

## Optimization of the water leaching parameters of tantalum and niobium contained in Manono ore in the Democratic Republic of Congo by fusion in the $\text{NH}_4\text{HF}_2$ -KOH system

Bertin Kitungwa K.,<sup>1,2</sup>, Phalaris Yuma M.,<sup>1</sup>, Clarisse Kateule M.,<sup>1</sup>,  
Crépin Kyona W.,<sup>1</sup>, Isidore Wakenge B.<sup>1</sup>

<sup>1</sup>Department of Chemistry, The Inorganic Chemistry Unit, Faculty of Sciences, University of Lubumbashi, P.O. Box 1825, Likasi Avenue, Haut Katanga Province (DRC)

<sup>2</sup>Laboratory of Chemical of Africa, Shalina Group, City of Lubumbashi, Haut Katanga Province, DRC.

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**Abstract:** This research highlights the benefit of using the mixture of two fluxes,  $\text{NH}_4\text{HF}_2$ -KOH during the fusion and in the optimization of the water leaching parameters of niobium and tantalum contained in the Manono ore in the Republic Democratic of Congo. The ore studied is a columbite containing approximately 53% in  $\text{Nb}_2\text{O}_5$ , 30% in  $\text{Ta}_2\text{O}_5$ , 7% in  $\text{SiO}_2$ , 5% in  $\text{SnO}_2$  and 3% in  $\text{Fe}_2\text{O}_3$ . Indeed, the use of ore/  $\text{NH}_4\text{HF}_2$ /KOH charge in a respective mass ratio of 1,0 /2,5 / 1,0 has an advantage insofar as the better efficiency of leaching water with niobium and tantalum are respectively obtained at approximately 97% and 94% at 160°C for 90 minute of fusion and 30 minutes of agitation leaching against 89% and 84% when  $\text{NH}_4\text{HF}_2$  is used alone at 250°C. This advantage comes from the fact that the addition of KOH to the ore/ $\text{NH}_4\text{HF}_2$  mixture causes a spontaneous and exothermic reaction.

**Key Word:** leaching parameters; tantalum niobium; fusion system;  $\text{NH}_4\text{HF}_2$ -KOH

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### I. Introduction

Tantalum and niobium are two highly stressed metals because of their unique properties which guarantee their use in electronics, optics, aerospace and nuclear power. Anatoly A., (2004). Niobium remains the essential element in the manufacture and obtaining of High strength low alloy steels (HSLA). While around 57% of tantalum is mainly used for the manufacture of superalloys and capacitors, representing respectively 23% and 34% Wei S., et al., (2019) and Wang X., et al., (2009). Growing demand for tantalum and niobium by high-tech industries has pushed researchers to implement several extraction and purification methods. These elements are slightly acidic due to the nature of their pentoxides Ross W., (1964), which means that their dissolution is still not easy. Dissolving tantalum and niobium using molten salts was the first method to be applied for industrial exploitation Eckert J., (1995). Although this method is the first to be used industrially, the cost linked to high temperature during melting remains a major challenge for researchers interested in the recovery of these two metals. It is for this reason that several researches propose different fondant types in order to be able to significantly decrease the melting temperature of the target metals while guaranteeing good recovery efficiency. Among these researches, we can cite among others those who used on the one hand an ammonium bifluoride system ( $\text{NH}_4\text{HF}_2$ ) as molten salt and presented efficiency of leaching of tantalum and niobium in the respective order of approximately 98% and 95% for a melting temperature of 250°C in an ore/flux ratio of 1/30 for 180 minutes Kabangu M., (2013). And on the other hand, those who used potassium hydroxide (KOH) as flux with recovery efficiency of approximately 95% and 94% respectively for niobium and tantalum at 400°C in a ratio of 1/2 of ore/flux for 60 minutes of fusion. Wang X., et al., (2019). The chemistry of molten salts often uses the eutectic mixture fluxes to further decrease the melting temperature that a system would give a melting salt. This investigation presents part of our thesis research and assesses the possibility of combining  $\text{NH}_4\text{HF}_2$  and KOH in the same system in order to determine the contribution of the mixture on the eutectic of fusion while optimizing the conditions of leaching of tantalum and niobium. This reasoning is motivated by the fact that the reaction between these two reagents is strongly exothermic with release of water Rakov E., and Mel'nichenko E., (1984).

