtained which was further cleaned by heating flotation and a final concentrate with the grade 56.9% WO_3 at the recovery 51.9% was achieved.

Usually wolframite is industrially recovered by gravity concentration methods including using shaking tables, spirals and centrifugal separators etc. But as the mineral particle size decreases the concentration efficiency of gravimetric methods becomes low. For instance, in processing of wolframite slimes materials from the wolframite mines in Jianxi China by gravity concentration methods normally the recoveries of WO_3 are only 45-50% [14]. Recently, the industrial experiments of beneficiation by flotation for the wolframite slimes from a wolframite mine in this area were carried out [14]. In the concentration plant of this mine fine shaking tables and centrifugal separators are used as the beneficiation equipment for wolframite ore dressing. The slimes had the grade of 0.45% WO_3 . In flotation testwork chelating collectors were used. A concentrate by flotation with the grade of 30.2% WO_3 at the recovery of 80% was obtained from the industrial testwork.

1.2.2 METALS COMPREHENSIVE RECOVERIES AND UTILIZATIONS OF TUNGSTEN CONTAINING TAILINGS

Tungsten mine tailings usually not only contain tungsten but also include other valuable metals such as Cu, Mo and Bi and non-metal minerals which could be comprehensively recovered or utilized [15].

Comprehensive recoveries of Cu, W and Sn were achieved from tin tailings containing tungsten (0.64% WO_3) and also Cu and Sn in Bolivia. The combined different techniques (such as chlorination, flotation, high intensity magnetic and gravity separations) are applied in the process [16]. After the chlorination, segregation flotation, high intensity magnetic separation and gravity separation were applied, the technological parameters are optimized as follows: the segregation temperature 950 °C, segregation time 45 min, calcium chloride dosage 3%, coke dosage 3%, primary grinding fineness $\text{P}_{95} < 74 \mu\text{m}$, magnetic field intensity of high intensity magnetic separation $H=1.0$ Tesla, and secondary grinding fineness $\text{P}_{95} < 38 \mu\text{m}$. Under the optimal conditions, the copper concentrate with Cu grade of 25.04% at recovery of 83.19%, tungsten concentrate with WO_3 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.

Mining and quarrying activities in Europe generate approximately 55% of total industrial wastes, according to a recent Eurostat report. Most of these wastes are directly dumped on land or deposited in landfill sites [17]. The potential for reuse of waste-rock piles of Panasqueira tungsten mine was discussed [17]. Such materials must have suitable properties for technical-artistic value added applications, such as conservation, restoration and/or rehabilitation of historic monuments, sculptures, decorative and architectural intervention, or simply as materials for building revetments.

Using tungsten mine tailings as the main raw material, ceramic substrates were successfully prepared by conventional ceramic sintering process [18]. Material properties including density, porosity, corrosion resistance performance, mechanical strength were measured and showed that the ceramic substrate from tungsten mine tailings could be potential in applications.

1.2.3 INNOVATIVE STUDIES IN ENVIRONMENTAL PROTECTION OF TUNGSTEN CONTAINING TAILINGS

The stability and safety of the mine tailings reservoirs are important for tailings mining and environmental protection. High sulphides such as pyrite are usually contained in tailings. The oxidation of these sulphide minerals could cause acidity of the tailings reservoirs. The effects of pyrite oxidation were studied [5] by combining geological exploration and experimental data. The chemical and mineralogical analyses were conducted. The transport performance of heavy metal ions in the tailings reservoirs and the variations of the physical and dynamical properties of the reservoirs were investigated and simulated. The results showed that the effects of pyrite oxidation mainly occur in the surface shallow layers. As coarse particles decrease and powders and clay particles increase, the density of tailings material increases and the permeability coefficient decreases. In the paper [19] the slope stability of the tailings dam in a tungsten mine in China was studied. Based on the measurements of the dam microscopic parameters a mathematic model was established using a software (PFC2D) for analyzing the stability of the tailings dam, in which the tension variation curves and the particles transportation are applied to predict the instability failure and the development process of the dam structure. The stability of tungsten mine's tailings dam was also studied by using probabilistic analysis method [20].

Seepage control is a critically important aspect in the design, construction, and operation of a tailings dam as it directly affects: the stability of the downstream slope; internal erosion due to piping; and pollution of ground and surface waters downstream of the dam [21]. The seepage control for a tungsten mine's tailings dam was investigated [22]. The geological properties of the tailings dam's geotechnical engineering, the soil permeability and the reasons of seepage were analyzed. Based on the study horizontal seepage drainage pipes

were installed through which the penetration water in the tailings dam could be led to the drainage ditch timely.

1.3 INNOVATIVE PROCESSING TECHNOLOGIES FOR THE HYDROMETALLURGICAL RECOVERY OF TUNGSTEN

In the following different innovative concepts are presented for the hydrometallurgical recovery of tungsten. These concepts are not (yet) state-of-the-art, but might be a powerful tool to address the future challenges for a cleaner, cheaper and more efficient recovery of tungsten from low-grade primary or secondary resources.

1.3.1 ACIDIC LEACHING WITH NITRIC AND PHOSPHORIC ACID

The state-of-the-art process for industrial scheelite leaching is the treatment with sodium hydroxide or sodium carbonate in an autoclaving process [23, 24]. However, these two leaching processes usually require high temperature and relatively large amounts of reagents to obtain high yields. This high excess of reagents causes a decrease of the leaching rate. The digestion had to be performed at high liquid/solid ratio, with a corresponding increase in heat consumption and decrease in the equipment capacity [25]. Additionally, the scheelite can be treated in an acidic leaching step with hydrochloric acid to produce tungstic acid [23]. This process has several disadvantages, as a solid-colloidal layer of tungstic acid covers the unreacted particles and hinders the reaction [26].

In a study of Zhang et al. [25, 27], scheelite was leached with a mixture of phosphoric in nitric acid (less corrosive to equipment than HCl) to produce a phosphotungstic acid solution, which is further treated by solvent extraction and the raffinate is recycled to the ore leaching stage. Here, the phosphoric acid acts as chelating agent and avoids tungstic acid precipitation. The acid consumption and waste water amount greatly decrease and the results show high recovery rates [27]. The proposed flowsheet is depicted in **Figure 1.1** Because of the acidic leachate, there is no further acid needed prior the solvent extraction step.

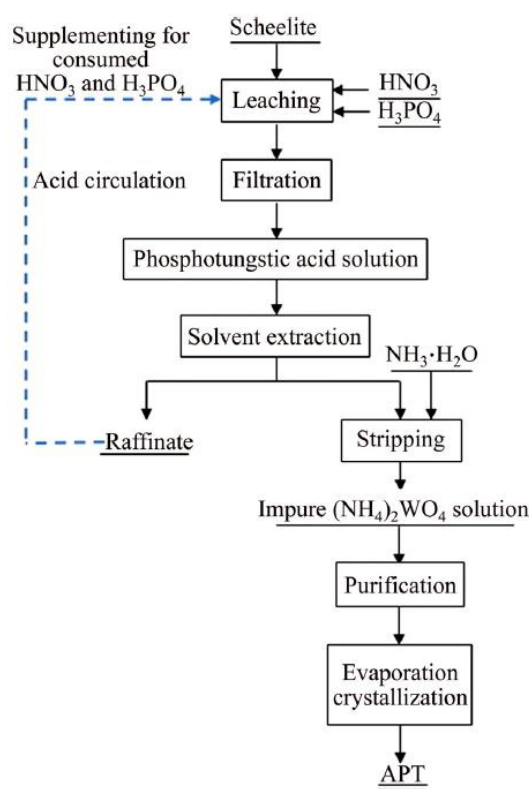


Figure 1.1 Flowsheet for APT production with acidic leaching with nitric and phosphoric acid.[27]

1.3.2 BIOSORPTION

In a study of Ogi et al. (2016) [28] tungsten is recovered selectively from tungsten-bearing scrap by biosorption. Traditional hydrometallurgical methods (solvent extraction, ion-exchange) usually consume high amounts of chemicals and energy and additionally generate toxic sludges and other waste products. Therefore, this study aims for the development of a more effective and environmentally friendly technology for the recovery of tungsten. Biosorption has been applied to several metals, for example Ag, Au, Cr, Cu, Fe, In, Ni, Pb, Pd, Pt, Rh, U, Re, Zn [29, 30] using bacterial species. For tungsten biosorption, *E. coli* and beer yeast have high uptake capacities of 0.16 g tungsten/g biosorbent and 0.29 g tungsten/g biosorbent respectively, which is comparable to ion-exchange resins.

A flowsheet of recycling of used WC tip is shown in **Figure 1.2**. First, the WC scrap is calcinated at 950 °C for 12 h yielding WO₃ and CoWO₄ powder, which is treated with NaOH to obtain a Na₂WO₄ solution. At this stage, the biosorbent is added to the solution and the pH is adjusted to approximately 1, where W is adsorbed selectively and impurities like molybdenum and vanadium remain in solution. The W-adsorbed beer yeast is separated by centrifugation and dried at 80 °C for 12 h. After that, the beer yeast is burnt off in a furnace. Finally, the purified WO₃ powder is transformed into WC by reduction and calcination.

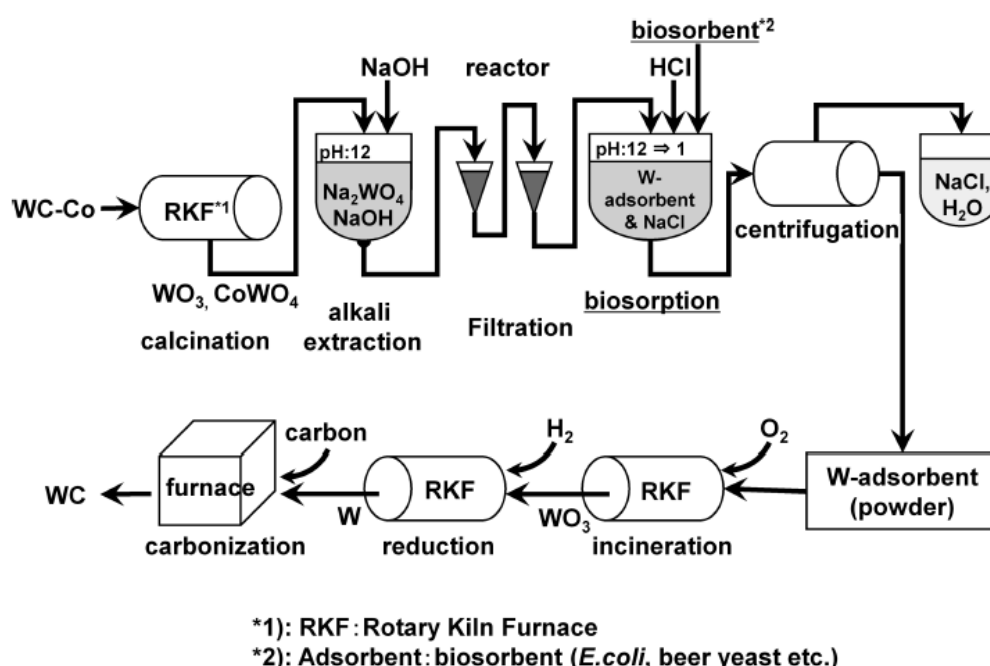


Figure 1.2 Flowsheet of tungsten recovery by biosorption. [28]

A feasibility study reveals that this biosorption process is still more expensive than that of the ion-exchange resin D301 (**Table 1.1**), but the required amount of chemicals are relatively small; large amounts of acid and base substances are not necessary to remove tungsten from the adsorbent, which is a significant advantage.

