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**Development of a process for the concentration of the strategic tantalum and niobium oxides from tin slags**

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**Abstract**

The extraction of tin through smelting of cassiterite ( $\text{SnO}_2$ ) has generated considerable amounts of slag in the main production areas of South-East Asia, Africa, and South America. Tantalum and niobium naturally occur in cassiterite deposits and are concentrated in the slag during the smelting process. Tin slags have often been disposed as industrial waste despite contents of tantalum and niobium ranging from 2 to 25 %. Conventional hydrometallurgical processes for the concentration of tantalum and niobium oxides utilizing high concentration of strong acids such as HF or  $\text{H}_2\text{SO}_4$  are environmentally and economically challenging. This paper describes an original and greener approach for the selective dissolution of the slag amorphous matrix, and the concentration of tantalum and niobium oxides in a solid residue. Starting from a slag containing about 15 %  $(\text{Ta,Nb})_2\text{O}_5$ , sequential alkaline and acid leaching stages resulted in the production of a 63 %  $(\text{Ta} + \text{Nb})$  oxides concentrate, which is comparable to commercial grade of mineral concentrates.

**Keywords:** Tin slag, Tantalum and niobium oxide, Leaching, Concentrate

## 1. Introduction

Tantalum and niobium are two refractory metals in group 5 of the periodic table. These metals have fairly similar chemical properties and frequently occur in the same minerals. However, their respective abundance in the earth crust is 2 ppm for tantalum and 20 ppm for niobium (Parker and Fleisher, 1968). The major mineral sources of tantalum and niobium are pyrochlore, microlite, tantalite, columbite, columbo-tantalite, etc.

Brazil is by far the leading supplier of niobium, accounting for about 90% of the world production (Papp, 2013). Most of the niobium production is marketed as ferro-niobium, which is utilized to manufacture high-grade steels and alloys (super alloys) (Schwela, 2010). On the other hand, Australia and Brazil accounted for more than 60 % of the total production of tantalum in 2008 (Papp, 2013). About 24 % of tantalum production was used for the manufacturing of capacitor grade tantalum powder in 2011. Other major uses are in metal products, tantalum chemicals, metallurgical grade powders, and tantalum carbides.

Tantalum and niobium compounds have a growing importance in aerospace, military, and clean energy developments, placing these two metals in the category of strategic materials. The European Union consumption of these metals almost totally relies on importation, and both metals are part of the so-called EU 27 critical materials group as defined in 2017. As shown in Fig 1. (Anonymous, 2017), the “criticality” is a measure correlating the importance of a given material to the economy versus the risk of supply disruption. The high supply risk of critical raw materials is mainly due to the high share of the worldwide production supplied by China (antimony, fluorspar, gallium, germanium, graphite, indium, magnesium, rare earths, tungsten), Russia (platinum group metals), the Democratic Republic of Congo (cobalt, tantalum) and Brazil (niobium and tantalum) (Anonymous, 2017). Further, the risk factor in the supply chain of some raw materials is increased by their so-called “conflict minerals” status (e.g. columbo-tantalite and wolframite). Additionally, strategic metals and/or materials are used in unique applications with limited alternatives and substitutions. Hence, developing more diversified and

secondary sources of critical metals such as tantalum and niobium became of great importance. Tin slags represent a relatively well geographically scattered secondary source of tantalum and niobium (Allain, 1993). The global supply of tantalum historically has been 70 percent from concentrates, 10 percent from tin slag, and 20 percent from recycling and synthetic concentrates (Schwela, 2010). The exploitation of tin slag through economically and environmentally viable processes could help mitigate supply risks.

