

Potential Slow Release Fertilizers Based on K_2MgSiO_4 Obtained from Serpentinite

Fabiane C. Ballotin,^a Wedisson O. Santos,^b Edson M. Mattiello,^c Ottávio Carmignano,^d
Ana Paula C. Teixeira^a and Rochel M. Lago^{b,*a}

^aDepartamento de Química, Universidade Federal de Minas Gerais, 31270-901 Belo Horizonte-MG, Brazil

^bInstituto de Ciências Agrárias, Universidade Federal de Uberlândia, 38410-337 Uberlândia-MG, Brazil

^cDepartamento de Solos, Universidade Federal de Viçosa, 36570-000 Viçosa-MG, Brazil

^dDoutorado Inovação/Mineradora Pedras Congonhas, Universidade Federal de Minas Gerais,
31270-901 Belo Horizonte-MG, Brazil

In this work, a potassium magnesium silicate mineral based on phase K_2MgSiO_4 was prepared from serpentinite rock and studied as a potential K and Mg slow-release fertilizer. The material was prepared by impregnation of serpentinite/KOH and calcination at 700 °C to produce K_2MgSiO_4 phase, olivine and forsterite. The release patterns of K and Mg in the stirred-flow trial and leaching through the soil columns showed that K_2MgSiO_4 -based materials released K on lower rates than KCl and $MgSO_4 \cdot 7H_2O$, however, there was no evidence of Mg release. The extraction with 1 mol L⁻¹ NH_4OAc showed a considerable content of Mg and K for K_2MgSiO_4 -based materials, due to exchange of NH_4^+ and Mg^{2+} . X-ray diffraction (XRD) analysis of materials impregnated with K and calcined showed peaks relative to K_2MgSiO_4 . After leaching, the peaks intensity diminished, supporting that part of K leached. Therefore, the samples showed great potential as slow-release K-fertilizers when compared with KCl source.

Keywords: fertilizer, potassium, serpentinite, slow release, stirred-flow

Introduction

Fertilizers use is essential to achieve high crop yields under tropical soil conditions, which are generally poor in nutrients such as K and Mg. In the case of K, Brazilian agribusiness is highly dependent on importation of K-salts to meet the current agricultural demand.¹

In highly weathered soils, as the most of those occurring in tropical agricultural areas, the low cation exchange capacity (CEC)² limits the cationic retention, including K^+ . In these conditions, unsuitable managements of traditional K-sources, such as KCl, may lead to risks associated to soil salinity, plant toxicity or losses by leaching across soil profile.³ Therefore, these reports evidence the need to prospect fertilizer technologies which release K in a controlled process according to plant demands aiming to improve fertilizer efficiency, including the reduction of both on K loss and the need of split application.^{4,5} In fact, several studies have been performed into using different materials as slow-release K-fertilizer, such as rice husk ash for the synthesis of

silicon and potassium,⁶ K-feldspar ($KAlSi_3O_8$)⁷ and chrysotile/ K_2HPO_4 .⁸

Serpentinite, a metamorphic rock with general approximate formula $[Mg_3Si_2O_5(OH)_4]$, is found in different places on the surface of the world with global reserves estimated in hundreds of millions kg.⁹ The basic serpentine structure is a layer composed of Mg-rich octahedral units $[MgO_2(OH)_4]^{6-}$ linked to tetrahedral silicate moieties $[Si_2O_5]^{2-}$.

Serpentinite is typically used as building stone generating a fine fraction as industrial residue, which potentially can be used as fertilizer.¹⁰ Indeed, due to the basicity, serpentinite has been used as a Mg source and replacement of lime.¹¹ In addition, due to the thermal properties of serpentinite it is also used as flux agent to produce thermal-phosphate fertilizers.¹²

Previous studies have shown that alkaline metals, such as Li^+ , Na^+ and K^+ can be intercalated in the serpentinite structure and upon thermal treatment form different Mg silicates such as Li_4SiO_4/MgO ,¹³ $Na_2Mg_2Si_2O_7$ ¹⁴ and K_2MgSiO_4 .¹⁵ The phase K_2MgSiO_4 showed several physical-chemical behaviors such as alkalinity and low solubility in water and acidic media.

*e-mail: rochel@ufmg.br

Therefore, the K_2MgSiO_4 phase produced from the available and low-cost serpentinite can be a source of K or Mg in slower release rates compared with traditional soluble sources, which could be highly advantageous as potential fertilizers.

The goal of the study was to investigate the performance of products from chemical treatment followed by calcination (fine fraction impregnated with KOH and thermally treated) of serpentinite in terms of release pattern of K and Mg and plant availability.

Experimental

Material synthesis

Serpentinite (composed of lizardite and antigorite associated with talc) samples obtained from Pedras Congonhas Mine in Nova Lima (Minas Gerais, Brazil) were impregnated with KOH (20 wt.% K) and calcined at different temperatures (500, 700 and 900 °C) according to methodology described by Ballotin *et al.*¹⁵ The samples were named according to calcination temperature, where K_{500} , K_{700} and K_{900} indicate that materials were impregnated with KOH and calcined at specific temperatures. The materials SER (serpentinite) and SER_{700} (serpentinite calcined at 700 °C) were also used.

Material characterization

The X-ray diffraction (XRD) analyses were performed on a Shimadzu diffractometer, model XRD-7000 with $CuK\alpha$ with a scan speed of 4° min^{-1} . SEM (scanning electron microscopy) samples were also metallized with gold and the images were obtained on a Quanta 200 equipment.

The total content of K and Mg in the materials were extracted using HCl conc.¹⁶ First, 0.5 g of the samples were extracted with 10 mL of HCl 36.5% (m/m) until next to dryness. Then, 30 mL of 2 mol L^{-1} HCl were added until boiling for 10 min.

