Short communication

Potassium chloride production by microcline chlorination

Pablo Orosco[a,b,*], María del Carmen Ruiz[a]

[a] Instituto de Investigaciones en Tecnología Química (INTEQUI), Chacabuco y Pedernera, San Luis, Argentina
[b] Facultad de Química, Bioquímica y Farmacia, Universidad Nacional de San Luis, Chacabuco y Pedernera, San Luis, Argentina

ABSTRACT

The potassium chloride is one of the most important fertilizers used in agriculture. The current demand of this salt makes interesting the study of potassium chloride production from unconventional potassium resources. In this work the potassium chloride production by chlorination of microcline was investigated. The starting reagents were microcline, hydromagnesite and chlorine.

Non-isothermal and isothermal chlorination assays were carried out in a thermogravimetric device adapted to work in corrosive atmospheres. The temperature effect on potassium extraction and the phase transformations produced during chlorination of microcline were studied. The reagents and reaction products were analyzed by X-ray fluorescence (XRF) and X-ray diffraction (XRD). The experimental results indicated that by chlorination of microcline an important extraction of potassium in the temperature range from 800 to 900 °C was produced. Moreover, at 800 °C the forsterite, enstatite and magnesium aluminate spinel phases were generated.

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1. Introduction

Nowadays, the fertilizers have an important role in the efficient production of agricultural products. Potassium chloride (KCl) is one of the most important fertilizers as it supplies potassium to plants, which is an essential element for most of them. This salt performs the function of activating numerous enzymes from vegetal cells. Moreover, it is the main osmotic potential contributor due to its abundance in the cells. Worldwide, the potassium chloride is employed mainly in the fertilizer industry and in less extent in chemical industry for manufacturing hydroxides, carbonates and nitrates. In Argentina, the use of KCl is limited to the agricultural sector. This country is a great consumer of potassium chloride; however, it does not have a big production of this salt. At the present, Argentina imports potassium chloride, mainly from Germany and Canada, principal producers of this salt [1,2].

Argentina has deposits of KCl located in the south of Mendoza province and in the north of Neuquén province. In these deposits, the potassium chloride contains impurities such as NaCl, CaSO$_4$ and clays. The methods of purification and concentration used are washing and attrition, flocculation with polyacrylamide, and crystallization and flotation [2,3].

Taking into account the small amount of deposits in Argentina and the cost of processing involved in the commercial elaboration of potassium chloride, it is interesting to study new methodologies to process KCl from deposits and the use of other potassium sources.

Several researchers have studied the potential use of rocks rich in K such as K-feldspars, micas and feldspathoids as potassium sources. The extraction of potassium was carried out through processes of crushing, milling and leaching using HNO$_3$ as leaching agent. However, the results obtained showed a low efficiency in extracting this metal [4–6]. Kleiv and Thornhill [7] have used mechanical activation and leaching with distilled water and HNO$_3$ to extract potassium from nepheline syenite and microcline, reaching a considerable metal recovery. Despite the efficient extraction that was achieved, this method requires a high quantity of energy.

The pyrometallurgical process of chlorination can be an alternative way for extracting potassium as KCl from microcline. This method has been effectively used in the extraction of various metals of oxides and minerals in the last decades. This is due to the high reactivity of the chlorinating agent, the selectivity of the reaction, simple treatment of effluents, and low cost of the processes [8–10].

The main aim of this work is to study the feasibility of producing potassium chloride by chlorination of microcline.

2. Experimental procedures

2.1. Materials and procedure

The solid reagents used in this work were microcline from San Luis, Argentina, supplied by *Minera Piedra Grande S.A.* and hydromagnesite p.a. quality, provided by Sigma–Aldrich.

The gases used in the different thermal treatment analysis were chlorine 99.5%, supplied by Cofil, Argentina and nitrogen 99.99% provided by Air Liquide, Argentina.

The minerals were mixed in a ratio of 70% (w/w) of hydromagnesite and 30% (w/w) of microcline. This ratio was established in order to generate new phases that promote reactivity of the chlorine with the potassium. The preparation of the mixture, denominated M, was made in a disk mill, and the mixing time was 4 min.