Table 1.1 Comparison of cost performance of beer yeast and ion-exchange resin for 1 ton of recycled WC[28].

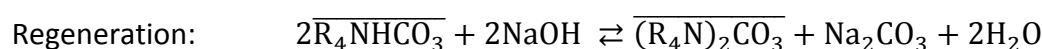
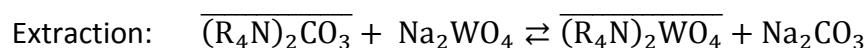
adsorbent	chemicals ^a	chemical amount needed (kg)	price of chemicals ^b (US\$/kg)	price of chemicals needed for 1 ton of W recovery (US\$)	sum of prices needed (US\$)	displacement (L)
biosorption (beer yeast)	15% HCl	4880	0.20	488	1508	13388
	beer yeast	3400	0.30	1020		
ion-exchange resin (D301)	NH ₄ Cl	735	0.17	124	489	71280
	25% NH ₄ OH	400	0.39	156		
	12% NaClO ₄	192	0.90	173		
	NaOH	24	0.01	0.24		
	D301	8573	1.00	36 ^c		

^aChemicals required for ion-exchange resin are based on ref 23. ^bThese values are for reference only. The prices of all materials were based on currently available prices from Alibaba.com (official site). ^cIon-exchange change (D301), assumed to be recycled 240 times.

1.3.3 DIRECT SOLVENT EXTRACTION FROM ALKALINE MEDIUM

The traditional hydrometallurgical recovery of tungsten includes an alkali leaching, which is followed by a solvent extraction step [31 – 33]. This solvent extraction has to be conducted in acidic media (pH 2 - 3), as most of the industrial extractants (tertiary or secondary amines/quaternary ammonium salts) work in that range most efficiently. Thus, lots of acid is

needed to neutralize and acidify the leach liquor and the valuable alkali (Na_2CO_3 or NaOH) and acid (H_2SO_4 or HCl) become useless inorganic salts. Additionally, anionic impurities of P, As, Si, Sn cannot be removed, because of the formation of heteropoly acid. The precipitation of those impurities leads to a loss of tungsten [34]. Therefore, the direct solvent extraction of tungsten from alkaline medium was proposed and studied [35]. The breakthrough was the application of quaternary ammonium carbonate salts as extractants, where the main reactions are expressed as [36]:



Two major problems have restricted the industrial application for this process: poor phase separation and a relatively low tungsten concentration in the strip liquor (aprox. 100 g/l) resulting in high energy consumption in the following crystallization of APT by evaporation.

In a new study of Zhang et al. (2016) [37], this direct solvent extraction from alkaline medium has been optimized to promote the application in commercial scale. Therefore, pilot (multi-stage mixer-settler system) and industrial (multi-stage annular centrifugal extractor) test plants were run over a longer period of time. Trioctyl methyl ammonium chloride was transformed into quaternary ammonium carbonate and used as extractant. The results of the pilot test with NaOH leaching liquor of wolframite concentrate are summarized in **Table 1.2**.

Table 1.2 Pilot test with NaOH leaching liquor of wolframite concentrate. [37]

Item	WO_3	Mo	P	As	SiO_2	Sn	Cl^-	F^-
Feed (g/L)	146.5	0.63	1.44	0.701	0.321	0.0018	3.09	2.62
Strip liquor (g/L)	152.5	0.92	<0.005	0.009	0.034	0.0001	1.82	0.25
Raffinate (g/L)	2.14	0.041	1.20	0.623	0.480	0.0006	0.42	1.69
Scrub raffinate (g/L)	10.9	0.027	/	/	/	/	0.69	0.51
Extraction (%)	98.00	89.48	/	/	/	/	/	/
Removal (%)	/	/	99.67	98.77	93.60	94.66	43.40	90.83

The extraction rate reaches 98 %. Molybdenum is coextracted and needs to be removed in a consecutive precipitation step [23]. Other impurities like P, As, Si and Sn are almost removed quantitatively.

A flowsheet of the overall process is shown in **Figure 1.3**. The organic and the aqueous phase form closed cycles in the leaching-solvent extraction process, as well as Na_2CO_3 and NaOH . There is no consumption of acid and the precipitation of P, As and Si by precipitation is not

necessary. Compared with the traditional technology, this technology shows the advantages of a shorter process, a high recovery rate, a low consumption of chemicals, and dramatically reducing the amount of waste water with obvious economic and environmental benefits, producing a final product which meets the quality standards. It is reported, that the overall costs can be reduced by about US\$ 400 per ton APT [37].

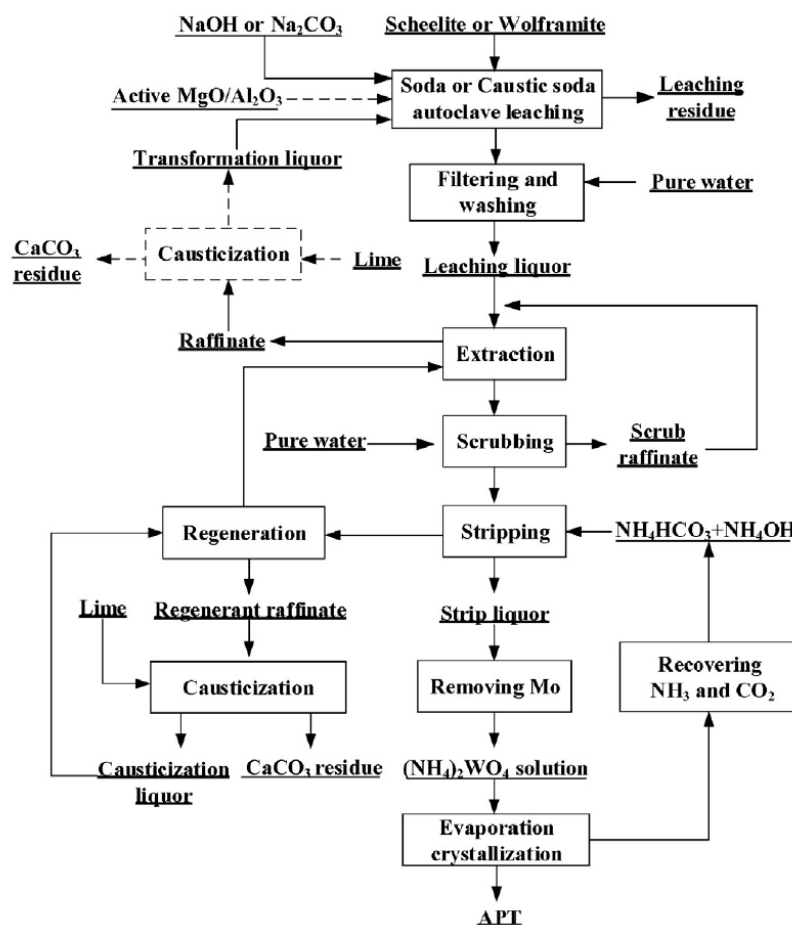


Figure 1.3 Flowsheet of tungsten hydrometallurgy based on direct solvent extraction from alkaline medium. [37]

1.3.4 EMULSION LIQUID MEMBRANES

Emulsion liquid membrane (ELM) techniques have been extensively investigated for the separation of metal ion, hydrocarbons and other biological compounds. ELM combines the two consecutive steps extraction and stripping within one single operation [38]. Therefore, the emulsion membrane phase (w/o emulsion) consists of a homogeneous mixture of extractant, organic diluent, an internal aqueous stripping phase and a surfactant for stabilizing the emulsion. The solute species from the external feed phase gets dissolve in the organic phase and diffuses into the internal strip phase. Finally, the enriched solute can be recovered by breaking of the emulsion (electro-coalescer, temperature etc.) [39]. This

transport of the solute through the liquid membrane is coupled with counter-transport of ions (H^+ or OH^-) from the internal stripping phase to the external feed phase (“facilitated transport”), which is the main driving force and allows high enrichment concentrations. On the other side, this driving force triggers an osmotic water flow and results in swelling or shrinking of the internal stripping phase and hence a loss of performance. Safety issues are another problem for an industrial realization. The first and only industrial ELM plant for zinc recovery in Austria burnt down due to a malfunction in the electro-coalescer [40].

Lende & Kulkarni (2015) [41] investigated the ELM technique for the selective recovery of tungsten from a multi-component waste stream of printed circuit boards (**Figure 1.4**) in a stirred tank. Here, Aliquat 336 in hexane was used as organic phase and NaOH as internal strip phase. The two reaction mechanisms write as follows:

1. Extraction: $WO_4^{2-} + 2\overline{(R_3CH_3N^+Cl^-)} \rightleftharpoons \overline{(R_3CH_3N^+)_2WO_4^{2-}} + 2Cl^-$
2. Stripping: $\overline{(R_3CH_3N^+)_2WO_4^{2-}} + 2Na^+ \rightleftharpoons Na_2WO_4 + \overline{(R_3CH_3N^+)_2}$

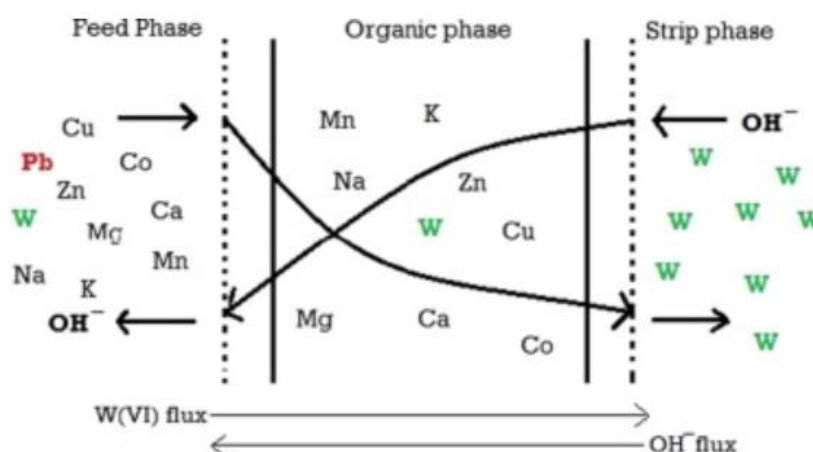


Figure 1.4 ELM process of selective tungsten recovery. [41]

In this study W(VI) (600 ppm) was selectively extracted from a multi-component feed, which mainly contains Pb (150 ppm) as co-elements. Under optimized conditions, the extraction efficiency was found to be 80 % with 4 times enrichment in the stripping phase. The separation factor for W(VI) vs. other co-ions was found to be very high thereby indicating selective recovery of W(VI) from the wastewater by using ELM process.

ELM is often conducted non-dispersively in hollow fiber modules [42], where the emulsion is easier to split afterwards by a temperature shift, because of lower surfactant concentrations. The basic properties of ELM operations such as low-solvent inventory and high surface area make them ideal for the separation of solutes from dilute aqueous streams [43].

