CAPÍTULO 17

SLOW-RELEASE FERTILIZER FROM A ROCK CONTAINING GLAUCONITE BY THERMAL PROCESSING WITH ADDITIVES

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ABSTRACT: Glauconite is a monoclinic mineral, of green color, a potassium and iron hydrated phyllosilicate. It is an alternative source of potassium, but still not being commercially exploited in a large scale for this purpose, due to the lack commercial technology that makes the business economically viable. This work investigated the dissolution of potassium in a solution of citric acid 2% (m/m) after thermal and chemical processing, with additives ($CaCO_3$, $MgCl_2.6H_2O$), of a rock containing glauconite at six temperatures: 660°C, 700°C, 740°C, 780°C, 820°C and 860°C, 60 minutes and granulometry smaller than 0.15mm. The mass ratio (rock, $CaCO_3$, $MgCl_2.6H_2O$) was: (1.0: 0.2: 0.3). A rock containing glauconite with a content of 11.9% K_2O and 58% glauconite was selected. The potassium extraction was evaluated by extraction in 2% citric acid solution (m/m) at 95°C for 15 minutes and in water at 90°C. The solubility in water was 21% (770°C) and in citric acid the highest potassium extraction was 78% at the temperature of 770°C. The curve passes over a maximum (770°C), showing that there is a limit to the temperature in the thermal processing. Above this value, there is a drop in the extraction indicating different mechanism of reaction between the rock and additives. By considering that in water, the solubility of potassium was 4 times lower than in citric acid, it can be concluded that the thermal processing makes Verdete ore a potential alternative source of potassium for the production of slow release fertilizer.

KEYWORDS: potassium; slow release fertilizer; thermal processing; glauconite.

1 I INTRODUCTION

Silicates constitute an important group of minerals in the soils, constituting about 40% of the common minerals. They make up more than 90% of the earth's crust and occur in both primary minerals, inherited from igneous or metamorphic rocks, and secondary minerals formed by the intemperance of primary mineral products. The possibility of the use of silicate rocks for the production of fertilizers is an important strategy, since they are well distributed in all regions of the world (Castro *et al.*, 2005; Almeida *et al.*, 2006; Theodoro et al., 2006; Van Straaten, 2007; Martins *et al.*, 2010; Tchouankoue *et al.*, 2014).

Slow-release fertilizers use phyllosilicates as a potassium-providing raw material because of the low mobility of this potassium in water, dilute acids or weak organic acids. In order to increase the kinetics release of this potassium, several studies in this subject have been published (Tokunaga, 1991; Valarelli, 1993; Piza et al, 2011, Orioli Jr & Coutinho, 2009; Mangrich et al, 2001). Results obtained in these surveys indicate that rocks containing reasonable amounts of glauconite may constitute alternative sources of potassium for agricultural use. These researches were emphasized between the years of 1970 and 1980. Biotite, leucite, nepheline syenite, micaschists, potassium feldspar, chloriteschists, muscovite and Verdete were some of the evaluated materials (Lopes *et al*. 1972; Faquin, 1982; Leite, 1985).

One way to increase the availability of potassium is by promoting the modification of the mineral structure by thermal processing (Francisco et al, 2007; Silva et al, 2012; Van Straaten, 2007). Mazumder et al (1993) Mazumder et al. (1993) investigated the dissolution of glauconite potassium in distilled water after thermal processing (between 700°C and 850°C) using a mixture of sandstone containing the mineral and calcium chloride, varying the calcination time between 5 and 180 minutes and granulometry from 300µm to 75µm. The leaching in distilled water was performed at a temperature ranging from 40°C to 90°C, achieving extractions greater than 90% from 10 minutes of leaching, for calcination at 850°C. To reach such extractions, the ratio was 1.0:0.5 sandstone and calcium chloride, in a calcination time of 60 minutes.