Soil preparing

The study was developed at the facility of Soil Science Department at Federal University of Viçosa, Minas Gerais, Brazil, using two different soils with contrasting textures (sandy soil, from Três Marias-MG and clay soil, from Viçosa-MG). Air dried soil samples were ground and sieved (mesh size 2 mm). The sandy soil had the following physical and chemical properties: clay 19%, silt 2%, sand 79%; pH (H_2O) 4.36; K (Mehlich-1 extractor) 15 mg dm^{-3} ;

Mg (KCl extractor) $0.023 \text{ cmol}_c \text{ dm}^{-3}$ and 1.01% organic carbon. The clay soil had the following physical and chemical properties: clay 55%, silt 10%, sand 35%; pH (H_2O) 5.73; K (Mehlich-1 extractor) 13 mg dm^{-3} ; Mg (KCl extractor) $0.28 \text{ cmol}_c \text{ dm}^{-3}$ and 1.52% organic carbon.

Soil acidity were corrected reaching bases saturation to about 60%. For that, lime ($CaCO_3$) was mixed in all soil volume (2.5 dm^3), remaining incubated for 15 days with humidity maintained at 80% of water-holding capacity.¹⁷ Subsequently, the soil was air-dried, ground and passed through a 2-mm sieve for physical and chemical characterization.

Stirred-flow trial

The releasing kinetics of K and Mg from serpentinite samples were performed using a stirred-flow technique equipped with a piston coupled with a ultra-high performance liquid chromatography (UHPLC) pump system. A 15 mL stirred-flow acrylic chamber was used in the experiments to which 50 mg of each fertilizer (containing 10 mg of K) were added. Deionized water was used as desorbing solution and a 25 mm diameter cellulose filter membrane with $0.45 \mu\text{m}$ pore size were used in the reaction chamber.

Upon sealing the reactor chamber, deionized water was flowed through the chamber at 1 mL min^{-1} , and the dispersion in the reactor chamber was stirred by a magnetic stir bar at 400 rev min^{-1} . Time zero was defined as the moment of entry of the first drop of effluent solution into the first tube of the fraction collector. The leached was collected with a fraction collector set to collect 2 mL of solution *per* tube for 360 min. The releasing kinetics trial were performed in triplicate. Total leaching concentrations of K and Mg were quantified by flame emission and absorption spectrometry, respectively.

Average of cumulative leached K or Mg data were plotted as a function of time and were calculated by multiplying the leaching amount at each time *per* mass of fertilizer and volume of the reaction chamber.

Column soil trial

The leaching of K and Mg in soil was evaluated by a soil leaching column trial. For that, 50 cm^3 of both, sandy and clay soils were packed into a column (60-mL removable Luer Lock syringe, 3-cm diameter), corresponding to a height of 8 cm.

The base of the column was covered with a layer of glass wool before packing. The columns were then leached

top to bottom with 15 mL of water and brought to water-holding capacity. Fertilizers giving a 150 mg dm⁻³ K and 132 mg dm⁻³ Mg were placed on the top of the soil at 0.5 cm deep. Leaching was performed by adding 15 mL of deionized water on top and applying suction with a syringe to draw the water through the column. The leachate was sampled until 46 days after fertilization (DAF), at different intervals, as follows: 1, 2, 3, 6, 9, 13, 16, 20, 23, 27, 30, 34, 37, 40, and 46 DAF. Between leaching events, the columns were incubated at 25 °C. Potassium and Mg concentrations in the leachate were determined by flame emission and atomic absorption spectroscopy, respectively.

The acidity of leachate (pH) were measured by potentiometry.

The recovery rate of K and Mg were calculated following the equation 1.

$$\text{Recovery rate (\%)} = \frac{w_{\text{recover}} - w_{\text{control}}}{w_{\text{added}}} \times 100 \quad (1)$$

where, w_{recover} is the K and Mg content in the leachate of the fertilized treatment; w_{control} is the K and Mg content in the control treatment, and w_{added} is the total of added K and Mg in each experimental unit. The experiment was performed using a factorial scheme (7 + 1) × 2 × 15, corresponding to seven materials, one control treatment, two soils and fifteen incubation times. The trial was a completely randomized design with three replications.

K and Mg availability in soil

Potassium and Mg fertilizes with 150 mg dm⁻³ K and 132 mg dm⁻³ Mg were incubated with 15 cm³ of limed soil (clay and sandy) and maintained watered at 80% of water-holding capacity.

The experiment was performed using the factorial scheme (7 + 1) × 2 × 6, corresponding to seven sources of K or Mg, one negative control treatment, two soils and six incubation times (5, 10, 15, 30, 60 and 90 DAF). The experimental design was completely randomized with three replications.

By the end of each incubation day, the soil samples were air dried, ground and sieved (2 mm). Available K or Mg contents was extracted using NH₄OAc as test (1 mol L⁻¹, pH 7.0), considering a relation m v⁻¹ soil:solution of 1:10, which was stirred at 200 rev min⁻¹ for 10 min, followed by a rest of 16 h.¹⁸ Potassium and Mg concentrations were determined by flame emission and absorption spectroscopy, respectively. The soil extractable elements (EE) contents (available) were calculated according to the equation 2.

$$\text{EE (mg dm}^{-3}\text{)} = \frac{w_{\text{recovered}}}{V_{\text{soil}}} \quad (2)$$

where, $w_{\text{recovered}}$ is K and Mg ions extracted with NH₄OAc and V_{soil} is the soil volume used in the experiment (5 cm³).

The recovery rate by extractor of K and Mg were calculated according to equation 3:

$$\text{Recovery rate (\%)} = \frac{w_{\text{recovered}} - w_{\text{control}}}{w_{\text{added}}} \times 100 \quad (3)$$

where, w_{control} is the K and Mg content in the control soil, and w_{added} is the total of added K and Mg in each experimental unit.

Results and Discussion

Chemical composition of the materials

The serpentinite sample (named hereon as SER) presented 29.1 wt.% MgO, 39.9 wt.% SiO₂, 10.1 wt.% Fe₂O₃ and 1.7 wt.% Al₂O₃. Upon thermal treatment of pure serpentinite at 700 °C (SER₇₀₀) the Mg content increased to ca. 18% (Table 1) due to dehydration processes. After KOH addition and thermal treatment at 500, 700 and 900 °C (K₅₀₀, K₇₀₀ and K₉₀₀), the Mg contents decreased to the range 10-14%, due to K addition as KOH. Potassium contents in these samples were ca. 12.2-14.5 wt.% (Table 1).

