A STUDY ON APPLICATION OF PHLOGOPITITE AS A SLOW RELEASE POTASSIUM FERTILIZER

Adriana de A. S. da Silva[a, b], Silvia C. A. França[a], Célia M. Ronconi[b] , João A. Sampaio[a], Adão B. da Luz[a], and Diego de Sousa da Silva[a, b]

[a] CETEM – Centro de Tecnologia Mineral, Ministério de Ciência e Tecnologia
Av. Pedro Calmon, 900 - Cidade Universitária, CEP: 21941-908, Rio de Janeiro – Brazil
Phone +55(21) 38657334, Fax: +55(21) 2290-9196,
e-mail: asoeiro@cetem.gov.br.

[b] Instituto de Química, Universidade Federal do Rio de Janeiro (UFRJ), Av. Athos da Silveira Ramos, 149, CP 68563, 21941-909, Rio de Janeiro, RJ, Brazil.

ABSTRACT

In Brazil, the domestic production of minerals used in the agriculture is not enough to supply the needs of the country in its activities, making necessary to import those minerals. Based on the vocation of agricultural activities in Brazil, the use of fertilizers increases, aiming to increase productivity in the crops. Thus, the needs for fertilizers will always be increasing.

In the South hemisphere, Brazil is the only producer of potassium, with one mine in operation (Northeastern Brazil, in the state of Sergipe), producing around 750,000 t of KCl in 2007, which represents just around 8% of the domestic consumption in potassium. Based on this scenario, the investigation of industrial minerals and rocks that contain potassium and can be used in agriculture as an alternative source of potassium will be very welcome.

Micas can be considered a rich source of potassium. The minerals classified on this group are hydrate aluminum silicates, with isomorphic substitutions of K, Na, Mg and Fe ions, which generate materials with different chemical and physical properties, allowing their large variety of industrial application.

In this work, chemical and mineralogical properties of a phlogopitite rock from the state of Bahia (Northeastern Brazil) were investigated to evaluate the possibility of its use as a slow release potassium fertilizer. Preliminary results showed that the mineral phlogopite contains around 8.6% grade of K_2O. The goal in this paper is to study the availability of potassium, under environmental and soil condition for plantation, to this nutrient be caught by the plants. For that purpose, kinetic experiments were run to determine the nutrients release capacity by the mineral and also the need of submitting it to chemical or structural modifications that allow the availability of potassium.

Key words: Agrominerals, phlogopitite, potassium fertilizer.

INTRODUCTION

The symbol K for the chemical element potassium comes from the Latin word derived *Kalium* of the Arabic *qali* that means alkali. Due to its dimensions and ionic charges, it concentrates in the final phases of the magmatic activity and, although it exists with certain abundance in the earth crust (ahead of magnesium, titanium, hydrogen and phosphorus), it rarely forms economical deposits (Nascimento, 2004).

In Southern Hemisphere there is a single silvinite (KCl + NaCl) mine in operation, the one of Taquari Vassouras plant, in the state of Sergipe, Brazil. Producing 750 thousand tons of equivalent KCl in 2007, it satisfied only 8% of the domestic needs in potassium.

Potassium (K) is a macronutrient that is essential for the growth of plants and its required to promotes and regulates enzymes activation, supports the translocation of carbohydrates, increase water use efficiency and resistance to drought seasons (van Straaten, 2007). It is an important nutrient for crops like sugarcane, sugar beat, potatoes, grapes, fruits and cereals.

Rocks or industrial minerals that present high potassium grades, like mica, feldspars and other silicates, can be used as alternative sources for the production of potassium salts or to direct application in the soil as slow release fertilizers (Cavalcante *et al*, 2005).

Slow-release fertilizers are excellent alternatives to the soluble fertilizers. Because nutrients are released at a slower rate throughout the season, plants are able to take up most of the nutrients without waste by leaching. A slow-release fertilizer is more convenient, since less frequent application is required. Fertilizer burn is not a problem with slow-release fertilizers even at high rates of application; however, it is still important to follow application recommendations. Slow-release fertilizers may be more expensive than soluble types, but their benefits outweigh their disadvantages (Bennett, 1996).

However, to apply these minerals source of potassium as a fertilizer is necessary to understand it chemical and structural availability.

Phlogopite, a mineral from the mica group with chemical formula $KMg_3(AlSi_3O_{10})(OH)_2$, is a trioctahedral layer silicates that usually contains K as the interlayer cation – around 9% grade of K -, which compensates a negative charge arising from cation substitutions within the layer structure.

