Thermal and chemical solubilization of verdete for use as potassium fertilizer

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ABSTRACT

Thermal and chemical treatments were used to investigate the solubilization of potassium from verdete, a glauconitic rock. Fluxing agents were evaluated at distinct temperatures and proportions. Chemical dissolution of verdete was studied with increasing amounts of acids or bases at different temperatures and reaction times. In the calcination test, the presence of fluxing agents was critical to increasing the rock solubility, in addition to the effects of temperature and material ratios. The content of water-soluble K was 100, 100, 85, and 42% when using the salts LiCl, $CaCl_2.2H_2O$, Na_2CO_3, NaCl, respectively, as fluxing agents. The salts $CaSO_4$, $CaCO_3$ and $Ca_3(PO_4)_2$ were ineffective as fluxing agents. In the chemical treatments, the reaction with the base NaOH was more efficient than the acids to solubilize K. It was possible to solubilize up to 60% of K from verdete with 4.0 mol L^{-1} NaOH, at 150 °C for 120 min. Among the acids, H_3PO_4 was the most efficient, promoting solubilization of up to 42% K, with 4.0 mol L^{-1} H_3PO_4, at 225 °C, for 120 min. When using the concentrated acid waste and shaking for 144 h, up to 75% of K could be solubilized from the rock. It was concluded that the heated treatments were most effective in solubilizing verdete, followed by the acid waste, which are processes required for the production of soluble potassium fertilizers from unconventional sources of low reactivity.

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Contents

1. Introduction

The limited reserve of soluble potassium (K) minerals in the world and the growing consumption of this nutrient have caused concerns in countries which import K fertilizers. Water soluble K fertilizers are usually obtained by the exploitation of evaporite deposits, such as

sylvite (KCl), sylvinite (KCl and NaCl), or carnallite (KMgCl3 · 6.H2O). These deposits occur mainly in Canada, Russia, Belarus and Germany, which together are the source of approximately 85% of worldwide imports (Fertecon, 2011).

Brazilian imports of K fertilizers supplied more than 90% of internal demand in 2011 (Oliveira, 2012). Brazil is the third largest worldwide consumer of this nutrient (IFA, 2013) and has only one sylvinite mine in operation, in the state of Sergipe (Lopes, 2005).

The high dependency on foreign K sources in Brazil has stimulated the search for alternative non-conventional sources for use in the production of K fertilizers. Among these sources, verdete, a metasedimentary rock, stands out. It is composed of glauconite, quartz, feldspar and potassium feldspars, with a total K_2O content ranging from 50 to 150 g kg^{-1} (Loureiro et al., 2009; Piza et al., 2011). Evaluations made by METAMIG (Alecrim, 1982) indicated that in the municipality of Cedro do Abaeté, MG, there are 57.4 million tons of verdete available to mine. The *in natura* use of the finely ground rock exhibits low agronomic efficiency (Nascimento and Loureiro, 2004) and, for that reason, the development of solubilization and/or concentration processes are fundamental to making this source viable. The release of K from these minerals is difficult due to the energy with which K is bonded in the chemical structure and the high stability of this mineral. In regard to micas, according to Curi et al. (2005), this stability is due to K ions (K$^+$) occupying the interlayer spaces where they are strongly bonded to tetrahedral oxygens, compensating for the deficiency of structural charges. This bond impedes separation of the layers and expansion of the mineral.

By heating this type of material, it may promote rapid release of K from the silicate structures. Calcination, for example, has proven to be a promising route for solubilization of the K from micas and feldspars (Valarelli and Guardani, 1981; Nascimento, 2004). For improved efficiency of this method, $CaCl_2$ and carbonates were used as fluxing agents, which, in addition to lowering the melting point of rock minerals, may enrich the product obtained with other nutrients, such as Ca and Mg. Mazumder et al. (1993) calcinated ground glauconite with $CaCl_2$ at 1200 and 1300 °C at different reaction times and found that, in general, the solubilized K contents increased with increasing temperature and reaction time. The K obtained was easily solubilized in water at ambient temperature. Nascimento (2004) also extracted practically all the K from mineral rock rich in microcline by calcination with $CaCl_2$ at 900 °C over a 2-hour period. Calcination resulted in the formation of anorthite and sylvite, and K was easily leached in water.

Chemical reagents can also used to solubilize K from silicate minerals. This process is more efficient when combined with heating, adding pressure or shaking. It was found that 96% of the K from K feldspar was leached into water after treatment with 4 mol L^{-1} NaOH and under pressure (Nascimento, 2004). Varadachari (1992) solubilized K by treating muscovite with H_3PO_4 at a temperature from 250 to 350 °C.

