Effect of Na$^+$ ion on the dissolution of ferrocolumbite in autoclave

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ARTICLE INFO

ABSTRACT

The effect of different leaching media on the dissolution of ferrocolumbite from the province of San Luis, Argentina, in an autoclave was investigated. The leaching agents used were aqueous solutions of HF–NaF or HF–Na$_2$C$_2$O$_4$.

The researched parameters were temperature and different types and concentrations of the leaching media. The obtained results show that the values of Nb and Ta extractions from ferrocolumbite with diluted HF are substantially modified when NaF or Na$_2$C$_2$O$_4$ are added to the leaching medium, and separation of Ta from the other components present in the sample is successfully accomplished while working under certain conditions of temperature and reagent concentrations.

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1. Introduction

Niobium and tantalum have a wide range of applications, such as in the manufacture of alloys and super alloys used in nuclear and aerospace industries; in the production of microalloys used in the automotive, marine, mining and transport industries; in the obtaining of high-strength steels wear and corrosion; in the chemical industry in general; and in electronics for the construction of capacitors and conductors. Tantalum is also used in medicine and niobium in optics (Gupta and Suri, 1994; Habashi, 1997).

The industrial methodology most studied and used for the treatment of materials containing niobium and tantalum is the leaching process with concentrated HF. After the digestion, the solution is diluted in water, and the residue is separated. The recovery of both metals usually takes place by solvent extraction with methyl isobutyl ketone (Habashi, 1997; Köck and Paschen, 1989; Zhu and Cheng, 2011). Finally, the residual F$^-$ can be removed by precipitation with the addition of a calcium salt to the leach liquor. The fluoride, recovered as synthetic calcium fluoride, may be reused as raw material or additive in several industrial applications (Aldaco et al., 2005).

Even though the leaching pressure of materials containing Nb and Ta has not been widely studied, we can mention some authors who have conducted some researches in this field. Baram (1965) studied the kinetics of the dissolution of tantalite in an HF–H$_2$SO$_4$ medium, and determined that the dissolution rate of the mineral is controlled by a diffusional phase. A few years later, this author performed kinetic studies on the leaching of niobium and tantalum pentoxide with HF, and arrived to

the conclusion that the dissolution of Ta oxide occurs through physical control, and that the dissolution of Nb oxide occurs through chemical control, with apparent activation energies of 23.85 kJ/mol and 49.79 kJ/mol, respectively, Baram (1972). Pyrochlore leaching with HCl in an autoclave to obtain technical grade Nb$_2$O$_5$ was investigated by Habashi and Toromanoff (1983).

The study of the dissolution of columbite and tantalite in the HF medium, carried out in order to determine the influence of the ions F$^-$ and H$^+$, led Majima et al. (1988) to conclude that both ions are required for rapid dissolution of minerals, and also, that the increase of their concentration and temperature, increases the dissolution of the mineral. Krasilshckik et al. (1991) used pressure leaching to dissolve poorly soluble materials, including Nb and Ta oxides. Welham (2001) studied the effect of the degree of milling on the dissolution of niobium and tantalum concentrates, finding that the mechanical pre-treatment affected the rate and extent of dissolution in NaF–HF and HCl media.

Rodriguez et al. (2015) investigated the pressure leaching process of ferrocolumbite in hydrofluoric acid media. These authors concluded that the best values of extraction of niobium and tantalum are obtained whilst working with amounts of HF lower than the ones industrially used. This considerably reduces the amount of HF used in the leaching process, favoring it over the industrial processes, both economically and environmentally.

