Hydrometallurgical extraction of Al and Si from kaolinitic clays

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Abstract

Herein is presented the results of a study on the hydrometallurgic extraction and recovery of aluminum and silicon by leaching of kaolinitic clays with HF. The studied extraction parameters were: temperature, reaction time, solid/liquid ratio, concentration, and precipitating agent mass. In the leaching process, mineral dissolutions near 100% were obtained when working at 348 K, solid/liquid ratio 2% w/v, HF 12% v/v, for 120 minutes. The HF leach liquor generated from the dissolution of kaolinitic clays contains H_2SiF_6 and H_3AlF_6. Studies were conducted to recover the two valuable fluorides as K_2SiF_6 and Na_3AlF_6 by precipitation with alkaline salts from the leach liquor. Phases of precipitated fluorides were identified by XRD and surface morphology by SEM. The purity of the K_2SiF_6 precipitate was 98.8%, whereas for Na_3AlF_6, it was 89.3%. Also, both synthesized solids are of high commercial value due to their industrial applications.

Keywords: extraction, kaolinitic clays, aluminum, synthesis, cryolite.

1. Introduction

Kaolin is a mineral widely used in different industries, among which the ceramics industry is highlighted, which uses it for the manufacture of a wide variety of products, such as tableware, sanitary ware, stoneware, tiles, electrical porcelain, ornamental ceramics and refractory (Rivera *et al*., 2016). Also, kaolin is a widespread source of aluminum, whose aluminum mass content is between 10-20%. The industrial production of aluminum is carried out by the Bayer and Hall-Herault processes, using bauxitic rocks as raw materials, which contain an aluminum mass content between 20 and 30% (Habashi, 1997).

A large number of studies have described the dissolution reaction of silicates with different inorganic acids. Terry (1983a and 1983b) classified the silicates according to their reactivity with acids in the following way: those that are not readily decomposed by acids; those from which the cations, but not the silica, can be readily dissolved; and those from which the cations and silica are readily dissolved. Further researchers studied the dissolution of metakaolin using HCl (Hulbert *et al*., 1970, Altiokka *et al*., 2003, Bazin *et al*., 2007), HNO_3 (Hulbert *et al*., 1970) and H_2SO_4 (Altiokka *et al*., 2010, Colina *et al*., 2002).

Furthermore, there are a series of studies concerning the effect of fluoride ions as additives on different acid leaching clays. Gajam and Raghavan (1985) and Bailey and Chapman (1987) looked into the effect of adding fluoride ions on the dissolution of clays with HCl, and concluded that its addition increases the dissolution rate. Adams and van Dalen (1979) found that the addition of fluorsilicic acid, leads to an increase in the dissolution rate of silicate ores with H_2SO_4. Kline and Fogler (1981) have studied the relationships between the kinetics of dissolution of silicates, and the chemical species present in aqueous hydrofluoric acid. They concluded that the measured rates of dissolution are attributed entirely to the attack by the HF molecules, rather than by F^- or HF_2^- ions. The rate of reaction is proportional to the concentration of HF molecules adsorbed at surface lattice bonds.

Kumar *et al*. (2010) reported precipitation of Na_2SiF_6 and Na_3AlF_6 from leach liquors by dissolution of low grade molybdenite ore with HCl/HF. They proposed the recovery of these compounds by increasing the pH of the solution with Na_2CO_3. Both compounds are the most common and widely used alkali fluorides in industry

(Rosales *et al*., 2013).

The hieratite (K_2SiF_6) is a compound especially used in the manufacture of special glasses and vitreous enamels, insecticides and wood preservatives. Cryolite (Na_3AlF_6) is mainly used as a flux in the production process of metallic aluminum; other minor applications are as enamel bleaches, glass opacifier and insecticide's active agent (Rosales *et al*., 2013).

Herein, a new process for the synthesis of cryolite and hieratite from leach liquor obtained by dissolution of calcined kaolin with HF is proposed, wherein the operating parameters of the dissolution reaction were optimized. Furthermore, this process can be applied to calcined kaolin and also to waste from the ceramic industry.