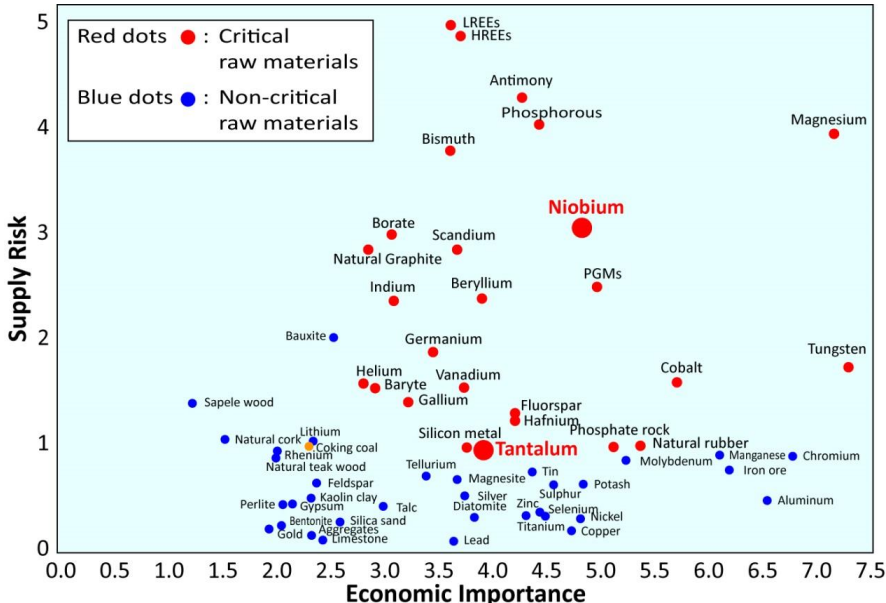


Figure 1. Correlation between economic importance and supply risk of raw materials for the European Union (*adapted from Anonymous, 2017*).

One may mention that the different minerals of tantalum and niobium occur in their own distinct deposits but they are also frequently present as inclusions in cassiterite ( $\text{SnO}_2$ ), which is the main mineralogical source of tin. During the smelting of tin, the process concentrates tantalum and niobium in slags along with other elements such as rare earth elements, titanium, zirconium, silicon, aluminum, iron, calcium, etc (Hasbi et al.1983). The content of tantalum and niobium in tin slags varies as function of tin deposit's geochemistry and the smelting process, but ranges from 1 to 25 %  $(\text{Ta}+\text{Nb})_2\text{O}_5$ , approximately. Conventional methods used for the extraction of these elements from slags consist in their full dissolution by highly concentrated hydrofluoric acid, mixture of hydrofluoric and sulfuric acids, or smelting in electric furnaces (Borchers and Korinek, 1981). Process viability is limited either

by economic or by environmental considerations (Albrecht et al. 1990). According to the work of Brocchi and Moura (2008) the leaching of a tin slag with HCl increased the niobium and tantalum pentoxide content only from 3.3% and 4.1% to 7.2% and 8.4%, respectively. Dry halogenation methods are often used for the recovery or separation of the halogenated compounds of refractory metals (including tantalum and niobium) from their bearing materials (Allain, 1993; Gaballah, Allain and Djona, 1997; Kanari, Gaballah and Allain, 1999, 2000, 2001; Brocchi and Moura, 2008; Adipuri et al. 2011; Pienaar, Wagener and Crouse, 2012).

This paper summarizes the results of a greener approach for the selective dissolution of the slag amorphous matrix resulting in a  $(\text{Ta,Nb})_2\text{O}_5$  concentrate grade that is comparable to commercial grade mineral concentrates. Effects of various leaching parameters (reaction time & temperature, solid concentration, concentration of the reagents, leaching cycles, etc. ) on the concentration and recovery rate of tantalum and niobium oxides in a solid concentrate were investigated.

## **2. Experimental**

### ***2.1. Physico-chemical characterization of tin slags***

The average composition (mass %) of tin slags from six different locations was determined by electron microprobe (EMP) analysis and the results are displayed in Table 1. Note that the EMP device (Cameca SX50) used a microprobe, which is limited to the analysis of fourteen elements simultaneously. As expected, the slags are mostly composed of aluminum, silicon, calcium and iron oxides while the average content of  $(\text{Ta,Nb})_2\text{O}_5$  ranged from 1.1 % (Malaysia) to 24.9 % (Thailand). The residual tin content is generally less than 2.0 %. The slag from the Democratic Republic of Congo was the raw material selected to develop the process described in this paper. This specific tin slag was characterized by a 12.7 %  $(\text{Ta,Nb})_2\text{O}_5$  content and by a high  $\text{SiO}_2$  content (41.9 %). The scanning electron microscope (SEM) used for characterizing the microstructure and qualitative composition of the slag is a Cambridge-Stereoscan 250 device (Cambridge Instruments, UK), utilizing a beam energy of 25 kV

coupled to the same manufacturer data acquisition software, while the explored spectrum range was from about 1 to 20 keV. Fig. 2 (a) displays the microstructure of this slag examined by SEM. The qualitative composition of the different phases present in the slag was determined through energy dispersive spectroscopy (EDS) analysis. Fig. 2 shows clearly the presence of two distinct phases in the slag: a matrix phase (Fig. 2-b) forming the bulk of the slag and composed mostly of silicon, aluminum, calcium, iron, manganese oxides with a low concentration of tantalum and niobium oxides, and a dendritic phase (Fig. 2-c) embedded in the matrix and containing high amounts of tantalum, niobium, titanium, and calcium oxides. The X-ray diffraction indicated the amorphous nature of all tin slag samples.

The composition and microstructure of this slag strongly suggest that the hydrometallurgical process used to treat this slag will require a selective dissolution of the matrix phase to concentrate the tantalum and niobium oxides mostly contained in the dendritic phase (Allain, 1993).

