

Thermal behaviour of ground and unground acid leached vermiculite

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Abstract Acid leaching of vermiculite is an interesting procedure to prepare high surface area porous silica. Thermal behaviour of unground and ground vermiculite leached with HCl solutions has been studied by TG, DTA, ETA and high temperature XRD. Important differences have been observed in the thermal behaviour of unground and ground vermiculite after the acid treatments. Thus, for the acid-treated unground vermiculite, dehydrated vermiculite, enstatite and cristobalite were formed during the heating, while for the acid-treated ground vermiculite only iron oxides and cristobalite phases were observed. Structural modifications due to acid treatment were responsible for changes in the transport properties determined by ETA for the vermiculite samples.

Keywords Vermiculite · Grinding · Acid leaching · DTA · TG · EGA · Emanation thermal analysis

Introduction

Vermiculite is a layered mineral of practical importance as a raw material for technical ceramics, as sorbent for

contaminants of the environment, as thermal insulator, etc. [1]. For many applications of natural vermiculite the particle size of the starting material has to be in the nanometer, submicron and micron size. Mechanical treatments like ultrasound and wet or dry grinding have been proposed for delaminating and reducing the particle size of the clay minerals. The mechanical treatment causes modifications of the clays such as in their surface area, structure, morphology, porosity and reactivity [2–9]. For vermiculite, it has been observed that ultrasound causes a considerable particle size decrease, reaching nanometer sizes, while keeping the initial structure [10]. Besides, grinding causes a decrease in particle size, as well as an intense structural degradation of vermiculite, resulting in a loss of the lamellar shape and in a progressive amorphization, accompanied with the formation of hard agglomerates by cold-welding [11].

Selective leaching by acid has been used to prepare porous silica from various clay minerals, including vermiculite [12–15]. The presence of iron in the vermiculite structure influences the value of the surface area obtained after the acid treatment [16]. Grinding of clay minerals significantly influences their leaching behaviour [17]. Ground vermiculite shows a considerable particle size reduction with increasing grinding times, which induces structure degradation. The increased surface area, increased porosity and structural defects produced by grinding of vermiculite influences its leaching behaviour [12]. A very high surface area, i.e. $720 \text{ m}^2 \text{ g}^{-1}$, for the product prepared by acid leaching of the ground vermiculite has been recently reported [12]. The prepared sample contains amorphous phase (silica) and akaganeite (β -Fe-OOH). The presence of iron in the product obtained after acid treatment is important in the preparation of amorphous silica with a high surface area, which made possible to enlarge the field of the material application.

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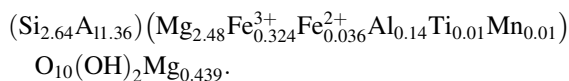
Mechanical treatment influences the thermal reactivity of the clay as well as the formation of high temperature phases [18–25]. Thermal behaviour of vermiculite samples ground by vibratory mill has been characterized using thermal methods [26]. The comparison of the results obtained by different methods contributed to better understanding of the effects of grinding on the vermiculite clay mineral [26].

Considering that grinding, leaching and the thermal treatment caused significant modifications in the clay, this paper aimed to study the thermal behaviour of unground and ground vermiculite samples leached with HCl solutions. The thermal behaviour has been characterized by DTA, TG, high temperature XRD, as well as by emanation thermal analysis (ETA). The ETA has been already advantageously used in the characterization of thermal reactivity due to microstructure changes of clays [27].

Experimental

Starting material

Vermiculite from Santa Olalla (Huelva, Spain) was used as starting material. Its half-unit cell composition is [10]:



Initial vermiculite (V) was obtained by a knife-mill (using the Retsch ultracentrifuge mill, model 255 M-1 equipped with a sieve of 80 μm).

Preparation of samples

The investigated samples were prepared by grinding of V in batches of 10 g by using a vibratory mill Herzog HSM-100 at 1500 rpm, the grinding time was 3 min. Both V and the vermiculite sample ground for 3 min (GV) were treated with 0.25, 0.5, and 1 M HCl solutions at a solid/acid mass ratio of 1:20. The suspensions were maintained at 80 °C and stirred for 24 h. The treated samples were washed with distilled water until the supernatant was free of acid.

