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Article

Modeling Controlled Potassium Release from Phlogopite in Solution: Exploring the Viability of using Crushed Phlogopitite Rock as an Alternative Potassium Source in Brazilian Soil

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As propriedades químicas e mineralógicas do flogopitito, uma rocha que contém flogopita, foram estudadas tendo em vista o emprego como fonte alternativa de potássio. A caracterização mineralógica da rocha foi realizada por difratometria de raios X, fluorescência de raios X, microscopia eletrônica de varredura e espectroscopia na região do infravermelho. De acordo com os resultados, flogopita contém 82,6 g K_2O kg^{-1} (ca. 9%). A cinética de liberação do íon potássio a partir do mineral foi avaliada em meio ácido (nítrico, cítrico, oxálico e Mehlich-1) e em uma solução salina (tetrafenilborato de sódio, $Na[B(C_6H_5)_4]$). Os resultados experimentais obtidos a partir dos estudos cinéticos foram ajustados para determinar uma relação matemática entre a concentração de íons potássio liberada em solução e o tempo de liberação.

The chemical and mineralogical properties of phlogopitite, a rock containing the mineral phlogopite, were studied aiming at employment as an alternative source of potassium. Mineralogical characterization of this rock was performed using X-ray diffractometry, X-ray fluorescence, scanning electron microscopy and infrared spectroscopy. According to the results, phlogopite contains approximately 82.6 g K_2O kg^{-1} (ca. 9%). The kinetics involved in the release of the potassium ions from the mineral were examined using acidic solutions (nitric, citric, oxalic and Mehlich-1) and a salt solution (sodium tetraphenylboron, $Na[B(C_6H_5)_4]$). The experimental results from the kinetic studies were used to determine the mathematical relationship between the concentration of potassium released and the reaction time.

Keywords: phlogopitite, phlogopite, potassium source, potassium release, kinetic studies

Introduction

Brazil is one of the world's most important agricultural producers. However, the domestic production of fertilizer is insufficient to meet the needs of the region. In addition, Brazilian soils are acidic and lack nutrients; therefore, they require the extensive use of fertilizers to improve the agricultural production.[1] Alternative mineral sources are needed to address this problem. Potassium is one of the essential nutrients for crops, such as sugarcane, sugar beet, potatoes, grapes, fruits and cereals, because it promotes and regulates enzyme activation, supports carbohydrate translocation and increases water use efficiency as well as drought resistance.[2-4] Potassium fertilizers are widely used in agriculture around the world.[5]

One mine that operates in the Northeast of Brazil (in the Sergipe State) produces approximately 606.710 t *per* year of KCl, which is only 10% of the domestic consumption. Given this discrepancy, the investigation of K^+-containing minerals and rocks that can be directly used in soil as an alternative potassium source is an important step toward decreasing agricultural production costs. Moreover, rock fertilizers may also become an environmental solution to soil fertilization because they do not require chemical processing and can be used as mined.[6-8]

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Because of their structure, minerals from the mica group are rich in K^+ and are ideal candidates for ion exchange[9] when their particle size is controlled.[10,11] The minerals classified in this group are hydrated aluminum silicates with isomorphic substitutions of K, Na, Mg and Fe ions; these substitutions result in the generation of materials with different chemical and physical properties for a wide variety of industrial applications.[12] Among this mica mineral group, phlogopite [$KMg_3(AlSi_3O_{10})(OH)_2$],[13] a trioctahedral layered silicate, typically contains K^+ (approximately 9% grade) as an interlayer cation to compensate for the negative charge from cation substitutions in the layered structure.[14]

In Brazil, tons of phlogopitite are discarded as an emerald mining byproduct. Thus, our group investigated the viability of utilizing this residue as a potassium source for crops. The availability of K^+ in phlogopite was studied using different acid and salt solutions as extractants. To examine the K^+ release capacity, kinetic experiments were performed in which a kinetic equation was used to describe the potassium release profile as a function of time.

Experimental

Chemical and mineralogical properties of phlogopitite

Phlogopitite rock from Pindobaçú city in Bahia State, Brazil, was used in this investigation. The sample was first crushed into particles smaller than 50 mm and then ground using a roll crusher. Finally, the sample was passed through 3.35 to 2 mm sieves to produce a material with a size distribution less than 2 mm. This material was homogenized in a stockpile, and small samples (1 kg) were collected for this study.