2. Experimental

2.1 Equipment and materials

The reagents used were HF, KCl and NaCl, all being of analytical grade. The mineral used was commercial kaolin, with particle size minor to 75 µm, extracted from "Sur del Río" deposit located in the province of Chubut (Argentina). The experimental tests were performed in a closed batch reactor of 500 mL built in Teflon®, and equipped with magnetic stirring and temperature control systems.

The sample was characterized by X-ray fluorescence (XRF) using a Philips PW 1400 equipment and X-ray diffraction (XRD) was carried out in a Rigaku D-Max III C diffractometer. Morphological analysis was done by SEM with a LEO 1450 VP microscope which was equipped with an X-ray dispersive spectrometer EDAX, Genesis 2000, used to determine the semi-quantitative composition of the synthesized compounds by EPMA analysis.

2.2 Preparation and characterization of the sample

The sample was calcined in a muffle furnace at 1073 K for 3 hours, causing its transformation from the crystalline phase kaolinite, to the amorphous phase metakaolinite; according to Gajam and Raghavan (1985) this phase exhibits greater reactivity towards acid dissolution. The characterization of the sample by thermogravimetry shows two zones of mass loss, the first zone exhibits a mass loss, between 373 and 423 K approximately, of 2% w/w that corresponds to the removal of physically adsorbed water on the kaolin surface and the second region corresponds to kaolinite dehydroxylation that begins at 723 and ends at 1073 K approximately, according to Equation (1).

$$Al_2Si_2O_5(OH)_{4(s)} \rightarrow Al_2O_3 2SiO_{2(s)} + 2H_2O_{(g)} \quad (1)$$

Kaolinite mineral is composed by tetrahedral (SiO_4) and octahedral (AlO_6) sheets. These sheets form elemental clusters based on the tetrahedral-octahedra combination. The combination among *n* elemental clusters through the hydrogen bond provided by OH^- ions of the octahedral sheet builds up the mineral structure. This structure exhibits an order along a, b, and c axes. During the process of transformation of kaolinite into metakaolinite by calcination, the hydrogen bond is broken followed by a process of dehydroxylation and a change in the co-ordination of aluminum from six to four. Order is maintained along the axes a and b, but disappears along the axis c (according to Gastuche *et al*., 1963); this alteration explains the greater reactivity of metakaolinite towards chemical reagents.

The bulk composition of the ore is shown in Table 1, as determined by XRF.

Component	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	K_2O	Na_2O	CaO	MgO	Other
% w/w	65.20	22.30	1.07	0.27	0.51	0.28	0.66	0.21	9.50

Table 1
The bulk composition of the ore.

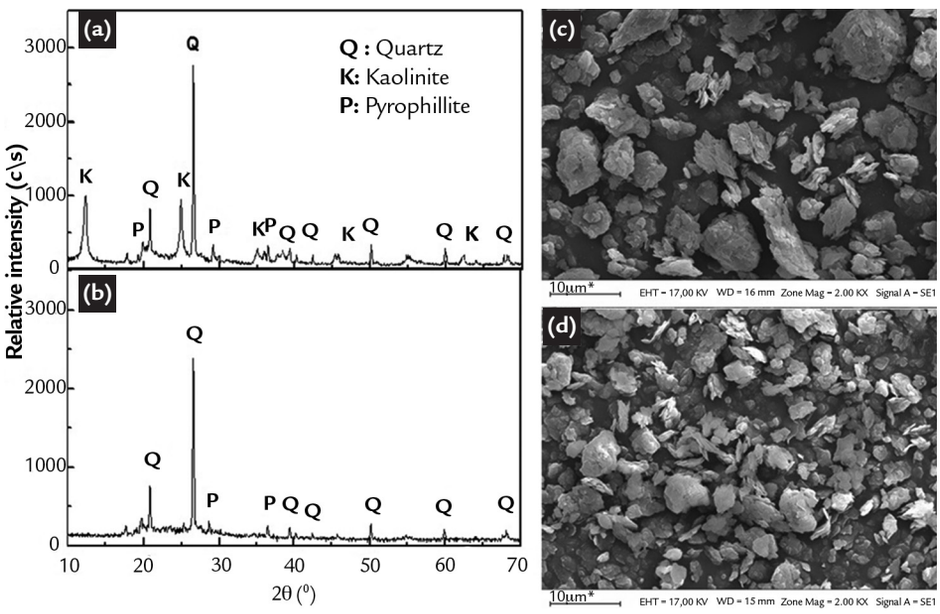

Figure 1
XRD (a) and SEM (c) of kaolin and XRD (b) and SEM (d) of metakaolin.