In this paper the use of phlogopite as a source of K is being studied. Chemical and structural analyses were run to determine the properties of this material, specially the availability of K ions in the natural raw material under soil and environmental conditions, aiming to use this material as a rock for crops.

MATERIALS AND METHODS

The sample

The sample studied in this paper is a rock phlogopitite from Campo Formoso, state of Bahia, Brazil. Primarily, the material received was crushed below 50 mm and milled to produced a material with size distribution below 2,0 mm. This material was homogenized in a stockpile and small samples (1 kg) were grabbed to the next steps of beneficiation.

Sample Characterization

The sample characterization was based on the following steps:

i) Chemical analysis, to determine the composition by X-ray fluorescence (Spectra plus v.1.6, standardless method);
ii) Mineralogical analysis, to determine the mineral phases present in the sample, by X-ray diffraction (Bruker-D4 Endeavor, Co $K\alpha$ (40 kV/40 mA));
iii) Morphology was studied by scanning electron microscopy;
iv) Particle size distribution, using screening process (Tyler series).

The importance of different techniques to characterize the sample is due to the complementation among the results, to a better comprehension of the responses of the material to the chemical and physical procedures for nutrients release.

Kinetic experiments

Kinetic experiments are generally carried out to determine the type of reaction and its efficiency related to the time. In this paper, this experiment aimed to evaluate the potassium release from the mineral phlogopite.

In some cases, the amount of nutrient present in a mineral (result from chemical analysis) it is not easily released to the crops. Therefore, it is necessary to quantify the solubility of these nutrients to determine its real available amount to guarantee it application as a fertilizer.

Aiming to investigate the potassium solubility under different soil conditions, were carried out tests on distilled water and nitric acid solution (HNO_3 – 0.01M). The use of acidic solutions aims to promote chemical conditions similar to that ones existing in the soil/roots interface (rizosphere), which can improve extractions processes.

The kinetic studies were run under the same conditions to 10 different size fractions, obtained by screening. This procedure aimed to investigate the efficiency of potassium release as a function of particle size, to determine the appropriate particle size distribution to the application of phlogopite as slow release fertilizer.

In these experiments, 5 g of sample were added in Erlenmeyer, with 50 mL of acidic solution or distilled water, which were shake in an orbital shaker for 4 hours, as maximum retention time, under 300 rpm agitation and room temperature.

The samples were taken from the flask at pre-determined retention time - 1, 2, 3 and 4 h, by using pipette, and filtered in semi-quantitative filter paper; the filtrate was analyzed by atomic absorption spectrophotometry, to K ions quantification.

RESULTS AND DISCUSSIONS

Sample characterization

The total chemical analysis for the head sample is showed in Table 1. The results show that this phlogopitite sample contains around 7.2% K but it also contains high grade of MgO, 17.5%, that is another important nutrient to the plants. It is important to observe that raw materials to be used as a fertilizer must have very low or none heavy metals grade. In this sample were measured 0.5% Cr_2O_3 and 0.04% ZnO. According to Coelho (2008), the maximum concentration of Cr in fertilizers is 200 ppm.

Table 1: Chemical compositions of phlogopitite (head sample)

Oxides	grade (%)	Oxides	grade (%)
Al_2O_3	10.09	MoO_3	0.02
CaO	0.54	NiO	0.14
Cr_2O_3	0.51	P_2O_5	0.09
Cs_2O	0.11	Rb_2O	0.33
F	3.35	SiO_2	39.89
Fe_2O_3	8.6	SO_3	0.06
K_2O	8.26	TiO_2	0.22
MgO	17.48	ZnO	0.04
MnO	0.18	Total	88.67

The results of the mineralogical composition of the phlogopitite obtained by XRD are presented in the Figure 1. It is possible to observe that the main minerals in the rock are phlogopite and talc. Certainly, the presence of talc explains the high grade of MgO, presented in the Table 1.

