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Innovation potential in the recovery of refractory metals from primary resources

Authors : Pr. Jason YANG (GTK) Florent Bourgeois (LGC), Kathy Bru (BRGM), Witold Kurylak (IMN), Eugen Andreiadis and Daniel Meyer (CEA), Stefan Willersinn (UNIKL), Sami Virolainen and Markku Laatikainen (LUT), Xianfeng Hu, Lena Sundqvist Ökvist and Guozhu Ye (MEFOS), Yongxiang Yang (TUDELFT)

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Author(s)	Pr. Jason YANG Florent Bourgeois (LGC), Kathy Bru (BRGM), Witold Kurylak (IMN), Eugen Andreiadis and Daniel Meyer (CEA), Stefan Willersinn (UNIKL), Sami Virolainen and Markku Laatikainen (LUT), Xianfeng Hu, Lena Sundqvist Ökvist and Guozhu Ye (MEFOS), Yongxiang Yang (TUDELFT)
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INNOVATION POTENTIAL IN THE RECOVERY OF REFRACTORY METALS FROM PRIMARY RESOURCES

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Contributors

MINING:

Jason Yang, GTK (W, Mo)

MINERAL PROCESSING :

Florent Bourgeois, LGC (Ta, Nb); Kathy Bru, BRGM (W) ; Jason Yang, GTK (W, Mo), Witold Kurylak, IMN (Nb, Ta, Re)

Hydro-metallurgy:

Eugen Andreiadis and Daniel Meyer, CEA (Ta, Nb) ;

Stefan Willersinn, UNIKL (W) ; Tuomo Sainio, Sami Virolainen and Markku Laatikainen, LUT (Mo)

Pyro-metallurgy:

Xianfeng Hu, Lena Sundqvist Ökvist and Guozhu Ye, MEFOS (W, Mo) ; Yongxiang Yang, TUDELFT (Mo) ; Bertrand Dusanter, ERAMET (Ta, Nb)

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INTRODUCTION

In the previous report D2.2 the technologies of mining, mineral processing and extractive metallurgy (hydrometallurgy and pyrometallurgy) are reviewed on recovery of refractory metals from primary resources. Based on the report D2.2 the innovative investigations of these technologies on tungsten, molybdenum, tantalum and niobium are presented. The technological innovations of the pyro and hydrometallurgical processing of rhenium are covered in the work package 3 for secondary resources because rhenium is produced as by-product in Mo and Cu processing, or in other words, rhenium is mainly recovered from the secondary resources.

In addition, the economics and environmental impact estimations related to mining, mineral processing and extractive metallurgy of refractory metals from primary resources are briefly discussed.

MINING TECHNOLOGY

INTRODUCTION

Innovations in mining are considered very slow. Despite centuries of technological development, the mining industry still goes about its business in pretty much the same way as it always has. Machines have become larger and more sophisticated in mining but operations today would be completely similar to time 50-100 years ago [1]. The reasons for mining to lag behind other industries in deployment of new technologies were attributed to three factors: failure, success and information. 1) Failure: mining is inherently a risky business. With new mines, despite our best efforts, it is often not known precisely what is going to come out of the ground, or how it is going to behave in a plant, until operations actually start. Furthermore, the profitability of a new mining venture depends largely on the price that will be obtained for the product – something over which we have no control. 2) Success: In some ways, success in mining can be as big a barrier to technology development as the fear of failure. Once a new mine is successfully and profitably operating with its tried and true equipment, the impetus for technological change can be relatively small. So if fear of failure causes us to start with proven (old) technology, and success causes us to stay with it as long as possible. 3) Information: solids are often extremely difficult to deal with. Solids are, by their nature, not homogeneous. They can vary immensely in composition and size, they segregate and they resist mixing. They stick when we don't want them to stick, and they fall apart when we want them to hold together. Metering the flow of solids is extremely difficult; measuring the precise composition of a flow of solids is even worse. It is practically impossible to know exactly the composition, size and mass flow of ore at every part of most mining processes at all times.

Studies on mining technology are mainly involved in the fields of rock mechanics, mining technology, intelligent mining, filling technology, rock slope engineering, blasting engineering, ground pressure monitoring etc.

INNOVATION REVIEW

Slope stability is very important for the safety of mining operations. At an open-pit tungsten mine in Yunnan China a numerical model of slope stability was established using a software GEO-Studio to simulate the infiltration, and the distributions of slippery surface and line at the conditions of different rainfall amounts and durations [2][6].

Rockburst is a spontaneous, violent fracture of rock that usually occurs in deep mines. The rockburst prediction was studied at a tungsten mine in China using the maximum principal stress criterion in the deep roadway and

the results showed that at the 450-1050 m depth of the surrounding rock roadway the rockbursts of moderate to high degrees probably occur and depending on rock types the highest degree of the rockburst would happen for granodiorite porphyry type of rock [3]. In a molybdenum mine in China the water-weakening properties of weathered rock masses and their influences on roadways stabilities were investigated [14]. The results showed that, influenced by natural moisture content, natural swell ratio and lateral confinement swell ratio, the deformation and failure of roadways were usually occur for altered hornstone and altered granite porphyry, for which weakening property, disintegration tendency and physical environment were the key factors. In addition, the clay mineral content and underground water were the intrinsic and external factors for the roadway failure.

Measurements of the mechanical properties provide important data for the mining operations. The mechanical properties of cracked rock for a tungsten ore were measured including uniaxial compression, uniaxial compression deform and tensile tests [5]. The Brazil splitting test was carried out to analyze the effects of sample thickness of rock on the rock splitting strength and tensile modulus of elasticity for a lime stone rock [9].

At Sandaozhuang tungsten mine in Henan China the micro-seismic signals, including rock fracture signal, rock blasting signal and noise signal, were monitored and identified in site which was used to predict any disasters happening and evaluate the rock stability [4]. To remain the authenticity and integrity of blasting signal the de-noising was investigated for blasting vibration signal by using EEMD method [7].

The waste rock filling of a mined-out area (nearly 200 million m³) at a large wolframite mine was studied [8]. Some issues about waste rock preparation and transportation, waste rock filling project layout and construction were discussed. In another study a model for prediction of filling body strength was established in which parameters of slurry density, cement-sand ratio, cement content and slag powder mix content were contained [11].

The shape of ore body at deep area is complex at a tungsten mine. To increase mining efficiency a combined mining technology was applied which combining common hole shrinkage stoping method with sublevel caving method. By using this new method the operation safety factor was increased. The stope mining cycle was decreased by 0.5 to 1.5 year. The mining loss rate and the mining dilution rate were reduced by 5% and 6%, respectively [10]. In drifting blasting a delay time identification technology was used at a tungsten mine. By optimizing the short-delay time interval the explosive energy was fully allocated and utilized [12]. In a large molybdenum-tungsten mine depending on the thickness the caving mining and the no pillar sublevel caving were used. A method was developed to remove intruded gangues and decrease the mining dilution rate by controlling proportion of ore and ore cutoff grade [13]. In a copper-molybdenum mine in Anhui China for study of the deep mine structural stability a stoping process simulation system was established by which the mine geological mining conditions were analyzed; the mining scheme was determined, and the 4 steps excavation process was numerically simulated [15]. In Xigou molybdenum mine in China the linear planning theory was used to analyze the parameters in ore proportioning [16].

Filling mining technology is an advanced mining technology and application in mining operations. The experiences in industrial applications show that this technology is higher in mining safety and more efficient than other mining technologies [18]. The soft interlayer of a slowly inclined thin to medium thickness ore deposit mining technology was studied [17].

Cavability of ore-rock is an important parameter to judge if the block caving method can be used. By Monte-Carlo simulation theory, the characteristics of the joint surface's distributional space was researched, and the reasonable advantage of joints were selected, the related parameters which are thought important were analyzed. A 3d model was established and Makeblock software system was used to evaluate the cavability of ore-rock. This method was applied to ore-rock fragmentation evaluation on No. 3 mining area in Jinchuan mine [19].

Blasting vibration propagations were measured in the Jinduicheng open pit mine for different blasting methods and software for blasting vibration prediction was established [20]. A numerical model of mining was established by mechanical parameter of rock analysis and stress, safety rate and plastic zone during mining were calculated [21]. The A*algorithm method was used to optimize the truck transportation system in an open-pit mine [22].

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MINERAL PROCESSING

TUNGSTEN ORES

As the increase of exploitation the primary tungsten resources become poorer in grade, finer in grain size and more complex in mineralogy which cause the mineral processing of the tungsten ores more difficult [26]. Generally, the researches and innovations are concentrated in selective reagent development, using combined gravity-magnetic-flotation process, improving Petrov's process for scheelite concentration, using fine bubble flotation techniques such as column flotation, and applying high gradient/intensity magnetic separators, centrifugal concentrators etc.

INNOVATIONS IN VERY FINE W MINERAL RECOVERY

Many flotation operations need to improve liberation by grinding minerals to very fine sizes, in order to increase recovery for low grade and finely disseminated mineral deposits [39]. Lot of mineral values are lost in the form of fines and slimes. The need for the development of specialized processes/units to recover values in the fines and slimes is much greater today, as the ores treated now become poorer in grade, more disseminated, with liberation at a very fine size [3]. The mineral processing technologies for very fine particle recovering were reviewed [11].

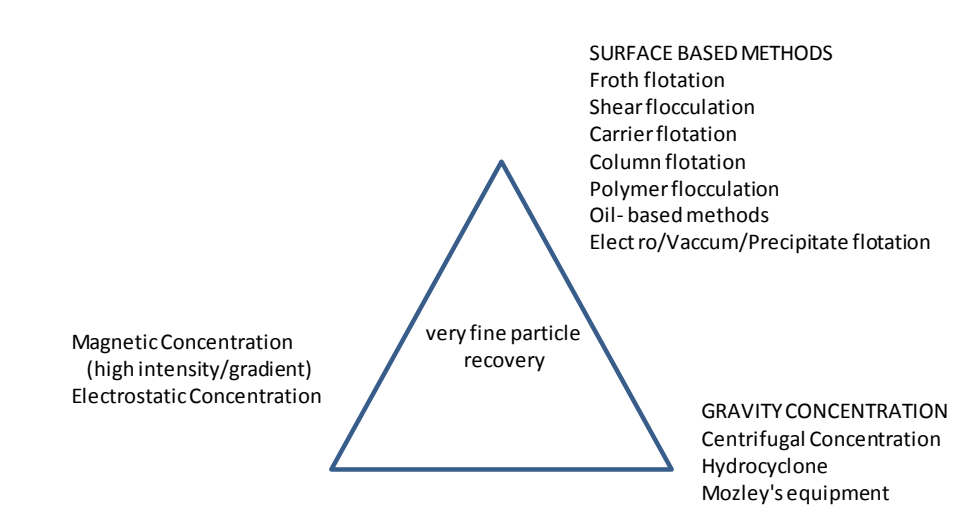


Figure 1 Beneficiation technologies for very fine particle recovery [11]

As shown in Figure 1 it is recognized that gravity concentration and magnetic concentration, particularly the high intensity/gradient and superconducting systems and centrifugal concentration, are as good as flotation method. They can also be better/more convenient under appropriate circumstances. It is also recognized that the approach to the problem of very fine particles through modifications of well-established surface-based methods is better than developing entirely new processes. An example of the former is hydrophobic association. The selective flocculation process is an example of the latter [11]. In this review, it is first attempted to put together the available basic knowledge as relevant to the problem of very fine particle recovery. This enables a closer look at certain aspects of the problem. Secondly it is attempted to analyse the various surface-based (flotation) methods. This identifies some research areas to be followed up. Of them the important ones are:

(a) Aggregation of very fine particles by hydrophobic association. A scheelite/ fluorite system has already been studied. (b) Development of column flotation. (c) Physical and chemical characterization of the surface chemical composition and the surface heterogeneity.

The low flotation rate and recovery of hydrophobic fine particles (<20 μm) are mainly due to their low collision efficiency, EC, with bubbles. Their EC values can be increased by decreasing the bubble size and by aggregating the fine particles to an optimum size for flotation [39]. A decrease in the bubble size not only increases the bubble–particle collision efficiency but also increases the bubble–particle attachment efficiency and the number of generated bubbles in the case of constant gas flow rate. These factors also increase the flotation rate and recovery of fine particles but might cause higher water recovery, which increases entrainment of gangue minerals. The bubble size can be decreased by mechanical and physicochemical methods. In mineral flotation mechanical methods are more common, whereas physicochemical methods have been widely used in water treatment practice, where selectivity is not needed.

For fine particles, it is experimentally and theoretically clear that the flotation rate increases with increasing particle size. Thus, many techniques have been developed which try to increase particle size and mass and decrease surface energy. All these techniques have the same feature that fine particles are induced to form flocs or aggregates. Again, a lack of selectivity in aggregation has restricted their applicability in mineral flotation [39].

Various bubble–particle collision and attachment efficiency models have been reviewed and the factors influencing collision and attachment efficiencies were discussed. It was seen that for fine particles, the main collision mechanism is interception, whereas submicron particles are also affected by Brownian motion, and larger particles by inertia. Bubble–particle attachment models were developed on the premise that the particle sliding time has to be longer than the induction time or the kinetic energy of the particle has to be larger than the energy barrier between the bubble and the particle. Both theoretical and experimental studies in the literature showed that the bubble–particle attachment efficiencies in potential and Stokes flow conditions increase with decreasing particle and bubble size and increasing particle contact angle and electrolyte concentration [39].

For fine particle flotation, the bubble–particle stability can be assumed to equal unity because if fine particles are able to form a three-phase contact line with a bubble, the formed aggregate is stable even in turbulent conditions. In practice, fine particle flotation can be improved by allowing long residence times and working at high collector coverages (large contact angles). New approaches are required, which could include very high energy zones for bubble–particle contact or completely novel ways of introducing particles directly to the water–vapour interface [39].

Improvements in gravity processes had been made since 1980s to increase the efficiency of fine mineral concentrations. But more researches focus on flotation. The developments and researches on scheelite ore flotation were reviewed from three aspects of unit, reagent and equipment [6]. Applications of combined processes, combined flotation reagents and new types of flotation machines have improved flotation efficiency of scheelite. In addition, the advances of research on the processing of mixed wolframite-scheelite ores in China were reviewed [9]. These ores have the features of complex compositions, fine grain size and low head grade of tungsten. New flotation reagents and new beneficiation equipments had been developed for processing these types of ores. The process of flotation combined with gravity and magnetic separations had been commercially applied in tungsten concentrators.

Effects of size distribution (content of fine fraction (<10 μm)) on scheelite flotation were studied by testing and theoretical calculations [1]. The results show that particle size influences the scheelite recovery and the performance of combined reagents. The scheelite recovery was decreased by adding fine particles (<10 μm)

into the pulp containing coarse particles. According to the extended DLVO (EDLVO) theory the interaction energy between particles and shear forces of the fluids are related to particle size, which might explain why the fine fractions influence the scheelite flotation.

Carrier flotation is an effective method for increasing very fine minerals recovery. Carrier flotation of scheelite with the size of $-19\ \mu\text{m}$ was studied using polystyrene particles of $-100\ \mu\text{m}+50\ \mu\text{m}$ as the carrier for the fine scheelite [14]. At the conditions of alkaline atmosphere and high agitation conditioning using sodium oleate as the collector the fine scheelite was effectively recovered. It was found by observation under an electronic microscope that hydrophobic adsorption between the surface of polystyrene and scheelite particles and the hydrophobic potential was calculated by EDLVO theory.

