Extraction of Potassium from Microcline by Chlorination

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Abstract: A pyrometallurgical route for the extraction of potassium from microcline was investigated. The reagents used were microcline, calcite and chlorine gas. Isothermal and non-isothermal chlorination assays were performed using experimental equipment adapted for working in corrosive atmospheres. The effects of temperature and reaction time on the chlorination reaction of the microcline-calcite mixture were studied. The reaction mechanism was also investigated. The techniques used to characterize reagents and products were thermogravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM), and electron probe microanalysis (EPMA). The experimental results showed that the extraction of potassium in the form of KCl begins at 700 °C for 15 min. Anorthite also starts to be produced under these conditions. The optimum conditions for quantitative extraction of potassium and selective formation of anorthite were 900 °C for 60 min.

1. Introduction

Potassium is the third major plant and crop nutrient after nitrogen and phosphorus. This element plays an important role in a number of physiological processes essential to growth, development, stress resistance, yield, and quality of crops [1]. On Earth, potassium is the seventh most abundant element, comprising about 2.6% of the crust volume [2]. However, most of the potassium is incorporated in the crystal lattice structure of minerals and thus not directly available for plant uptake. By contrast, soluble potassium resources are scarce [3]. The most abundant K-bearing minerals are microcline ($KAlSi_3O_8$), muscovite ($KAl_3Si_3O_{10}(OH)_2$), and biotite ($K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$) [4].

Microcline is very difficult to decompose by conventional chemical methods due to the high stability of its structure [5]. Several methods have been developed to extract soluble potassium from microcline, including roasting [6,7], hydrothermal processes [8,9], bioleaching [10,11], and leaching [5,12,13]. However, these processes encounter some disadvantages such as high processing temperature, high energy consumption [6,7], generation of secondary phases during the process [8,9], long reaction times [10,11] or the requirement of expensive reagents and equipment [5,12,13]. Therefore, it is necessary to develop a simple, selective, and low-cost technique to extract soluble potassium from microcline. Previous work carried out in our research group on minerals chlorination using magnesium carbonate and chlorine gas showed that potassium chloride was extracted during chlorination of a microcline and hydromagnesite mixture, with forsterite and magnesium aluminate spinel being generated as well [14].

In this work, the chlorination of microcline using calcite and chlorine gas as reagents was studied with the purpose of extracting quantitative potassium and obtaining anorthite ($CaAl_2Si_2O_8$), a ceramic material used in electronic and refractory industries.

2. Materials and Methods

2.1. Materials

The minerals used in this work were microcline and calcite, both from San Luis, Argentina. The gases used in the different assays were chlorine gas 99.05% *v/v* (Cofil, Argentina) and nitrogen 99.99% *v/v* (AGA, Argentina). The mixture of the minerals, denominated Mi, was prepared in a ratio of 65% *w/w* of microcline and 35% *w/w* of calcite. The minerals were mixed in a disk mill for 4 min. This ratio was selected, taking into account the reactivity of chlorine gas with calcite and microcline mixture. The reaction of Mi chlorination is represented by the following reaction:

$$CaCO_3 + 2KAlSi_3O_8 + Cl_2(g) \rightarrow CaAl_2Si_2O_8 + 2KCl + 4SiO_2 + CO_2(g) + 0.5O_2(g) \qquad (1)$$
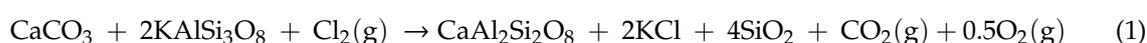
The chemical composition of the minerals and the Mi sample are shown in Table 1. The crystalline phases present in Mi are shown in Figure 1.

Table 1. Chemical composition (%*w/w*) of the starting minerals and the mixture of the minerals (Mi).

	Mineral		**Sample**
	Microcline	**Calcite**	**Mi**
Al_2O_3	20.91	-	13.52
SiO_2	67.93	-	44.12
K_2O	10.28	-	6.72
CaO	0.18	55.94	19.58
Fe_2O_3	0.68	-	0.42
LOI	-	44.02	14.36
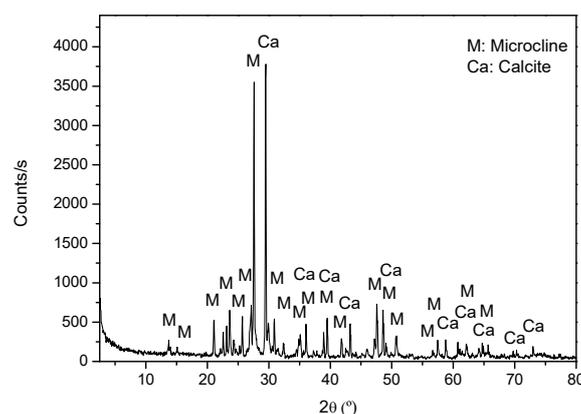
Figure 1. XRD pattern of the Mi sample.

Data on Table 1 indicates that the microcline used has a high degree of purity. In addition, this ore contained a high percentage of potassium.