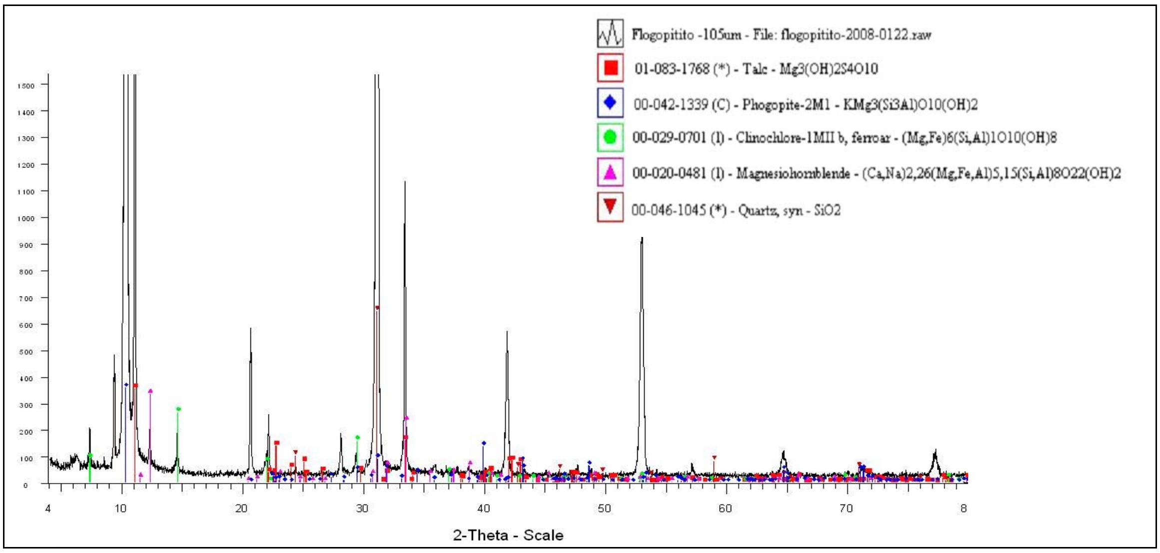

Figure 1: X-ray diffraction patterns from phlogopitite

Layers that can be split or delaminated into thin sheets compose the crystalline structure of phlogopite. The ions K are placed interlayer (between tetrahedral layers), under strong bonds, which make difficult it release from this structure (Figure 2).

Aiming to improve the releasing of potassium some studies are being developed (Castilhos and Meurer, 2001) to run the extraction experiments under acidic conditions, by using organic acids solutions like citric and oxalic acids, aiming to improve the mineral weathering forming metallic-organic complexes. This procedure can improve the potassium availability from the crystalline structure of phlogopite.

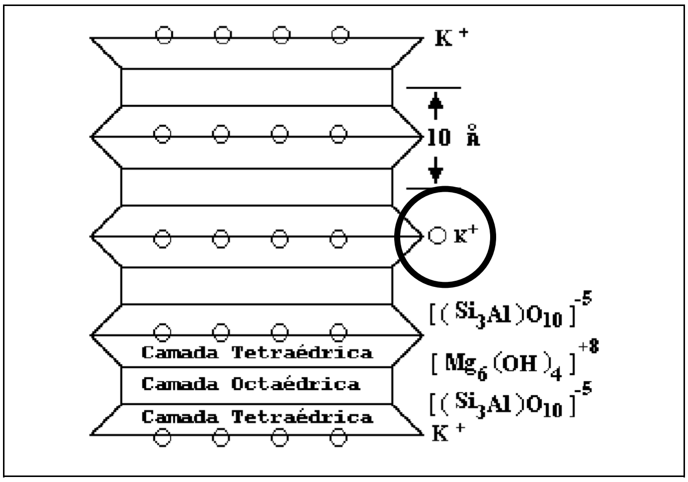

Figure 2: Crystalline structure of phlogopite (Bigham *et al.*, 2001)

The morphology of the sample (Figure 3), obtained by scanning electron microscopy technique, shows the platelets like structure of phlogopite, with poor delamination.

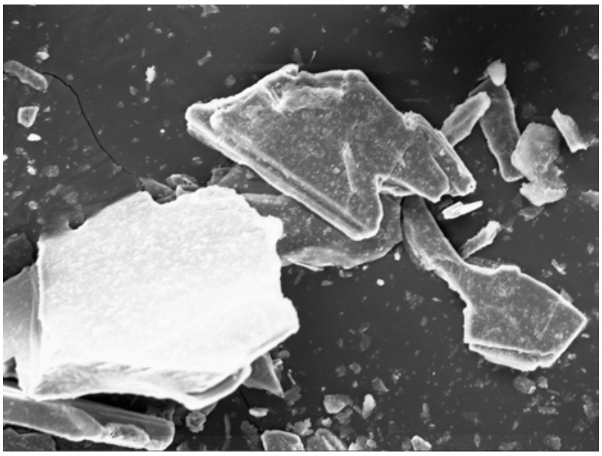

Figure 3: Image of scanning electron microscopy for the phlogopite sample

Table 2 presents the particle size distribution to the ground sample. It is possible to see that about 34% of the sample was in the fraction –420+149 μm; about 10% correspond to the fine fraction.