COMBINED GRAVITY-MAGNETIC-FLOTATION PROCESS

Wolframite is usually recovered by gravity and magnetic separations in industry. For fine particles of wolframite flotation would be a more efficient method. The flotation of wolframite using sodium hydroxamate as collector was investigated [2]. The process mechanism was studied by determining collector-mineral adsorption, zeta potentials and infrared spectra measurement, and solution chemistry calculations. Multilayer adsorption of collector was found necessary for selective flotation the metal hydroxamate was identified the major adsorbed species on wolframite. The optimal flotation condition observed experimentally agreed well with that predicted from solution chemistry calculations. The calculation also predicted a wider pH range of effective flotation with increasing collector concentrations. Meanwhile, flotation of the slimes of a wolframite ore was studied [22]. Effects of the surface properties of wolframite and ions in slurry on flotation were discussed.

The beneficiation of a carbonate type wolframite-scheelite ore was investigated including mineralogical studies and beneficiation testwork. The process of high intensity magnetic separation followed by gravity separation using shaking tabling for wolframite concentration, and heated flotation followed by acid leaching for scheelite concentration. The wolframite concentrate with grade 33.6% WO_3 and the scheelite concentrate with grade 66.6% WO_3 were obtained at the total recovery of W 69.2% [18]. In another wolframite-scheelite mine the concentration process was improved [20]. In the rough bulk wolframite-scheelite flotation stage a high gradient magnetic separation was added to recover wolframite; at the cleaning flotation stage wolframite and scheelite were concentrated separately in different streams, the wolframite cleaning tailings returning to the rough flotation circuit and the scheelite cleaning tailings being processed using a suspension vibration cone concentrator to recover wolframite.

In a scheelite mine in Jianxi China the ore has a low grade of W and complex compositions of gangue minerals. A combined process of pre flotation of sulphides followed by gravity concentration, room temperature rough flotation and heated cleaning flotation. Na_2CO_3 , water glass (Na_2SiO_3) and BK-418 were used as pH regulator, the depressant for gangues and the collector for scheelite. For the ore with head grade 0.18% WO_3 good results were obtained: scheelite concentrate with grade 67.6% WO_3 and recovery of W 71.4%, and the operational cost was lower than previous process [21].

A process of wolframite-scheelite ore concentration was developed [23] which contains size classification, followed by gravity concentration in size and slimes flotation. In the flotation circuit a combined collector was used and a centrifugal concentrator was used in the gravity concentration circuit. For the ore with head grade 39.3% the coarse and fine W concentrates with grades 58.5% and 26.2% WO_3 were obtained and the total recovery was 77.0% (coarse 62.0%, fine 15.0%).

CONVENTIONAL PETROV'S PROCESS FOR SCHEELITE FLOTATION AND NEW DEVELOPMENTS

The conventional Petrov's flotation process is used for scheelite cleaning concentration which involves steaming of bulk concentrate in 2-4% solutions of Na_2SiO_3 at 80-90°C using fatty acids as the collectors [5]. Experimental studies of heated cleaning flotation were conducted for a rough concentrate of scheelite with grade 5.4% WO_3 . The dosage of Na_2S was found to be important for the concentrate grade and recovery of W. The mechanism was investigated. The component HS^- in the slurry repels the adsorption of the collector on the surface of gangue minerals such as calcite and fluorite and meanwhile, the component S^{2-} in the slurry reacts with metallic ions to form the unsolvable precipitation and the activation function of Pb^{2+} to the gangue minerals are reduced [17]. For a skarn type scheelite ore from Africa the room temperature and heated cleaning concentrations were compared and it was found that the latter was more efficient. For the ore of head grade 0.21% by the process of room temperature rough flotation and heated cleaning flotation the final concentrate with grade 63.6% WO_3 at recovery 82.6% was achieved.

Recently, new cleaning flotation processes of scheelite at room temperature have been developed in China by using different collectors from Petrov's process. A study of new cleaning flotation process at room temperature for scheelite concentration was conducted was at Sizhuoyuan scheelite concentrator in China [4]. A ligand collector called M-COMPLEX was used and salted water glass as the depressant for gangues. This process was used for processing the rough concentrate with the grade of 17.6% WO_3 and the cleaning concentrate with the grade of 63.2% WO_3 at the recovery of 95.0% was achieved.

A case study was carried out on scheelite flotation for a scheelite ore from Yunnan China which has complex associations between scheelite and gangue minerals and a low grade of WO_3 (0.28%) [7]. After grinding (grinding size 82.9% passing 74 μm) sulphides were removed by flotation, and then scheelite was floated using NaOH as pH regulator, Na_2SiO_3 and ferrous sulfate as the depressant of gangue minerals, and No. 733 collector (an oxidized paraffinum sodium salt). One rougher, five cleaners and three scavengers were included in the process and the final cleaning concentrate had the grade of 69.9% WO_3 at the recovery 87.3%. Another study was conducted for a scheelite-molybdenite ore from the skarn scheelite deposit in Jiangxi China [10]. The ore has low concentrations of tungsten (0.16% WO_3) and molybdenum (0.026% Mo). The molybdenite has very fine grain size and closely associated with pyrite. A process of bulk molybdenite and pyrite flotation, molybdenite/pyrite separation after regrinding, scheelite flotation at room temperature from the tailings. Effects of the parameters of grinding size, collector dosage, dosage of sodium carbonate, sodium silicate type and dosage were investigated by experiments. At the optimized conditions of the locked cycle experiment a molybdenum concentrate with grade 46.1% Mo and recovery 88.7% and a tungsten concentrate with grade 65.1% WO_3 and recovery 85.4% were achieved [10].

NEW DEPRESSANTS FOR CALCIUM CONTAINING GANGUES IN SCHEELITE ORES

Scheelite has similar surface properties and floatability to some calcium containing gangue minerals such as calcite and fluorite. There are two approaches of research on the reagent development in scheelite flotation. One is to develop more selective collectors for scheelite and another one is to develop effective depressants of the calcium containing gangues [12]. The depression mechanism of organic and non-organic depressants of these calcium containing gangues was studied and their applications were reviewed [12]. The addition of particular hydrophilic groups on the structures of depressants was suggested a useful method in the development of efficient depressants for the calcium containing gangues. In another study [15] different depressants of calcium containing gangues were compared on the depression performance and combined ferrous sulfate and sodium silicate was selected for real ore testing using a scheelite ore from Yunnan China.

Using no. 733 collector (an oxidized paraffinum sodium salt) at pH 10.5 and at room temperature by 6 time cleaners and 2 time scavengers calcite and fluorite were effectively depressed and scheelite concentrate of grade 63.2% WO₃ at recovery 86.3% was achieved.

RECOVERY OF ASSOCIATED Mo, Cu AND Bi SULPHIDES FROM TUNGSTEN ORES

Some valuable metals such as Mo, Cu and Bi are associated in the tungsten ores in the form of sulphides [13]. A study on the flotation of Cu and Bi sulphides and pyrite from tungsten ore was conducted [16]. The process of bulk Cu-Bi-pyrite flotation and Cu-Bi/pyrite separation was used at the grinding size of 76.3% passing 76 µm. The reagent named Z-200 was used as the collector for the bulk flotation and lime was used at the Cu-Bi/pyrite separation stage. From the locked cycle test a Cu concentrate with grade 21.4% Cu at recovery 94.8% and a bulk Bi-pyrite concentrate with grade 3.0% Bi at recovery 85.2% were obtained. The tailings as the tungsten concentrate had the grade of 38.2% WO₃ with the recovery 89.3%. Process optimization for the middlings of shaking tables in a wolframite concentrator was conducted [8]. The material had low concentration of W and Sn, but the contained Cu, Mo, and Zn as associated components were not effectively recovered in the original process. The original process was optimized by adding the units of the middling regrinding and the associated components (Cu, Mo and Zn) recovery through gravity concentration.

Testwork on the selection of combined collector and dosage was carried out at a tungsten mine for improving the process of Bi and Mo sulphides flotation and separation [19]. In the Mo flotation circuit the combined collector of butyl xanthate at dosage 80 g/t and kerosene at dosage 35 g/t was determined; in the Bi flotation circuit the combined collector of diethyldithiocarbamate at dosage 263 g/t and butyl xanthate at dosage 87 g/t was determined.

For a tungsten ore containing Cu and Zn sulphides and high pyrrhotite an experimental study was conducted [24]. The process of pre flotation of Cu, magnetic separation of pyrrhotite, Zn flotation, pyrite flotation and re-concentration of tailings for scheelite recovery was applied. For the ore with head grades 0.47% Cu, 0.91% Zn, 0.51% WO₃ and 21.1% S the Cu concentrate with grade 22.95% Cu and recovery 89.2%, the Zn concentrate with grade 45.6% Zn and recovery 74.0%, the scheelite with grade 50.9% WO₃ and recovery 79.0% were achieved. The total sulphide recovery was over 93.0%.

INNOVATIONS IN SELECTIVE FRAGMENTATION

As mentioned before, exploitation of ores with a low content of metals is facing several comminution bottlenecks. In particular the selective liberation of minerals, i.e. liberation of minerals without overgrinding, can be mentioned and is currently investigated within the FAME project with an innovative technology called high voltage pulse (HVP) technology. This technology is based on highly energetic electrical pulses (150 – 750 J/pulse) with a very fast voltage ramp-up time (<500 ns) which are applied to the material immersed in water. These pulses cause dielectric breakdown in the material leading to electrical discharge and the formation of tiny plasma channels through the feed material which then generate very strong shockwaves resulting into a huge tensile stress regime within the material. Discontinuities in electrical properties of minerals generate cracks at the grain boundaries allowing full liberation of components (with or without the need of further crushing steps). This technology has been tested on a W-skarn ore and the results have showed an improvement of the scheelite liberation and a decrease in the grinding energy (<http://www.fame-project.info/media/>).

MOLYBDENUM ORES

STUDIES ON FLOTATION PROCESS AND OPERATIONAL INNOVATIONS

In the Copperton Concentrator of Bingham Canyon mine several operational changes have been made in the bulk flotation circuit to capitalize on the findings including the separate treatment of an ore type containing problematic silicate minerals and the optimization of the frother to collector ratio to ensure adequate froth stability [27]. Effects of aluminosilicate minerals on copper–molybdenum flotation from Sarcheshmeh porphyry ores were studied [28].

Nitrogen was industrially used to replace air in the molybdenite flotation circuit at the Sarcheshmeh mine [30]. The Sarcheshmeh copper deposit located in Iran contains 1 billion tonnes of ore averaging 0.7% copper and 0.025% molybdenum with processing capacity 41,000 t/d. Molybdenite as a by-product is recovered in two separate stages, bulk copper–molybdenum concentration and separation. The recovery of molybdenite in the first and second stages is 65% and 85–90%, respectively. The yearly production of molybdenite concentrate varies between 3500 and 4000 t. Sodium sulphide is used as the depressant of the copper and iron bearing minerals which due to a rather high consumption (17.7 kg/t) constitutes one of the major cost items of the plant (i.e., 58% of total reagents cost). Nitrogen for the plant was supplied from an oxygen plant used for the smelter through a 1400 m long pipeline. After using nitrogen in the plant for a period of 21 months, the consumption of sodium sulphide (Na₂S) was reduced from 17.7 to 14.2 kg/t at constant metallurgy. The reduction was lower than expected which was mainly due to the type of sodium sulphide used and the lack of any automatic instrument to control the depressant (sodium sulphide) dosage [30]. In addition, nitrogen has been also used in Mo–Cu separation circuit at the High Valley Copper concentrator in Canada.

Bulk Cu–Mo flotation followed by separation is the normal industrially used process. Three flotation approaches, bulk flotation followed by separation, selective Cu flotation followed by bulk flotation and then separation, and preferential Mo flotation followed by Cu flotation, were compared using the ore from Dexing porphyry Cu–Mo deposit in Jiangxi China. The bench-scale flotation results demonstrated that comparing to other two flotation approaches, the preferential Mo flotation approach using a new non-thiol collector could achieve a higher recovery of molybdenite, while the tailings of molybdenum circuit was treated by copper flotation to obtain a high recovery of other co-present metal values. The industrial flotation tests indicated that a cleaner concentrate containing 0.655% Mo with 88.49% Mo recovery was obtained, and Mo recovery and grade were increased by over 34.0% and 0.4% and Na₂S consumption was saved by 50% comparing to the bulk Cu–Mo flotation followed by separation process [32].

Effects of water in Mo flotation circuit were tested at a Mo concentrator in Henan China by using four different waters including the recycled water from the circuit and three fresh waters from different sources and it was indicated by the testwork that the water containing higher calcium could cause the precipitation in the slurry and the froth being stick when the pH was high and the mixed water of the circuit recycled water and one fresh water with the ratio of 1:4 was suggested to be used in the process [33]. At another Mo concentrator in China the Mo recovery was low. Laboratory testwork was conducted and it was found that the low liberation degree was the reason to cause the loss of Mo in the concentrate. An innovation was carried out by regrinding the tailings from rough cleaner and rough scavenger circuit after dewatering and de-reagent. The industrial application showed that the Mo recovery was increased by 1% [36].

Molybdenite flotation in the bulk copper/molybdenum flotation circuit at Kennecott Utah Copper was studied by means of a combination of plant metallurgical surveys, laboratory flotation tests, mineralogical analysis (QEM-Scan), surface analysis (ToF-SIMS) and contact angle measurements [29]. It was demonstrated that

molybdenite recovery is influenced by flotation feed solids percent and the mineralogy of the host rock. Molybdenite recovery was consistently higher at reduced flotation feed solids percent. Furthermore, the recovery of molybdenite was significantly lower from flotation feeds with high limestone skarn ore content. The major factors affecting the flotation recovery of molybdenite from both porphyry and skarn copper ores are discussed. It is suggested that the lower flotation recovery of molybdenite compared to the copper sulphide is determined by several factors, including particle morphology, inherent hydrophobicity and possible formation of slime coatings in the presence of gangue minerals typical of skarn ores. Implications on plant performance are discussed, and solutions to restore molybdenite recovery presented [29].

STUDIES OF FLOTATION REAGENTS

Experiences in AMAX plants and laboratories have shown that petroleum hydrocarbons differ in their effectiveness for enhancing the natural floatability of molybdenite. A research program was carried out to identify the characteristics of a petroleum hydrocarbon which make it suitable as an oily collector for molybdenite flotation. To provide a systematic set of flotation oils commercial refinery base stocks were blended with diesel fuel. The effects on molybdenite flotation of the following properties of the blended oils were investigated: average molecular weight, kinematic viscosity, molecular structure, density, and weight fraction of base stock in the blend. Standard laboratory batch-flotation tests were conducted using 40 different blended oil collectors. These data were compared with the molybdenite flotation results obtained with the Amoco and Texaco oils regularly used at the AMAX plants and the test results correlated by step-wise multiple-regression analysis. The experimental evidence indicates that a two-component blend of a higher molecular-weight base stock and a lower molecular-weight diluent oil can be a better molybdenite collector than a single-component oil. Furthermore, the flotation oils blended from naphthenic base stock gave superior flotation results whereas those blended from aromatic stock resulted in inferior molybdenite flotation [38].

Some reagents to be potential frothers for copper-molybdenum sulfide mineral flotation were evaluated by using initial dynamic frothability index (IDFI) and initial dynamic froth collapse rate (IDCR) [31]. Flotation testwork using these reagents as frothers for copper-molybdenum flotation was conducted to determine the metallurgical performance of these potential frothers.

Pb sulphides are usually associated with molybdenite in Mo ores. Depression of Pb in Mo-Pb separation circuit was investigated using three depressants of Pb, phosphate Nokes reagent (PN), STC and DX for an Mo ore with high Pb content (0.065%). The dosages of the three depressants added at the cleaning stage were determined by the testwork. A good result was obtained [34]. In the Mo concentrator in Jinduicheng Mo mine Nokes reagent was used as the depressant for Pb in the Mo-Pb separation circuit. A new STC depressant was tested for the Mo ore from the concentrator. Comparing to the Nokes reagent the advantages of the STC depressant were good stability, lower consumption and less toxicity [35]. In addition, in Huanlong Mo mine in China the Mo concentrate contains 3-5% Pb. a study was conducted for removal of Pb and the Pb grade was decreased to 0.3% [37].