Table 1. Average composition\* (mass %) of slags as determined by microprobe analysis, after conversion into oxides.

Slag origin	(Ta, Nb) <sub>2</sub> O <sub>5</sub>	TiO <sub>2</sub>	WO <sub>3</sub>	ZrO <sub>2</sub>	SnO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	FeO	SiO <sub>2</sub>	MnO
DR Congo	12.7	1.3	0.2	0.9	0.7	11.2	11.6	3.3	41.9	3.7
Indonesia	2.7	13.3	0.0	8.4	0.8	8.0	14.1	11.9	23.3	0.4
Malaysia	1.1	6.6	1.4	1.1	1.6	10.3	14.4	27.7	27.5	0.7
South Korea	10.8	17.8	0.1	3.2	0.8	4.7	29.2	12.2	11.9	0.7
Spain	18.7	7.3	0.1	0.5	0.1	6.9	18.7	0.9	32.4	1.7
Thailand	24.9	15.5	1.0	4.8	0.7	7.0	11.8	9.2	15.3	2.1

\*: The balance constituents are assumed to be carbon dioxide (as carbonate), structural water, bonded OH group, as well as minor oxides (chromium, vanadium and rare earth elements oxides).

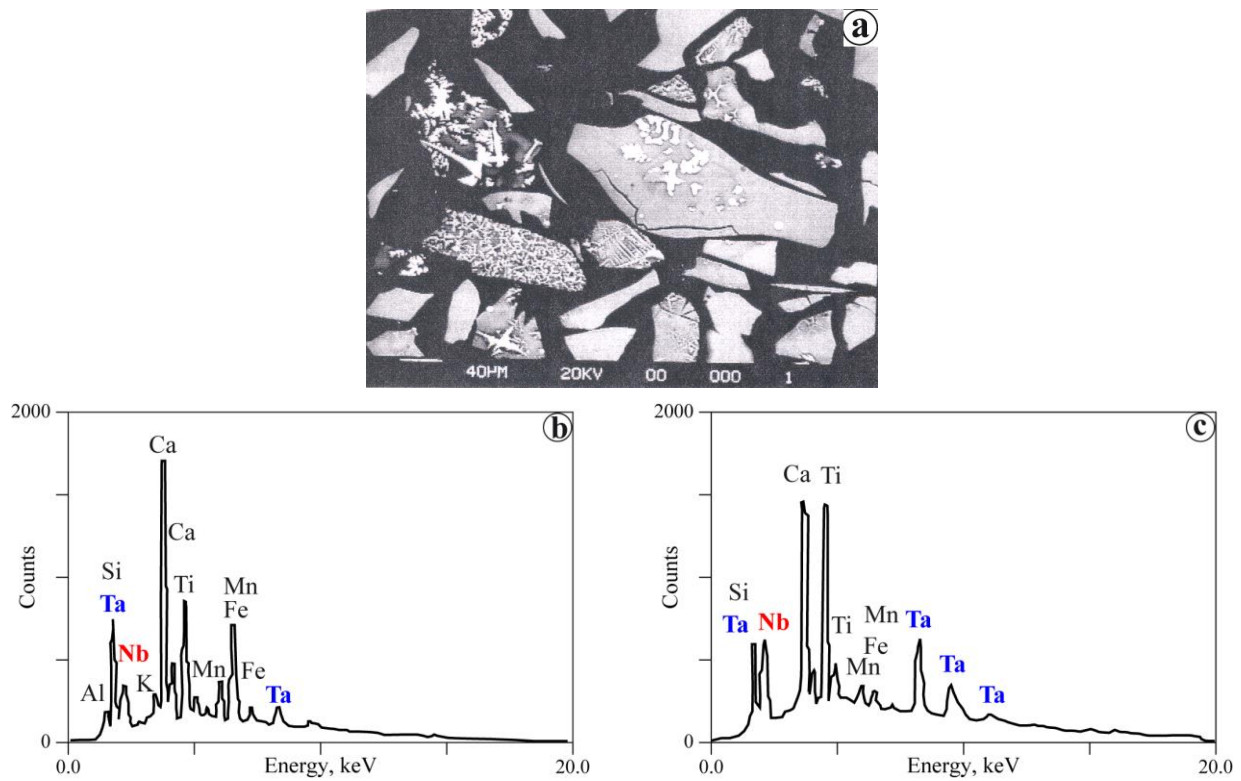


Figure 2. SEM/EDS examination results of the Thailand slag sample: SEM micrograph of the slag sample (a); spectrum (b) and (c) represent the qualitative elemental composition of the matrix and dendritic area, respectively.