The objective of this work was the study of a rock containing glauconite (Verdete ore) as an alternative source of potassium for the production of a slow release fertilizer. More precisely, to evaluate the influence of the temperature on the thermal processing of the rock, with additives, on the solubility of potassium in a solution of citric acid 2% (m / m) and in water.

2 I MATERIAL AND METHOD

Chemical and mineralogical characterization

For chemical and mineralogical characterization, the samples were reduced into grain size suitable for analysis. Scanning electron microscopy (JEOL, JSM 35C and X-ray Dispersive Energy Spectrometer, NORAN, Voyager 3050 model) was applied to identify the mineral phases and their elements.

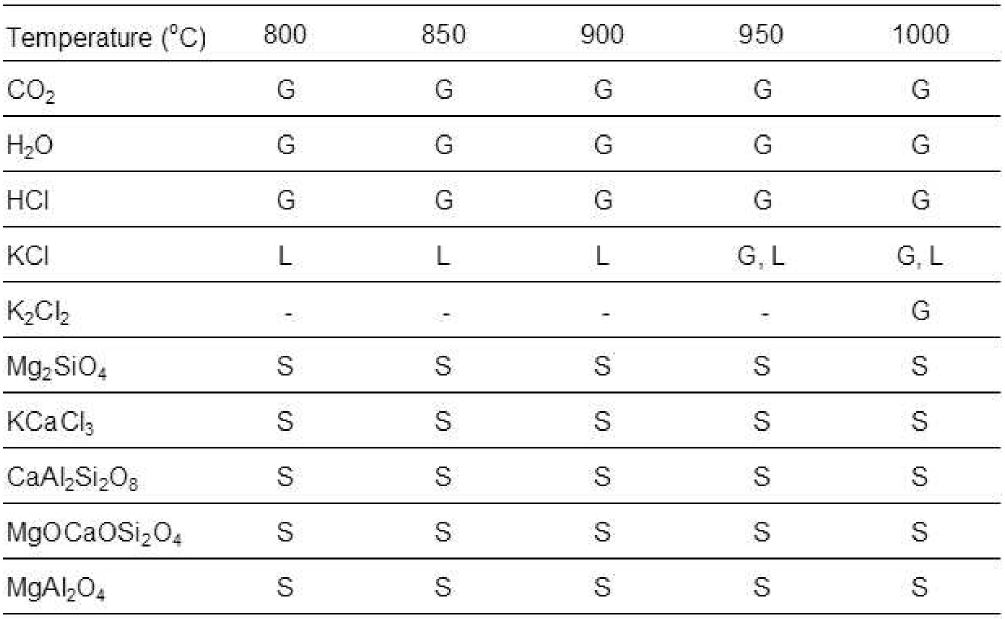
For the analysis of the crystalline components of the sample, X-ray diffractometer, Philips-PANalytical PW 1710 from the X-ray laboratory of the Department of Metallurgical Engineering and Materials of UFMG, was used with a voltage of 40mV, current of 20mA and angle of incidence ranging from 3° to 80°, with a variation of 0.05°. In the generated diffractograms, the diffraction peaks were indexed according to the standards presented in the ICCD database. For the analysis by ICP/OES, the preparation of the sample followed the procedures listed below:

- ✓ Lithium metaborate melting: the melting involved the complete dissolution of the sample in a molten flow;
- ✓ Optical Emission Spectrometry with Inductively Coupled Plasma Direct reading – ICP/OES: the equipment used in this work was the ICP/OES model Perkin Elmer Optima 7300DV.

Thermal Processing

The glauconite under study comes from rock (Verdete ore) containing this mineral that occurs in Serra da Saudade, in the region of the municipality of Cedro de Abaeté, state of Minas Gerais, Brazil. For the thermal processing, the system was considered: (rock+$CaCO_3$+$MgCl_{2.}6H_2O$), in the mass ratio (1.0: 0.2: 0.3).