NIOBIUM AND TANTALUM ORES

The elements niobium and tantalum do not occur in the free state and in a form of sulphides. Because of their chemical similarity both mentioned elements occur together [40-45]. There are over 50 known niobium and tantalum containing minerals [45]. The most common minerals of these metals are: columbite (Fe, Mn)(Nb, Ta)₂O₆, tantalite (Fe, Mn)(Ta, Nb)₂O₆, tapiolite (Fe, Mn)(Ta, Nb)₂O₆, pyrochlore NaCaNb₂O₆F or (Na, Ca)₂Nb₂O₆(OH, F), microlite (Na, Ca) ₂Ta₂O₆ (O, OH, F), euxenite (Y, Ca, Ce, U, Th)(Nb, Ta, Ti)₂O₆. Furthermore, niobium and tantalum are present as an impurity in the titanium minerals, ilmenite or rutile [44]. The vast majority of global demand for niobium (over 90%) is covered by deposits of pyrochlore mined in Brazil and Canada. In Addition, approximately 7.5% of the demand is met by the extraction of columbite (Brazil, Nigeria) and about 2.5% by tantalite production [41,42].

Recovery and processing of tantalum deposits is more varied. In this case Brazil is the largest producer of tantalum, however, its market share is about 40%. Successive producers are Australia (20%), China and the countries of south-east Asia (10%) and the remaining market constitute African countries [43].

Among the prospective sources of niobium and tantalum worth mentioning are phosphate deposits in the region of Prairie Lake (Ontario, Canada). The expected size of the deposit (ET - exploration target) is 515 - 630 million Mg, in which the content of Nb₂O₅ and Ta₂O₅ are respectively 0.09 - 0.11% (0.9 - 1.1 kg / Mg) and 18 - 21 ppm (18 - 21 g / Mg). The total amount of niobium oxide (V) contained in the deposit is 465.5 – 693 thousand Mg. The total amount of tantalum oxide (V) is 9.27 - 13.23 thousand Mg. Administrators of deposits are convinced that when you start mining phosphate, recovery of niobium and tantalum will be economically justified. [46, 47]. As reported by literature presence of both metals was found in deposits on the bottom of the oceans. Currently, it is impossible to clearly define the development prospects for the extraction of these metals from the bottom of the seas and oceans. [48]

As highlighted throughout the literature, tantalum is characterized by a refractory nature, low natural abundance, extensive solid solution, few known deposits, sporadic supply and difficult metallurgy. It is therefore a complex, critical and high tech metal of the future. Niobium being by and large associated with Tantalum at the mineralogical level, improvements in processing technology that apply to Tantalum will also benefit production of Niobium.

It is also true to a large extent that the improvements in processing that are deemed beneficial to Ta concentration are not specific to Ta-bearing ores. In other words, the current trends in mineral processing that target lower grade polymetallic ores are directly relevant to Ta and Nb processing.

What was described in the present report on W processing, which would benefit from improvement in column flotation, magnetic separation and gravity separation for instance, in relation to the need for improving fines and ultrafines recovery, apply to ta ore processing also. To such an extent, innovations in processing that have been described in the tungsten section are applicable to Ta processing, and the reader is invited to report to the section on beneficiation of tungsten ores.

Natural Ta-Nb bearing ores exhibit specific properties that make processing difficult. These properties include:

- Brittleness, and therefore a propensity to produce fines (difficult to recover) during handling. Grinding being a key processing step in tantalum beneficiation, technologies that will selectively liberate Ta-bearing phases while limiting the production of fines are deemed highly relevant to improving Ta recovery. It would seem relevant in this respect to also research avenues for inducing selective micro-fracturing at the interfaces between phases, such as to promote selective liberation of Ta-Nb bearing phases. Possibilities would include

using microwaves heating, high voltage pulse power fragmentation or cryogenic grinding for example. Advanced flotation techniques are also necessary to recover the Ta-bearing fines in order to reduce Ta loss during beneficiation, however the improvement needed in flotation technology for recovery of Ta fines are not specific to Ta-bearing ores and are at the subject of numerous research programs throughout the world. One problem associated with flotation worth stressing here is the high consumption of additives required for flotation processing of Ta-Nb fines, which is costly and a pollution issue. Thinking beyond current developments of improved processing technologies, where mineral processing is separate from extraction, one may think of coupling extraction and liberation so that liberated fines are leached as they are being produced, which would avoid losing valuable fines in the process. It is unknown at this stage if such a solution, which relates to process intensification, has been tested with Ta ores.

- A high specific gravity, hence conventional and enhanced gravity separation techniques are a matter of significance when it comes to Ta beneficiation, and any improvement in these technologies has some relevance to Ta recovery improvement. The experience gained from Cabbott Corp. at the now closed Tanco mine on the use of Falcon concentrators is one significant example along these lines. This work has shown that enhanced gravity separation is a significant vector for improving the recovery of Ta fines from dilute flotation product streams. This is also associated to the unwanted production of fines during processing of mineralogically complex ores, which is one of the most significant problems with mineral processing today.

- A complex mineralogy as tantalum is highly intergrown with sulfide and other oxide minerals. Textural associations and micro-chemical composition play a critical role in determining a deposit's amenability to metallurgical processing. Hence every development in quantification of complex mineralogy and sampling are deemed relevant for improvement of tantalum ores' recovery. It is also a fact that the complex mineralogy is responsible for the production of fines and ultrafines with existing mineral processing technologies. In recent years, researchers in the mineral processing sector, particularly in the comminution-flotation area, have started thinking about what one may refer to as the "mechanical texture" of ores, rather than the mineralogical texture. The underlying idea is that ores are processed mechanically, so that it is their physical properties which govern their behavior under stress, not their mineralogy. Research about linking the physical properties of the ore and their texture would be of significant value to the mineral processing at large, and to Ta beneficiation in particular.

In addition, regular or high intensity magnetic separation are important in the cleaning stages of Ta beneficiation, and improving of their efficiency is also an factor to be considered for recovery improvement.

RHENIUM ORES

USGS estimated the total global source of rhenium at 12,500 Mg, it is equivalent to more than two hundred years of production at current rates of extraction. Reserves, which are cost-effective and recyclable, and which are now being recovered are much lower, at around 2,500 tons, enough to sustain current production levels for some fifty years. The main reserves of rhenium have been identified in Chile, Canada, Kazakhstan, Peru, Russia and the United States. One-fourth of the total world reserves of rhenium is in Chile, which also is the source of the largest production in the world. Chilean reserves are located in four giant porphyry copper deposits: Chuquicamata, El Salvador, El Teniente and Andina, all of which are operated by Corporación Nacional del Cobre de Chile (Codelco). The rhenium content of the molybdenum concentrates varies depending on the mine and is as follows:

- Chuquicamata 220ppm
- Andina 300ppm

- El Teniente 400ppm
- El Salvador 500ppm

Chuquicamata mine, which is part of Norte Division belonging to Codelco, has the lowest content of rhenium from four mines producing molybdenum. Nevertheless, in 2006, Norte Division covered the 65% of molybdenum, Codelco and it was probably the main source of rhenium.

In the former Soviet Union the reserves are located mainly in Russia and Kazakhstan, with significant deposits exploited also in Uzbekistan and Armenia.

American reserves are located mainly in Arizona and Utah, while smaller amounts are also found in New Mexico and Nevada. All current production comes from Sierrita deposits in Arizona, where rhenium is recovered from concentrates of molybdenum.

In Peru, the largest reserves are located in bed porphyritic Toquepala deposits. Other provisions are found in Europe and Africa, but none are at the present time operated to extract rhenium. In Europe, we are dealing with porphyry deposits, while in Africa are sedimentary deposits of copper-cobalt [51, 52].

So far, existence of only one pure rhenium mineral is confirmed that occurs in the vicinity of the volcano Kudriav on the Kuril Islands in Russia. The mineral is rhenium sulphide (ReS_2), and it's extraction and processing is still not possible [53, 54].

In 2016 an article was published which contains information about finding a rhenium and osmium containing deposit in the territories of Yukon and Northwest in Canada [55].

Presence of rhenium has also been found in deposits of crude oil extracted in Europe and metalliferous deposits in the provinces of Nunitang and Guangdong in China and in the high-sulphuric coal in China. This coal can be seen as a potential source of rhenium production [56-60].

At the moment recovery of rhenium from all those newly found sources is not planned.

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HYDROMETALLURGY

TUNGSTEN

INTRODUCTION

Due to the high dependence from Chinese exports, innovative concepts are necessary to guarantee a sustainable supply of tungsten, especially for resource-poor countries 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.

FUTURE CHALLENGES

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 D 2.2, 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, 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 questions are, how can the treatment of the raffinate (digestion, waste reduction, energy saving) and stripping (stripping agent, ionic strength) be improved [2]?

INNOVATIVE PROCESS TECHNOLOGY 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.

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 [4, 5]. 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 [6]. Additionally, the scheelite can be treated in an acidic leaching step with hydrochloric acid to produce tungstic acid [4]. This process has several disadvantages, as a solid-colloidal layer of tungstic acid covers the unreacted particles and hinders the reaction [7].

In a study of Zhang et al. [6, 8], 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 [8]. The proposed flowsheet is depicted in Figure 1. Because of the acidic leachate, there is no further acid needed prior the solvent extraction step.

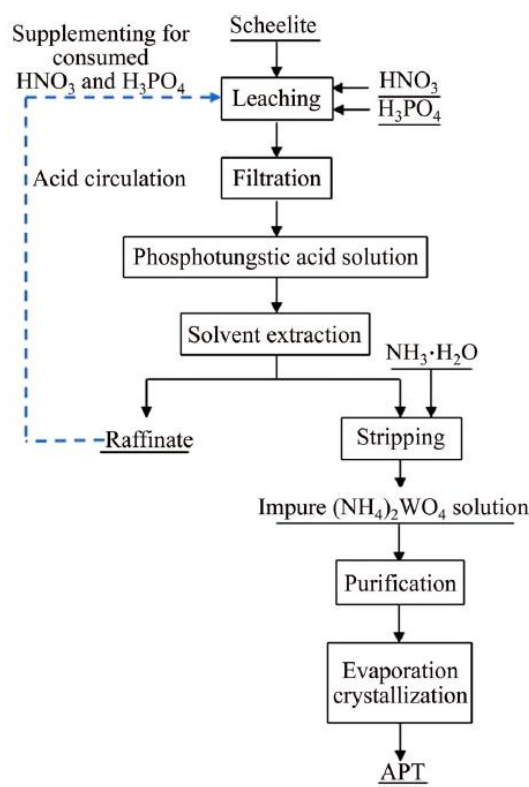


Figure 1 Flowsheet for APT production with acidic leaching with nitric and phosphoric acid [8].

BIOSORPTION

In a study of Ogi et al. (2016) [9] 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 [10, 11] 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 2. First, the WC scrap is calcinated at 950 °C for 12 h yielding WO_3 and $CoWO_4$ powder, which is treated with NaOH to obtain a Na_2WO_4 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 WO_3 powder is transformed into WC by reduction and calcination.

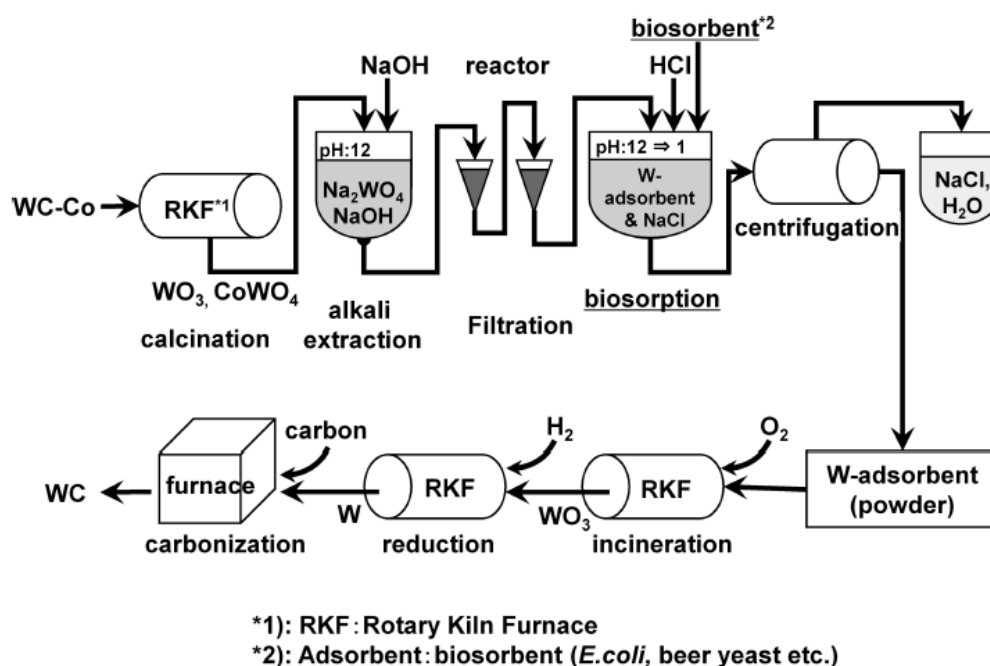


Figure 2 Flowsheet of tungsten recovery by biosorption [9].

A feasibility study reveals, that this biosorption process is still more expensive than with the ion-exchange resin D301 (Table 1), but the required amount of chemicals are relatively small; large amounts quantities of acid and base substances are not necessary to remove tungsten from the adsorbent, which is a significant advantage.

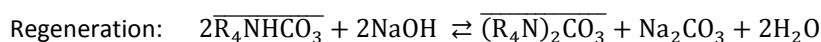
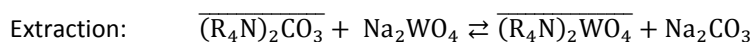
Table 1 Comparison of cost performance of beer yeast and ion-exchange resin for 1 ton of recycled WC [9].

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.

DIRECT SOLVENT EXTRACTION FROM ALKALINE MEDIUM

The traditional hydrometallurgical recovery of tungsten includes an alkali leaching, which is followed by a solvent extraction step [12 – 14]. 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 (Na₂CO₃ or NaOH) and acid (H₂SO₄ 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 [15]. Therefore, the direct solvent extraction of tungsten from alkaline medium was proposed and studied [16]. The breakthrough was the application of quaternary ammonium carbonate salts as extractants, where the main reactions are expressed as [17]:



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) [18], 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 2.

Table 2 Pilot test with NaOH leaching liquor of wolframite concentrate [18].

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 [4]. Other impurities like P, As, Si and Sn are almost removed quantitatively.

A flowsheet of the overall process is shown in Figure 3. The organic and the aqueous phase form closed cycles in the leaching-solvent extraction process, as well as Na₂CO₃ 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 [18].

