

Fluoride aided potassium extraction from Verdete rock by thermal processing with ferrous sulfate heptahydrate.

Extração de potássio auxiliada por flúor da rocha de Verdete por processamento térmico com sulfato ferroso hepta-hidratado.

Recebimento dos originais: 28/02/2019

Aceitação para publicação: 22/03/2019

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ABSTRACT

Glauconite is a green-colored monoclinic mineral with hydrated phyllosilicate of potassium and iron. It has low resistance to weathering and is usually found in sandstones and shales, as well as in marls and impure limestones. It is a secondary mineral formed from the modification of iron-rich micas, such as biotite. Even though it is an alternative source of potassium, it is still not extracted commercially on a large scale due to the lack of commercial technology that makes the business viable economically. Ferrous sulfate heptahydrate is a residue or by-product formed during the pickling of iron and steel and also in the manufacture of titanium dioxide from the ilmenite. Iron, as a raw material for the production of reagents, is abundant in the tailings of this metal. The use of ferrous sulfate as a sulfating agent has the advantage of being more selective and less aggressive during processing, in addition to the property of being thermosensitive. Fluorine accelerates this sulfation process due to an ionic substitution action on the structure of glauconite and on compounds that prevent the reaction, such as calcium sulfate. This work has investigated the release of potassium by dissolution in a 2% (w/w) citric acid solution in water, after previous thermal and

chemical processing of glauconite rock (10% K₂O) from Cedro doAbaeté - MG - Brazil with ferrous sulfate heptahydrate and NaF in the ratio (1.00: 0.70: 0.01), respectively. Potassium soluble in citric acid and not soluble in water characterizes a slow acting fertilizer. Thermal processing was performed at temperatures of 500°C and 700°C for 6h in a fluidized bed oven. The selection of ferrous sulphate was based on a thermodynamic evaluation of the system. The results showed that the thermal processing of the rock and ferrous sulfate mixture alone was not effective for the release of potassium in aqueous solution and in citric acid. The extraction of potassium from raw rock in citric acid was 7%. The mixture of rock and ferrous sulfate, without fluoride, in citric acid had an extraction rate of 6.8%. However, the same mixture with addition of 29ppm of fluorine had different results, in water (20% at 700°C) and mainly in citric acid (52.1% at 700°C), increasing the availability of potassium in more than 7 times when compared to the availability of rock potassium in natura. This study confirms that the combined effects of fluorine and temperature of thermal processing increase the release of potassium from glauconite.

Keywords: fertilizer, potassium, fluoride, glauconite, ferrous sulfate.

RESUMO

A glauconite é um mineral monoclinico de cor verde com filossilicato hidratado de potássio e ferro. Tem baixa resistência ao intemperismo e é geralmente encontrado em arenitos e folhelhos, bem como em margas e calcários impuros. É um mineral secundário formado a partir da modificação de micas ricas em ferro, como a biotita. Embora seja uma fonte alternativa de potássio, ainda não é extraída comercialmente em larga escala devido à falta de tecnologia comercial que torna economicamente viável o negócio. O sulfato hepta-hidratado é um resíduo ou subproduto formado durante a decapagem do ferro. e aço e também na fabricação de dióxido de titânio a partir da ilmenite. Iron, como matéria-prima para a produção de reagentes, é abundante nos rejeitos deste metal. O uso de sulfato ferroso como um agente de sulfatação tem a vantagem de ser mais seletiva e menos agressiva durante o processamento, além da propriedade de ser termossensível. Fluorina acelera este processo de sulfatação devido a uma ação de substituição iônica na estrutura da glauconite e em compostos que impedem a reação, como o sulfato de cálcio. Este trabalho investigou liberação de potássio por dissolução em solução de ácido cítrico a 2% (p / p) em água, após processamento térmico e químico prévio de rocha glauconita (1 0% K₂O) de Cedro doAbaeté - MG - Brasil com sulfato ferroso hepta-hidratado e NaF na proporção (1,00: 0,70: 0,01), respectivamente. Potássio solúvel em ácido cítrico e não solúvel em água caracteriza adubo de ação lenta. O processamento térmico foi realizado a temperatura de 500 ° C e 700 ° C por 6h em um forno de leito fluidizado. A seleção de sulfato ferroso foi baseada em uma avaliação termodinâmica do sistema. Os resultados mostraram que o processamento térmico da rocha e mistura de sulfato ferroso sozinho não foi eficaz para a liberação de potássio em solução aquosa e em ácido cítrico. A extração de potássio de rocha crua em ácido cítrico foi de 7% .A mistura de rocha e sulfato ferroso, sem flúor, em ácido cítrico teve uma taxa de extração de 6,8%. Entretanto, a mesma mistura com adição de 29ppm de flúor apresentou resultados diferentes, em água (20% a 700 ° C) e principalmente em ácido cítrico (52,1% a 700 ° C), aumentando a disponibilidade de potássio em mais de 7 vezes comparado ao th A disponibilidade de rocha potássica in natura. Este estudo confirma que os efeitos combinados do flúor e da temperatura do processamento térmico aumentam a liberação de potássio da glauconita.