Methods of samples characterization

X-ray diffraction (XRD) patterns were obtained by using a Philips X'pert Pro instrument equipped with an X'celerator using Cu K α or Co K α radiation. The XRD measurements were performed at a voltage of 40 kV and an intensity of 40 mA. Qualitative analysis was performed with the HighScorePlus software package (PANalytical, The Netherlands, version 3.0), Diffrac-Plus software package

(Bruker AXS, Germany, version 8.0) and JCPDS PDF-2 database [28]. For quantitative analysis of XRD patterns we used Diffrac-Plus Topas (Bruker AXS, Germany, version 4.2) with structural models based on ICSD database [29]. This program permits to estimate the weight fractions of crystalline phases by means of Rietveld refinement procedure. The degree of crystallinity was also calculated by means of Diffrac-Plus Topas program. In the high temperature chamber the XRD patterns of the sample were collected every 50 °C.

Surface area values were determined by using the B.E.T. method. The adsorption of N $_2$ was measured with Multi-Station High Speed Gas Sorption Analyzer (Quantachrome Instruments NOVA 4200). The samples were outgassed by heating at 200 °C.

The emanation thermal analysis (ETA) measurements were performed on samples of 0.05 g in air flow (flow-rate 40 mL/min) at a heating rate of 6 K/min, by using modified NETZSCH ETA DTA 404 equipment.

The ETA is based on the measurements of radon release rate from samples previously labelled. The samples for ETA were labelled with acetone solution containing traces of ^{228}Th and ^{224}Ra . The specific activity of a sample after labelling was 10 5 Bq/g. Atoms of ^{220}Rn were formed by the spontaneous α -decay of ^{228}Th and ^{224}Ra . The ^{224}Ra and ^{220}Rn atoms were incorporated into the sample to a maximum depth of 80 nm due to the recoil energy (85 keV/atom), which the atoms gain by the spontaneous α -decay. The maximum depth of ^{220}Rn penetration was 80 nm as calculated with the TRIM code.

TG, DTA and evolved gas analysis (EGA) measurements were carried out on heating in synthetic air by using the NETZSCH STA (QMS) 409/429-403 equipment. Sample amount was 0.05 g.

The chemical compositions of the raw material and the residues after leaching were determined in triplicate by X-ray fluorescence (Siemens SRS 3000).

Results and discussion

Characterization by thermal analysis methods

Thermal behaviour of vermiculite samples was characterized by TG and DTA results.

Results of not acid leached vermiculite samples

The thermal behaviour of the V and GV samples substantially differ, as shown in Figs. 1 and 2. Thus, the dehydration process of V sample is characterized by two distinct endothermic effects on heating up to 250 °C, while the dehydroxylation is characterized by an endothermic

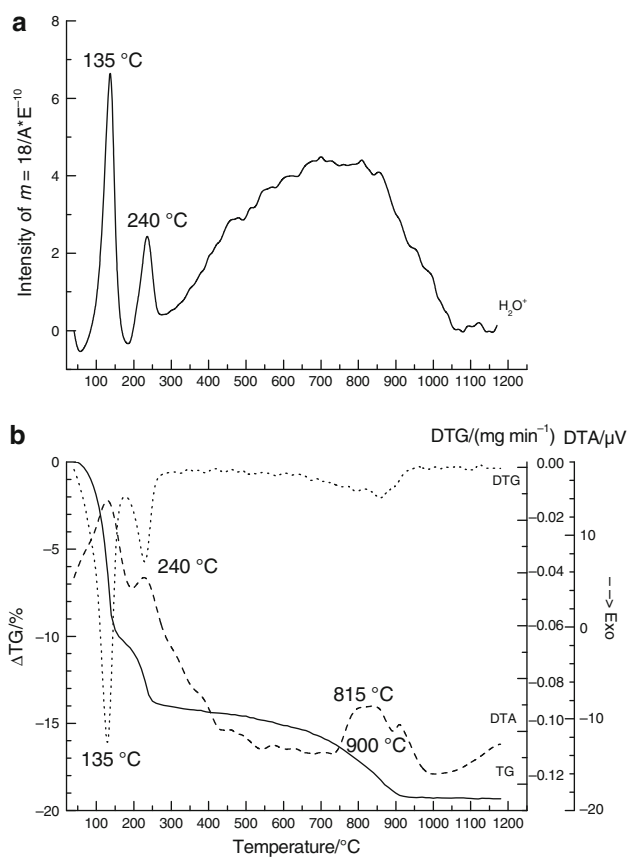


Fig. 1 EGA curve showing the water release ($m/z = 18$) (a) and DTA, TG and DTG curves (b) for V