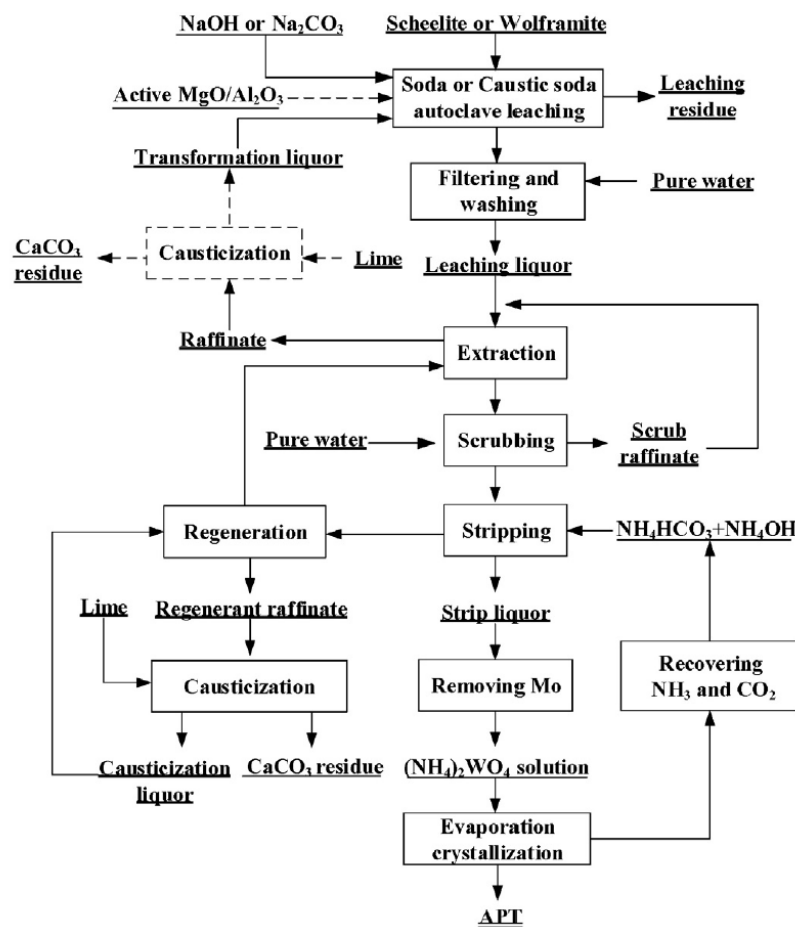


Figure 3 Flowsheet of tungsten hydrometallurgy based on direct solvent extraction from alkaline medium [18].

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 [19]. 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.) [20]. 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 [21].

Lende & Kulkarni (2015) [22] investigated the ELM technique for the selective recovery of tungsten from a multi-component waste stream of printed circuit boards (Figure 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: $WO_4^{2-} + 2(R_3CH_3N^+Cl^-) \rightleftharpoons (R_3CH_3N^+)_2WO_4^2 + 2Cl^-$
2. Stripping: $(R_3CH_3N^+)_2WO_4^2 + 2Na^+ \rightleftharpoons Na_2WO_4 + (R_3CH_3N^+)_2$

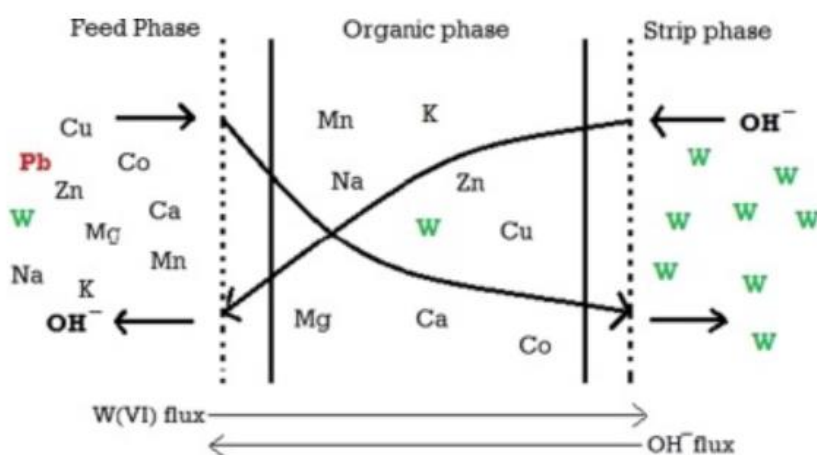


Figure 4 ELM process of selective tungsten recovery [22].

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 [23], 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 [24].

MICROSTRUCTURED EXTRACTION PROCESSES

Recent developments in micro process engineering helped successfully to intensify existing solvent extraction processes of various metals [25, 26]. 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 [27]. 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.

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MOLYBDENUM

INTRODUCTION

Primary molybdenum resources include the molybdenite (MoS_2) mineral and the Mo-Ni black shales in China. In 2015, the share of primary Mo production was around 40 % [1]. Conventionally, the molybdenite concentrates obtained by flotation and other beneficiation methods are roasted to technical-grade MoO_3 . Moreover, standard hydrometallurgical purification methods are used to produce high-purity Mo chemicals.

Innovation potential for hydrometallurgical processing is related to alternative and improved leaching methods and to new ways to purify and/or concentrate the Mo-bearing process streams. The leaching step has been modified to adapt for low-grade ores and to reduce the environmental load. Bio-leaching, for example, has been considered practically useless for Mo recovery but some recent studies indicate that this may not be true.

In separation and purification, new ideas focus on treatment of dilute side-streams and utilization of novel materials. This report aims to review these developments.

INNOVATIVE TECHNOLOGIES FOR MOLYBDENUM EXTRACTION FROM PRIMARY RESOURCES

LEACHING

Direct oxidative leaching of molybdenite concentrates is already utilized along with the pyro-metallurgical roasting. The shift towards hydrometallurgy is motivated by increasing use of low-grade concentrates but also by needs to reduce gaseous emission from the extraction process. Innovation potential can be found in processes, where the Mo yield and purity are improved and the amount of gaseous emissions and solid or liquid wastes can be reduced. Moreover, the conventional flotation-roasting method is not suitable for alternative resources, like the Ni-Mo black shales.

In existing pressure oxidative leaching (POX) processes, nitric acid is frequently used to increase the Mo recovery. Some modifications have been tested to decrease the NO_x emissions; Smirnov et al. [3] have used only “catalytic” amount of HNO₃ and Wang et al. [4] used activated carbon to improve Mo extraction. The role of carbon in Mo extraction is not clear but it is also claimed to adsorb impurities and thereby increase the product purity. In both case, standard molybdenite concentrate was used and it was leached at 180 °C and at a total pressure of 2-2.5 MPa. 99 % recovery of Mo was achieved and no NO_x emissions were produced.

Zhao et al. [5] have studied pressure leaching of Ni-Mo shales under alkaline conditions. Good recovery of Mo (>98 %) was obtained during 10 h at 80 °C and at NaOH concentration of 2.5 mol/L. Main advantage of the alkaline leaching is that Mo is completely solubilized and Ni remains in the solid residue. Drawbacks include high consumption of NaOH and formation of large amounts of Na₂SO₄ waste [6]. In acidic leaching of Ni-Mo shales, on the other hand, Ni is dissolved and part of the oxidized Mo remains in the solid phase. Moreover, the Mo recovery has been found to be substantially lower at acidic conditions [4].

Oxidative leaching using air as the primary oxidant requires rather harsh conditions and requirements for the reactor materials are high. NaClO has been tested as an alternative oxidant, because practically complete extraction of Mo from concentrates can be attained at moderate temperatures. The method involves, however, serious waste problems, because large amounts of both NaCl and Na₂SO₄ are produced. Therefore, it has been proposed mainly for extraction of Mo from secondary copper concentrates or from low-grade Ni-Mo shales. Liu et al. [7] extracted Mo from low-grade Ni-Mo ore using hypochlorite leaching under mechanical activation in a planetary ball mill. High Mo recovery was found at 70 °C and at mildly basic conditions (pH 11). The hypochlorite oxidant can be generated also in-situ from NaCl using the electro-oxidation leaching process. Cao et al. [8] obtained >99 % Mo recovery from a molybdenite concentrate at room temperature, when a current density of 800 A/m² was used in 4 M NaCl and at pH 9. In this process alternative, NaCl can be recycled but no exact process configuration has been reported.

Bio-leaching of molybdenite ores has been studied to some extent and the general conclusion is that molybdenite is very resistant to bacterial attack and the soluble Mo species are toxic for the micro-organisms. Olson and Clark [9] have shown that a mixed *Acidithiobacillus* and *Leptospirillum* culture can extract 85 % of Mo contained in finely ground high-purity MoS₂ samples provided that the redox potential is high (750-800 mV SHE). The leaching rate was, however, much less than that found e.g. in bio-leaching of pyrite. It was also found that in the presence of Fe(III), the toxicity of Mo species decreases and Mo concentrations of few g/L are possible in the pregnant solution. Another process configuration to avoid the toxicity problem has been

proposed by Chen et al. [10]. They utilized a membrane bio-reactor (MBR) to extract Mo and Ni from a low-grade Ni-Mo ore using a *Sulfolobus metallicus* culture. The Mo concentration was kept at 0.4 g/L by means of the membrane separator and after 20 d leaching at 65 °C, 56 % of Mo and 80 % of Ni were extracted.

SEPARATION AND PURIFICATION

PRECIPITATION

In conventional Mo processing, precipitation is mainly utilized to obtain the desired molybdate salt from the ammoniacal solution. Precipitation is also applied to some extent to remove impurities before crystallization.

New developments include the Fe(III) co-precipitation method of Li et al. [11], where the pregnant solution obtained in alkaline leaching of Ni-Mo ores is treated with freshly precipitated $\text{Fe}(\text{OH})_3$ to bind the soluble Mo. After separation of the Mo-loaded solid, molybdenum was released using NH_4OH and finally, an ammonium molybdate solution containing 100 g Mo/L was obtained. NaHCO_3 was added for pH control and the FeCl_3 recovered by HCl treatment was recycled. The purpose of this step was mainly to concentrate the Mo solution before crystallization and the fate of impurities like W, V, As and P was not discussed. All these impurities probably co-precipitate with Mo but exact amounts have not been reported. In an earlier publication [5], the same authors used a smaller dose of $\text{Fe}(\text{OH})_3$ to remove the impurities.

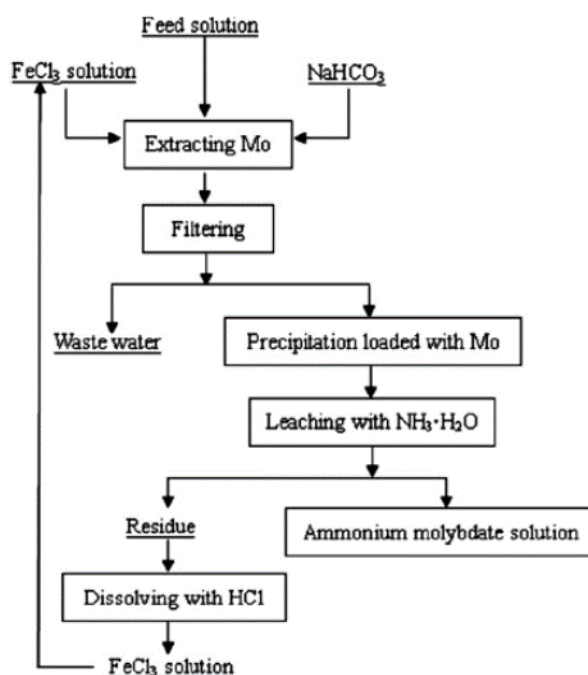


Figure 5 Treatment of the Mo leach liquor with $\text{Fe}(\text{OH})_3$ [11].

SOLVENT EXTRACTION

In solvent extraction (SX), the innovation potential is related to treatment of dilute side streams in order to improve the overall Mo recovery and to new extractants offering higher Mo selectivity.

An et al. [12] have studied Mo recovery from wash solution stemming from acid treatment of technical MoO_3 . The washing step is included to remove copper, iron and other impurities and the solution contains 10-15 g/L of Mo and Cu and 2 g/L of Fe(III). The process comprising of 2-stage extraction and stripping steps is shown in

Figure 6. Conventional ion exchange extractant Alamine 304 (tri-n-octylamine) was used with isodecanol as modifier.

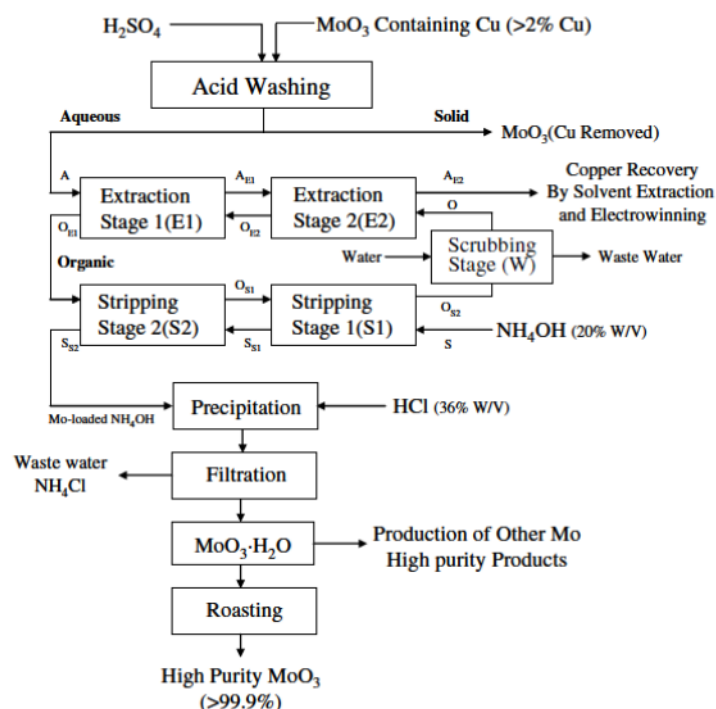


Figure 6 Mo SX for an acid wash solution [12].

The process was tested in industrial scale with a wash solution processing capacity of 30 t/d and high Mo recovery (99 %) and purity (99.9 %) were obtained.

Quite similar separation problem is involved in treatment of acidic sea nodule leach solutions typically containing 0.5, 12, 15 and 2 g/L of Mo, Cu, Ni and Co, respectively. Parhi et al. [13] used the same extractant as above in a 2-stage extraction-stripping process to recover and concentrate Mo. Ammonium molybdate concentration in the rich electrolyte was nearly 100 g Mo/L and after crystallization and thermal decomposition, MoO₃ was obtained with a purity of 99.9 %.

Simple amine extractants work well, when separation of Mo from transition metals only is needed. In more complicated systems, either synergistic effects from secondary extractant or more specific extractants can be used. Separation of Mo and Re using a secondary amine (bis-(3,5-dimethylhexyl-4-methylhexyl)amine, N298) and tributylphosphate (TBP) as synergistic extractants has been studied by Xiong et al. [14]. Laboratory-scale experiments showed that addition of the solvating extractant TBP has much larger influence on Re distribution, while highest Mo selectivity was obtained with pure amine extractant.

Zhu et al. [15] have studied separation of Mo(VI) and V(V) using Cyphos IL 101 trihexyl(tetradecyl)phosphonium chloride, Cytec) as a Mo-selective extractant. They used a synthetic leach solution containing 0.5 g/L of Mo and V as well as 1 g/L of Cu, Fe, Al and Mn. It was found that good Mo/V separation can be obtained at pH 0.5 and both metals can be easily separated from the impurities. V was stripped with 0.5 M H₂SO₄, while Mo needed much higher concentration of 4-6 mol/L. Cytec has also developed a modified phosphinic acid extractant Cyanex 600, which is specially designed for Mo extraction from acidic copper SX raffinates [16]. No data seem to be available on applications, where acidic leaching liquors from primary Mo resources were extracted.

ION EXCHANGE AND ADSORPTION

In analogy with SX, ion exchange (IX) and adsorption are used to purify and/or concentrate the Mo-containing leaching liquors before crystallization. After alkaline leaching processes, the cation is also changed from Na⁺ to NH₄⁺.

Treatment of low-grade Ni-Mo ores gives low Mo concentration in pregnant leach solution (PLS). After oxidative leaching at alkaline conditions, Zhao et al. [5] first acidified the purified PLS to pH 2.5 and then loaded Mo in a weak anion exchange resin. Loaded Mo was subsequently eluted with 8 M NH₄OH to obtain an ammonium molybdate solution, where the Mo concentration was about ten times higher than in the original PLS. Weak anion exchangers is the standard choice for Mo separation at moderate acidic conditions because of formation of the highly charged anionic Mo species. Strong anion exchangers with quaternary ammonium functional groups have also been tried [17] but desorption of Mo may be more difficult. At more acidic conditions, anionic chloro and sulfato complexes are formed. This explains the high Mo distribution coefficients found in HCl medium with weakly acidic aminophosphonic acid resin (Purolite S950) [18] and in H₂SO₄ medium with weakly anionic resins [19].