The ore sample was analyzed by XRD and SEM before and after the thermal treatment and the results are

shown in Figure 1. The Figure 1 (a) shows diffraction lines of kaolinite (ICDD 01-072-2300) and as accessory minerals, quartz and pyrophillite (JCPDS 033-1161 and JCPDS 012-0203, respectively). In Figure 1 (b) lines of quartz and pyrophillite can be observed more clearly because the metakaolinite does not have a crystalline structure. The morphological analysis of kaolin, Figure 1 (c), and metakaolin, Figure 1 (d), shows that both samples have particles with a laminar structure. This is because after dehydroxylation, some degree of organization is still present.

2.3 Experimental procedure

The experimental procedure was shown in Figure 2.

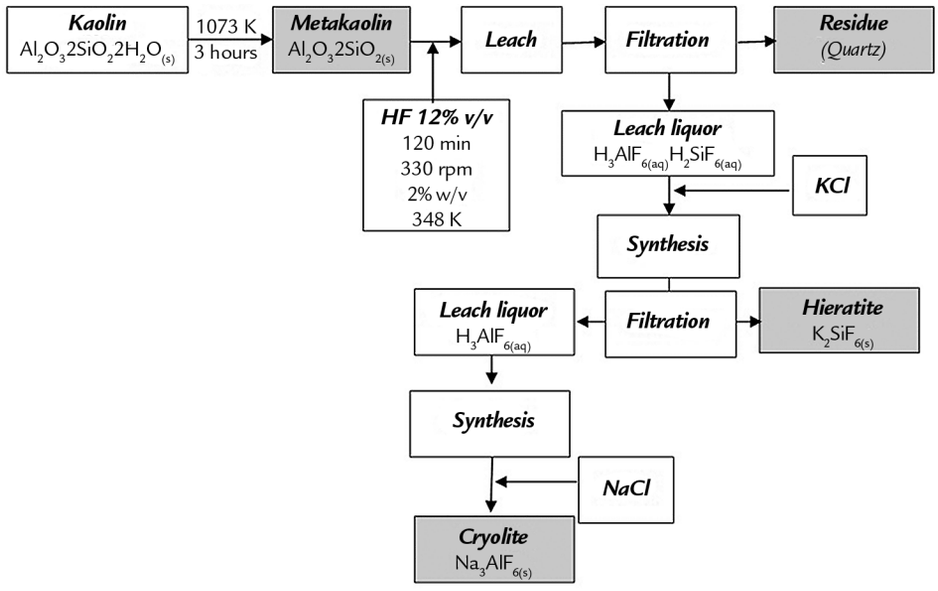

Figure 2
Flow sheet of the proposed process.

2.3.1 Leaching experiments

In accordance with the bibliography, (Rosales *et al*. 2013, 2014), we found that the dissolution reaction of metakaolin in HF occurs as follows:

$$Al_2O_3\ 2SiO_{2(s)} + 24HF_{(aq)} \longrightarrow 2H_3AlF_{6(aq)} + 2H_2SiF_{6(aq)} + 7H_2O \quad (2)$$

The dissolution efficiency (Rosales *et al*. 2013, 2014) was calculated by using Equation (3):

$$X(\%) = [(m_0 - m_r) / (m_0)]\ 100 \quad (3)$$

where: X is the dissolution efficiency; m_0 is the initial mass of the solid reactant and m_r is the mass that remains unreacted after the reaction.

The studied parameters were: concentration of HF (6-15% v/v), temperature (288-363 K), reaction time (0-120 min) and solid/liquid ratio (1-5% w/v) at two temperatures (308 and 348 K).