In this study, it is a question of optimizing the conditions of tantalum and niobium water leaching contained in Manono ore in the Province of Tanganika in Democratic Republic of Congo by fusion in the  $\text{NH}_4\text{HF}_2$ -KOH system. To get this, fusion tests are carried out each time followed by leaching with water in order to determine the influence:

- the ore / flux mass ratio on the recovery yields of tantalum and niobium;

- adding KOH to the ore / NH<sub>4</sub>HF<sub>2</sub> mixture on the temperature, the melting time, the quantity of the melting mass and the efficiency of dissolution of tantalum and niobium.

## II. Material and Methods

### II.1. Material

About 10 kilograms of tantalum and niobium ore were collected according to standard sampling methods Ross X., (1964) at Manono-center in Tanganika Province in Democratic Republic of Congo, the latitude of which is 7°13'40.8 " and longitude 27°19'44 ' . At a distance of about 500 kilometers northwest of the city of Lubumbashi. Dewaele S., et al., (2015). The ore was placed in a bag of raffia in the laboratory of the Faculty of Science at the University of Lubumbashi. An oven drying at 110°C for 24 hours was carried out before undergoing a process of fragmentation and milling to obtain a particle size of 200 mesh Ross X., (1964). The reagents, NH<sub>4</sub>HF<sub>2</sub> and KOH used during the fusion were of analytical purity (United Scientific (Pty) Ltd. [www.unitedscientific.CD.Z](http://www.unitedscientific.CD.Z) . And distilled water was used in the leaching process. Analysis of the chemical elements was carried out by ICP-OES of Arcos-Ametek brand for the liquid resulting from leaching and by XRF of Olympus-Delta Professional brand with anode in Rhenium tube for solid residues. Whereas the mineralogical analysis was carried out using a binocular optical microscope in polarized and reflected transmitted light.

### II.2. Experimental methods

The experiment was carried out in two stages:

- the merger: for this step, several parameters were evaluated under the conditions below:
  1. to evaluate the influence of ore/ flux ratio on the recovery efficiency of tantalum and niobium, the temperature of 250°C Kabangu M., (2013), the time of 60 minute Wang X., (2009) and the mass of 10 grams of ore were kept constant. The amounts of 1.5; 2.0; 2.5; 3.0 mass of ore were respectively used as mass of the flux, NH<sub>4</sub>HF<sub>2</sub> by milling it with the ore.
  2. To determine the influence of the addition of KOH to the best ore/NH<sub>4</sub>HF<sub>2</sub> ratio obtained in the previous point on the temperature, the melting time and the efficiency of dissolution of tantalum and niobium, the addition each time 10 grams of KOH in the ore/NH<sub>4</sub>HF<sub>2</sub> mixture was kept constant during the tests. At each respective time of 30; 60; 90 and 120 minutes. For an optimal time obtained, the tests were carried out by varying the melting temperature of 220; 190; 160 and 130°C.
  3. At the best times and temperatures, the influence of the melting charge or melting mass on the melting time and the metal leaching efficiency is evaluated by varying the melting mass of 11.25g; 22.50g; 33.75g and 45.00g each due to an ore / NH<sub>4</sub>HF<sub>2</sub> /KOH mass ratio of 1.00/2.50 /1.00g respectively.
- the leaching tests were carried out under the following conditions Wang X., et al (2009) and Kabangu M., (2013) :
  1. weigh 10 grams of the fusion product;
  2. take 100 ml of distilled water;
  3. agitation speed 500 rpm;
  4. agitation time 30 minutes.

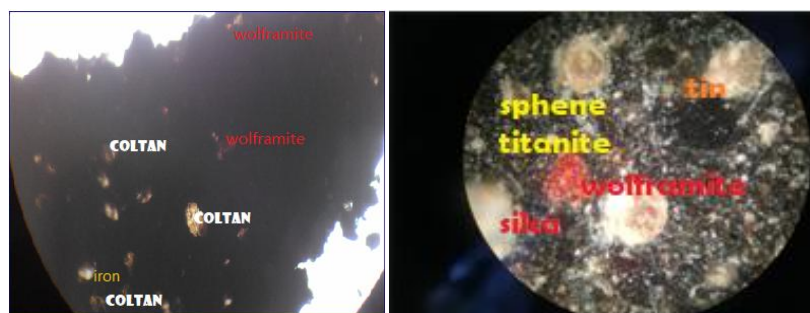
## III. Results and discussion

### III.1. Chemical and mineralogical analysis

Table 1. Chemical analysis of the sample of tantalum niobium ore from Manono center (% by weight)

