

Effects of sulphuric acid dissolution on the physical and chemical properties of a natural and a heated vermiculite

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The effects of high-temperature (90°C) sulphuric acid dissolution on the physical and chemical properties of a commercial vermiculite sample, in natural and heated forms, were investigated using chemical, X-ray diffraction, Fourier transform infrared spectroscopy and thermal analyses, and specific surface area measurements. The X-ray diffraction analyses showed that vermiculite and mixed-layer mica-vermiculite structures in the natural sample were completely destroyed following dissolution in 4 N H₂SO₄, whereas the basal peak related to mica, which exist in minor amounts in the natural sample, was observed in the X-ray diffraction patterns even after the dissolution in 8 N H₂SO₄. As a result of the destruction of main clay structures in both samples by acid dissolution, hydrous amorphous silica phases were formed. The maximum specific surface area values were obtained after dissolution in 4 N H₂SO₄ solution, where the increases in surface area values were approximately 150 (from 3.3 up to 494.6 m²/g) and 24 (from 14.0 up to 335.2 m²/g) times in the natural and heated samples, respectively. The results of all experiments indicated that the heated sample had higher resistance to acid dissolution than the natural sample, probably due to its dehydrated and collapsed mica-like layer content, which was formed by the heating process at 900°C applied before the dissolution experiments. Besides, in this study, the changes in some of the magnetic properties of the heated sample, before and after dissolution, were also determined.

Key words: Dissolution. Mica. Sulphuric acid. Vermiculite.

Introduction

Vermiculite, as a mineralogical term, is the name of a group of hydrous 2:1 layer planar hydrous phyllosilicates with a layer charge between smectite and mica and having hydrated exchangeable cations in interlayer spacings (Guggenheim et al., 2006). Commercially, vermiculite is a term used to describe micaceous minerals exhibiting exfoliation when heated quickly to elevated temperatures. The exfoliated vermiculite is lightweight, chemically inert, fire-resistant, odourless and finds use in various construction products, agriculture, horticulture and other industrial applications (Rau, 1985; Hindman, 1994; Harben, 1995; Cuillo, 1996). Other than thermal exfoliation method, dissolution in inorganic acids, i.e. sulphuric (Okada et al., 2006; Steudel et al., 2009; Su et al., 2011; Chmielarz et al., 2012), hydrochloric (Suquet et al., 1991; Ravichandran and Sivasankar, 1997; Temuujin et al., 2003; Temuujin et al., 2008; Maqueda et al., 2009; Chmielarz et al., 2012; Yu et al., 2012; Ritz et al., 2014) and nitric (Chmielarz et al., 2010; Alves et al., 2014; Santos et al., 2015) acids can be used as a modification technique to alter the properties of vermiculites. In our previous study (Ehsani et al., 2014), we investigated the leaching behaviour of a vermiculite in 1 M H₂SO₄ at 20°C and 90°C, and it was found that high-temperature leaching was the most effective way to alter the properties of vermiculite.

As a continuation of our previous study, in this work, we investigated the effects of dissolution in high-temperature (90°C) sulphuric acid solutions at different concentrations on the physical and chemical properties of a commercial vermiculite sample, in natural and heated forms, using chemical, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and thermal (TG/DTA) analyses, and specific surface area measurements. In this work, the magnetization curves of some of the selected samples were also obtained.

Materials and methods

The natural vermiculite sample is micron-grade Palabora vermiculite, which was supplied kindly by Palabora Europe Ltd. The heated vermiculite (HV) sample was prepared by heating of the natural vermiculite (NV) sample for 1 hour at 900°C in a muffle furnace starting from the room temperature. The chemical composition of the natural sample can be found in Ehsani et al. (2014).

In a standard dissolution experiment, 50 g of the natural or heated vermiculite sample was added into 500 mL of 1, 4 and 8 N hot (90 °C) aqueous sulphuric acid under intensive mixing. After one hour, the undissolved solids were separated by filtration, washed, dried at 105 °C and then stored in sealed bottles for further characterization. The chemical compositions, B.E.T. specific surface area values (Quantachrome, nitrogen adsorption, after degas for 2 hours at 105 °C), XRD patterns (Rigaku, CuK α radiation, measured after equilibrating with room atmosphere), FT-IR spectra (Bruker, KBr pellet method, in the frequency range of 4000-

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400 cm⁻¹) and TG/DTA curves (Setaram, heating rate of 10°C/min, static air atmosphere, measured after equilibrating with room atmosphere) of the natural and heated vermiculites, and the undissolved solids obtained after the dissolution were determined. The magnetization curves (Quantum Design, vibrating sample magnetometer module of Physical Properties Measurement System) of the selected samples were also registered for the characterization purposes.