Table 1. Total content of K and Mg in both serpentinite rock (SER) and products from its impregnation with KOH over different calcination temperatures

Material	Mg / wt.%	K / wt.%
SER	14.3 ± 1.9	–
SER ₇₀₀	18.1 ± 0.4	–
K ₅₀₀	13.2 ± 0.5	12.2 ± 0.7
K ₇₀₀	13.6 ± 0.3	14.3 ± 0.3
K ₉₀₀	10.9 ± 1.4	14.5 ± 0.8

SER: serpentinite; SER₇₀₀: serpentinite thermally treated at 700 °C; K₅₀₀, K₇₀₀ and K₉₀₀: serpentinite impregnated with K and thermally treated at 500, 700 and 900 °C, respectively.

SEM images of the samples showed that SER is a compact material with particles around 50 µm. The thermal treatment caused particles agglomeration (Figure S1, Supplementary Information (SI) section) and the impregnation with KOH and calcination did not promote any significant change in terms of morphology. Similar results have been observed in a previous work.¹⁵

XRD analyses (Figure S2, SI section) revealed that SER is basically composed of antigorite (JCDPS 44-1447), lizardite

(JCDPS 9-444), $Mg_3Si_2O_5(OH)_4$ and talc ($Mg_3Si_4O_{11}H_2O$) (JCDPS 2-66), hydrated phases of magnesium silicates.¹⁵ When these minerals are thermally treated at 700 °C, the peaks relative to these phases become less intense, and new phases are formed due to dehydration of the serpentinite, such as olivine (Fe,Mg) $_2SiO_4$ (JCPDS 2-1326) and forsterite, Mg_2SiO_4 (JCPDS 4-768).

For the samples impregnated with KOH and thermally treated (Figure S3, SI section), the potassium magnesium silicate phase, K_2MgSiO_4 (JCPDS 39-1426) was detected. As an expected general trend, the increase of calcination temperature led to a decrease of XRD peaks intensity relative to hydrated phases while the intensity of the peaks related to K_2MgSiO_4 phase increased.¹⁵

Potassium and Mg release pattern

Kinetic release of K from the materials revealed different patterns (Figure 1). After 50 min of release, 100 wt.% of K was leached, when the source was KCl. For the same time, the materials K_{500} , K_{700} , K_{900} released 80, 53 and 70 wt.% of total K, respectively. The K release diminished for all sources after 50 min of leaching. However, even with a lower rate of leaching, after 6 h, the K leached accumulated 84, 73 and 80% of total K, respectively for sources K_{500} , K_{700} , K_{900} (Figure 1).

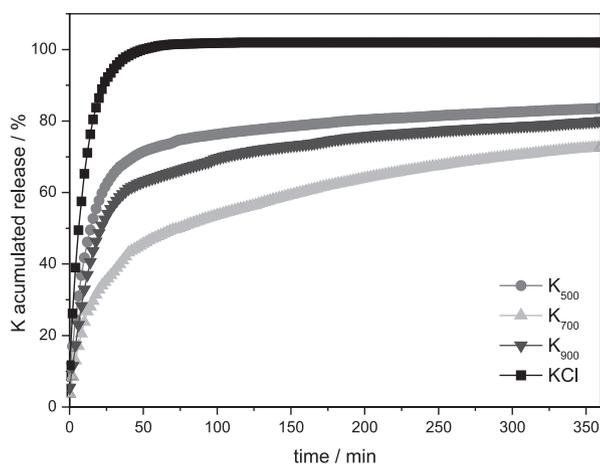


Figure 1. Cumulative release of K in water flux during 6 h, at rate of 1 mL min⁻¹, for materials K_{500} , K_{700} and K_{900} (serpentinite impregnated with K and thermally treated at 500, 700 and 900 °C, respectively) and KCl.

Differences among materials in terms of releasing patterns can be attributed to different calcination temperatures on formation and stability of K phases. At 500 °C, serpentinite is not totally decomposed and probably the phase K_2MgSiO_4 has low crystallinity, leaving K ions more leachable, since reacting surface increases when the crystallinity of any phase decreases.¹⁵ The temperature increase promoted a higher

leaching of structural elements, including K. Thus, at 900 °C, the K can be expelled of crystal structure, while at 700 °C, the K is strongly bounded to the new formed phase.¹⁵

Comparing the synthesized materials with KCl, it can be observed that they release K in lower rates, once KCl is an ionic salt with high solubility, different from materials obtained by serpentinite calcination, which generally have low water-solubility, due to silicates slow dissolution kinetics.¹⁹ The K-release patterns of the materials suggest their potential as slow release fertilizers, however, the synchrony with crops still have to be evaluated. For Kakoulides,²⁰ materials which release nutrients slowly have more advantages if they release in strict synchrony with crop demand, reducing the potential for groundwater contamination by mobile elements on soil, due to leaching, soil salinization and the reduced need of reapplications during the crop cycles.^{5,21}

Magnesium releasing patterns were low after 200 min of leaching (Figure 2a), and there was a low linear increase trend for Mg over the time for materials SER_{700} , K_{500} and K_{700} . For SER and K_{900} , the release was negligible. However, as expected, the material $MgSO_4 \cdot 7H_2O$ (Figure 2b) released its total Mg content over 200 min. Magnesium was likely not leached from the serpentinite-based due to the insoluble crystalline structures formed. However, studies of serpentinite solubilization with inorganic acids showed that Mg could be extracted in presence of acidity species,²² and although the structure is maintained, silicate sheets is disrupted resulting in amorphous phase.²³

After 6 h of release, the remaining solid materials were dried at 80 °C for 12 h for performing XRD analyses. Figures S2 and S3 (SI section) contrast XRD spectra from these materials before and after leaching trial. The

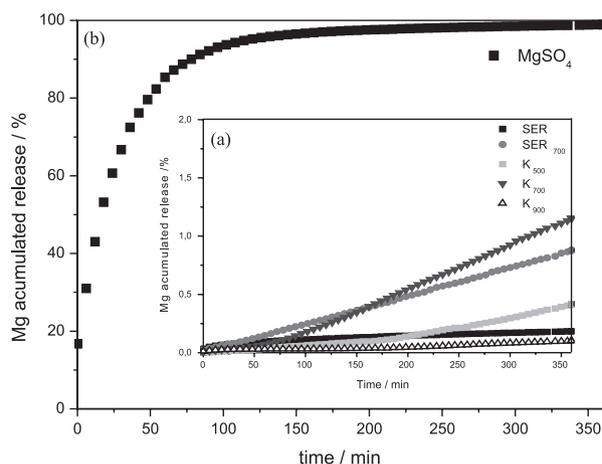


Figure 2. Cumulative release of Mg in water, during 6 h, rate of 1 mL min⁻¹, for materials SER (serpentinite), SER_{700} (serpentinite thermally treated at 700 °C), K_{500} , K_{700} and K_{900} (serpentinite impregnated with K and thermally treated at 500, 700 and 900 °C) (a), and $MgSO_4$ (b).