Nb <sub>2</sub> O <sub>5</sub>	Ta <sub>2</sub> O <sub>5</sub>	SiO <sub>2</sub>	SnO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	WO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>
52,56	30,05	7,23	5,26	3,47	0,73	0,39	0,33	0,21

it comes out from table 1 that the sample under examination is a columbite, the presence of the proportions of SiO<sub>2</sub> and SnO<sub>2</sub> would be due to a trace of cassiterite. To confirm these results, a mineralogical analysis was carried out and the results of which are recorded in the figures below:



These figures above show that there are minerals that are visible under a microscope in transmitted light and those that are in reflected light. Thus, we can detect the presence of columbite-tantalite of brown color, iron of gray-white color, colorless silica, tin of yellow-brown twin color, wolframite of red color, rhombic titanite of yellowish color, opaque minerals and other minerals. These results are consistent with chemical analysis and are in agreement with the geology and mineralization of Manono Kitotolo as shown by Dewaele S., et al., 2015.

### III.2. Effect of the ore / $\text{NH}_4\text{HF}_2$ ratio on the leaching efficiency of metals

Leach efficiency will be limited to metals such as Niobium, tantalum, tin, silicon and iron due to their proportion in the starting sample.

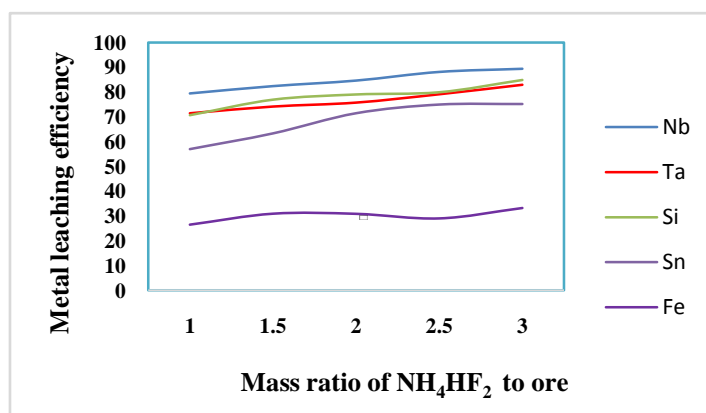


Fig. 3. Impact of the ratio of ore/ $\text{NH}_4\text{HF}_2$  on the leaching efficiency of metals

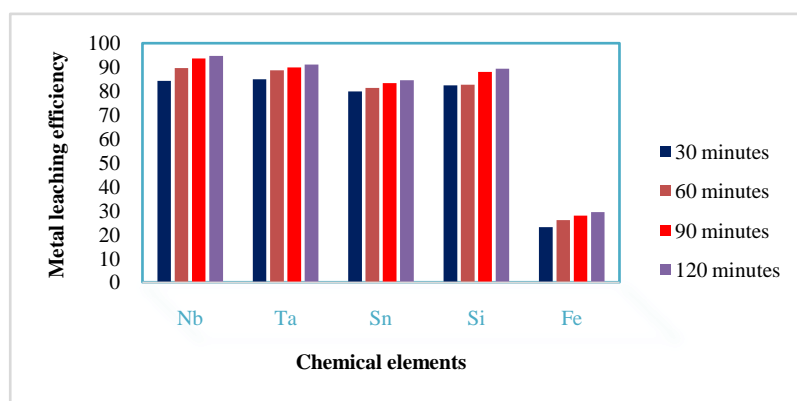
Figure 3 above reveals that the ore/flux ratio has a great influence on the leaching of niobium and tantalum after fusion with  $\text{NH}_4\text{HF}_2$  at  $250^\circ\text{C}$ . The more this ratio increases from 1.0 to 3.0, the efficiency of these two metals go respectively from 79% and 71% to about 86% and 80%. These results, although a function of the mass of  $\text{NH}_4\text{HF}_2$  during the fusion, a slight reduction in the leaching yield is observed, unlike the results obtained by Kabangu M., (2013) and even a reversal of the solubilization ratio of niobium and tantalum in water. It seems to us that this slight difference in the results obtained can be justified on the one hand by the mineralogical nature of the ore studied. The ore under examination is a columbite associated with the trace of tin and silicon and on the other hand, this difference would be due to the quantity of  $\text{NH}_4\text{HF}_2$  which is 30 times the mass of the ore whereas in this study, we do considered that the ratio of 1.0/3.0 of ore/flux. Indeed, these results are logical the researches of Rokov E., and all (1984) which also revealed that after fusion with  $\text{NH}_4\text{HF}_2$ , they find ammonium oxofluoroniobate whose fusion begins at a temperature of  $130^\circ\text{C}$  by forming ammonium hexafluorooxonioate,  $(\text{NH}_4)_3\text{NbOF}_6$ . While Ravov E., (1984) shows that the reaction of  $\text{Ta}_2\text{O}_5$  with  $\text{NH}_4\text{HF}_2$  how already between  $156\text{--}190^\circ\text{C}$ . The yields of silicon and tin are almost similar and range from 61% and 57% to approximately 75% respectively depending on the mass of  $\text{NH}_4\text{HF}_2$  at  $250^\circ\text{C}$ . It has been demonstrated by Rokov E., and Mel'nichenko E., (1984) that in this temperature range, silicon reacts with ammonium bifluoride to form a double salt,  $(\text{NH}_4)_2\text{SiFe}_6\text{-NH}_4\text{F}$  while tin would form two compounds,  $\text{NH}_4\text{SnF}_3$  and  $\text{NH}_4\text{Sn}_2\text{F}_5$  which are soluble in water. While the low yield of solubilization of iron although evolving slightly with the mass ratio of the flux, is justified by the fact that the  $(\text{NH}_4)_3\text{FeF}_6$  formed around  $170^\circ\text{C}$  is the soluble form whereas all the other forms of iron are insoluble in water (Rokov E., and Mel'nichenko I., (1984), but soluble in acid solutions Albert C., and Geoffrey W., (1980).