2.3.2 Recovery experiments

The leach liquor used for the synthesis was prepared by leaching metakaolin with HF, within the optimal operational variables, as studied in section 3.1 "Leaching of metakaolin". Recoveries of Al and Si from the leach liquor were performed via chemical precipitation with alkaline salts. The studied parameter was the precipitating agent's mass.

The recovery tests were conducted in two steps; in the first one, the precipitation of Si was studied by adding KCl, according to reaction step 1. This salt was precipitated as K_2SiF_6 and then separated by filtration. The second step was performed with the liquor obtained in step 1 (without Si) by addition of NaCl as reaction step, in order to precipitate Na_3AlF_6.

Step 1: Recovery of silicon

$$2KCl_{(s)} + H_2SiF_{6(aq)} + H_3AlF_{6(aq)} \rightarrow K_2SiF_{6(s)} + H_3AlF_{6(aq)} + 2HCl_{(aq)} \quad (4)$$

Step 2: Recovery of aluminum

$$3NaCl_{(s)} + H_3AlF_{6(aq)} \rightarrow Na_3AlF_{6(s)} + 3HCl_{(aq)} \quad (5)$$

3. Results and discussion

3.1 Leaching of Metakaolin

3.1.1 Effect of concentration leaching agent

Tests for leaching metakaolin with different concentrations of HF were performed at: 348 K, 330 rpm and 60 min. The leaching agent (HF) concentrations used were: 6, 8, 10, 12 and 15% v/v. The results shown in Figure 3 a), demonstrate that when the HF concentration increases, the metakaolin dissolution also increases, which is because more reagents are available to react with the mineral and form the products (Habashi, 1980), and the plateau of this curve is reached at an HF concentration value of 12% v/v. The greatest dissolution of the calcined mineral was obtained by leaching with HF at 12% v/v. It is worth mentioning that high mineral dissolutions are achieved with HF 6% v/v. For the following assays, the concentration of HF used was 12% v/v.

3.1.2 Effect of reaction temperature

The dissolution tests for studying the effect of temperature were performed under the following conditions: concentration of HF 12% v/v; reaction time 60 min; stirring speed, 330 rpm and solid-liquid ratio, 2% v/w. The results are presented in Fig. 3 b), an augmentation in the temperature increases the dissolution of the mineral; 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. In addition the increase of the temperature increases the reactivity of the solid and the solubility of the formed products (Habashi, 1980 and Quiroga *et al*., 1996, Rosales *et al*., 2013, Rodriguez *et al*., 2015). Even though higher leaching, around 92%, is obtained at temperatures above 348 K, important extractions, about 70%, are also achieved at room temperature, 298 K (Habashi, 1980 and Quiroga *et al*., 1996). This is of great importance for carrying out the process on a larger scale because energy consumption decreases considerably in the mineral dissolution step.

3.1.3 Effect of reaction time

The experiments were carried out at 348 K, 330 rpm, 2% w/v solid/liquid ratio and 12% v/v HF. The results of test performances are shown in Figure 3 c). It can be observed that for the same leaching temperature, increased reaction time leads to an increase in the dissolution of metakaolin. Therefore, the increase in the contact time between solid and fluid phases increases the dissolution of the mineral (Habashi, 1980, Quiroga *et al*., 1996 and Rodriguez *et al*., 2004 and 2015). The maximum value of dissolution, 96%, was obtained in 120 min of reaction. Additionally, important dissolutions of the mineral (around 90%) working at lower reaction times (< 60 min) are achieved.