In this paper we researched the dissolution of ferrocolumbite when different concentrations of Na$^+$ cation (as Na$_2$C$_2$O$_4$ or NaF) were added to the leaching medium containing an HF aqueous solution. The influence of these salts was studied, in order to diminish the concentration of the HF used in the leaching process and to establish the best conditions for separation and recuperation of Nb and Ta in these media, as their corresponding solid fluoride complexes. The obtained results
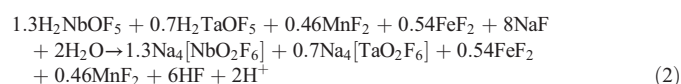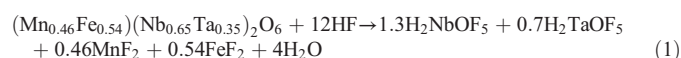
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were compared to those achieved by studying the effect of the concentration of HF in the absence of Na^+ cation.
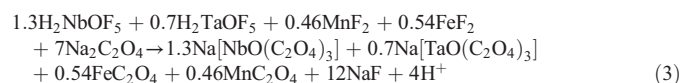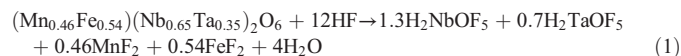
1.1. Basis of fluoride complexes precipitation

The dissolution of minerals with high contents of Nb and Ta with concentrated HF medium leads to the formation of acid complexes $H_2[NbF_7]$ and $H_2[TaF_7]$ (Gupta and Suri, 1994; Gibalo, 1970; Agulyansky, 2004; Zhu and Cheng, 2011). When this dissolution is carried out at low HF concentrations, the complexes $[NbF_6]^-$ and $[TaF_6]^-$ appear, which in aqueous solution hydrolyze the oxyfluoride $[MeOF_5]^{2-}$ $[MeOF_4]^-$ $[MeOF_6]^{3-}$ and $[MeO_2F_5]^{4-}$. The presence of oxalic acid leads to the formation of complexes of the $H[MeO(C_2O_4)_2]$ (Me: Nb or Ta) type (Gibalo, 1970). The operating conditions used in this research suggest, in agreement with the literature mentioned above, the following reactions for the dissolution of ferrocolumbite with HF–NaF and HF–$Na_2C_2O_4$:

Mineral–HF (5% v/v)–NaF (between 2 and 5% w/v):

$$(Mn_{0.46}Fe_{0.54})(Nb_{0.65}Ta_{0.35})_2O_6 + 12HF \rightarrow 1.3H_2NbOF_5 + 0.7H_2TaOF_5 + 0.46MnF_2 + 0.54FeF_2 + 4H_2O \quad (1)$$

$$1.3H_2NbOF_5 + 0.7H_2TaOF_5 + 0.46MnF_2 + 0.54FeF_2 + 8NaF + 2H_2O \rightarrow 1.3Na_4[NbO_2F_6] + 0.7Na_4[TaO_2F_6] + 0.54FeF_2 + 0.46MnF_2 + 6HF + 2H^+ \quad (2)$$

Mineral–HF (5% v/v)–$Na_2C_2O_4$ (between 2 and 5% w/v):

$$(Mn_{0.46}Fe_{0.54})(Nb_{0.65}Ta_{0.35})_2O_6 + 12HF \rightarrow 1.3H_2NbOF_5 + 0.7H_2TaOF_5 + 0.46MnF_2 + 0.54FeF_2 + 4H_2O \quad (1)$$

$$1.3H_2NbOF_5 + 0.7H_2TaOF_5 + 0.46MnF_2 + 0.54FeF_2 + 7Na_2C_2O_4 \rightarrow 1.3Na[NbO(C_2O_4)_3] + 0.7Na[TaO(C_2O_4)_3] + 0.54FeC_2O_4 + 0.46MnC_2O_4 + 12NaF + 4H^+ \quad (3)$$

The Reactions (1), (2) and (3), show that both NaF and $Na_2C_2O_4$ are not involved in the opening of the mineral. The anions of these species, F^- and $C_2O_4^{2-}$, behave as additional complexing agents. On the other hand, the presence of Na^+ cation leads to the formation of insoluble complexes of Nb and Ta (Gibalo, 1970; Agulyansky, 2004).

2. Experimental

2.1. Equipment and materials

The experimental tests were conducted in an autoclave, built in Monel alloy, 450 mL capacity, equipped with electromagnetic stirring, a heating mantle, and a control unit. The Monel alloy is resistant to the attack of HF.

