

OPTIMIZATION OF THE LEACHING CONDITIONS OF AN AUTOCLAVE. APPLICATION TO THE DISSOLUTION OF FERROCOLUMBITE FROM SAN LUIS PROVINCE, ARGENTINA

M.H. RODRIGUEZ and M. del C. RUIZ

Instituto de Investigaciones en Tecnología Química Universidad Nacional de San Luis-CONICET. Chacabuco y Pedernera, C.C. 290, 5700 San Luis, Argentina. mrodriguez@uncu.edu.ar (Mario H. Rodriguez)

Abstract— The optimum working conditions of a Parr laboratory autoclave for minerals dissolution were studied and the results obtained were applied to the leaching with HF of a Nb and Ta mineral, from the San Luis, Argentina. The optimized variables were heating rate, liquid volume, stirring speed, inert solid addition and cooling rate. Changes in the liquid volume, stirring speed and presence of an inert solid did not produce modifications in the actual heating rate. The optimum heating programs ranged between 5 and 10°C/min and depended on the programmed final temperature. The cooling period was 25 min. The results indicated that, using the optimum working conditions, more than 90% of mineral might be dissolved at 220°C. It was also observed that the dissolution of mineral was slightly affected by the stirring speed and the particle size whereas temperature, HF concentration, solid-liquid relation and reaction time strongly influenced the extraction of elements.

Keywords— Parr autoclave, Ores, Leaching, Operating variables, Ferrocolumbite.

I. INTRODUCTION

Metal extraction by hydrometallurgy is a technology of increasing importance in the extractive metallurgy. Leaching is one of the procedures used for the extraction of metals from minerals and concentrates and also for the refinement of metals and their recovery from the leaching solutions (Sarkar, 1983; Habashi, 2005). The use of autoclaves has greatly increased in the hydrometallurgical activities since, as they are closed vessels, they cause minor pollution (Habashi, 1971, 1999; Dreisinger, 1995). From the industrial point of view, closed vessels are more useful, when compared with other reactors, because many industrial dissolution processes usually require temperatures above the water boiling point in order to proceed at a reasonable speed (Sarkar, 1983; Dreisinger, 1995).

In the past decades, common minerals such as sulphurs (Cu, Zn, Pb, Co and Au) were treated by pressure leaching (Berezowsky, 1991). Serova *et al.* (1993), using an autoclave, studied the distribution of In between the aqueous and the solid phases during the oxidizing leaching of zinc sulphide concentrates. This device was also used to treat a mineral containing rare earths (Silva and Barbosa, 1993).

In the last years, many researchers have tried to determine the kinetics of mineral leaching in closed ves-

sels. Antonijevic *et al.* (2004) investigated the kinetics of chalcopyrite leaching with hydrogen peroxide in sulphuric acid. Jiang *et al.* (2004) using the same leaching medium, studied the kinetics of pyrolusite leaching from manganese-silver associated ores. The kinetics of sand leaching in alkaline medium and of malachite in sulphuric medium was investigated by Mgaidi *et al.* (2004) and Bingöl and Canbazoglu (2004), respectively.

The industrial process used to extract Nb and Ta from minerals by hydrometallurgy at atmospheric pressure makes use of HF at 70% v/v in order to obtain high dissolutions of the mineral (Gupta and Suri, 1994). Although the pressure leaching with low HF concentrations has some advantages, such as minor acid consumption, minor corrosion of the reactor, minor negative effects on the environment and fewer difficulties in the dissolution of these slight soluble minerals, there is little information about the dissolution in an autoclave of minerals containing Nb and Ta. Habashi and Toromanoff (1983) studied the dissolution of pyrochlore with HCl in an autoclave with the aim of obtaining Nb₂O₅ of technical grade. Krasilshchik *et al.* (1991) used pressure leaching for low solubility materials, such as Nb and Ta oxides. Rodriguez *et al.* (2004, 2007) have investigated the influence of carboxylic acids on the leaching of ferrocolumbite with HF and have proposed a kinetic model for the leaching of ferrocolumbite with HF.

On the other hand, a reliable kinetic study of a solid-liquid hydrometallurgical reaction in an autoclave requires a carefully determination of the equipment working conditions to obtain an adequate reproducibility and the control of the important parameters. It is important to emphasize that the optimum working conditions of an autoclave may vary from vessel to vessel. Consequently, it is essential to know them all, and the most convenient way to determine these conditions is through experimentation.