XRD of SER (Figure S2a), showed mainly the presence of antigorite, lizardite and talc,¹⁵ while SER₇₀₀ diffraction pattern (Figure S2b) indicated the disappearance of serpentinite characteristic peaks and the formation of new phases, such as olivine and forsterite. After the 6 h of releasing, an expressive decrease of peaks intensity from both materials, SER and SER₇₀₀, occurred.

X-ray diffraction of materials impregnated with KOH and calcined at 500, 700 and 900 °C before and after leaching is shown in Figure S3 (SI section). In general, peak intensities relative to the phase K₂MgSiO₄ diminished noticeably after leaching. In fact, the dissolution of the mineral phase leads to a decrease in both the crystallinity of the phase and its final concentration, leaving mainly the phases MgSiO₄ and (Mg,Fe)SiO₄.¹⁵

For K₅₀₀, it can be inferred that before leaching, the material still presents peaks of antigorite and lizardite, showing that 500 °C was not enough to totally decompose serpentinite phases. Furthermore, olivine, forsterite and K₂MgSiO₄, non-hydrated phases, are also present. After leaching, however, the peaks due non-hydrated phases were no longer observed. Probably, 500 °C was not sufficient to form stable phases.¹⁵

X-ray diffraction of K₇₀₀ before leaching showed only non-hydrated phases. Although after leaching the peaks intensity diminished, the phases of olivine, forsterite and K₂MgSiO₄ maintained. On the other hand, the XRD of K₉₀₀ was similar to K₇₀₀, and the phases intensity were higher, which is likely explained by the temperature of thermal treatment.¹⁵ Ballotin *et al.*¹⁵ also showed that when K₂MgSiO₄ is in contact with a solvent (methanol), fractions of K are leached and the intensity of XRD peaks for the K₂MgSiO₄ phase decreases.

In order to understand the material solubility, sample K₇₀₀ was left in contact with water and HCl_{conc} for 24 h. After this time, the material was analyzed by XRD (Figure 3). After contact with water, XRD data showed that only the peak relative to phase K₂MgSiO₄ disappeared, probably

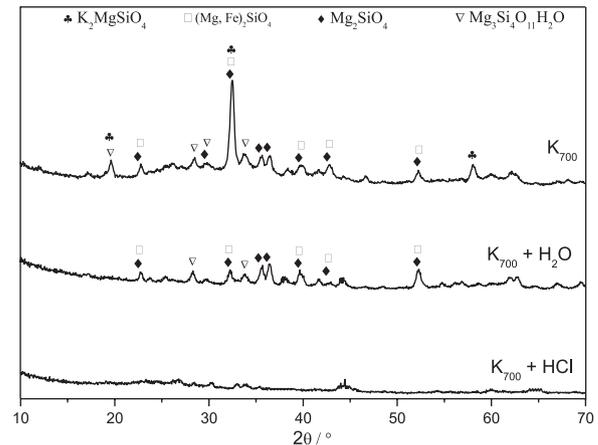


Figure 3. X-ray diffraction patterns of K₇₀₀, K₇₀₀ after reacting with water and HCl for 24 h under stirring.

due to K release. However, after contact with HCl, all the mainly peaks disappeared due to a collapse of the silicate structure in acid medium.

Thus, based on K and Mg release patterns, as well as XRD before and after release, it can be inferred that when in contact to water, K is released from the material structure, letting the phase Mg₂SiO₄ (Figure 4).

Leaching tests on soil columns

Leaching tests of the materials on soil columns showed different patterns among the materials, and soil textures (Figure 5). Indeed, for sandy soil in general more quantity of K was recovered from all the sources. Curiously, the KCl source presented variations on leaching ratio, being decreasing on time intervals 0-4; 5-28 and 29-49 days, when it was recovered 24, 12 and 3% of the total of added K. For materials K₅₀₀, K₇₀₀ and K₉₀₀, at same time intervals, were recovered 8.3, 16.9 and 5.0; 8.2, 20.1 and 6.1; 6.2, 20.2 and 6.9% of total K, respectively.

Different from kinetics initial study, except for KCl, the other materials presented different K-release patterns. At

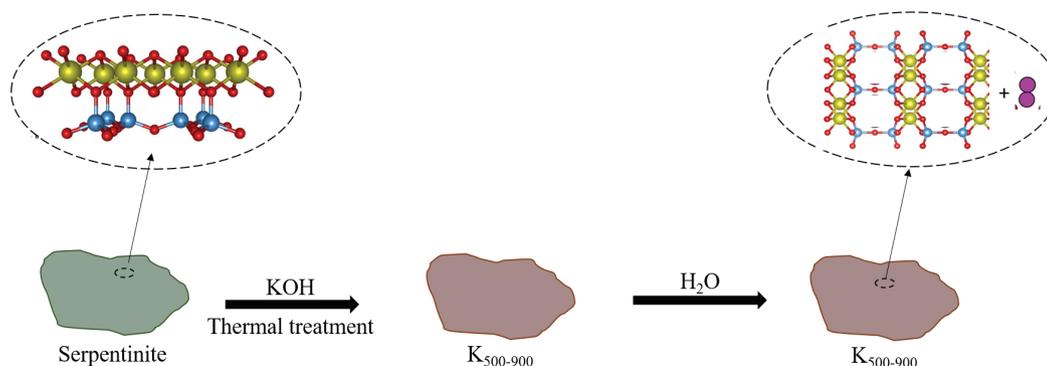


Figure 4. Scheme of K release from serpentinite structure.