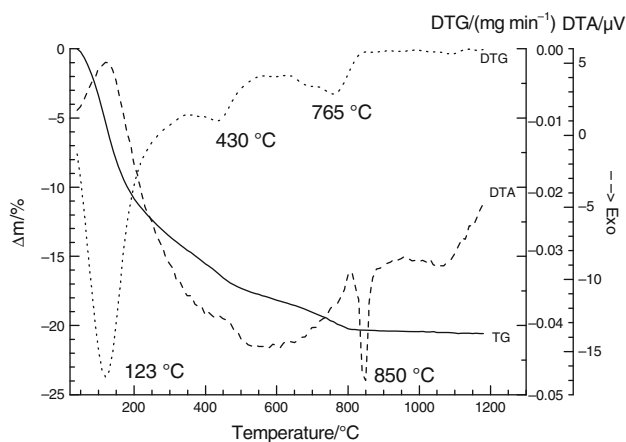


Fig. 2 DTA, TG and DTG curves for GV

effect at about 800 °C (Fig. 1b). These processes are characterized by water release in the evolved gas curve (Fig. 1a). Besides, the small exothermic effect at about 900 °C corresponds to the formation of new phases (Fig. 1b).

For the GV sample (Fig. 2), the endothermic dehydration effects on the DTA curve on heating up to 250 °C are

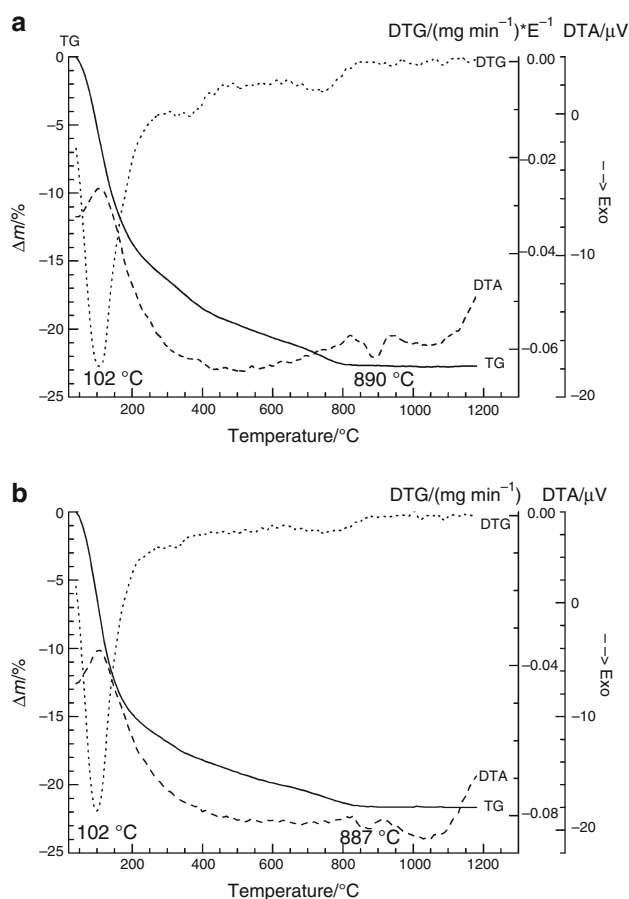


Fig. 3 DTA, TG and DTG curves for GV treated with 0.25 M HCl solution (a) and DTA, TG and DTG curves for GV treated with 0.5 M HCl solution (b)

not resolved in two peaks. On the other hand, the exothermic effect at about 850 °C, corresponding to the formation of the new phases, is more intense for the GV sample as compared to the V one.

Results of leached vermiculite samples

Figure 3a and b depicts DTA and TG results of the GV sample leached with 0.25 and 0.5 M HCl, respectively. These results demonstrate that the behaviours of these samples are similar to that of GV (Fig. 2); but the intensities of thermal effects in the temperature range from 300 to 900 °C are smaller for the acid-treated samples.