The purpose of this work is to establish the optimum working conditions of a Parr laboratory autoclave and to carry out experimental assays in order to obtain reliable data for the dissolution reaction of a ferrocolumbite with HF, under high pressure conditions.

II. MATERIALS and METHODS

A. Equipment

The equipment used was a 4562 Parr autoclave, which is shown in Fig. 1.

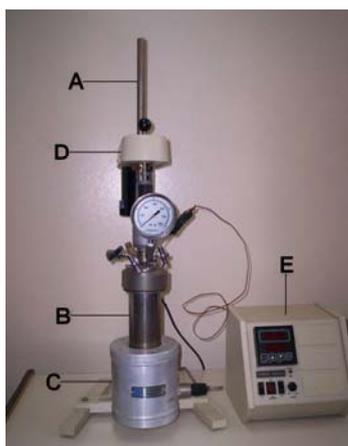


Figure 1. Experimental equipment. A: Support; B: Reactor; C: Heater mantle; D: Stirring system; E: Control unit.

The equipment included a 450 ml reactor built in Monel; a stirring system and a heater mantle, through which movement and power were transferred to the autoclave, respectively; all these parts were mounted on a support and connected to the control unit, by means of which the stirring speed and power supply were monitored.

B. Materials

The materials used in this work were: distilled water, high purity quartz as inert solid, Merck HF at 40% p/v and an Nb and Ta mineral extracted from “Las Cuevas” mine in the Province of San Luis, Argentina.

The mineral was characterized using different methodologies. The analyses by X-ray diffraction (XRD) were carried out in a Rigaku D-Max III C equipment, operated at 35 kV and 30 mA, with radiation K_{α} of Cu, filter of Ni, $\lambda=0.15418$ nm, and the mineral diffractogram shows the presence of ferrocolumbite, feldspar and quartz (Fig. 2).

The mineral morphology was studied by scanning electron microscopy (SEM) using both a Philips 515 and a LEO 1450 VP equipments. Figure 3 shows a micrograph of the particles of minerals, and particles of irregular shape, with flat sides can be observed.

The specific surface, determined by the Brunauer Emmet and Teller method (BET), was $1.2 \text{ m}^2/\text{g}$. The mineral composition was obtained by X-ray fluorescence (XRF), and the Nb_2O_5 , Ta_2O_5 , FeO and MnO contents were 41.2%, 36.8%, 9.5% and 6.8%, respectively, Ruiz *et al.*, 2004. The presence of SiO_2 and Al_2O_3 , corresponding to the gangue (quartz, feldspar) was also observed.

C. Procedure

Optimization of the working variables

A series of experiments were carried out in order to know the effect of the following parameters on the actual or experimental heating rate: theoretical heating rate for different temperatures, liquid volume, stirring speed and solid mass. The optimum cooling period for the working temperatures was also determined. The methodology described below was used for all the assays.

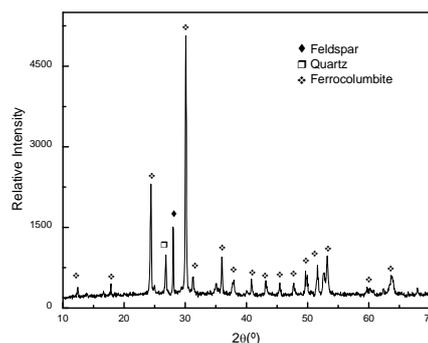


Figure 2. Mineral diffractogram

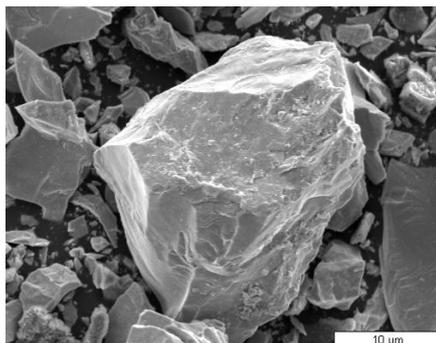


Figure 3. Mineral micrograph.

First, an adequate volume of distilled water was placed in the reactor vessel, and the water amount did not exceed three fourths of the available space. The assays with solids were carried out adding between 1 and 10 g of quartz at a determined water volume, thus obtaining the pulp.