Results and discussion

The amounts of the main chemical components of the natural and heated samples following dissolution in sulphuric acid were given in Fig. 1. It can be seen that the structural aluminium, iron and magnesium contents of both samples after dissolution drastically decreased with the increasing acid concentrations from 1 to 4 N. For example, Al₂O₃, Fe₂O₃ and MgO contents of the natural sample decreased from 8.90, 8.36 and 19.91 % to 7.93, 7.91 and 17.60 % following the dissolution in 1 N H₂SO₄, and to 0.44, 1.44 and 3.07 % following the dissolution in 4 N H₂SO₄, respectively. The K₂O content of the natural sample, which indicated the presence of interstratifications (Muiambo and Focke, 2012; Hillier et al., 2013), was also decreased from 4.63 to 4.28 % after the dissolution in 1 N H₂SO₄ and to 0.26 % after the dissolution in 4 N H₂SO₄, respectively. Above 4 N H₂SO₄ concentration, the dissolution was leveled off for both samples, and Al₂O₃, Fe₂O₃, MgO and K₂O contents of the undissolved solids became 0.21, 0.93, 2.76 and 0.12 %, respectively, after the dissolution of the natural sample in 8 N H₂SO₄. On the other hand, the heated sample, which was formed from dehydrated and collapsed mica-like layers due to the applied heating process, was found to be more resistant to the acid dissolution. The Al₂O₃, Fe₂O₃, MgO and K₂O percentages of the heated sample decreased from 10.09, 9.31, 21.69 and 5.20 % to 0.49, 1.31, 2.95 and 0.48 %, respectively following the dissolution in 8 N H₂SO₄. Due to the dissolution of interlayer and the main structural components, the amounts of SiO₂ in the undissolved solids increased. The SiO₂ content of the natural sample (41.02 %) increased to 82.00 and 84.39 %, and of the heated sample (44.39 %) increased to 79.85 and 83.78 % after dissolution in 4 and 8 N H₂SO₄, respectively. It was also observed that the colours of the undissolved solids obtained from both samples after dissolution in 8 N H₂SO₄ turned to white and the single flakes, being the original morphology of both samples were also preserved following acid dissolution.

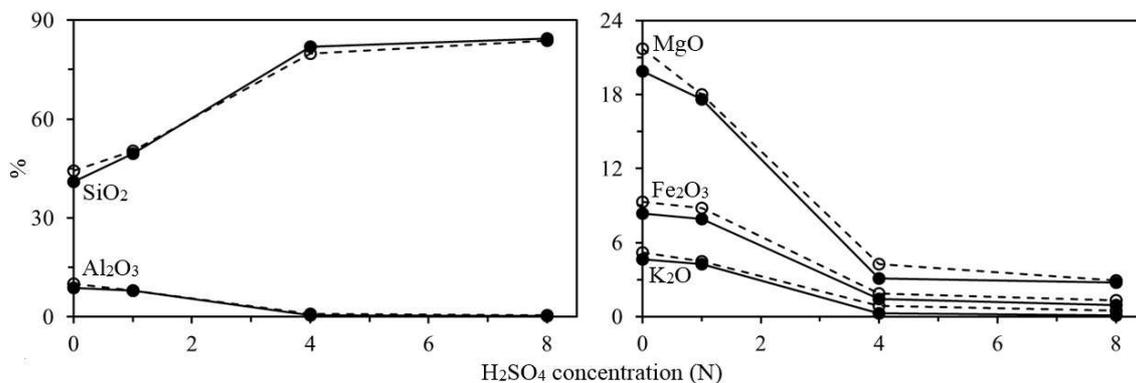


Fig. 1. Changes in the main chemical components of the natural and heated samples following dissolution in sulphuric acid at indicated concentrations (full markers: natural samples, empty markers: heated samples).

Because of the dissolution of structural components from the clay layers, the specific surface area of both samples increased (Tab. 1). The maximum specific surface area values were reached following the dissolution in 4 N H₂SO₄, where the increases in specific surface area values were approximately 150 and 24 times for the natural and heated samples, respectively. The dissolution in acid solutions at a higher concentration (8 N) leads to the decrease of the specific surface area values, which was also observed in the related literature (Temujin et al., 2003; Yu et al., 2012; Santos et al., 2015). As a comparison with the similar experimental conditions in the literature studies using micron-grade South African natural vermiculite, Temujin et al. (2003) reached surface area values of 581 and 501 m²/g after the dissolution in 4 M HCl at 80°C for 0.5 and 2 hours, respectively, and Okada et al. (2006) reached 265 and 470 m²/g after the dissolution in 1 M H₂SO₄ at 70°C for 1 and 2 hours, respectively. Again, as a comparison, Temujin et al. (2008) reached 547 and 559 m²/g after the dissolution of the 600 °C-heated vermiculite in 2 M HCl at 80 °C for 0.5 and 2 hours, respectively. Besides, with the increase in the specific surface area values, the moisture content of the undissolved solids was observed to increase, as expected (Fig. 2).