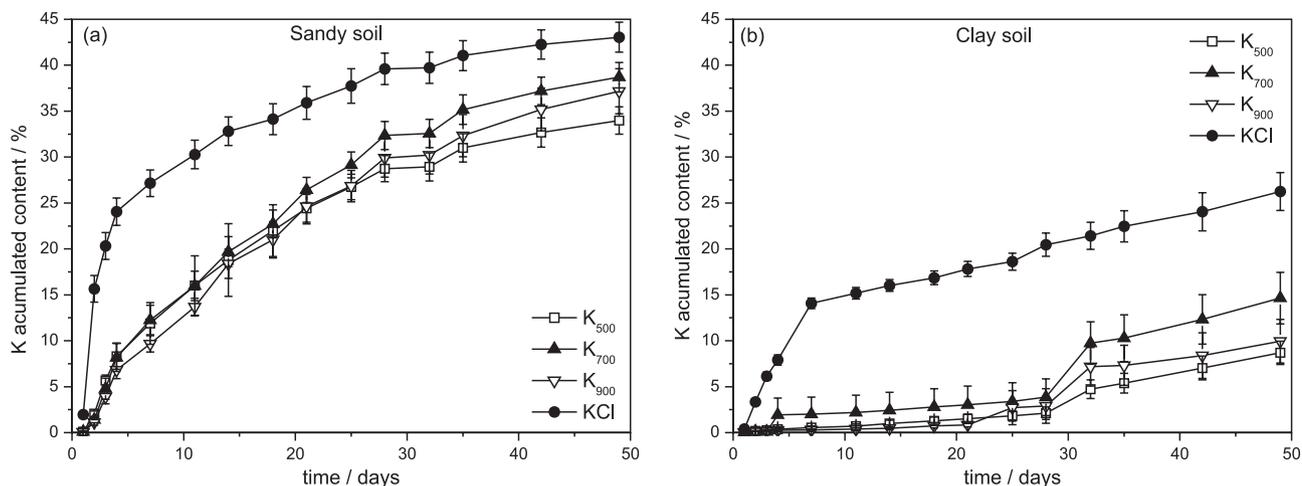


Figure 5. Leached fraction (cumulative) of K (% of total applied) of materials (K_{500} , K_{700} , K_{900} and KCl) using soil columns of different textures: (a) sandy and (b) clay. K_{500} , K_{700} and K_{900} are serpentine impregnated with K and thermally treated at 500, 700 and 900 °C, respectively.

49 days, the total of K leached were 43, 39, 37 and 34% of total applied for KCl, K_{500} , K_{700} and K_{900} , respectively, while on release tests, the leached fraction was higher: 100, 80, 53 and 70% for KCl, K_{500} , K_{700} and K_{900} . Probably this difference could be attributed to soil addition on column trials, which has negative charges that could adsorb K.²⁴ Moreover, for the clay soil, it was observed a different leaching trend among materials. For KCl, it was observed two distinct ratios, between 0-4 and 5-49 days.

For other sources, the ratio varied over time, being higher between 27-32 days, 28-49 days and lower between 0-27 days. After 49 days, the K recovery were 26% when the KCl was the source and 9, 15 and 10% for K_{500} , K_{700} and K_{900} , respectively.

As previously shown for continuous flow experiment, on column trial, the calcined materials did not release significant amount of Mg over the leaching time. However, the soluble

Mg-source ($MgSO_4 \cdot 7H_2O$) promoted leaching of 32 and 23% in sandy and clay soil, respectively, after 50 DAF (Figure 6). It was also observed that leaching rates of Mg ($MgSO_4 \cdot 7H_2O$) on sandy and clay soil differed all over the time. On sandy soil, the high release ratio was observed between 0-4 days (28%), followed by a low ratio (4%) between 5-49 DAF, indicating a decrease on release ratio over time.

Although both soils presented similar values of CEC, 4.19 $cmol_c dm^{-3}$ for clay and 3.99 $cmol_c dm^{-3}$ for sandy soil, the recovered content of K^+ and Mg^{2+} in sandy soil was higher than in clay soil, promoting less retention of K^+ or Mg^{2+} , resulting in higher leaching of K^+ or Mg^{2+} .²⁵

Recovery rate and available soil content

The recovery rate represents the amount of fertilizer applied to the soil that are able to be recovered by an

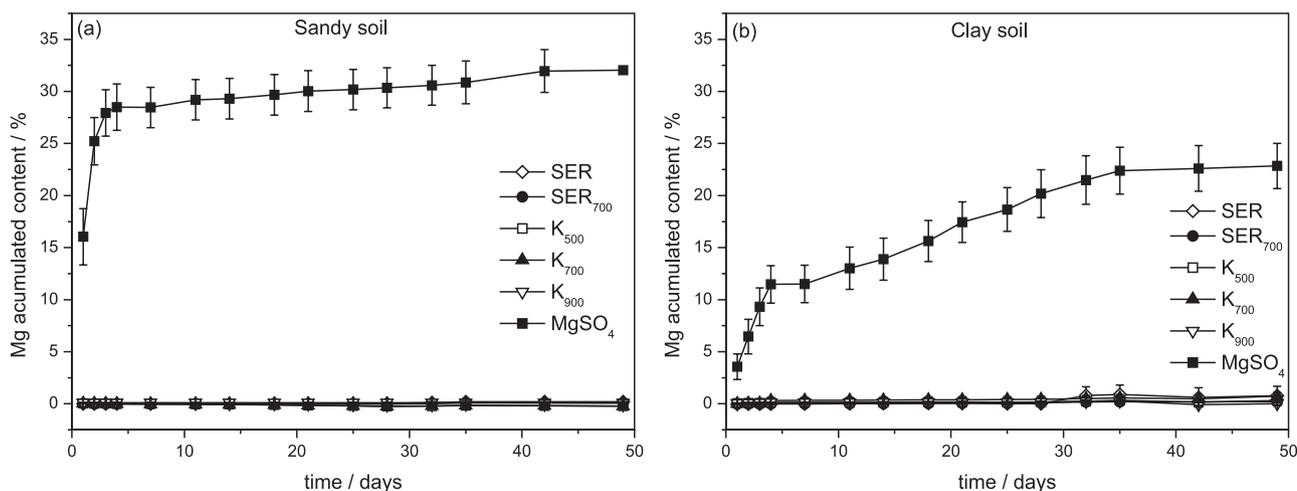


Figure 6. Leached fraction (cumulative) of Mg (% of total applied) of different materials (serpentine, SER₇₀₀, K_{500} , K_{700} , K_{900} and $MgSO_4 \cdot 7H_2O$) using soil columns of different textures: (a) sandy and (b) clay.