Separation of Mo from metals like V and W is largely related to utilization of secondary resources but similar needs can be found also in treatment of leaching liquors from primary resources. In leaching of low-grade Ni-Mo shales, some V is found in the leach liquors and it is conventionally removed by precipitation as NH₄VO₃. As an alternative method, Li et al. [20] have studied chelating ion exchange resins for V removal from a PLS containing 90 G Mo/l and 0.4 g V/L. Resins containing aminomethylpyridine (AMP), iminodiacetate (IDA) or aminomethylphosphonate (AMPA) groups were tested in laboratory scale. The authors claim that the AMP resin adsorbs V with high selectivity at pH values around 8 and V can be recovered from the resin using NH₄OH.

Activated carbon adsorption has been studied for purification of the Mo-bearing leach liquors [21]. Selective adsorption of Mo was found at pH 2, probably because of high affinity of the polyanions on the carbon surface, and pure ammonium molybdate solution was obtained after desorption with NH₄OH. Another example of activated carbon utilization is a carbon-in-leach (CIL) process to improve Mo extraction [4] in acidic oxidative leaching. No details were, however, reported and actual function of carbon remains unclear.

MEMBRANE SEPARATION

No data seem to be available on direct use of ultra- or nanofiltration in treatment of Mo-bearing process solutions. This is quite surprising when considering the size of the Mo polyanions formed in moderately acidic solutions. The membrane-related studies are mainly focused on the use of supported liquid membranes, where the SX extractants are used as carriers. These are typically anion exchange extractants for Mo [22, 23]. In fact, the same phenomena are operative in liquid membranes and SX. The liquid membranes have been studied in laboratory-scale for several decades but no indications have been found on pilot or industrial-scale experiments. As is well-known, the main drawback of supported liquid membranes is the insufficient physical stability.

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TANTALUM AND NIOBIUM

INNOVATIVE LEACHING PROCESSES

The first step in the industrial hydrometallurgical process is the extraction of Nb and Ta from high grade Nb and Ta concentrates, after ore and/or pyrometallurgical processing. This extraction was carried out by acid digestion in a mixture of hydrofluoric acid HF with other mineral acids, generally sulfuric acid H₂SO₄. Sulfuric acid lowers the partial pressure of hydrofluoric acid, thereby reducing volatilization losses and acid consumption. The mineral acid improves also the dissolution process, increasing the Ta and Nb leaching yields, therefore high concentrations can be obtained (several tens g/L). All commercialized solvent extraction processes are indeed exclusively operated in the presence of fluoride ions, because of the speciation differences between Nb and Ta in a such medium, favoring their separation. However, HF is not ideal for the decomposition stage because the process is accompanied by the loss of about 6–7% HF due to volatilization, which is hazardous. Furthermore, a large amount of fluoride-containing wastewater that needs to be treated is generated.

Using ammonium bifluoride as an alternative to hydrofluoric acid, the leaching process is performed with water and large amounts of impurities are precipitated in the form of insoluble compounds that can be separated from the solution by filtration (Kabangu et al., 2012). Ammonium bifluoride is also easy to handle compared to aqueous HF. In addition, large quantities of inexpensive ammonium bifluoride are becoming available as byproduct from plants producing e.g. NF₃. The leach liquor prepared in this way shows consistent concentrations of Ta and Nb. The optimum digestion conditions were determined to be: a tantalite-to-bifluoride mass ratio of 1:30; a reaction temperature of 250 °C; a reaction time of 3 h. Under these conditions the leach recoveries of niobium and tantalum were 95% and 98.5% respectively. This can be treated by liquid–liquid extraction using both collective and selective methods after an appropriate acidity adjustment. The extraction of both niobium and tantalum improved considerably with the introduction of sulfuric acid into the feed solution. The best results (DTa = 530, DNb = 4.5, SFTa/Nb = 115) were obtained using 2-octanol as extractant at 6 M sulfuric acid (Kabangu et al., 2012).

Due to environmental concerns and the relatively high solubility of niobium and tantalum in alkaline media, hydrometallurgical processes using concentrated solutions of KOH or NaOH are catching growing attention for the treatment of Nb and Ta ores. A process for the leaching of low-grade refractory niobium–tantalum ores with KOH sub-molten salt was proposed with the objective to eliminate fluorine pollution at the source (Zhou et al., 2005). In this process, the ore is decomposed in concentrated KOH solution (sub-molten salt) at

atmospheric pressure, giving about 10% higher decomposition than that for the HF process. However, a large amount of KOH solution is required to be evaporated and recycled in this process, which is very energy intensive. In order to optimize this process and reduce the energy consumption, a new process was proposed (Wang et al., 2009) to reduce the amount of KOH. The new process is based on the decomposition of the ore minerals by molten KOH into $K_3(Ta,Nb)O_4$, followed by hydrolysis to the soluble hexametalate salt $K_8(Ta,Nb)_6O_{19} \cdot nH_2O$ which is leached in water. However, due to a side reaction leading to the formation of insoluble $KTaO_3$ and $K(Ta,Nb)O_3$, less than 80% Nb and Ta can be effectively leached by water. Increasing the ratio of Nb:Ta in the ore can significantly increase the leach recovery. Therefore, the improved process included first adding a certain amount of Nb_2O_5 to the ore, then decomposing the enriched ore with solid KOH at about $400^\circ C$ and finally leaching the decomposition products with water. After filtration, the leach solution containing niobium and tantalum can be treated by evaporation and crystallization to obtain $K_8(Ta,Nb)_6O_{19}$ and transformed by dilute acid solution into high purity (99.3%) $(Nb,Ta)_2O_5$. In comparison with the sub-molten salt method, the alkali-to-ore mass ratio used in this process dropped from 7:1 to 2:1 resulting in reduced energy consumption. From a process point of view, the Nb_2O_5 used for enriching the niobium–tantalum ore can be recycled from some of primary Nb_2O_5 product or realized by mixing with another ore in which the Nb_2O_5 -to- Ta_2O_5 mass ratio is high. The general flow sheet of this process is shown in Figure 7.

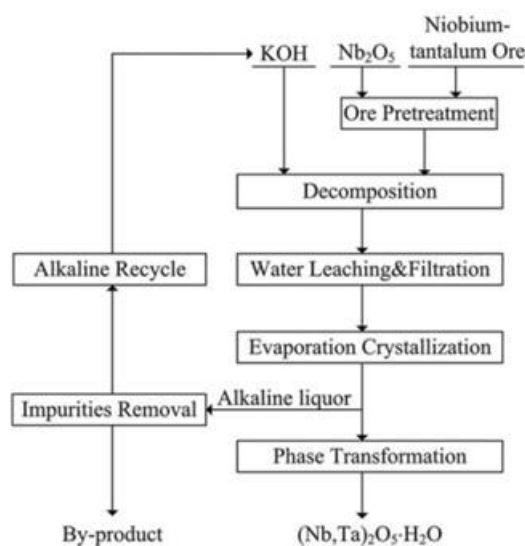


Figure 7 Flow sheet for the molten KOH leaching and recovery of niobium and tantalum.

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 (Gupta, 1994). These metals are usually present in the aqueous phase as niobates, tantalates, and complex ions, such as fluorides, thiocyanates, and other ions. The stability of these complexes and the tendency to form solvation complexes with the organic extractant depend greatly on the chemistry of the aqueous phase. By varying this, it is entirely feasible to extract selectively either niobium or tantalum or co-extract both niobium and tantalum into the organic phase. The separation of niobium and tantalum in the latter case is then accomplished by selective back extraction/stripping of the desired species.

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 (Polyakov and Polyakova, 2003):

- 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 (Nikolaev et al., 2007):

- 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 TaF₅ and NbF₅ in different acidic media was recently made (Ungerer et al., 2014). 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 (HNO₃), sulfuric acid (H₂SO₄) and perchloric acid (HClO₄), 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)F₅. 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 H₂SO₄. This implies that Ta and Nb obtained from Ta(Nb)F₅ could be separated using PA and D2EHPA in the organic phase and H₂SO₄ in the aqueous phase. This result is advantageous for the SX industry where Ta/Nb containing minerals are traditionally leached with high concentrations of H₂SO₄ 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)F₅, the extraction of Ta from Nb can be achieved without the use of additional HF, as has been used previously.

Amines

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 SFTa/Nb in a TOA-fluoride system under optimum conditions is of the order of 400.

In the case of HF medium, the re-extraction of niobium from organic to aqueous stream can be carried out with 7% HCl, 6 to 10% HNO₃, or 14 % NH₄Cl, and the re-extraction of tantalum can be carried out with concentrated

HNO₃ (9.5 to 12.5 M HNO₃) or 25% NH₄OH. Generally, the extraction of tantalum is favored from fluoride media; the extraction of niobium, on the other hand, is favored from HCl acid solutions with acidity of over 4 to 6 M or from solutions containing a high concentration of chloride ions. Extraction of tantalum from HCl acid media can be improved to an almost quantitative level by the addition of about 0.25 M HF. The extractability also depends on the nature of the diluent used and the chemistry of the aqueous phase.

El hussaini and Rice (2004) 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 (Bhattacharyya and Ganguly, 1984). 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 (CCl₄) were studied to extract niobium and tantalum from the sulphuric acid–oxalic acid system (Djordjevic et al., 1966). No obvious differences were found in extraction distribution coefficients among the three amines tested. The highest distribution coefficients were obtained with the lowest H₂SO₄ concentration. When the H₂SO₄ concentration increased to more than 3.5 M, the extraction distribution coefficients of both niobium and tantalum decreased to lower than 1. With lower H₂SO₄ concentrations of less than 2.5 M, the extraction of niobium was higher than that of tantalum. In the H₂SO₄ 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 CCl₄.

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 (Niwa et al., 1987) 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.

Octanol

A process developed for an Egyptian ore material containing valuable metal oxides (RE₂O₃ 6.65%, Nb₂O₅ 5.36% as well as TiO₂ and ZrO₂ 6.15% and 4.50%, respectively, besides Ta₂O₅ 0.47%) has been developed using a breakdown by potassium bisulfate fusion (El-Hazek et al., 2012). The optimum conditions for dissolving the interesting metal (ore/potassium bisulfate ratio of 1/3, time 3 h and temperature 650 °C) give dissolution efficiencies of 98%, 99.3% and 94% for Nb, Ta and Ti, respectively, as well as complete REE dissolution. Recovery of interesting metals (REEs, Nb, Ta and Ti) from bisulfate leach liquor involved several steps. First,

direct precipitation technique was used for recovering REEs and Ti by 10% oxalic acid at pH 1.9 followed by re-dissolving in HCl and separation between them by KOH at different pH values where Ti precipitates at pH 1 but REEs precipitate at pH 6–7. Then, Fe and Al are precipitated at a pH range of 2.5–4 before applying solvent extraction for Nb and Ta. Subsequently, Ta and Nb recovered by solvent extraction technique using octan-2-ol (100%) at different contact times and pH values and stripped by distilled water or different concentrations of HF and H₂SO₄. Ta is extracted at 100% octan-2-ol, A/O 1/1, pH 2.0 and contact time 15 min and stripped by distilled water, A/O 1/1 and contact time 20 min. Then, Nb is extracted at 100% octan-2-ol, A/O 1/1, pH 0.7 and contact time 5 min and stripped by 7 M HF + 6 M H₂SO₄, A/O 1/1 and contact time 20 min. The technical flowsheet proposed is shown in Figure 8.

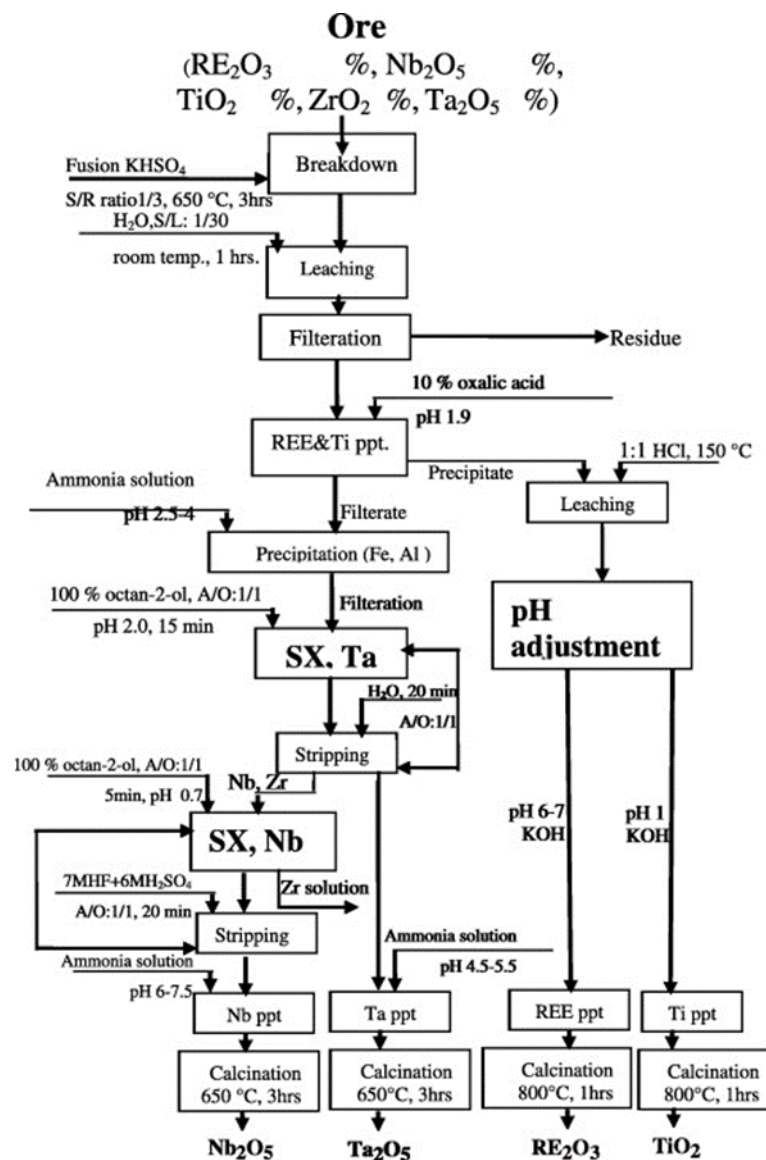


Figure 8 Technical flowsheet proposed for a REE-Ti-Nb-Ta ore based on KHSO₄ fusion

Other extractants

The separation of niobium and tantalum from impurities such as iron, tin, titanium, manganese and silicon to obtain their pure products was reported to be more efficient with TBP than with MIBK in the HF / H₂SO₄ system and in the pure HF system (Zhu, 2011). In a solution containing 10 M HF and 6 M H₂SO₄, at an A/O of

1:1 with undiluted TBP, the separation factors (SF) of niobium and tantalum over the impurities of concern are very high with a minimum of 6000, suggesting very good separation with this system.