1.3.5 MICROSTRUCTURED EXTRACTION PROCESSES

Recent developments in micro process engineering helped successfully to intensify existing solvent extraction processes of various metals [44, 45]. Here, a higher specific interfacial area and shorter diffusion distances lead to a higher number of theoretical stages. This is especially of interest for dilute feed streams for low-grade ores or tailings. Microextraction processes are either designed as slug-flow in a microchannel with alternating drops of aqueous and organic phase, non-dispersively in surface-modified microchannels or with an additional separating membrane between the two phases [46]. The advantage of a higher extraction efficiency is outweighed by a lower throughput compared to conventional extraction equipment. A higher throughput is achieved by numbering-up of many identical modules. Despite the superior extraction efficiency, the throughputs of big mixer-settler plants in extractive metallurgy cannot be realized.

1.4 ECONOMICS AND ENVIRONMENTAL IMPACT ESTIMATIONS

1.4.1 ECONOMICS AND ENVIRONMENTAL IMPACT ESTIMATIONS FROM TAILING TREATMENT

To improve environmental, social and economic outcomes alternative tailings management methods were reviewed [47]. Three approaches in particular were highlighted: paste and thickened tailings; tailings reuse, recycling and reprocessing; and proactive management (e.g. the integration of sulphide flotation with cemented paste backfill). In the future models could be constructed to optimize environmental, social and economic outcomes of tailings management across the value chain through integrated orebody characterization, mine planning, processing, disposal, re-processing, recycling and reuse [47]. On the viewpoint of economics avoiding of tailings was considered the most preferable and reducing, reusing, recycling, recovering, treatment and disposal of the tailings are less preferable in sequence [48]. Innovations in all these items are the most important.

Mining wastes can affect the environment through one or more of the following intrinsic criteria [49]: chemical and mineralogical composition; physical properties; volume and surface occupied, and waste disposal method. The increase in demand (quantity and diversity) and metal prices leads to a renewed interest in the historical mining waste which can be considered as potential source of base metals and critical metals. One major difficulty regarding mining waste reprocessing concerns the quantification and distribution of elements and minerals on all scales from the nano-scale to the macroscale in space and time (for example considering the oxidation of sulphide). Developing predictive tools and reliable, field-tested modelling of long-term mining waste behavior are among the greatest challenges. Such data and tools are needed to establish the recycling and reuse potential of

these materials; geochemists and mineralogists have a significant role to play in this endeavor [19].

Any operation will require a cost and benefit approach to ensure its feasibility, which should take into account restocking of the remaining mining wastes after their reprocessing including to ensure their long term safe disposal, and to prevent or at least minimize any long term negative effects for example attributable to migration of airborne or aquatic pollutants from the mining waste facility. This new approach should consider the following strategy: engage the operation if the economic value of the recovered metal is superior to the reprocessing costs and the final disposal of the remaining mining wastes; If not, include the long term environmental and social benefits (especially regarding ground water and surface water impact reduction) of the remaining materials long term safe disposal [19].

1.4.2 ECONOMICS AND ENVIRONMENTAL IMPACT ESTIMATIONS FROM RECYCLING

ECONOMICS ESTIMATION

Tungsten recycling is less energy intensive than virgin production. According to **Table 1.3** [1], virgin production results in roughly 10,000 kWh/t of tungsten (Mittersill, Austria), depending on the grade and cut-off (usually 0.2 %), whereas tungsten from recycling (zinc process) accounts for < 6,000 kWh/t. Despite these energy savings, recycling is not necessarily cheaper than buying ore concentrate, depending on the market conditions, the costs of tungsten scrap may even be higher (for example approx. US\$ 15,000 per t of carbide scrap [50] and US\$ 14,000 per t of Chinese concentrate [51]).

The above mentioned case studies and innovative processes are usually (still) more expensive than the conventional tungsten recovery processes, but further research initiatives or developments might lead to economically more competitive processes. For example, if biosorbents are used as waste products from other fermentation processes or other, cheaper ones were found, the main cost driver for that technology will be significantly reduced. Basically, all the innovative concepts aim to reduce the energy or reagent consumption (e.g. acid, base, stripping solution etc.) or waste (water) amount, which is often outweighed by a consumption of other reagents or a lower yield. Only an overall and detailed analysis of the specific production costs and yield will judge, if the specific technology is competitive enough.

Table 1.3 Energy estimates for APT production [1].

Processing step	Energy (kWh/t)	Comments
Ore mining & extraction		
Drilling	0.4*	USA best practice across the whole metals sector
Blasting	2.2*	
Digging	1.5*	
Ventilation	1.3*	
Dewatering	0.2*	
Materials handling	14.7*	
Beneficiation and processing		
Crushing	0.4*	USA best practice
Grinding	14.4*	USA best practice
Beneficiation general	12.8*	Wolframite ore in India
Ore mining & extraction plus beneficiation and processing in Mittersill mine, Austria	31.7*	Scheelite concentrate production from ore in Mittersill, Austria
APT production from concentrate	1600	Solvent extraction method (99.87% efficiency)
APT production from scrap	2000	Anodic dissolution method
Powder from concentrate	12,000–20,000	Chemical and electrolytic methods
Powder from WC recycling	4,000–6,000	Zinc process (>95% efficiency)

ENVIRONMENTAL IMPACT ESTIMATION

Tungsten mining and beneficiation processes often account for high losses (10 – 40 %) and high amounts of waste rock and landfill. Although primary production cannot be entirely substituted by recycling, because the demand is growing year by year [51] recycling methods require lower processing energies, and hence, produce lower carbon emissions and avoid waste rock, waste water and leachates from mining operations [1]. Additionally, many of the mentioned innovative technologies lead towards a greener tungsten processing industry by reducing the amount of reagents needed and/or reducing the production of harmful or useless by-products (e.g. salts from neutralization reactions).

1.5 BARRIERS OF RECYCLING

According to Leal-Ayala et al. (2015) tungsten recycling is not necessarily restricted by technological availability. The main barriers for achieving higher recycling rates are dispersion, dilution and the lack of collection infrastructure [1]. The market price is an

additional constraint. Even if the price for tungsten concentrates has been increasing since the last decades, recycling is in most of the cases still too expensive. Besides recycling, substitution by other materials might be a more convenient alternative for some applications. Additionally, the material efficiency is often increased by re-designing the same products with less tungsten. In some cases about 90 % of the tungsten content was reduced by re-designing specific carbide tools [1].

1.6 SOLUTIONS TO INCREASE RECYCLING

The first step to increase the recycling rates is a reliable identification and estimation of available secondary resources. Although large tungsten-bearing tailings in Europe have been identified in deliverable D3.1, various other potential feed streams remain undiscovered. Especially, various kinds of industrial waste (mill tailings, grinding sludge, dust, sweepings) is disposed elsewhere and withdrawn from the value chain of recycling. Towards an enhanced recycling management several possible solutions may be applicable.

1.6.1 INCREASING THE AWARENESS AND SIGNIFICANCE OF METAL RECYCLING AND SUSTAINABILITY

For a sustainable society, a sophisticated recycling management system is inevitable. Over the last decades immense efforts and research activities have been spent on the development and implementation of recycling strategies into the value chains of various other waste industries, like for example paper and plastic waste and to some extent for electronical devices, light bulbs or batteries. Additionally, because of the limited availability of fossil resources, the energy market has slowly been shifting towards a greener and more sustainable production, especially in resource-poor countries like in the European Union. All these examples show, that the economy is aware of the importance of a sustainable production, which needs more support for other branches in order to increase the recycling rates, especially here for the metals industries. Primary resources are finite, the existing ores and minerals are becoming more and more low-grade, which will raise the price for the recovery process. At some point, the recycling alternative has to become the cheaper method.

1.6.2 CENTRAL WASTE COLLECTION CENTERS AND CHANNELING WASTE STREAMS

Grinding sludges and floor sweepings are usually dumped as general waste, especially in small factories, where only small amounts of waste are generated. Mill scale is recycled internally as raw material in big plants, but in small plants, it is often sent to landfills [52]. Big recycling plants are only economically operable, if a continuous supply of metal scrap can be guaranteed in sufficient amounts. Therefore, centralized waste collection centers might

provide continuously those recycling plants with fresh feed material by channeling those waste streams of different waste-types and grades.

Practical initiatives like take back schemes between manufacturers and end-users have already been reported [1]. Additionally, some companies of the tungsten industry e.g. H.C. Starck (Germany) [53] and Wolfram Bergbau und Hütten AG (Austria) [54] buy scrap (powder, grinding sludges or WC hard scrap etc.) from end-users and mix them into their production process.

1.6.3 REWARD SYSTEM & INCENTIVES

From a political point of view, special incentives might reward those tungsten producers or processors, who maintain a recycling management system in order to increase the recycling rates. This potential benefits should provide incentives to investors and companies, who are willing to explore and develop new tungsten resources and re-evaluate known resources outside China and reduce the dependence on Chinese exports and prices [1].

1.6.4 PENALTY & CONTINGENTS

In the opposite direction, tungsten producers or processors are fined, if they don't implement a recycling management system into their value chain or exceed an assigned contingent (similar to emission contingents).

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CHAPTER 2 MOLYBDENUM

2.1 MINING AND RE-PROCESSING OF MOLYBDENUM CONTAINING TAILINGS

2.1.1 INNOVATIVE STUDIES ON MINING AND RE-PROCESSING TECHNOLOGIES

At Erdenet processing plant in Mongolia there are three tailings, bulk rougher flotation tailings (tailings I), middling concentration tailings (tailings II) and bulk cleaner concentration tailings (tailings III). Beneficiation investigation for tailings III for recovery of bulk Cu and Mo was conducted [1]. The concentrations of Cu and Mo in the material of tailings are 0.2–0.5% and 0.1–0.2%, and 55% of Cu and 20% of Mo are in the fraction of $-8\ \mu\text{m}$. Mo occurs mainly in molybdenite (content 0.4%) and Cu in chalcopyrite (content 1.4%). The re-concentration flowsheet is shown in **Figure 2.1** which contains selective flotation to separate Cu and Mo, recleaner Mo flotation to get final Mo concentrate, rough Cu concentrate washing and regrinding, Cu and pyrite flotation circuits to get final Cu and pyrite concentrates. For the tailings with the grades of Cu 0.31% and Mo 0.25% the experiment results showed: molybdenum concentrate with 45.04% Mo at the recovery of 66.25%, copper concentrate with the grade of 15.4% at the recovery of 53.24% and pyrite concentrate with the grades of 45.12% Fe and 52.1% S at the iron recovery of 89.16%, and the secondary tailings contains 0.13% Cu and 0.09% Mo were achieved.

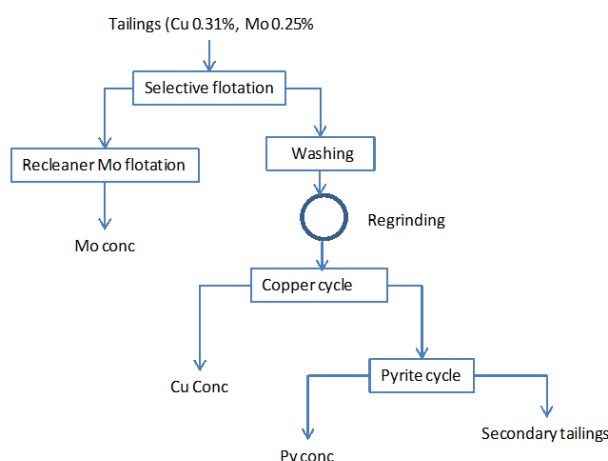


Figure 2.1 Flowsheet of tailings processing at Erdenet processing plant in Mongolia.