By considering some conclusions of the study by Aitta et al (1986), the following particle size was adopted: 100% smaller than 0.15 mm for the sample subjected to thermal processing. To select the temperature, in thermal processing, simulations of the phase equilibrium were performed considering the input components. The simulations were performed in the application FactSage module Equilib. For the system (rock + $CaCO_3$ +$MgCl_{2.}6H_2O$), the phases likely to be formed are found in Table 2:



Temperature (°C)	800	850	900	950	1000
CO_2	G	G	G	G	G
H_2O	G	G	G	G	G
HCl	G	G	G	G	G
KCl	L	L	L	G, L	G, L
K_2Cl_2	-	-	-	-	G
Mg_2SiO_4	S	S	S	S	S
$KCaCl_3$	S	S	S	S	S
$CaAl_2Si_2O_8$	S	S	S	S	S
$MgOCaOSi_2O_4$	S	S	S	S	S
$MgAl_2O_4$	S	S	S	S	S

Table 1: Phases in the glauconite/$CaCO_3$/$MgCl_2.6H_2O$ system. G-Gas, L-Liquid and S-Solid.

Due to the appearance of KCl in the gas phases at temperatures above 950°C and the decrease of the $KCaCl_3$ solid phase above 900°C, the temperatures chosen were: 660°C, 700°C, 740°C, 780°C, 820°C and 860°C. The choice of $CaCO_3$ had the function of reducing the loss of HCl due to the decomposition of $MgCl_2.6H_2O$. The thermal processing was performed in a ceramic crucible (alumina) with an initial mass of 50g of rock, maintained in the temperature for 1h. The components of the mixture were PA reagents.

Extraction of the systems thermally processed in citric acid and water

The extraction of potassium in water was performed at 90°C, according to MAPA (Mapa, 2014).

For extraction in citric acid a 2% solution was prepared with 10 g of crystallized citric acid, monohydrate and analytical grade (Prolab) - $C_6H_8O_7.H_2O$ - dissolved in distilled water. Then, the solution was transferred to a 500-mL volumetric flask and increased. Regarding the dissolution test, 0.1000g (for the 1: 500 ratio) of each product of the calcination reactions is weighed and added in 100mL beakers. After that, 50mL of the extracting solution was added and brought to the heating plate, maintaining the temperature of 95°C for 15 minutes without boiling. After heating, the solution was cooled, filtered through a 0.45-µm membrane and 25 mL of the filtrate were transferred to a 100-mL volumetric flask and increased (Mapa, 2014).

3 I RESULT AND DISCUSSION

Chemical and mineralogical characterizaton

The chemical composition of the sample was (Table 1):

Compound	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	Na_2O	SiO_2
%	15.1	<0.03	6.7	11.9	3.0	0.0	62.2

Table 2: Chemical composition of Verdete sample used in the study.

The mineralogy of the sample is represented in the graph in the Figure 1.