An important factor in the extraction of K from silicate minerals is the acidity of the medium. Feigenbaum et al. (1981) affirmed that at pH 3, H$^+$ behaves as a strong interlayer K exchanger in glauconite. With an increase in pH, most notably above 8.5, silicate activity is increased (Mello and Perez, 2009), and K may be solubilized by the attack of OH$^-$ groups on the structure of the potassium minerals (Varadachari, 1992).

The aim of this study was to evaluate the effect of thermal and chemical treatments on solubilization of K from verdete for the purpose of obtaining water-soluble potassium fertilizer.

2. Materials and methods

The present study was conducted in the laboratories of the Soil Department of the Universidade Federal de Viçosa (Federal University of Viçosa, Viçosa, MG, Brazil). Verdete rock was used as a source of K in this study. This is a rock found in the state of Minas Gerais in the Bambuí formation on the Serra da Saudade lithoface in the São Francisco Cráton (Valarelli et al., 1993).

As previously stated, glauconite is the main K mineral present in the verdete rock. It is a hydrated aluminosilicate with the chemical formula $K_2(Mg,Fe)_2Al_6(Si_4O_{10})_3(OH)_{12}$ and a density ranging between 2400 and 2950 kg m^{-3} (Luz et al., 2010). According to Fassbender (1975), glauconite is a mica from the illite group, which is distinct from other illites due to a greater isomorphic substitution of Al^{3+} by Fe^{2+} in octahederal structures. This mineral is formed by a process called glauconitization, which occurs in the marine environment by slow sedimentation under reducing conditions. During this process, under conditions of low dendritic input, there is loss of aluminum oxide and silicon dioxide, accompanied by enrichment with Fe and K (Pettijohn, 1963; Fassbender, 1975; Lima et al., 2007).

In the Bambuí formation, where verdete rock is found in Brazil, glauconite is identified by a greenish color and it generally has a particle size of less than 3 μm. Stratigraphically, glauconite is located in zones below the sedimentary input, with its genesis occurring through slow halmyrolysis within a reducing micro-environment (Guimarães, 1997). In the glauconitization process, the initial material resembles a Fe aluminosilicate, undersaturated with alkalis, similar to amorphous smectites (Lima et al., 2007).

2.1. Collection and preparation of samples

Fourteen samples of verdete were collected in the Central region of Minas Gerais (MG), within the domain of the municipalities of Cedro do Abaeté and Quartel Geral (Fig. 1). Samples were collected in a random manner from the landscape in outcroppings of this rock. Pickaxes were used to remove fragments from the rock and approximately 10 kg of verdete were obtained in different collection locations, which were geo-referenced. Localization of the collection points and their coordinates are shown in Fig. 1 and Table 1, respectively.

The samples were ground and passed through a sieve (steel Solotest) with a −150 μm mesh for chemical and mineralogical analyses. The samples were treated with a tri-acid digestion procedure (EPA 3052, 1996) and the concentration of K was determined by flame emission spectrophotometry. Verdete samples with total contents greater than 80 g kg^{-1} of K_2O were selected, sieved (−150 μm mesh) and used in the solubilization studies.

2.2. Calcination

The effect of calcination of verdete on the solubilization of K was studied by the factorial combination $(7 \times 2 \times 3) + 3$: seven salts were evaluated as fluxing agents ($CaCl_2.2H_2O$, $CaCO_3$, $CaSO_4$, $Ca_3(PO_4)_2$, NaCl, Na_2CO_3 and LiCl), in two verdete:cation proportions (w/w) (10:1 and 10:2.5), three temperatures (300, 700 and 1100 °C) and three additional treatments consisting of the rock without addition of salts, heated at the temperatures of 300, 700 and 1100 °C. The experimental units were arranged in a randomized complete design with three replications.

Samples of 10 g of verdete, which had passed through a sieve with a −150 μm mesh, were mixed with the respective quantities of salts. Quantities of 4 g of this mixture were placed in porcelain crucibles and calcinated in a muffle furnace for 45 min. The heating ramp was linear with a duration of 60 min. The different heating rates established were: 4.58, 11.25 and 17.92 °C min^{-1}, for 300, 700 and 1100 °C, respectively. After calcination, the products were crushed in an agate mortar and passed through a sieve with a −150 μm mesh. In this material, K soluble in water and in 2% citric acid was determined by flame emission spectrophotometry.