Table 2: Particle size distribution for the phlogopitite (ground sample)

Nominal aperture size (μm)	% Mass	Nominal aperture size (μm)	% Mass
+2000	6.76	-210+149	9.49
-2000+1680	3.39	-149+105	9.16
-1680+1200	7.58	-105+74	5.95
-1200+841	3.38	-74+53	3.73
-841+595	7.55	-53+44	1.86
-595+420	8.31	-44+37	1.96
-420+297	10.50	-37	6.27
-297+210	13.97	Total	98.88

Kinetic experiments

The kinetic experiments were run to determine the potassium release capacity. The first test was carried out with H_2O. In this test was possible to see that the potassium has not a good release in H_2O (Figure 4), to the experimented time. Analyzing the potassium extraction efficiency in function of the particle size, the finer fractions showed, as expected, better extraction capacity due to the higher values of surface area. As expected, the –37 μm fraction reached extraction efficiency of 5.5 mg/L, which is the double when compared to the ones in the fractions +37 μm (1.5 to 2.5 mg/L).

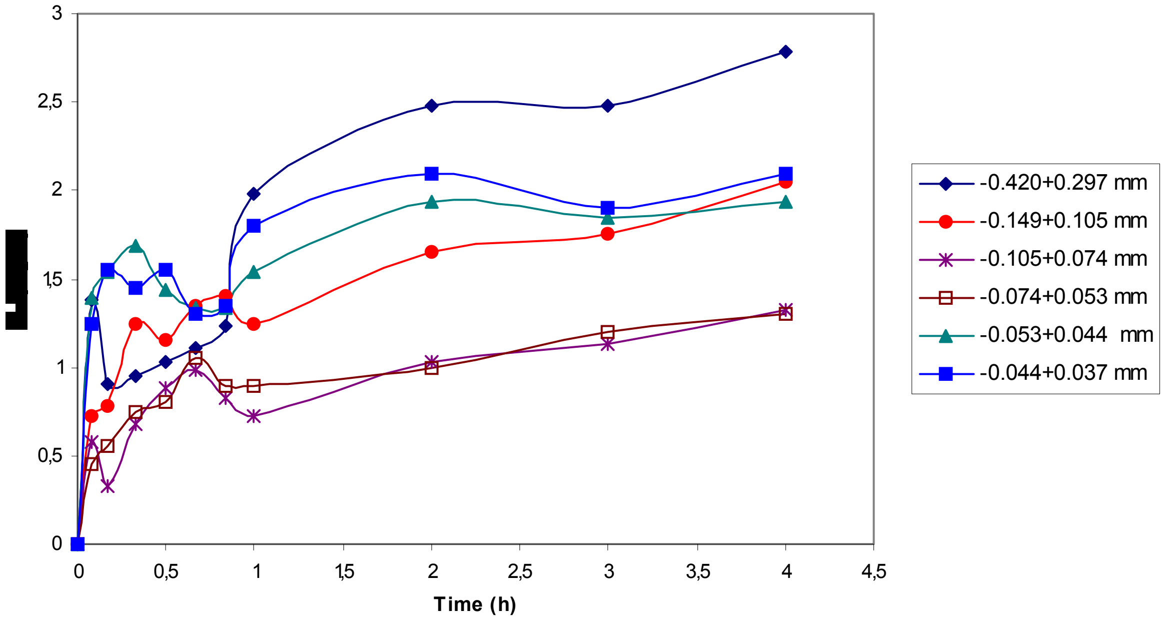

Figure 4: Potassium releasing in distilled H_2O

Considering the low concentration of potassium in distilled water, around 0.12%, it was observed that the extraction rates are higher in the first two hours, showing a reduction in the driving force after this time. These results showed a low solubility of potassium in water; so aiming to improve the potassium extraction the experiments were run in acidic media, nitric acid, to avoid the weathering in the sample and as a result better potassium extraction rates. The results are showed in Figure 5. In these tests the kinetic parameters were not evaluated in the first hour of experiments.