3.1.4 Effect of solid/liquid ratio

Experiments were performed with a solid/liquid ratio in the range of 1 to 5% w/v, while other parameters remained constant at the following values: temperature, 308 K; HF concentration, 12% v/v; reaction time, 30 min and stirring speed 330 rpm. The obtained results are plotted in Figure 3 d) and show that at a low solid/liquid ratio, dissolution of the solid is high. These results were expected since the magnitude of the complexation depends not only on the values of the formation constants but also on the concentration of the active form of the complexing reagent (Inczédy, 1976, Rodriguez *et al*., 2004). Therefore, with increasing solid/liquid ratios the available, concentration of the complexing agent is lower, and the magnitude of dissolution decreases. In addition, the extraction for the S/L ratio to 2% w/v corresponding to 30 min and 308 K, is lower than its analogue at 348 K and 60 min, although the operating conditions at which this leaching value is obtained, considerably decreases energy consumption not only with the operating parameter related with the temperature increase but indirectly with the stirring speed parameter, since the reaction time is lower. In addition, operating at a lower temperature and time decreases the corrosion of the equipment.

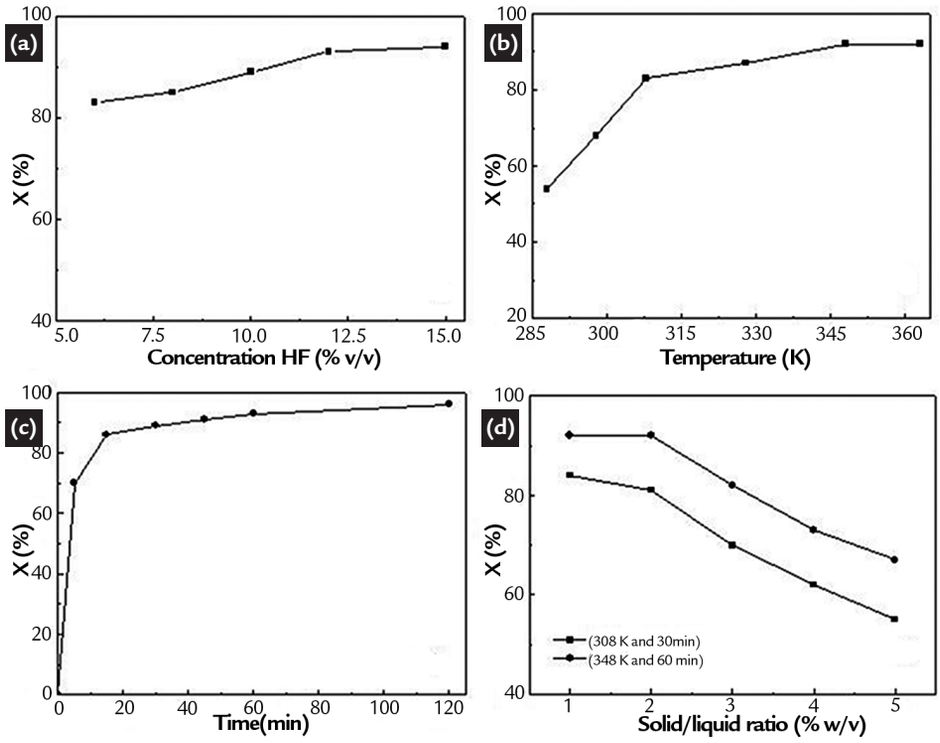

Figure 3
Effect of: a) concentration, b) temperature, c) time and d) solid/liquid ratio on the dissolution of metakaolin.

3.2 Recovery of Al and Si

The leach liquor used in the assays for the recovery and synthesis of compounds of aluminum and silicon was performed using the data obtained from the study of operating parameters "section 3.1. Leaching metakaolin". The selected operating conditions were: 50 g of metakaolin were dissolved in 2.5 L of a solution of HF obtaining a mineral dissolution of 96%.

To determine the recovery values of K_2SiF_6 and Na_3AlF_6, precipitation tests were carried out by adding different amounts of KCl and NaCl to the leach liquor, in a range above and below the stoichiometric values necessary for the occurrence of the reactions of the steps 1 and 2. The assays were performed by adding KCl in the first step; thus synthesizing hieratite. After all the silicon was recovered, NaCl was added to precipitate cryolite.