## 2.2. Experimental Apparatus and Method

The initial lots of slag consisted of homogeneous batches of 80 to 100 kilograms issued from tin slag factories. After successive crushing, grinding, and screening to a size  $\leq 80$  micrometers, a subset of 10 kg of slag was quartered using a riffle quartering tool, and subdivided in adequate samples of 100 g each, used for the leaching experiments. The tin slags leaching experiments were carried out in the jacketed glass reactor illustrated in Fig. 3. The reactor was heated at the desired temperature through circulation of water heated in a temperature-controlled water bath. The agitation velocity was controlled by adjusting the speed of an electric motor. The acids or alkaline reagents were premixed to desired concentrations and fed into the reactors prior to feeding the tin slags. Once the desired reaction time was reached, the resulting slurry was released through the bottom valve and filtered.

The typical experimental procedure for the leaching of the tin slags is shown in the flow chart Fig. 4. The leaching method consisted of separated acid “A” and alkaline “B” stages alternated in the

sequences: A-B-A, or B-A-B. The acid reagent was composed of a mixture of hydrochloric (HCl) and hydrofluoric (HF) acids while the alkaline solution consisted in concentrated NaOH. The filtration of the slurry produced by each individual acid or basic step resulted in: (1) a white residue high in tantalum and niobium oxides, (2): a solid dark residue lower in tantalum and niobium oxides and reprocessed through the subsequent step, (3) a liquid filtrate discarded after neutralization.

During acid leaching, the effect of various parameters (HCl and HF concentrations, initial solid concentrations, leaching time and temperature,... etc.) on dissolution extent of the sample was investigated. More detailed information on the variation of the parameter range is given in the next section.

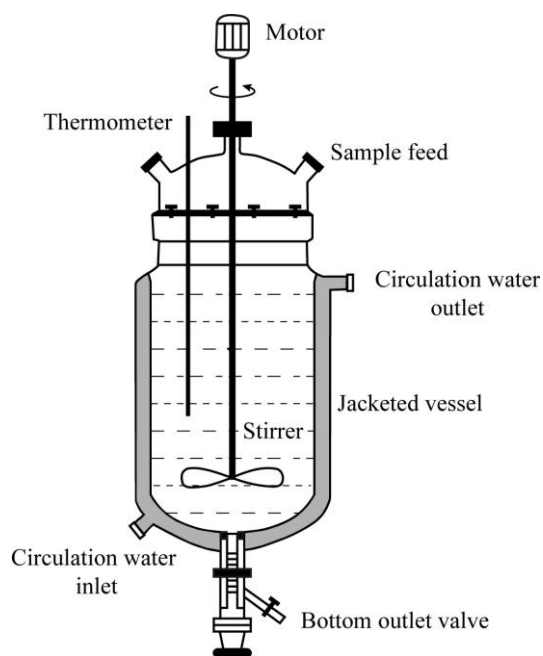


Figure 3. Experimental set-up used for the leaching of tin slags.

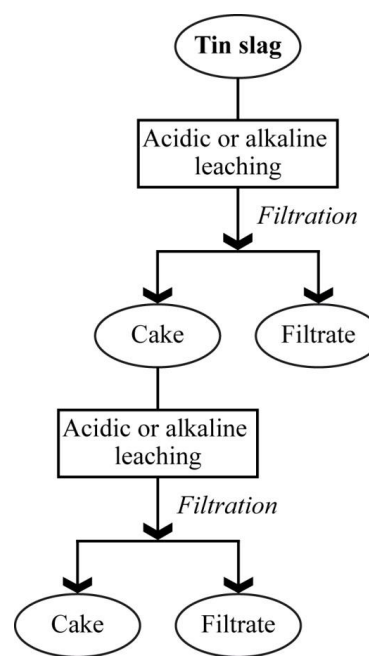


Figure 4. Experimental procedure for the leaching of tin slags.

### 3. Results and Discussion

Figure 5 shows the mass loss of the investigated slag as function of time for separate acid and alkaline leaching runs using the standard conditions mentioned below. These leaching tests were conducted in triplicate and error bars are also shown with the mean values of the mass loss. One can observe that both individual acid (HCl) and alkaline (NaOH) leaching runs resulted in relatively modest mass loss reaching a plateau very quickly at a level of about 15 %, and 2.5 %, respectively. The single acid or



basic leaching steps performed within this study standard conditions were not sufficient to achieve a commercial grade tantalum and niobium oxides concentrate.