One of challenges in re-concentration of the Mo tailings is that the mineral of molybdenite in the tailings materials usually has very fine particles size and difficult to be recovered efficiently by conventional methods of flotation, magnetic and gravity separations. The low flotation rate and recovery of hydrophobic fine particles ($<20\ \mu\text{m}$) is mainly due to their low collision efficiency, EC, with bubbles. There are two approaches to increase EC values. One is by decreasing the bubble size such as using flotation columns in which fine bubbles are

generated and the other one is by aggregating the fine particles to an optimum size for flotation [2],[3].

The investigation was conducted for recovering molybdenite from an ultrafine waste tailings by oil agglomerate flotation (OAF) [4]. Neutral oils like kerosene, diesel, transformer and rapeseed oil were used as collectors or bridging reagents in OAF. The average size of collected particles (dp 50), agglomerates (da 50) and their distribution of the froth concentrate were determined by laser particle size analyzer or sieve analysis. Conventional flotation froth cannot catch the ultrafine particles, so it is an ineffective process to recover molybdenum metal in the waste tailings, while OAF has some advantages to recover fine minerals. It was shown from the study that the best result was obtained from transformer oil due to its appropriate length of carbon chain, kinematic viscosity and cyclical structure. The oil amount plays a very important role on average size of the particles, with the increase of transformer oil from 2.0 to 13.8 kg/t, da 50 increases from 0.15 to 0.68 mm and dp50 decreases from 9.06 to 2.05 μm . The experiments indicated that the bigger the da 50, the smaller the dp 50, and the higher the recovery of molybdenite. The appropriate conditions for recovering ultrafine molybdenite were determined as follows: dosage of frother: 0.5 kg/t, natural pH: 6.2, stirring time: 3 min, and stirring intensity: 400–600 r/min. Lastly, the closed cycle test and industrial application in the producing scale of 500 t/d were carried out, and result showed that 95% molybdenum was recovered with a satisfied grade of 22.62%.

The dispersion-selective hydrophobic flocculation was used in the flotation circuit to recover ultrafine molybdenite from a cleaning concentration tailings at a molybdenum mine in China [5]. That is, the slurry of the tailings was firstly dispersed by adding a dispersant and then the ultrafine Mo and Cu minerals were flocculated by adding a flocculant, and finally the collector and frother were added for bulk Cu and Mo flotation. In the Cu-Mo separation stage the dispersant and the flocculant were still added prior to the addition of the Cu depressant, Mo collector and frother. Over 85% recovery of Mo was achieved but the grade of the Mo concentrate was only 9.2%. The low Mo concentrate grade could be attributed to the low selectivity of flocculation.

Experiments were carried out to recover Mo and Cu from the cleaning concentration tailings at a molybdenum concentrator of Junduicheng Molybdenum Company in China by using a type of unconventional flotation column with fine bubbles called the cyclone-static micro bubble flotation column [6]. A closed cycle flowsheet was used including roughing and cleaning concentration stages. The roughing concentration stage contained one rougher, one cleaner and two scavengers and the cleaning concentration stage contained three cleaners and one scavenger. The Mo concentrate with the grade 34.2% Mo at the recovery 74.0% and the Cu concentrate with grade 16.8% Cu at the recovery 67.5% were obtained.

Some other innovations were developed to increase the recovery of ultrafine molybdenite from mine tailings including using new reagents and optimizing technical flowsheets and parameters.

A patent was reported in ultrafine molybdenite flotation from an iron mine tailings [7] in which by fine grinding and using a combined depressant the recovery of Mo was increased. Flotation of the molybdenum oxides from a molybdenum flotation tailings, which was produced from a sulfide-oxidized molybdenum ore, was studied by adjusting reagent and dosage and optimizing technical flowsheet [8]. A technological process including tailings regrinding, desliming and molybdenum oxide flotation was determined. In the molybdenum oxides flotation an amphoteric collector was used for floating the minerals of calcium molybdate. This tailings contains 0.095% Mo. The grade of Mo in the final concentrate reaches 8.1% at the recovery 77.5%.

A mechanochemical leaching method by using a stirred mill was studied for the treatment of a molybdenum containing slag. The effects of grinding size and time, solid/liquid ratio and $\text{Na}_2\text{CO}_3/\text{Mo}$ mole ratio, and pH on the molybdenum leaching rate were studied. The molybdenum leaching rate was increased by 15% comparing to traditional process [9].

2.1.2 STUDIES IN COMPREHENSIVE UTILIZATIONS AND ENVIRONMENTAL PROTECTION OF MO CONTAINING TAILINGS

In a molybdenum mine in China the variation of physical and mechanical properties of the tailings with time in the range of 16 years at an upstream high stack tailings reservoir was studied. It was revealed that the shallow buried tailings is greatly affected by the oxidation of pyrite. The research provides data for the design and analysis of the tailings dam [10].

For comprehensive utilizations of the molybdenum mine tailings or molybdenum containing slags the studies on recovery of non-metallic minerals from these materials were also conducted. Recovery of non-metallic minerals including quartz and feldspar from a Mo mine tailings in Shaanxi China was investigated [11]. The process includes two stages, bulk quartz and feldspar concentration and quartz and feldspar separation. In the first stage operations of pre-screening, magnetic separation and two times of flotation were applied in sequence to get bulk quartz and feldspar concentrate, and in the second stage quartz and feldspar the operations contain pre-screening, magnetic separation, classification and two time flotation to get quartz and feldspar concentrates. In addition, the beneficiation of another molybdenum mine tailings from a large molybdenum mine in Anhui China by flotation to extract potassium feldspar was experimentally studied [12]. Through experiments and optimization the determined process was in sequence de-sliming, high intensity magnetic separation for iron removal and potassium feldspar flotation. In the potassium feldspar flotation a combination of anionic and cationic collectors in a suitable ratio was applied to

separate potassium feldspar and quartz. The greatest potential to improve the recycling of the metals (e.g. refractory metals) used in small quantities in highly mixed products is collection. However, for the recovery of these metals from the tailings the re-concentration technology is crucial.

2.2 INNOVATIVE TECHNOLOGIES FOR MOLYBDENUM EXTRACTION FROM SECONDARY RESOURCES

Conventional secondary molybdenum resources include side streams from copper and uranium production. In fact, the output from these resources exceeds the primary Mo production and in 2015 the shares were 60 and 40 %, respectively [13]. As reported in D3.2, the industrial wastes/residuals containing molybdenum are miscellaneous. According to the primary production of molybdenum (largely from Mo mines and Cu-Mo mines) and primary use of molybdenum (~ 80% for steel products[14]), it is believed that copper slag and mill scale (generated during the hot metal working of steels) are of significant interest for recycling molybdenum from the listed industrial wastes/residuals. Spent catalysts, fly ashes and steel-making dusts are other potential resources. In this report catalysts are considered as secondary resources rather than resources from urban mining.

The innovative technologies for extracting molybdenum secondary resources are described as the following.

2.2.1 MOLYBDENUM EXTRACTION AS BY-PRODUCT FROM COPPER PRODUCTION

INNOVATION IN APPLYING NEW EXTRACTANT

Mo recovery in copper smelting is well-established technology and not considered here. More innovation potential is found in Mo separation from solvent extraction-electrowinning (SX-EW) circuits. Mo concentrations are usually low but because of the very large liquid volumes, Mo recovery may be feasible. A new extractant, Cyanex 600 (Cytec), has been developed for such purposes and pilot-scale testing has shown that a Mo concentrate containing 60 g Mo/L can be obtained from a copper SX raffinate containing 75 ppm Mo and 40 g/L of H_2SO_4 [15]. Scrubbing of Mo as oxo-anions at relatively high PH from the organic phase in copper SX has been proposed by Paatero and Virolainen [16].

INNOVATIVE POTENTIAL IN RECYCLING MO-CONTAINING COPPER SLAG

Direct reduction - a pyro-metallurgical process

The molybdenum in the copper slag is bound in an insoluble spinel, which belongs to the $2FeO \cdot MoO_3 - Fe_3O_4$ series.[17] When the copper slag is subjected to a direct carbothermic reduction, molybdenum and iron in the slag are recovered as Fe-Mo alloy. 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. The flow sheet of Mo recovery by this direct reduction process is shown in **Figure 2.2**[18].

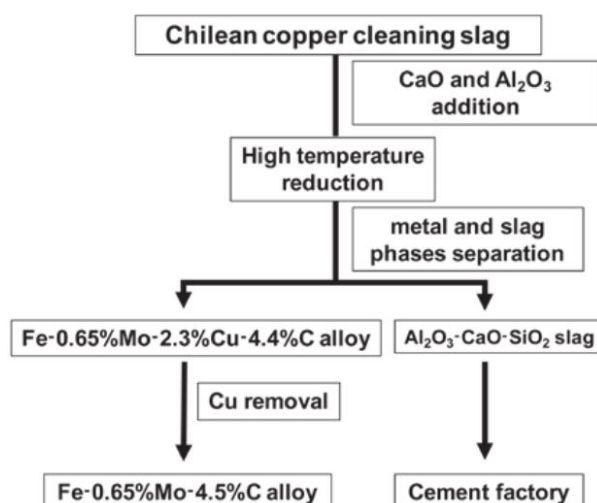


Figure 2.2 Flow sheet of Mo recovery from Chilean copper slag.[18]

Roasting-leaching process: a hybrid pyro- and hydro-metallurgical process

As molybdenum in the copper slag is bound to the spinel type phase $2\text{FeO} \cdot \text{MoO}_3 - \text{Fe}_3\text{O}_4$ series, extraction of molybdenum by direct hydro-metallurgical process have low feasibility with respect to the leaching degree. However, conversion of this spinel phase by roasting provides a possibility. One example of this roasting-leaching process is presented in [19]. In that work, the copper slag was roasted under oxidative atmosphere (90% air and 10% SO_2), during which molybdenum and iron were oxidized to their highest states at 700°C . Then, the molybdenum was selectively recovered from the oxidized slag by acid (H_2SO_4) leaching. The results showed that the molybdenum recovery from the slag was influenced by the magnetite content in the slag during the leaching process (low magnetite content leads to a high recovery of molybdenum); a molybdenum recovery higher than 80% was obtained. The obtained results confirmed the feasibility for recovering molybdenum using two-step processes, i.e., oxidative roasting followed by an acidic leaching.

No pilot scale trials have been carried out regarding the proposed processes for recycling Mo from copper slag at the moment; therefore more efforts should be put to investigate the industrial feasibility.

2.2.2 INNOVATIVE POTENTIAL IN RECYCLING MO-CONTAINING MILL SCALE

MICROWAVE HEATING

Microwave heating is a potential process for recycling mill scale, as the reaction rate is very high and there is no need to pelletize the mill scale.[20] In this proposed process, mill scale is well mixed with excessive amount of carbonaceous materials and heated in the microwave oven. The mill scale can be reduced into metallic droplets in around 15 minutes. The obtained metallic droplets can be mechanically separated from the leftover carbonaceous materials, which can be further recycled and used as reducing agents. Besides the iron component, the other components containing alloying elements (such as Cr, Ni and Mo) can also be reduced into the metallic, which can be used as a feed for Mo-containing steel production by charging it, for example, in the Electric Arc Furnace. The proposed flow chart for recycling mill scale by microwave heating is shown in **Figure 2.3**. Though the process is of great interest, it is far away for industrial applications, as there is no available microwave furnace for industrial use at the moment.