Petroleum sulfoxide extractants are essentially similar to TBP, but with an increased efficiency and charge capacity. These compounds, however, have the disadvantage of high viscosity, which can be circumvented to some extent by dilution with alcohols. Tantalum and niobium from a solution containing about 115 g/L Nb₂O₅, 8.7 g/L Ta₂O₅, 40 g/L HF, and 300 g/L H₂SO₄ have been extracted with petroleum sulfoxide dissolved in C₆-C₈ alcohols. The extracted volume contained 140 g/L Nb₂O₅ and 15 g/L Ta₂O₅. Niobium was recovered by re-extraction with water, whereas tantalum was recovered by re-extraction with 50 g/L of ammonium fluoride. (Gupta, 1994)

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PYRO-METALLURGY

TUNGSTEN

DIRECT ALLOYING STEEL WITH TUNGSTEN BY TUNGSTEN ORE

Besides dominant use of tungsten for making cemented carbide, some tungsten (< 9% of the total tungsten application) is also used to produce W-alloyed steels, such as high speed steels. The alloying of steel with tungsten is commonly made by adding ferrotungsten into the steel melt. Due to the laborious and costly ferrotungsten production, the alloying of steel with tungsten by this process is not economic. Direct alloying steel with tungsten by tungsten ore is a promising technology; in this process, tungsten ore can be mixed with carbonaceous materials and be charged into the melting furnace to alloy the steel directly with tungsten, and the yield of tungsten can reach >95%.[1] Due to the integration of ferrotungsten production process and tungsten alloying process, the new technology implies cost and energy efficiency. It is known that some pilot trials have made in China and this technology has been applied in some mini plants, where tungsten ore is available. Secondly, it is also reported that steel can simultaneously be alloyed with tungsten by directly using tungsten ore and technical grade MoO₃. [2] This can be very interesting for producing some steels, in which W and Mo are important alloying elements.

It should be noted that this process is more competitive to be applied in the plant, in which there are tungsten ore and/or technical grade MoO₃ available. Secondly, this process cannot completely replace the use of ferrotungsten, as the final stage composition tuning of the steel will anyhow need to use ferroalloy.

TUNGSTEN CARBIDE PRODUCTION BY ONE-STEP CARBONIZATION METHOD

As shown in D2.2 tungsten carbide production needs two steps: one step for reduction WO₃ into tungsten powder and one step for carbonization of tungsten powder. To get the tungsten powder with desired particle size range, a grinding process is normally needed. One-step production of tungsten carbide is a promising technology, as the costly two-step production process will be tailored into a single one; and it has the advantage of producing WC powder with finer crystal structure of nanometer and with improved mechanical properties.[3] The innovative processes include direct carbothermic reduction of WO₃, scheelite or wolframite,[4]–[6] direct carbonization of WO₃ by CH₄-H₂ mixtures,[7] direct carbothermic reduction of carbon coated WO₃. [8] Here, another one-step production process, tungsten carbide production by mechanical alloying,[9] is introduced. In this process, tungsten oxide is mixed with carbon powder and then the mix is mechanically processed in a mill, during which large amounts of energy are generated and tungsten oxide is transformed into tungsten carbide without using other technological steps. This one-step preparation of tungsten is reported successful in the laboratory scale. The drawbacks of the process lie in the fact that it requires a prolonged period of grinding with very demanding conditions (high rotational speed of the jars and relatively high working temperature). So far, it is difficult to foresee an industrial application from the above proposed one-step tungsten carbide processing process; however, this will still be the interest for future industrial exploration.

ELECTROLYTIC PROCESS FOR THE PREPARATION OF TUNGSTEN POWDER AND TUNGSTEN CARBIDE

Electrolytic process is a promising process for the preparation of materials. In this process, the metal oxide is made into cathode and soaked in the molten salt. Under the driving force of the direct current, oxygen in the metal oxide is ionized and be transported to the anode through the molten salt. The net result is the production of metal at the cathode and evolution of CO/CO₂ at a graphite anode or O₂ at an inert anode. Compared to the traditional reduction process, the electrolytic process exhibits a high yield and increased energy efficiency for preparation of materials. It is reported that many metals and alloys have been produced by this electrolytic process and the process is now being scaled up for the production of tantalum, titanium and uranium.[10] The electrolytic preparation of tungsten powder and tungsten carbide are newly proposed process.[10]–[12] The principles and the advantages of electrolytic process for the preparation of tungsten and tungsten carbide are basically the same as above mentioned. The problems of the process include: (1) the formation of volatile tungsten oxychloride when WO₃ have contact with the molten salt CaCl₂; (2) the dissolution of CaWO₄ in the molten salt; (3) low tungsten yield due to (1) and (2); (4) further treatment of the formed phase may be needed.

More fundamental studies are needed in the future to optimize the process and industrial application can be expected.

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MOLYBDENUM

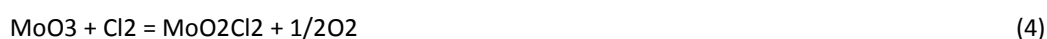
ALTERNATIVES OF TRADITIONAL OXIDATIVE ROASTING

LOW-TEMPERATURE OXIDIZING-CHLORINATING ROASTING

As presented in D2.1, molybdenite concentrates are normally subjected to oxidation in air at temperatures of 500-650 °C in the multi-level hearth furnaces to facilitate the transformation of molybdenite into technical grade MoO_3 , an important intermediate of molybdenum. During this process, a large amount of dust and sulfurous gas are emitted, and this has been regarded as the drawback of this process. Unfired purely hydrometallurgical process (such as nitric acid leaching) can be an alternative to avoid the generation of dust and sulfurous gas; However, nitric acid is costly and the process is only deemed to be commercially effective with concentrates containing more than 50% Mo.[1] As another alternative, low-temperature oxidizing-chlorinating roasting of molybdenite concentrates is proposed in 2014.[2] In this patented process, molybdenite concentrates are roasted together with NaCl in air at the temperature around 450 °C (low than the traditional process temperature, 500-650 °C).

The mechanism of the roasting process can be explained by the following steps:

- (i) Molybdenum disulfide (MoS_2) in the charge is oxidized to molybdenum oxide (MoO_3) in the initial stage according to the reaction (1).
- (ii) Sodium chloride contained in the charge couples evolving sulfur dioxide (SO_2) into sodium sulfate in the presence of oxygen according to the reaction (2);
- (iii) Molybdenum oxide formed in step (i) is removed from the MoS_2 – MoO_3 system according to the reactions (3-4).
- (iv) Other molybdenum compounds (such as molybdenum dioxydichloride and molybdate) are also formed during the process.



After roasting, ~60 - 75% molybdenum remains in ash, while its remaining amount is chlorinated and distilled in the composition of chlorides and oxychlorides being completely caught in the settling chamber and absorbers. Molybdenum from the ash is extracted from the ash by two-stage leaching (first stage with water and second stage with alkali solution); molybdenum in the molybdenum chlorides and oxychlorides is extracted by leaching with alkali. General benefits of the proposed process include the reduction of evolving of dioxide of sulfur in

the atmosphere, the reduction of roasting temperature to 450 °C and formation of water-soluble compounds of molybdenum during roasting. The claimed process makes it possible to recover molybdenum no lower than 98%. The flow chart of the proposed innovative process is shown in Figure 1.

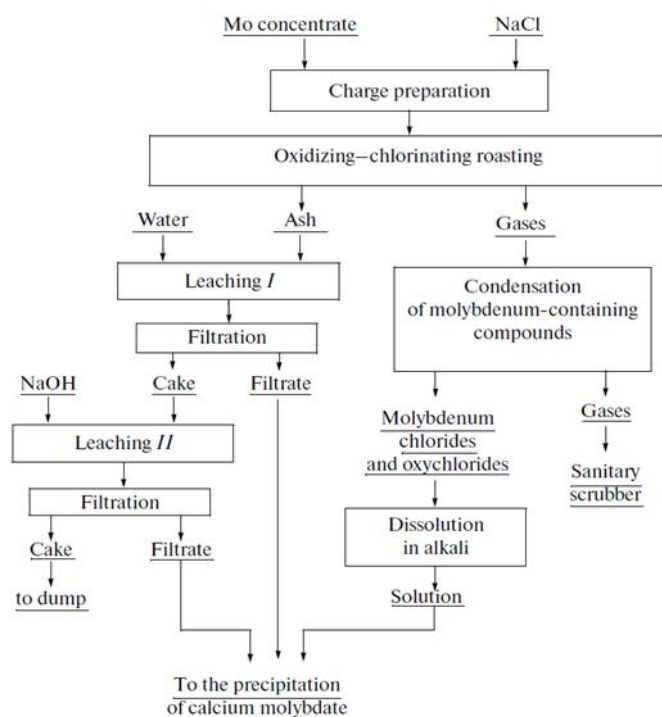
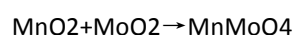
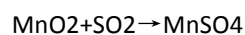
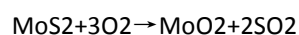
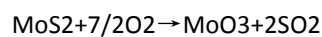


Figure 1 Flow chart of processing molybdenite concentrates using oxidizing-chlorinating roasting [2]

CO-ROASTING MOLYBDENUM CONCENTRATE AND PYROLUSITE (MnO₂)

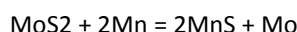
In this patented method, molybdenum concentrate are roasted together with pyrolusite (a mineral consisting essentially of manganese dioxide MnO₂) in air at 450-600 °C [3]. During the roasting, the following reactions will occur:



The roasting products can be leached with H₂SO₄. The leaching solution thereafter can be treated by ammonia for the production of ammonium molybdate and manganese sulfate. The advantages of the proposed process include: (i) lower roasting temperature; (ii) shorter roasting time; (iii) improved Mo recovery; (iv) less emission of SO₂, CO and CO₂; (v) co-production of ammonium molybdate and manganese sulfate.

DIRECT REDUCTION WITH M_N

Molybdenum in the molybdenum concentrate (MoS_2) can be extracted by sulfide forming reducing agent Mn, which is less expensive. In general, the reduction reaction takes place as the following:



The process can be applied to directly convert molybdenite concentrate to ferro-molybdenum with the help of a melt of ferromanganese or a mixture of ferromanganese and iron in an electric arc furnace, induction furnace, or converter. The sulfur is thereby transferred to the sulfide-bearing slag.[4]

REFRAINING THE VOLATILIZATION OF MoO_3 DURING THE ALLOYING PROCESS FOR STEELMAKING

Adding MoO_3 to steel accounts for the major use of MoO_3 . As reviewed in D2.1, MoO_3 can be added into various converters/furnaces to alloy the steel with molybdenum. The main issue with MoO_3 addition into the converters/furnaces lies in the high volatility of MoO_3 at temperatures above $\sim 800^\circ C$, leading to the loss of molybdenum into the exhaust dust and consequently low Mo recovery into the steel. For example, the molybdenum loss can be more than 7% when MoO_3 was used as a raw material for molybdenum alloying in the EAF.[5] The innovative techniques involve the design of new alloying precursors, by using which the volatilization of MoO_3 can be refrained. One of these alloying precursors is proposed to be “mill scale + MoO_3 + carbon”, and the Mo recovery by using this alloying precursor can reach as high as 98%.[6] The principal of the alloying process is based on in-situ formation of more stable compounds of molybdenum from MoO_3 and industrial grade Fe_2O_3 (mill scale). This innovative alloying technology is known to be already applied by the steelmaking industry in Sweden.

PROCESSING OF LOW-GRADE MO CONCENTRATES [LASHEEN ET AL. 2015]

The availability of higher grade sulfide-molybdenum concentrates (48-56% Mo, or 80-93% MoS_2) will be reduced in the longer term. At the same time, demand for molybdenum products will continue to grow. As a result, it is essential that alternative, economical processing routes for treating different types of raw materials should be developed. An ever-increasing quantity of complex low-grade molybdenite concentrates (20-45% Mo) is being produced from secondary sources as a by-product of copper and uranium mining. However, low-grade ores and raw materials comprise lower grade sulfides, oxides, and uranium by-product. Traditional methods of molybdenum extraction, namely flotation-leaching-roasting of molybdenite concentrate at high temperatures, are applicable for high-grade MoS_2 concentrates derived from the primary molybdenum ores and as a by-product from copper–molybdenum porphyry ores. Such secondary low-grade MoS_2 concentrates require extensive modification in the already complex conventional routes. Therefore, several research studies have studied the development of molybdenum extraction routes.

Among these methods, plasma smelting and lime-scavenged reduction are useful for highgrade concentrates only. On the other hand, pressure oxidative leaching, alkali fusion, nitric acid break down, hypochlorite leaching, oxidative roasting followed by sulfuric acid and water leaching, pyrochlorination, lime-scavenged reduction, and bioleaching appear to be suitable for the treatment of low-grade concentrates. Bioleaching offers good prospects for recovering valuable metals and, at the same time, generates much less environmental pollution. However, more research work is needed prior to its commercial application. Further R&D efforts are recommended on five inherently attractive routes for molybdenum separation, including

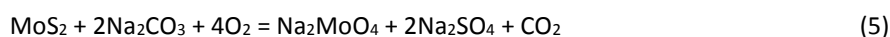
oxidative roasting followed by sulfuric acid and water leaching, lime-scavenged reduction, pressure oxidative leaching, pyrochlorination, and bioleaching.

OXIDATIVE ROASTING

The same as processing of high-grade Mo concentrates.

LIQUATION SMELTING

Liquation smelting makes it possible to concentrate selectively the rock-forming and molybdenum ore components, including impurity elements, in immiscible liquid phases. Thermochemical processing of copper-molybdenum concentrates by liquation smelting is discussed by Urbazayeva, Khanturgayeva, and Nikiforov (1999), in which the copper-molybdenum concentrate was fused with sodium carbonate content in charge 80–100% and lump silicate content 20% in an electrothermic furnace at 950–1150 °C. Under these conditions, the extraction of molybdenum into the liquation salt amounts to 80%, and the extraction of copper and bismuth into the matte amounts to 95% and 100%, respectively. The smelting reaction can be presented as:



PLASMA SMELTING

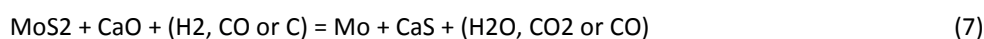
The possibility of effective application of a plasma technology to decompose the molybdenum sulfate concentrate, molybdenite, was reported by several investigators (Huska and Clump 1967; Munz and Gauvin 1975; Gauvin, Kubanek, and Irons 1981; and Evans, Pickles, and Toguri 1988). Direct production of ferro-molybdenum in a three-phase 47-kW plasma arc furnace (at 2300 °C) in the presence of lime and iron scrap as per reactions was reported (Prasad et al. 2002):



A study by Timoshevsky et al. (2006) showed that, in the case of the real system which contains quite a few carbon (~26%), the initial feedstock decomposes through a stage of refractory molybdenum carbide Mo_3C_2 formation. The accuracy of the thermodynamic calculations has been proven experimentally. It has been demonstrated that 100% decomposition of molybdenum sulfide is reachable under the specified experimental conditions (the reactor was heated up to 2500–2600 K, and then the feedstock feeder was switched on). The developed technology enables one to prevent the carry-away of companion rare-earth metals. Specific energy consumptions were of approximately 40 kW · h/kg of Mo.

DIRECT REDUCTION OF MOLYBDENITE

Direct reduction of metal sulfides in the presence of powerful sulfur acceptors like lime has the inherent advantages of enabling the development of a single-step extraction process, bypassing the difficult metallurgical operation of roasting, and aiding in SO_2 pollution abatement (Prasad, Mankhand, and Prasad 1997).



Kay (1965) reported that a high-grade molybdenite concentrate can be reduced by hydrogen in the presence of

lime to the extent of 82.8% at 1255K in 20.2 ks. In another limited study, Habashi and Dugdale (1973) observed only 40% reduction at 1073K in 3.6 ks using a theoretical amount of lime and a hydrogen flow rate of 3.93 cm³/s. Mankand and Prasad (1982) proposed a leach-reductionmelting approach for the treatment of even low-grade molybdenite concentrates. The resultant metal from this approach was of 96–97% purity at 1173K which could be consolidated and refined by electron beam melting to 99.9% purity. Following such successful attempts, further investigations have been conducted on the carbothermal (Padilla, Ruiz, and Sohn 1997).