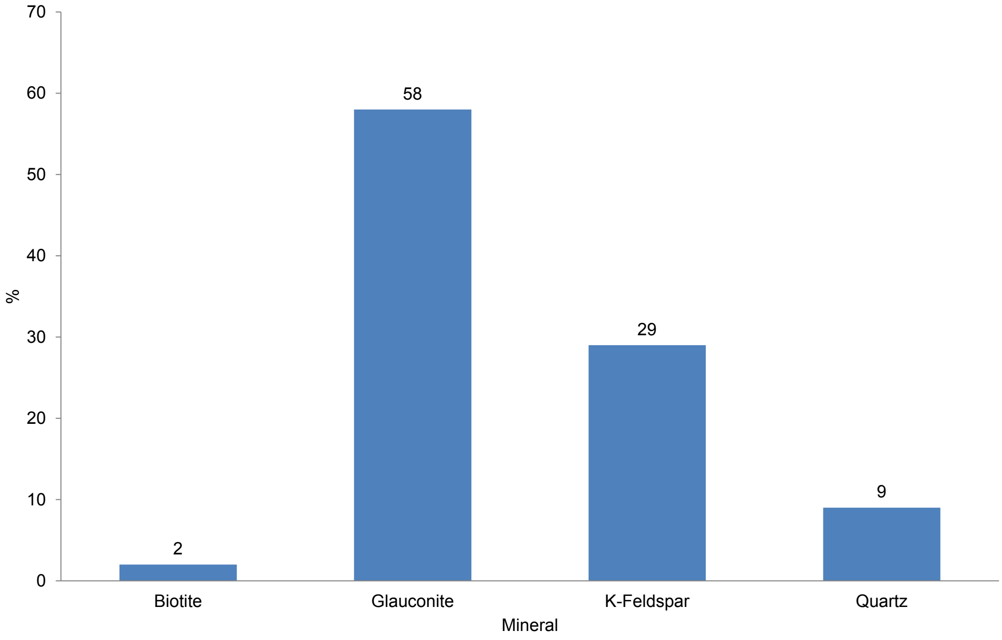


Figure 1: composition of Verdete sample used in the study.

Figure 1 represents the diffractogram of the Verdete rock with its main readings.

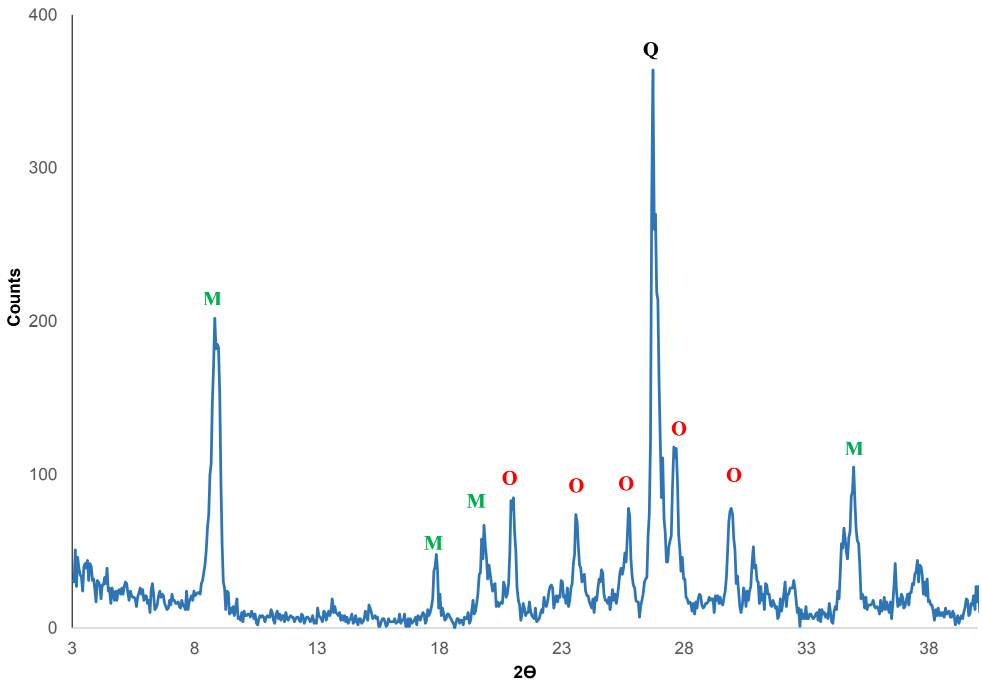


Figure 2: Diffractogram of Verdete ore: M – Mica, Q – Quartz, O– Orthoclase (K-Feldspar).

The images in the MEV (Figure 3) show a predominant matrix of a phyllosilicate of the Verdete rock.