The chemical composition of the minerals and the M sample was determined by X-ray fluorescence (XRF). The results obtained are presented in Table 1.

The primary minerals which are present in the mixture under study were identified by X-ray diffraction (XRD). The diffractogram of the M sample (Fig. 1) shows the presence of the crystalline phases microcline and hydromagnesite.

2.2. Equipment

The experimental chlorination assays were performed in a thermogravimetric system designed in our laboratory [11]. The device is provided of a quartz reactor placed inside an electric furnace equipped with a temperature controller.

The measurement system of mass is an analytical scale (Mettler Toledo AB204-S/FACT, maximum sensitivity of 0.0001 g) connected to an automatic data logger.

The X-ray diffraction analysis of reactants and reaction products was performed on a Rigaku D-Max-IIC equipment with Cu Kα, operated at 35 kV and 30 mA. The composition of microcline and hydromagnesite mixture and the chlorination residues were determined by X-ray fluorescence using a Philips PW 1400 equipment.

2.3. Procedure

Isothermal and non-isothermal chlorination assays were carried out using masses of approximately 1 g of powder sample. For the different thermal treatments, flows of 50 ml/min of N_2 and 100 ml/min of Cl_2/N_2 (50%, v/v) were used.

In each non-isothermal experiment, the samples were calcined in the gaseous mixture Cl_2/N_2 (50%, v/v) at a heating rate of 5 °C/min until a temperature of 900 °C was reached. The mass change was recorded as a function of temperature.

In each isothermal assay, the reaction temperature was set and N_2 fed into the reactor. Once this temperature was reached, the sample was placed inside of the reactor and the Cl_2/N_2 (50%, v/v)

Table 1
Chemical composition (%, w/w) of the starting minerals and M sample.

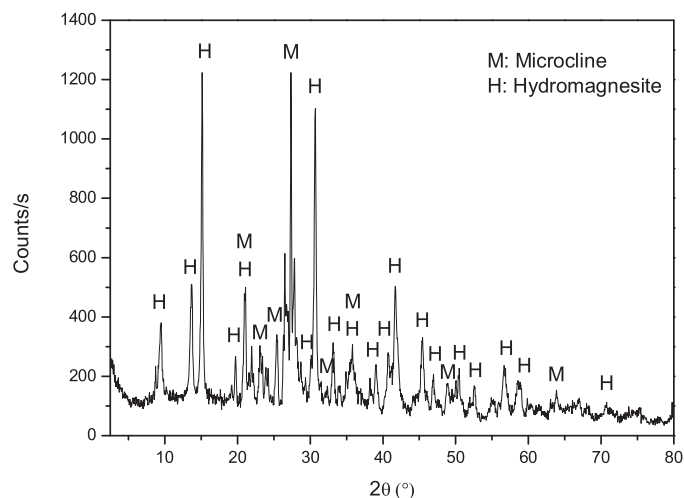|	Mineral		Sample
	Microcline	Hydromagnesite	M
Al_2O_3	20.87	–	6.26
SiO_2	67.70	–	20.31
K_2O	10.45	–	3.14
CaO	0.19	–	0.06
MgO	–	43.10	28.01
Fe_2O_3	0.70	–	0.02
LOI	–	56.90	39.94

Fig. 1. M sample diffractogram.

was allowed to flow during a reaction time of 15 min. When this period of time was over, the flow of Cl_2 was interrupted, and the sample was purged with N_2 while the reactor was cooled down.

2.4. Additional trials

Isothermal chlorination assays were carried out between 650 and 900 °C in Cl_2/N_2 (50%, v/v) atmosphere during 120 min to determine the optimum temperature for potassium chloride production.

2.5. Washing and filtration of the chlorination residues

All the residues from the isothermal chlorination assays performed to reaction times of 15 min and 120 min were subjected to processes of washing and filtration with water at room temperature in order to remove the chlorides generated during the reaction. Then, the residues obtained were dried in an oven at 100 °C. In some cases, the filtering liquid was evaporated in an oven at 100 °C.