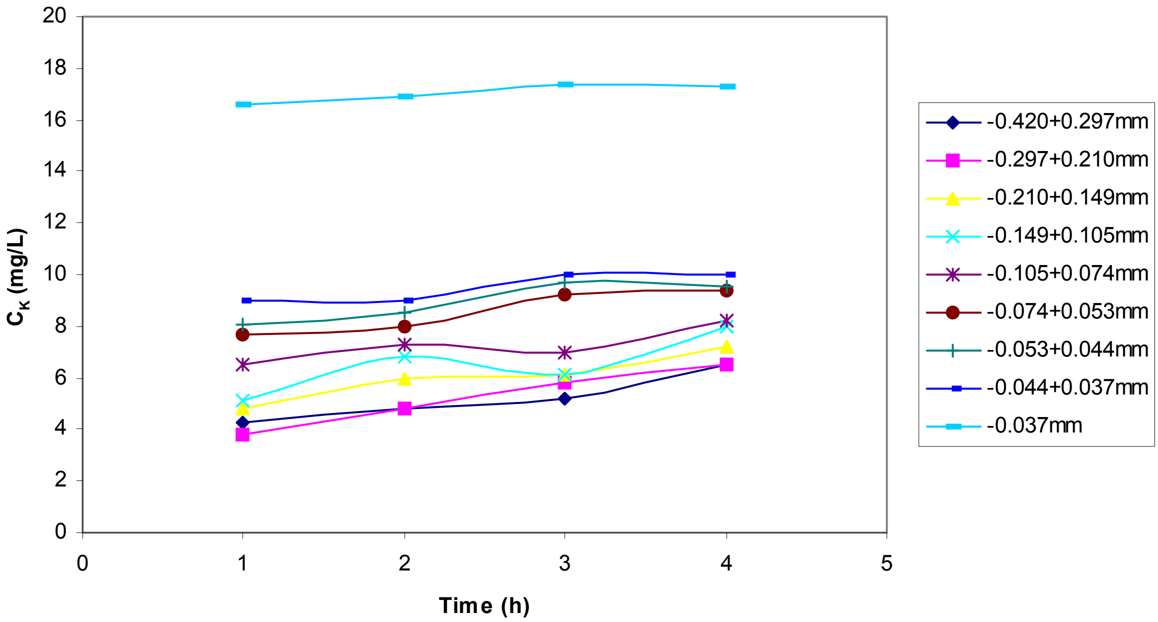

Figure 5: Potassium releasing in HNO_3 solution (0.01M)

Based on the results showed in Figure 5 it can be noticed that the efficiency of potassium extraction in acidic media is better than in distilled water. In accordance to Castilhos (2001), the acids can improve the weathering of the mineral and make the potassium release easier. The extraction efficiencies obtained in acidic media, for all particle sizes, were around three times higher than the same process run in distilled water. To the –37 μm fraction, the extraction efficiency reached values around 17 mg/L while to the fractions +37 μm the efficiencies were in the rate of 6.5 to 8.5 mg/L.

Other extractors like Mehlich-3 solution, citric acid and oxalic acid are being tested. Oxalic acid, for example, is an effective agent for extraction of cations from micas through a combination of proton attack and complexation reactions (Girgin and Abut, 2002). Results obtained to kinetic experiments, run with Mehlich-3 extractor solution during 168 hours (7 days) reached around 4% potassium extraction efficiency. This result is corroborated by Castilhos (2001), which ran experiments to tropical soil samples (Planosoil) during 3.000 hours and got around 2.1% potassium extraction efficiency, using oxalic acid as extractor solution.

Based on these results, the phlogopite can be considered a potential mineral to be applied in perennial plantation crops for which slow-release agromineral inputs are suitable and in use.

CONCLUSIONS

The phlogopitite presented low solubility of potassium in H_2O. However, in acidic solution the values of solubility are higher, thereabout 3 times more soluble. Anyway, these values are still very low to the application of phlogopite as a slow release fertilizer.

There is no significant variation in potassium releasing between 1 and 4 hour.

The results obtained until the moment are preliminary. Other extractors are being studied to increase potassium releasing. These extractors are citric acid, oxalic acid and Mehlich-3 solution. There is also the possibility of using microorganisms, like fungi or bacteria, as an alternative biological process to induce the potassium release.

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