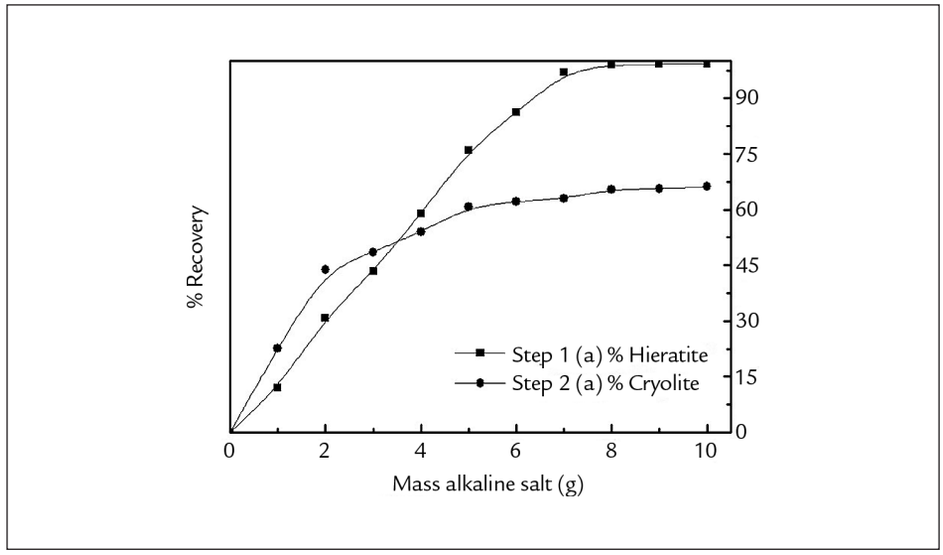

Figure 4
(a) Step 1, effect of KCl addition and (b) step 2, effect of NaCl addition.

In Figure 4, it can be seen that increasing the addition of the mass of both the salts, leads to an increase in the recovery of Si and Al. The best recoveries of Si, > 99% as hieratite, are obtained by adding amounts of KCl greater than 7 g. Whereas for Al, the best recoveries for cryolite (70%) are obtained by adding a NaCl mass greater than 6 g.

In Figures 5 a) and b), the characterizations by XRD and SEM of the solids obtained in step 1 are shown. It can be observed that the only crystalline structure present corresponds to hieratite, K_2SiF_6, (ICDD 01-085-1382) as proposed; whereas, in the micrograph, it is seen that the particles have an isometric hexoctahedral shape with sharp edges, coinciding with the crystalline structure of the hieratite. In Figures 5 c) and d), characterizations of the solids obtained in step 2 are presented; XRD shows that the only crystal structure detected corresponds to cryolite, Na_3AlF_6 (ICDD 01-082-0217) and SEM analysis shows that these particles have a monoclinic prismatic shape and well defined edges.

The resulting compounds Na_3AlF_6 and K_2SiF_6 were analyzed by microanalysis EPMA and XRF to determine the purity of the solid precipitates. Table 2 shows the purity of these compounds.