Prasad, Mankhand, and Suryaprakash (1993) investigated the reduction of molybdenite in the presence of lime by different reductants (H₂, CO, and C); the results showed that, lime tremendously enhances the reduction rates and drastically reduces sulfur emission into the off-gases. The lime-scavenged reduction process has been observed to be very complex, and it may proceed through a number of successive and parallel reactions. The process seems to involve a sulfur-oxygen exchange reaction (as a prerequisite) resulting in the intermediate formation of MoO₂ and CaMoO₄. In carbothermic as well as CO reduction of molybdenite, complications arise due to in-situ carburization of the product metal.

CHLORINATION

Chlorination of sulfide ore as an alternative to roasting has drawn considerable interest for the processing of low-grade sulfide concentrate. The high reactivity of chlorine, relatively low temperature operation, and possibilities of recovering sulfur in a nonpolluting form are some of the advantages that can be harnessed from this process.

The reaction between MoS₂ and Cl₂ in the presence of oxygen is:



whereas with MoS₂ and Cl₂ alone, it is:



Senderoff and Labrie (1955) were the first to chlorinate molybdenite concentrate at 823K to form molybdenum pentachloride for use in the fused-salt electrorefining of molybdenum. Hayer, Uchida, and Wong (1968), in their attempt to recover sulfur by chlorination at 675 K, ended up with a product consisting of MoCl₅ and S₂Cl₂.

Molybdenite concentrate can be successfully processed by direct chlorination, either in a static bed reactor in the presence of oxygen at 573K (Nair, Bose, and Gupta 1978) or a fluidized-bed reactor in the presence of oxygen at 300K (Nair et al. 1987, 1988) However, for an exothermic reaction, the fluidized bed is more suitable than the static bed. Therefore, direct chlorination of molybdenite concentrate using the fluidized-bed technique is a more favorable option (Figure 2).

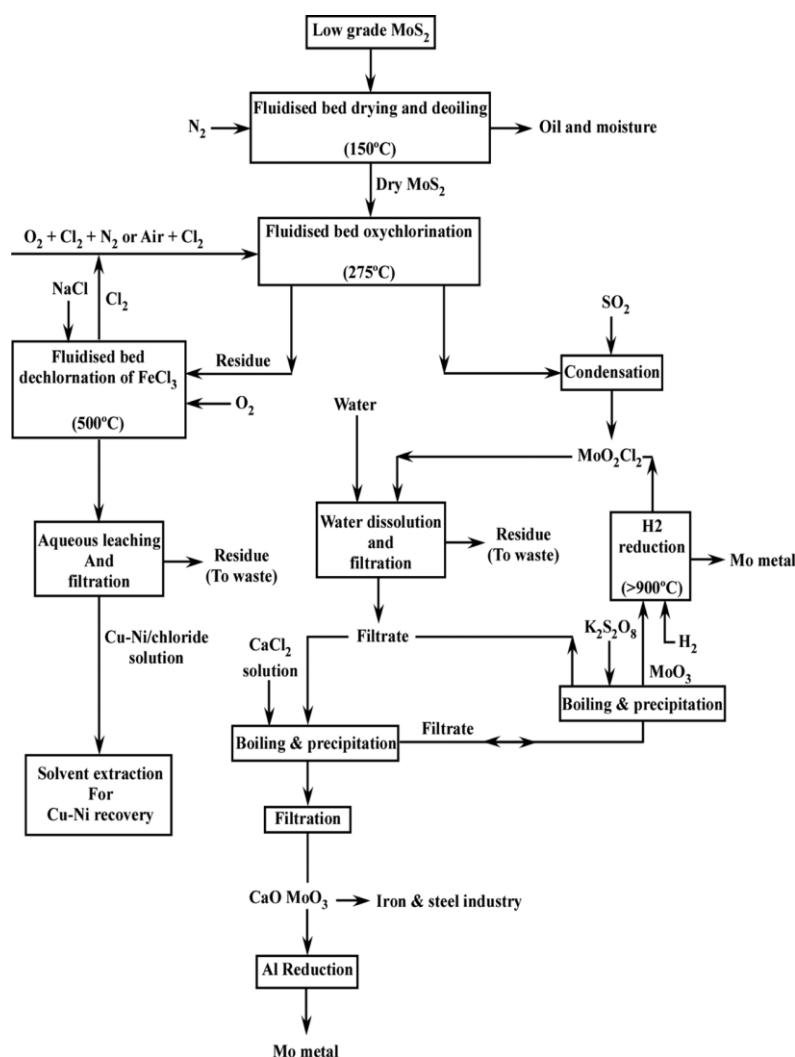


Figure 2. Flow-sheet for the extraction of molybdenum from low-grade molybdenite concentrate by oxychlorination (Nair et al. 1988).

COMBINED PYRO-HYDRO PROCESSING

A pyrometallurgical pretreatment followed by hydrometallurgical processing plays an important role in the treatment of low-grade molybdenum ores. Wang and Wang (2010) have recently applied oxidative roasting followed by sulfation roasting and water leaching for raw carbonaceous Ni–Mo ores. The results showed that, during the oxidation-roasting process, molybdenum and nickel sulfides are oxidized and a molybdenum-bearing phase—powellite (CaMoO_4)—is generated. After sulfation roasting, the powellite vanishes. The generated molybdenum and nickel sulfates are easily leached in water. Under optimum conditions (roasting temperature 240 °C for 1 h; 32mL sulfuric acid=100 g roasted Ni–Mo ore, water leaching for 2 h at 98°C, and a liquid-to-solid ratio of 2:1), the maximum extraction of molybdenum and nickel was 92.1% and 83.5%, respectively. In a novel process by Wang, Wang, and Liu (2009), Ni–Mo ore was roasted at 650 °C for 4 h, followed by leaching with Na_2CO_3 and NaOH mixed solution, as shown in Figure 2. The recovery efficiency of molybdenum reached 92.32%.

Experimental studies by Wang et al. (2011) showed that the most effective method to extract molybdenum and nickel from the carbonaceous Ni–Mo ore is calcification roasting—sulfation roasting—water leaching. Adding 36

g CaO to 100 g the raw carbonaceous Ni–Mo ore can not only protect the environment against SO₂ pollution but also promote the formation of bunsinite (NiO) during calcification roasting. After sulfation roasting with 70mL 98% sulfuric acid at 240°C for 2 h, the bunsinite vanished. The generated molybdenum and nickel sulfates were readily leached in water and, the maximum extraction of molybdenum and nickel achieved were 97.23% and 93.16%, respectively, at 98°C with stirring for 2 h with a liquid=solid ratio of 2:1.

A study by Berg et al. (2002) showed the treatment of low-grade sulfidic molybdenum ores by using a combined processing route for a comprehensive recovery of molybdenum, copper, and other minor elements as shown in Figure 3. As the first step, oxidative roasting was used to give 85–90% sulfur removal. The final sulfur content at the roast could be reduced to approximately 1.9–2.0% at (620°C–670°C) within 5–5.5 h of roasting. Then, both water leaching at 85°C for 6 h, at liquid/solid ratio of 2.85 with magnetic stirring, and dilute sulfuric acid leaching with 5.0 and 7.5 vol.% sulfuric acid at 60 and 80°C for 2 h were done. The liquid-to-solid ratio is approximately 2.85. Both copper and molybdenum were recovered one after another from the filtrates via cementation by iron powder under controlled temperature and pH conditions. Recovery for both elements was, in all cases, more than 99%.

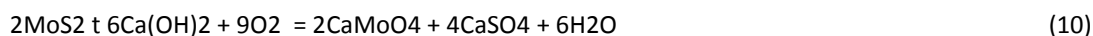
Cementation of copper and precipitation of molybdenum from the H₂SO₄ leach filtrate resulted in a rather poor separation efficiency for molybdenum, cakes after copper cementation and molybdenum precipitation contained equal amounts of molybdenum. After the two precipitation steps almost all of the molybdenum was precipitated from the solution. The separation efficiency for copper was much better, about 80–98% of copper was distributed in the first copper cake, and after both precipitation steps all of the copper was recovered from the solution. Cementation of copper and precipitation of molybdenum from the H₂O leach filtrate resulted in a moderate separation efficiency for molybdenum. 60–90% of molybdenum was reported to the second molybdenum cake. Almost all of the molybdenum in the water-leach solution was removed by both precipitation steps. The separation efficiency for copper is excellent, almost all the copper was removed from the solution during the first cementation step and after both precipitation steps the filtrate contained less than 1 ppm copper.

The pH of the solution during the copper cementation should be lower than 0.9. At a pH=2.0 no cementation reaction was observed. For molybdenum precipitation, initial pH of the solution should not be lower than 1.0, and a value close to 1.0 gives a better precipitation efficiency. Repulping of the wet H₂SO₄ leach cake results in a removal of about 48% of the total sulphate content and no loss of molybdenum to the filtrate, while Ba(OH)₂ addition removes about 88% of the total amount of sulphate but gives also a significant loss of molybdenum (about 60%).

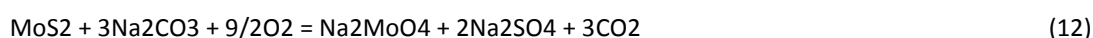
Rao, Natarajan, and Padmanabhan (2001) studied the roasting of bulk sulfide float (BSF) of an Indian uranium ore, The optimum conditions for roasting have been found to be T = 550°C, residence time 4 h, and the addition of 12% Li SO₄. Leaching of the roasted mass under these optimum conditions with water yielded 98% of Cu values, 65% of Ni values, 93% of Co values and approximately 50% of molybdenum values in the leach liquor. Leaching with NaOH solution of the acid leach residue yielded additional 43% of molybdenum values into the alkaline leach liquor that is free of any other metals. Thus, the overall recovery of molybdenum in both leach liquors is 93%.

Roasting of molybdenite in the presence of lime results in the conversion of molybdenum and rhenium values into calcium molybdate and calcium perrhenate, respectively. The SO₂ generated during roasting is fixed as CaSO₄. Calcium perrhenate [Ca(ReO₄)₂], being water soluble, can be selectively extracted from the calcine by leaching with water, whereas calcium molybdate (CaMoO₄) can be solubilized by leaching with dilute sulfuric acid (Singh et al. 1988). Juneja, Singh, and Bose (1996) extracted molybdenum and rhenium values from low-grade Indian molybdenite concentrate by roasting in the presence of slaked lime and soda ash, followed by

hydrometallurgical treatment of the roasted products. In the lime-roasting process, molybdenum recoveries of approximately 99% were achieved when a charge containing a slaked lime to concentrate ratio of 0.875 was roasted at 550°C for 1 h and the calcine was leached twice with 1M sulfuric acid at 80–90°C for 2 h. The roasting reaction in presence of lime can be presented as follows:



In the soda-ash-roasting process, more than 99% of the molybdenum could be extracted when a charge containing a sodium carbonate to concentrate ratio of 1.05 was roasted at 650°C for 1 h and the roasted mass was leached with water at 80–90°C for 2 h. The roasting reaction in presence of soda ash can be presented as follows:



Shariat, Setoodeh, and Dehghan (2001) treated a MoO_3 calcine (60.9% Mo, 1.3% Cu, 2.9% Fe, 0.16% S, and 1.2% SiO_2) by first dissolving it in ammonium hydroxide. The leach liquor was then treated with ammonium disulfide to remove copper and other base metals before precipitating molybdic acid (H_2MoO_4) at pH 2. The precipitate was then dissolved again in ammonium hydroxide from which ammonium paramolybdate ($3(\text{NH}_4)_2\text{O} \cdot 7\text{MoO}_3$) was re-crystallized at 60°C. The final roasted MoO_3 product contained less than 1mg/kg each of Ca, Fe, Cu, As, and 10 mg/kg of Sb.

A two-step procedure comprising oxidation roasting and water leaching can be used for the treatment of high-impurity ferromolybdenum (Shi et al. 2011). Under optimum experimental conditions (CaO/ Na_2CO_3 mole ratio of 0.76; Na_2CO_3 and CaO added total mole number of 0.57/100 g ferromolybdenum powder; oxidation roasting at 700°C for 2 h; water leaching for 2 h at 98°C with liquid/solid ratio of 3:1), the extraction of molybdenum was 97.5%, and the leached rate of impurities phosphorus, arsenic, and silicon were only 16.2%, 18.1%, and 41.2%, respectively.

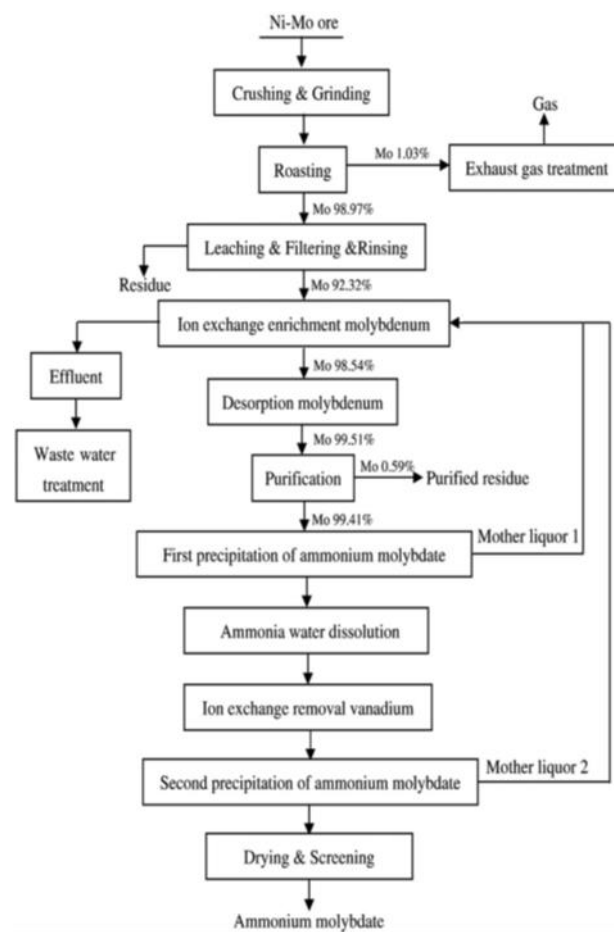


Figure 3 Flow sheet of molybdenum extraction from Ni-Mo ore (Wang, Wang, and Liu 2009).

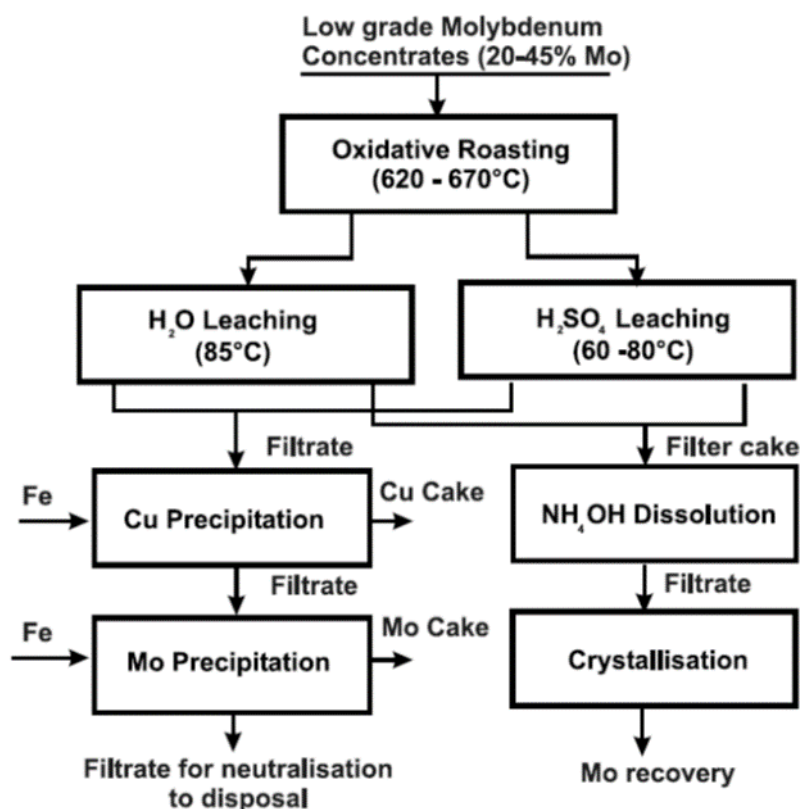


Figure 4 Flow sheet of treatment of low-grade sulphidic molybdenum ores (van den Berg et al. 2002).