In order to increase the tantalum and niobium oxides concentration, different slags were subjected to sequential acid and basic leaching stages. Table 2 compares the mass loss of seven slags subjected to sequential acid-basic (AB) or basic-acid (BA) leaching trials. The mass loss changes as function of the slag origin due to differences in chemical composition, but it is evident that the combined leaching mass losses are systematically higher in comparison to single acid or basic leaching steps. Actually, Table 2 shows that the mass loss produced by acid leach preceded by an alkaline leaching is about 18 % higher than a single acid run while the basic leach preceded by an acid leaching is about 64 % higher than a single basic leach.

The higher mass loss of the basic leaching during the sequential acid-basic (AB) can be attributed to the dissolution of the chloride/fluoride compounds produced during the acid leach and soluble in alkaline condition. On the other hand, the higher mass loss of the acid leaching during the sequential basic-acid (BA) can be attributed to the production of insoluble hydroxide species during the basic leach, followed by the formation of soluble chlorides and fluorides during the acid leaching step (Allain, 1993).

Standard conditions of tin slags leaching experiments were as follows: initial solid concentration: 50 g/L; HCl concentration: 6 Mol/L; HF concentration: 0.14 Mol/L; temperature: 70 °C; time: 18 hours.

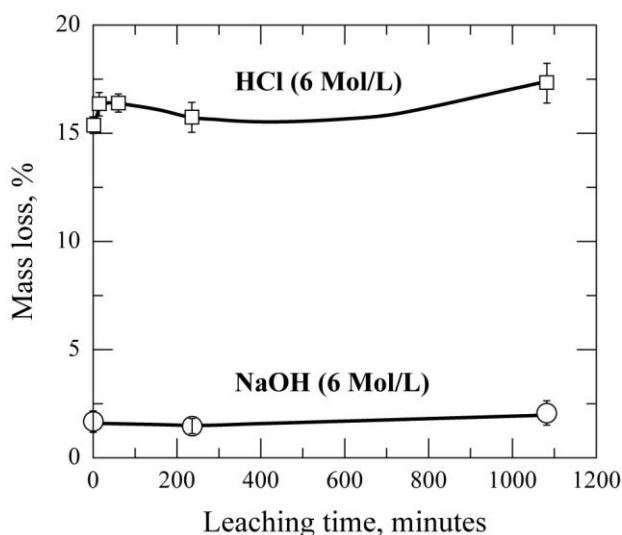


Figure 5. % Mass loss of tin slag during acid and alkaline leaching as function of time (results shown are mean values and error bars).

Table 2. Mass loss of different tin slags subjected to sequential acid and basic leaching stages.

Slag origin	% ML LA <sup>*</sup>	% ML LB <sup>+</sup>	% Total AB	% ML LB	% ML LA	% Total BA
Spain	31.64	47.80	64.32	0.68	41.28	41.68
Indonesia	46.34	54.64	75.66	0.26	76.43	73.36
Malaysia	38.16	52.80	70.82	2.00	71.65	71.08
South Korea	47.52	29.20	62.84	2.24	53.65	52.61
Thailand	45.40	26.00	59.60	2.82	58.10	59.10
DR Congo I	46.64	48.15	72.34	8.44	56.68	60.74
DR Congo II	41.88	32.75	60.92	1.62	64.15	64.74
Average	42.51	41.62	66.64	2.58	60.28	60.47

\* Mass loss after acid leach, + Mass loss after basic leach

% Total AB: Mass loss after acid-basic leach, % Total BA: Mass loss after basic-acid leach.

The effect of the HF concentration and the leaching time on the percent mass loss of tin slags is shown in Figure 6. As in previous case, the error bars are displayed as a result of triplicate runs for several experimental tests. This chart indicates that the mass loss of the tin slag increases almost linearly as a function of the concentration of hydrofluoric acid. Moreover, Figure 6 shows that there is only a modest difference in mass loss between 1 hour and 18 hours reaction times showing that the acid digestion of the slag takes place very quickly over the full range of HF concentrations. This type of kinetic is characteristic of a superficial or catalytic reaction mechanism (Allain, 1993). Based on the experiments illustrated in Fig 7, the activation energy of the acid leaching was calculated to be around 8 kJ/mol which is in good agreement with the reaction mechanism mentioned above.

Table 3 lists the experimental parameters investigated during this study and their most favorable values based on highest concentrations of  $(\text{Ta+Nb})_2\text{O}_5$  measured in the leaching concentrates. The more favorable leaching sequence is Acid-Basic-Acid and that the highest  $(\text{Ta+Nb})_2\text{O}_5$  contents were obtained using a relatively moderate concentration of hydrofluoric acid (HF) of 1.2 mol/L.

Figure 8 exhibits the correlation between the slag mass loss and the content of  $\text{Nb}_2\text{O}_5$  and  $\text{Ta}_2\text{O}_5$  in the final leach residue. The most favorable leaching conditions for an Acid-Basic-Acid sequence led to a 75 % mass loss and to the production of a 63.3 weight % of  $(\text{Ta+Nb})_2\text{O}_5$  concentrate, which is comparable to the grade of commercial concentrates obtained from their primary mineral sources (Simandl, 2001; Gibson, Kelebek and Aghamirian, 2015).