The washed and dried residues, corresponding to a chlorination period of 15 min were analyzed by XRD. Also, the crystallized solid from evaporation of filtering liquid obtained by washing of the chlorination residue of the M sample at 700 °C was analyzed by XRD.

The washed and dried residues from the chlorination assays performed during 120 min were analyzed by XRD and XRF.

3. Results and discussion

The results of non-isothermal calcination assays performed in Cl_2/N_2 mixture are shown in Fig. 2.

The thermogravimetric curve of M sample presents three zones of mass change. The first and second zones correspond to the phenomena which produce mass losses, whereas a mass gain occurs in the third zone. The first region can be observed in the range between 90 and 360 °C. The second zone takes place in the range between 360 and 480 °C. The last region can be noted between 700 and 900 °C.

With the purpose of clarifying the phenomena that may occur during thermal treatments in Cl_2, additional isothermal assays in Cl_2/N_2 mixture were performed in the temperature interval ranging from 360 to 900 °C. The residues of these assays were analyzed by XRD. Fig. 3 shows the diffractograms of the
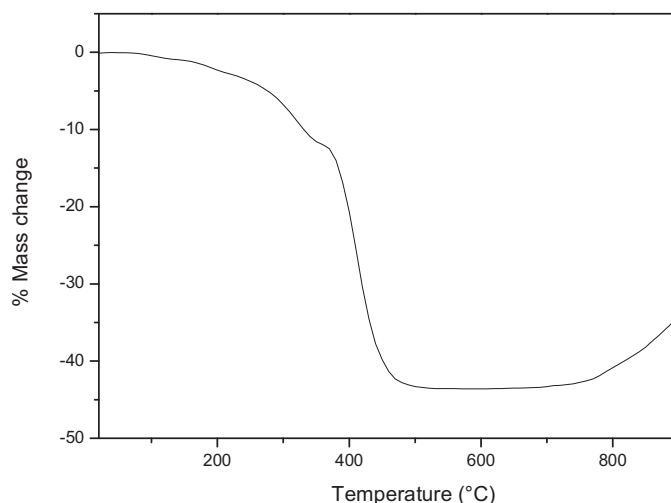
Fig. 2. Thermogram corresponding to the M sample calcined in Cl_2/N_2.

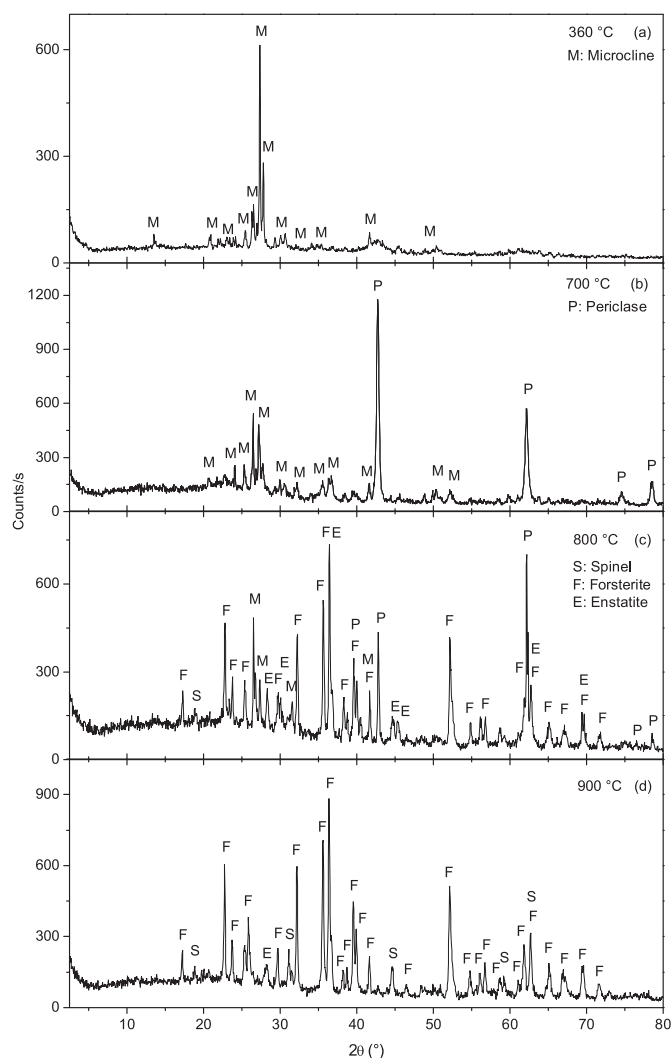chlorination residues obtained at different temperatures and reaction times of 15 min.