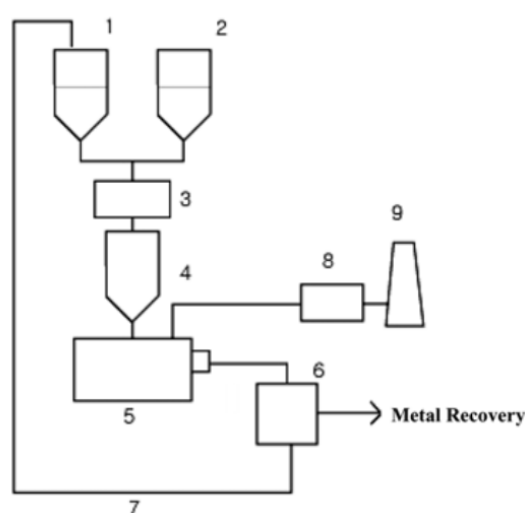


Figure 2.3. A flowsheet for the recovery of metallic components from mill scale: (1: carbonaceous materials, 2: mill scale, 3: mixer, 4: supplier, 5: microwave furnace, 6: gravitational separator, 7: recharge of remaining particles, 8: cooling tower, 9: chimney).[20]

SPONGE IRON POWDER PRODUCTION BY REDUCTION OF MILL SCALE

Sponge iron is normally produced by the reduction of iron ore. Due to the high iron content, mill scale is also expected to produce sponge iron by carbothermic reduction[21] or hydrogen reduction[22]. During the reduction, the alloying elements, such as Cr, Ni and Mo in the mill scale are also expected to be reduced. The reduction of mill scale provides another means to obtain sponge iron, which on one hand can be used as the metallic feed in the steel manufacturing process (such as in the Electric Arc Furnace steelmaking process), on

the other hand, can be used as alloyed iron powder for the production of iron-base powder metallurgy parts.

SMELTING REDUCTION MILL SCALE BRIQUETTES IN THE EAF FOR PRODUCING STAINLESS STEEL

Molybdenum is used as an alloying element in many types of stainless steels. Therefore, Mo-containing mill scale can be used to produce stainless steels, during which the Mo content in the mill scale is used. In one pilot study, oily mill scale, coke and other wastes were made into briquettes and being charged into the EAF (3.4 wt.% of charged steel scrap) for recycling the mill scale[23]. The results show that the smelting process can proceed smoothly in the EAF and the alloying elements can be almost completely reduced.

USING “MILL SCALE + MoO_3 + COKE” AS A MOLYBDENUM ALLOYING PRECURSOR

As presented in D2.2 “mill scale + MoO_3 + coke”[24] is regarded as an innovative alloying precursor for molybdenum alloying in the EAF. In this sense the Mo-containing mill scale can be used here to recycle the molybdenum content in the Mo-containing mill scale.

2.2.3 MOLYBDENUM EXTRACTION FROM STEEL-MAKING DUSTS

Virolainen et al. [25] have used water leaching to obtain an alkaline solution (pH 14) containing about 2 g Mo/L. Solvent extraction (SX) was then used to obtain pure Mo solution. The leachate was purified using quaternary ammonium salt (Aliquat 336) as the extractant. At optimum conditions, other metals except Cr could be removed from the Mo solution.

2.2.4 MOLYBDENUM EXTRACTION FROM SPENT CATALYSTS

Spent hydro-treating catalysts form an important potential resource for secondary recovery of Mo. After roasting pre-treatment, the catalysts are leached at acidic or alkaline conditions [26]. Kar et al. [27] have used soda ash roasting at 600 °C to recover 92% of Mo contained in a hydro-refining catalyst. After water leaching, a Na-molybdate solution was obtained and can be converted to high-purity MoO_3 as shown in **Figure 2.4**. Adsorption on activated carbon was used to purify the pregnant leach solution (PLS) before crystallization as ammonium molybdate.

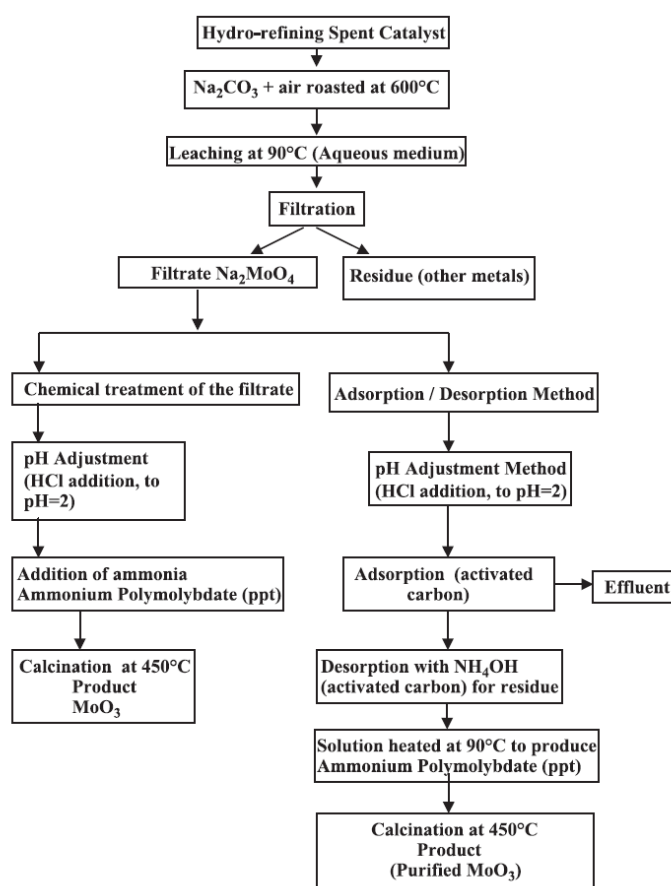


Figure 2.4 Recovery of MoO_3 from spent hydro-refining catalyst [27].

Instead of roasting at high temperature, Park et al. [28] have studied direct oxidative leaching of a hydrodesulfurization (HDS) catalyst. H_2O_2 was used to convert MoS_2 to MoO_3 and it was leached in an aqueous Na_2CO_3 . At optimum conditions, 84% of Mo could be recovered and after precipitation of phosphorus with MgCl_2 , precipitation of ammonium molybdate and thermal decomposition, MoO_3 was obtained in 97.3 % purity.

Separation of Mo(VI) and V(V) is often needed in Mo recovery from spent catalyst and several methods have been proposed for treatment of the leach liquors. Ion exchange has been studied by Guo and Shen [29]. They used an iminodiacetic acid (IDA) resin for separation of Mo and V from other metals in the loading step and for selective desorption of Mo and V. V and Mo were desorbed sequentially using 5 M H_2SO_4 and 5.5 M NH_4OH . Nguyen and Lee [30] used standard strong anion exchanger and they found that Mo anions can be selectively exchanged at PH around 1. Desorption was made with 3.5 M NaOH.

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CHAPTER 3 NIOBIUM AND TANTALUM

3.1 INTRODUCTION

Waste and scrap recycling accounted for 48% of United States Ta imports in 2014. The 21% is from Sn slag refining in Thailand and Malaysia. Historically, Sn slags have accounted for up to 40% of global Ta production [1]. In 2012, 30% of Ta production came from scrap recycling, 20% as by-product of Sn mining (Thailand, Malaysia, Nigeria, Zaire, etc.).

Niobium is a strategic metal with a wide variety of uses ranging from niobium carbide- and niobium nitride- steel alloys through piezoelectric compounds, such as LiNbO_3 , to superconducting niobium-tin magnets [2]. These industries are a first potential source of secondary resources of niobium. Also, large quantities of niobium tailings are discarded during the processing of the ores in mines, resulting in a complete waste, from which niobium can be recovered [3].

3.2 INNOVATIVE PROCESSING TECHNOLOGIES FOR NIOBIUM AND TANTALUM EXTRACTION FROM SECONDARY RESOURCES

3.2.1 INNOVATIVE SOLVENT EXTRACTION PROCESSES

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. A large number of solvent extraction processes using over 200 combinations of various organic solvents and mineral acids have been investigated for the extraction and separation of niobium and tantalum [4]. These metals are usually present in the aqueous phase as niobates, tantalates and complex ions, such as fluorides, thiocyanates, and other ions. The stability of these complexes and the tendency to form solvation complexes with the organic extractant depend greatly on the chemistry of the aqueous phase. By varying this, it is entirely feasible to extract selectively either niobium or tantalum or co-extract both niobium and tantalum into the organic phase. The separation of niobium and tantalum in the latter case is then accomplished by selective back extraction/stripping of the desired species.

Although a lot of extractants have been studied for separating and purifying Nb and Ta, methyl-iso-butyl ketone (MIBK) is still widely used industrially, despite of several disadvantages, such as relatively high solubility in water, low flash point and high volatility. These obvious drawbacks 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.

Niobium and tantalum separation by solvent extraction is industrially 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. There is therefore a strong incentive for the development of innovative hydrometallurgical separation processes limiting or avoiding the use of fluorides.

Current hydrometallurgical methods of processing tantalum–niobium concentrates have some serious problems [5]:

- Permanent loss of reagents and large amounts of residues,
- The amount of dissolved impurities equates that of Nb and Ta in the leaching solutions,
- The loss of substantial quantities of fluorine in the process, and the costs associated with its regeneration,
- Solid wastes created amount more than an order of magnitude greater than that of useful products.

Innovative improvements of the hydrometallurgical technology for processing niobium and tantalum concentrates could be expected in the following aspects:

- The application of more robust extractants with higher stability and lower water solubility,
- Less HF or no HF used for the digestion of concentrates and the metal separation with SX, and
- Recycling reagents as much as possible to reduce liquid and solid wastes.

With the aim of simplifying the extraction technology, reducing the consumption of the main reactants and improving the purity of the end products, several recommendations can be made [6]:

- Control of the concentration of free HF by countercurrent leaching of raw material or by binding of free HF to form slightly soluble compounds, e.g., rare-earth metal fluorides, which are commercial products. At a low concentration of free HF, the niobium and tantalum extraction selectivity is higher.
- Washing of metal-containing extracts with aqueous fluoride solutions containing the element being purified. In practice, purified solutions directly from the process (back extracts) can be used. The application of metal-containing solutions as washing solutions leads to a noticeable increase in the concentration of the metal being purified in the system

and to more efficient displacement of impurity elements from organic to aqueous solutions. The used washing solutions are combined with the initial solutions to be extracted; therefore, this procedure does not lead to a loss of metal.

- Back extraction of metals should be performed with water or weak HF solutions, which simplifies the composition of back extracts before isolation of niobium and tantalum compounds from solutions. Back extraction with water is more efficient when using neutral oxygen-containing solvating extractants such as MIBK or octanol.
- Pyrolysis as a reagentless method for isolating Nb and Ta compounds as commercial products and for regenerating the main process reagent HF. This method also allows one to control the fluorine impurity concentration in the end product. In conventional extraction processes, the use of pyrolysis is complicated by the complex composition of solutions, hence the recommendation of performing the extraction in the absence of other mineral acids except HF.
- Flotation of emulsified and partially dissolved extractant from raffinates, which decreases the loss of extractant and its concentration in waste solutions.