By comparing the results obtained at the ratio of 2.5 to those of 3.0; we realize that there is not a big difference with regard to the paces of the curves obtained. The ore / NH<sub>4</sub>HF<sub>2</sub> ratio of 1.0 / 2.5 seems rational to us for the rest of the experiments.

### III.3. Effect of adding KOH to the ore / NH<sub>4</sub>HF<sub>2</sub> mixture on the temperature, the melting time and the leaching efficiency of tantalum and niobium

These series of fusion experiments followed by leaching are carried out under the conditions of 10 grams of ore ground with 25 grams of NH<sub>4</sub>HF<sub>2</sub> to which 10 grams of KOH are added to the crucible before just melting since the reaction between KOH and the ore / NH<sub>4</sub>HF<sub>2</sub> mixture is spontaneous and exothermic Rokov E., and Mel'nichenko E., (1984). The results are reported in Figures 4,5 and 6 below.

#### III.3.1. Effect of adding KOH to the ore / NH<sub>4</sub>HF<sub>2</sub> mixture on the melting time and the dissolution yields of metals at 220°C



**Fig 4. Influence of adding KOH to the ore / NH<sub>4</sub>HF<sub>2</sub> mixture on the melting time and leaching efficiency of Nb, Ta, Sn, Si and Fe at a temperature of 220°C**

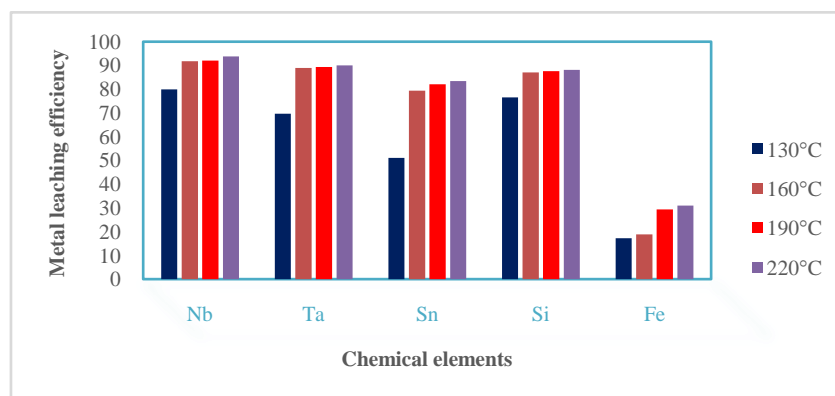
Figure 4 shows that the leaching process of Nb, Ta, Sn, Si and Fe is influenced on the one hand by the melting time for a constant temperature. And on the other hand, by adding KOH. Indeed, the addition of KOH to the ore / NH<sub>4</sub>HF<sub>2</sub> mixture to have a mass ratio of 1.0 / 2.5 / 1.0 respectively for the ore, NH<sub>4</sub>HF<sub>2</sub> and KOH has significantly improved the solubilization efficiency metals under examination, in this case niobium and tantalum since their respective efficiency increased from approximately 86% and 83% to 90% and 89% when the KOH was added to the mixture before melting. The mixture of KOH, NH<sub>4</sub>HF<sub>2</sub> and the ore offers several possibilities:

- $6\text{KOH (crystalline)} + (\text{Nb, Ta})_2\text{O}_5 \text{ (crystalline)} = 3\text{K}_2(\text{Nb, Ta})\text{O}_4 \text{ (crystalline)} + 3\text{H}_2\text{O (gas)}$  compound capable of being hydrolyzed into soluble K8 and of regenerating KOH. Wang X., et al (2009)(1)
- $3\text{K}_2(\text{Nb, Ta})\text{O}_4 \text{ (crystalline)} + n.\text{NH}_4\text{HF}_2 \text{ (crystalline)} = 3\text{NbOF}_3.\text{NH}_4\text{F (crystalline)} + 3\text{TaF}_5.\text{NH}_4\text{F (crystalline)} + 6\text{KHF (crystalline)} + n\text{H}_2\text{O (gas)}$  Motlalepula N., (2013) and Mel'nichenko E., (1984).(2)
- $\text{KOH (crystalline)} + \text{NH}_4\text{HF}_2 \text{ (crystalline)} = \text{KHF}_2 \text{ (crystalline)} + 2\text{NH}_3 \text{ (gas)} + \text{H}_2\text{O (gas)}$  Rokov E., et al (1984) and Newton F., (1929). (3)

In view of the results observed during the experiment, we realize that not only are we witnessing the spontaneous reaction between KOH and NH<sub>4</sub>HF<sub>2</sub> but also the cold attack of the ore mixed with ammonium bifluoride. This attack would lead to the production of potassium oxofluoroniobate, K<sub>2</sub>NbOF<sub>5</sub> Newton F., (1929),. In any case, the tantalum leaching efficiency is always slightly lower than that of niobium due to the fact that its content is low compared to niobium but also by the fact that during the reaction, we also witness the formation of a certain proportion on insoluble K(Nb,Ta)O<sub>3</sub> Wei S., et al., (2019) and Rokov E., et al., (1984). This influence of KOH is also observed on the leaching yields of tin and silicon. The water leaching of silicon is better and is close to that of niobium because, the reaction of SiO<sub>2</sub> with NH<sub>4</sub>HF<sub>2</sub> is exothermic and already begins around the temperature of 100°C by forming the (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub>.NH<sub>4</sub>F which is easily below in aqueous solutions Uspenskie V., et al., (1975). While the iron solution yields still do not exceed 29%, which is a good thing because iron is an annoying impurity which is supposed to be eliminated in the purification step by solvent extraction for a process full.

To clearly highlight the influence of adding KOH to the ore/ $\text{NH}_4\text{HF}_2$  mixture, the melting time of 90 minutes is rational for the continuation of experiments. For the rest, the temperature is varied from 220°C, 190°C, 160°C and 130°C in order to evaluate the influence of the  $\text{NH}_4\text{HF}_2$ -KOH- $\text{H}_2\text{O}$  system on the melting temperature and solubilization of metals.

**III.3.2. Effect of adding KOH to the ore /  $\text{NH}_4\text{HF}_2$  mixture on the melting temperature and the dissolution yields of metals during 90 minutes of melting**



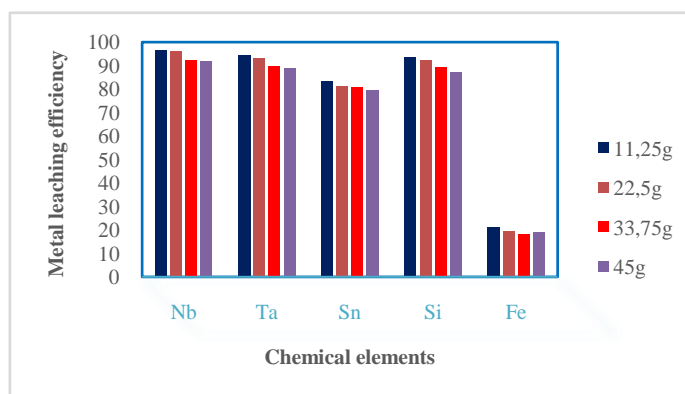
**Fig.5. Influence of the addition of KOH to the ore /  $\text{NH}_4\text{HF}_2$  mixture on the melting temperature and the leaching yields of Nb, Ta, Sn, Si and Fe during 90 minutes of melting**