The X-ray diffractogram (XRD) pattern of the minerals mixture shows the presence of two crystalline phases (microcline and calcite). SEM images of Mi sample are shown in Figure 2. The particles marked with the symbols □ and ○ in Figure 2a,b were identified by electron probe microanalysis (EPMA) (Table 2) as microcline and calcite particles, respectively. The size of the particles of Mi sample is varied. Microcline has a particle size distribution from 3 to 20 μm and calcite has a particle size distribution from 5 to 70 μm.
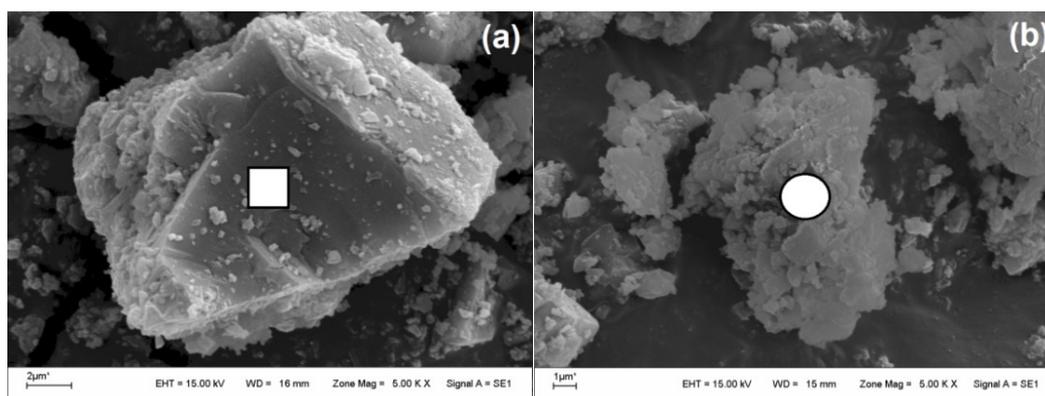
Figure 2. SEM micrographs corresponding to Mi sample: (**a**) microcline particle, (**b**) calcite particle.

Table 2. Electron probe microanalysis (% atomic) corresponding to particles present in Mi sample.

Particle	Al	Si	Ca	K	O
Microcline (□)	10.32	34.73	-	8.71	46.23
Calcite (○)	-	-	38.62	-	46.86

2.2. Equipment

The experimental chlorination assays were performed in a thermogravimetric system designed in our laboratory [15]. This device includes a quartz reactor placed inside an electric furnace equipped with a temperature controller.

The chemical composition of the minerals and the mixture, as well as the residues from thermal treatment of the mixture in chlorine, was determined by XRF using Philips PW 1400 X-ray equipment (Philips, Almelo, The Netherlands). The analysis by XRD on mixture and chlorination residues was performed on a Rigaku D-Max-IIIC (Rigaku Co., Tokyo, Japan), Cu-Ka, which was operated at 40 kV, 30 mA.

2.3. Calcination Procedure

The assays in the thermogravimetric system were carried out using approximately 0.5 g masses of powder sample. For the thermal treatment, flows of 100 mL/min of Cl_2/N_2 (50% *v/v*) were used.

2.3.1. Procedure for Non-Isothermal Chlorination

In each non-isothermal experiment, the samples were calcined in a 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.

2.3.2. Procedure for Isothermal Chlorination

In each isothermal assay, the sample was placed inside the reactor and calcined in a N_2 atmosphere at a heating rate of 5 °C/min, until the working temperature was reached. Once this temperature was stabilized, $Cl_2(g)$ was fed into the reactor, generating the Cl_2/N_2 (50% *v/v*) mixture. The sample was kept under this atmosphere during the reaction time. Subsequently, the $Cl_2(g)$ flow was interrupted, and the sample was purged with N_2 while the reactor was cooled down.

The isothermal assays were conducted in the temperature range between 500 and 900 °C and periods of reaction from 15 to 120 min.

2.3.3. Washing and Filtration of the Chlorination Residues

The residues of these chlorination assays were subjected to washing and filtration with hot water in order to remove calcium chloride present in the chlorinated sample. The residues obtained were then dried in an oven at 100 °C. The washed and dried residues of filtration were analyzed by XRD.