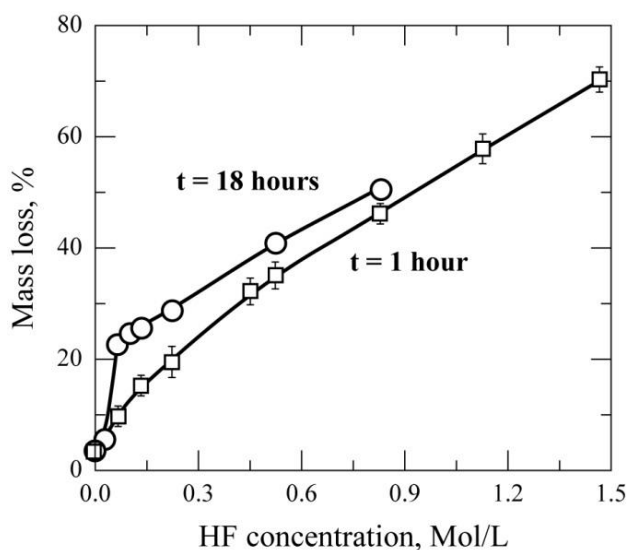


Figure 6. Effect of the HF concentration and the leaching time on the mass loss of a tin slag sample (results shown are mean values and error bars for  $t = 1$  hour only).

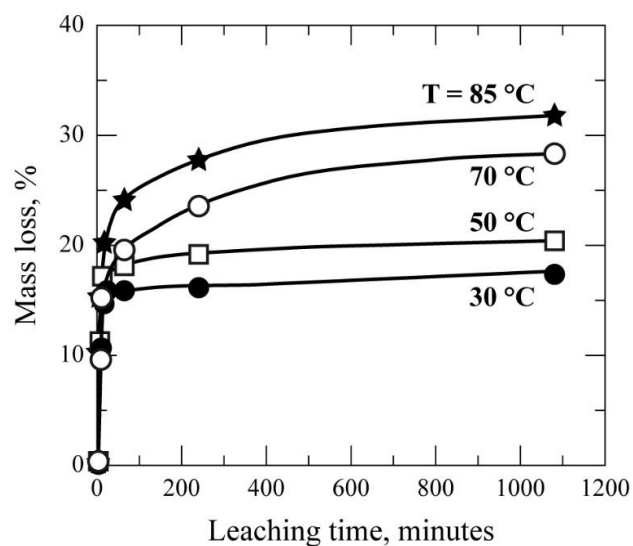


Figure 7. Effect of the temperature on the mass loss of a tin slag sample at different reaction times.

Table 3. Experimental parameters investigated and their most favorable values.

Parameter	Investigated interval	Effect on dissolution rate of matrix	Most favorable value
Time	2 min to 24 hours	After 1 h, time has almost no effect on acid or basic leaching	4 h
Temperature	20 to 85 °C	Temperature has little effect, $E_a = 8$ kJ/mol	70 °C
Initial solid concentration	12.5 to 450 g/L	Decreases as the solid concentration increases	50 g/L
HCl concentration	0.5 to 8 mol/L	Dissolution rate increases as the HCl concentration increases up to 2 mol/L	2 mol/L
HF concentration	0 to 1.5 mol/L	Dissolution of matrix increases but high HF concentration lead to dissolution of Ta, Nb and Si	1.2 mol/L
NaOH concentration	0.5 to 4 mol/L	Dissolution rate increases as the NaOH concentration increases up to 2 mol/L	2 mol/L
Cycle of leaching	Simple Acidic, Basic & altered (A-B-A; B-A-B)	Sequential /altered acid - basic leaching leads to the best results for the dissolution of the matrix	acid-basic-acid