2.3. Chemical solubilization

To evaluate the effect of acid and alkaline attack on solubilization of K from verdete, the treatments were defined in a factorial combination $(5 \times 2 \times 3 \times 2) + (3 \times 2)$, composed of five reagents (H_2SO_4, HCl, H_3PO_4,
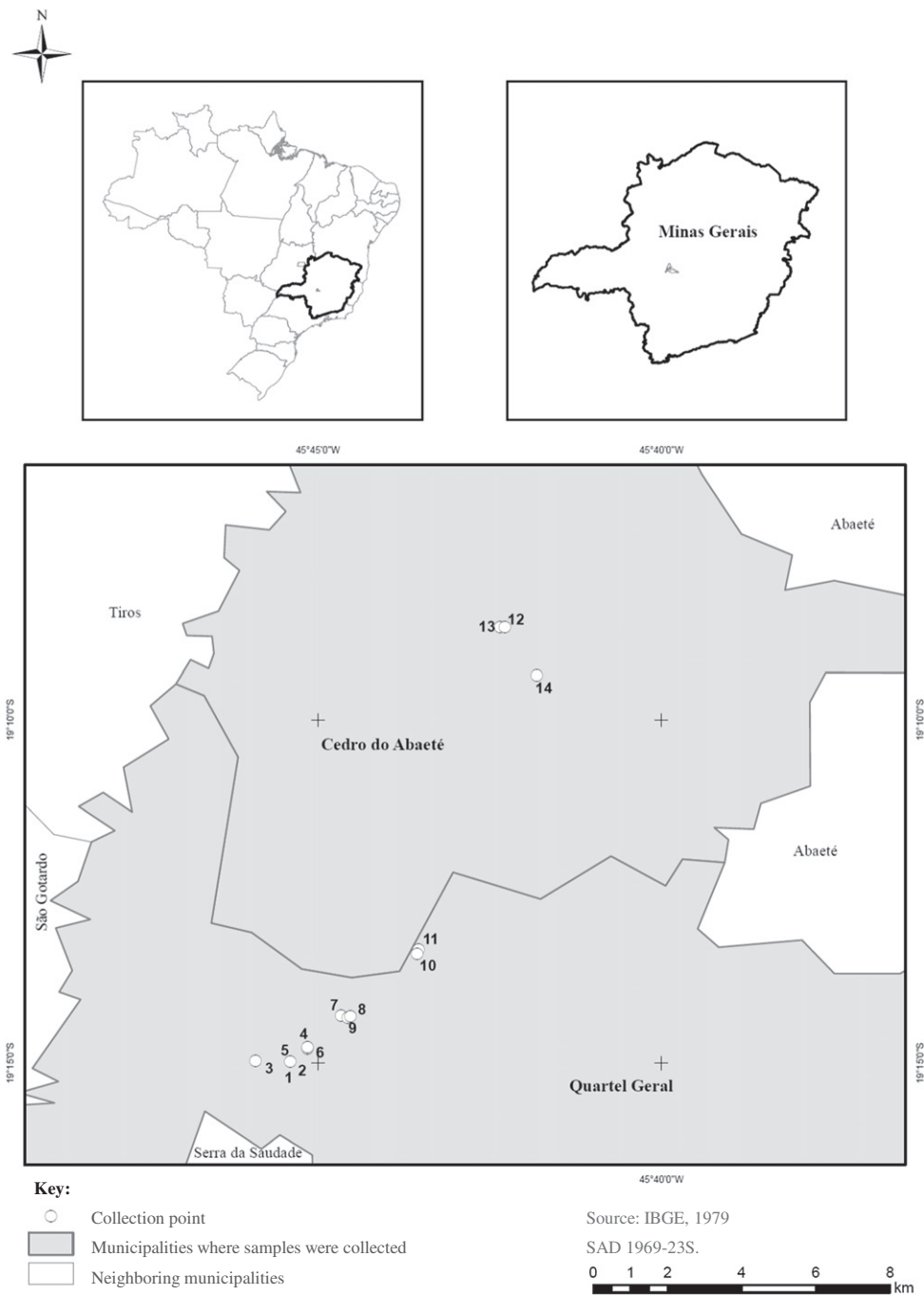
Fig. 1. Localization map of collection points of the verdete samples in the municipalities of Quartel Geral and Cedro do Abaeté in the state of Minas Gerais, Brazil.

HNO_3 and NaOH), in two concentrations (1 and 4 mol L^{-1}), at three temperatures (25.8, 150 and 225 °C), and two equilibrium times (30 and 120 min). The second factorial (3×2) refers to the verdete with distilled water subjected to three temperatures and two reaction times. A randomized block design with three replications was used for the experimental units.

For this experiment, 2 g of verdete was transferred to digestion tubes together with 10 mL of the reagent, and the reaction occurred in a digester block (Te-040/25RP Tecnal). The heating ramp was linear with a duration of 30 min. Upon reaction completion, the volume of the material was made up to 50 mL with distilled water. This solution was then filtered through Whatman Grade 595 filter paper (4–7 μm). The K concentration in the extract was determined by flame emission spectrophotometry (B462—Micronal).