Several techniques were used to characterize the phlogopitite sample: X-ray diffractometry (XRD) (Bruker-AXS D5005) using Co K_α radiation (λ at 1.78897 Å) at 35 kV and 40 mA; infrared spectroscopy (IR) (Bomen-Hartmann & Braun, MB102, DTGS FTIR detector) with measurements from 4000 to 400 cm^{-1}; X-ray fluorescence (XRF) (Bruker-S4, standardless method); and scanning electron microscopy (SEM) (Leica F440, high-vacuum mode). For the X-ray diffraction measurements, the phlogopitite sample was deposited onto a glass sample holder; for the SEM analyses, the samples were adhered to SEM studs using carbon tape and then coated with gold using a sputter-coater (BAL-TEC, SCD 005) for 3 min at 30 mA. For the X-ray fluorescence analysis, 8.0 g of phlogopitite were compacted under 20 t of pressure for 3 min using a Teclago PCA40M/20ton manual pelletizing press. IR spectrum was generated using KBr discs.

K^+ release using different extractants

The potassium (K^+) exchange capacity of phlogopitite was first investigated using deionized water and then using acidic solutions of 0.01 mol L^{-1} oxalic acid ($H_2C_2O_4$), 0.01 mol L^{-1} citric acid ($H_8C_6O_7$), 0.01 mol L^{-1} nitric acid (HNO_3) and Mehlich-1 (0.05 mol L^{-1} HCl + 0.0125 mol L^{-1} H_2SO_4). These solutions were used to mimic the chemical environment of the soil/root interface (i.e., the rhizosphere).[15] Microbial activity is high in the rhizosphere and is responsible for producing organic compounds such as amino acids, enzymes and organic acids, resulting in an acidic medium. Finally, the potassium (K^+) exchange capacity of phlogopitite was also investigated in a salt solution composed of 1.0 mol L^{-1} NaCl, 0.2 mol L^{-1} $NaB(C_6H_5)_4$ and 0.01 mol L^{-1} EDTA (NaTpB).

In each experiment, 5.0 g of phlogopitite were added to an Erlenmeyer flask with 0.05 L of deionized water or an acid or salt solution. The flask was subsequently shaken at 300 rpm. Each sample was agitated for 1-168 h at room temperature; 0.05 L of sample was then collected and filtered. These experiments were performed in triplicate. The potassium in each solution was quantified using atomic absorption spectroscopy (Varian AA6, λ at 248.3 nm, air/acetylene). A commercially available K^+ standard solution (1000 mg dm^{-3}) provided by Vetec (Rio de Janeiro, Brazil) was used throughout the experiments.

K^+ release kinetics

To evaluate the potential application of phlogopitite as an alternative fertilizer, mathematical models were used to describe and predict the behavior of the exchangeable K^+ release over time in solution, as reported by Jalali,[16] Zhou and Huang[17] and Darunsontaya *et al.*[18]

The experimental conditions were adjusted to vary the results from the kinetic studies. Non-exchangeable K^+ release can be described using the following differential equation.[19]

$$\frac{dK_t}{dt} = k_2(K_0 - K_t) \quad (1)$$

The algebraic equation from the integration of equation 1 is as follows:

$$\ln(K_0 - K_t) = \ln K_0 - k_2 t \quad (2)$$

where K_t is the non-exchangeable K^+ released at any time t, K_0 is the non-exchangeable K^+ released at the maximum

release time (determined from the experimental data), and k_2 is the non-exchangeable K^+ release-rate coefficient.

The adjustments can be compared to the results generated by Martin and Sparks[19] and by Jalali,[16] who used similar equations to evaluate the kinetics in certain clay soil systems. The power-function (3), parabolic-diffusion (4) and Elovich (5) equations are presented as follows.

$$\ln K_t = \ln a + b \ln t \quad (3)$$
$$K_t = a + b\, t^{1/2} \quad (4)$$
$$K_t = a + b \ln t \quad (5)$$

Results and Discussion

Phlogopitite characterization

Table 1 shows the complete chemical analysis for phlogopitite rock using the X-ray fluorescence technique. The sample contains approximately 8.3% K_2O, which is equivalent to 68.9 g kg^{-1} total K^+, high-grade MgO (17.5%) (an additional important plant nutrient) and 0.54% CaO.