Tab. 1. Specific surface area values of the natural and the heated vermiculite samples following dissolution in sulphuric acid.

H ₂ SO ₄ conc. [N]	Specific surface area [m ² /g]	
	Natural vermiculite	Heated vermiculite
0	3.3	14.0
1	79.4	74.7
4	494.6	335.2
8	451.9	302.4

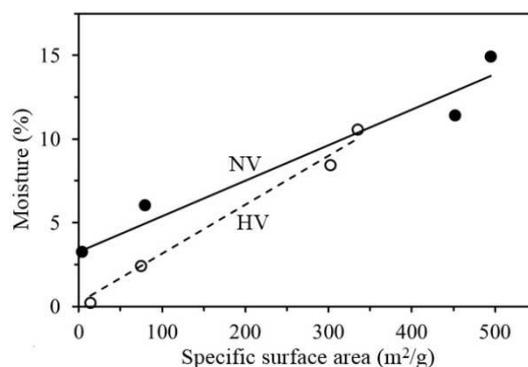


Fig. 2. The relationship between specific surface area values and moisture content of the natural and heated samples following dissolution in sulphuric acid (full markers: natural samples, empty markers: heated samples).

The XRD patterns of the natural and heated samples following dissolution in sulphuric acid were given in Fig. 3. The XRD peaks at $2\theta=3.48^\circ$, 6.22° , 7.18° , 7.48° , 8.80° and 10.54° in the pattern of the natural sample (Fig. 3, NV) indicated that this sample contained dominantly mixed-layer mica-vermiculite and vermiculite, and minor amounts of mica phases (Bassett, 1959; Marwa et al., 2011; Muiambo et al., 2015). On the other hand, the XRD peak at 8.86° in the pattern of the heated sample (Fig. 3, HV) indicated that this sample was formed from the dehydrated and collapsed mica-like layers. The clay layers in the natural sample can be destroyed totally by heating at 1200°C (Turianicová et al., 2014). The dissolution process in 1 N H₂SO₄ drastically reduced the intensity of vermiculite basal peak and the dissolution in 2 (Ehsani et al., 2014), 4 and 8 N H₂SO₄ completely destroyed the vermiculite structures in the natural sample, as can be concluded from the disappearance of the peak at 6.22° . Although the dissolution process in 2 N H₂SO₄ greatly reduced the peak intensities (Ehsani et al., 2014), the dissolution in 4 and 8 N H₂SO₄ completely destroyed mixed-layer mica-vermiculite structures in the natural sample, as can be observed from the disappearance of the peaks at about 3.5° , 7.3° and 10.5° . In contrast, even after the dissolution of the natural sample in 8 N H₂SO₄, the basal peak belonging to mica at about 8.8° could still be seen in the XRD pattern of the undissolved solids (Fig. 3, NV-8N), although its intensity was reduced. In addition to the changes dealing with the basal peaks, the dissolution of clay layers could also be observed, due to a formation of a hump-type XRD peak at about $22\text{--}23^\circ$ belonging to the hydrous amorphous silica phases. Especially, this effect could be seen in the case of the dissolution of both samples in acids with the concentrations 4 and 8 N (Fig. 3, NV-4N, NV-8N, HV-4N and HV-8N).