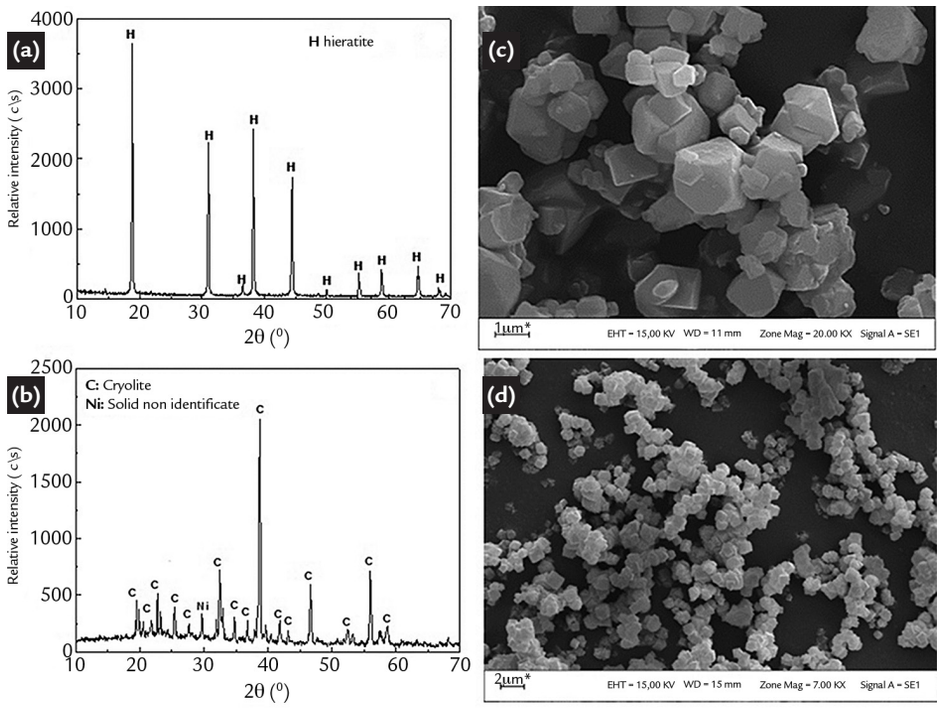

Figure 5
a) XRD and c) SEM of solid precipitated step 1, b) XRD and d) SEM of solid precipitated step 2.

Figure	Compounds	Purity	%F	%Na	%K	%Si	%Al	%O	%Fe	Other
5c)	K_2SiF_6	98.8	47.00	---	35.30	16.70	1.20	---	0.40	0.60
5d)	Na_3AlF_6	89.3	40.01	33.80	1.80	2.50	15.69	4.20	0.21	1.79

Table 2
Analysis of the solid precipitate Figs. 5 (c) and (d) in atom %.

The results shown in Table 2 are in agreement with the analysis by XRD (Figures 5a and c). Furthermore, it was established that the precipitate in step 1 (hieratite) solid has a purity of 98.8% and the compound obtained in step 2 (cryolite) has a purity of 89.3%. Kumar *et al.*, 2010 obtained a precipitate of Na_2SiF_6 (malladrite) and Na_3AlF_6 (cryolite) from the leach liquors of low-grade molybdenite containing alumino-silicates. The near complete recovery of Na_2SiF_6 and the cryolite was found to be contaminated with sodium ferric-fluoride and recovery about 95%. Rosales *et al.* 2013 obtained, by precipitation with NaOH, a mixture of cryolite and malladrite, from spodumene liquors, achieving a recovery of 92% of aluminum and silicon.

The high purity hieratite and technical grade cryolite obtained with the leach liquor from metakaolin with HF, is presented. These products, K_2SiF_6 and Na_3AlF_6, have numerous industrial applications, as already mentioned in the introduction. In addition, the SiO_2 generated as a byproduct, is used as an abrasive agent in the cutting of rocks, as well as a flux in smelting operations. Also, it is used for manufacturing porcelain and sandpaper.

4. Conclusions

From the experimental results, it can be inferred that the dissolution process of metakaolin with HF is an efficient way to extract Al and Si. The best obtained value of the mineral dissolution, 96%, was achieved, working at 330 rpm, HF concentration of 12% v/v, solid/liquid ratio of 2% w/v for 120 min and 348 K. The recovery of aluminum and silicon by the chemical precipitation methodology with alkali salts is a viable method, achieving 99% recovery of silicon, as hieratite with a purity of 98.8% and about 70% aluminum, as cryolite, with an 89.3% purity.

References

ADAMS, M.J., Van DALEN, E. Effect of adding fluoride on the sulphuric acid extraction of alumina from silicate ores. ***Light Met.,*** W.S. Peterson (Ed.), TMS, p.205-216, 1979.

ALTIOKKA, M.R., AKALIN, H., MELEK, N., AKYALÇIN, S. Investigation of the dissolution kinetics of meta-kaolin in H_2SO_4 solution. ***Ind. Eng. Chem. Res.,*** v.49, p.12379-12382, 2010.

ALTIOKKA, M.R., HOŞGÜN, H.L. Investigation of the dissolution kinetics of kaolin in HCl solution. ***Hydrometallurgy,*** v.68, p.77-81, 2003.