Table 1. Chemical composition of the phlogopitite sample obtained using the X-ray fluorescence technique

Oxide	Grade / %	Oxide	Grade / %
Al_2O_3	10.1	MnO	0.18
CaO	0.54	NiO	0.14
Cr_2O_3	0.51	Rb_2O	0.33
Fe_2O_3	8.60	SiO_2	39.9
K_2O	8.26	TiO_2	0.22
MgO	17.5	M.L.[a]	12.0

[a]Mass loss.

The X-ray diffraction pattern (Figure 1) shows the mineral phases in the phlogopitite rock. The primary mineral in the rock is phlogopite [$KMg_3(AlSi_3O_{10})(OH)_2$], which exhibits a lamellar structure oriented along the (001) direction. The basal spacings, which were determined using Bragg's equation for the most intense peaks in the diffractogram, were 10.1 Å (001) and 3.36 Å (003). These values are consistent with those reported in the literature for dehydrated phlogopite.[14,20,21] An additional mineral was identified as talc (basal spacing of 9.54 Å). The presence of talc likely explains the high grade of MgO observed in the X-ray fluorescence spectrum (Table 1) because the ideal formula for talc is $Mg_3Si_4O_{10}(OH)_2$.[13]

The rock composition was also investigated using infrared spectroscopy, and the spectrum is shown in Figure 2. The characteristic bands for phlogopite [$KMg_3(AlSi_3O_{10})(OH)_2$] were observed. The band at 3719 cm^{-1} is the OH stretching vibration of the $Mg_3(OH)$ groups. This band is typically observed in the 3704-3712 cm^{-1} range of natural phlogopites.[14] An additional typical band was observed at 817 cm^{-1} and was attributed to vibrations of the apical Al–O bond in the AlO_4 tetrahedral. The bands at 661 and 729 cm^{-1} are associated with Al–O–Si bonds.[21] The spectrum of the sample also shows a band at 1620 cm^{-1}, which is attributed to adsorbed water molecules.

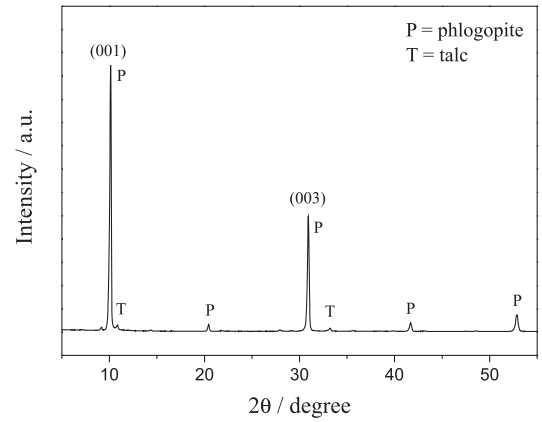

Figure 1. X-ray diffraction pattern of the phlogopitite sample.

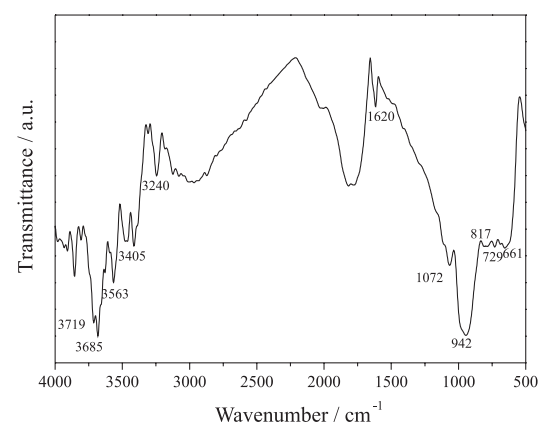

Figure 2. Infrared spectrum of the phlogopitite sample.

The SEM micrographs (Figure 3) confirm that the samples have typical mica-like structures characterized by highly parallel layers. These layers, particularly for this sample, are poorly delaminated from each other because of the grinding method used during the preparation of the sample.