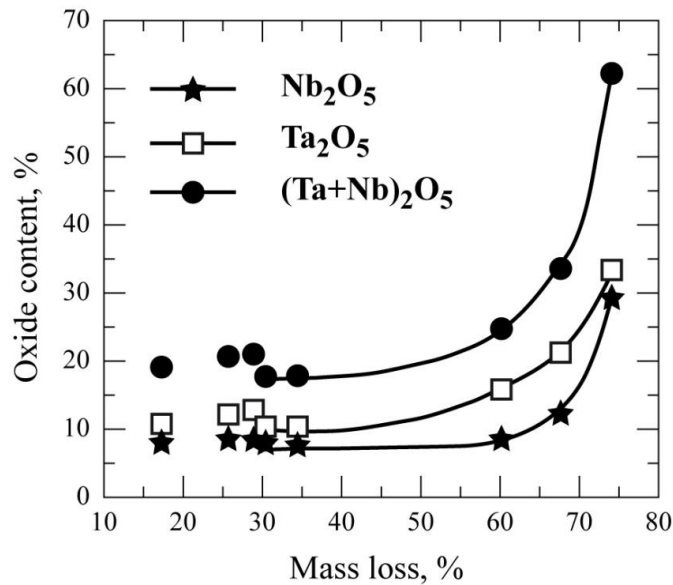


Figure 8. Correlation between the sample % mass loss and the content of Nb<sub>2</sub>O<sub>5</sub> and Ta<sub>2</sub>O<sub>5</sub> in the final leaching residue.

The mass balance and process flow of tin slag leaching are shown in Figure 9 confirming the production of a high grade (Ta+Nb)<sub>2</sub>O<sub>5</sub> solid concentrate yielding about 86 % weight of the total (Ta+Nb)<sub>2</sub>O<sub>5</sub>

contained in the raw slag. The balance of these oxides is included in a solid residue containing about 3 % weight of the total  $(\text{Ta+Nb})_2\text{O}_5$ , recyclable into the leaching process, and in a liquid effluent holding about 11 % weight of the total  $(\text{Ta+Nb})_2\text{O}_5$ . Weight percentages are derived from masses of  $(\text{Ta+Nb})_2\text{O}_5$  indicated in grams in Fig. 9.

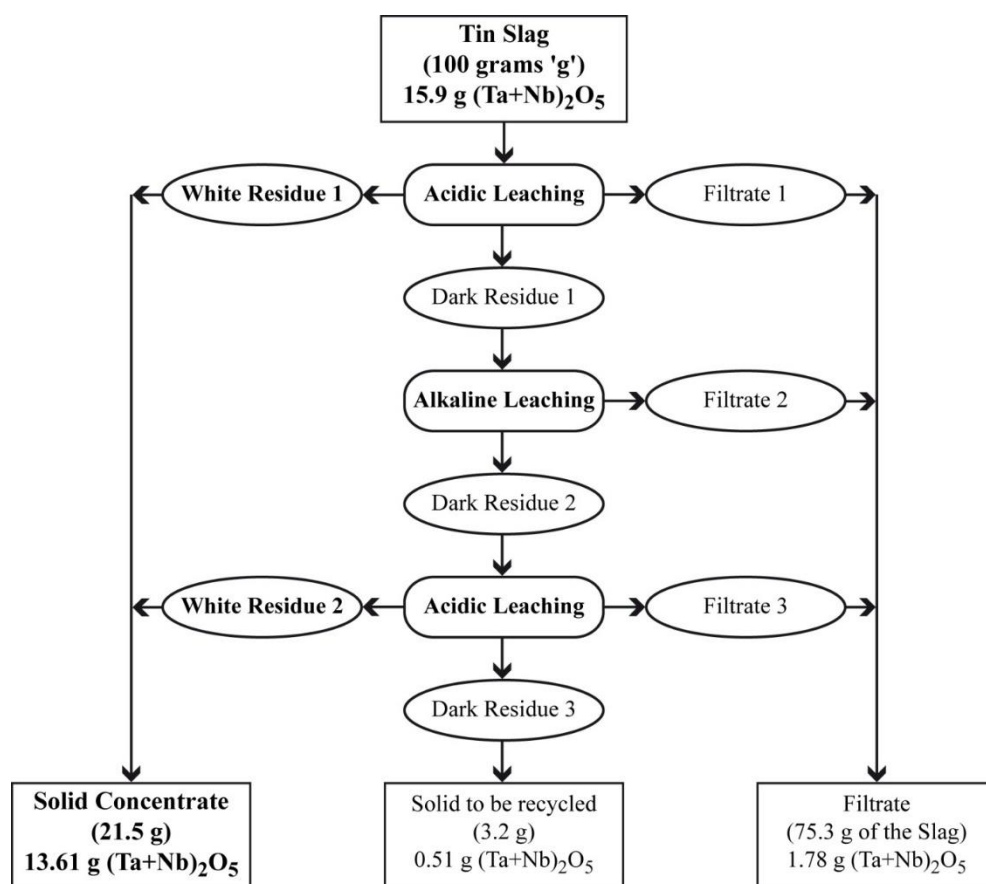


Figure 9. Schematic representation of the flow-sheet and mass balance for the tin slag leaching.

