Separation and Purification Technology 162 (2016) 180–187

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

# Selective recovery of niobium and tantalum from low-grade concentrates using a simple and fluoride-free process

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ARTICLE INFO

*Article history:*
Received 23 December 2015
Received in revised form 12 February 2016
Accepted 13 February 2016
Available online 13 February 2016

*Keywords:*
Niobium–tantalum ore
Hexaniobate
Alkaline process
NaOH
Purification

ABSTRACT

The current hydrometallurgical processes used for niobium and tantalum recovery are operated in strongly acidic and fluoride-containing solutions. To avoid the use of these highly toxic media, a fluoride-free process was developed to recover Nb and Ta from low-grade industrial concentrates. The process is based on the caustic conversion of the raw material with $NaOH_{(aq)}$ at atmospheric pressure and at relatively low temperature which then allows the selective dissolution of sodium hexaniobates. Finally, Nb is recovered as purified hydrous oxide by acidification of the hexaniobate solution. The influence of many industry-relevant parameters (temperature, initial NaOH concentration, residence time, impurity content in the initial concentrate, pH of precipitation) was studied in order to optimize the recovery and purification of the valuable metals. Finally, the process was validated in continuous operation at a pilot scale. High recovery yields for Nb and Ta (65%) were obtained as well as high separation factors toward Ti, Fe, P, S, Th and U. The results demonstrate that it is possible to recover and purify Nb and Ta from industrial concentrates without using fluoride solutions.


## 1. Introduction

Niobium (Nb; $Z = 41$) and tantalum (Ta; $Z = 73$) are two group V elements which remain largely unknown to the general public even if their unequaled properties make them essential for many key sectors. For example, Nb is a strategic ingredient in the manufacture of high-strength low-alloy (HSLA) steels [1]. The addition of Nb strengthens the steels without impairing their ductility. Moreover, the cost related to the Nb-alloying is generally insignificant compared to the final value of these steels. Hence even if the HSLA steels contain a low percentage of Nb, typically less than 1% (w/w), they account for nearly 90% of the niobium usage [2]. These low-grade Nb alloys are essential to the automotive market, the pipeline industry and the building and construction sectors. In a lesser extent (about 10% of the Nb market), Nb compounds are used as superconducting magnets, electronic components, nuclear fuel claddings, optical lenses, medical implants, catalysts, collection coins, etc. [3,4]. The most remarkable application of Nb is probably its use as NbTi superconducting magnets at the Large Hadron Collider (LHC) and as NbTi and $Nb_3Sn$ superconducting magnets at the international nuclear fusion reactor project ITER [5–7]. The tantalum market is smaller than the niobium one, with a production of 500–2000 t of Ta per year compared to about 100,000 t per year for Nb [8]. The main application of Ta is the manufacture of electronic components. Because of their high melting point and low thermal expansion, tantalum alloys are also used in cutting tools, military projectiles and in the aircraft industry.

### 1.1. Hydrometallurgical processes for Nb and Ta recovery

The numerous applications and the expanding market push the industrial and the academic researchers to develop new processes for the recovery of Nb and Ta from their ores and concentrates. Nb raw concentrates or colombo-tantalite concentrates (which typically contain 20–50% (w/w) $Ta_2O_5$ and 25–60% (w/w) $Nb_2O_5$ [8]), are usually treated by hydrometallurgical processes in highly acidic media due to the low solubility of Nb(V) and Ta(V) under mild aqueous conditions [9–11].

The fluoride media have been extensively studied for the extraction of the two metals. Actually, the first industrial process for the extraction and purification of Nb and Ta, called Marignac's process, required concentrated HF solutions [12]. This process allowed the production of high purity compounds and helped developing the Nb and Ta industries. In the current processes, the first step is generally the digestion of the Nb–Ta raw material

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http://dx.doi.org/10.1016/j.seppur.2016.02.025
1383-5866/

in a concentrated solution of fluoride ions (HF or $NH_4F$) and in the presence of a mineral acid (most frequently $H_2SO_4$ and HCl). The main advantage of these processes is that Nb(V) and Ta(V) are highly soluble in the fluoride media. Solutions containing up to 5 mol/L of Nb can be obtained in HF 20 mol/L at 25 °C [13]. An extensive review of the chemistry of Nb and Ta in fluoride media has been done by Agulyanski [14]. Another advantage of the fluoride media is that Nb and Ta can form distinct complexes depending on the acidity and the metal concentration. Indeed, niobium forms $NbOF_5^{2-}$ at low acidity and $NbF_6^-$ at high acidity whereas tantalum forms $TaF_7^{2-}$ at low acidity and $TaF_6^-$ at high acidity. This difference in the speciation of the two metals allows their separation, so that, all the commercialized solvent extraction (SX) processes for the Nb–Ta separation are operated in fluoride media. An intensive effort is still being made to improve the Nb–Ta separation by SX in such media [15–20]. Nonetheless, the fluoride solutions are highly toxic and a large amount of effluents containing fluoride ions are generated by the processes mentioned above. Moreover, the fluoride processes are only appropriate for high-grade Nb–Ta concentrates [21].