2.4. Solubilization with an acid waste product

The effect of waste from tantalum oxide (Ta) and niobium (Nb) production, which were extracted by pegmatite three-acid leaching (H_2SO_4/HF/HCl), was evaluated on solubilization of verdete. It has a high acidity (pH 0), density of 1.8 kg L^{-1} and contains SO_4^{2-}, Cl^-, F^-, NO_3^- and PO_4^{3-} at concentrations of 712, 128, 109, 18 and 15 g L^{-1}, respectively.

Initially the acid waste product was diluted with distilled water to obtain solutions with a content of 25, 50, 75 and 100% of waste product. Then, samples of verdete (3 g) with different dilutions of acid waste product (12 mL) were placed in centrifuge tubes and were shaken at 150 rpm in a horizontal laboratory shaker (Te:14-Tecnal). After shaking, the tubes were heated in a water bath at 90 ± 5 °C for 4 h in a fume hood

Table 1
Coordinates for localization of collection points of the verdete samples in the municipalities of Quartel Geral and Cedro do Abaeté in the state of Minas Gerais, Brazil.

Collection point	UTM coordinates (UTM Zone 23 S)	
	X	Y
1	420763.1	7871570.4
2	420763.1	7871570.4
3	419654.6	7871575.9
4	421120.1	7871937.6
5	421136.3	7871929.0
6	421142.7	7871878.0
7	421843.8	7872863.6
8	421873.2	7872788.0
9	422032.9	7872736.5
10	423725.6	7874215.9
11	423738.8	7874334.6
12	426090.9	7882653.2
13	425888.3	7882636.0
14	426728.6	7881766.5

to reduce or eliminate concentrations of F for safety reasons. The material was then transferred to glass beakers and dried in an air circulation oven at 105 °C for 72 h. After cooling, this material was ground in an agate mortar and passed through a sieve with a −150 μm mesh. The K concentration soluble in water and 2% citric acid, were then determined. In this same material, the total concentration (water-soluble concentration) of other elements was also determined for nutrients: Ca, Mg, P, S, Zn, Cu, Mn, Fe, B, Mo and Ni, and undesirable elements for fertilizer composition: Pb, Cd, Cr, Na, Ti, V and Zr by inductively coupled plasma-optical emission spectrometry (ICP-OES) (8300-Perkin Elmer). With the exception of Si, which was determined by energy dispersive X-ray spectroscopy (EDX) (Medx1300-Shimadzu). Calculation of the Si concentration was possible using the relationship between relative proportions of K with Si using EDX analysis and the original concentration of K in the rock previously determined by atomic emission spectrometry.

2.5. Solubilized potassium

The values of K solubilized from verdete in water, in 2% citric acid, and in acid or alkaline solutions that underwent the various previously described treatments were obtained by calculating the ratio between their quantities in the solution and rock according to Eq. (1):

$$\text{Dissolution of } K(\%) = (K_1/K_t) \times 100, \tag{1}$$

where K_1 and K_t are the amounts of K in the solution and in the initial rock, respectively.

3. Results

3.1. Calcination

The absence of fluxing agents during calcination of verdete limited solubilization of K. As expected, the K contents extracted in 2% citric acid were greater than those extracted in water. A maximum of 1.97% of the total K from verdete soluble in water was measured at the calcination temperature of 700 °C. At temperatures of 300 and 1100 °C, solubilization in water was 0.57 and 0.26% of the total K, respectively.

In the presence of fluxing agents, the verdete:cation proportion and the calcination temperature had significant effects on K solubilization. All K from the verdete became soluble in water through the use of LiCl and CaCl$_2$.2H$_2$O, with LiCl being the most efficient fluxing agent considering the lower temperatures and verdete:cation ratio necessary (Table 2).

Calcination with LiCl as the fluxing agent raised the water-soluble K content with the increase of calcination temperature to 700 °C, without

a change in this content beyond this temperature in both the verdete:Li proportions. With the use of CaCl$_2$.2H$_2$O as fluxing agent at the 10:1 verdete:Ca proportion, an increase in the water-soluble K content was observed for the temperature of 700 °C and reduction for 1100 °C. In the 10:2.5 verdete:Ca proportion, greater water-soluble K contents were obtained with the increase in temperature over the temperature range.

With NaCl as fluxing agent, there was generally an increase in K solubilization upon increasing the proportion of the fluxing agent and temperature, obtaining up to 50% of the total water-soluble K at the verdete:Na proportion of 10:2.5 and temperature of 1100 °C (Table 2).

The fluxing agents CaCO$_3$, CaSO$_4$ and Ca$_3$(PO$_4$)$_2$ were not efficient in solubilization of K from verdete, reaching maximum values of 5.7, 4.7 and 14.8% of the total water-soluble K, respectively (Table 2).