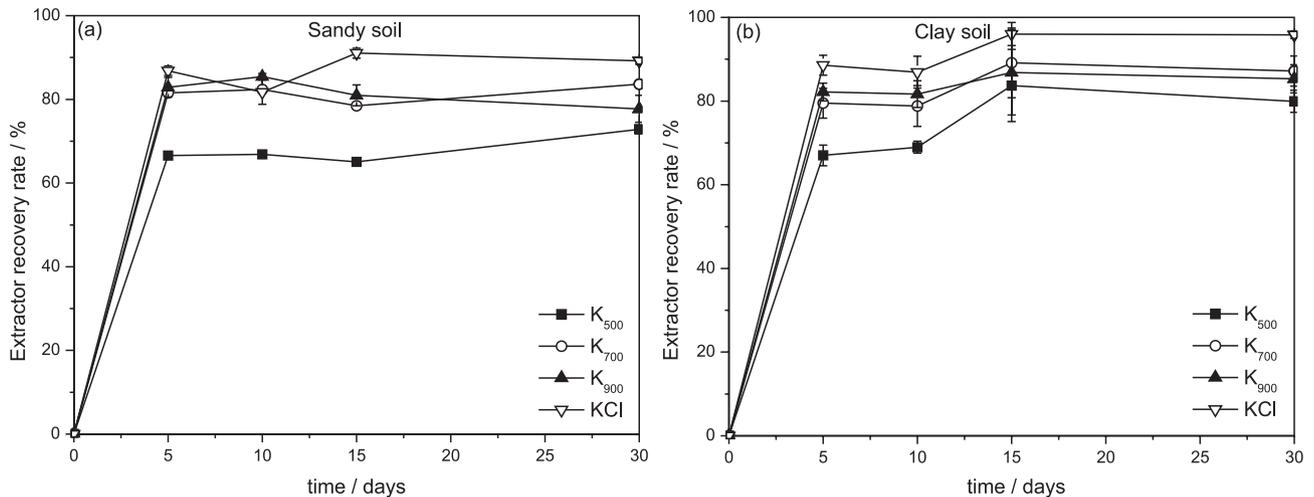


Figure 7. K recovery rate by 1.0 mol L⁻¹ NH₄OAc extractant at pH 7.0 after 60 DAF with K₅₀₀, K₇₀₀, K₉₀₀ and KCl in soils of contrasted textures: (a) sandy and (b) clay.

extractor. Assuming that non-exchangeable K is negligible in both soils, increasing on recovery rate over time means, therefore, that there is an increasing on K releasing from the materials. In this sense, the extractor NH₄OAc was used to evaluate how K recovery rate varied among the sources throughout the incubation times (Figure 7).

For sandy soil the recovery rate of K after 60 DAF was 90% for KCl and 73, 84 and 78% for materials K₅₀₀, K₇₀₀ and K₉₀₀, respectively. On clay soil, the recovery rate was higher, 96, 80, 87 and 85% for KCl, K₅₀₀, K₇₀₀ and K₉₀₀, respectively, after 60 days of soil incubation. The lower releasing of K of SER based materials compared to KCl could indicate differences on agronomic effectiveness among them, especially in terms of leaching and salt index. In fact, if the releasing rate of these materials met the initial plant demand and lasts longer, there is an expectation that they can be agronomically more efficient for crop fertilization,

and therefore with high value as fertilizers. However, we do not know when the remaining K in these materials would be released over the time. If these remaining K species are highly insoluble or less reactive it would be not advantageous.

According to van Raij,²⁶ the K availability for plant nutrition is based on the exchangeable K contents, which are readily available to the plants.²⁷ This exchangeable K is retained electrostatically by negative charges present in organic or mineral colloids from the soil and is released by exchange with cations of saline solutions.²⁸ Studies have shown that the extractor 1.0 mol L⁻¹ NH₄OAc is the most recommended to determine the available K content for plant demand.^{26,29}

The total recovery of Mg²⁺ (Figure 8) in the sandy soil was around 58, 0.2, 29, 24, 21 and 18% for MgSO₄, SER, SER₇₀₀, K₅₀₀, K₇₀₀ and K₉₀₀, respectively, after 30 DAF. For