It appears from FIG. 5 that the addition of KOH to the ore/ $\text{NH}_4\text{HF}_2$  mixture has a great influence on the melting temperature and leaching of the metals under examination. It is interesting to note that already at a melting temperature of 130°C., niobium, silicon and tantalum have yields which exceed 70% for the first two elements and around 70% for the last. It seems to us that this observation is the result of the exothermic reaction observed before the fusion as soon as KOH was added to the ore/ $\text{NH}_4\text{HF}_2$  mixture. These results confirm the argument of Ravov E., (1984) and Uspenskie V., et al., (1975) who respectively argued that fluoroniobate can already be found already at a temperature of 130°C and  $(\text{NH}_4)_2\text{SiF}_6 \cdot \text{NH}_4\text{F}$  below this temperature.

These forms are soluble in water as we have already pointed out above. The results of the dissolution of tin are more influenced by the temperature and do not exceed 83% following the presence of tin fluorides which are insoluble in water but soluble in bases Albert C., and Geoffrey W., (1980) while the soluble part of the tin is in the form of potassium stanate ( $\text{K}_2\text{SnO}_3$ ) Wang X., et al (2009). While iron leaching increases slightly with the temperature of 190 and 220°C.

In view of the results obtained during this experiment and taking into account the energy boost, the temperature of 160°C seems rational to us for the rest of the work.

**III.3.3. Effect of the quantity of the melting mass on the melting and the dissolution yields of the metals at 160 ° C. and for 90 minutes of melting**



**Fig. 6. Impact of the melting mass on the fusion and the leaching yields of Nb, Ta, Sn, Si and Fe at a temperature of 160 ° C. and for 90 minutes of fusion**

Fig. 6 reveals that the melting mass also influences the time, the melting temperature and the leaching efficiency of the metals. The efficiency decrease with the increase in the quantity of the melting mass for the same crucible capacity during melting. This observation shows that the more the amount of the melting mass increases, this no longer allows good heat circulation during the melting. The addition of KOH to the ore/ $\text{NH}_4\text{HF}_2$  mixture promotes an exothermic cold reaction as we have already mentioned in the introduction while facilitating the diffusion of heat during melting. It seems to us that this reality would be favorable for saving time and for melting temperature. Indeed, Turkdogan E., (1985) maintains that the quantity of the charge to be melted in an oven is a function of the capacity of the crucible and the mass ratio of ore/melting. In view of the results obtained, the mass ratio of 5g/12.5g/5g respectively for the ore /  $\text{NH}_4\text{HF}_2$  / KOH for a Zirconium or Teflon crucible with a total capacity of 90 grams of flux gives us a better compromise.

#### IV. Conclusion

It appears at the end of the investigations that the use of the  $\text{NH}_4\text{HF}_2/\text{KOH}$  system for the fusion of a columbite ore offers a better advantage because it made it possible to obtain good leaching efficiency with niobium water at about 97 % and 94% tantalum for a melting temperature of 160°C unlike the experiment where  $\text{NH}_4\text{HF}_2$  is used alone at 250°C. It is also possible because of the tantalum and niobium content in the starting ore that the bulk of it melts over time at 130°C and dissolves from the water. This is due to the fact that the reaction combining  $\text{NH}_4\text{HF}_2$  and KOH is strongly exothermic.

Optimizing the melting and leaching conditions of niobium and tantalum with water revealed that the melting time and temperature are two important parameters for the leaching of these two metals with water. depend on the quantity of melting mass, the ore/flux ratio but also on the mineralogical nature of the ore of niobium and tantalum. The optimal conditions which made it possible to dissolve approximately 96% of niobium, 92% of tantalum and silicon, 81% of silicon and 19% of iron are the following:

- the charge to be melted must be in a mass ratio of 1.0/2.5/1.0 respectively for the ore/ $\text{NH}_4\text{HF}_2/\text{KOH}$ ;
- melting time 90 minutes;
- melting temperature 160°C;
- agitation time during leaching: 30 minutes.

In light of these results, our future report will determine:

- the different mineralogical forms in which niobium, tantalum, silicon, tin and iron are found in the melt after fusion at 130°C, 160°C, 190°C and 220°C and in the residues solids obtained after leaching of the melt by X-Ray Diffraction, XRD and Scanning Electron Microscope, SEM;
- the different ionic forms under which these elements pass in aqueous solution during leaching with water by infrared analysis, IR and by mass spectrometer, MS.

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