Then the reactor was connected to the measure and control units, and after checking for complete valves closed, the temperature controller was programmed according to the selected heating program, from an initial temperature near the environmental one (25°C). The stirring system and the heating program were then turned on. After each assay was completed, stirring was suspended, and the reactor was taken away from the heater mantle, leaving it to cool in two different ways, according to the working temperature. When it was lower than 100°C , the reactor was cooled at environmental temperature until reaching the initial temperature; when the experiments were performed at a temperature higher than 100°C , the reactor was left to cool for 10 min and then, submerged in a thermostatic bath with water recirculation until reaching the environmental temperature. When working with solids, the reactor content was filtered, the liquid was discarded and the inert solid was dried and re-used.

Mineral leaching

A mineral mass of 5 g and 275 ml of HF solution were placed in the reactor; after that, the pulp was heated with constant stirring and a heating program of 5 or $10^{\circ}\text{C}/\text{min}$, according to the working temperature. The reaction time was measured from the moment the working temperature was reached. When the assay was finished, the reactor was left to cool for 25 min without

stirring, the content was filtered, the solid was dried and calcined at 900°C for four hours, and then the residue was weighed.

III. RESULTS AND DISCUSSION

A. Optimization of the operating variables

The experimental data obtained from the optimization study of the reactor operating variables are shown in the Appendix A Tables.

Heating rate

The theoretical heating rate is the relation between the final temperature minus the environmental temperature (25°C) and the time programmed to reach the working temperature. The experimental or actual heating rate is the relation between the temperature recorded by the thermocouple and the time the system takes to stabilize the programmed final temperature, with a $\pm 2^\circ\text{C}$ error.

Different theoretical heating rates (from 1 to 15.3°C/min) were studied for every programmed final temperature, and the results are shown in Table I, Appendix A. The volume of distilled water was 150 ml, and the stirring speed was 330 rpm for all the experiments.

It was observed that the optimum theoretical heating rates were 5°/min and 10°/min to reach final temperatures ranging from 50 to 148°C and from 178 to 220°C, respectively. It was also observed that the actual heating rates were below the theoretical one.

The determination of the difference between both heating rates permits to know the pre-heating time of the mineral-leaching agent mixture, which is necessary to reach the working temperature. During this time, certain degree of the mineral dissolution may occur. These data have to be considered when carrying out kinetic studies to propose models and reaction mechanisms that represent with good approximation the dissolution of the material under study.

Liquid volume

In order to know the working conditions for the leaching stage, the study of this variable was carried out between 150 and 275 ml and at three temperature levels (50, 123 and 220°C). The stirring speed was 330 rpm and a series of heating rates were assayed for each temperature (see Table II, Appendix A).

The results showed that at the three studied temperatures, 50, 123 and 220°C, changes in the liquid volume did not cause significant modifications in the experimental heating rate since the heat transfer did not show significant differences. The small differences observed in the experimental heating rate, when changing the liquid volume at 123°C, might be attributed to an experimental error.

Stirring speed

Several assays ranging between stirring speeds of 110 and 550 rpm and at two temperature levels, 75 and 220°C, were carried out. For each temperature level, the

most adequate theoretical heating rate was selected and kept constant (5 and 10°C/min, respectively). The water volume, selected according to the results in Table III, Appendix A, was 275 ml in all cases.

The results permitted to conclude that it is possible to work between 110 and 550 rpm because a change in this operating variable did not produce changes in the experimental heating rate (Table III, Appendix A).

Inert solid addition

The influence of the solid material and pulp concentration on the experimental heating rate was studied at three temperature levels, using between 1 and 10 g of quartz, with constant stirring speed and liquid volume (330 rpm and 275 ml, respectively), and the most adequate theoretical heating rate for each temperature level.

The results indicated that the increase of pulp concentration did not modify significantly the experimental heating rate values, which ranged between 1.7 and 1.9; 3.2 and 3.4, and 4.8 and 5.1 for 50, 123 and 220°C, respectively (Table IV, Appendix A).

Cooling period

Experimental assays of the reactor content cooling were carried out in order to establish a similar cooling period for recovering an initial temperature of approximately 25°C, from different final temperatures. The results permitted to determine that it is possible to cool the system from working to initial temperature, 25°C, in 25 min with different cooling rates for each assayed temperature (Table V, Appendix A).

It was also observed that the cooling rate was directly proportional to the reached final temperature, and it decreased as the system neared the environmental temperature.

Optimum working conditions for leaching

The results described in items 3.1.1 to 3.1.5 permitted to determine the optimum Parr autoclave operating variables for the different leaching assays of the Nb and Ta mineral. These parameters are shown in Table 1.