As previously mentioned, to extract and quantify K^+ from the phlogopitite, several extraction experiments were performed using citric, oxalic and nitric acid solutions as well as a Mehlich-1 solution. As previously noted, these solutions were used to mimic the chemical environment in the rhizosphere.[15]

The Mehlich-1 solution, which is a mixture of two strong acids (HCl + H_2SO_4), is typically used to extract

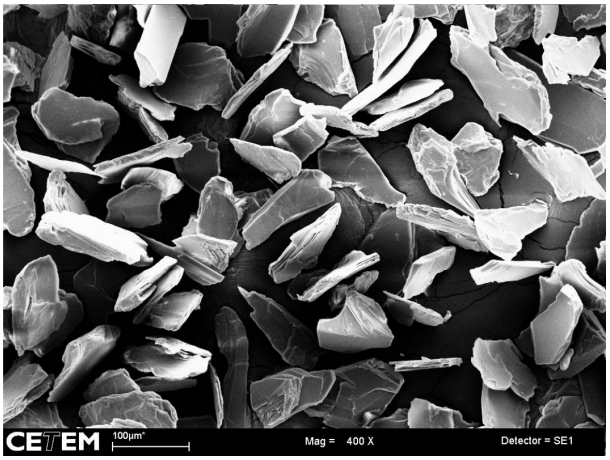

Figure 3. SEM micrograph of the phlogopitite sample.

strongly adsorbed nutrients through a dissolution process.[22] Sodium tetraphenylboron [$NaB(C_6H_5)_4$] was also used to extract K^+ from the phlogopite interlayers via ion exchange followed by precipitation.[18]

K^+-exchange experiments

The ion-exchange experiments were conducted to evaluate the K^+ release from phlogopite at room temperature in water or the acid or salt solutions, as described in the Experimental section. To determine whether the K^+ in phlogopite can be released for agricultural use (i.e., the available K^+), the extractants must be separated and quantified. These results will indicate whether the mineral can be applied as an alternative fertilizer.

The first experiment was conducted using deionized H_2O as an extraction medium. K^+ at 15 and 21 mg kg^{-1} was released over 1 h and 4 h of extraction, respectively. Thus, H_2O is inadequate for extracting potassium from phlogopite because of the low levels of K^+ extracted. The low extraction efficiency of H_2O may be related to its low ionic force.

Acidic media are more efficient than H_2O for extracting K^+ (Figure 4), most likely because the acid promotes mineral weathering, which can increase the rate of K^+ exchange from the interlayer spacing of phlogopite. The K^+ release rates for phlogopite sample in acidic solutions were substantially greater than in water. This result indicates that the acid solutions played a critical role in the K^+ release due to the increased H^+ concentration, which promotes weathering in the sample and increases the extraction yield. The K^+ exchange rate in phlogopite depends not only on the H^+ concentration from the extracting solution but also on the morphological characteristics of the sample, such as porosity, which can affect the weathering process of the mineral. A similar behavior was observed by Zhou and Huang,[17] who used phosphate and chloride solutions to extract K^+ from illite.

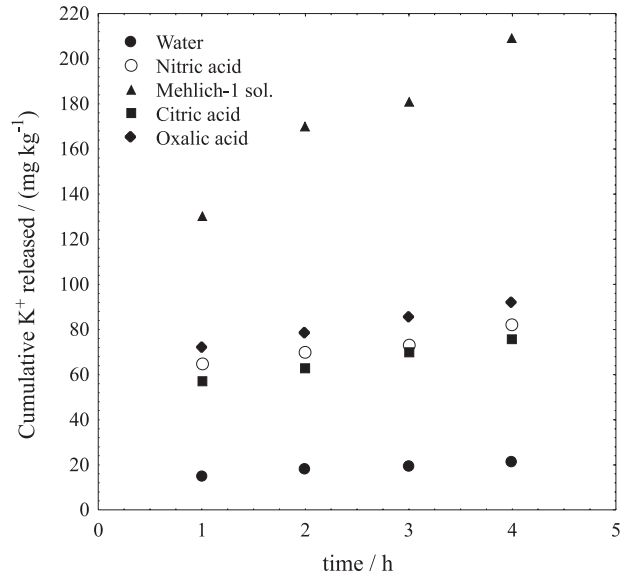

Figure 4. The cumulative levels of K^+ released in water and in certain acidic solutions (4 h extraction time).