3. Results

3.1. Non-Isothermal Thermogravimetry in Cl_2/N_2

The results of the non-isothermal treatment of the Mi sample in Cl_2/N_2 flow are shown in Figure 3a. The thermogravimetric curve of the sample presents two mass change regions. The first region can be observed in a temperature range between 420 and 700 °C, and corresponds to a mass gain of 2.9% approximately. The second region occurred in the range between 700 and 900 °C, and is associated with a mass loss of approximately 2.3%. This zone corresponds to a balance between mass gain and loss occurring in the sample as a consequence of phenomena taking place within this temperature interval.
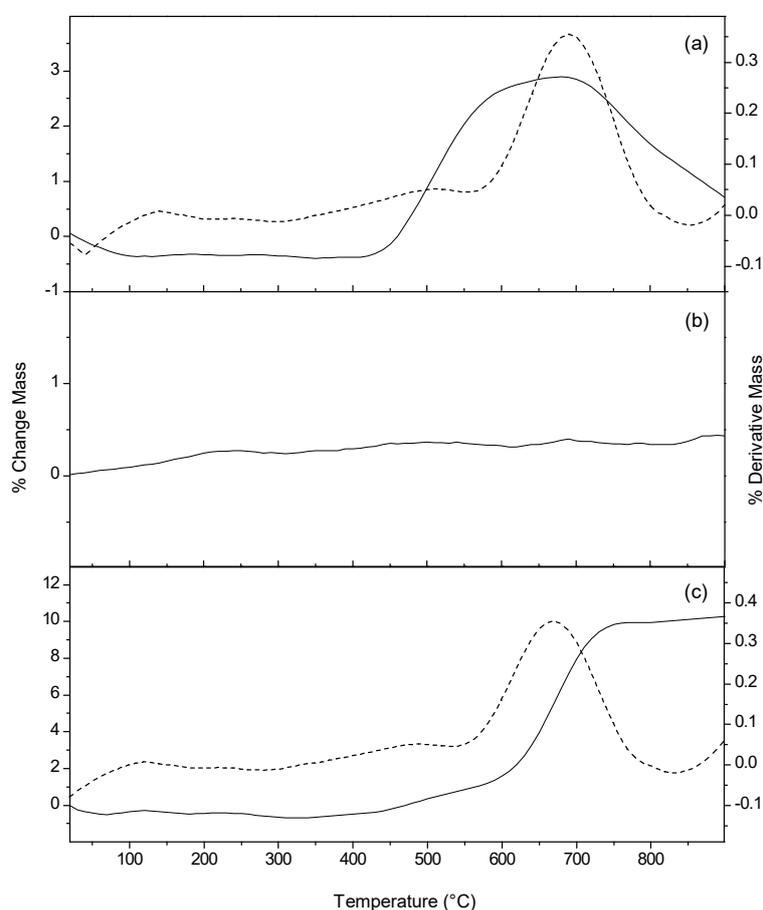
Figure 3. Thermogravimetric and derivative thermogravimetric curves corresponding to different samples calcined in $Cl_2(g)$: (**a**) Mi, (**b**) microcline and (**c**) calcite.

With the purpose of determining the phenomena that take place during the non-isothermal calcination of Mi in $Cl_2(g)$, non-isothermal chlorination assays of microcline and calcite, and isothermal chlorination assays of Mi at different temperatures for 15 min were carried out. The chlorination residues were then analyzed by XRD.

3.1.1. First Zone of Mass Change (420–700 °C)

The first region of mass loss observed in the thermogram of Figure 3a corresponds to the chlorination of calcite according to Reaction (2).

$$CaCO_3 + Cl_2(g) \rightarrow CaCl_2 + CO_2(g) + 0.5O_2(g) \tag{2}$$
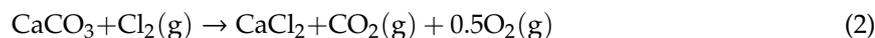
The occurrence of this reaction was demonstrated using the thermograms of calcite and microcline (Figure 3b,c), and the XRD pattern corresponding to the chlorination residue of the Mi sample at 600 °C without the filtration and washing treatments (Figure 4).
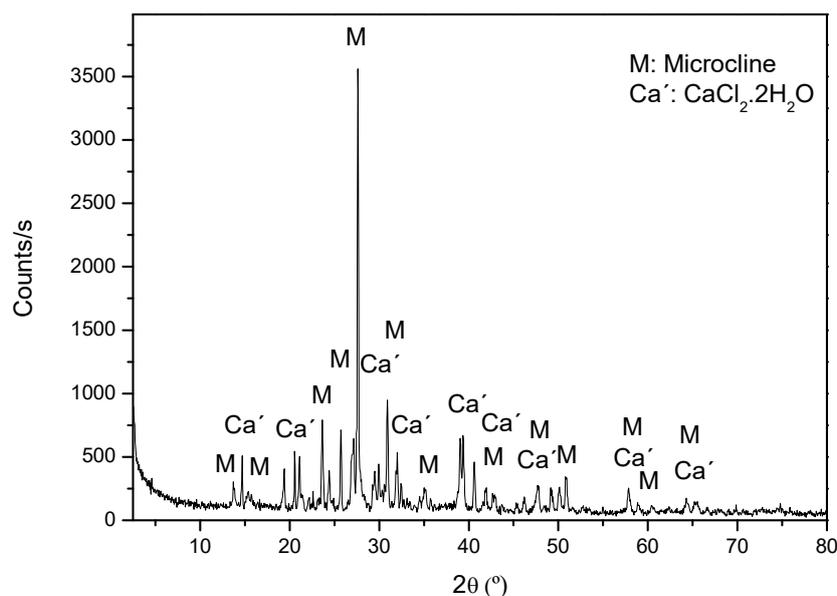
Figure 4. XRD pattern of the chlorination residue of the Mi sample at 600 °C for 15 min without filtration and washing treatments.

In the thermogram of microcline (Figure 3b) the mass remained constant, while in the thermogram of calcite (Figure 3c) a mass increase was observed, which was attributed to calcium chloride formation.