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TANTALUM AND NIOBIUM

INNOVATION REVIEW

In 1994, Gupta and Suri presented in a famous book « Extractive Metallurgy of Niobium » a thorough presentation of available techniques to recover the rare and difficult metals Niobium and Tantalum which can be summerized in the following way :

Initially, the recovery of Niobium and Tantalum happened through exploitation of tin slags at low production levels. These slags sometimes contains traces of Nb/Ta (cassiterite). A complex separative chemistry of Tantalum and Niobium appeared first, of which Niobium pentoxide was a byproduct. In this context, in the first part of the XXth century, the reduction techniques, which are more or less those of today, were discovered. Due to the impossibility to smelt tantalum nor niobium oxides into carbothermic furnaces, a number of metallothermic for metal production of Nb or Ta were developed as shown in Figure 5.

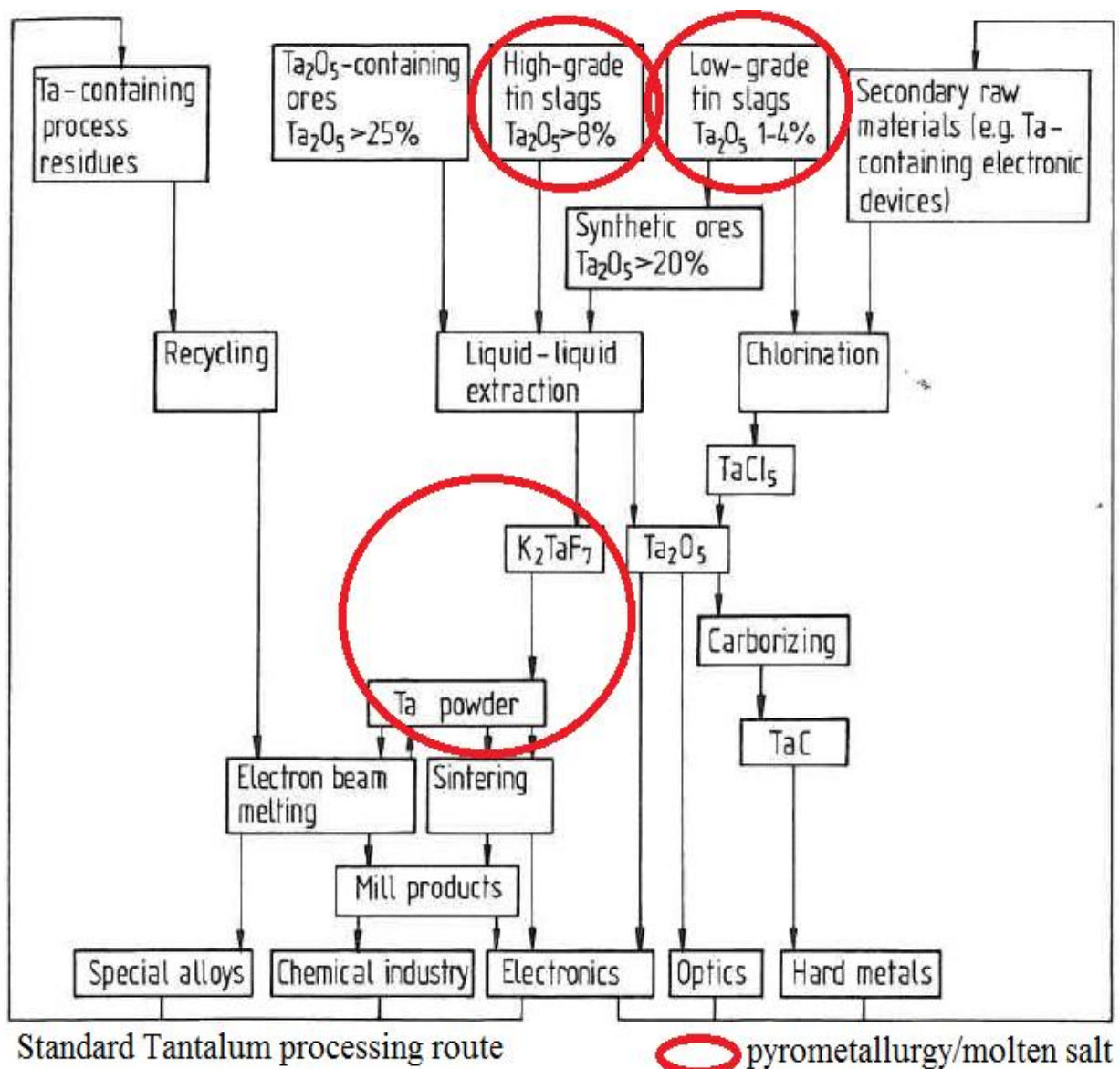


Figure 5 Production process of Niobium and Tantalum

- **sodiothermy** : Tantalum as metal was produced from its oxide or halide by oxygen exchange with sodium, but the reaction had to occur in molten salt medium, which acts a reaction retardant (diluting effect). All these methods for tantalum production with sodium need the intermediate K_2TaF_7 salt.
- **calciothermy** : this technique for Niobium was of limited interest, due to the fact that calcium-oxide which is produced during niobium reduction, has a melting point of $2580^\circ C$, which renders le slag/metal settling very difficult. This was more or less overcome by use of additional calcium chloride as fluxing agent, but the resulting metal still needed electron beam refining.
- **aluminothermy** : the reasonable price of aluminium and its relative high purity, and the melting point of its oxide ($2045^\circ C$) makes it the solution en general. The use of fluxing with quicklime, the progressive feeding of the charge into the converter and subsequent heat control, and the adjustable particle size of aluminium made the whole process mature for industrialization.

In 1966, CBBM invested in this metallurgy to produce ferroniobium from pyroxene. This production proved totally adapted to the needs of the niobium microalloying of steels, and paved the way to a total recomposition of the Nb metallurgy, turning the old rich tin-slugs route to a marginal industry.

In 1983, the company Mineracao Catalao in Brazil, Goias, reported a similar aluminothermic process.

Another technique, chloride reduction process was also put into production in 1986. A Japanese company Toho Titanium Co., who had been a user of the Kroll technology for titanium for 30 years, invested in a 30t/y niobium process based on chloride exchange with magnesium in gaseous conditions. The crude niobium though, was not pure enough and needed further vacuum distillation, sintering and electron beam melting. This process seems to have disappeared.

Yet, the last industrial breakthrough was made by CBMM, when in 1994, they invested in a new hybrid kind of furnace, being halfway between a traditional electric furnace and an aluminothermic converter. In this process, the energetic value to heat the charge to reduction temperatures that niobium oxide needs, is partly brought by arc electrodes and metallic iron, with a significant saving on aluminium charge. The process, though, is officially described as an EAF process as shown in Figure 6.

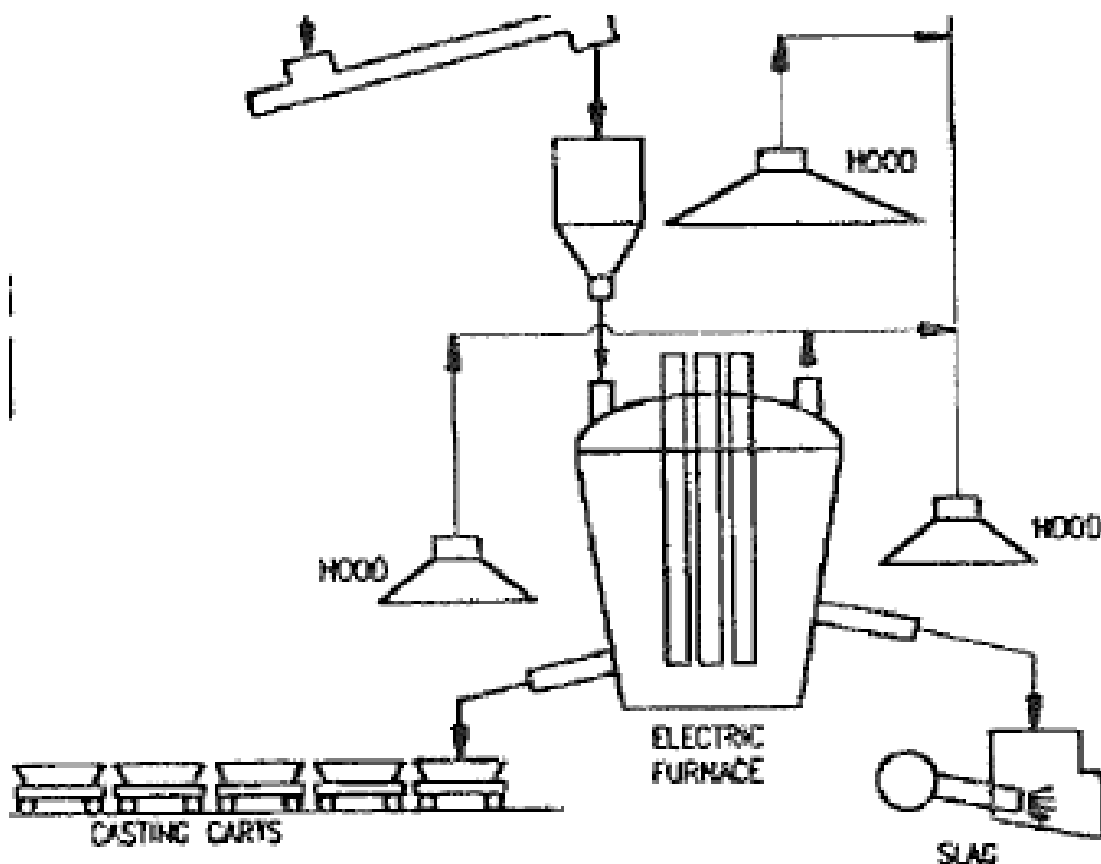


Figure 6 CBBM Electric furnace for aluminothermic FeNb 1994

Taking 1994 as a starting point, a bibliographic review of innovative processes for Niobium and Tantalum has been made in international databases, scientific journals and patents.

Most of the published material deal either with end-of-line recycling of intermediate niobium or tantalum valuable scraps, or with specific applicative metallurgy of the Nb or Ta products, - that means product

adaptability to the specific use - , mostly using already highly purified niobium oxides and being then out of the scope of this study.

Nevertheless, we found some very promising and innovating ways in few documents, which can be collected in 3 categories.

Indirect alloying of Niobium

- 1) The Patent CN102212637 makes use a Nb-rich slag on the top a steel melt, allowing Nb be reduced and enter the steelmelt. As such, the proposed patent belongs to the recycling process of niobium, but the conditions and specifications of Nb-bearing slags might help do more research on indirect alloying.
- 2) In a study, pyrometallurgical use of Niobium oxide is made in a specialty Copper Alloy (Cu-8, Cr-4). In order to avoid the use of costly pure metallic niobium, Nb-oxide is added and partial aluminothermic process is made in molten copper. Cr₂Nb precipitates are successfully produced in the grain boundary of the copper alloy.

Improved quality of FeNb alloy

The Patent RU2003132227 proposes a process which includes a two stage aluminothermic process, and the use of sodium nitrate in the charge.

Magnesiothermy of Tantalum/Niobium oxides with Magnesium in gas phase

- 1) The Patent US6171363 (2001) proposes a vacuum process based on volatilization of Magnesium, which permits at the same time purification of Magnesium, kinetic control of the reaction.
- 2) Followed, in 2003, a publication of the University of Tokyo proposing an alternate pre-sintered charge allowing a better Mg gas permeability, the rest of the process being close to the US6171363.

As a conclusion, it appears that the innovation potential in the pyrometallurgical extractive metallurgy of Niobium is low in the ferro-niobium market for microalloying of steels, and resides mostly in a collaborative research in molten salt process and/ or gaseous reduction. These specialty metallurgies hardly correspond to what is usually meant by pyrometallurgy.

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BRIEF DISCUSSIONS ON ECONOMICS AND ENVIRONMENTAL IMPACT ESTIMATIONS RELATED TO MINING AND PROCESSING TECHNOLOGIES

ECONOMICS ESTIMATION

Three methodologies in mining economics estimation were discussed [1]:

- 1) Strategic economic evaluation - exploring the economics of a project or operation;

Before we look in detail at one of the strategic economic tools at our disposal - marginal cost and revenue - we must first refresh our knowledge of the underlying concept of supply and demand equilibrium.

- 2) Tactical economic decision tools – cost control and efficiency;

Given the effort and investment placed into finding the most appropriate economic plan, it is vital that we comply with this plan during execution in the tactical short range horizon. Complying with these plans enables us to not only meet our strategic goals, but importantly, enables us to utilise the fixed costs efficiently.

- 3) The use of specialist systems and processes - to aid the strategic and tactical methodologies

Tungsten recycling is less energy intensive than virgin production. According to Table 1 [2], 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 [3] and US\$ 14,000 per t of Chinese concentrate [4]).

Table 1 Energy estimates for APT production [2].

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)

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.

A preliminary economic evaluation has been given for the POX-SX process proposed by Wang et al. [5]. Total investment of a plant processing annually 8 kt molybdenum concentrate is 37.3 M\$. Moreover, the auxiliary material costs are estimated as 710 \$ per ton of ammonium molybdate. At the prices of 2012, the net profits are 8.8 M\$/a.

ENVIRONMENTAL IMPACT ESTIMATION

Key environmental impacts of mining were described [6]. The first impact is the disposing of large quantities of waste. The impacts are often more pronounced for open-pit mines than for underground mines, which tend to produce less waste. Degradation of aquatic ecosystems and receiving water bodies, often involving substantial reductions in water quality, can be among the most severe potential impacts of metals extraction. Pollution of

water bodies results from three primary factors: sedimentation, acid drainage, and metals deposition. Mining may result in additional indirect impacts that emanate far from the mine site. The most obvious impact to biodiversity from mining is the removal of vegetation, which in turn alters the availability of food and shelter for wildlife. Often the larger-scale impacts from mining occur from indirect effects, such as road building and subsequent colonization.

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 [7] recycling methods require lower processing energies, and hence, produce lower carbon emissions and avoid waste rock, waste water and leachates from mining operations [8]. 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).

MAIN EU R&D PROJECTS

Several European projects involving in processing of refractory metals are currently running. In particular, the projects FAME, OptimOre and NewOres can be mentioned. The FAME project (Flexible and Mobile Economic Processing Technologies) focuses on addressing a number of economic and environmental challenges to improve processing technologies and to recover valuable materials from low grade and / or complex feedstock's ore by increasing the range of yields of recovered raw materials with lower energy consumption and minimising mine waste (<http://www.fame-project.info/research/>). Regarding the OptimOre project, it aims at increasing yield on Tungsten and Tantalum ore production by means of advanced and flexible control on crushing, milling and separation process (<https://optim-ore.eu/>). The objective of the NewOres project is to develop new models for the genesis of rare metal (W, Nb, Ta, Li) ore deposits from the European Variscan Belt and to valorize low grade and fine grained ore and mine tailings in particular from a major W mine (Panasqueira) from already mined deposits thanks to new intensive flotation devices, the combination with centrifugal gravity separation, and search to develop a new energy saving mineral processing (<http://www.agence-nationale-recherche.fr/?Project=ANR-14-EMIN-0001>).

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