### *1.2. The Maboumine process*

The environmental footprint of the current hydrometallurgical processes used for the extraction and purification of Nb and Ta forces ones to device cleaner methods. Especially, it appears essential to replace the fluoride compounds. In this regard, a fluoride-free hydrometallurgical process for the recovery of niobium from the Mabounié mine has been developed since the early 2000s. The so-called Maboumine project aims at recovering niobium, but also, tantalum, uranium and the REE from the Mabounié ore deposit located in Gabon. The Mabounié mine is a secondary Nb–Ta–REE–U deposit associated with carbonatite complexes [22] and contains pyrochlore minerals. The average composition of the ore is as follow (in % w/w): Fe 35%, Al 6.1%, P 2.7%, REE 1.4%, Nb 1.2%, Ti 1.2%, U 0.03% and Ta 0.02% [23]. The estimated resources are 360 MT at 1.02% $Nb_2O_5$ cut-off which makes the Mabounié mine one of the most important Nb deposit worldwide [24]. The general flowsheet of the up-stream part of the Maboumine process is given in Fig. 1 and more details have been published elsewhere [25,26].

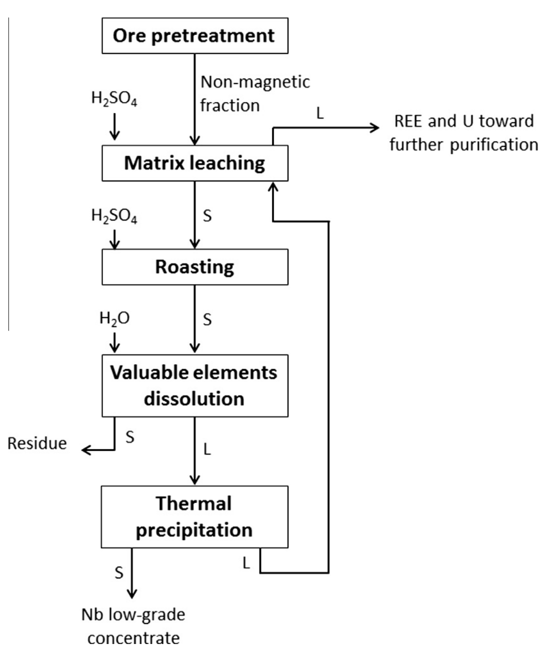


**Fig. 1.** Simplified flowsheet for the recovery of Nb from the Maboumine ore. Up-stream part of the process. Ore pretreatment consists in ore crushing, gravimetric and magnetic separation and sieving [25,26].

In the up-stream Maboumine process the non-magnetic fraction of the ore is first leached with concentrated $H_2SO_4$ in order to eliminate the goethite and crandalite minerals. The leaching residue, which contains the valuable elements, is mixed with $H_2SO_4$ and roasted at 250–300 °C which triggers the decomposition of the pyrochlore minerals. The roasted solid is then leached with water so that Nb, Ta, the REE and U are solubilized. Finally, Nb and Ta are precipitated selectively to the REE and U and the filtrates are recycled in the first leaching step to optimize the acid consumption. The filtrates containing the REE and U are processed in the down-stream part of the process. The method developed for the REE recovery is not discussed in the present paper but has been recently described [23]. Regarding the recovery of uranium, despite its low content in the Mabounié ore, this element can be recovered as a by-product using classical processes [27,28]. The extraction yields for the process depicted in Fig. 1 are about 99% for U, 90% for the REE and 85% for Nb and Ta. The typical composition of the Nb raw concentrate obtained by the up-stream Maboumine process is given in Table 1.

Although the Nb recovery is high, the Nb concentrate obtained has a low Nb content and still contains lot of impurities, especially Ti and Fe, so that it has no commercial value. Consequently further purification is needed. In the continuity of the up-stream process (Fig. 1), a fluoride-free hydrometallurgical process was developed to selectively recover Nb and Ta from this low-grade concentrate.

Alkaline media have caught growing attention over the past few decades for the extraction of Nb and Ta. For example, Hongming Zhou et al. [29] studied the recovery of Nb from ores containing ~25% of Nb, ~25% of Ta, ~3% of Ti and ~7% of Fe. The method was based on the decomposition of the ore with KOH at 150–350 °C followed by a water leaching step. The extraction of Nb was higher than 70% and the extraction of Ta and Ti ranged between 40% and 90%. More recently, Wang et al. [21] also investigated the recovery of Nb from a natural ore using KOH. The initial ore contained ~19% of Nb, ~21% of Ta, ~3% of Ti and ~8% of Fe. The proposed method requires adjusting the Nb/Ta ratio by adding pure $Nb_2O_5$ before roasting the mixture with KOH at 300–500 °C. After roasting, the dissolution yields in water were 85–100% for Nb and Ta, 35–50% for Ti and 15–20% for Fe. Then Nb and Ta were selectively precipitated as $K_8(Nb,Ta)_6O_{19}{\cdot}nH_2O$, namely hydrated potassium hexaniobate-tantalate. The salt was then dissolved in water and the solution was acidified with $H_2SO_4$ to produce a purified Nb–Ta hydrous oxide, $(Nb,Ta)_2O_5{\cdot}nH_2O$. Other studies, focused on the Nb recovery from synthetic concentrates by KOH roasting/leaching have also been published [30–32]. The main advantage of these processes is that Nb is highly soluble in KOH owing to the formation of hexaniobate ions $Nb_6O_{19}^{8-}$. Solubility data for

**Table 1**
Composition of the low-grade Nb concentrate obtained with the up-stream Maboumine process. Solid dried at 100 °C.

| Element | Nb | Fe | Ti | P | S | Ta | REE | U | Th |
|---|---|---|---|---|---|---|---|---|---|
| % (w/w) | 10–15 | 6–10 | 8–12 | 8–10 | 2–5 | 0.25 | <0.2 | <0.003 | <0.21 |
| Nb/impurity (w/w) | / | 1–3 | 1–2 | 1–2 | 2–8 | 40 | >50 | >3300 | >47 |