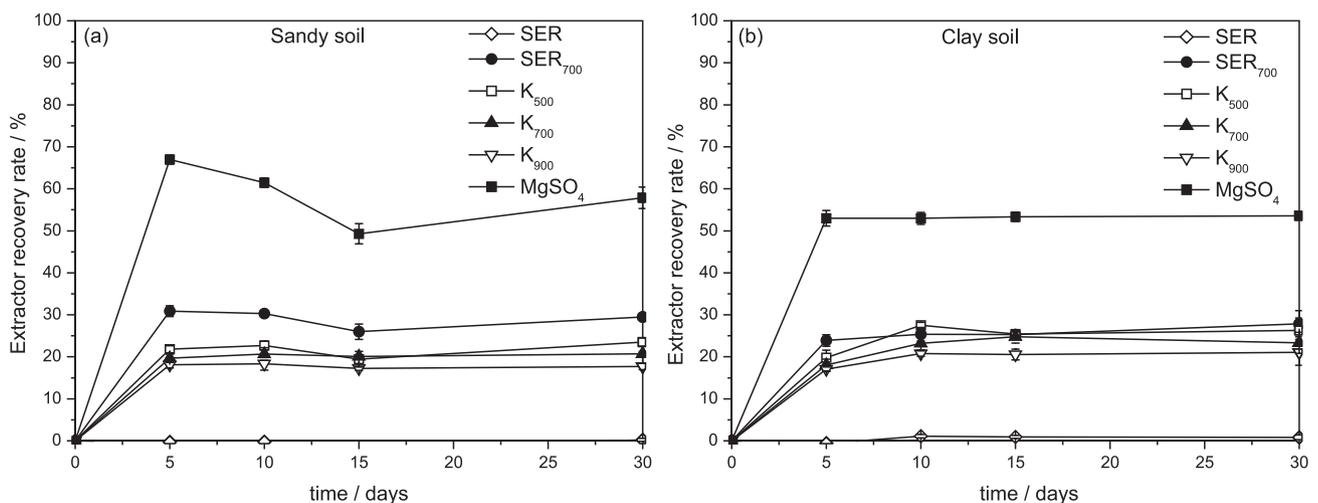


Figure 8. Mg recovery rate by 1.0 mol L⁻¹ NH₄OAc extractant at pH 7.0 of different sources (K₅₀₀, K₇₀₀, K₉₀₀ and KCl) and incubated soils of contrasted textures: (a) sandy and (b) clay.

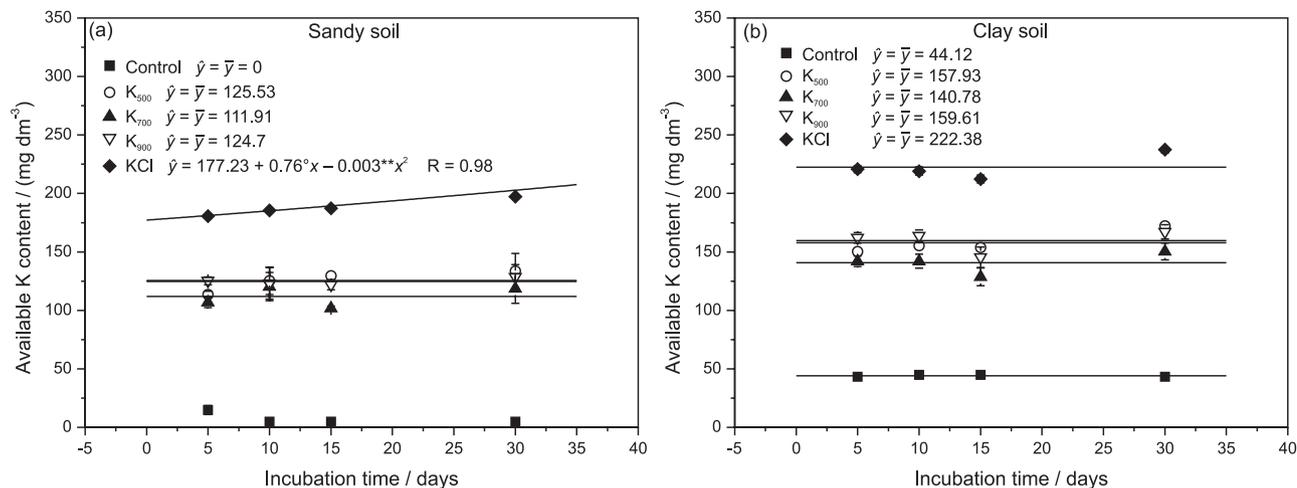


Figure 9. Available K contents ($1 \text{ mol L}^{-1} \text{ NH}_4\text{OAc}$, pH 7 test) extracted from soil of contrasting textures: (a) sandy, and (b) clay, which were incubated with products obtained from the calcination of serpentinite treated with KOH K_{500} , K_{700} and K_{900} .

the clay soil, the recovery after 30 days was 54, 0.8, 28, 26, 23 and 21% for $MgSO_4$, SER, SER $_{700}$, K_{500} , K_{700} and K_{900} , respectively. The low recovery of Mg on materials SER $_{700}$, K_{500} , K_{700} and K_{900} in water might occur because Mg is part of the material structure.

It is important to note that, during the leaching test, the released Mg and K were lower when compared to the available contents. This occurs because in the leaching trial, the fluxing water was used as an extractor and in the incubated soil trial, the extractor used was NH_4OAc . The phenomenon that occurs is the exchange of cations; NH_4^+ ions replace the cations present in the soil²⁷ releasing K and Mg.

The incubation time had no effect on the availability of K for all sources (Figure 9). For sandy soil, the availability of K for serpentinite sources was constant all over the time. The availability of K after 30 days were 5.0, 125.5, 111.9 and 124.7 mg dm^{-3} , respectively for control, K_{500} , K_{700} and K_{900} . The K availability for KCl had a slightly increase all over the days.

In the clay soil the available nutrient content in the soil was also constant for a long time. The available values after 30 days were 44.1, 157.9, 140.8, 159.7 and 222.4 mg dm^{-3} for the control, K_{500} , K_{700} , K_{900} and KCl, respectively. For both soils, K_{700} presented a lower K availability than K_{500} and K_{900} , which is related to the formation of phase K_2MgSiO_4 as previously discussed.

The available Mg^{2+} contents were constant over time. In the sandy soil, the control (soil without fertilizer application) and SER treatments promoted similar concentrations of available Mg (5.3 and 5.1 mg dm^{-3} of Mg^{2+} , $1 \text{ mol L}^{-1} \text{ NH}_4\text{OAc}$, pH 7 test). However, the materials K_{500} , K_{700} and K_{900} showed available 29.4, 27.9 and 25.8 mg dm^{-3} , respectively. Like expected, the water-

soluble source, $MgSO_4 \cdot 7H_2O$, showed a greater release on all evaluated times (90 mg dm^{-3}).

On clay soil, the Mg contents were also constant all over the time. It was observed that Mg^{2+} contents on clay soil were higher than sand soil. The control (soil without fertilizer) and SER treatments presented 29.4 and 31.7 mg dm^{-3} of available Mg. The available content was 55.9, 53.7 and 51.6 mg dm^{-3} for K_{500} , K_{700} and K_{900} .

The available Mg^{2+} content of SER treatment was different from K_{500} , K_{700} and K_{900} in both soils due to K addition and thermal treatment, which changes the material structure, becoming easier the exchange of Mg^{2+} and NH_4^+ . Although the materials with K showed available Mg contents when were extracted with $1 \text{ mol L}^{-1} \text{ NH}_4\text{OAc}$, the stirred flow trial as well as the soil column experiments, demonstrated no release of Mg^{2+} , being necessary studies with plants.

