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Technical note

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

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## 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–$Na_2C_2O_4$.

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 $Na_2C_2O_4$ 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.

## 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–$H_2SO_4$ 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 $Nb_2O_5$ 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 $Na_2C_2O_4$ 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 $K_\alpha$ 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).

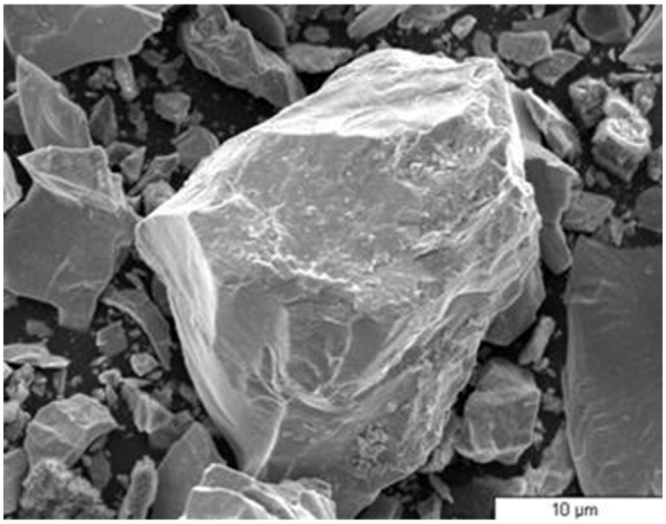

**Fig. 1.** Micrograph of the mineral.