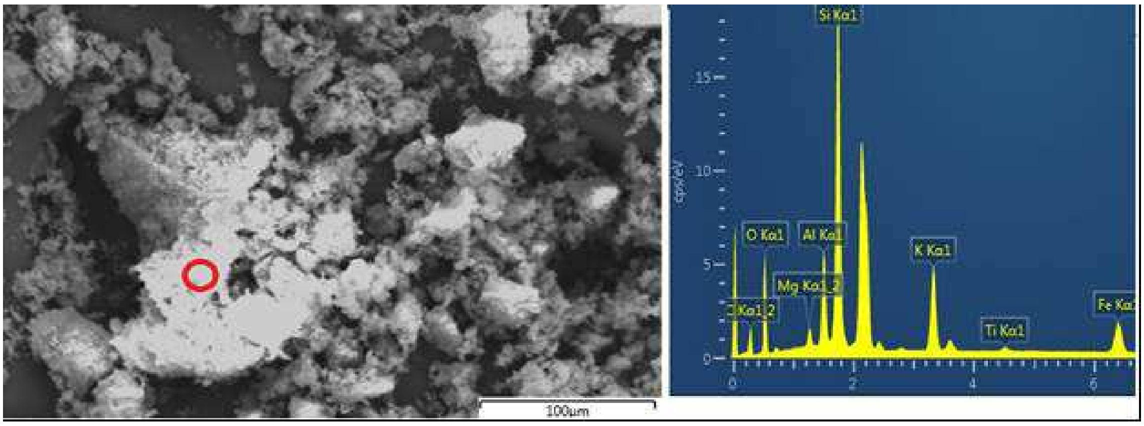


Figure 3: - Backscattered electron images of Verdete rock sample in Scanning Electron Microscope showing the predominance of a phyllosilicate matrix.

Thermal processing

The diffractogram of the heat-treated mixture at 780°C for 60 minutes is in Figure 4. The identified crystalline phases were: D - Diopside ($CaMgSi_2O_6$), M - Mica, O - Ortoclase ($KAlSi_3O_8$), Q - Quartz (SiO_2), S - Sylvite (KCl). The sylvite was formed by the displacement of the potassium of the structure of the glauconite by the chloride ion. At 780°C the residual mica is poorly identified, indicating almost complete transformation of this phase, considering that the detection limit of a XRD analysis is 5%. The formation of diopside, the phase rich in Ca and Mg, is further evidence of the unreacted ash-forming nucleus model which is the final inert phase.

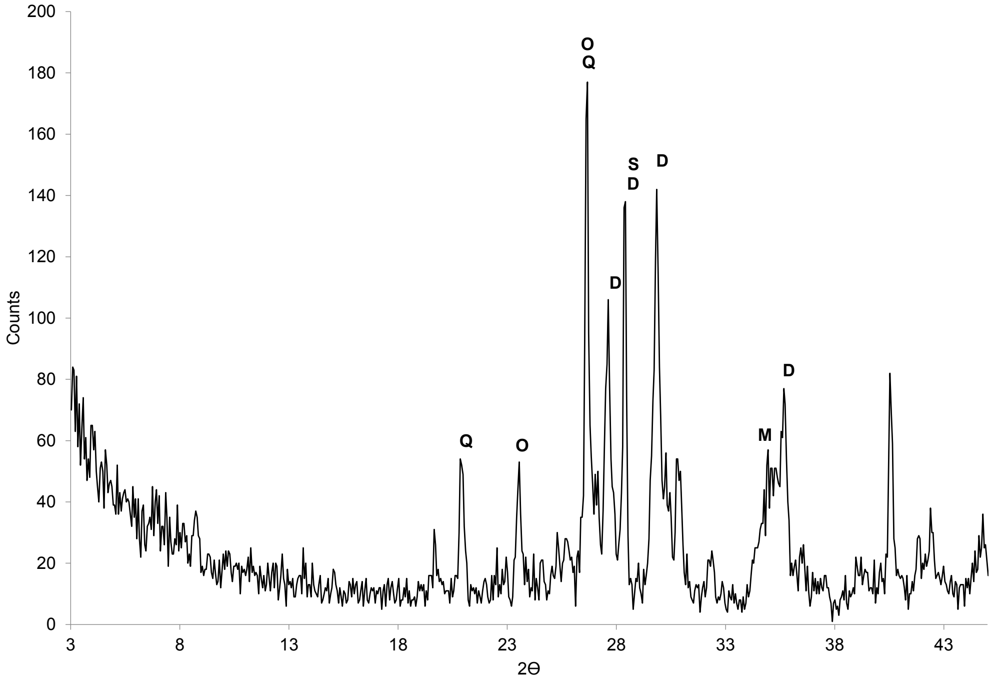


Figure 4: Sample diffractogram (mixture) at thermal treatment at 780°C. Identified phases: D – Diopside; M – Mica; O – Orthoclase; Q – Quartz; S - Sylvite.