The XRD pattern of the untreated chlorination residue (Figure 4) shows the presence of microcline and calcium chloride, which are the product of calcite chlorination (Reaction (2)). This chloride is hydrated because it suffers a hydration process after being extracted from the reactor.

3.1.2. Second Mass Change Zone (700–900 °C)

The phenomena that occur in this region are described by the following Reaction (3):

$$CaCl_2 + 2KAlSi_3O_8 \rightarrow CaAl_2Si_2O_8 + 2KCl + 4SiO_2 \tag{3}$$
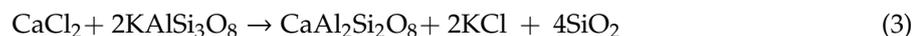
Potassium Extraction from Microcline

This phenomenon was corroborated using the thermograms of Mi, microcline and calcite. Comparison of the thermogravimetric curves indicates that the mass remains constant between 700 and 900°C in the thermogram of microcline, while the thermograms of calcite and Mi showed mass gain and mass loss, respectively.

The behavior of mass with temperature in Figure 3b indicates that chlorine gas does not react with microcline. The mass gain observed in Figure 3c was due to the formation of calcium chloride. The mass loss in Figure 3a was the result of a balance between the partial volatilization of KCl and the calcite chlorination (Reaction (2)). The volatilization of KCl was caused by the formation of a eutectic mixture between KCl and $CaCl_2$ not consumed by Reaction (3). In the flow system used in this work,

the volatile KCl generated was removed from the reaction zone, favoring the chlorination reaction of microcline, and the formation of more volatile KCl.

Anorthite Synthesis from Microcline and Calcium Chloride

The calcium chloride produced by calcite chlorination (Reaction (2)) reacted with the microcline generating anorthite (Reaction (3)).

The reaction was experimentally proved by the XRD patterns of the residues corresponding to the calcined sample between 700 and 900 °C (Figure 5a–c). The figures show the anorthite, quartz and microcline phases, which confirms the proposed reaction mechanism for the synthesis of anorthite.
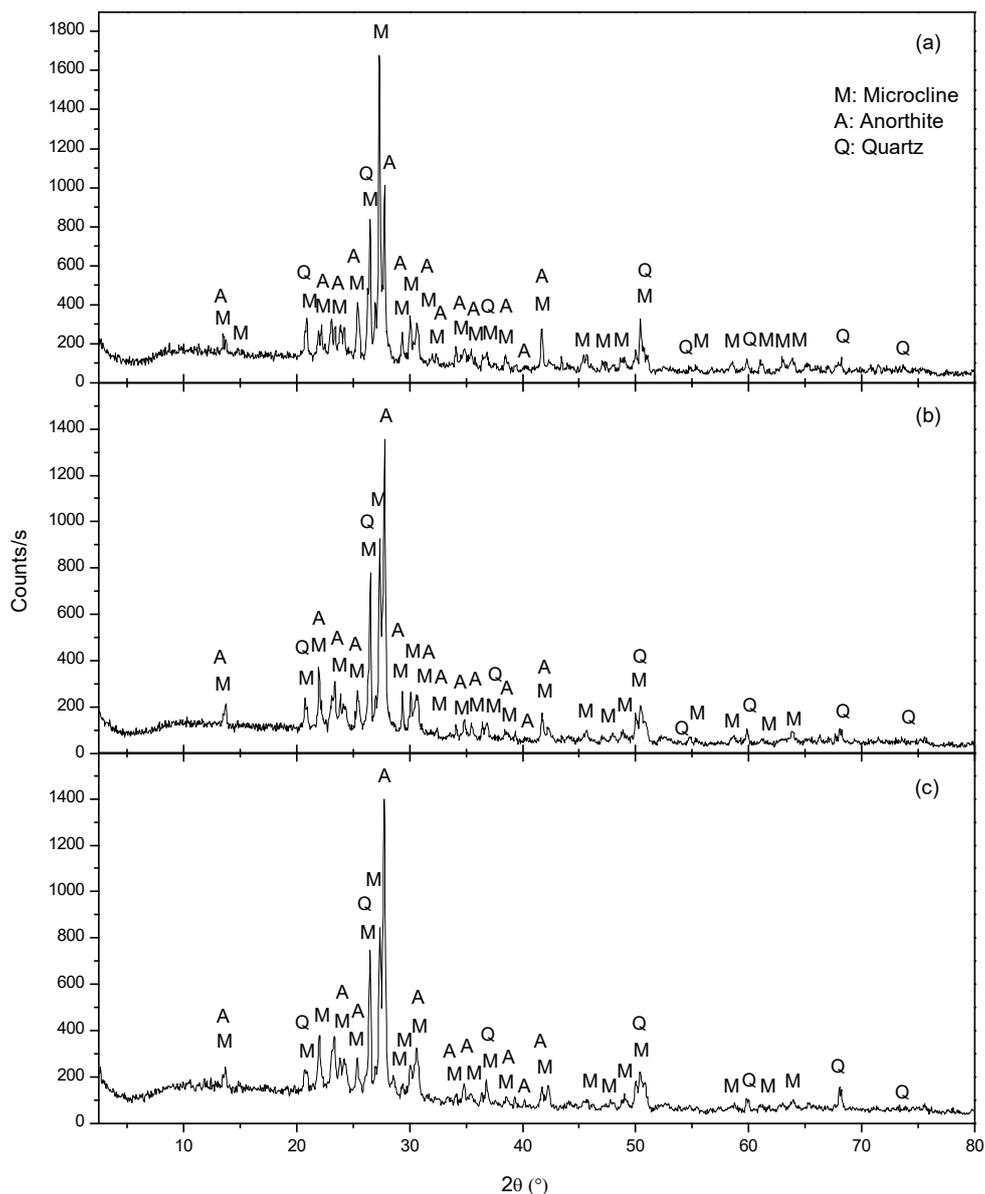
Figure 5. XRD patterns of the chlorination residue of the Mi sample at: (**a**) 700 °C, (**b**) 800 °C, (**c**) 900 °C and periods of 15 min.