Figure 4 represents results of TG, DTA and evolved gas analysis used for the detection of the release of H₂O and HCl for the GV sample treated with 1 M HCl solution. The endothermic effect observed in the DTA curve on heating at temperatures up to 200 °C can be assigned to the loss of bound water. In the temperature range 300–800 °C, the mass loss indicates the decomposition processes of β -FeOOH connected with the HCl release (Cl⁻ is an essential

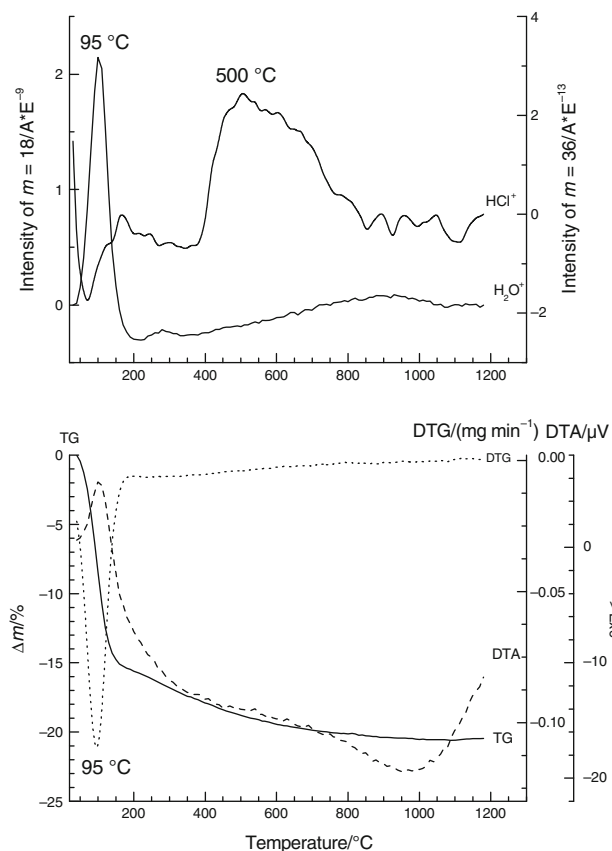


Fig. 4 DTA, TG and DTG curves for GV treated with 1 M HCl solution

component for stabilization of β -FeOOH structure [30–32] formed during the acid treatment). At temperatures above 800 °C the sample starts to crystallize. These results are supported by X-ray data as it will be shown in next section.

Figure 5 depicts DTA and TG results of V treated by 1 M HCl solution. It is of interest to compare the DTA results of V and GV after leaching with 1 M HCl (see Fig. 4). The V leached by 1 M HCl is characterized by an endothermic effect at 840 °C attributed to the dehydroxylation of vermiculite and an exothermic effect at 860 °C corresponding to the formation of new phases, as it will be confirmed by XRD study in next section. The DTA results of GV acid leached with 1 M HCl solution did not show the mentioned endothermal and exothermal effects (Fig. 4).

Structure characterization by X-ray diffraction during the heating

The high temperature XRD patterns in Fig. 6a characterize changes in the interlayer space for the V sample during heating. The d_{002} diffraction data at 14.4 Å decreases to 11.6 Å after heating at 100 °C and to 10 Å at 300 °C. These changes are attributed to the loss of hydration water

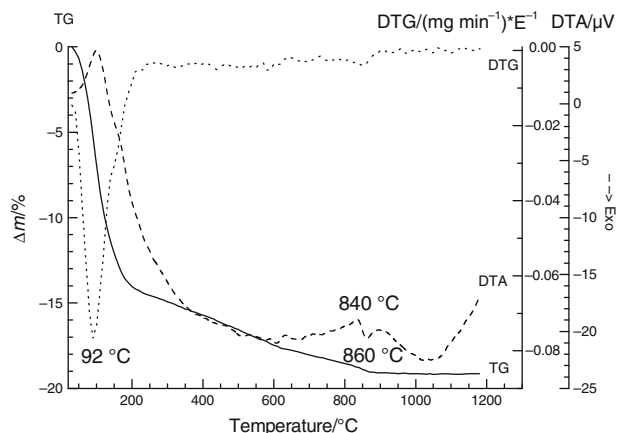


Fig. 5 DTA, TG and DTG curves for V treated with 1 M HCl solution

of the interlayer cation. On further heating at 900 °C, new crystalline phases, namely a talc-like structure and enstatite, are formed. Enstatite is the only phase detected at 1000 °C. The XRD patterns of GV (Fig. 6b) show broader peaks than V, suggesting heterogeneity in the interlayer distance formed by random displacement. The imperfection in the crystal order is mainly due to edge alteration [10]. On heating, the values of d_{002} shift towards smaller values. At 800 °C a talc-like phase is observed, being transformed, at higher temperatures, to enstatite.