Conclusions

This work has produced supporting evidences that serpentinite is a potential raw material to synthesize K-slow release fertilizers through chemical/thermal treatment. Thermal treatment of serpentinite with KOH produced mainly the phase K_2MgSiO_4 which showed to be an efficient source of K^+ species less water-soluble than KCl, and therefore with lower releasing rates. Studies involving biological responses with plants over long-term evaluations are necessary to investigate the effectiveness of these new materials as potential K-fertilizers.

Supplementary Information

Supplementary data are available free of charge at <http://jbcs.sbq.org.br> as a PDF file.

Acknowledgments

The authors acknowledge Pedras Congonhas Ltda. for the samples and the support of INCT Midas, CNPq, CAPES, FAPEMIG and Microscopy Center.

References

1. Mancuso, M. A. C.; Soratto, R. P.; Crusciol, C. A. C.; Castro, G. S. A.; *Rev. Bras. Cienc. Solo* **2014**, *38*, 1448.
2. Aprile, F.; Lorandi, R.; *J. Agric. Sci.* **2012**, *4*, 278.
3. Hanafi, M. M.; Eltaib, S. M.; Ahmad, M. B.; *Eur. Polym. J.* **2000**, *36*, 2081.
4. Chen, S.; Yang, M.; Ba, C.; Yu, S.; Jiang, Y.; Zou, H.; Zhang, Y.; *Sci. Total Environ.* **2018**, *615*, 431.
5. Jarosiewicz, A.; Tomaszewska, M.; *J. Agric. Food Chem.* **2003**, *51*, 413.
6. França, A. A.; Schultz, J.; Borges, R.; Wypych, F.; Mangrich, A. S.; *J. Braz. Chem. Soc.* **2017**, *28*, 2211.
7. Ciceri, D.; de Oliveira, M.; Allanore, A.; *Green Chem.* **2017**, *19*, 5187.
8. Borges, R.; Baika, L. M.; Grassi, M. T.; Wypych, F.; *J. Environ. Manage.* **2018**, *206*, 962.
9. Guillot, S.; Schwartz, S.; Reynard, B.; Agard, P.; Prigent, C.; *Tectonophysics* **2015**, *646*, 1.
10. Błońska, E.; Pająk, M.; Małek, S.; Januszek, K.; *Commun. Soil Sci. Plant Anal.* **2017**, *48*, 692.
11. Chittenden, E. T.; Stanton, D. J.; Watson, J.; Dodson, K. J.; *New Zeal. J. Agric. Res.* **1967**, *10*, 160.
12. Ranawat, P.; Kumar, K. M.; Sharma, N. K.; *Curr. Sci.* **2009**, *96*, 843.
13. Vieira, S. S.; Paz, G. M.; Teixeira, A. P. C.; Moura, E. M.; Carmignano, O. R.; Sebastião, R. C. O.; Lago, R. M.; *J. Environ. Chem. Eng.* **2018**, *6*, 4189.
14. Paz, G.; Vieira, S. S.; Bertoli, A. C.; Ballotin, F. C.; de Moura, E. M.; Teixeira, A. P. C.; Costa, D. A. S.; Carmignano, O.; Lago, R. M.; *J. Braz. Chem. Soc.* **2018**, *29*, 1823.
15. Ballotin, F. C.; Cibaka, T. E.; Ribeiro-Santos, T. A.; Santos, E. M.; Teixeira, A. P. C.; Lago, R. M.; *J. Mol. Catal. A: Chem.* **2016**, *422*, 258.
16. Ministério da Agricultura, Pecuária e Abastecimento (MAPA); *Manual de Métodos Analíticos Oficiais para Fertilizantes Minerais, Orgânicos, Organominerais e Corretivos*; MAPA/SDA/CGAL: Brasília, Brazil, 2014, p. 220.
17. Reichardt, K.; *Rev. Bras. Cienc. Solo* **1988**, *12*, 211.
18. de Camargo, O. A.; Moniz, A. C.; Jorge, J. A.; Valadares, J. M. A. S.; *Métodos de Análise Química, Mineralógica e Física de Solos do Instituto Agrônomo de Campinas*; Instituto Agrônomo de Campinas: Campinas, Brazil, 2009.
19. Krevor, S. C. M.; Lackner, K. S.; *Int. J. Greenhouse Gas Control* **2011**, *5*, 1073.
20. Kakoulides, E. P.; Valkanas, G. N.; *Ind. Eng. Chem. Res.* **1994**, *33*, 1623.
21. Cuevas, J.; Daliakpoulos, I. N.; Gueso, J. J.; Tsanis, I. K.; *Agronomy* **2019**, *9*, 295.
22. Teir, S.; Revitzer, H.; Eloneva, S.; Fogelholm, C.-J.; Zevenhoven, R.; *Int. J. Miner. Process.* **2007**, *83*, 36.
23. Styles, M. T.; Sanna, A.; Lacinska, A. M.; Naden, J.; Maroto-Valer, M.; *Greenhouse Gases: Sci. Technol.* **2014**, *4*, 440.
24. Sparks, D. L. In *Advances in Soil Science*; Stewart, B. A., ed.; Springer: New York, USA, 1987, p. 358.
25. Oliveira, M. W.; Trivelin, P. C. O.; Boaretto, A. E.; Muraoka, T.; Mortatti, J.; *Pesq. Agropec. Bras.* **2002**, *37*, 861.
26. van Raij, B.; *Fertilidade do Solo e Adubação*; Ceres: São Paulo, Brazil, 1991.
27. Oliveira, V.; Ludwick, A. E.; Beatty, M. T.; *Soil Sci. Soc. Am. J.* **1971**, *35*, 763.
28. Chapman, H. D.; Pratt, P. F.; *Soil Sci.* **1962**, *93*, 68.
29. Zarenia, M.; Hosseinpur, A. R.; Zarbizadeh, M.; Kiani, S.; *Ann. Biol. Res.* **2013**, *4*, 165.

Submitted: July 1, 2019

Published online: September 25, 2019