3.2. XRF Analysis of Mi in Cl$_2$/N$_2$

The results of the XRF analysis performed on sample Mi and the residues chlorinated at different temperatures and reaction times are presented in Figures 6 and 7.
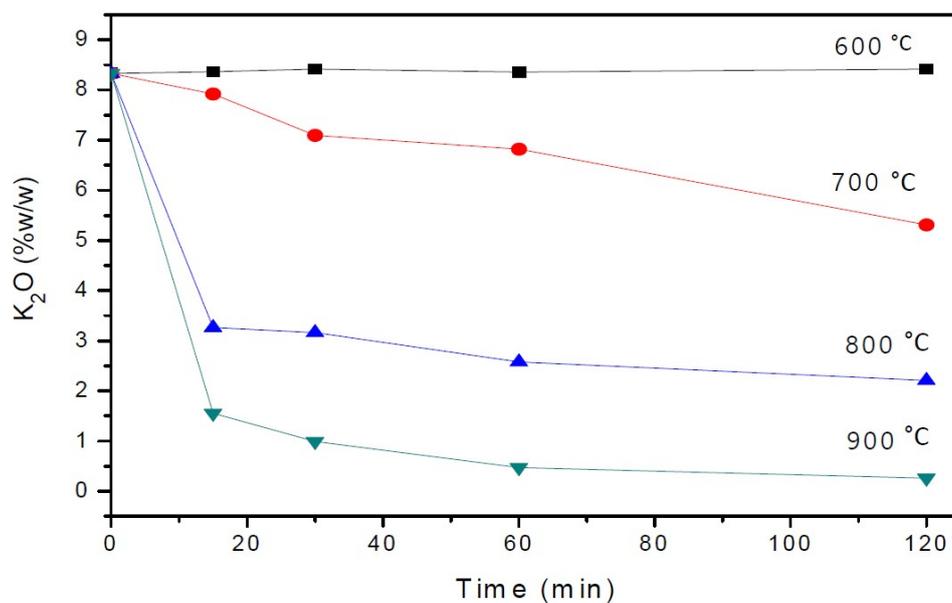
Figure 6. Content of K_2O in residues of the M1 sample calcined in $Cl_2(g)$ at different temperatures and reaction times.
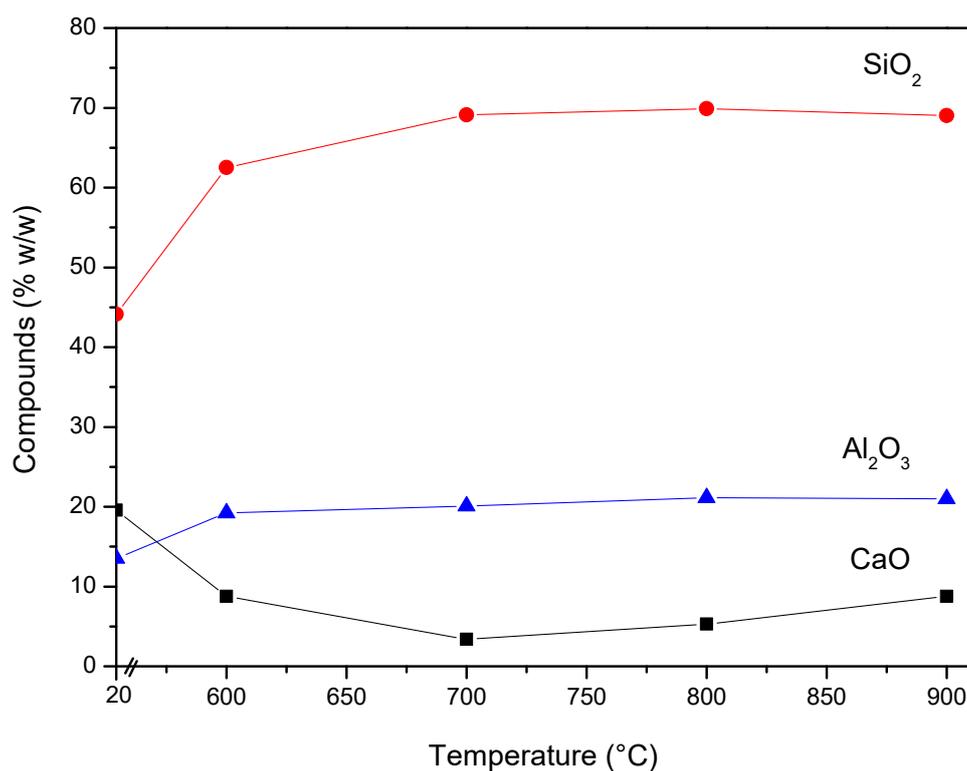
Figure 7. Content of SiO_2, Al_2O_3 and CaO in residues of the Mi sample calcined in $Cl_2(g)$ at different temperatures for 120 min.