Figure 5 represents SEM image and specific EDS analysis of the sample treated at 780°C revealing a crystalline structure containing phases rich in K and Cl. The image shows that the crystals begin to melt, corroborating with the melting point of pure KCl of 778°C.

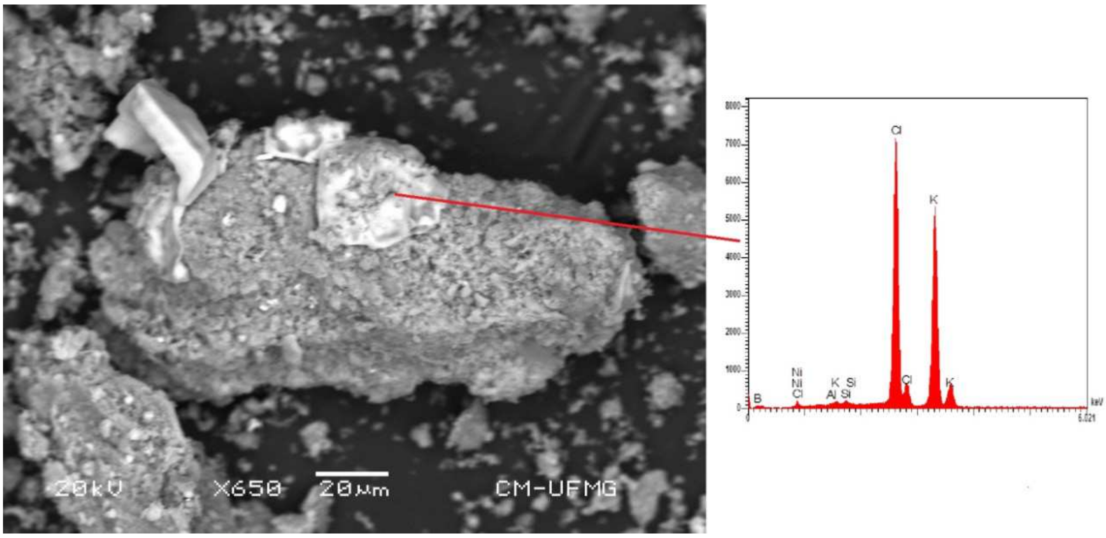


Figure 5: Image of SEM and EDS of a sample heated at 780°C, with addition of additives. EDS readings showing phases rich in K and Cl, with crystals in the melting process.

Extraction of the systems processed in citric acid

Figure 6 is the diffractogram of a sample after thermal treatment at 780°C (with additives) and after leaching with 2% citric acid solution. The identified crystalline phases were, as follow: D – Diopside; H–Hematite; M–Mica; O – Orthoclase; Q - Quartz. The increase in the crystallization of the hematite was most likely due to the iron released from the glauconite structure. It is also observed that the mineral phases of diopside, product of the reaction in the thermal treatment, have low solubility in 2% citric acid. Other studies may determine a better condition to solubilize this compound as it is a source of calcium and magnesium. The Orthoclase that did not react in the thermal treatment phase, remains as a component with non-exchangeable potassium. The sylvite phases was completely vanished.