The used mineral as a ferrocolumbite from "Las Cuevas" mine, located in the department of San Martín, San Luis Province, Argentina. The composition and stoichiometry of the mineral was obtained through X-ray fluorescence (XRF) in a Philips PW 1400, and the contents of Nb, Ta, Fe and Mn were 41.2, 36.8, 9.5 and 6.8%, respectively (Ruiz et al., 2002). In addition, we observed the presence of SiO_2 and Al_2O_3, corresponding to the gangue (quartz and feldspar) that accompanies the mineral. The stoichiometry of the mineral is as follows:

$$(Mn_{0.46}Fe_{0.54})(Nb_{0.65}Ta_{0.35})_2O_6$$
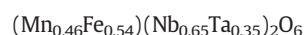
The characterization of mineral X-ray diffraction (XRD) was carried out in a diffractometer Rigaku D-Max III C, operated at 35 kV and 30 mA, using radiation K_α of Cu, and Ni filter, $\lambda = 0.15418$ nm. The diffractogram indicated the presence of the minerals ferrocolumbite, feldspar and quartz. The morphology of the mineral was studied by scanning electron microscopy (SEM) in a microscope LEO 1450 VP equipped with energy dispersive spectrometer (EDS), Genesis 2000. It was observed that untreated mineral particles exhibited an irregular shape and had flat faces, Fig. 1.

All other reagents were of analytical grade.

2.2. Methodology

A mass of 5 g of ore milled to a size of -45 μm was placed in the reactor and a volume of 275 mL of leaching solution was added. Then, N_2 was bubbled in order to remove air and reduce the corrosive effects that dissolved O_2 produces on the reactor in hot HF. The mixture was then heated through stirring, using a heating program from 5 to 10 °C/min, depending on the final temperature. The reaction time was measured once the set temperature was reached for each test. After that period, the reactor was let to cool down for about 25 min, without stirring. Finally, the content was filtered.

The heating and cooling times used in this study were standardized for each of the temperatures investigated. The optimal values for heating rate, volume of liquid and solid–liquid ratio were established in a previous study (Rodriguez and Ruiz, 2011).

In all the tests the solid–liquid ratio at 1.82% w/v, the stirring speed at 330 rpm and the reaction time at 80 min were kept constant. The studied parameters were temperature (between 75 and 123 °C), different types of the leaching media (HF–NaF or HF–$Na_2C_2O_4$) and different concentrations of NaF or $Na_2C_2O_4$ (between 2 and 5% w/v).

The amounts of Nb, Ta, Fe and Mn remaining in the residue were determined by XRF, using the technique developed by Ruiz et al. (2002). Some residues were characterized by XRD, SEM and EDS.

2.2.1. Leaching tests

The quantitative analytical determination for each studied oxide (Ta_2O_5, Nb_2O_5, FeO and MnO) was performed according to the methodology developed by Ruiz et al. (2002).
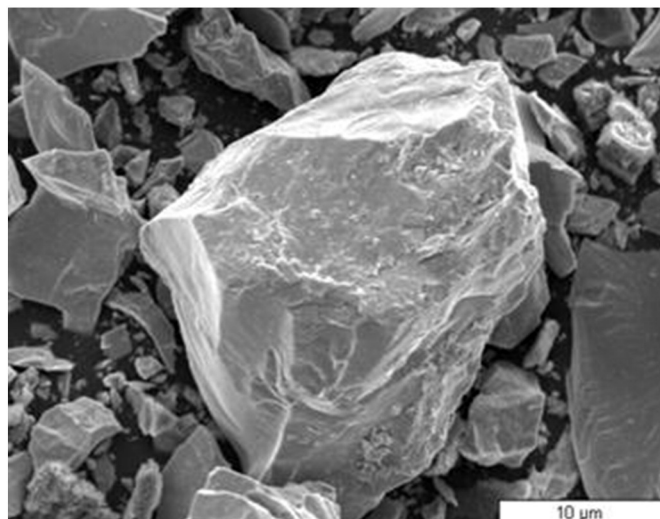

Fig. 1. Micrograph of the mineral.