Palavras-chave: fertilizante, potássio, flúor, glauconita, sulfato ferroso.

1 INTRODUCTION

The use of silicate rocks is a strategy for the production of fertilizers since they are well distributed in all regions of the world (Martins et al, 2010). Among these rocks, there are

alternative sources of potassium such as mica and feldspar. Glauconite, a mineral from the silicates group, with chemical formula $(K;Na)(Fe^{3+};Al;Mg)_2(Si;Al)_4O_{10}(OH)_2$, is found among these minerals (Srasra and Trabelsi-Ayedi, 2000). In the region of Cedro do Abaeté - MG - Brazil, an emerald mining region, there are large resources of glauconite-bearing rocks (Verdete ore), which are an important source of potassium that can be exploited (Eichler, 1983).

Potassium is one of the three basic plant nutrients, along with nitrogen and phosphorus. There is no substitute for potassium in agriculture and therefore it is essential to maintain and expand the food production (Marschner, 1995). The slow-release fertilizers mainly use phyllosilicates as raw materials for potassium due to the low mobility of the potassium in water, dilute acids or weak organic acids. To increase the kinetics of the potassium release, several works in this direction have been published (Tokunaga, 1991; Vallareli, 1993; Piza et al, 2011 Orioli Jr and Coutinho, 2009; Mangrich et al, 2001). Research results indicate that rocks containing reasonable amounts of glauconite may be alternative sources of potassium for agriculture. Biotite, leucite, nepheline syenite, micaschist, potassium feldspar, chlorite schist, muscovite and Verdete(containing glauconite) were some of the materials evaluated (Lopes et al 1972; Faquin, 1982; Leite, 1985).

To increase the availability of glauconite potassium, one can change the mineral structure by thermal treatment (Silva et al, 2012a7). Mazumder et al. (1993) have investigated the dissolution of glauconite potassium in distilled water after a thermal treatment between 700°C and 850°C using a mixture of sandstone (sedimentary rocks) containing the glauconite mineral and calcium chloride. The time of calcination was varied between 5 and 180 minutes, with particle size of 75µm to 300µm. Leaching was performed in distilled water at temperatures ranging from 40°C to 90°C, which resulted in extractions higher than 90% after 10 minutes of leaching for calcinations at 850°C. The ratio between sandstone and calcium chloride to achieve such extraction was (1.0:0.5) in a calcination time of 60 minutes.

Even though the thermal treatment can have low economic viability due to the high energy consumption, the great rise in the consumption and cost of production of fertilizers made from potassium support further studies (Jena et al. 2014).

Swamy and Prasad (1983) have investigated the kinetics of thermal decomposition of ferrous sulfate heptahydrate, which consists of three distinct steps: (i) the loss of six molecules of water, (ii) the loss of a single water molecule from the monohydrate, and (iii) the decomposition of the intermediate iron oxysulfate (III) and sulfur trioxide. The three processes have activation energy of 16, 24 and 132 kcal/mol, respectively. Data on the thermal decomposition of $FeSO_4 \cdot H_2O$ in various gaseous environments and different heating regimes indicate the formation of intermediate products such as $FeOHSO_4$ and $Fe_2O(SO_4)_2$. Studies on the mechanism and kinetics of the thermal

decomposition of various inorganic sulfates show the variety and the specific characteristics of the process. Depending on the type, the chemical composition of the initial sulfates and the experimental conditions, the possibility of evolution of thermal processes to different chemical mechanisms and kinetic parameters were confirmed. The control of the partial pressure of the gaseous components and the oxy-redox potential of the specific systems determine the formation of the products (Petkova and Pelovski, 2001).