A comparison of various extractants used for the separation of TaF_5 and NbF_5 in different acidic media was recently made [7]. The extractants tested included the cation exchangers di-iso-octyl-phosphinic acid (PA) and di-(2-ethylhexyl)-phosphoric acid (D2EHPA), the neutral solvating extractant 2-thenoyl-trifluoro-acetone (TTA), and the anion exchangers tri-n-octylamine (Alamine 336), tri-octyl-methyl ammonium chloride (Aliquat 336) and 1-octanol, 2-octanol and 3-octanol. In addition, four different acids, hydrochloric acid (HCl), nitric acid (HNO_3), sulfuric acid (H_2SO_4) and perchloric acid ($HClO_4$), were used at different concentrations to determine the best combination for extraction. From the eight extractants, PA and D2EHPA showed the best extraction and selectivity results for both Ta and Nb irrespective of the acid used when using $Ta(Nb)F_5$. Accordingly both Ta and Nb seem to preferentially form complexes with the cation exchangers PA and D2EHPA and less so with the anion exchangers (Alamine 336 and Aliquat 336), the neutral TTA and the octanols. When comparing the separation factors of the four acids tested using PA and D2EHPA as extractants, the highest selectivity was attained in H_2SO_4 . This implies that Ta and Nb obtained from $Ta(Nb)F_5$ could be separated using PA and D2EHPA in the organic phase and H_2SO_4 in the aqueous phase. This result is advantageous for the SX industry where Ta/Nb containing minerals are traditionally leached with high concentrations of H_2SO_4 implying that the leachate can be directly used in the SX process thus avoiding complicated and expensive transition plants. The results also show that although HF might still be required for the synthesis of $Ta(Nb)F_5$, the extraction of Ta from Nb can be achieved without the use of additional HF, as has been used previously.

The extraction of niobium and tantalum by anion exchange type of extractants, such as amines, takes place due to the exchange of complex metal ion in the aqueous phase with that of a correspondingly charged ion in the organic phase. Some of the liquid ion extractants used for niobium and tantalum are trioctylamine (TOA), tribenzyl amine (TBA), Amberlite LA-2, and Aliquat 336. Although no commercial application of amines has been found in the niobium and tantalum industry, they have been extensively studied and have the most possible potential for application.

Such extractants can be used to extract both niobium and tantalum collectively into the organic phase in the first instance. Subsequently, the re-extraction or back-extraction is carried out selectively to effect the separation. The extraction of tantalum by anion exchangers is relatively less sensitive than Nb to the concentration of hydrofluoric acid; e.g., the distribution coefficient of the tantalum remains constant at about 200 in the acidity range of 1 to 5 M HF. The distribution coefficient of niobium, on the other hand, decreases very sharply when the HF concentration is increased to 2 M. The separation factor $S_{Ta/Nb}$ in a TOA-fluoride system under optimum conditions is of the order of 400.

El hussaini and Rice [8] proposed a process for extracting niobium and tantalum from a fluorinated leach liquor with tertiary amine Alamine 336, using kerosene and xylene as diluents and n-decanol as a modifier. The effect of contact time, sulfate and fluoride concentrations in the aqueous phase, extractant concentration and aqueous to organic phase ratio were investigated. Both elements were extracted to different extents, with tantalum extraction slightly greater. The separation factor was greater for kerosene diluent. Selective stripping was performed using either 50 g/L potassium hydroxide or 25 g/L ammonium carbonate solutions for niobium and tantalum. Tantalum was stripped first and $Ta(OH)_5$ was precipitated during the stripping process. The separation of niobium from tantalum was achieved at this point and niobium was then precipitated by adding ammonia.

Niobium from chloride media can be extracted into tribenzyl amine TBA phase dissolved in chloroform [9]. As tantalum does not form chloro-complexes with a negative charge as readily as niobium, its extraction was significantly lower than that of niobium with amines. Taking this advantage, niobium can be separated from tantalum in HCl solutions by extraction with amines, leaving tantalum in the raffinate. No commercial application has been reported so far.

Tertiary amines, TOA (tri-n-octylamine), TDA (tri-n-decylamine) and TDDA (tri-n-dodecylamine) in tetrachloromethane (CCl_4) were studied to extract niobium and tantalum from the sulphuric acid–oxalic acid system [10]. No obvious differences were found in extraction distribution coefficients among the three amines tested. The highest distribution coefficients were obtained with the lowest H_2SO_4 concentration. When the H_2SO_4 concentration increased to more than 3.5 M, the extraction distribution coefficients of both

niobium and tantalum decreased to lower than 1. With lower H_2SO_4 concentrations of less than 2.5 M, the extraction of niobium was higher than that of tantalum. In the H_2SO_4 concentration range of 1.0–1.5 M, reasonably high separation factors of around 10–30 for niobium over tantalum (SFNb/Ta) can be obtained. This could provide a possible method for separating niobium from tantalum from sulphuric acid–oxalic acid system without the presence of HF, however the process needs to be optimized to allow extraction of macro-concentrations of metals using a less-toxic diluent than CCl_4 .

Niobium and tantalum have also been extracted as tartarate complexes in tri-n-octyl amine and as citrate complex in Aliquat 336.

High purity tantalum and tantalum-free niobium (99.999–99.9999%) can be obtained using quaternary ammonium salts as extractants from a hydrofluoric acid solution [11] containing various metallic impurities (alkaline or alkaline-earth metals, cobalt, manganese, iron, nickel, copper, etc.). This patented process can be applied to ore concentrates as well as scrap containing Nb and Ta, or Ta-rich tin slags.

3.2.2 EXTRACTION OF NIOBIUM AND TANTALUM FROM TIN SLAG

During the pyrometallurgical extraction of tin from cassiterite, oxides of Ta and Nb are concentrated in the slag. In particular, tin slags can contain up to 10% of tantalum oxide.

Gaballah et al. [12] 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 Ta_2O_5 chlorination was 246 kJ/mole. Below 600°C, E_a for carbochlorination was 74 kJ/mol for Nb_2O_5 and 110 kJ/mol for Ta_2O_5 . In the case of low grade tin slag (< 10% $\text{TaO}_2 + \text{Nb}_2\text{O}_5$), Odo et al. [13] have investigated the extraction of valuable metals (Nb/Ta) 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%).

3.2.3 NIOBIUM AND TANTALUM FROM COPPER SMELTING SLAG

Copper slag is produced during pyrometallurgical production of copper from copper ores. For every tone of metal production about 2.2 t of slag is generated. Slag usually contains a considerable quantity of valuable metals, in which niobium and tantalum are included. Among the various processing method for recovering metals from slag, physical separation by froth flotation is widely used. The use of alkyl, arylaryl or alkylaryl hydroxamates in the

flotation of minerals that chelate with hydroxamate is also known in the industry. Hydroxamates are powerful collectors in flotation due to their ability to selectively chelate at the surfaces of minerals that contain lanthanum or niobium [14].

3.2.4 EXTRACTION OF TANTALUM FROM CONCENTRATES

A novel hydrometallurgical process was developed to selectively extract Nb and Ta from Nb–Ti–Fe raw concentrates [15]. The process is based on the formation of sodium hexaniobate by reaction between the initial concentrate and concentrated NaOH at atmospheric pressure. After caustic conversion, the sodium hexaniobate are selectively dissolved in water. The optimum conditions for the caustic conversion step were determined to be $[\text{NaOH}]_{\text{initial}} = 400 \text{ g L}^{-1}$, $T = 110 \text{ }^{\circ}\text{C}$, $t = 5 \text{ h}$. Under these conditions, the dissolution of Nb reaches nearly 70% whereas less than 1% of Fe and Ti are dissolved. It was found that the Ti and Fe content of the initial concentrate is the main factor limiting the Nb recovery. The sodium hexaniobate solution is then acidified in order to precipitate a purified

$\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ concentrate. The best compromise between the acid consumption, the precipitation yield and the purification of Nb was to acidify the sodium hexaniobate solution to pH 4 at room temperature. Since Nb and Ta have similar chemical properties, Ta is also extracted by the proposed process. The global Nb and Ta recovery yields, measured in continuous operation at a pilot scale, were 65%. High purity $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ was obtained starting from low-grade industrial Nb–Ti–Fe concentrates. The present study demonstrates that fluoride-free process can be developed for the recovery and purification of niobium and tantalum.

3.2.5 NIOBIUM FROM BAYAN OBO TAILINGS

Many complicated factors such as low grade, fine-grained dissemination and complex mineral composition are the main problems encountered in the separation and recovery of Nb (and REE) from the Bayan Obo ore deposit. A number of different processes have been developed which are listed in the **Table 3.1** [16].

Table 3.1 Comparison of different processes for recovering Nb and Re from the Bayan Obo tailings [16].

Process	Process steps	Product/quality	Yield (%)	
			Nb	RE
Baogang Steel [17]	Smelting reduction – selective oxidation – dephosphorization – smelting	Nb–Fe alloys (~12.5 wt%Nb), RE-enriched slag (≥ 10 wt%REO)	~60	–
Yang et al. [18]	Magnetizing roasting – magnetic separation – plasma smelting	Nb–Fe alloys (22–32 wt%Nb)	~61	–
Fang et al. [19]	Selective pre-reduction – smelting separation – smelting	Nb–Fe alloys (~14 wt%Nb)	~83	–
Zhang et al. [20]	Briquetting – chlorination – segmented condensation – hydrolysis	Nb-enriched slag (~62 wt%Nb ₂ O ₅)	–	–
Li et al. [21]	Hydrochloric acid washing – sulfuric acid decomposition – leaching – N ₂₃₅ extraction – crystallization	Nb ₂ O ₅ (99.5–99.9 wt%)	~70	–
Chen et al. [22]	Selective pre-reduction – magnetic separation – hydrochloric acid washing	Nb-enriched slag (~30 wt%Nb ₂ O ₅)	–	–
Chen et al. [23]	Mixing – sulfuric acid roasting – leaching – filtering and washing	Leach solution (~2.6 g L ⁻¹ Nb ₂ O ₅ , ~22 g L ⁻¹ REO)	~86	~96
Liu et al. [24]	Grinding ore – sulfuric acid decomposition – leaching – hydrolysis and magnetic separation – neutralization and smelting	Nb–Fe alloys (~15.7 wt%Nb), RE _x O _y (~92 wt%)	~62	~72

In the 1950s, Baogang Steel developed ‘smelting reduction – selective oxidation – dephosphorization – smelting’ process in which the Nb in Bayan Obo ore was reduced by hot iron in a blast furnace and subsequently selectively oxidized in a converter. However, the high energy consumption and equipment cost were the disadvantages in this process. Besides that, the yield of Nb (~60%) is too low mainly due to the formation of NbC detained layer in blast furnace. In order to reduce the energy consumption and equipment cost of the Nb–Fe alloys preparation, Yang et al. developed the ‘magnetizing roasting – magnetic separation – plasma smelting’ process [18] in which hematite and limonite was reduced to magnetite which could be separated from the Bayan Obo ore by magnetic separation. Thus the Nb could be enriched in the tailings of magnetic separation. A smelting reduction in the

plasma at 2500–3000 °C was used to prepare the Nb–Fe alloys (22–32 wt% Nb) using the Nb-enriched tailings as raw materials. Compared to the process of Baogang Steel, the omitting of blast furnace and converter reduced the energy consumption and the equipment cost partly. Unfortunately, the yield of Nb (~61%) was still too low. Later, Reuter et al. introduced direct reduction to production of ferroniobium in an electric furnace (Reuter et al., 1994). Based on this method, Fang et al. [19] developed the ‘selective pre-reduction – smelting separation – smelting’ process in which the pellets made from Bayan Obo ore, carbon powders, and binders were fed into a rotary kiln, where iron oxides were reduced to metallic iron by selective pre-reduction at 1050 °C. Afterwards, the metallic iron was smelting separated from the slag which consisted of the oxides such as Nb₂O₅ in the electric furnace. Finally, the Nb–Fe alloys (~14 wt% Nb) were prepared by reduction in the other electric furnace and the yield of Nb was enhanced to 83%. Moreover, Chen et al. studied the gas-based pre-reduction of Bayan Obo ore using H₂/CO as the reducing agent, respectively [22]. Generally speaking, both the coal and gas-based pre-reduction processes improved the yield of Nb and economic efficiency. However, the high energy consumption and equipment cost were still unavoidable in the above-mentioned processes. Moreover, the application of low-grade Nb–Fe alloys and RE-enriched slags are limited. Thus, the large scale application of these pyrometallurgical processes has not been possible so far.