Figure 4 shows the heating and cooling periods for three temperatures under the following working conditions: stirring speed, 330 rpm; liquid volume, 275 ml; solid mass, 5 g and time of leaching to the programmed final temperature of 80 min.

Table 1. Optimum working conditions.

Temperature (°C)	Volume (cm ³)	Stirring speed (rpm)	Heating rate (°C min ⁻¹)	
			Theoretical	Actual
50	275	330	5	1.7
75				2.5
98				3.65
123				3.4
148				2.7
178			10	4.5
200				4.7
220				5.1

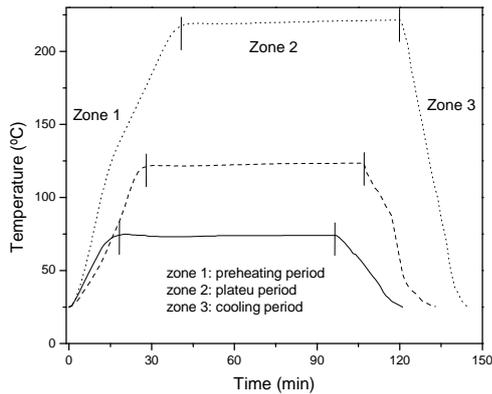
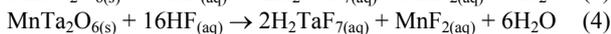
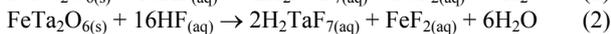


Figure 4. Actual heating and cooling periods for three final temperatures: — 75°C, ---- 123°C, 220°C.

B. Application of the autoclave optimum working conditions to ferrocolumbite dissolution in HF medium

The ferrocolumbite dissolution reaction with concentrated HF may be represented as follows (Gupta and Suri, 1994):



In all the assays, the HF concentration was always higher than the concentration calculated stoichiometrically for the mineral total dissolution, according to Eqs. (1) to (4) and to the gangue content.

The parameters studied in the leaching assays were temperature, reaction time, acid concentration, particle size and stirring speed.

The quantitative analytical determinations for each studied oxide (Ta_2O_5 , Nb_2O_5 , FeO and MnO) was performed according to the methodology developed by Ruiz *et al.* (2004). In each experiment, 100 mg of the residue was used for the preparation of the pellets for the analyses, and the mass of each oxide in the residues was obtained. With these data and the initial mass values of each oxide present in the mineral, the quantity of dissolved ferrocolumbite was calculated, in terms of global conversion, X%, defined as:

$$X\% = \frac{m_i - m_f}{m_i} \cdot 100 \quad (5)$$

where: m_i and m_f , are the addition of the masses of the Nb, Ta, Fe and Mn oxides, initial and final, respectively.

Effect of stirring speed, particle size and solid-liquid relation

The influence of these variables on mineral dissolution was studied at three different levels: stirring speed between 110 and 550 rpm, particle size between -175/+147 and -45 μm , and solid-liquid relation between 0.36 and 3.63% w/v. The remaining parameters were kept constant: temperature, 220°C; liquid volume, 275 ml; HF concentration, 9% v/v and reaction time, 80 min. The results are shown in Table 2.

Table 2. Effect of stirring speed, particle size and solid-liquid ratio.

Stirring speed (rpm)	X%	Particle size (μm)	X%	S-L ratio (% w/v)	X%
110	83.0	-175 +147	83.0	0.36	85.2
220	81.4	-147 +104	80.5	1.82	83.0
330	81.7	-75 +53	80.2	3.63	81.3
440	80.9	-45	81.7	-	-
550	84.3	-	-	-	-

The results indicated that changes in the stirring speed and particle size slightly affected the mineral dissolution in the studied ranges. In the case of the first variable, this result is attributed to the fact that the thickness of the solid-surrounding film, through which HF must flow to contact it and react, did not change when the speed increased, indicating that HF transfer from the solution bulk to the solid, through the boundary layer, is maximum for the assayed stirring speeds values. These results demonstrate that there was no diffusive control on the process global rate due to the boundary layer. Similar results have been reported by other authors, who worked at lower temperatures and with stirring speeds between 0 and 1.100 rpm (Baram, 1965 and 1972; Majima *et al.*, 1988; El Hussaini and Mahdy, 2002).