Table 1 presents a series of decomposition reactions of iron sulphates that served as the basis for establishing the methodology used. The equations of reaction 1 and 2 show that the pyrolysis of ferric or ferrous sulphate is not spontaneous ($\Delta G > 0$) in the temperature range between 500°C and 700°C. Reactions 3 to 6 suggest that the decomposition reaction is more favorable in an atmosphere saturated with water (such as reactions 3 and 4) or that the decomposition is by pyrohydrolysis (such as reactions 5 and 6) (Petkova et al, 2011). Due to these observations, the application of a water-saturated air stream was selected.

Table 1: Gibbs Energy Values as a function of temperature for various decomposition reactions of iron sulphates. Reference temperature: 25°C.

Reaction	Chemical equation	Temperature (°C)			
		350	500	700	800
		ΔG (kcal)			
1	$\text{FeSO}_4 = \text{FeO} + \text{SO}_3(\text{g})$	34.9	28.3	19.6	15.3
2	$\text{Fe}_2(\text{SO}_4)_3 = \text{Fe}_2\text{O}_3 + 3\text{SO}_3(\text{g})$	55.6	36.3	10.6	-2.1
3	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O} = \text{FeO} + \text{SO}_3(\text{g}) + 7\text{H}_2\text{O}$	19.6	0.1	-27.5	-41.7
4	$4\text{FeSO}_4 \cdot 7\text{H}_2\text{O} + \text{O}_2(\text{g}) = 2\text{Fe}_2\text{O}_3 + 4\text{SO}_3(\text{g}) + 28\text{H}_2\text{O}$	-20.7	-89.5	-188.6	-239.6
5	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O} = \text{FeO} + \text{H}_2\text{SO}_4(\text{g}) + 6\text{H}_2\text{O}$	10.8	-6.7	-31.0	-43.2
6	$4\text{FeSO}_4 \cdot 7\text{H}_2\text{O} + \text{O}_2(\text{g}) = 2\text{Fe}_2\text{O}_3 + 4\text{H}_2\text{SO}_4(\text{g}) + 24\text{H}_2\text{O}$	-55.7	-116.8	-202.6	-245.9

The selection of ferrous sulphate instead of ferric sulphate was due to reactions 4 and 6 (Table 2). Even though they are complex reactions, they show very favorable free energy of formation, besides the fact that the beginning of the process of generation of sulfuric anhydride, or even hydrogen sulphate (H_2SO_4), occur at low temperature. These are the agents (SO_3 or H_2SO_4) responsible for the availability of glauconite potassium, either in aqueous medium or by extraction with citric acid.

Fluoride is used due to the formation of melting points during the reaction, as free micro droplets in the matrix, which affect the structure of the filosilicate (substitution reactions), besides destroying physical barriers of sulfates formed in the sulphation reaction, mainly due to $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Due to the similarity of the atomic rays, the fluorine ion ($r_{\text{F}^-} = 1.33\text{\AA}$) can replace the oxygen ion ($r_{\text{O}^{2-}} = 1.32\text{\AA}$) in the vitreous reticulum of silicate particles (Navarro, 1991).

The objective of this work is to investigate the action of fluoride in the sulfation process of glauconite as an alternative source of potassium for the production of slow-release fertilizers. More

precisely, to evaluate the release and solubilization of potassium originated from the structure of this mineral through the extraction with an organic acid, after previous thermal and chemical processing of the mixture of reagents (ferrous sulfate and fluoride) with rock (Verdete) containing this mineral.

2. MATERIAL AND METHODS

Figure 1 represents the steps of the mineral processing for the provision of potassium from Verdete rock (glaucónitic) by extraction with mineral acid and organic acid (citric acid).