Presumably, longer reaction times for the rock and acid solutions would increase the potassium release rates. Thus, additional experiments were conducted to verify the efficiency and process for achieving a steady state after 168 h (Figure 5).

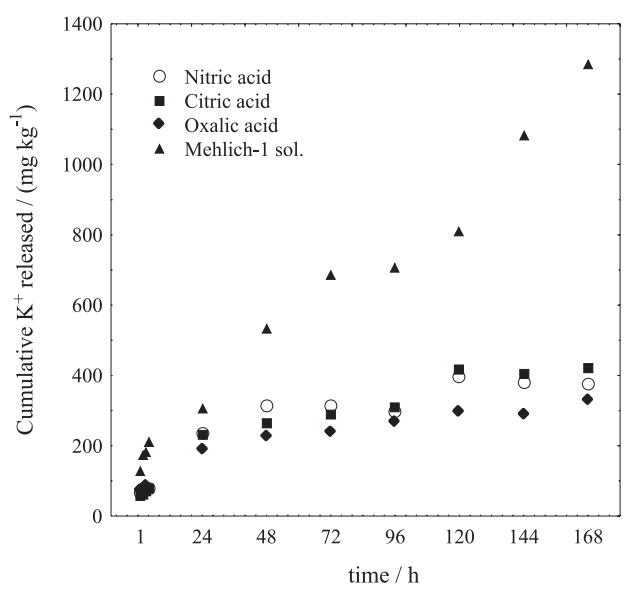

Figure 5. The cumulative levels of K^+ released into the extracting solutions (168 h extraction time).

For the extractants analyzed, the best results (Figure 5) were obtained with the Mehlich-1 solution, which resulted

in 1.29 g kg^{-1} K^+; because the phlogopitite sample contained 68.9 g kg^{-1} K^+ (total K^+), 1.9% of K^+ was extracted into the solution after 168 h. For this solution, the extraction curve indicates that K^+ was continually released from the phlogopitite (i.e., the concentration changed significantly) and did not reach equilibrium.

The data for K^+ release as a function of time were fitted using the following mathematical models: a power-function equation (Figure 6), a parabolic-diffusion equation (Figure 7) and the Elovich equation (Figure 8), as previously discussed. The coefficients of determination (r^2) were calculated by a least-squares regression of the measured *vs.* predicted values using the Statistica® version 7 software package. In these equations, the constant *b* requires special attention and analysis because it indicates the K^+ release rate. These data were generated for the K^+ extraction experiments and are provided in Table 2.

The statistical analysis (Table 2) indicates that the power function resulted in the best fits and linearity for the nitric,

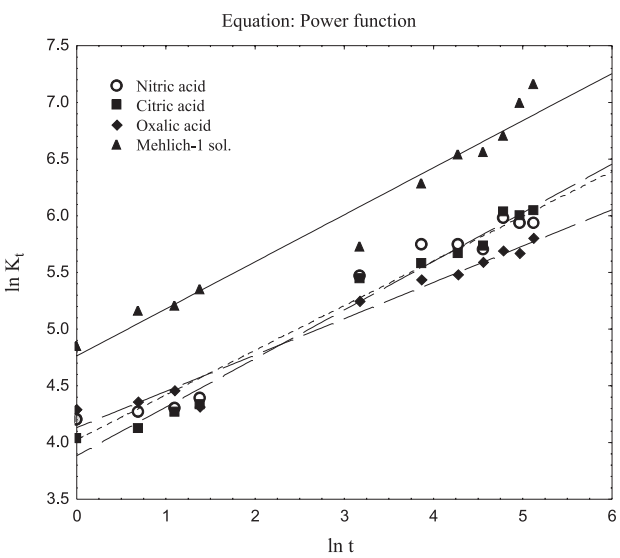

Figure 6. The relationship between the observed and predicted K^+ release kinetics from phlogopitite described by the power function.