Besides, the same table shows that changes in the particle size slightly affected the mineral dissolution in the studied ranges. This result suggested that for these granulometries the maximum degree of mineral liberation was reached, and consequently the particle size did not modify the mineral dissolution mechanism. On the other hand, the determination values of the mineral BET surface area did not show significant changes in relation to the granulometry variation, and consequently, the contact surface of the solid and the leaching agent was similar in the range of the assayed particle sizes.

Table 2 also shows that the mineral dissolution decreased when the solid-liquid relation increased. This behaviour is similar to the HF concentration effect described below.

Temperature and reaction time effect

The temperature and reaction time influence on the mineral dissolution was studied selecting the optimum leaching working conditions. The temperature was investigated in an interval from 50 to 220°C for a reaction time of 80 min; the reaction time was studied between 45 and 180 min at different temperatures ranging between 50 and 220°C. The remaining variables were kept constant: HF concentration, 9% v/v; mineral mass and particle size, 5 g and <45 μm , respectively. The results are shown in Table 3.

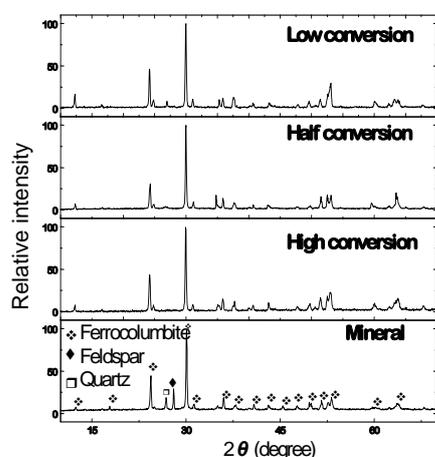
Table 3 shows that when the temperature increased, the mineral dissolution also increased. These results were in agreement with the fact that solid-liquid reactions are sensitive to temperature since the changes on this variable affect the solids reactivity (Habashi, 1980; Quiroga *et al.* 1996). Other authors found similar re

Table 3. Effect of reaction time at different temperatures.

Time (min)	(X%)					
	50°C	75°C	98°C	123°C	178°C	220°C
45	19.7	28.2	-	71.2	-	82.9
80	22.8	39.9	64.7	72.0	81.5	81.7
120	25.6	48.5	-	73.4	-	82.3
150	28.4	51.9	-	73.7	-	81.3
180	30.1	53.8	-	80.0	-	82.7

Table 4. Effect of HF concentration at different temperatures.

[HF] (%v/v)	(X%)		
	75°C	123°C	220°C
5	27.7	68.7	67.0
9	39.9	72.0	81.7
15	63.0	78.4	89.3
20	68.9	84.5	91.1

**Figure 5.** Diffractograms of the ore and three residues of the leaching of mineral.

sults when investigating the temperature effect on the oxides and minerals dissolution in an acidic medium. Baram (1972), Majima *et al.* (1988), El Hussaini and Mahdy (2002), observed that the increase of the leaching temperature favored the recovery of metals present in those materials.

Table 3 also shows that, at temperatures ranging between 50 and 123°C, the mineral dissolution was higher when the reaction time increased. These results indicated that under these working conditions the formed products were soluble and their solubility increased with the increase of these variables. Besides, these experimental observations are in agreement with the well-known fact that the dissolution reactions between a mineral and a fluid reagent are in general slow and non-reversible, whether the reagent is an acid or a base. Therefore, when the contact time between the solid and the fluid phase increased, the mineral dissolution also increased (Habashi, 1980; Quiroga *et al.*, 1996).

The mineral dissolution was slightly affected by the reaction time, and the most dissolution value was reached at 220°C and 45 min. The X-ray diffractograms of the residues, Figure 5, from these assays indicated that they were composed only by non-reacting mineral. This fact can be explained because at first the mineral

particles with the highest reactivity are dissolved due to the presence of uranium in its structure (Rodriguez *et al.*, 2004); then, the dissolution of the remaining mineral is more difficult.

Effect of HF concentration at different temperatures

The effect of HF concentration on the mineral leaching was studied at three temperature levels: 75, 123 and 220°C. The remaining parameters were kept constant: liquid volume, 275 ml; mineral mass and granulometry, 5 g and <45 μm, respectively; reaction time, 80 min and stirring speed, 330 rpm (Table 4).

