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Technical note

Extraction of niobium and tantalum from ferrocolumbite by hydrofluoric acid pressure leaching

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ABSTRACT

Pressure acid leaching was used to extract niobium and tantalum from a ferrocolumbite ore. The leaching was carried out in a pressure reactor using hydrofluoric acid as leachant. Various parameters, such as temperature, reaction time, HF concentration, stirring speed, particle size and solid-to-liquid ratio in the leaching process, were optimized. The reactants and products were characterized by X-ray fluorescence (XRF), X-ray diffraction (XRD) and specific surface area (BET). Experimental results showed that the maximum extraction of Nb and Ta, 90 and 80% respectively, it was achieved at an HF concentration of 9% v/v, reaction temperature of 220 °C, particle size of −45 μm, solid-to-liquid ratio of 1.82% w/v and reaction time of 80 min. Crystalline structures, different from those originally present in the ore, were not detected by XRD analysis of the leaching residues.

1. Introduction

Pyrometallurgical and hydrometallurgical methods at atmospheric pressure have been widely used for the extraction of Nb and Ta from minerals and other Nb-Ta-bearing materials. However, pressure leaching at elevated temperatures has not yet been extensively studied (Gupta and Suri, 1994; Habashi, 1980).

The production of technical grade Nb_2O_5 by digestion of pyrochlore concentrate with HCl at 200 °C in a pressure reactor has been explored by Habashi and Toromanoff (1983). Niobium and tantalum oxides were found solely to dissolve under pressure leaching conditions (Krasilshckik, 1991).

Majima et al. (1988) investigated the dissolution of columbite and tantalite in acidic fluoride media in the presence of both H^+ and F^- in the leachant. Their experimental results have shown that increases in H^+ and F^- concentration and reaction temperature are effective in the enhancement of the dissolution rate. In addition, it was found that mechanical activation used in the columbite leaching process affects substantially the rate and degree of its dissolution in HF and NaF-HCl media (Hoberg and Götte, 1985; Welham, 2001).

The operating variables affecting the autoclave leaching of a ferrocolumbite ore in HF-carboxylic acid media have also been investigated, and it was found that the addition of tartaric and oxalic acids led to Nb and Ta recoveries over 90% (Rodriguez et al., 2004). In addition, the authors studied the leaching kinetics of ferrocolumbite in HF medium, and their results indicated that the model, based on the nucleation and nuclei growth concept, fitted well the experimental data. Furthermore, the value of the apparent activation energy suggested that the controlling step, after the reaction interface has been formed, is the rate of chemical reaction (Rodriguez et al., 2007).

Other authors investigated the recovery of niobium and tantalum from ore by using highly concentrated caustic potash as an alternative to hydrofluoric acid and they concluded that almost complete extraction of both niobium and tantalum is achieved at temperatures above 300 °C (Wang et al., 2009; Zhou et al., 2005).

The extraction kinetics of tantalum using methyl isobutyl ketone (MIBK) from a Ta–Nb alkaline leach solution was investigated (Yang et al., 2013). The salts obtained at this stage were converted to TaF_7^{2-} by adding HF. Kinetic results indicated that the rate of TaF_7^{2-} extraction by MIBK is controlled by the rate of chemical reaction at the aqueous–organic interface rather than in the bulk phase.

The extraction of Ta (V) from aqueous sulfate/fluoride solution using trioctyl phosphine oxide (TOPO) in MIBK was also investigated (Sanda and Taiwo, 2012). The aqueous solution was produced by leaching tantalite-columbite with $HF\text{-}H_2SO_4$. Regarding the use of TOPO as extractant, kerosene proved to be better diluent than xylene. The synergism observed concerning tantalum extraction using TOPO in MIBK can reduce the number of extraction stages.

The present study aimed to establish the optimal operational conditions for Ta and Nb extraction from a ferrocolumbite ore by HF pressure leaching.

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2. Experimental

2.1. Materials

The ferrocolumbite ore was collected in San Luis Province, Argentina. This ore was ground in a disk mill to a particles size ranging between +147 and −45 μm. The BET analysis with N_2 adsorption at 77 K in a Micromeritics Acusorb 2100E showed a low specific area (1.2 m^2/g) indicating a low porosity of ferrocolumbite grains. The chemical analysis of the raw ore by X-ray fluorescence with Philips PW1400 equipment indicated that the mineral formula is (Ruiz et al., 1993):

$$(Mn_{0.46}Fe_{0.54})\ (Nb_{0.65}Ta_{0.35})_2O_6.$$

The XRD diffractogram, obtained in a Rigaku D-Max III C equipment, operated at 35 kV and 30 mA, using K_α radiation of Cu (Ni filter $\lambda = 0.15418$), showed the presence of ferrocolumbite (JCPDS 33-659, 1993), quartz and feldspar; the last two minerals are present in the ore sample as gangue. All other chemicals used in this work including hydrofluoric acid were of analytical grade.