The data shown in Table 1 and Figure 6 indicated that the content of potassium in the starting sample (6.72% *w/w*) was less than the content of potassium in the chlorination residue calcined at 600°C (8.36% *w/w*). This is due to the fact that the CaCl$_2$ not consumed by reaction (3) was removed by processes of washing and filtering, which generates a relative increase in the content of potassium in the residues. Therefore, comparison of the potassium content in the stoichiometric mixture without CaCl$_2$ excess (Reaction (1)), which was (8.33% *w/w*), with that in the chlorination residues is necessary to

determine the starting temperature for potassium extraction. Thus, it could be inferred that potassium extraction starts at 700 °C. It can be noted that a considerable increase in potassium extraction was produced in the temperature range between 700 and 800 °C. These results can be attributed to the fact that $CaCl_2$ (melting point 762 °C) changes from solid to liquid state, which favors reaction (3). At 900 °C a quantitative recovery of potassium was produced, reaching an extraction extent of 97% *w/w* for periods of 120 min.

The figure also shows that the highest level of potassium extraction was produced at 800 and 900 °C during the first 15 min.

In addition, the effect of chlorine gas and temperature on sample Mi causes changes in the concentration of SiO_2, Al_2O_3 and CaO as shown in Figure 7. These changes are the result of a balance between mass gain and loss occurring in the sample as a consequence of the phenomena which take place during the chlorination. On the other hand, the process of washing and filtration carried out on chlorination residues after the thermal treatment affected the concentration of these compounds in Mi. The chlorination residue of Mi at 600 °C showed an increase in the concentration of SiO_2 and Al_2O_3 and a decrease in the concentration of CaO in relation to sample Mi, which results from the removal by washing and filtering of the calcium chloride generated by Reaction (2). Between 700 and 900 °C, the concentration of CaO increased significantly with temperature mainly due to the formation of anorthite. In this temperature interval, the concentration of SiO_2 and Al_2O_3 remained constant, which is a consequence of two phenomena: the extraction of potassium from Mi and the anorthite synthesis.

3.3. Conditions for Efficient Extraction of Potassium and Selective Formation of Anorthite

The quantitative extraction of potassium from microcline was produced at 900°C for 60 min according to the data obtained by XRF (Figure 6).

Phase evolution during anorthite synthesis was investigated using the XRD patterns of chlorination residues at different temperatures and reaction times (Figure 8).

Figure 8a,d show that anortithe formation in the presence of chlorine starts at 700 °C and continue until the final investigated temperature. This can be inferred by comparing the XRD patterns of the chlorination residues of the Mi sample obtained between 700 and 900 °C and different periods of time, since the intensity of typical peaks of anorthite increases with temperature.

The disappearing of typical peaks of microcline occurred at 900 °C for 60 min (Figure 8c) and a significant crystallization of anorthite was observed at 900 °C for 120 min (Figure 8d). This indicates that anorthite formation is selective at 900 °C for the time period range of 60 to 120 min.

SEM micrographs of the anorthite obtained at 900 °C and a reaction time of 60 min are shown in Figure 9. In the SEM image of Figure 9a, a large number particles of irregular shape and varied size can be observed. Figure 9b reveals that anorthite particles are porous.

The obtained results indicate that the optimum conditions of chlorination for the extraction of potassium from microcline and synthesizing anorthite is 900 °C for 60 min, while for longer periods of time a significant recovery of potassium was not observed and for shorter periods of time anorthite was not selectively formed.