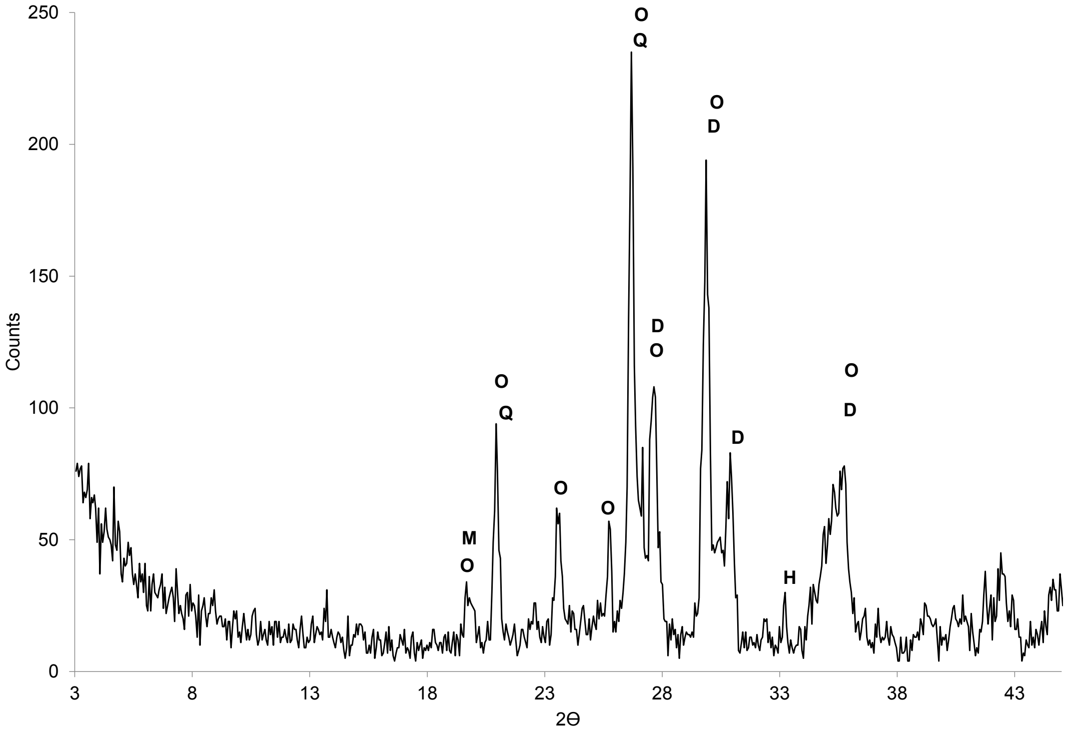


Figure 6: - Sample diffractogram after thermal treatment at 780°C (with additives) and leached with 2% citric acid solution. D – Diopside; H – Hematite; M – Mica; O – Orthoclase; Q – Quartz.

Figure 7 is SEM image and specific EDS analysis of the sample treated at 780°C and after solubilization in 2wt% citric acid solution. No phase rich in sylvite was identified, indicating total extraction of this phase by citric acid.

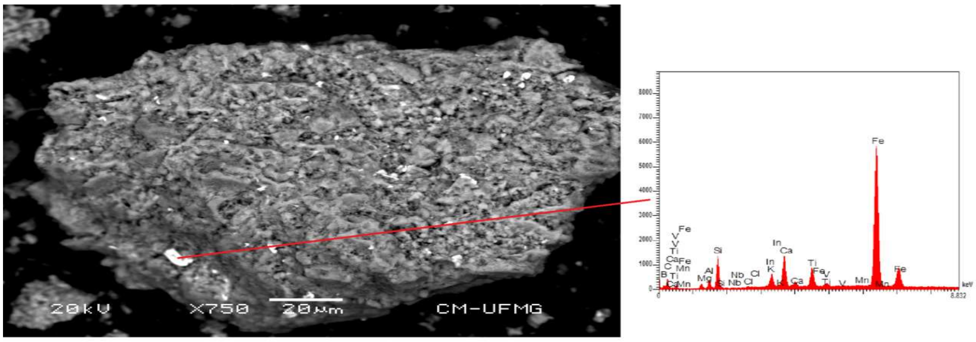


Figure 7: SEM and EDS images of the sample heated at 780°C, with the addition of additives and after leaching with 2% citric acid solution. EDS readings did not identify Sylvite-rich phases.