2.2. Leaching equipment and procedure

The reactor consisted of a 450 mL Monel autoclave. The reactor was assembled on a support stand and connected to the control system, where stirring speed and heat supply were monitored by a control unit.

For each test, the ore and the leaching solution were put into the reactor. The content was heated under constant stirring and at a heating rate of either 5 or 10 °C/min, depending on the working temperature (Rodriguez and Ruiz, 2011). Once the set temperature was reached, the reaction time began to be monitored. At the end of the experiment, the system was cooled, and the slurry in the reactor was filtered. The resultant solid was dried, calcined at 900 °C for 4 h, cooled and weighed. The concentrations of Ta and Nb in the residues were determined by XRF (Ruiz et al., 2004). The solid residues were also analyzed by XRD.

3. Results and discussion

Taking into account the mineral formula and the fact that the dissolution with hydrofluoric acid is not selective, the reaction of dissolution of ferrocolumbite with HF may be represented by the following reaction:

$$(Mn_{0.46}Fe_{0.54})(Nb_{0.65}Ta_{0.35})_2O_{6(s)} + 16HF_{(aq)} \rightarrow 1.3H_2NbF_{7(aq)} + 0.7H_2TaF_{7(aq)} + 0.46MnF_{2(aq)} + 0.54FeF_{2(aq)} + 6H_2O. \quad (1)$$

The oxide mineral conversion (X) was calculated as follows:

$$X\% = ((m_i - m_f)/m_i) \quad (2)$$

where: m_i, is the initial mass of the oxide calculated taking into consideration the mineral added to the reactor and the content of the oxide in the raw ore; and m_f, is the final mass of the oxide determined as follows: 100 mg of the residual sample was weighted, and further analyzed by XRF and the oxide content in that sample was determined with a calibration curve built using the pure oxide methodology.

The parameters studied in the leaching tests were temperature, solid-to-liquid ratio, acid concentration, reaction time, stirring speed and particle size.

3.1. Effect of temperature

The effect of temperature on the leaching of Ta and Nb was evaluated in the range of 75 to 220 °C. Conditions of the autoclave leaching were as follows: particle size, −45 μm; HF concentration, 9% v/v; solid-to-liquid ratio, 1.82% w/v; reaction time, 80 min and stirring speed, 330 rpm. The experimental results are shown in Fig. 1.

In Fig. 1 it is illustrated that under the same working conditions, the extraction of both Ta and Nb from their oxides increases as the temperature increases. These results are consistent with the facts that solid–liquid reactions are sensitive to variations in temperature and that increasing temperature improves the dissolution of most solids (Habashi, 1980; Quiroga, 1996).

3.2. Effect of solid-to-liquid ratio

The effect of solid-to-liquid ratio on leaching of Ta and Nb was studied from 0.36 to 3.64% w/v. Conditions of the autoclave leaching were as follows: temperature varying from 75 to 220 °C; particle size, −45 μm; HF concentration, 9% v/v; stirring speed, 330 rpm and reaction time, 80 min. The results are shown in Fig. 2.

Fig. 2 shows that the recovery of the metals is the highest for the solid-to-liquid ratio of 0.36% w/v, and begins to decrease for higher values. Such decline could be attributed to the following reasons: for a fixed HF concentration, the amount of acid available to react with the mineral is higher as the solid-to-liquid ratio decreases. It is also known that in complexation reactions, the amount of complex formed increases with the concentration of the complexing agent (Inczédy, 1976).

3.3. Effect of acid concentration

The effect of acid concentration on the leaching of Ta and Nb was investigated from 5 to 20% v/v at three different temperatures: 75, 123 and 220 °C. The leaching process was carried out under the following conditions: particle size, −45 μm; solid-to-liquid ratio, 1.82% w/v; reaction time, 80 min and stirring speed, 330 rpm.

The results shown in Fig. 3 indicate that the extraction of Nb and Ta increases as the acid concentration increases in the experiments run at 75 and 123 °C. At 220 °C, the amount of such metals in the leaching solution increases when leaching agent concentration varies from 5 to 15% v/v. As the acid concentration increases from 15 to 20% v/v, the extraction of Nb and Ta remains almost constant.