3.2. Chemical solubilization

The results from the use of acids and alkaline solution show a significant effect for reagent, concentration, temperature and reaction time on solubilization in water of the total K from the verdete. NaOH was more efficient in solubilization of K than the acids, especially upon increasing the reaction time and concentration of this alkaline solution. It was possible to solubilize up to 60% of the K from the verdete when the alkaline solution at a concentration of 4 mol L^{-1} was used at a temperature of 150 °C and a reaction time of 120 min, however, the solubilization decreased at the higher temperatures (Table 3).

Among the acids, H$_3$PO$_4$ was the most efficient, followed by H$_2$SO$_4$. Reaction time and the concentration of the acid had a significant effect on the solubilization of K. It was possible to solubilize up to 42.3% of the total K from the verdete with H$_3$PO$_4$, at 4 mol L^{-1}, 225 °C and a reaction time of 120 min. There was no significant effect of reaction time observed for H$_2$SO$_4$, however, increases in solubilization of K occurred with an increase in temperature. At 4 mol L^{-1} of H$_2$SO$_4$ at 225 °C and a reaction time of 120 min, it was possible to solubilize up to 35.8% of the K. The HCl and the HNO$_3$ were not highly efficient in solubilization of K, instead a stabilization or decrease was observed in efficiency as of 150 °C. Although effects of reaction time and acid concentration were observed, solubilization was less than 15% of the total K content of the verdete, demonstrating the low effectiveness of these acids (Table 3).

3.3. Acid waste product

The acid waste product effectively solubilized the K of the verdete, especially at higher concentrations (less water added during dilution step). There was a significant effect of the concentration of the acid waste product and reaction time on solubilization of K, without interaction between these variables (Fig. 2). Overall the effect of acid waste product concentration was more significant than the reaction time. Up to 75% of the total K soluble in water was obtained when the pure waste product (without dilution in water) and the longest reaction time (144 h) were used.

Table 2
Percentages of the total K from verdete solubilized in water (%), for various fluxing agents, verdete:cation proportions (w/w) and calcination temperatures.

Salt	Verdete:cation proportion (w/w) 10:1			Verdete:cation proportion (w/w) 10:2.5		
	300 °C	700 °C	1100 °C	300 °C	700 °C	1100 °C
CaCl$_2$.2H$_2$O	0.98	39.79	30.09	1.09	70.41	100.00
CaCO$_3$	0.66	2.32	0.28	0.71	5.72	0.55
Ca$_3$(PO$_4$)$_2$	1.31	4.39	0.87	2.42	14.81	8.69
CaSO$_4$	1.41	3.60	0.30	1.67	4.73	1.44
LiCl	0.99	100.00	100.00	1.09	99.63	100.00
Na$_2$CO$_3$	1.01	14.30	1.72	1.85	38.33	41.91
NaCl	1.33	10.66	16.42	1.21	19.07	50.00

Table 3
Percentages of the total K from verdete solubilized in water (%), for a range of acids and for NaOH at various concentrations, temperatures and reaction times.

Reagent	30 min						120 min					
	1 mol L^{-1}			4 mol L^{-1}			1 mol L^{-1}			4 mol L^{-1}		
	25.8 °C	150 °C	225 °C	25.8 °C	150 °C	225 °C	25.8 °C	150 °C	225 °C	25.8 °C	150 °C	225 °C
H_2SO_4	3.6	8.2	28.0	1.0	19.1	35.6	1.0	9.4	28.1	1.1	20.3	35.8
H_3PO_4	0.4	3.3	10.4	0.2	11.7	26.1	0.5	9.9	9.5	0.4	35.8	42.3
HCl	0.8	6.8	7.0	0.9	12.0	11.9	0.7	8.7	6.2	0.9	14.2	12.4
HNO_3	0.8	3.9	4.3	0.9	7.0	6.7	0.9	6.2	4.0	0.9	10.0	7.6
NaOH	0.4	11.6	18.7	0.5	13.2	33.5	0.4	22.5	13.0	0.5	60.0	44.5

Chemical characterization of the waste product revealed low levels of toxic elements that will not be of concern, hence, the waste product does not require any modification to be in accordance with Brazilian legislation on fertilizers (values not shown).