The conversion percentage, %X of each oxide constituent of the mineral, was expressed as follows:

$$\%X = \frac{m_i - m_f}{m_i} 100$$

where m_i is the initial amount of each oxide, whose value was calculated by relating the mass of mineral added to the reactor, to the concentration of oxide present in the mineral; m_f is the final mass of each oxide, which was determined as follows: in each experiment, 100 mg of the residue were used for the preparation of the pellets for the analyses, the mass of each oxide in the residues was obtained, the content of each oxide was determined by XRF, with a calibration curve built using the pure oxides methodology.

3. Results and discussion

3.1. Dissolution in HF–NaF medium

The study of the effect of adding NaF to the leaching medium was performed at 75 and 123 °C, with a constant concentration of HF 5% (v/v) and two concentrations of NaF (2 and 5% (w/v)). The experimental data is shown in Table 1. Once again, in order to compare both results, we present the results obtained in similar working conditions, using HF 5% (v/v) as the leaching medium.

Data in Table 1 indicate that the addition of NaF to the leaching media, and therefore, the changes in the concentration of this species, as well as differences in temperature, significantly affect the extraction of Nb, Ta, Fe and Mn with respect to the results obtained in an HF medium.

In general it can be observed that the addition of NaF did not affect the rate of the dissolution reaction of the ferrocolumbite. These results are consistent with those reported by Majima et al. (1988), who, working with different leaching media noted that the increased concentration of F^- ions, did not affect the rate of the dissolution reaction. These authors also highlight that the presence of F^- and H^+ ions is necessary for the opening of the minerals.

Table 1 also shows that working at 75 °C and at a concentration of NaF 2% (w/v), the dissolution of Ta decreases to 12% and that those of other metals constituting the ferrocolumbite are practically inhibited, conversely to what happens in HF 5% (v/v). This phenomenon is attributed to the presence of Na^+ in the medium, which favors the formation of insoluble complexes of Nb, Ta, Fe and Mn, being the Ta complex the most soluble.

When working with HF (5%) (v/v)–NaF (2%) (w/v) at 123 °C, a slight increase in the recovery of Ta and a marked decrease in Nb, Fe and Mn can be observed. This allows us to separate Ta from other metals.

At both temperatures, when the amount of NaF is increased, there is a decrease in the extraction of Fe and an increase for the rest of the metals.

These results are due to the characteristics of the complexation reactions with formation of a precipitate. In these reactions there is a

concentration value of metal:ligand for which precipitate formation is the greatest. Then, the increase in the concentration of ligands may lead to redissolution of the precipitate (Rodriguez et al., 2004; Inczédy, 1976).

3.2. Dissolution in HF–Na₂C₂O₄ medium

The study of the effect of adding $Na_2C_2O_4$ was conducted at two different temperatures and $Na_2C_2O_4$ concentrations, 75 and 123 °C and 2 and 5% (w/v), respectively. We worked with HF 5% (v/v). The experimental data is shown in Table 2.

The values of extraction achieved at 75 °C indicate that the presence of sodium oxalate increases slightly the recovery of Ta, while those of Nb, Fe and Mn decrease drastically and become almost zero when the concentration of sodium oxalate is 5% (w/v).

Therefore, it can be said that the addition of sodium oxalate to the leaching medium brings about two important effects. On the one hand, the recovery of Ta increases and on the other hand, the recovery of Nb, Fe and Mn decreases, with extraction values lower than 1%. Although the recovery values are low under these working conditions, the separation of Ta from the rest of the elements is achieved.

When operating at 123 °C, the addition of $Na_2C_2O_4$ 2% (w/v) causes an increase in the recovery of Ta, Nb and Mn, but not in that of Fe. However, when increasing the concentration to 5% (w/v), the recovery of Nb and Ta decreases and becomes practically null for Fe and Mn.

The results obtained in the leaching with HF 5% (v/v) and $Na_2C_2O_4$ in different concentrations can be explained taking into account the peculiarities of the complexation reactions as displayed above.

