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Research paper

Structural changes on vermiculite treated with methanol and ethanol and subsequent microwave irradiation

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ABSTRACT

Present work reports the alcohol treatment and subsequent irradiation with microwave of commercial vermiculites. Alcohol treatment resulted in slight delamination of the layers and the color of the samples changed into brilliant golden and no expansibility was observed ($k \leq 1.3$). Samples treated with alcohol and subsequently irradiated with microwaves expanded; the greater expansibility ($k = 8$ for 1 h) was provided by the most complex sample and treated with methanol. The structural changes were studied by using X-ray diffraction (XRD), thermogravimetric analysis (TG and DTA), infrared spectroscopy and carbon analysis. The results of these analysis indicated dehydration-hydration and order–disorder which would be related to the entry of alcohol into the vermiculites and the loss of water content. The changes occurred in a similar way to the temperature and vacuum, and were less pronounced for the purest vermiculite. The crystallite size and lattice strain values which reflect changes in crystallinity and structural order varied slightly regardless of treatment and time. Alcohol treatment and subsequent microwave irradiation may be the procedure for obtaining purest vermiculite from less pure sample.

1. Introduction

Vermiculites belong to the 2:1 group of phyllosilicates. The 2:1 layer is composed of one octahedral sheet between two tetrahedral sheets. The positive charge deficiency is compensated by hydrated exchangeable cations (as Mg^{2+}, Ca^{2+}, Na^{+} and K^{+}) located in the interlayer space between the parallel 2:1 layers. Vermiculite has water layers between the silicate layers and, therefore, it can undergo processes of dehydration-hydration which depend on temperature, pressure, chemical composition, size and relative humidity (Mathieson and Walker, 1954; Walker, 1956; Vali and Hesse, 1992; Collins et al., 1992; Reichenbach and Beyer, 1994, 1995, 1997; Ruiz-Conde et al., 1996; Marcos et al., 2003, 2009; Marcos and Rodríguez, 2010). The hydration state of vermiculite is defined by the number of water layers in the interlayer space, with a development corresponding to different phases, such as zero-, one- and two-water layer hydration states (0-, 1- and 2-WLHS, respectively) (Suzuki et al., 1987). As an example, for Mg-vermiculites the basal spacing are 9.02 Å for 0-WLHS, 11.50 Å for 1-WLHS and 14.40 Å for 2-WLHS (e.g.: Suzuki et al., 1987; Ruiz-Conde et al., 1996; Marcos et al., 2003, 2009).

As a result of their lamellar structure, vermiculite shows the diversity of properties related to the structural characteristics, such as layer charge associated with the numerous isomorphic substitutions and mixed layered structure, and to dehydration–rehydration ability (Mathieson and Walker, 1954; Shirozu and Bailey, 1966; Grim, 1968; Brown and Brindley, 1980; de la Calle and Suquet, 1988; de la Calle and Suquet, 1988; Marcos et al., 2004; Argüelles et al. 2009 and 2010). It is an interesting mineral as a model system in physics, chemistry and the biological sciences (Satapathy et al., 2011; Wu et al., 2011; Eom et al., 2011), but it is also an attractive material due to its numerous thermal and insulation applications (Strand and Stewart, 1983; Suzuki et al., 1989; Suzuki and Suzuki, 2001; Hindman, 1992; Bergaya et al., 2006; Klein and Dutrow, 2007; Abollino et al., 2008; Zhang et al., 2009; Marcos et al., 2012; Marcos and Rodríguez, 2014).

Numerous studies on the intercalation of polar organic molecules by clay minerals have been carried out. In addition to water, inorganic or organic substances can be adsorbed in the expandable interlayer space (Brigatti et al., 2005; Jiménez de Haro et al., 2005). The adsorption properties of alcohols is the most widely studied (Yariv and Cross, 2002; Bergaya et al., 2006). Vermiculite soaked with alcohol is used e.g. to improve superficial scald development on 'Granny Smith' (Chervin et al., 2001) or to treat colonies against *Varroa destructor* (Emsen and Dodologlu, 2011.

The results obtained from the research on commercial vermiculites treated with methanol and ethanol are presented in this work and the structural changes induced in the samples were detected by using X-

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ray diffraction, thermogravimetric analysis, infrared spectroscopy and carbon analysis.

2. Experimental

Vermiculite samples from Santa Olalla (Huelva, Spain), Libby (Montana, EEUU) and China (provided by Vermiculita y Derivados S.A. company of Gijón, Spain). The received samples, smaller than 5 × 5 mm in size, were used in the experiments after elimination of other minerals by hand-picking. Chemical and thermogravimetric analyses of the samples were previously published (Marcos and Rodríguez, 2010, 2014). Differences between the compositions of the three studied minerals were observed by K_2O, iron and potassium contents. First, it was found that the samples from Libby and China have a higher K_2O (5.614 and 9.682%, respectively) content are not pure vermiculites, since K_2O content is higher than 0.033% (Velde, 1978; Justo et al., 1986). They are referred as "commercial vermiculites", which are the vermiculite mined and beneficiated particles larger than 1 mm in size. Later, the order in the iron and potassium content for samples was determined as: Santa Olalla < China < Libby.