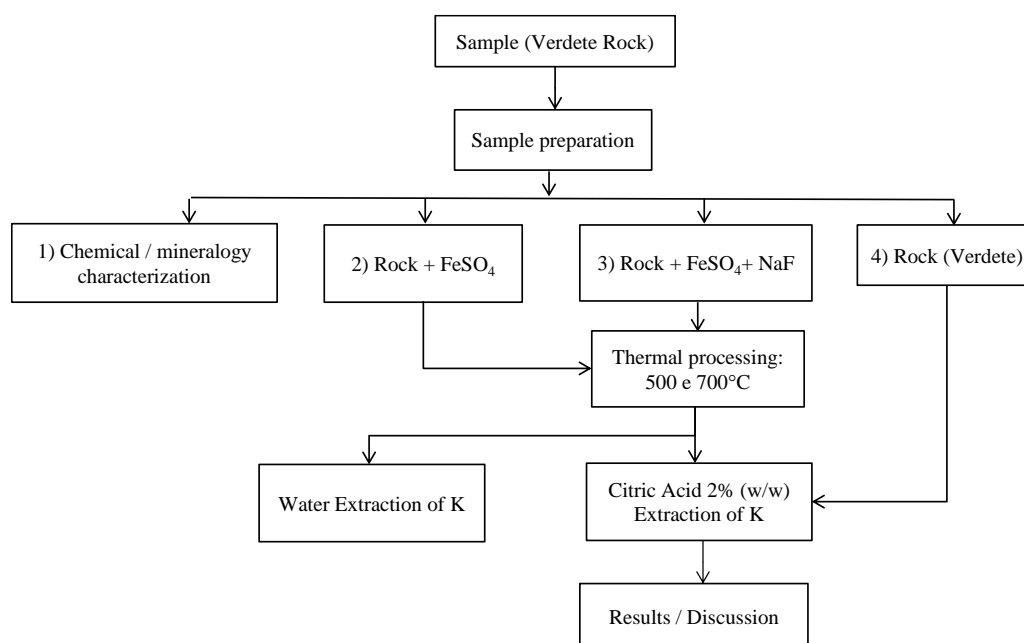


Figure 1: Flowsheet describing the methodology used in the study of the availability of potassium from Verdete rock

The crude sample is fragmented and divided into four aliquots. The first aliquot (sample 1) is used for chemical and mineralogical characterization. The second aliquot (sample 2) is reserved for the mixture with ferrous sulphate heptahydrate. The third aliquot (sample 3) is reserved for the mixture of ferrous sulphate heptahydrate and sodium fluoride, which is the main objective of this investigation, and the fourth aliquot (sample 4) is unmixed comminuted rock for the evaluation of the extraction of potassium in acid without thermal processing.

Samples 2 and 3, duly mixed with the reagents, proceed to the thermal processing in a fluidized bed in a vertical oven. After calcination, the sample 2 is subjected to extraction in citric acid and sample 3 is subjected to extraction of potassium in water and citric acid. In this study, analytical-grade reagents, NaF (Synth); $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Synth); Citric Acid (Prolab); H_2SO_4 (Hexis), were used.

The sample, properly homogenized, was ground and classified in 100% less than 0.15mm. For mineralogical characterization, sample 1 was pulverized in a pan mill for 20 seconds and samples were generated for chemical and mineralogical analyses. For the analysis of the crystalline

components of the sample, an X-ray diffractometer was used, with a voltage of 40mV, current of 20mA and angle of incidence varying from 3° to 80° with variation of 0.05°. Finally, the analysis of the mineral association was performed with an optical microscope.

Table 2 shows the mass proportions of the mixtures and thermal processing temperature used in the tests.

Table 2: Mass ratio of the reagents in the mixture for thermal processing.

Test	Rock	Aliquot	Temperature (°C)	Rock	FeSO ₄ .7H ₂ O	NaF	Air (70 °C)
1	Verdete	3	500	1	0,7	0,01	Moist
2	Verdete	3	700	1	0,7	0,01	Moist
3	Verdete	2	500	1	0,7	0	Moist
4	Verdete	2	700	1	0,7	0	Moist

A 9000W Linder-type bipartite vertical tubular oven was used with three heating zones. The oven had built-in resistances in ceramic fiber boards for maximum temperature of 1100°C, internal dimensions of 200mmx700mm, and a PLC (Programmable Logic Controller).

Two sulfation temperatures were evaluated for the tests: 500°C and 700°C for two samples (2 and 3 of the flowchart in Figure 1), as presented in Table 2.

The fluidization of the oven charge was performed in moist air at 70°C and flow rate between 6 and 8L/min. Humidification of the air was done by bubbling air in water by immersion in a thermostatic bath at 70°C. The residence time in the oven was 6h. Once the reaction time was reached, the reacted mixture was cooled inside the oven, then the final mass was measured and the sample was collected for chemical analysis.