In addition, Fe and Mn form insoluble compounds with anion $C_2O_4^{2-}$ such as FeC_2O_4 and MnC_2O_4 (Laitinen and Harris, 1975). In this study, the formation of a precipitate which is deposited on the unreacted mineral was experimentally observed. After filtration and calcination, this precipitate was analyzed by XRD and the results are discussed in Section 3.3.

3.3. Characterization of the leaching residue

Some residues from mineral leaching under different working conditions were characterized using the techniques of XRD, SEM and EDS.

Fig. 2 shows the diffractograms of unreacted mineral and residue calcined at 900 °C after leaching.

From Fig. 2, it can be inferred that working with the two leaching mixtures (HF–NaF and HF–Na₂C₂O₄), the dissolution of ferrocolumbite occurs, and besides, it enhances the intensity of the diffraction lines corresponding to new structures (Fig. 2a–d). The peaks of these new structures correspond to the files of Mn_3O_4 (JCPDS, 13-162) and Fe_3O_4 (JCPDS, 19–629), identified in Fig. 2 with an "O", and to the files of $NaTaO_3$ and $NaNbO_3$ (JCPDS 19-1221 and 25-863), identified in Fig. 2 with "N_E". In both cases, for each pair of compounds, a superposition of diffraction lines of the new structures was observed.

Table 1
Effect of NaF added.

Leaching media (% v/v)–(% w/v)	T (°C)	(X%)			
		Ta_2O_5	Nb_2O_5	MnO	FeO
HF (5%)	75	28	27	29	25
HF (5%)–NaF (2%)		12	<1	<1	<1
HF (5%)–NaF (5%)		14	10	12	<1
HF (5%)	123	52	52	56	48
HF (5%)–NaF (2%)		54	<1	<1	<1
HF (5%)–NaF (5%)		54	44	44	<1

Table 2
Effect of adding Na₂C₂O₄.

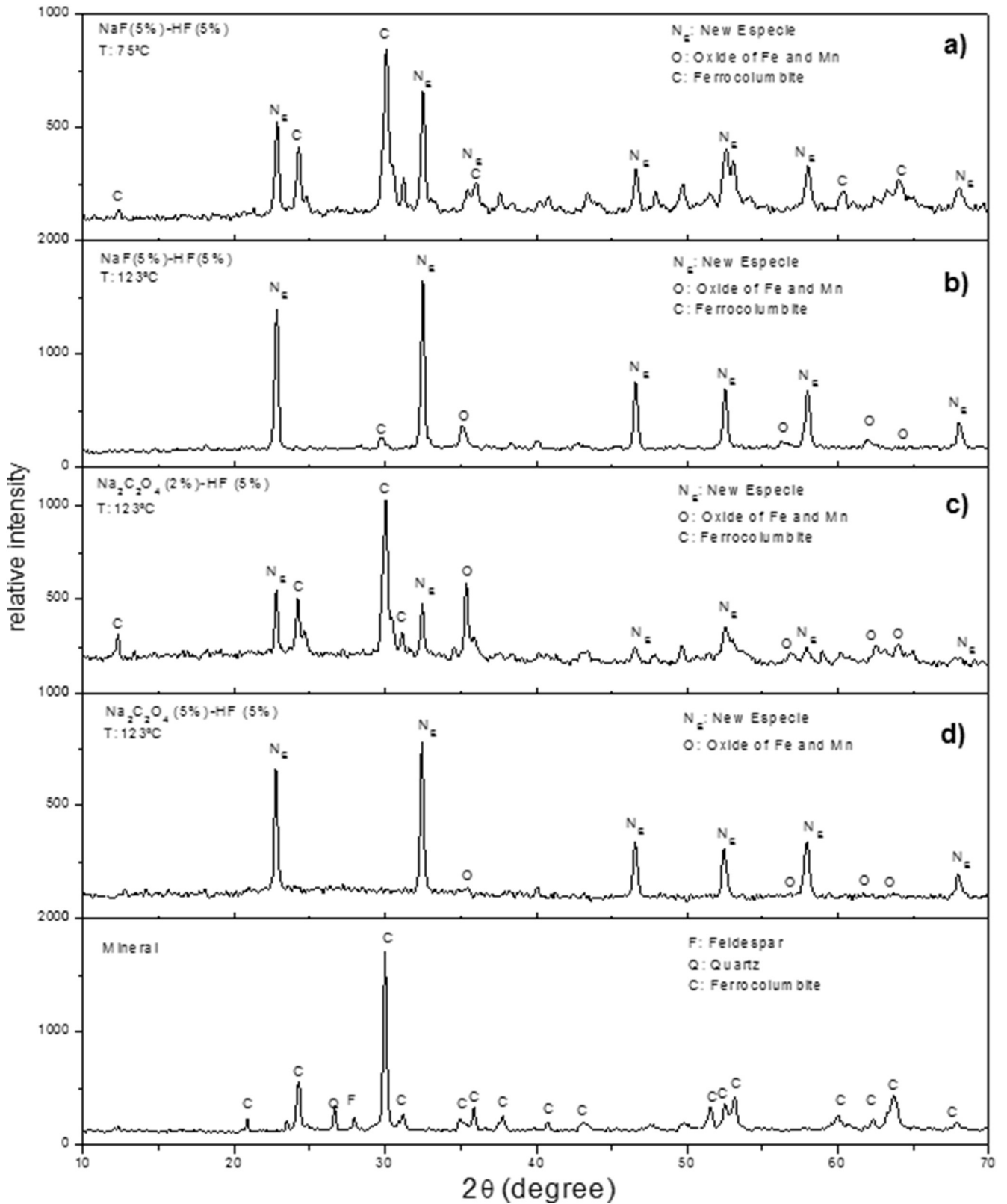| Leaching media (% v/v)–(% w/v)	T (°C)	(X%)			
		Ta_2O_5	Nb_2O_5	MnO	FeO
HF (5%)	75	28	27	29	25
HF (5%)–Na₂C₂O₄ (2%)		30	2	8	<1
HF (5%)–Na₂C₂O₄ (5%)		30	<1	<1	<1
HF (5%)	123	52	52	56	48
HF (5%)–Na₂C₂O₄ (2%)		84	72	62	39
HF (5%)–Na₂C₂O₄ (5%)		47	34	<1	<1