Fig. 3. Diffractograms of the chlorination residues of the M sample at different temperatures and reaction times of 15 min.

3.1. First zone of mass change (90–360 °C)

This region corresponds to dehydration and partial decomposition of hydromagnesite, which generated magnesite.

This can be deduced from the results shown in Fig. 3a, where the disappearance of hydromagnesite phase is observed as a result of a partial release of water vapor and carbon dioxide of the hydromagnesite structure.

3.2. Second zone of mass change (360–480 °C)

The second zone of mass loss observed in the thermogram of Fig. 2 corresponds to the thermal decomposition of magnesite generated by reaction (1):

$$MgCO_3 \rightarrow MgO + CO_2(g) \tag{1}$$

This phenomenon can be deduced from the results shown in Fig. 3b. The diffractogram shows the appearance of periclase as a consequence of magnesite decomposition.

3.3. Third zone of mass change (700–900 °C)

The changes that took place in this mass gain region can be explained using diffractograms of residues calcined at 800 and 900 °C in a Cl_2 atmosphere (Fig. 3c and d). The results of the analysis performed by XRD allowed to infer the occurrence of the following phenomena:

3.3.1. Generation of $MgCl_2$ by reaction between periclase and Cl_2

This region corresponds to periclase chlorination, according to reaction (2):

$$MgO + Cl_2(g) \rightarrow MgCl_2 + \frac{1}{2}O_2(g) \tag{2}$$
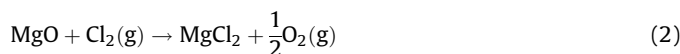
$$\Delta G° = (0.024T - 12.65)(kcal/mol\ MgCl_2)$$

The formation of the non-volatile $MgCl_2$ could be observed in Fig. 2 as mass gain starting at 700 °C. This phenomenon is corroborated using the solid from evaporation of filtering liquid obtained by washing of the chlorination residue of the M sample at 700 °C (Fig. 4). The XRD pattern of this solid shows the presence of $MgCl_2$ which is the product of the chlorination of periclase.
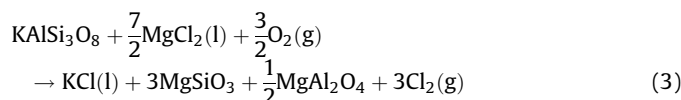
The chlorides shown in Fig. 4 are hydrated because they suffer a hydration process after being extracted from the reactor.
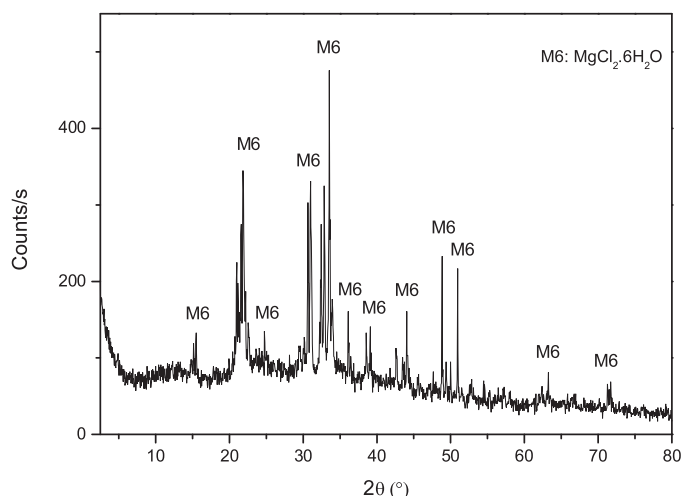
Fig. 4. Diffractogram of solid from the evaporation of filtering liquid obtained by washing the M sample chlorination residue at 700 °C.