As shown in Table 4 an increase in the concentration of the leaching agent led to an increase in the mineral dissolution. The higher dissolution of the mineral was obtained at 220°C with HF 20% (v/v). This is due to the great availability of the complexing ions, F⁻ and H⁺, to react with the mineral in each case, since in a complexation solid-liquid reaction, the magnitude of the formation of metallic complexes is directly proportional to the complexing agent concentration. These results coincided with those reported by Majima *et al.* (1988) who found that when HF concentration increased, there was higher availability of F⁻ and H⁺ ions to form the metal complexes, favouring mineral dissolution and soluble compounds formation. Similar results were reported by Baram (1965, 1972) who carried out kinetic leaching studies of minerals or oxides, containing Nb and Ta, in HF and HF-H₂SO₄ media. The author found that the increase in the concentration of acids in the leaching media increased the dissolution of the mineral and of the oxides. This effect is more clearly seen when working in a mixed medium composed by HF- H₂SO₄. The best dissolution of these minerals (higher than 99%) was obtained by using an HF- H₂SO₄ mixture (42%-92% v/v), at 80°C for a 4-hour period at a stirring rate of 500 rpm.

IV. CONCLUSIONS

The optimum working conditions determined in a Parr autoclave of 450 ml to carry out the minerals dissolution are: 275 ml of leaching liquid, a stirring rate of 330 rpm, and theoretical heating rates of 5°C/min and 10°C/min for the temperature intervals ranging between 50 and 148°C and between 175 and 220°C, respectively. Besides, a cooling standard time of 25 min was determined by using different rates, according to the temperature at which the leaching assay was carried out.

The ferrocolumbites leaching may be carried out in an autoclave with diluted HF. The leaching temperature, reaction time, HF concentration and the solid-liquid relation strongly influence mineral dissolution whereas the stirring speed and the size particle slightly affect it, under the studied working conditions. The yield of dissolution of about 80% was obtained with 9% (v/v) HF at 220 and 123°C, and with reaction times of 45 and 180 min, respectively. With 15% (v/v) HF working to 220°C about 90% of mineral was dissolved in 80 min.

The optimum working conditions of a laboratory Parr autoclave permitted to obtain reliable data for a kinetic-chemical study on the dissolution of a mineral containing Nb and Ta.

ACKNOWLEDGMENTS

The authors of this work wish to thank Universidad Nacional de San Luis, Consejo Nacional de Investigaciones Científicas y Técnicas and Fondo para la Investigación Científica y Tecnológica of Argentina for financial support.

REFERENCES

- Antonijević, M.M., Z.D. Janković and M.V. Dimitrijević, "Kinetic of chalcopyrite dissolution by hydrogen peroxide in sulphuric acid," *Hydrometallurgy*, **71**, 329-334 (2004).
- Baram, I.I., "Cinética de la disolución de los pentóxidos de niobio y tantalio en ácido fluorhídrico," *Zh. Prikl. Khim.*, **38**, 2181-2188 (1965).
- Baram, I.I., "Cinética de la disolución de tantalita en una mezcla de ácidos fluorhídrico y sulfúrico," *Tsvet. Met. (The Soviet Journal of Non-Ferrous Metals)*, **15**, 97-99 (1972).
- Berezowsky, R.M., "The commercial states of pressure leaching technology," *JOM*, **43**, 9-15 (1991).
- Bingöl, D., and M. Canbazoglu, "Dissolution kinetics of malachite in sulphuric acid," *Hydrometallurgy*, **72**, 159-165 (2004).
- Dreisinger, D., "R & D Opportunities for pressure hydrometallurgy," *JOM*, **43**, 8 (1995).
- El-Hussaini, O.M. and M.A. Mahdy, "Sulfuric acid leaching of Kab Amiri-niobium-tantalum bearing minerals, Central Eastern Desert, Egypt," *Hydrometallurgy*, **64**, 219-229 (2002).
- Gupta, C.K. and A.K. Suri, *Extractive Metallurgy of Niobium*, CRC Press, Florida (1994).
- Habashi, F., "Pressure hydrometallurgy: key to better and nonpolluting processes," *Engng. Min. J.*, **172**, 96-100 (1971).
- Habashi, F., *Principles of Extractive Metallurgy. Vol. I*, Gordon and Breach Science Publishers Inc., New York (1980).
- Habashi, F., *Textbook of Hydrometallurgy*, Ed. Les Copies de la Capitale Inc, 2^o ed., Québec (1999).
- Habashi, F., "A short history of hydrometallurgy," *Hydrometallurgy*, **79**, 15-22 (2005).
- Habashi, F. and I. Toromanoff, "Hydrometallurgical production of technical niobium oxide from pyrochlore concentrates," *J. of Less Common Metals*, **91**, 71-82 (1983).
- Jiang, T., Y. Yang, Z. Huang, B. Zhang and G. Qiu, "Leaching kinetics of pyrolusite from manganese-silver ores in the presence of hydrogen peroxide," *Hydrometallurgy*, **72**, 129-138 (2004).
- Krasilchik, V.Z., Zhiteleva, O.G., Sokol'skaya, N.N. and Chupakin, M.S. "Autoclave vapor-phase decomposition of some difficulty soluble substances," *Zh. Anal. Khim.*, **41**, 586-590 (1991).
- Majima, H., Y. Awakura, M. Mishima and T. Hirato, "Dissolution of columbite-tantalite in acidic fluoride media," *Metall. Trans. B*, **19B**, 355-363 (1988).
- Mgaidi, F., D. Jendoubi, M. Oulahna, El Maaoui and J.A. Dodds, "Kinetics of dissolution of sand into al-