These results can be explained bearing in mind that increasing acid concentration results in an increase of the amount of F^- and H^+ ions

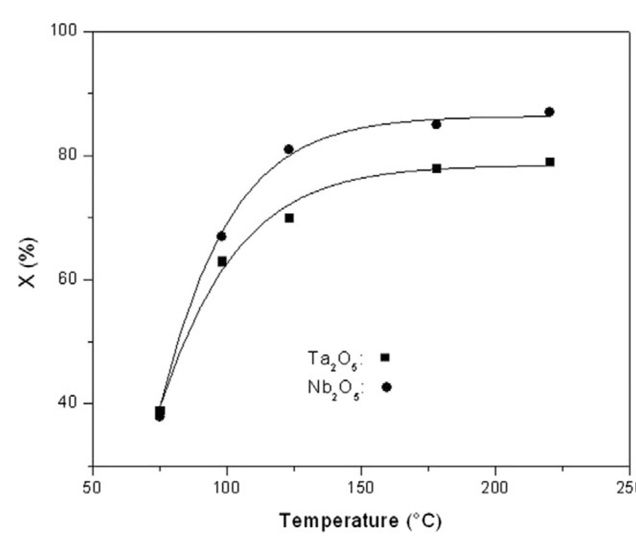

Fig. 1. Effect of temperature on the dissolution of ferrocolumbite (solid-to-liquid ratio, 1.82% (w/v); HF concentration, 9% (v/v); reaction time, 80 min; particle size, −45 μm and stirring speed, 330 rpm).

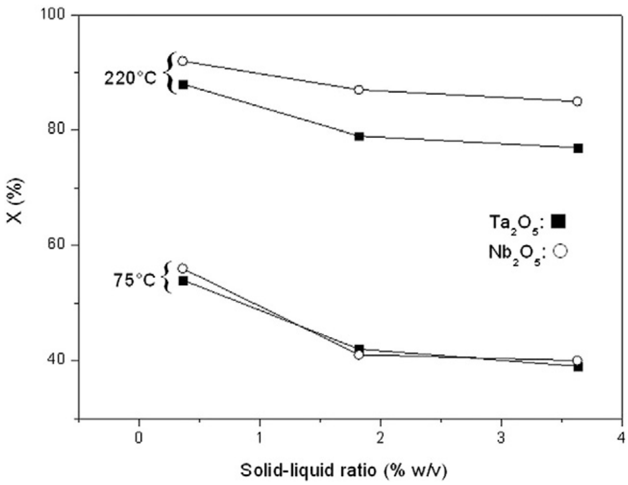

Fig. 2. Effect of solid-to-liquid ratio on the dissolution of ferrocolumbite at 75 and 220 °C (HF concentration, 9% (v/v); reaction time, 80 min; particle size, −45 μm and stirring speed, 330 rpm).

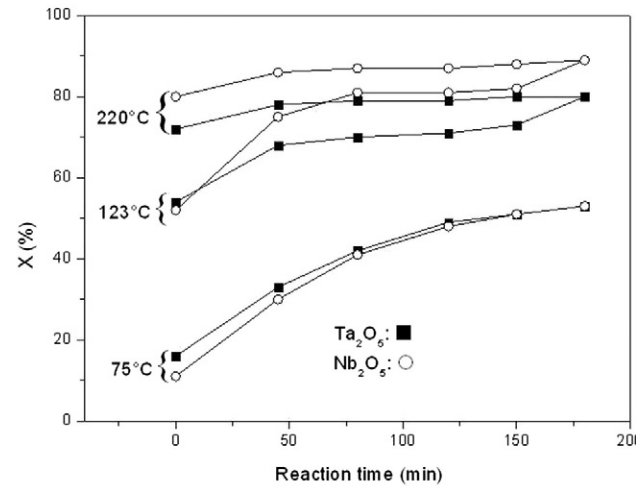

Fig. 4. Effect of reaction time on the dissolution of ferrocolumbite from 75 to 220 °C (solid-to-liquid ratio, 1.82% (w/v); HF concentration, 9% (v/v); particle size, −45 μm and stirring speed, 330 rpm).

available to react with the mineral to form, thus, soluble complexes corresponding to the metals that constitute the ferrocolumbite structure. In addition, it appears that this effect is enhanced by increasing the reaction temperature.

3.4. Effect of reaction time

The influence of reaction time on the Ta and Nb extraction at different temperatures is shown in Fig. 4. The tests were carried out under the following conditions: particle size, −45 μm; HF concentration, 9% v/v; solid-to-liquid ratio, 1.82% w/v and stirring speed, 330 rpm at a temperature range of 75 to 220 °C.

Fig. 4 shows the effect of reaction time on the extraction of Ta and Nb, which increases as the reaction time increases from 0 to 45 min. Further increases in time over 45 min do not improve their extraction.

These experiments agree with the known fact that the heterogeneous reaction between a mineral and a fluid reactant, either an acid or a base, is generally slow and sensitive to temperature (Habashi, 1980). Therefore, the increase in the contact time between solid and fluid phases increases the dissolution of the mineral.