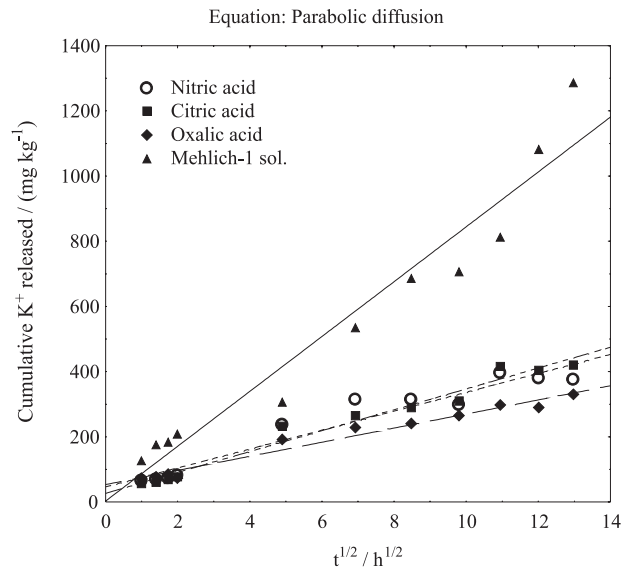

Figure 7. The relationship between the observed and predicted K^+ release kinetics from phlogopitite described by the parabolic diffusion equation.

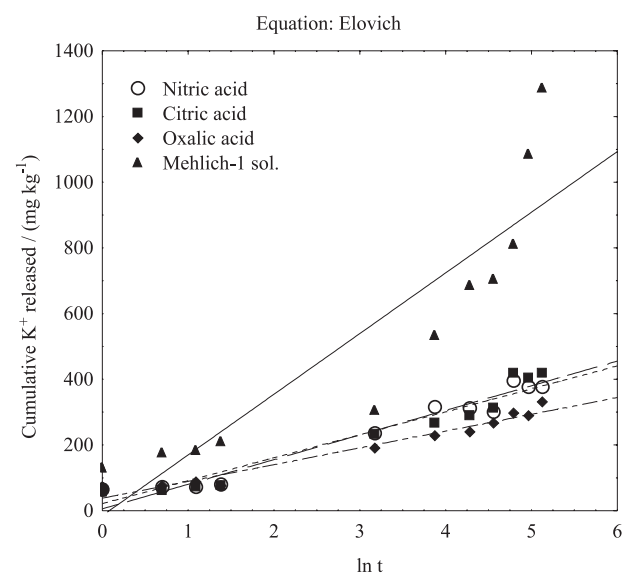

Figure 8. The relationship between the observed and predicted K^+ release kinetics from phlogopitite described by the Elovich equation.

Table 2. Results for the K^+ release kinetics: comparison of the parameters for the power-function, parabolic-diffusion and Elovich equations

Extractant solution	Release kinetic model								
	Power function			Parabolic diffusion			Elovich equation		
	b / (mg kg^{-1} h^{-1})	r^2	SE[b]	*b* / (mg kg^{-1} h$^{-1/2}$)	r^2	SE[b]	*b* / (mg kg^{-1} h^{-1})	r^2	SE[b]
Nitric acid	0.394	0.966	0.0246	29.02	0.931	2.627	69.91	0.957	4.939
Citric acid	0.429	0.983	0.0189	32.02	0.972	1.825	74.99	0.944	6.097
Oxalic acid	0.320	0.970	0.0186	21.64	0.972	1.221	51.08	0.959	3.512
Mehlich-1	0.415	0.956	0.0284	84.15	0.941	7.027	184.8	0.803	30.48
NaTpB[a]	0.303	0.957	0.0455	606.1	0.944	104.2	434.3	0.945	73.80
Water[a]	0.233	0.984	0.0209	5.749	0.980	0.584	4.116	0.980	0.418

[a]4 h experiment. [b]Standard error.

citric, oxalic and water extractions. The K^+ release rates, which are represented by the *b* parameter in the equations, exhibited the highest values for the extractions performed in citric acid solution (Table 2). The Mehlich-1 and NaTpB solutions were excluded from the *b* parameter analyses because the adjustments to the mathematical models (Figures 6 to 8 and Table 2) are not well suited for these extractants. The strong increase in K^+ solubility in the latter stages of the experiments in which the Mehlich-1 solution was used indicates a different release mechanism compared with that related to the other acid solutions. Zhou and Huang[17] discussed the efficiency and strength of the H^+ ion for K^+ exchange using data from Norrish.[23] At low acid concentrations (< 10^{-3} mol L^{-1}), H^+ behaves as any other cation and replaces the interlayer K^+, whereas, at high H^+ concentrations, the octahedral mica sheets can be attacked, and the structure can be destroyed.