- kaline solutions: application of a modified shrinking core model," *Hydrometallurgy*, **71**, 435-446 (2004).
- Quiroga, O.D., J.R. Avanza and A.J. Fusco, *Modelado Cinético de las Transformaciones Fluido-Sólido Reactivo*, Editorial Universitaria de la Universidad del Nordeste, Corrientes (1996).
- Rodriguez, M., J. Rivarola and M. del C. Ruiz, "The effects of carboxylic acid addition on hydrofluoric acid autoclave leaching of a ferrocolumbite," *Hydrometallurgy*, **74**, 39-46 (2004).
- Rodriguez, M., O. Quiroga and M. del C. Ruiz, "Kinetic study of ferrocolumbite dissolution in hydrofluoric acid medium," *Hydrometallurgy*, **85**, 87-94 (2007).
- Ruiz, M. del C., M. Rodriguez, E. Perino and R. Olsina, "X-ray fluorescence analytical methodology for the determination of Nb, Ta, Fe and Mn extracted in hydrometallurgical processes," *Lat. Am. Appl. Res.*, **34**, 23-27 (2004).
- Sarkar, K., "Selection of autoclaves in hydrometallurgical operations," *Trans. Instn. Min. Metall, Section C*, **94**, 184-194 (1983).
- Serova, N.V., L.I. Kulagina, V.I. Goriachkin, N.V. Polikarpova, V.I. Korsunski and V.B. Smirnova, "Indium behavior in autoclave oxidizing leaching of zinc sulfide concentrates," *Isvent. Met.* **4**, 12-14 (1993).
- Silva, F.T. and L.A. Barbosa, "Alkaline decomposition of a xenotime concentrate in autoclave," *Proc. of the III Meeting of the Southern Hemisphere on Mineral Technology*, 108-119 (1993).

APPENDIX A

Table I. Heating rate effect.

Final temperature (°C)	Working conditions			
	Theoretical		Actual	
	Heating rate (°C min ⁻¹)	Time (min)	Heating rate (°C min ⁻¹)	Time (min)
50	1.5	17	1.25	20
	1.7	15	1.3	19
	3.6	7	1.7	15
	5	5	1.8	14
	8.3	3	1.6	16
75	1	50	1	50
	2	25	1.9	26
	2.5	20	2.1	24
	3.3	15	2.5	20
	5	10	2.6	19
98	10	5	2.4	21
	3	24.5	2.35	31
	3.65	20	2.8	26
	5	14.5	3.65	20
	6.6	11	3.2	23
123	10	7.25	2.7	27
	3	33	2.3	43
	3.3	30	2.6	38
	4	24.5	2.9	34
	5	19.5	3.5	28
148	10	9.75	3.3	30
	12.25	8	2.0	48
	3	41	2.1	59
	3.6	34	2.3	53
	5	24.5	2.7	45
	12.3	10	(^a)	>60

Final temperature (°C)	Working conditions			
	Theoretical		Actual	
	Heating rate (°C min ⁻¹)	Time (min)	Heating rate (°C min ⁻¹)	Time (min)
178	10.2	15	4.6	33
	15.3	10	4.5	34
200	3.9	45	3.4	51
	4.6	38	3.9	45
	10	17.5	4.7	37
	13.5	13	4	44
	14.5	12	(^a)	>60
220	3.9	50	3.8	51
	4.6	42.5	4.2	46
	7.2	27	4.75	41
	10	19.5	5.1	38
	14.4	13.5	(^a)	>60

(^a): Strokes lines ("---") indicate that the system, at this theoretical heating rate, fails to reach the programmed final temperature in a warm-up time of 60 min or so.