Figure 7 represents the XRD patterns of V treated with 1 M HCl solution and heated to temperatures in the range between 30 and 1200 °C. The sample is characterized during heating by changes in the interlayer space, still present after the acid treatment of the sample, and by the high temperature formation of new phases, like enstatite and cristobalite.

Figure 8a–c depicts the XRD patterns of the GV treated with 0.25, 0.5 and 1 M HCl solutions, respectively. From the XRD patterns, in Fig. 8a and b, it can be stated that on heating of the GV treated with 0.25 and 0.5 M HCl solutions in the range between 30 and 200 °C, the samples are characterized by the d_{002} diffraction values of 14.4 Å; this result confirms that vermiculite peaks still remains in the sample after the acid treatment. At higher temperatures, the d_{002} diffraction peak of the sample treated with higher acid concentration (Fig. 8b) becomes broader while its intensity decreases with the temperature; eventually, at 750 °C, it practically disappears. These data characterize the alteration of the structure produced during grinding. Enstatite phase is already detected at 850 °C. The enstatite phase together with the small proportion of cristobalite is present in the sample at 1050 °C. At 1150 °C, cristobalite is the main phase. Small differences are observed between the samples treated with 0.25 and 0.5 M HCl. Thus, the 14.4 Å diffraction peak is broader and less intense for the sample

Fig. 6 XRD patterns of V (a) and GV (b) vermiculite before acid treatment measured at various temperatures (E = enstatite)

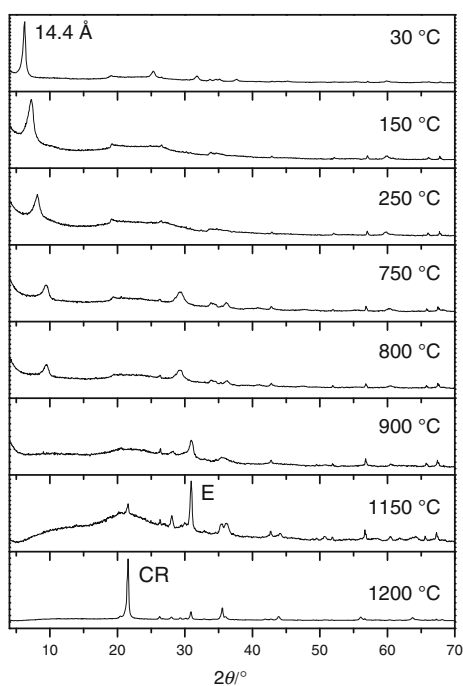
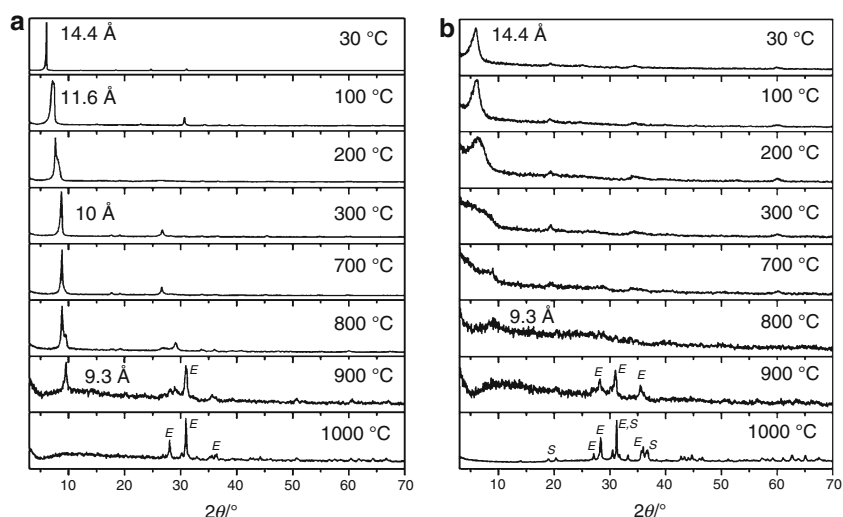