Fig. 5. Diffractogram corresponding to the residue of the mixture KAlSi$_3$O$_8$/MgCl$_2$ calcined in air at 800 °C.

3.3.2. Chlorination of microcline

Liquid MgCl$_2$ (melting point 714 °C [12]) and O$_2$(g), produced by periclase chlorination react with microcline at 800 °C, generating liquid potassium chloride, enstatite, magnesium aluminate spinel and chlorine, according to reaction (3).

$$KAlSi_3O_8 + \frac{7}{2}MgCl_2(l) + \frac{3}{2}O_2(g)$$
$$\rightarrow KCl(l) + 3MgSiO_3 + \frac{1}{2}MgAl_2O_4 + 3Cl_2(g) \qquad (3)$$

$$\Delta G° = (0.008T - 9.057)(kcal/mol\ MgCl_2)$$

Subsequently, enstatite reacts with MgCl$_2$(l) and O$_2$(g), producing forsterite and releasing chlorine (reaction (4)).

$$MgSiO_3 + MgCl_2(l) + \frac{1}{2}O_2(g) \rightarrow Mg_2SiO_4 + Cl_2(g) \qquad (4)$$
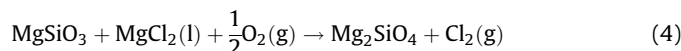
$$\Delta G° = (0.017T - 7.77)(kcal/mol\ MgCl_2)$$

The presence of chlorine prevents magnesium chloride from being transformed into periclase. This assumption was confirmed experimentally by the calcination of a mixture MgCl$_2$/microcline with a ratio of 1:1 at 800 °C for 15 min in air (50 ml/min). The XRD pattern of the calcined mixture is shown in Fig. 5. The presence of periclase phase confirms that in absence of Cl$_2$, MgCl$_2$ reacts with oxygen to form periclase.

The occurrence of the reactions (3) and (4) has been verified by the diffractogram of the residue corresponding to the sample calcined at 800 °C (Fig. 3c). The figure shows the phases generated in the products. Forsterite, enstatite and magnesium aluminate spinel phases can be observed in this figure, which confirms the proposed reaction mechanism for the microcline chlorination.

In addition, a new calcination assay of a mixture MgCl$_2$/enstatite with a ratio of 1:1 at 800 °C, in Cl$_2$/air (50%) flow with a rate of 50 ml/min was carried out to prove the reaction (4). Fig. 6 shows the phases generated during the mixture chlorination. The appearance of forsterite indicates the occurrence of the chlorination reaction between enstatite, oxygen and MgCl$_2$ at 800 °C.