Table II. Liquid volume effect.

Final temperature (°C)	Vo-lume (cm ³)	Working conditions				
		Theoretical		Actual		
		Heating rate (°C min ⁻¹)	Time (min)	Heating rate (°C min ⁻¹)	Time (min)	
50	150	1.6	16	1.25	20	
		1.7	15	1.3	19	
		3.1	8	1.7	15	
		5	5	1.8	14	
		1.6	16	1.25	20	
123	275	1.7	15	1.3	19	
		3.1	8	1.7	15	
		5	5	1.8	14	
		3	32	2.3	42	
		4	24.5	2.9	34	
220	150	5	19.5	3.5	28	
		10	9.75	3.3	30	
		3	32	2.4	41	
		4	24.5	3.0	33	
		5	19.5	3.4	29	
	275	200	10	9.75	3.2	31
			3	32	2.5	39
			4	24.5	2.9	34
			5	19.5	3.4	29
			10	9.75	3.2	31
220	150	3.9	50	3.8	51	
		4.5	43	4.2	46	
		5	39	4.5	43	
		10	19.5	5.0	39	
		14.4	13.5	(^a)	>60	
	275	200	3.9	50	3.8	51
			4.5	43	4.3	45
			5	39	4.5	43
			10	19.5	5.1	38
			14.4	13.5	(^a)	>60

(^a): Strokes lines ("---") indicate that the system, at this theoretical heating rate, fails to reach the programmed final temperature in a warm-up time of 60 min or so.

Table III. Stirring speed effect.

Final temperature (°C)	Stirring speed (rpm)	Working conditions			
		Theoretical		Actual	
		Heating rate (°C min ⁻¹)	Time (min)	Heating rate (°C min ⁻¹)	Time (min)
75	110			2.5	20
	220			2.6	19
	330	5	10	2.5	20
	440			2.5	20
	550			2.5	20

Final temperature (°C)	Stirring speed (rpm)	Working conditions			
		Theoretical		Actual	
		Heating rate (°C min ⁻¹)	Time (min)	Heating rate (°C min ⁻¹)	Time (min)
220	110			4.9	40
	220			5.0	39
	330	10	19.5	5.1	38
	440			5.0	39
	550			5.1	38

Table IV. Effect of an inert solid addition.

Final Temperature (°C)	Solid mass (g)	Working conditions			
		Theoretical		Actual	
		Heating rate (°C min ⁻¹)	Time (min)	Heating rate (°C min ⁻¹)	Time (min)
50	0			1.8	14
	1			1.9	13
	5	5	5	1.7	15
	10			1.8	14
	0			3.4	29
123	5			3.4	29
	10	5	19.5	3.4	29
	15			3.2	31
	0			5.1	38
	1			5.0	39
220	5			5.1	38
	10	10	19.5	4.9	40
	15			4.75	41

Table V. Cooling period.

Time (min)	Cooling program temperature (°C)					
	50	75	98	123	178	220
0	50	75	98	123	178	220
1	49	74	96	117	175	218
2	47	73	94	114	172	210
3	45	71	92	110	167	203
4	44	69	90	106	161	190
5	42	67	88	104	155	181
6	41	65	86	101	149	171
7	39	62	83	98	143	161
8	38	61	79	94	138	152
9	37	59	76	91	133	142
10	35	57	71	88	128	132
11	34	54	66	78	123	121
12	33	52	62	68	116	113
13	32	49	58	58	108	105
14	31	47	55	48	101	98
15	31	45	53	42	95	86
16	30	42	51	39	90	78
17	30	39	47	37	80	69
18	29	36	43	35	68	55
19	28	33	39	34	53	46
20	28	31	36	32	42	38
21	27	29	32	29	36	35
22	26	28	29	28	31	31
23	26	27	27	27	28	27
24	25	26	26	26	26	26
25	25	25	25	25	25	25

Received: June 5, 2010

Accepted: December 2, 2010

Recommended by subject editor: Pedro Alcântara Pessôa