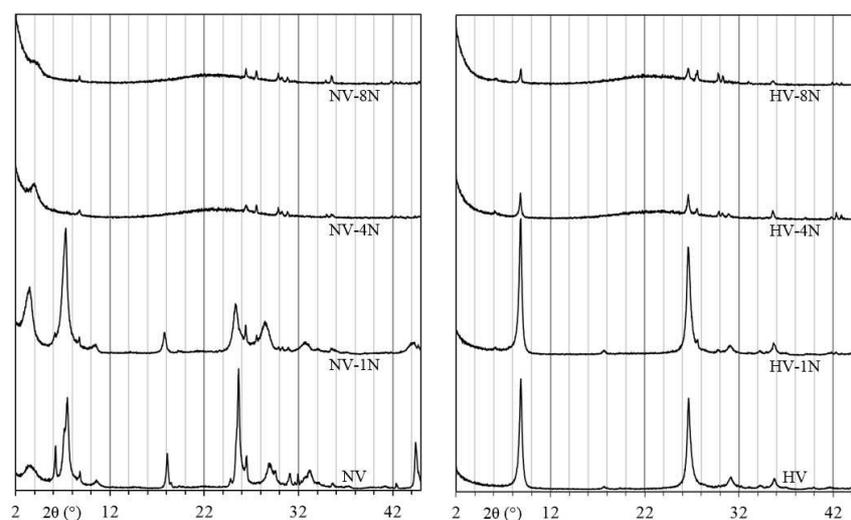


Fig. 3. XRD patterns of the natural and heated samples following dissolution in sulphuric acid at the indicated concentrations.

The intensity of the basal peak at about 8.8° , representing the dehydrated and collapsed mica-like layers in the heated sample decreased with the increase in acid concentration. As was also observed for the natural sample, even the dissolution in 8 N H_2SO_4 , the basal peak belonging to mica at about 8.8° again could be seen in the XRD pattern of the undissolved solids (Fig. 3, HV-8N) obtained from the heated sample. On the other hand, a new peak of very low intensity at about $6.1-6.2^\circ$ was observed in the XRD patterns of the undissolved solids obtained after the dissolution of the heated sample in acid solutions. This probably indicated the introduction of hydrogen and/or other cations released from the sample into the exchange sites of undissolved clay layers during the dissolution experiment (Jozefaciuk and Bowanko, 2002).

The FT-IR spectra of the natural and heated samples following dissolution in sulphuric acid were given in Fig. 4. Because, the FT-IR identification of vermiculites can be found in the related literature (da Fonseca et al., 2007; Kehal et al., 2010; Matějka et al., 2010; Muiambo and Focke, 2012; Marcos and Rodríguez, 2014; Ritz et al., 2014; Turianicová et al., 2014), only important changes created by acid dissolution were mentioned. In accord with the results of XRD analyses, the acid dissolution caused dissolution of the clay layers and the formation of hydrous amorphous silica phases, which could be observed mainly by the disappearance of absorption bands near 1000 cm^{-1} and between $600-750\text{ cm}^{-1}$, and the appearance of new bands especially at 800, 951, 1086 and $1200\text{ (shoulder)}\text{ cm}^{-1}$ for both samples.

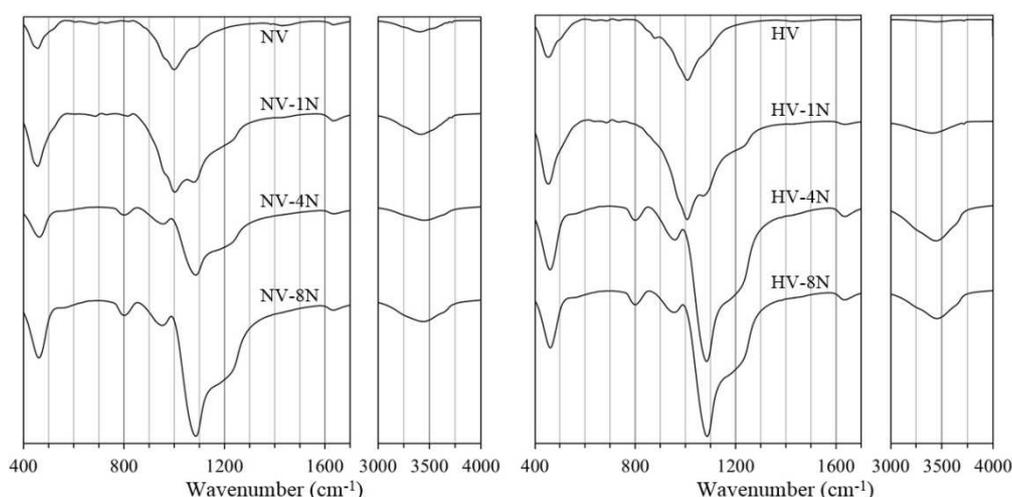


Fig. 4. FT-IR spectra of the natural and heated samples following dissolution in sulphuric acid at the indicated concentrations.