The preparation of the 2% citric acid solution was done by adding 10g of crystallized citric acid, monohydrate, C₆H₈O₇.H₂O in 500 ml of distilled water. For the extraction of potassium, 0.1g of the sample to be evaluated was weighed and placed in a 100ml beaker. 50mL of the extraction solution was added and placed in a hotplate at 95°C for 15 minutes. After heating, the solution was cooled, filtered through a 0.45µm membrane and an aliquot of 25mL of the filtrate was transferred to a volumetric flask of 100mL. The evaluation of potassium in the solution was performed by ICP/OES on a Perkin Elmer Optima 7300DV equipment.

The potassium content was obtained from the equation: $K (\%) = K_s / K_t \times 100$, where K_s is the mass of potassium solubilized in the 2% citric acid solution and K_t is the mass of the potassium from the initial rock sample, proportional to the aliquot tested.

3 RESULTS AND DISCUSSION:

3.1. CHEMICAL AND MINERALOGICAL CHARACTERIZATION

The sample consisted of 10.4% of K_2O , 10% of Fe_2O_3 , 15.7% of Al_2O_3 , 3.0% of MgO , 56.7% of SiO_2 , 0.04% of CaO and 0.1% of Na_2O as the main elements. Based on the values of F obtained in an analysis of variance for the results of 4 samples, the homogeneity of the lot was confirmed ($\alpha=0,05$; $F_{calculated}=17861 \gg F_{critical}$). The standard error for the potassium analysis was 0.11%.

The main minerals found in the sample were glauconite (58%), potassium feldspar (31%) and quartz (9%). Figure 2 represents the diffractogram of the Verdete rock with its main components.

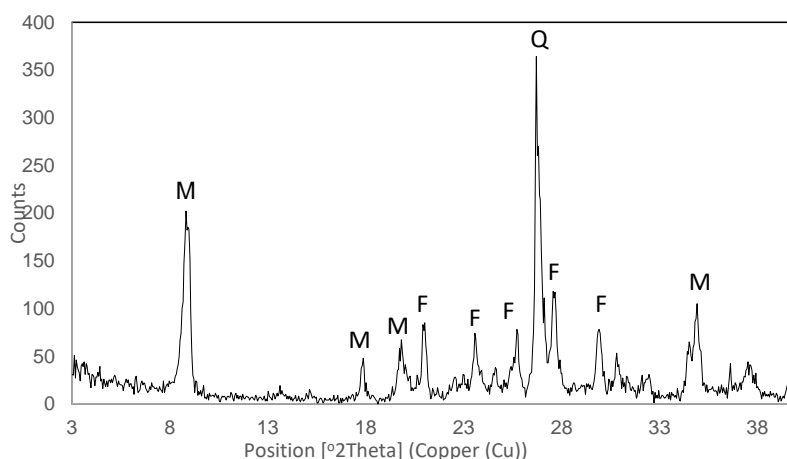


Figure 2: Diffractogram of the Verdete rock: M-Mica, Q-Quartz, F- potassiumfeldspar.

Figure 3 presents images obtained by light microscopy. Note that, even in the size range of less than $54\mu m$, there is a large amount of mixed particles, which indicates that a process of separation/concentration of minerals is not feasible and that the ore must go straight to a metallurgical extraction route.