An analysis of Figures 6 to 8 reveals that exchangeable K^+ remains in phlogopite for release into the Mehlich-1 solution; therefore, a longer experiment is required to analyze the time and release rate up to the K^+ release equilibrium. Thus, a new series of experiments and different mathematical models must be further investigated for the Mehlich-1 extraction.

Sodium tetraphenylboron (NaTpB) was used to assess phlogopitite K^+ availability. This salt can extract interlayer potassium from micaceous minerals because K^+ introduced into the NaTpB solution is almost entirely precipitated as potassium tetraphenylboron (KTpB), as described by the following equation:

$$KMg_3(AlSi_3O_{10})(OH)_{2(s)} + Na[B(C_6H_5)_4]_{(aq)} \rightleftharpoons NaMg_3(Si_3AlO_{10})(OH)_{2(s)} + K[B(C_6H_5)_4]_{(s)} \quad (6)$$

Precipitation of the insoluble potassium salt $[K[B(C_6H_5)_4]_{(s)}]$ decreases the K^+ concentration in the solution, and the equilibrium shifts to the right. To evaluate the NaTpB efficiency for the extraction of K^+ from phlogopitite, a new series of experiments was conducted using 0.2 mol L^{-1} NaTpB for extraction. Figure 9 shows a comparison of the K^+ release in NaTpB with that in the other acid solutions. A similar study on K^+ release was reported by Darunsontaya *et al.*,[18] who extracted a clay soil fraction in 0.3 mol L^{-1} NaTpB from 0 to 168 h.

Figure 9 shows that the NaTpB extractant is clearly effective in releasing K^+ from the phlogopite interlayer. The maximum value produced using NaTpB was 1.7 g kg^{-1} K^+, which corresponds to approximately 2.5% of the total K^+ in the mineral (from 68.9 g kg^{-1} total K^+) after 4 h of extraction.

The kinetic study was conducted using the same equations used for the acid extractions: the power-function, parabolic-diffusion and Elovich equations. The results

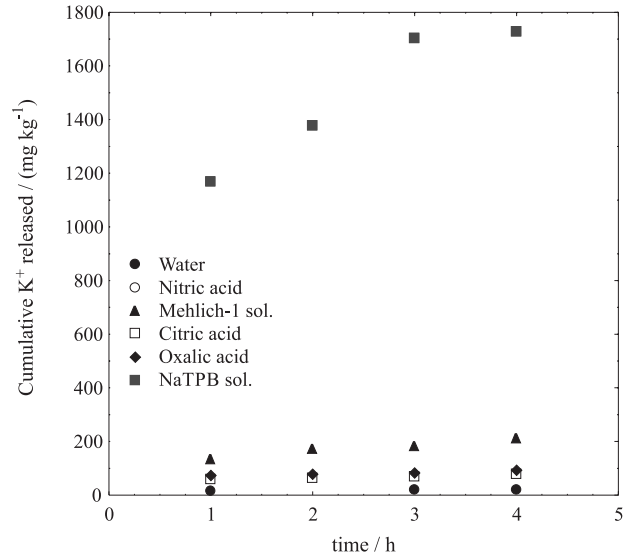

Figure 9. The cumulative levels of K^+ released in water, acid and NaTpB solutions (4 h extraction time).

from the statistical study presented in Table 2 demonstrate that, even though the *b* parameter values were highest for parabolic diffusion and the Elovich equations, the r^2 values were low, which indicates that more experimental data are necessary for a statistical analysis of this extraction. Notably, the NaTpB solution was the best extractant; however, its use in practical applications is limited. Because extraction in the acid medium was relatively low, NaTpB was used for extraction to discern whether K^+ could be released at higher levels.