Fig. 7 XRD patterns of V after treatment with 1 M HCl solution measured at various temperatures (E = enstatite, CR = cristobalite)

treated with 0.5 M HCl than for that treated with 0.25 M HCl solution and it disappears at lower temperatures. On the other hand, cristobalite phase is formed at lower temperatures and in higher concentration for the sample treated with 0.5 M HCl than for the sample treated with 0.25 M HCl. Due to the degradation produced by grinding, the leaching induces the formation of new phases at lower temperatures for GV than for V.

Figure 8c represents XRD patterns of GV leached by 1 M HCl measured from 30 to 1200 °C. The XRD patterns of the sample measured at 30 °C showed diffraction peaks at 0.3796, 0.337, 0.253 nm, etc., attributed to akaganeite,

i.e. β -FeOOH (11.8%), together with a high background caused by amorphous silica (87%), a small quantity of quartz was also present. The initial crystalline phase changed to amorphous on heating at about 300 °C. Thus, the sample heated in the range between 300 and 850 °C is practically amorphous. This is in agreement with previous results that show that akaganeite (β -FeOOH) decomposes to the amorphous or poorly crystalline phase β -Fe₂O₃, being transformed to crystalline α -Fe₂O₃ [30, 32, 33]. On heating at 850 °C, the sample showed for the first time some crystallinity. At the temperature of 1050 °C, the sample is fully crystalline, consisting of quartz, cristobalite, α -Fe₂O₃ and ε -Fe₂O₃.

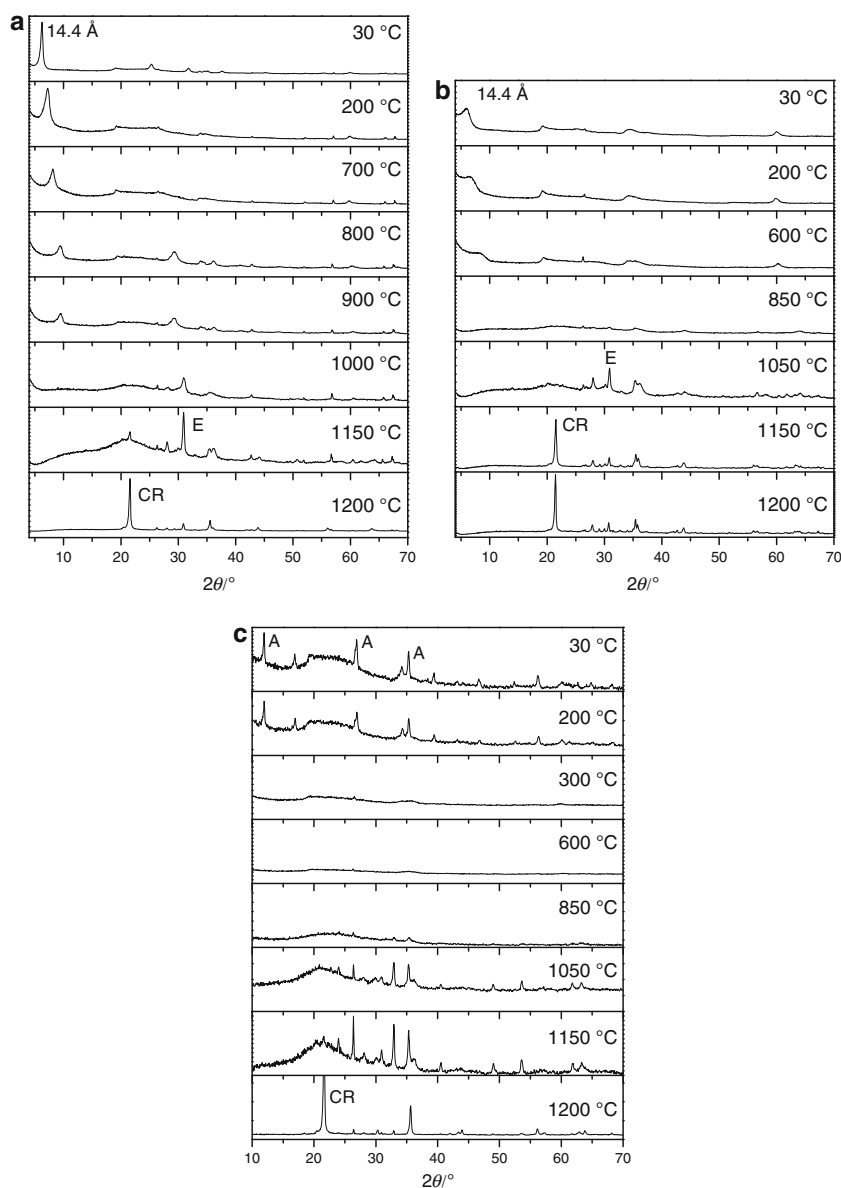
Results of emanation thermal analysis and structure changes of vermiculite samples on heating