Fig. 2. XRD patterns of the mineral and residue under different leaching conditions. N_E: NaNbO$_3$, NaTaO$_3$; O: Fe$_3$O$_4$ and Mn$_3$O$_4$.

The new phases identified in the NaF–HF medium come from the oxyfluoride and flouride complexes, Na$_4$NbO$_2$F$_6$; Na$_4$TaO$_2$F$_6$; MnF$_2$ and FeF$_2$, which are formed during the leaching process and precipitate onto the unreacted mineral. When this mineral is calcined at 900 °C, it converts to Fe$_3$O$_4$, Mn$_3$O$_4$, NaNbO$_3$ and NaTaO$_3$.

During the leaching process in an HF–Na$_2$C$_2$O$_4$ medium, and after the opening of the mineral and the formation of the oxyflouride complexes (Reaction (1)), the substitution reaction (Reaction (3)) takes place. This leads to the formation of the following complexes: Na[NbO(C$_2$O$_4$)$_3$]; Na[TaO(C$_2$O$_4$)$_3$]; FeC$_2$O$_4$ and MnC$_2$O$_4$. These complexes
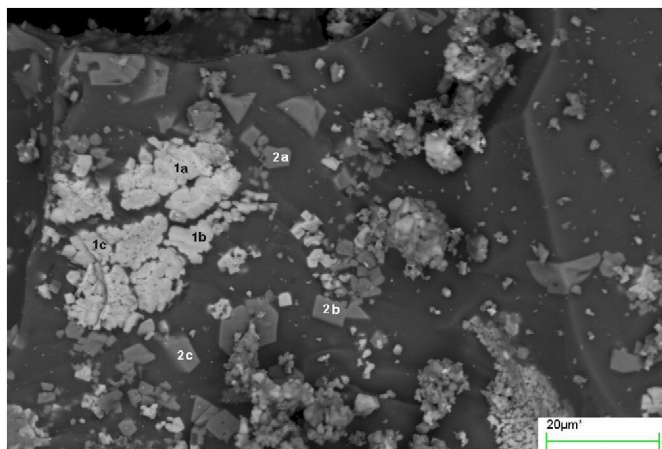
Fig. 3. SEM micrograph of a leaching residue in a NaF 5% (*v/v*)–HF 5% (*v/v*) medium, at 123 °C.
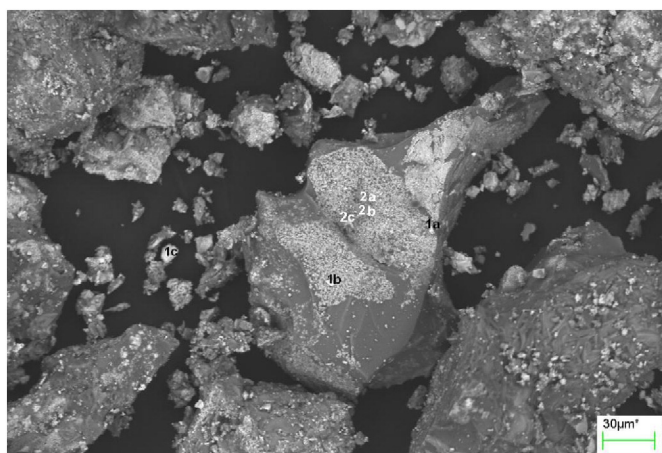

Fig. 4. SEM micrograph of the leaching residue in a $Na_2C_2O_4$ 5% (*v/v*)–HF 5% (*v/v*) medium, at 123 °C.

will then precipitate onto the unreacted mineral and will become $Na[NbO(C_2O_4)_3]$; $Na[TaO(C_2O_4)_3]$; FeC_2O_4 and MnC_2O_4 after calcined.

Figs. 3 and 4 show the SEM micrographs of retrodiffused electrons of two residues from the dissolution of the mineral in different leaching media and calcined at 900 °C. In Tables 3 and 4 the results of the microanalysis of the particles indicated in each figure are presented. These results were obtained through EDS.

Figs. 3 and 4 show the appearance of new solids with different morphology and chemical composition than the original mineral. A difference in the tonality of the marked particles, with respect to the other constituents in the residue, can be observed due to chemical contrast. In Tables 3 and 4 the values of elemental composition of the particles identified as 1a, 1b and 1c and; 2a, 2b and 2c are shown. Those belonging to the first group have a high content of Nb and Ta, and small amounts of

Table 3

Elemental composition of the particles marked in Fig. 3, in atomic %.

Analyzed region	%Nb	%Ta	%Fe	%Mn	%O
1a	23.28	30.89	1.10	0.63	29.77
1b	35.29	10.07	4.00	2.37	25.68
1c	18.79	14.95	5.82	3.19	34.07
2a	2.84	4.59	20.63	12.96	25.46
2b	2.56	7.05	59.76	42.50	38.06
2c	0.66	1.63	9.73	22.45	41.94

Table 4

Elemental composition of the particles marked in Fig. 4, in atomic%.

Analyzed region	%Nb	%Ta	%Fe	%Mn	%O
1a	21.24	16.47	0.55	0.47	26.06
1b	23.23	40.28	1.35	1.78	21.63
1c	21.27	35.80	1.20	1.58	19.24
2a	0.48	3.44	21.78	34.89	29.52
2b	2.03	1.97	19.25	29.69	36.45
2c	5.25	3.44	13.12	17.98	22.62

Fe and Mn, which corresponds to the appearance of $NaNbO_3$ and $NaTaO_3$. The second group has high contents of Fe and Mn, and small amounts of Nb and Ta, and comprehends a mixture of Fe_3O_4 and Mn_3O_4. These results are consistent with those observed when analyzing the residue by XRD.