Fig. 10 illustrates the SEM/EDS microstructures of the tin slag before and after an A-B-A leaching cycle. Micrograph and EDS spectra (a) display the initial microstructure and qualitative composition of the slag confirming the presence of dendritic phases high in tantalum and niobium oxides, and embedded in the vitreous phase. Additionally, Micrograph and EDS spectra (b) display the microstructure and qualitative composition of the final leaching residue produced from the same slag sample. It is noteworthy that only the dendritic “skeletons” remain in the residue indicating that the

sequential leaching cycles (A-B-A) totally dissolved the amorphous phases of the slag, leaching out the lower value elements such as silicon, calcium, iron and aluminum into the liquid filtrate, while selectively concentrating tantalum and niobium oxides in the solid residue. One may emphasize that the balance of the solid residue is essentially composed of silicon oxide, which makes this concentrate very suitable for subsequent purification processes through gas solid reactions such as chlorination or carbochlorination (Allain, 1993; Gaballah, Allain and Djona, 1997).

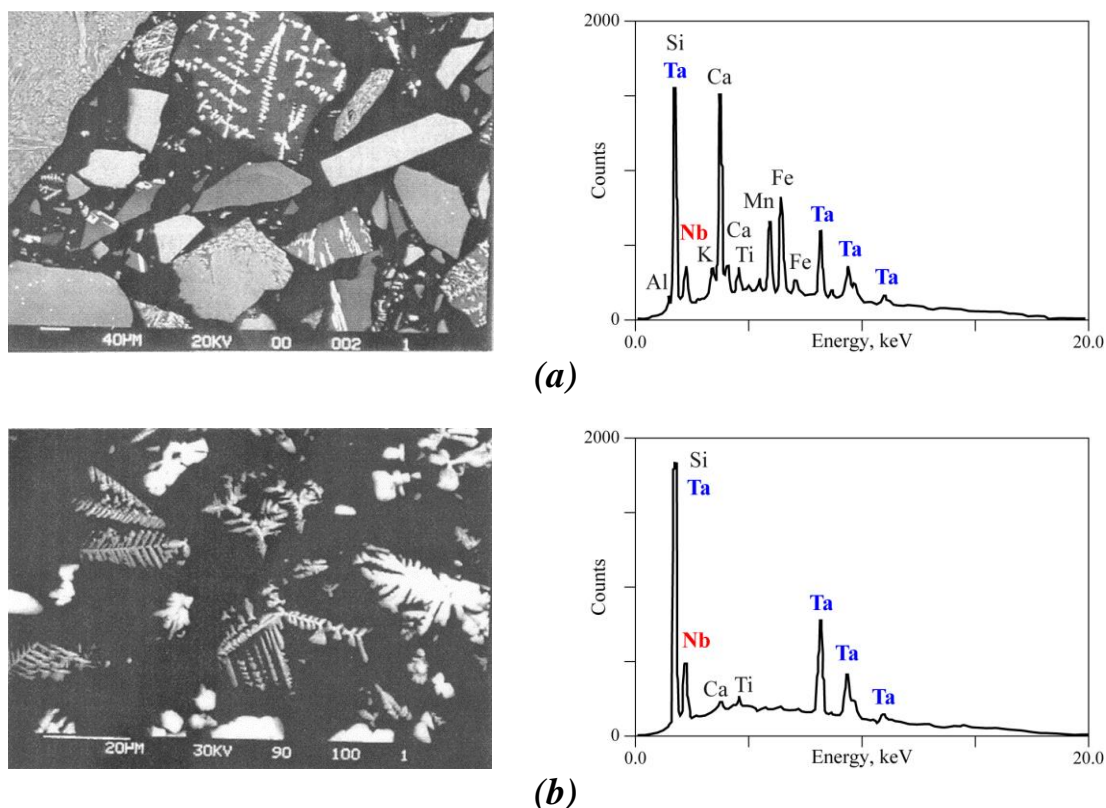


Figure 10. SEM/EDS aspects of the tin slag before (a) and after leaching (b).

#### **4. Conclusion**

An original approach was tested for the concentration of tantalum and niobium oxides contained in tin slags through sequential acid and alkaline leaching steps. The main results obtained within this study can be summarized as follows:

- Sequential acid and alkaline leaching steps produced higher mass losses than single acid or basic steps.
- The mass losses observed during the basic or acid leaches are almost instantaneous and are attributed to a catalytic mechanism as attested by a calculated 8 kJ/mol activation energy.
- The sequential acid and alkaline leaching process selectively concentrated refractory metals such as tantalum and niobium in a solid residue while leaching lower value elements such as silicon, calcium, iron and aluminum into a liquid filtrate.
- The selection of the most favorable sequence of Acid-Basic-Acid leaching led to the production of a commercial grade concentrate containing about 63 % weight  $(\text{Ta} + \text{Nb})_2\text{O}_5$  suitable for subsequent purification steps using chlorination or carbochlorination processes.

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