The synthesis of forsterite and magnesium aluminate spinel continues until the final investigated temperature. This can be seen in the diffractograms of the residues obtained at 800 and 900 °C (Fig. 3c and d) as temperature rises, the peaks intensities corresponding to forsterite and magnesium aluminate spinel
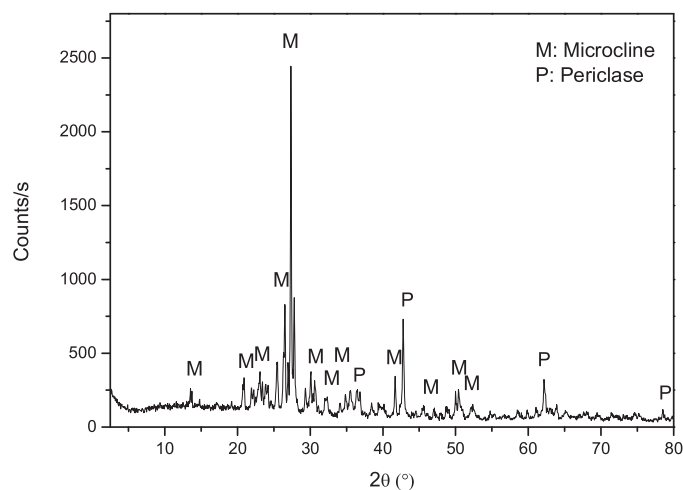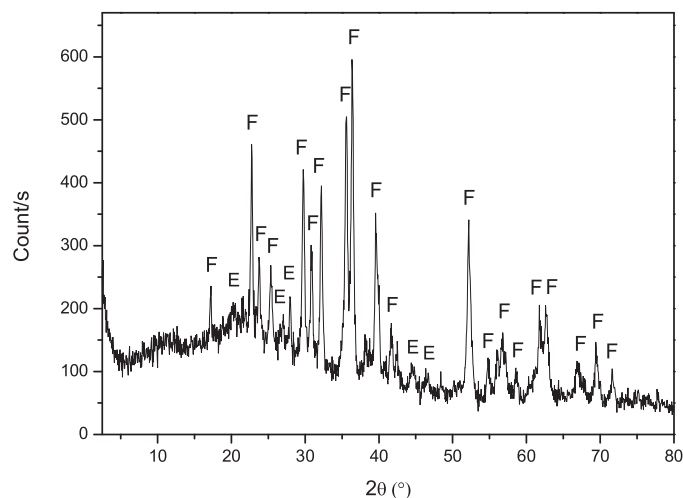
Fig. 6. Diffractogram corresponding to the residue of the mixture MgCl$_2$/MgSiO$_3$ calcined in Cl$_2$/air at 800 °C.

phases increase. Moreover, the disappearance of several of the peaks corresponding to enstatite was observed in this temperature range.

3.4. Analysis of potassium in chlorination residues

Fig. 7 shows the results of the potassium analysis performed by XRF on M residues which result from the chlorination at different temperatures for 120 min and treated as indicated by Section 2.5.

The extraction of potassium from microcline starts at about 700 °C. At 750 °C and 800 °C, the extraction is 35% (w/w) and 80% (w/w), respectively. The chlorination of microcline (reaction (3)) is complete at 800 °C, which favors the potassium recovery. This fact can be corroborated with the diffractogram as shown in Fig. 8 that indicates the disappearance of microcline phase and the appearance of forsterite, enstatite, and magnesium aluminate spinel phases. At 900 °C, the extraction of potassium is 93% (w/w).

The Purity of KCl was determined through the XRF analysis performed on the crystallized solid obtained after washing of the sample chlorinated at 900 °C for 120 min. The results indicate that the purity is 63%; this is due to the mixing of the product KCl with the MgCl$_2$ not consumed by reaction (4).