4. Conclusions

The addition of NaF and $Na_2C_2O_4$ to a medium composed of HF leaching 5% (*v/v*), markedly affects the dissolution reaction of ferrocolumbite. Under the following working conditions: HF (5% (*v/v*))–NaF (2% (*w/v*)) at 123 °C and HF (5% (*v/v*))–$Na_2C_2O_4$ (5% (*w/v*)) at 75 °C a partial separation of Ta occurs. This is due to the formation of insoluble compounds of Nb, Fe and Mn, which leaves Ta in the solution. Leaching at 123 °C with mixing HF (5% (*v/v*)) and $Na_2C_2O_4$ (2% (*w/v*)) allows dissolution of Nb of 72% and Ta of 84% and decreases the removal of Fe and Mn to 39 and 62%, respectively.

References

Agulyansky, A., 2004. The Chemistry of Tantalum and Niobium Fluoride Compounds. Elsevier Inc., Amsterdam.
Aldaco, R., Irabien, A., Luis, P., 2005. Fluidized bed reactor for fluoride removal. Chem. Eng. J. 107, 113–117.
Baram, I.I., 1965. Cinética de la disolución de los pentóxidos de niobio y tantalio en ácido fluorhídrico. Zh. Prikl. Khim. 38 (10), 2181–2188 (translated to Spanish).
Baram, I.I., 1972. Cinética de la disolución de tantalita en una mezcla de ácidos fluorhídrico y sulfúrico. Tsvetn. Met. 15, 97–99 (translated to Spanish).
Gibalo, I.M., 1970. Analytical Chemistry of Niobium and Tantalum. Ann Arbor-Humphrey Science Publishers, London.
Gupta, C.K., Suri, A.K., 1994. Extractive Metallurgy of Niobium. CRC Press, Florida.
Habashi, F., 1997. Handbook of Extractive Metallurgy. III. Wiley-VCH, Germany.
Habashi, F., Toromanoff, I., 1983. Hydrometallurgycal production of technical niobium oxide from pyrochlore concentrates. J. Less-Common Met. 91, 71–82.
Inczédy, D., 1976. Analytical Applications of Complex Equilibria. Ellis Horwood, Budapest.
Köck, W., Paschen, P., 1989. Tantalum-processing, properties and applications. JOM 41, 33–39.
Krasilshckik, V.Z., Zhiteleva, O.G., Sokol'skaya, N.N., Chupakin, M.S., 1991. Autoclave vapor-phase decomposition of some difficulty soluble substances. Zh. Anal. Khim. 41 (4), 586–590 (translated to Spanish).
Laitinen, H.A., Harris, W.E., 1975. Chemical Analysis. Mac-Graw-Hill Kogakusha, Ltd., Tokyo.
Majima, H., Awakura, Y., Mishima, M., Hirato, T., 1988. Dissolution of columbite-tantalite in acidic fluoride media. Metall. Trans. B 19B, 355–363.
Rodriguez, M., Ruiz, M.C., 2011. Optimization of the leaching conditions of an autoclave. Application to the dissolution of ferrocolumbite from San Luis province, Argentina. Lat. Am. Appl. Res. 41 (4), 317–323.
Rodriguez, M., Rivarola, J., Ruiz, M.d.C., 2004. The effects of carboxylic acid addition on hydrofluoric acid autoclave leaching of a ferrocolumbite. Hydrometallurgy 74, 39–46.
Rodriguez, M., Rosales, G.D., Pinna, E.G., Suarez, D., 2015. Extraction of niobium and tantalum from ferrocolumbite by hydrofluoric acid pressure leaching. Hydrometallurgy 156, 17–20.
Ruiz, M.C., Rodriguez, M.H., Perino, E., Olsina, R., 2002. Determination of Nb, Ta, Fe and Mn by X-ray fluorescence. Min. Eng. 15, 373–375.
Welham, N.J., 2001. Effect of extended grinding on the dissolution of a Ta/Nb concentrate. Can. Metall. Q. 40 (2), 143–154.
Zhu, Z., Cheng, C.Y., 2011. Solvent extraction technology for the separation and purification of niobium and tantalum: a review. Hydrometallurgy 107, 1–12.