In order to improve the product quality of the Nb-enriched slag (5–10 wt% Nb₂O₅) obtained in the Baogang Steel process, some benefit attempts were tried via extracting Nb from the Nb-enriched slag. In the chlorination process developed by Zhang et al. [20], Nb-enriched slag was mixed with coal powders and briquetted. Then the niobium in the briquette was chloridized to NbCl₅ at 800–900 °C, meanwhile, the manganese, iron and part of silicon was chloridized too. Next, the NbCl₅ was collected by segmented condensation and then hydrolyzed to the product (~62 wt% Nb₂O₅). Guo et al. prepared Nb₂O₅ from Nb-enriched slag by the extraction process with oxalic acid–N₂₃₅ system [21]. The Nb-enriched slag was washed with hydrochloric acid and decomposed with sulfuric acid. Then, the Nb was leached with oxalic acid and extracted with the tertiary amine (N₂₃₅). Finally, the product of Nb₂O₅ (99.5–99.9 wt%) could be prepared by reversing and crystallization. Obviously, the product quality was improved greatly by the above mentioned hydrometallurgy processes compared with the low-grade Nb–Fe alloys, although the total yield of Nb was still low. It can be seen that the hydrometallurgy process has obvious advantages in improving the product quality.

The chlorination process and the oxalic–N₂₃₅ extraction process are both extensions of the process of Baogang Steel. In order to get rid of smelting in blast furnace and converter, Chen et al. developed the ‘selective prereduction – magnetic separation – hydrochloric acid washing’ process [22]. After selective pre-reduction and magnetic separation, the Nb concentrate was washed with hydrochloric acid for removal of the iron, phosphorous and other impurities. The grade of Nb₂O₅ was improved to 30 wt%. Unfortunately, the extraction of Nb and RE had not been further studied. Chen et al. decomposed a concentrated ore

containing tantalum, niobium and rare-earth elements by roasting the mixture of the concentrated ore, concentrated sulfuric acid and sulfate at 180–400 °C [23]. Then the tantalum, the niobium and the rare-earth elements enter the solution by filtering and washing the mixture, wherein the leaching ratios of Nb and RE were comparatively high. This treatment approach provided a good method for recovering Nb and RE from Bayan Obo ore. Liu et al. adopted a similar method to decompose the concentrated ore containing Nb, Ti, Fe and RE elements, and then recovered Nb and RE from the sulfuric acid leach solution by the processes of grinding ore, sulfuric acid decomposition, leaching, hydrolysis and magnetic separation, neutralization and smelting [24]. Finally, the rare earth complex oxides and the Nb–Fe alloys were prepared. The multiple hydrometallurgy technologies were used in this process except the smelting of Nb–Fe alloys, hence the process cost was greatly reduced and the purity of the products was improved especially for the rare earth complex oxides. However, the low grade of Nb–Fe alloys still limited the application prospect of the product. Moreover, the total yields of Nb and RE in this process were yet to be improved.

Compared to the pyrometallurgical process, the production cost and energy consumption of the above hydrometallurgy processes is relatively low, and the product quality is remarkably improved.

Wang et al. studied a method to extract niobium from the mine tailings of Bayan Obo Mine. The method consisted in flotation-microwave magnetic roasting-magnetic separation, and they recovered up to 68% of the niobium contained in the tailings [25].

A large quantity of Fe can be separated from this ore by reduction roasting and magnetic separation [26]. The results showed that the separation efficiency of Fe increased up to 80% by increasing the reduction temperature. Moreover, the mass fractions of Nb₂O₅ and REO in magnetic separation tailings were also significantly increased by these treatments at the optimum temperature of 1100°C. Aiming at Nb and REE recovery, a H₂SO₄ solution was used in the leaching of the magnetic separation tailings at 160°C. Approximately 98 % of Nb and 99 % of REE were extracted, while some of the Fe, Ti, and Al leached into the leaching solution.

3.2.6 NIOBIUM AND TANTALUM FROM CARBIDE SLUDGE

Tungsten carbide is used for various metallurgical tools due to its hardness. Tool scrap is an important secondary source for recycling niobium and tantalum. Typical sludge contains 5.6 % niobium and 7.2% tantalum [4]. No studies related to Nb and Ta extraction from carbide sludge have been found.

3.2.7 TANTALUM FROM ALLOY SCRAP

Conversion of tantalum alloy scrap into high-value, electronic-grade tantalum nano-powders is a significant economic and technological advancement. At present, it is only possible to recycle tantalum alloy scrap into low-value tantalum mill products. A new technology platform based on the iodization of tantalum alloy scrap produces volatile tantalum (V) iodides that can be condensed to form fine powders. Subsequent hydrogen reduction of the iodide powders in a plasma furnace produces high surface area tantalum metal powder precursors, which, after annealing, yield high-purity nano-powders with uniform particle size distribution, low oxygen content, and high surface area and capacitance. The hydrogen iodide produced during plasma reduction can be captured, dissociated into molecular hydrogen and molecular iodine, and recycled. The total process flow sheet is presented in **Figure 3.1** [27].

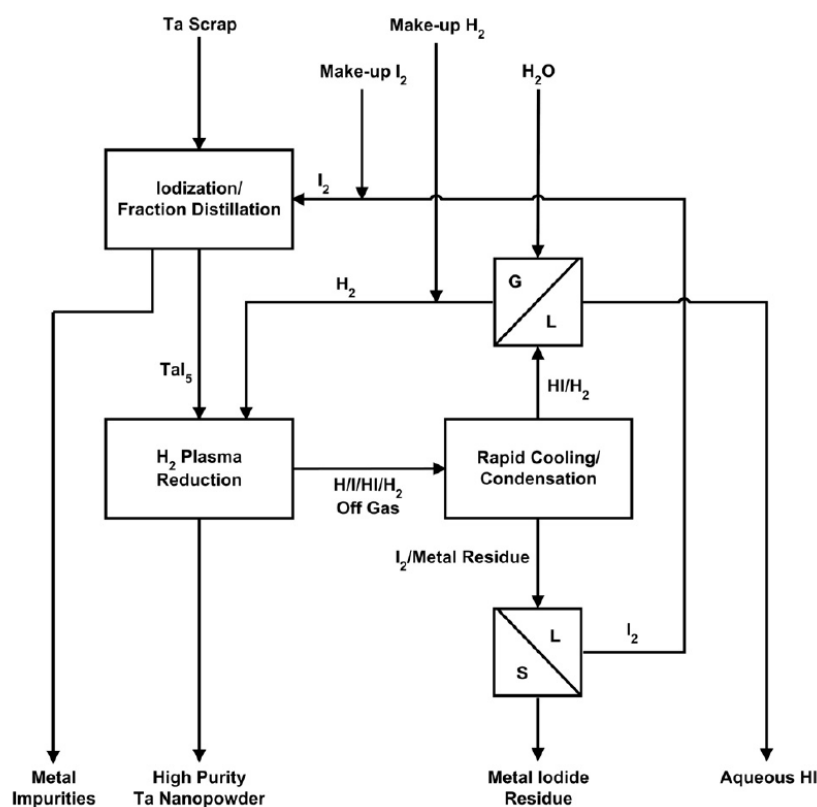


Figure 3.1 Production of high purity Ta fine powders from tantalum scrap processing [27].

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CHAPTER 4 RHENIUM

4.1 RECOVERY OF RHENIUM FROM INDUSTRIAL WASTES

Rhenium is one of the rarest elements in Earth's crust, so it is important to use or reuse all of its possible sources. In the first decade of XXI century the demand for rhenium increased from 35 Mg to 65 Mg. This increase was caused by the development of superalloys containing rhenium, which found their application in aircraft engines and stationary gas turbines. However, in recent years the demand for rhenium has stabilized and its price has lowered significantly. Nowadays the demand for this metal largely depends on changes which occur in aviation industry [1].

Rhenium is not a typical merchandise, because it is obtained as a byproduct; usually rhenium is acquired from copper-molybdenum ores, which are mainly the source of copper. In case of the production of molybdenum, it occurs as a co-product, and all operational decisions are usually made based on the prevailing conditions in the copper market, not because of demand for molybdenum or rhenium.

A large part of rhenium is recovered from dusts and gases from molybdenum roasting processes, if the proper apparatus is installed. It should be mentioned here that not all of roasting plants have the installations for rhenium recovery, so around 15 Mg per year of rhenium is not being recovered, which is the potentially important source of this element. In Kazakhstan rhenium is also produced from copper residues. In Poland rhenium occurs in domestic copper concentrates [1]. Due to high volatility of the oxidized forms of rhenium during the processing of copper concentrates in pyrometallurgical processes, rhenium accumulates in dusts and gases. In classical technology of shaft furnace rhenium partially distillates and accumulates in the sludge in a form of a sulphide. The rest remains in copper matte from which, after the Bessemer process, rhenium as a rhenium (VII) oxide transfers to the gas phase. From gas phase it is washed in the washing and cooling section of sulphuric acid plant (FKS). In the case of fluidized-bed furnace, rhenium distillates as an oxide and with other gases goes to sulphuric acid plant, where in the washing and cooling installation of this plant passes to the weak acidic waste effluent. Dusts from shaft furnace, sludge from scrubbing, dusts from converters and dusts from fluidized-bed furnace are directed to the lead smelter. During the smelting of lead in oscillating-rotary furnace, rhenium contained in processed gases passes partially to the gas phase, where it is recovered in secondary dusts. In the production cycle of recovery of lead the byproduct – Fe-As alloy is formed. From the processes described above, we can identify five materials containing rhenium: three washing acids, secondary dusts and Fe-As alloy. The compositions of this materials are shown in the Table 4.1.

Table 4.1 Composition of materials containing rhenium in Polish smelter.

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

It should be mentioned that nowadays in most of smelters rhenium is recovered from acidic effluents; there are some notifications about rhenium recovery from dusts, but scarce only. In Polish smelter rhenium is recovered only from acidic effluents by ion exchange method. So according to the shown data, the potential sources for rhenium recovery in Poland are secondary dusts and Fe-As alloy. Potentially 1.5-2.5 Mg of rhenium per year could be recovered from these materials. It should be mentioned, that dusts are being reversed to the process, and can be only withdrawn from circulation partially, and Fe-As alloy is a convenient way to secure accumulation of arsenic and is a extremely difficult material to process, so the profitability of this type of investment is low.

As it was mentioned, rhenium is recovered from acidic effluents with application of selective hydrometallurgical techniques. These are: solvent extraction, ion exchange and membrane methods. The first two methods are used on industrial scale for rhenium recovery in many smelters and roasting installations.