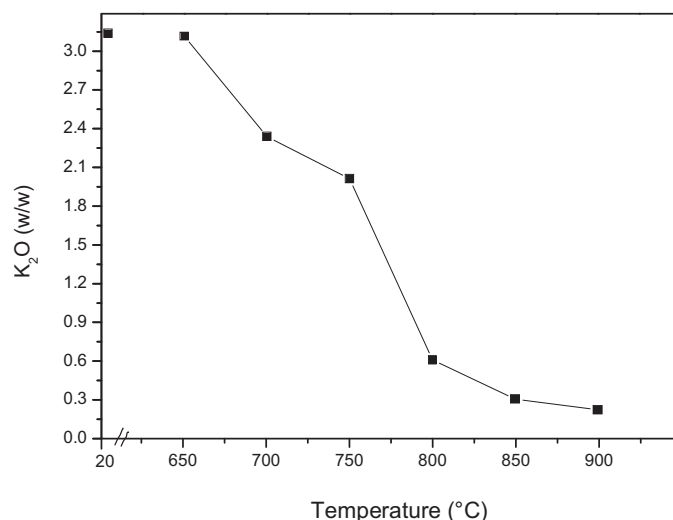**Fig. 7.** K$_2$O in residues of the M sample chlorinated at different temperatures.
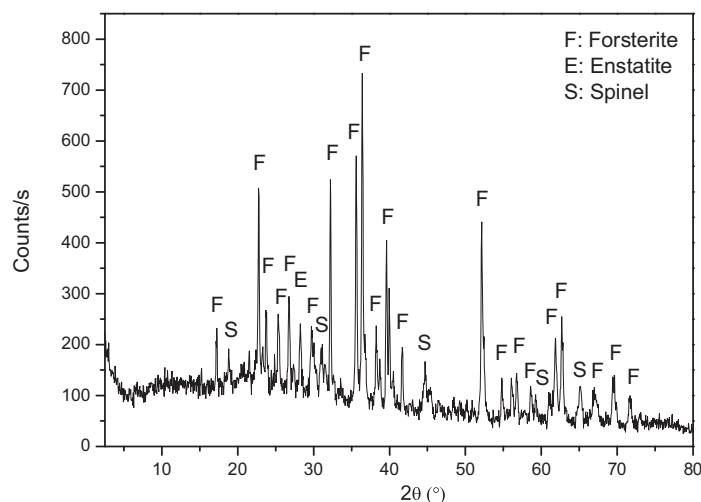

Fig. 8. Diffractogram of the chlorination residue of the M sample at 800 °C and reaction time of 120 min.

4. Conclusions

The pyrometallurgical process of chlorination investigated has demonstrated to be an efficient method for the production of potassium chloride. The experimental results indicate that in temperature range between 800 and 900 °C a considerable recovery of potassium as KCl is reached. At 900 °C the extraction of potassium is about 93% (w/w). Moreover, at this temperature interval forsterite, magnesium aluminate spinel and enstatite phases are produced as a consequence of microcline chlorination.

Acknowledgments

References

[1] A. Colombo, Panorama Minero, Suplemento 344 (2008) .

[2] SEGEMAR-UNSAM, Sales. Seminario de estudios sobre el ciclo de minerales-materiales, 3 al 5 de diciembre de 2003, Buenos Aires, publicación técnica N° 9.

[3] M. Balod, Proyecto potasio Río Colorado. Recursos minerales de la República Argentina, Vol. II, SEGEMAR 35 (1999) 1077–1081.

[4] H. Gautneb, A.K. Bakken, Crushed rocks, minerals and mine tailings as sources of potassium in agriculture, Nor. Geol. Unders. 427 (1995) 119–122.

[5] A.D. Harley, R.J. Gilkes, Factors influencing the release of plant nutrients from silicate rock powders: a geochemical overview, Nutr. Cycling Agroecosys. 56 (2000) 11–36.

[6] M. Heim, Norwegian rock powder in (organic) agriculture: history, status quo, challenges and possibilities, Nordisk Mineral Symposium, 23–24 April, Trondheim, 2001, pp. 16–21.

[7] R.A. Kleiv, M. Thornhill, Production of mechanically activated rock flour fertilizer by high intensive ultrafine grinding, Miner. Eng. 20 (2007) 334–341.

[8] F.M. Túnez, P. Orosco, J.A. González, M. del C. Ruiz, Kinetic study on the chlorination of indium oxide, Thermochim. Acta 524 (2011) 151–156.

[9] R.P. Orosco, M. del C. Ruiz, J.A. González, Purification of talcs by chlorination and leaching, Int. J. Miner. Process. 101 (2011) 116–120.

[10] L.I. Barbosa, G. Valente, R.P. Orosco, J.A. González, Lithium extraction from β-spodumene through chlorine gas chlorination, Miner. Eng. 56 (2014) 29–34.

[11] F.M. Tunez, J. González, M. del C. Ruiz, Aparato de Laboratorio para Realizar Termogravimetrias en Atmosferas Corrosivas y no Corrosivas, P060100450, 2007.

[12] HSC Chemistry for Windows Software V. 5.1, 2003. Outokumpu Research, Pori, Finland.