4. Discussion

Calcination of verdete in the absence of fluxing agents did not efficiently solubilize K. This shows that by reaching or exceeding the temperature the glauconite mineral structure begins to be destroyed at ~900 °C (Mashlan et al., 2012) and was not sufficient at releasing soluble forms of K. Using optical microscopy, thermal analysis (DTA), DRX and Mossbauer spectroscopy, Mashlan et al. (2012) observed that temperatures below 800 °C did not affect the glauconite structure, however, progressive oxidation of Fe^{+2} to Fe^{+3} occurs.
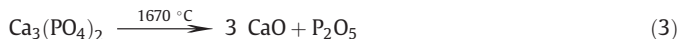
According to Tedrow (1966), glauconite presents four endothermic curves in DTA analysis, at 150, 360, 560 and 925 to 975 °C. Between 150 °C and 360 °C, evaporation of the water between interlayers occurs. Similarly with illite, the endothermic peak at 560 °C and 925 to 975 °C corresponds to the dehydroxylation of the glauconite structure (Tedrow, 1966). In relation to trioctahedral micas, thermal behavior is controlled by the octahedral and interlayer cations (Fanning et al., 1989). According to Jackson (1975), the temperature at which dehydroxylation occurs is defined by the type of the octahedral cations. Irrespective of this, in relation to the results obtained in this study, it is probable that a large part of the K released from the glauconite structure upon heating formed low solubility compounds during cooling, such as spinel at 980 °C (Roy, 1949) and leucite at 1050 °C (Tsvetkov and Valyashikhina, 1956).

The use of fluxing agents proved to be most efficient for the release of K from verdete, resulting in the highest concentration of soluble K in water, with significant interactions between fluxing agents,
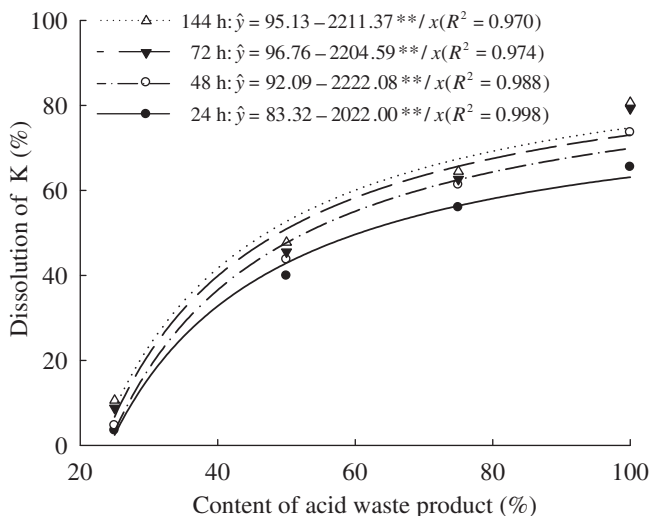

Fig. 2. Dissolution of K with respect to the content of acid waste product in the solution over different reaction times and regression equations.

proportions of the cations of these salts and the verdete, and calcination temperatures. The melting point of the fluxing agents appears to be an important factor in solubilization of K from verdete. Considering the glauconite as a silicate of K predominant in verdete (Piza et al., 2011), for salts that have a melting point (mp) below or near the temperature at which the glauconite starts to collapse (900 °C) i.e. $CaCl_2$ (mp = 775 °C), LiCl (mp = 610 °C), NaCl (mp = 800.7 °C) and Na_2CO_3 (mp = 856 °C) (Haynes, 2013); (Mashlan et al., 2012), then this leads to greater solubilization of K. The mp of $CaCl_2$ rather than $CaCl_2.2H_2O$ was considered because during the calcination of $CaCl_2.2H_2O$, monohydrate and anhydrous $CaCl_2$ are formed in the first and second steps, respectively. Regardless, a direct relationship was not observed between these variables, and this is likely to be due to the establishment of eutectic interactions between the verdete and the LiCl. These interactions appear to be unpredictable, and may optimize energy consumption during the melting of materials (Sial and McReath, 1984). This is a reasonable explanation because with LiCl at 700 °C it was possible to solubilize almost 100% of the K from the verdete at only 90 °C above its melting point. The same effect was achieved only with $CaCl_2.2H_2O$ at 325 °C above its melting point.

The low efficiency of the salts $CaCO_3$, $Ca_3(PO_4)_2$ and $CaSO_4$ may be related to their non-transition to the fluid phase, which makes less effective interactions with the rock minerals. For these salts, a possible common product of the thermal decomposition is CaO, which has a mp of 2613 °C (Haynes, 2013), and this is well above the maximum temperature used in the experiment (1100 °C).

Other possible products from thermal decomposition are CO_2 (g), P_2O_5(s) and SO_3 (s) from $CaCO_3$, $Ca_3(PO_4)_2$ and $CaSO_4$, respectively (Eqs. (2), (3) and (4)). However, the SO_3(s) can be sublimed at 44.5 °C and the P_2O_5 can exist as a fluid form only between 562 °C (mp) and 605 °C (bp) (Haynes, 2013). The CO_2 (g) formed should to attempt the atmosphere equilibrium, decreasing the concentration in the sample. Thus, it is unlikely that these products affect the solubilization of the K silicates from verdete rock.

$$CaCO_3 \xrightarrow{\text{600-850 °C}} CaO + CO_2 \tag{2}$$

$$Ca_3(PO_4)_2 \xrightarrow{\text{1670 °C}} 3\ CaO + P_2O_5 \tag{3}$$

$$CaSO_4 \xrightarrow{\text{1460 °C}} CaO + SO_3. \tag{4}$$

*Source: Copyright Haynes (2013) and Navarro et al. (2009).