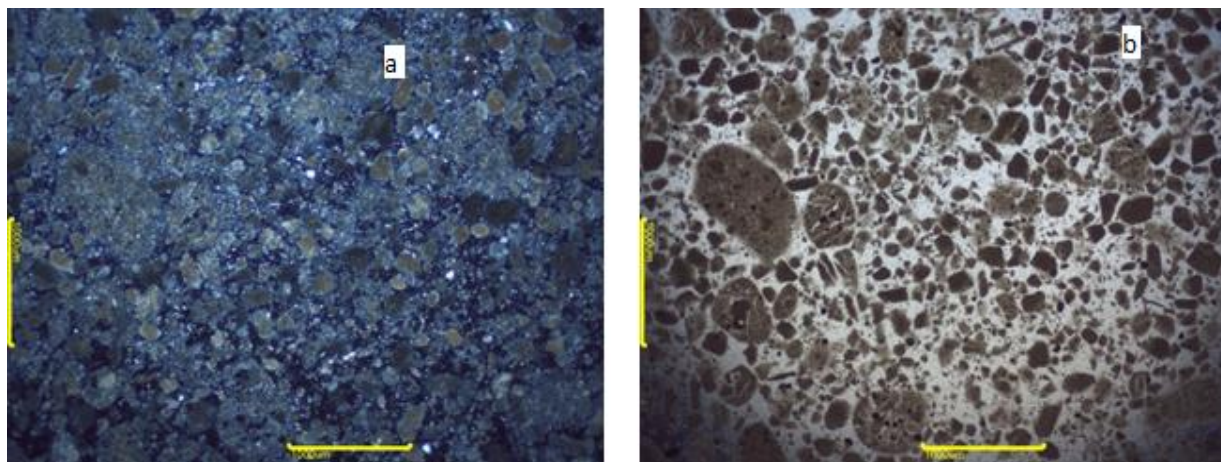


Figure 3: Images of Verdete obtained by optical microscopy, particles $<54\mu m$. a) Crossed Nicols; b) Parallel Nicols.

3.2. THERMAL PROCESSING

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For the thermal process, temperatures of 500°C and 700°C were selected based on the energy of formation values presented in Table 1 and to obtain a slow-release fertilizer with low energy consumption. The temperature values in the system were recorded every 10 minutes. The heat transfer was adjusted in such a way that the desired temperature was reached in 130 minutes. After reaching the processing temperature, the material was kept in the oven for 6h.

The thermal system temperature records, that is, when the thermal processing temperature was reached, were statistically evaluated (for tests 1 to 4) (Table 3):

Table 3: Statistical data for temperature at 500°C and 700°C (tests 1 to 4) during thermal processing.

500°C		700°C	
Mean	509	Mean	722
Variance	37	Variance	1504
Number of measurements	36	Number of measurements	36

The statistical parameters show that the sample subjected to the processing at 700°C was influenced by external agent or by transformations due to the phase change or chemical reactions. The statistical parameter that mostly evidences this difference is the variance, showing great dispersion of the data in the test at 700°C. This indicates changes in temperature outside the control adopted.

The control of the flow of moist air to fluidize the bed load in the oven is an important variable, since it is fundamental to the thermal decomposition (pyrohydrolysis). The flow records (l/min) were performed every 10 minutes and the statistical evaluation showed that the control was effective between 6l/min and 8l/min, due to the small standard error: (6.71 ± 0.08) l/min at 500°C and (6.55 ± 0.09) l/min at 700°C.

3.3. EXTRACTION OF THE CALCINED MIXTURES IN CITRIC ACID

The values of the dissolution of potassium in citric acid at 25°C are presented in Figure 4:

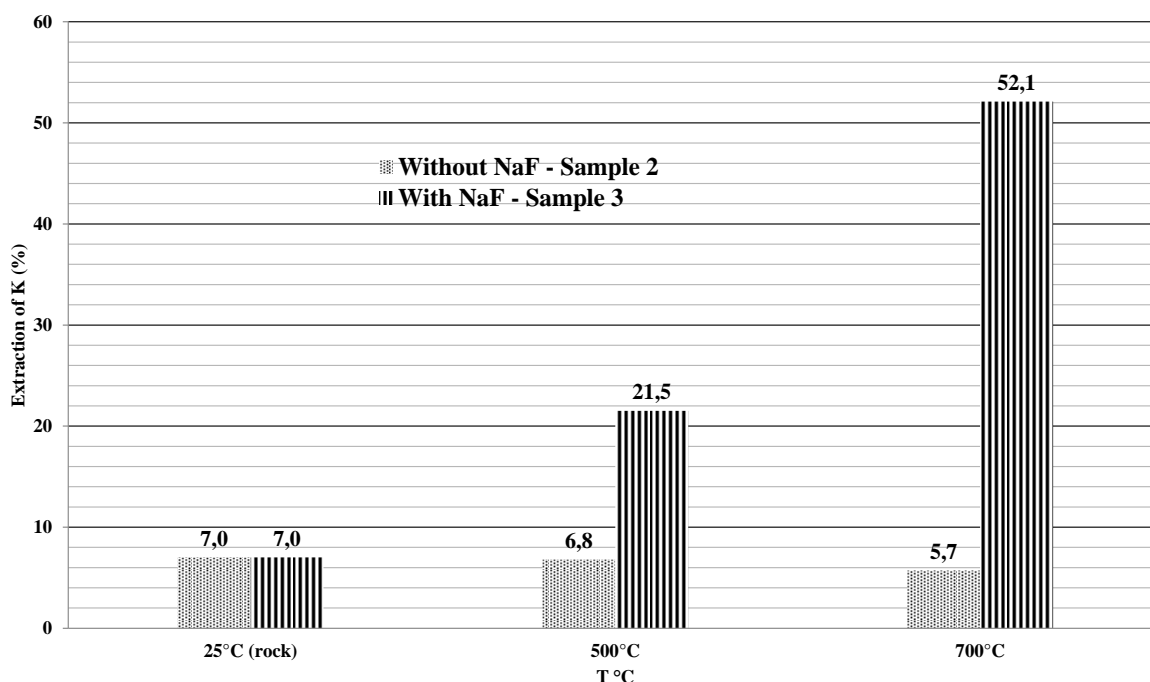


Figure 4: Extractions of K in citric acid 2% (w/w): Rock (Verdete) without thermal processing and rock with thermal processing mixtures: (Rock + FeSO₄) and (Rock + FeSO₄ + NaF).

The "in natura" rock (sample 4) had a 7% potassium solubility in 2% citric acid solution. This means that the rock applied to the soil in the form of powder can provide only 7% of the total potassium contained in that rock.

The potassium solubility of the Verdete rock in 2% citric acid solution when mixed with ferrous sulfate (sample 2) in the ratio (1.0:0.7) and heat-treated for 6 hours at 500°C (test 3) was of 6.8%, indicating that no alteration occurred in the solubility of K in citric acid 2% (w/w). Repeating the test at 700°C (test 4), the potassium extraction was 5.7%, which is below the value of soluble potassium of the "in natura" rock. We conclude that it is not possible to release potassium from glauconite in a mixture of rock containing this mineral with ferrous sulphate, even when the mixture was activated by thermal processing. The final E_h and pH values for the 500°C and 700°C processing were: 575mV, 488mV and 1.1 and 1.6, respectively. The pH drop was due to hydrolysis of the ferric sulphate formed in the processing and the Eh values due to Fe³⁺ concentration in solution. At 700°C (E_h = 488mV), there is lower concentration of Fe³⁺ in solution than at 50°C (E_h = 575mV), which can be explained by the ΔG values of reaction 6 (Table 1).

The mixture of rock (Verdete) with ferrous sulfate heptahydrate and sodium fluoride (29ppm fluorine in the final mixture) (sample 3) in the ratio (1.00: 0.70: 0.01) (Test 1), had the following

values of extraction of potassium in water after thermal processing: 7.0% at 500°C and 20% at 700°C. This test shows the effectiveness of fluorine along with temperature in the release of potassium in water. The values of extraction of potassium in 2% citric acid were: 21.8% at 500°C (test 1) and 52.1% at 700°C. Keeping fluoride fixed, the increase in temperature favors the release of potassium in citric acid.

In sum, it was observed that the temperature and the presence of fluorine (around 30ppm) are factors that favor the availability (solubilization) of potassium in citric acid. These parameters influence the production of slow-release fertilizers of potassium by thermal processing of rock mixtures containing glauconite and ferrous sulphate heptahydrate activated by fluorine.

4 CONCLUSIONS

The evaluation of various reactions through the Gibbs free energy has indicated hydrated ferrous sulfate as the best compound for sulphation of glauconite potassium for the formation of potassium sulphate. However, this was not verified at the temperatures investigated, with extractions of 6.8% in water and 6.8% and 5.7% (of total potassium) in citric acid at 500°C and 700°C, respectively, similar to the value of solubility of the rock in citric acid (7.0% of total potassium). The addition of a small amount of sodium fluoride (rock, $\text{Fe}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$, NaF) (1.00: 0.70: 0.01) to the mixture of Verdete rock and ferrous sulfate heptahydrate (29ppm F in the mixture) resulted in a significant increase of the soluble content of potassium in citric acid. In water, a solubilization of 20% of the total potassium was observed. The influence of fluoride was more evident for the potassium soluble in the 2% (w/w) citric acid solution when the value increased from 22% at 500°C to 52% at 700°C. The temperature and the presence of fluoride (conjugates) favor the availability of potassium by extraction in 2% citric acid solution, that is, they are important in the formulation of slow-release fertilizers of potassium from rock containing glauconite treated thermally with ferrous sulfate heptahydrate.

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