Two experiments were made: 1) Immersion of each vermiculite sample into alcohol at room temperature for different periods of time and 2) Irradiation of the samples with microwaves for 20 s (40 for Santa Olalla) after alcohol treatment. The procedure for the first experiment consists of: 1) Preparation of three sets of two 30 ml beakers. One of the two beakers of each set contains 10 ml of methanol and the other 10 ml of ethanol. 1) Preparation of three sets of two 30 ml beakers. One of the two beakers of each set contains 10 ml of methanol and the other 10 ml of ethanol. 2) Measure 1 ml of each vermiculite sample. The operation was performed twice for obtaining 2 lots of 1 ml volume of each vermiculite sample. The volume was measured by tipping the loose fragments into a measuring glass cylinder without compaction. 3) Weighing of each vermiculite sample. 4) Immersion of each sample into one beaker containing alcohol. 5) Separation of the solids by filtration, after the completion of alcohol treatment. 6) The samples were again weighed after the treatment. The second experiment 7) microwaves irradiation of alcohol treated vermiculite for 20 or 40 s to expand. Finally, the analysis (expansibility calculation, X-ray diffraction, etc.) of the untreated and treated samples were made separately for comparison.

The methanol (99.8%) and ethanol (99.9%) used were from Baker. The trace impurities (Cu, Fe, Ni) of methanol were <0.1 ppm and heavy metals (as Pb) < 0.5 ppm. The trace impurities (Al, Ca, Cu, Zn, Sn, Pb, Mg, B, Ba, Cu, Fe, Ni) of ethanol were up to 1.93 ppm.

The expansibility, k (k = density of the raw sample/density of the treated sample), was measured by the change of the apparent density (Justo et al., 1989). Each sample was measured in triplicate.

The experiments with microwave irradiation were carried out using a SHARPR64sT microwave oven working at 2.45 GHz of frequency with 800 W of energy.

The thermogravimetric analyses were performed between 25 °C and 1100 °C using a Mettler Toledo Stare System thermobalance with a heating rate of 10 °C/min. The total mass loss attributed to the water loss was determined gravimetrically by heating the samples in air at 1000 °C.

The X-ray diffraction patterns were taken with a PANalytical X'pert Pro diffractometer. Setting conditions: 40 mA and 45 kV (Cu-K_α radiation; λ = 1.5418 Å), 2θ 3–12, 2θ step scans of 0.007° and a counting time of 1 s per step. The standard reference material used was 660a NIST LaB_6 with Full Width at Half Maximum (FWHM) of 0.06° for 2θ = 21.36°. Changes in the intensity and position of the basal reflections were used to indicate changes in the structural order and hydration states. The crystal sizes and lattice microstrains of materials were evaluated using the PANalytical software (X'Pert Plus). Authors like Pérez-Maqueda et al. (2001) or Pérez-Rodríguez et al. (2002) used these parameters in delamination experiments of vermiculite, and Kaur et al. (2014) used them with gamma-irradiated vermiculite.

The infrared spectra were obtained with a Varian 670-IR equipped with a ATR "Golden Gate", in the range of 600–4000 cm^{-1}, with a resolution of 4 cm^{-1} using 16 scans for both the sample and the background. The sample was placed on diamond crystal and pressed to ensure the contact between the sample and the crystal. The infrared spectroscopy was used to characterize the starting and treated vermiculites.

Three carbon analysis of each studied sample were carried out with the Elemental Analyzer C, N, H, S Elemetar Vario utilizing combustion technique.

3. Results

Chemical treatment of raw vermiculites with alcohol resulted in slight delamination of the layers and the color of the samples changed into brilliant golden.

3.1. Expansibility

The weight loss of the samples after treatment with methanol and ethanol was very low (≤2%). The change in the volume of the samples was little and a slight expansibility was observed (k ≤ 1.3) (Table 1). The expansibility of the microwave irradiated samples was higher than the expansibility of the samples treated with methanol or ethanol and subsequently microwave irradiated. In the second case, the expansibility of the China and Libby samples was higher than the

Table 1
Expansibility coefficient k of the vermiculites treated with alcohol (methanol and ethanol), and alcohol and subsequently irradiated with microwaves, and only irradiated with microwaves. The standard deviation was lower than 0.002.

Sample	Treatment time (hours)	k				
		Methanol	Methanol + microwaves	Ethanol	Ethanol + microwaves	Microwaves
Santa Olalla	–					2.1
	1	1.1	1.7	1.0	1.2	
	24	1.1	2.1	1.2	1.4	
	168	1.1	1.5	1.3	1.2	
China	–					7.3[a]
	1	1.1	8.0	1.0	2.8	
	24	1.1	6.0	1.0	3.0	
	168	1.1	4.8	1.0	3.2	
Libby	–					6.8[b]
	1	1.1	3.9	1.0	4.0	
	24	1.1	5.5	1.1	5.0	
	168	1.2	5.6	1.1	5.7	

[a] Values from Marcos and Rodríguez (2011).
[b] Values from Marcos and Rodríguez (2014).