Some studies have demonstrated that β-tricalcium phosphate (β-TCP) is in a stable form below 1125 °C. With an increase in temperature, the β-TCP form, monoclinic space, is transformed into α-TCP, rhombohedral space, that is stable up to 1430 °C and is fused at 1756 °C (Elliot, 1994; Roux et al., 1978; Mathew and Takagi, 2001). Thus, considering these explanations are associated with the solubilization of K, up to 14.82% using $Ca_3(PO_4)_2$ as a fluxing agent (Table 2), suggests that the occurrence of unknown interactions between $Ca_3(PO_4)_2$ and minerals from the rock occur during the calcination process. It is possible that these reactions occurred during calcination due to the oxidation of Fe^{+2} to Fe^{+3} (Mashlan et al., 2012) or dehydroxylation of

the glauconite structure (Tedrow, 1966) and are associated with the presence of $Ca_3(PO_4)_2$.

Thermic decomposition of the $CaCO_3$ in CaO and CO_2 was investigated by Navarro et al. (2009). These authors found that this conversion began around 600 °C and was complete by 850 °C. Above 800 °C Bragg peaks of calcite disappeared, and at 1150 °C higher intensity to CaO peaks were observed. Thus, due to the temperature range in this study (300–1100 °C) which is associated with temperatures that cause decomposition of calcite as well as the thermal properties of the products obtained, it is reasonable that minimal solubilization of the K from verdete occurred using this agent.

Upon investigating the thermal conductivity of the Li (87.4 $Wm^{-1} K^{-1}$), Ca (200 $Wm^{-1} K^{-1}$) and Na (141 $Wm^{-1} K^{-1}$) cations, there was no correlation of this property with the effects of the salts as fluxing agents. In relation to the classes of the salts (sulfates, phosphates, carbonate sand chlorides), thermal conductivity of the chlorides (8 $Wm^{-1} K^{-1}$) is approximately 2.5 times greater than the other anions tested. This means that the chloride-based fluxing agents are more efficient in the transfer of thermal energy. This observation, however, is not sufficient to define the capacity of the salts in affecting melting of the verdete and release of K. It may, however, explain the fact that many chloride-based fluxing agents are efficient (e.g., KCl, NaCl, LiCl, $CaCl_2$ and $ZnCl_2$). Another possible explanation for the increased efficiency of the chloride-based fluxing agents (LiCl, $CaCl_2.2H_2O$, NaCl) in relation to the others ($CaCO_3$, $CaSO_4$, $Ca_3(PO_4)_2$, Na_2CO_3) may be related to the need for less activation energy for the formation of KCl in relation to the formation of K_2CO_3, K_2SO_4 and K_3PO_4.

In solids, heat transfer occurs through conduction and is due to the electrons of conduction or vibration of the crystalline structure of minerals (Incropera and Witt, 1981). These phenomena depend on the physical, chemical and crystallographic characteristics of the substances. For the fluxing agents, it is expected that thermal diffusivity, calorific capacity, thermal conductivity and melting point are the determining properties in the fluxing effect of some salts during the calcination of different minerals.

Another factor that may explain the behavior of salts in the increased solubility of the calcinated compounds is the presence of network modifying ions, such as Na^+ and Ca^{2+}. This framework is due to the fact that atoms such as Na and Ca bond ionically to oxygen during the melting of silicates and interrupt the continuity of the network, since some of these atoms are no longer shared between two tetrahedrons (Akerman, 2000). These cations act in breaking covalent bonds, such as Si–O–Si, which results in non-bonded oxygens, in this way, they may affect the stability of the mineral compounds formed (Oliveira, 2009).

It appears that isolated analysis of the characteristics and properties of the fluxing agents does not explain the effects of the fluxing agents in a satisfactory manner, moreover, there may be differentiated interactions between fluxing agents and rock components.

In relation to chemical solubilization of the K of verdete, the better performance of NaOH in comparison to acids may be related to the increase of Si activity with the increase in pH of the medium (Mello and Perez, 2009). Verdete is a rock rich in quartz and other silicate minerals, such as glauconite and feldspars (Piza et al., 2011), therefore, the increase in solubility of Si may lead to greater instability of the mineral and the release of K. These phenomena are due to the attack of OH^- groups on the silicate structure, and this process is accelerated with heating (Varadachari, 1992).