BAILEY, N.T., CHAPMAN, R.J. The use of coal spoils as feed material for alumina recovery by acid leaching routes V: the effect of fluoride additions on the extraction of aluminum with hydrochloric acid. ***Hydrometallurgy,*** v.18, p.337-350, 1987.

BAZIN, C., EL-OUASSITI, K., OUELLET, V. Sequential leaching for the recovery of alumina from a Canadian clay. ***Hydrometallurgy,*** v.88, p.196-201, 2007.

COLINA, F.G., ESPUGLAS, S., COSTA, J. High-temperature reaction of kaolin with sulfuric acid. ***Ind. Eng. Chem. Res.,*** v.41, p.4168-4173, 2002.

GAJAM, S.Y., RAGHAVAN, S. A kinetic model for the hydrochloric acid leaching of kaolinite clay in the presence of fluoride ions. ***Hydrometallurgy,*** v.15, p.143-158, 1985.

GASTUCHE, M.C., TOUSSAINT, F., FRIPIAT, J.J., TOUILLEAUX, R., Van MEERSCHE, M. Study of intermediate stages in the kaolin → metakaolin transformation. ***Clay Miner.,*** v.5, p. 227-236, 1963.

HABASHI, F. ***Principles of Extractive Metallurgy,*** v I. New York: Gordon and Breach Science Publishers Inc., 1980.

HABASHI, F. ***Handbook of Extractive Metallurgy.*** Germany: Wiley-VCH, 1997.

HULBERT, S.F., HUFF, D.E. Kinetics of alumina removal from a calcined kaolin with nitric, sulphuric and hydrochloric acids. ***Clay Miner.,*** v.8, p.337-345, 1970.

INCZÉDY, J. ***Analytical applications of complex equilibria.*** Budapest: Ellis Horwood, 1976.

KLINE, W.E., FOGLER, H.S. Dissolution of silicate minerals by hydrofluoric acid. ***Ind. Eng. Chem. Fundam.,*** v.20, p.155-161, 1981.

KUMAR, M., NANI BABU, M., MANKHAND, T.R., PANDEY, B.D. Precipitation of sodium silicofluoride (Na_2SiF_6) and cryolite (Na_3AlF_6) from HF/HCl leach liquors of alumino-silicates. ***Hydrometallurgy,*** v.104, p.304-307, 2010.

QUIROGA, O.D., AVANZA, J.R., FUSCO, A.J. ***Modelado cinético de las transformaciones fluido-sólido reactivo.*** Argentina: EUDENE, 1996. (In Spanish).

RIVERA, O., PAVEZ, O., LI KAO, J., NAZER, A. Metallurgical characterization of kaolin from Atacama, Chile. ***REM: Int. Eng. J.,*** v.69, 4, p.473-478, 2016.

RODRIGUEZ, M.H., RIVAROLA J., RUIZ, M. C. The effects of carboxylic acid addition on hydrofluoric acid autoclave leaching of a ferrocolumbite. ***Hydrometallurgy***, v.74, p.39-46, 2004.

RODRIGUEZ, M.H., ROSALES, G.D., PINNA, E.G., SUAREZ, D.S. Extraction of niobium and tantalum from ferrocolumbite by hydrofluoric acid pressure leaching. ***Hydrometallurgy,*** v.156, p.17-20, 2015.

ROSALES, G.D., RUIZ, M. C., RODRIGUEZ, M.H. Alkaline metal fluoride synthesis as a subproduct of β–spodumene leaching. ***Hydrometallurgy,*** v.139, p.73-78, 2013.

ROSALES, G.D., RUIZ, M. C., RODRIGUEZ, M.H. Novel process for the extraction of lithium from β-spodumene by leaching with HF. ***Hydrometallurgy,*** v.147, p.1-6, 2014.

TERRY, B. The acid decomposition of silicate minerals. Part I: reactivities and modes of dissolution of silicates. ***Hydrometallurgy,*** v.10, p.135-150, 1983a.

TERRY, B. The acid decomposition of silicate minerals. Part II: hydrometallurgical applications. ***Hydrometallurgy,*** v.10, p.151-171, 1983b.

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