The graph in Figure 8 represents the extraction of potassium in citric acid after tests of the mixture (with additives) at several temperatures. The curve went through a maximum (around 770°C), showing that there was a limit to the temperature. Above this value, there was a decrease in the extraction, indicating that other secondary and irreversible reactions began to overlap the mixed control of the initial reaction (diffusion and chemistry).

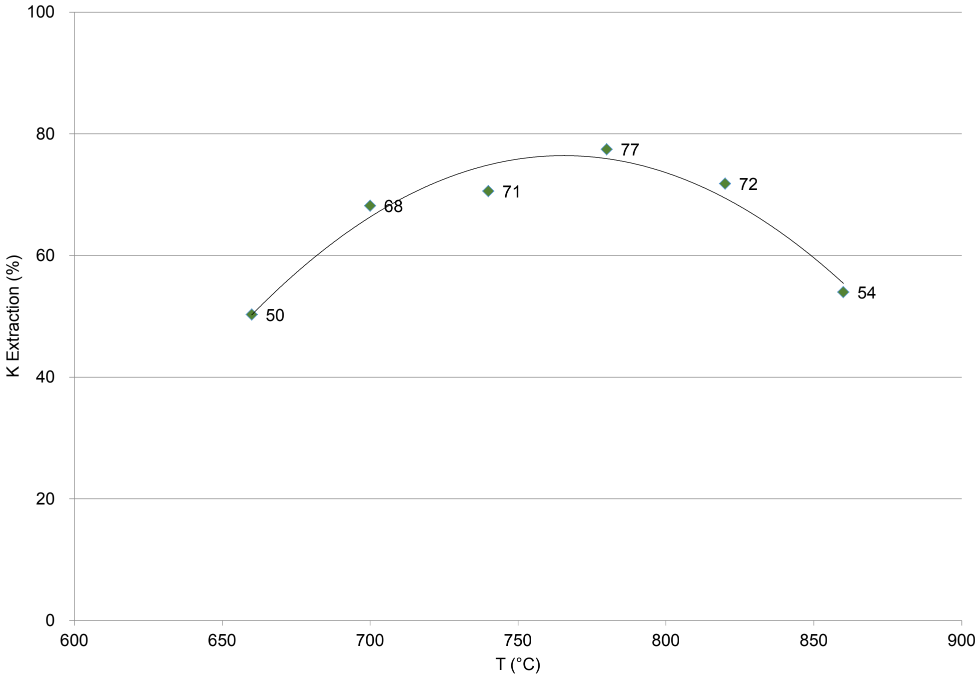


Figure 8: Potassium extraction in 2% citric acid solution (m/m).

4 I ACKNOWLEDGEMENTS

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5 I CONCLUSION

The thermal processing of the mixture (rock, $CaCO_3$, $MgCl_2.6H_2O$) in the mass ratio of (1.0: 0.2, 0.3) was effective, resulting in the extraction of 78% of the potassium in a 2wt% citric acid solution. There was formation of sylvite (KCl) proving the displacement of potassium from the structure of phyllosilicates. After solubilization in citric acid, no sylvite phase was identified, both in the X-ray analysis and in SEM images and EDS, therefore, dissolved in the solution. The extraction increases with temperature, rising to a maximum (78%) at 770°C. Above this value, the potassium extraction decreases. Up to this maximum temperature, the system is governed by gas-solid reaction, where gas is generated by the pyrohydrolysis of magnesium chloride. Above this temperature, other reactions with different mechanism begin to interfere, reducing the solubility of potassium in citric acid. The difference between the solubility of potassium in water, 21%, and the solubility in citric acid, 78%, makes glauconite a potential alternative source of potassium for the production of slow release fertilizer, when thermally processed using chlorine additive.

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