The decrease in solubilization of K by NaOH at 4 mol L^{-1} at a reaction time of 120 min at 150 °C (Table 3) may be a result of the formation of new mineral phases at temperatures greater than 150 °C which are not soluble in water, or the interference of diffusion processes of the metal. Nascimento (2004), working with alkaline leaching in K feldspar, noted the formation of hydroxycancrinite and cubic analcime at 180 °C and after a reaction time greater than 120 min. In this case, these phases were considered soluble. For the diffusion of metals during congruent dissolution of silicates, Terry (1983) affirmed that the formation of

silicone gels may interfere in the release of the element in the short term. The hypothesis is that with the increase in reaction time (from 30 to 120 min), there was greater release of Si from the verdete, which polymerized, forming silicone gels, and this hindered the diffusion and leaching of K.

Evaluating the better performance of H_3PO_4 compared to the other acids, it may be inferred that the capacity of the phosphate in substituting hydroxyls or silicates of the minerals, leading to their collapse (Rajan and Fox, 1975), may have favored greater chemical solubilization of the verdete, leading to greater release of K. Investigating the dissolution kinetics of muscovite by H_3PO_4, Varadachari (1992) confirmed that the breakdown of the structure of this mineral is due to attacks of OH^- groups. The same author observed that these groups are produced during polymerization of H_3PO_4 when heated at temperatures above 150 °C. This observation is supported by another study which verified an increase in solubilization of K from verdete at temperatures above the boiling point (bp) of H_3PO_4 (407 °C) (Haynes, 2013).

The better efficiency of H_2SO_4 in comparison to HNO_3 and HCl is attributed to its relatively high boiling point (bp = 337 °C), which allows for an increase in its efficiency with increased heating. Alternatively, HNO_3 has bp = 83 °C, and HCl, bp = 85 °C (Haynes, 2013), resulting in low performance when heated.

In studies on leaching of K from glauconitic sandstones in India, Yadav and Sharma (1992) chose HCl as the best leaching agent, in comparison to H_2SO_4, H_3PO_4 and HNO_3. In this same study, up to 96% of the total K from the glauconitic sandstones was solubilized with 6 mol L^{-1} HCl at 105 °C, shaking at 450 rpm for 180 min. The low values obtained with the use of H_2SO_4 and HNO_3 were attributed to the high solubilization of Fe and Ca from the rock. The efficiency of HCl, was correlated with the formation of ferrous and ferric chlorides.

The results obtained in this study on the chemical solubilization of K, show that verdete is a rock that is highly susceptible to the attack of OH^- on H^+ since NaOH and H_3PO_4 exhibited better performances. The behavior of these reagents in this study is corroborated by the results obtained by Nascimento (2004) and Varadachari (1992), who were able to solubilize K from silicate minerals using NaOH and H_3PO_4.

The chemical stability of the silicate during acid dissolution, according to Terry (1983), is determined by the combination of structural factors and properties of the metallic cations in the silicates. The type of anion in the acid and the type of compound it may form with the metal of the rock are highly influential factors in acid dissolution of minerals.

The pH of the waste product (pH 0) is an important factor in the solubilization of K from verdete. At pH ≤ 3, the exchange of K^+ by H^+ is well established for glauconite (Feigenbaum et al., 1981), with initial reactions being of greater intensity, through easier release of K from the mineral edges and surfaces. The presence of F in the waste product may have also promoted additional effects in solubilization of K. This element is extremely reactive and may displace the O in oxides, F has great affinity for silica, and this is strengthened in the presence of strong acids (Hekim and Fogler, 1977). The results of solubilization of K from verdete with the use of the acid waste product stimulate the utilization of industrial residues in fertilizer production at a lower cost from nonconventional sources. Likewise, qualification and quantification of environmental risks through the presence of potentially toxic elements in the final products are necessary.

Solubilization of K from silicate potassium is the first step in the production of soluble potassic fertilizers to supply some of the demand for countries where there are not sufficient deposits of soluble potassic minerals.

5. Conclusions

This study has shown that the heated treatments were more effective in releasing K from verdete rather than the acid or alkaline treatments, which are processes required for the production of soluble K

fertilizers from unconventional sources. Calcination in the presence of fluxing agents is efficient in the release of K from verdete. It is possible to extract almost 100% of the K from the verdete through the use of LiCl and $CaCl_2.2H_2O$ as fluxing agents, making the K highly soluble in water. Overall, solubilization of K from verdete is increased in an alkaline medium compared to an acid medium, hence, there are optimum conditions for each reagent. The use of the acid waste product is effective in solubilization of the K from verdete, making it a useful addition in this viable approach to producing water-soluble fertilizers.

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