Conclusions

The phlogopitite rock, which is a byproduct of emerald mining in Brazil, was crushed to ca. 2.0 mm and characterized using several techniques. The X-ray fluorescence results indicated that this rock contained approximately 9% K_2O; therefore, kinetic studies on potassium release from this mineral were conducted. The extent and rate of potassium release from phlogopitite were highly dependent on the extraction solution. The quantities and rates of K^+ release from phlogopitite were greater in the Mehlich-1 solution than in water or in citric, nitric or oxalic acid solutions. Although the NaTpB solution was the best extractant, its use in practical applications is limited. In conclusion, the phlogopitite investigated in this work may be used to improve the potassium level in Brazilian soil over the long term; however, it may not be used as an alternative to fertilization with potash (KCl and K_2SO_4). Despite the undoubted value of the chemical measurements performed in this work, phlogopitite K^+ bioavailability in Brazilian soil requires further field

studies. Thus, these results are the first step in discerning the bioavailability of phlogopitite K^+ for crops.

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References

1. Nascimento, M.; Loreiro, F. E. L. In *Série de Estudos e Documentos*; Peiter, C. C., ed.; CETEM/MCT: Rio de Janeiro, Brasil, 2004.
2. Van Straaten, P.; *Agrogeology: the Use of Rocks for Crops*; Enviroquest: Ontario, Canada, 2007.
3. Simonsson, M.; Andersson, S.; Andrist-Rangel, Y.; Hillier, S., Mattsson, L.; Öborn, I.; *Geoderma* **2007**, *140*, 188.
4. Naderizadeh, Z.; Khademi, H.; Arocena, J. M.; *Geoderma* **2010**, *159*, 296.
5. Barré, P.; Velde, B.; Fontaine, C.; Catel, N.; Abbadie, L.; *Geoderma* **2008**, *146*, 216.
6. Van Straaten, P.; *An. Acad. Bras. Cienc.* **2006**, *78*, 731.
7. Manning, D. A. C.; *Agron. Sustain. Dev.* **2010**, *30*, 281.
8. Silva, D. R. G.; Marchi, G.; Spehar, C. R.; Guilherme, L. R. G.; Rein, T. A.; Soares, D. A.; Ávila, F. W.; *Rev. Bras. Cienc. Solo* **2012**, *36*, 951.
9. Stout, S. A.; Cho, Y.; Komarneni, S.; *Appl. Clay Sci.* **2006**, *31*, 306.
10. Cho, Y.; Komarneni, S.; *Appl. Clay Sci.* **2009**, *43*, 401.
11. Cho, Y.; Komarneni, S.; *Appl. Clay Sci.* **2009**, *44*, 15.
12. Baltar, C. A. M.; Cavalcante, P. M. T.; Sampaio, J. A. In *Rochas e Minerais Industriais*; Luz, A. B.; Lins, F. F., eds.; CETEM: Rio de Janeiro, Brasil, 2008, ch. 29.
13. Dana, J. D.; *Manual de Mineralogia*; Livros Técnicos e Científicos Editora S.A.: Rio de Janeiro, Brasil, 1978, ch. 5.
14. Wypych, F.; Adad, L. B.; Mattoso, N.; Marangon, A. A. S.; Schreiner, W. H.; *J. Colloid Interface Sci.* **2005**, *283*, 107.
15. Castilhos, R. M. V.; Meurer, E. J.; *Cienc. Rural* **2001**, *31*, 979.
16. Jalali, M.; *Geoderma* **2006**, *135*, 63.
17. Zhou, J. M.; Huang, P. M.; *Geoderma* **2007**, *138*, 221.
18. Darunsontaya, T.; Suddhiprakarn, A.; Kheouruenromne, I.; Gilkes, R. J.; *Appl. Clay Sci.* **2010**, *50*, 376.
19. Martin, H. W.; Sparks, D. L.; *Soil Sci. Soc. Am. J.* **1983**, *47*, 883.
20. Brindley, G. M.; Brown, G.; *Crystal Structure of Clay Minerals and their X-ray Identification*; Mineralogical Society: London, UK, 1980.
21. Bigham, J. M.; Bhatti, T. M.; Vuorinen, A.; Tuovinen, O. L.; *Hydrometallurgy* **2001**, *59*, 301.
22. Sobral, L. F. In *Embrapa Tabuleiros Costeiros*; Resende, R. S., ed.; Boletim de Pesquisa e Desenvolvimento: Aracaju, Sergipe, Brasil, 2009.
23. Norrish, K. In *Proc. Int. Clay Conf.*; Serratosa, J. M., ed.; Div. de Ciencias: Madrid, Spain, 1973, p. 417.

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