The TG/DTA curves of the natural and heated samples following dissolution in sulphuric acid were given in Fig. 5. The natural sample showed characteristic dehydration peaks of magnesium vermiculites, but at lower temperatures, the first peak at about 121°C and the second one at about 232°C , probably due to the interstratification (Boettcher, 1966; Justo et al., 1993). The mass loss values obtained from TG curve of the natural sample between $20-200^\circ$, $200-400^\circ$ and $400-1000^\circ\text{C}$ were 3.88, 0.55 and 4.90%, respectively. The destruction of vermiculite structures can also be observed by the disappearance of double dehydration peaks in DTA curves of the undissolved solids obtained by dissolving natural sample in 2 (Ehsani et al., 2014), 4 and 8 N H_2SO_4 . At the same time, the formation of hydrous amorphous silica phases can also be observed by the appearance of a broad and single low-temperature endothermic dehydration peak. The weight loss values obtained from TG curves were also in a good correlation with the experimentally determined moisture values.

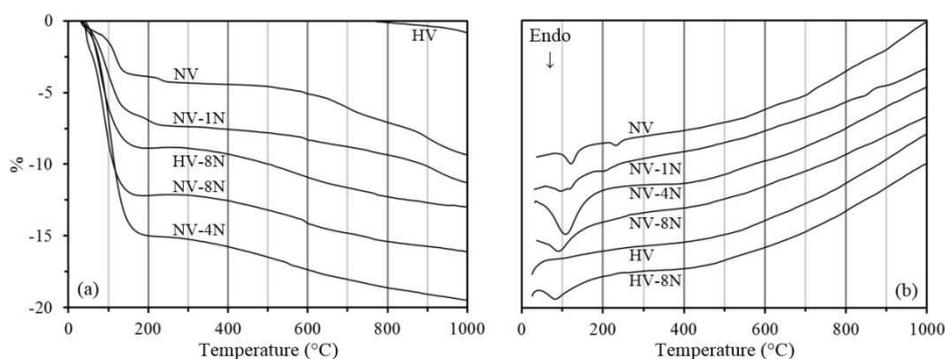


Fig. 5. TG/DTA curves of the natural and heated samples following dissolution in sulphuric acid at indicated concentrations (a: TG curves, b: DTA curves).

The magnetization curves of the heated sample and its undissolved solids obtained by dissolution in 8 N H₂SO₄ were given in Fig. 6. The maximum magnetization value of HV sample, 0.56 emu/g, was higher than the HV-8N sample, 0.13 emu/g, at a magnetic field value of 20 kOe, probably related with the Fe₂O₃ contents of the samples, which were 9.31 % for HV and 1.31 % for HV-8N. Besides, the magnetization curve of the HV-8N sample showed a very slight negative slope at higher magnetic field values, probably due to the increased SiO₂ content of this sample, which was 83.78 % (initially 44.39 % in HV). On the other hand, the magnetization curves indicated that both samples had very low coercivity values.

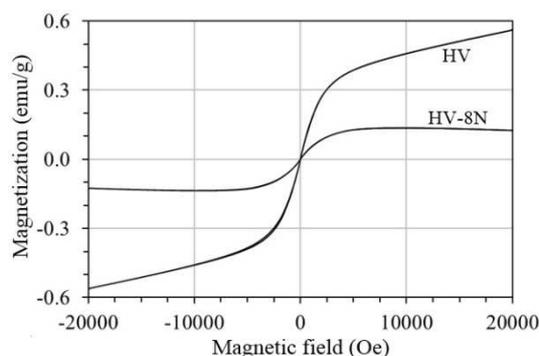


Fig. 6. Magnetization curves of the heated sample and its undissolved solids obtained by dissolution in 8 N sulphuric acid.

Conclusions

In this study, the influence of high-temperature (90 °C) sulphuric acid dissolution on the physical and chemical properties of a commercial vermiculite, in natural and heated forms, was investigated using different techniques. It was found that the dominant clay structures, namely mixed-layer mica-vermiculite and vermiculite, in the natural sample could be completely dissolved in 4 N H₂SO₄. On the other hand, as a minor constituent, mica in the natural sample resisted dissolution even if 8 N H₂SO₄ was used. Due to the dissolution of main clay structures in both samples, especially in the case of the application of 4 and 8 N acid, hydrous amorphous silica phases were formed. The maximum specific surface area values reached for the natural and the heated samples were 494.6 and 335.2 m²/g, respectively, both obtained after the dissolution in 4 N H₂SO₄. The experimental results indicated that because of the dehydrated and collapsed mica-like layer content in the heated sample resulting from the heating process applied before the dissolution experiments, the heated sample exhibited higher resistance to dissolution than the natural sample. In this study, the results of the magnetic properties of the heated sample, before and after dissolution, were also compared. Finally, high surface area and adsorptive solids can be prepared by high-temperature sulphuric acid dissolution. The preliminary tests indicated that some of the undissolved solids, especially those obtained after the dissolution of the natural sample in hot sulphuric acid could be potentially used in oil bleaching processes.

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