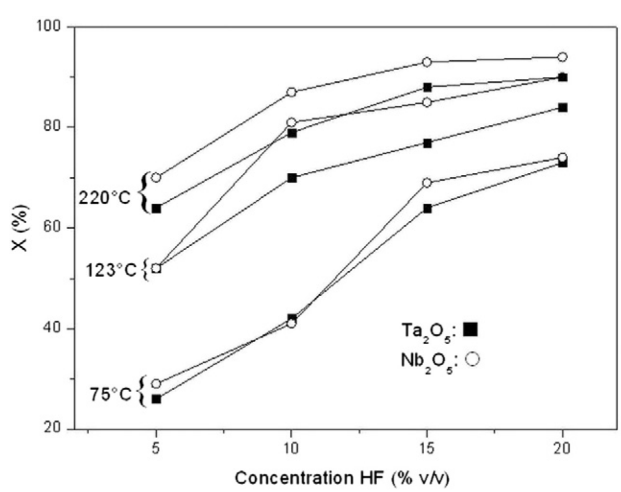

Fig. 3. Effect of acid concentration on the dissolution of ferrocolumbite at 75, 123 and 220 °C (solid-to-liquid ratio, 1.82% (w/v); reaction time, 80 min; particle size, −45 μm and stirring speed, 330 rpm).

3.5. Effect of stirring speed

The effect of stirring speed on ferrocolumbite dissolution was investigated from 110 to 550 rpm. The leaching conditions were as follows: solid-to-liquid ratio, 1.82% (w/v); particle size, −45 μm; temperature, 75 and 220 °C; reaction time, 80 min and HF concentration, 9% (v/v).

The experimental results showed that a variation in the stirring speed from 110 to 550 rpm does not affect the extraction of Ta and Nb. This would indicate that the rate-determining step is the chemical reaction.

3.6. Effect of particle size

The effect of particle size on the dissolution of Ta and Nb was studied from +147 to −45 μm at two temperatures, 75 and 220 °C. The experimental conditions of the autoclave leaching were as follows: HF concentration, 9% v/v; solid-to-liquid ratio, 1.82% w/v; stirring speed, 330 rpm and reaction time, 80 min.

The results indicated that changes in particle size affect slightly the extraction of niobium and tantalum in the range studied, which means that the increase in the solid surface area did not have a significant influence on the extraction of these metals, since, under such working conditions, the maximum degree of mineral liberation has been reached.

4. Characterization of residues

Fig. 5 shows the results of the characterization of leaching residues by XRD at different conversions. The obtained XRD patterns were compared to the XRD pattern of the ore.

The diffractograms of residues do not show formation of crystalline structures different from those identified in the ore pattern. In addition, Fig. 5 shows that as the conversion increases, the peaks corresponding to quartz and feldspar (gangue) disappear, which is due to the increase in solubility of the compounds formed by the reaction between the hydrofluoric acid and the gangue, with increasing temperature.

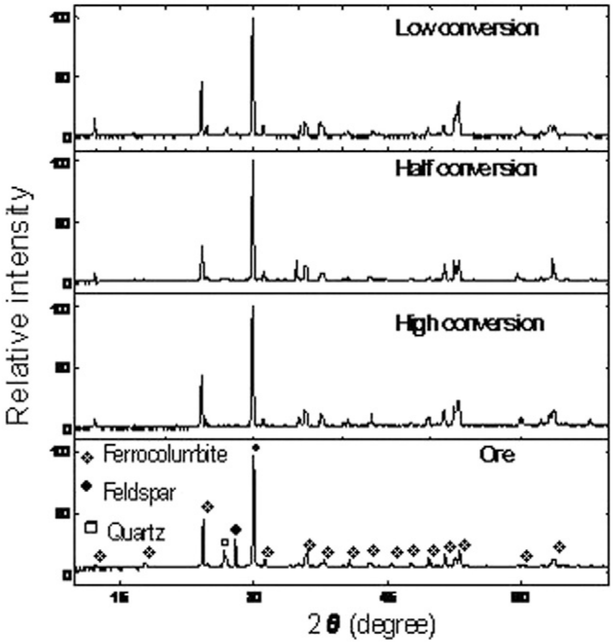

Fig. 5. XRD patterns of three acid leach residues.

5. Conclusions

In summary, a process including the pressure leaching with HF was employed to extract niobium and tantalum from ferrocolumbite. The experimental results indicate that the augment in the leaching temperature, reaction time and HF concentration increases the dissolution of Ta and Nb oxides. Furthermore, the decrease in the particle size and solid-to-liquid ratio enhances the oxide extraction. The optimal conditions to achieve a niobium and tantalum extraction of 90 and 80%, respectively were as follows: HF concentration, 9% v/v; reaction temperature, 220 °C; particle size, −45 μm; solid-to-liquid ratio, 1.82% w/v and reaction time of 80 min.

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