Figure 9 depicts the ETA results of V treated with 1 M HCl solution, as well as the ETA results of GV and GV leached with 0.25, 0.5 and 1 M HCl solutions to characterize changes of the transport properties and microstructure development during heating of the samples.

From comparison of ETA results in curve 1, and in curves 2–5, Fig. 9 it follows that the values of emanation rate, E , of the leached samples are higher as compared to the E values for V (curve 1, Fig. 9). This can be explained by the increase of surface area of the acid-treated vermiculite samples due to the changes in the microstructure and the formation of new phases.

The values of surface area and alumina content in the samples are presented in Table 1. From this Table 1, it is obvious that the surface area increases with the acid treatment of the samples, following the increase of the HCl concentration; thus, the smallest value of surface area is observed for V. The increase of the content of Al³⁺ in the GV sample treated with 0.25 and 0.5 M HCl solutions can

Fig. 8 XRD patterns of GV after acid treatment with 0.25 M (a) 0.5 M (b) and 1 M (c) HCl solutions measured at various temperatures (E = enstatite, CR = cristobalite, A = akaganeite)



be attributed to the leaching of Mg^{2+} by HCl. A different behaviour is observed for GV treated by 1 M HCl solution, where the vermiculite phase is not present due to its chemical degradation.

From the comparison of the ETA results with the TG and DTA results (Fig. 2) and the XRD patterns (Fig. 6b) for the GV, it follows that the emanation rate, E , of the sample is enhanced by the water release on heating. The sharp decrease in the emanation rate, E , is due to the structure changes of the sample characterized by XRD patterns in Fig. 6b. In the temperature range above 860 °C an increase in the emanation rate E takes place due to volume diffusion mechanism. The higher values of the emanation rate for the ground sample as compared with the unground one (figure not shown) can be also attributed to

the fact that the mechanical activation by grinding enhances the formation of new crystalline phases.

From the ETA results it follows that the microstructure development of the GV acid-treated with 0.5 M HCl solution (Fig. 9, curve 3) is similar to the GV treated with 0.25 M HCl solution (see Fig. 9, curve 2). Thus, the increase of the emanation rate E observed on samples heating up to 800 °C is due to the radon diffusion along open pores of the samples. These samples present relatively high surface area even after heating to 700 °C. Thus, the surface area of the GV treated with 0.25 and 0.5 M HCl solutions and heated at 700 °C are 115 and 175 m^2/g , respectively. The ETA results show the decrease of the emanation rate at about 800 °C, due to annealing of the microstructure irregularities and formation of the enstatite

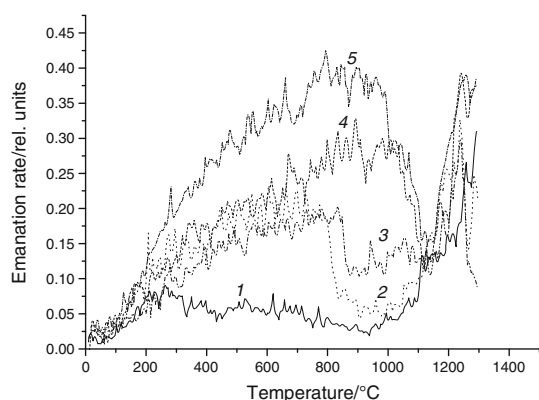


Fig. 9 Emission thermal analysis results. *Curve 1* GV; *curve 2* GV treated with 0.25 M HCl solution; *curve 3* GV treated with 0.50 M HCl solution; *curve 4* GV treated with 1 M HCl solution; *curve 5* V treated with 1 M HCl solution

mineral phase. The presence of enstatite is confirmed by XRD patterns (Fig. 8a, b). On heating above 1000 °C, the increase of emanation rate and the changes on the ETA curve corresponds to the formation of new phases in the range from 1000 to 1200 °C as confirmed also by XRD patterns by the transition of enstatite to cristobalite (see Fig. 8a).