With the aim of determining the effect of $CaCl_2$ on microcline, a calcination assay of a mixture microcline/$CaCl_2$ in a ratio 65/35 (%*w/w*) at 900 °C for 60 min, in N_2 (100 mL/min) was carried out. The XRD pattern of the calcined mixture is shown in Figure 10.
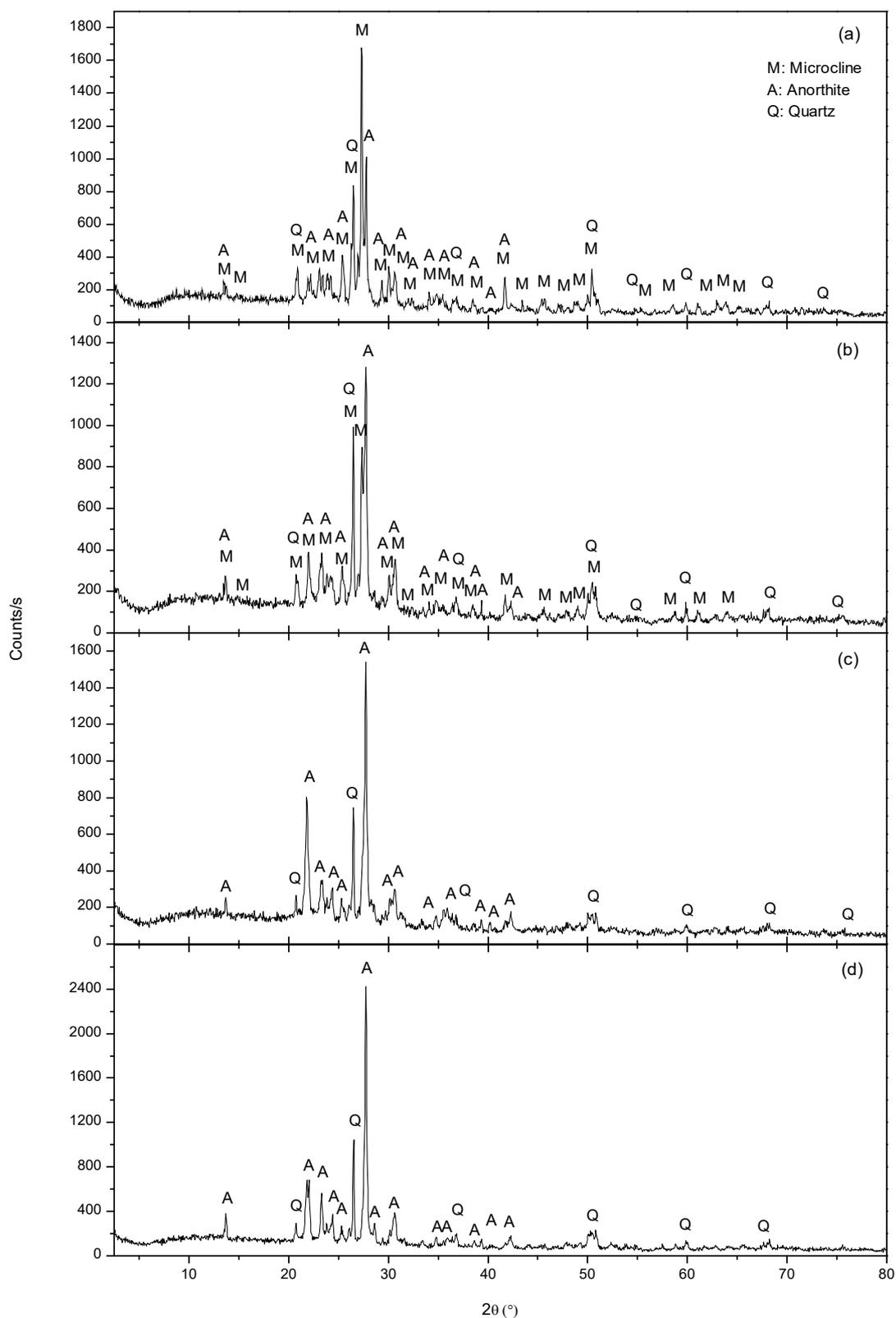
Figure 8. XRD patterns of Mi sample calcined in Cl₂(g): (**a**) 700 °C for 15 min, (**b**) 800 °C for 60 min, (**c**) 900 °C for 60 min, (**d**) 900 °C for 120 min.
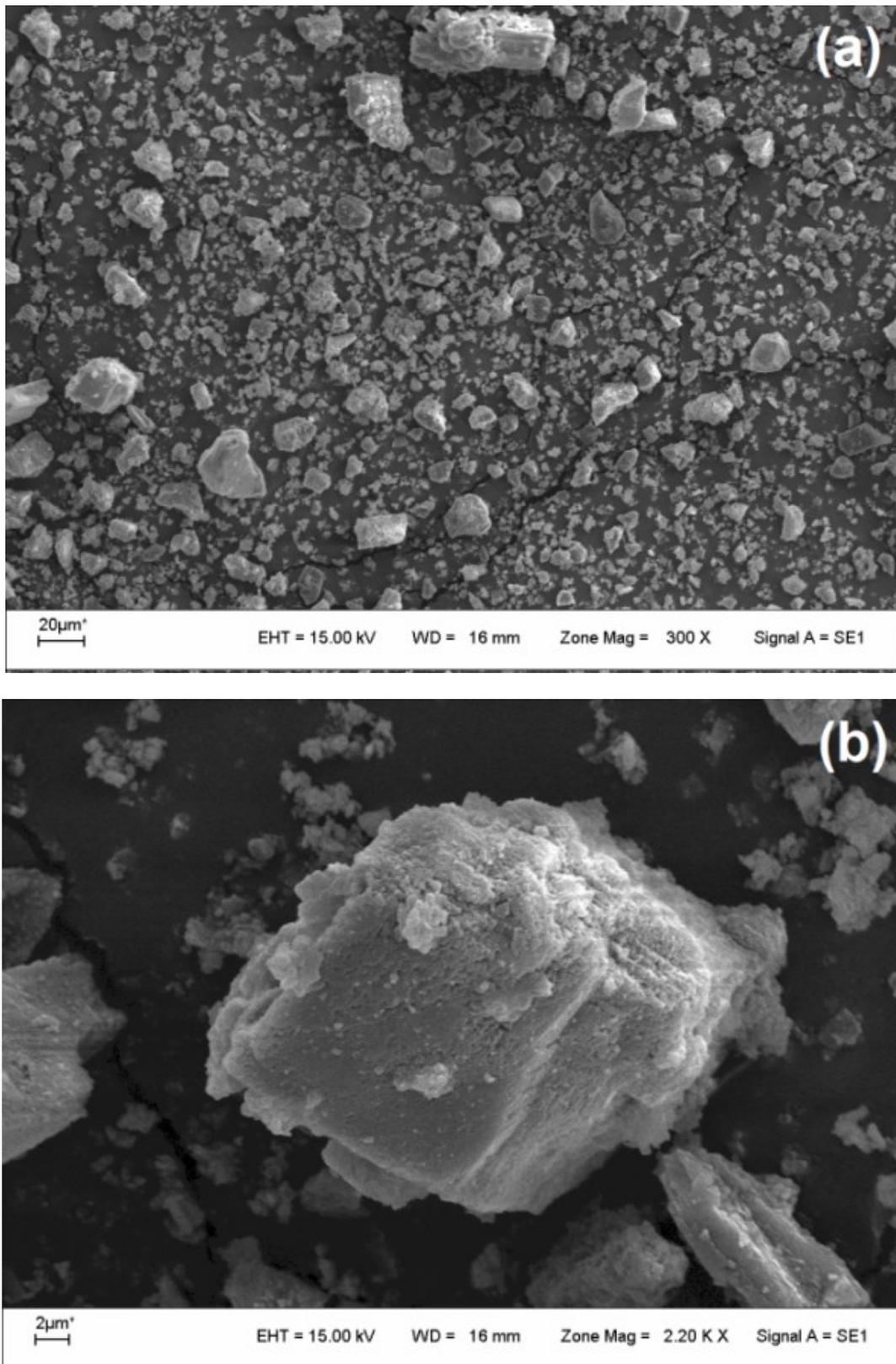
Figure 9. SEM micrographs of the anorthite obtained at 900 °C for 60 min: (**a**) overall view, (**b**) anorthite particle.
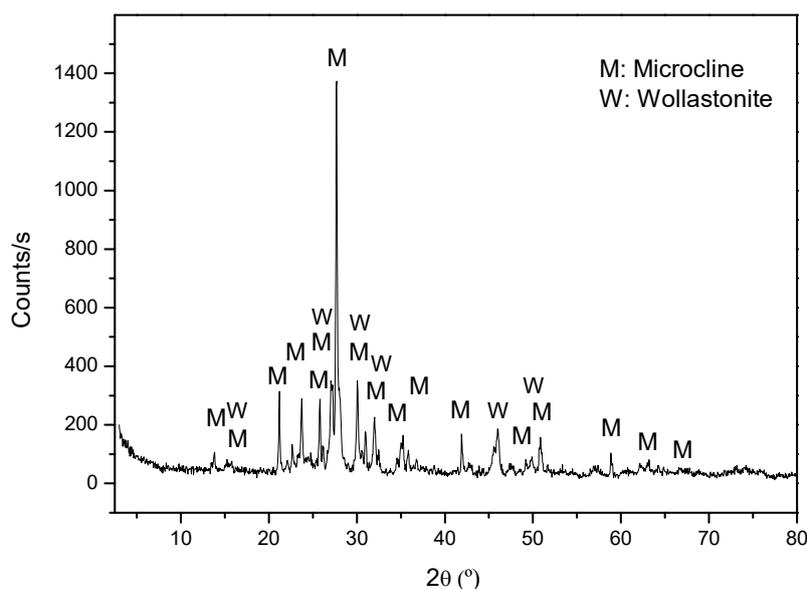
Figure 10. XRD pattern of the chlorination residue of the mixture $KAlSi_3O_8/CaCl_2$ calcined in N_2 at 900°C for 60 min.

This figure shows the presence of microcline and wollastonite ($CaSiO_3$). The high intensity of microcline characteristic peaks and low intensity of wollastonite typical peaks indicate that the calcination of microcline with $CaCl_2$ is not efficient method to extract potassium and produce new phases.

4. Conclusions

The results of the chlorination assays of a mixture containing microcline and calcite in a ratio of 65/35 (%*w/w*) prove that this process is an efficient method for the extraction of potassium from microcline and the synthesis of anorthite at moderate temperatures.

Potassium in the form of KCl is extracted from microcline in the temperature interval between 700 and 900 °C. At 900 °C for 120 min the extraction extent of potassium was about 97% *w/w*.

The formation of anorthite in $Cl_2(g)$ atmosphere started at 700°C for 15 min and was totally selective at 900 °C for 60 min.

The most favorable chlorination conditions for the extraction of potassium from microcline and synthesis of anorthite were 900°C and 60 min reaction time. These conditions allowed for efficient extraction of potassium and selective formation of anorthite.

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