Acidic effluents constitute difficult and heterogeneous by composition material, where amount of rhenium oscillates from 25 to 100 mg/L, which requires extremely selective extractants, membranes and resins.

In the case of solvent extraction commonly used as a rhenium extractants are: trioctylamine, di-isododecylamine or tributyl phosphate [2]. In the literature we can find also other, less frequently used substances, like: N-(2-hydroxy-5-nonylbenzyl)-B-hydroxyethylmethylamine [3], primary amine N1923 [4] or phosphorylated polyethers containing dimethylo- and o-phenylo- parts characterized by high rhenium extraction [5]. Until now, substances derived from amines and phosphates are mostly mentioned as potential rhenium extractants. The development of the synthesis of new extractants of metals, including rhenium, observed in recent years has a research potential for industrial application of new, more selective,

lasting, ecological and cheaper to produce extractants. It should be mentioned that the price of extractant is a significant cost of the recovery of rhenium, so the improvement of technological and economical factors of this process is essential.

For rhenium recovery there are also commonly used strong and weak basic resins of high selectivity for rhenium [2, 6]. The difference in rhenium sorption results from basicity, pore structure and the type of functionalization of resin [7]. These materials can be further divided into: gel, macroporous and composite. However, for industrial application macroporous resins are mostly used, because of their greater durability. Despite this, gel resins better bond the ions of rhenium than macro-structural polystyrene resins [8], on the other hand they have low resistance to the increase of temperature and impurities present in industrial acidic effluents containing rhenium. The other important process is elution of absorbed rhenium ions from resin – this process must be selective towards other anions, and eluent must enable separation of the desired product in a simple way, so in most of cases it is ammonium perrhenate (APR). Currently, as eluents of rhenium aqueous solutions of ammonia and ammonium chloride or ammonium thiocyanide are used. Ammonia solutions are the most appropriate, because APR can be crystallized from them directly.

It should be mentioned that the basic parameter demonstrating the utility of the resin to the recovery of rhenium is its high selectivity for rhenium and durability, and in the context of industrial use the high availability and low price. Currently, the resins used in the industry are very expensive made-to-order substitutes. Like in solvent extraction, the price of resin is a significant cost of rhenium recovery, so improvement of the technological (extend of the use of deposit) and economical (reduction in cost) factors are essential.

In conclusion, searching for new, more efficient methods of rhenium recovery based on solvent extraction and ion exchange require profound examination of the newest available ion-exchange resins and organic extractants in order to optimize the rhenium recovery process. Both methods generate lots of waste solutions. In this context the membrane techniques have high industrial potential to reduce the amount of waste solution and to provide more energy-efficient process.

Processing of dust due to the small amount of rhenium and rich elemental composition is not a priority, at present mainly due to the low price of rhenium, but also to the nature of the material. It may change in the future. The propositions of the recovery of rhenium from dusts are mainly based on hydrometallurgical methods – the leaching agents are acid or base solutions, but also sodium salts [9]. There are also pyrometallurgical and hybrid (combination of pyro- and hydrometallurgy) methods for processing of this type of materials [10, 11]. An interesting alternative is to use the pressure method for recovery of rhenium from dusts [12]. This technique allows increasing significantly the efficiency of rhenium recovery, while minimizing the time of leaching and decreasing the temperature of leaching.

It should be mentioned that the amount of rhenium in the dusts being in the circulation could differ a lot (from 1 to some dozens of ppm). Fluctuations in the amount of rhenium in this material may result in a total lack of profitability of technology implementation. In addition, the dusts in the circulation of the smelter are subjected to continuous recovery in a metallurgical furnace, so they were not considered as a secondary raw material and their withdrawal would bring changes in operation of smelter.

Fe-As alloy is the most troublesome rhenium containing material, however the proper research work about application of pyrometallurgical and hydrometallurgical processes for a comprehensive recovery of precious metals and management of toxic metals may allow developing effective technologically and economically methods, fulfilling the environmental requirements, especially as the load of rhenium in this material is relatively high.

4.2 INNOVATIVE TECHNOLOGIES FOR RHENIUM EXTRACTION FROM SECONDARY RESOURCES

4.2.1 RE EXTRACTION AS BY-PRODUCT FROM COPPER/MOLYBDENUM PRODUCTION

The technology for Re recovery from dusts and off-gases generated in Mo roasting is well-established. Moreover, the hydrometallurgical methods (mainly ion exchange but also solvent extraction) used in purification and concentrating the Re-bearing solutions have been thoroughly studied (see [13] and the references therein).

More innovation potential can be found in Re recovery from direct leach liquors and from side-streams that have been less studied. Nebeker and Hiskey [14] have studied direct ion exchange recovery of Re from copper heap-leaching PLS containing about 1 ppm Re. Weak base anion exchangers were used and after loading and elution with 1 M NaOH, a Re-rich solution containing 1.4 g Re/L was obtained. In pressure oxidation of molybdenite concentrates, Re ends up in the PLS and can be recovered by solvent extraction. A SX process shown in **Figure 4.2** has been proposed to recover both Re and Mo from a solution containing 60 ppm Re and 8.2 g Mo/L [15]. Re was extracted with tributylphosphate (TBP) at acidic conditions and stripped with NH_4OH to obtain an ammonium perrhenate solution.

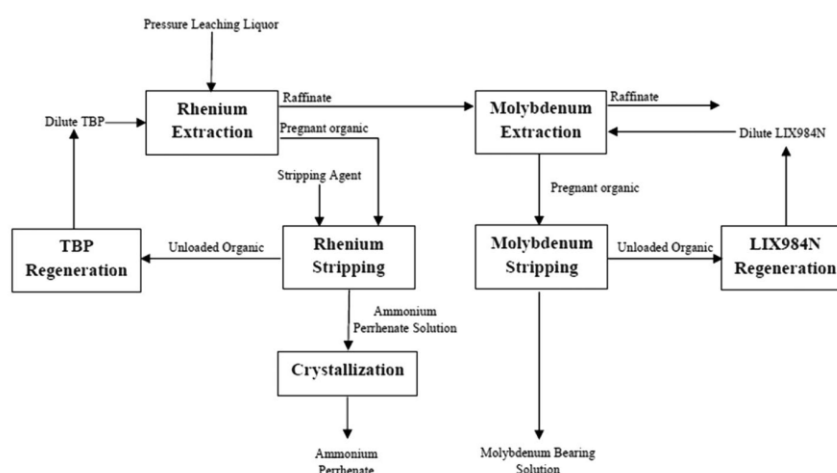


Figure 4.2 Extraction of Re and Mo from molybdenite leachate [15].

Selective extraction from alkaline leach solutions has also been studied [16]. Re was extracted from PLS containing 16.5 g Mo/L and 0.13 g Re/L at pH 9 using trioctylamine and TBP as synergistic extractants. After one-step extraction, 97 % recovery of rhenium was obtained and the Re concentration in the aqueous raffinate was 0.004 g/L.

Amer [17] has studied Re recovery from lead slime formed in making a copper concentrate. The slime containing 0.05 wt-% of Re was leached with water at 94 °C under O₂ pressure of 1.0 MPa. More than 90% of Re was extracted and the PLS, which contained 0.3 g Re/L as well as number of impurities, was treated with a strong base anion exchanger (IRA 410). After selective uptake of the perrhenate ions, they were desorbed using hypochloric acid. Paatero and Virolainen [18] have suggested a process, where Mo and Re are recovered from copper shaft residue by sequential leaching, solvent extraction and ion exchange. After acidic treatment, Mo and Re are leached at alkaline conditions and Re is recovered from the solution using standard anion exchangers.

4.2.2 RE EXTRACTION FROM SPENT CATALYSTS

Bi-metallic Pt-Re reforming catalysts and Co-Re catalysts used in the Fischer-Tropsch synthesis are important secondary resources for Re. In both cases two methods can be used; the alumina support is first decomposed or the metals are directly extracted from the spent catalyst [19]. Hydrometallurgy can be used in direct leaching and in the subsequent separation/purification steps.

Complete dissolution can be achieved using acid leaching or fusion with NaOH and the methods have been reviewed by Kasikov and Petrova [19]. Jafarifar et al. [20] leached a Pt-Re catalyst with HCl-HNO₃ and recovered the metal values using selective precipitation as shown in **Figure 4.3**. Leaching rate and product purity were enhanced by means of microwave-assisted heating.

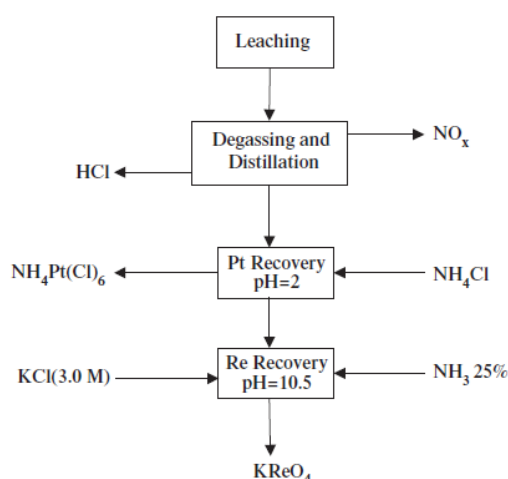


Figure 4.3 Recovery of Re and Pt from spent catalyst with acid leaching and selective precipitation [20].

Angelidis et al. [21] have proposed a milder treatment with NaHCO_3 to first extract Re followed by complete dissolution with H_2SO_4 . The two-step leaching simplifies separation of Re from PLS but no details were given on the purity of PLS or on the purification steps needed. Batch leaching of a Pt-Re/alumina catalyst at 40 °C using 0.1 M NaHCO_3 gave 97 % yield for Re when the catalyst was crushed before leaching. Similar Re extraction was also obtained in packed-bed leaching.

4.3 INNOVATION POTENTIAL OF PROCESSING TECHNOLOGIES FOR SECONDARY RESOURCES OF NB, TA AND RE: A SHORT SUMMARY

After a deep literature review of innovations to extract niobium, tantalum and rhenium from secondary sources (slags, mine tailings, ashes, scraps, etc.), it can be stated that this extraction is mainly carried out by hydro and pyro-metallurgical methods, normally not preceded by processing technologies, probably because the material size and characterisation fixes well with the extracting technique to be applied.

Specifically, for Rhenium, it has been found that processing technologies in the recovery of the metal from copper ores cannot be applied because rhenium is dissolved in the deposit so it is better to capture it from gases produced in the copper ore metallurgical processing. Anyway, the study of methods to recover rhenium directly from Cu and Mo ores can be a promising field of innovation.

Concerning niobium and tantalum, they can be mainly extracted from several secondary sources: tin slags, copper smelter slags, mine tailings, carbide sludge, alloy scraps. Very little information has been found about processing technologies in these fields. In case of tin slags, it has been found that in a study the slag had to be processed before extraction

methods to reduce its size. In the specific case of the study, the methods were crushing, grinding, and sieving, and then the leaching process was applied. In the case of copper smelting slags, hydroxamates are powerful in flotation to recover Nb and Ta. In the case of Bayan Obo mine tailings, the recovery of 68% of the niobium contained in the tailings was possible by a flotation-microwave magnetic roasting-magnetic separation. No innovations have been found of niobium and tantalum extraction from carbide sludge.

In general, the few information found in the upstream processing field suggests that there is a potential need of research as there are several secondary sources that are not been used industrially.

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