A special attention deserves the vermiculite samples leached with 1 M HCl. Thus, the increase of the emanation rate, E , values with temperature is more intense for higher concentration (1 M of the HCl leaching solution); this is due to a larger extraction of Al from the lattice of vermiculite (Table 1) by the acid treatment, which produces important modifications in the vermiculite structure.

Moreover, the thermal behaviour of V and GV leached by 1 M HCl solution can be characterized as follows (see curves 4 and 5, Fig. 9): the increase of the emanation rate E up to approximately 1000 °C is due to random diffusion in the sample, the decrease of emanation rate E on heating from about 1000 °C is due to the annealing of structure irregularities, and the changes of the E values observed on further heating of the samples up to 1300 °C corresponds to the crystallization of new phases.

Table 1 Values of surface area and the content of alumina (Al_2O_3) in ground and unground acid leached vermiculite samples

Sample	Treatment	BET surface area/ $\text{m}^2 \text{g}^{-1}$	Alumina content in the sample/%	ETA results presented in Fig. 9
GV	Not leached	32.05	15.47	Curve 1
GV	0.25 M HCl	261.45	21.10	Curve 2
GV	0.5 M HCl	485.70	21.00	Curve 3
GV	1 M HCl	689.11	1.8	Curve 4
V	Not leached	15.40	15.62	
V	1 M HCl	504.28	7.05	Curve 5

It should be mentioned that for V after treatment with 1 M HCl solution, the vermiculite phase still remains, as detected by XRD patterns (Fig. 7). On the other hand, in the GV treated with 1 M HCl solution, only amorphous silica and akaganeite ($\beta\text{-FeOOH}$) are present, while no vermiculite phase is observed by XRD (Fig. 8c). In GV treated with 1 M HCl solution, the amorphous silica transformation to cristobalite at about 950 °C is characterized by the decrease of the emanation rate E observed on heating. In the sample heated at 1200 °C the formation of composites of cristobalite and iron oxide has been determined by XRD and HRTEM methods [34]. The ETA results in curve 4, Fig. 9 indicates the formation of this composite by the effect in the temperature range from 1150 until 1250 °C. The curve 5, Fig. 9, characterizes the thermal behaviour of V treated with 1 M HCl solution using the ETA results. This sample shows a very high emanation rate (curve 5, Fig. 9) as compared with the non-leached sample (curve 1, Fig. 9), this behaviour can be understood considering the differences among these two samples in terms of surface area and Al^{3+} loss from the vermiculite lattice that produce important modifications on the vermiculite structure. Thus for the leached sample, its very high surface area facilitates the radon diffusion along open pores.

Conclusions

The thermal study of V and GV treated with HCl solutions characterized the structure changes of the vermiculite and the formation of new phases during heating. Important differences were obtained by means of DTA, TG, EGA and ETA methods for V and GV samples treated with 1 M HCl solution. The XRD patterns demonstrated that for V some vermiculite still remains after the acid treatment. Enstatite appeared after heating at high temperature, being transformed to cristobalite on further heating. On the other hand, in the GV treated with 1 M HCl solution, amorphous silica and iron oxides were observed. By heating from 300 to 900 °C an amorphous phase was formed. At higher temperatures a composite product composed of cristobalite and crystalline iron oxides was formed. In the vermiculite treated with 0.25 M HCl and 0.5 M HCl solutions the altered vermiculite was observed that transformed by heating to enstatite and to cristobalite.

Differences in the microstructure development due to grinding and acid treatment of the vermiculite samples were characterized by emanation thermal analysis. The transport properties of the samples characterized by ETA represent supplementary information to that obtained by other used methods.

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