Expansibility of vermiculites irradiated with microwaves
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1. Introduction

When vermiculites are strongly heated at high temperature (≈ 1000 °C) during a short period of time, the water situated between layers is quickly converted into steam disrupting the structure. As a consequence, a highly porous thermal-exfoliated material is formed. This material finds use in construction products, agriculture, horticulture, and other applications (Strand and Stewart, 1983; Hindman, 1992; Bergaya et al., 2006). The thermal exfoliation occurs in a direction approximately perpendicular to the layers. This property of exfoliation is explained as due to the explosive release of interlamellar water molecules by heating, and causes the vermiculite particles to expand to twenty or thirty times their original size normal to the basal planes. Several authors (Midgley and Midgley, 1960; Couderc and Douillet, 1973; Justo et al., 1989; Marcos et al., 2009) found that the better exfoliation was achieved in the case of vermiculite–mica mixed-minerals or vermiculites containing layers in different hydration states. Justo et al. (1989) appointed that the chemical composition should also influence the exfoliation process.

Marcos et al. (2003) studied the dehydration of vermiculites in vacuum pressure. Vacuum causes dehydrated vermiculite in a similar way as does heating, although a remarkable difference between both processes induced by temperature and by vacuum, respectively, was found. The formation of the hydrated states was slower and smoother in vacuum during heating. Under vacuum, the dehydration process seemed to be limited to the monolayer water state. A fully dehydrated phase was not observed either by decreasing the pressure or by increasing the time at a fixed vacuum pressure. Therefore, vacuum inhibited the dehydration–rehydration process.

In conventional processes, the vermiculites are heated at about 1000 °C. Reaction of vermiculite with H2O2 led to exfoliation below 100 °C (LIT). In some applications, as intumescent fire barriers, it is desirable that exfoliation of vermiculite should occur at intermediate temperatures, i.e. at 200–350 °C. Some authors (Wada, 1973a,b; Langer and Marlor, 1981) modified vermiculite with urea, thiourea or dihydrogenphosphate to obtain exfoliated particles at these intermediate temperatures. The present study revealed that exposing vermiculites to microwaves exfoliated the particles at temperatures ca. 100 °C.

Microwaves are a form of electromagnetic energy with associated electric and magnetic fields (Stuchly and Stuchly, 1983; Kingman, 1999). The materials which couple with (absorb) the microwave radiation are dielectrics and contain dipoles. The basic viewpoint is that microwave irradiation induces charged particles to migrate or rotate, which results in polarization of polar particles (dipoles align and flip around since the applied field is alternating). The lag between this polarization and rapid reversals of the microwave field creates friction among molecules to generate heat (when the microwaves are applied to dielectric materials) (Galema, 1997). Easy startup and volumetric heating, due to the penetration of microwaves, improve the efficiency and reduce process times, making it an attractive source of thermal energy. Chen et al. (1984) and Harrison and Rowson (1995) conducted experiments to quantify the heating rates of pure minerals. The first authors concluded that: most silicates, carbonates and sulphates, some oxides and some sulphides were transparent to microwave radiation. However, most arsenic sulphides and sulphosalts...
emitted fumes and melted when heated strongly (Standish et al., 1991; Whittington and Milestone, 1992; Kudra et al., 1993; Abdelghani-Idrissi, 2001; Long et al., 2002).

Considering the strong interaction between water and microwaves, the aim of this work was to study the behaviour of vermiculites during microwave irradiation and to make a comparison with the behaviour at high temperature and under vacuum.

2. Experimental methods

The vermiculite samples came from Santa Olalla (Huelva, Spain), Catalão (Goiás, Brasil), Paulistana (Piauí, Brasil), Palabora (South Africa) and three from China (named CHE, CHW and CHG). They were previously described by Marcos et al. (2009) and Marcos and Rodríguez (2010).

These commercial vermiculites were present in the form of small packets of a green color with different tints, with maximum dimensions of ca. 2–3 mm in diameter and 0.5–1 mm thick. Santa Olalla formed large packets with dimensions of 1–2 cm in diameter. Vermiculites were studied as received, after elimination of other minerals by hand-picking.

The experiments with microwave were carried out with a microwave oven (SHARP R64sT) working at 2.45 GHz of frequency with 800 W of energy. The temperature seemed not to exceed 100 °C (Walkiewicz et al., 1988; Obut and Yörükoğlu, 2003). In a microwave oven, heating depends on the potency of the oven and of contents of the water, density and sample quantity. Therefore, we used different containers and sample holders (glass Petri dishes with and without glass top, porcelain crucibles with and without porcelain tops, and glass dishes for microwave heating with and without tops) and different microwave exposure times (from 10 s to 600 s).

The expansibility, \( k \) (\( k = \text{density of the raw sample/density of the expanded sample} \)), was measured by the change of the apparent density. A known volume of the sample was weighed, expanded by introducing the sample in the microwave. The apparent volume was measured by tipping the loose fragments into a measuring glass cylinder without compaction.

The X-ray diffraction patterns were taken with a Philips X’pert Pro diffractometer, at 40 mA and 45 kV (Cu-Kα radiation; \( \lambda = 1.5418 \text{ Å} \)), 20 3–70°, 20 step scans of 0.02° and a counting time of 1 s per step.

Images of the expanded vermiculites after microwaves irradiation were taken with the JEOL-6100 scanning electron microscopy (SEM) and with a Leica MZ16A binocular microscope.
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 was determined gravimetrically by heating the samples in air at 1000 °C.

3. Results and discussion

The expansion of the vermiculite particles depended on the container type, the irradiation time and the sample size. For instance, CHG in glassy Petri dishes with glassy tops was expanded by 30% after 10 s and by 100% during 20 s, but only 50% were expanded in glassy microwave dishes.

Larger particles expanded better than the smaller ones (Obut and Yörükoğlu, 2003). In the case of Santa Olalla vermiculite, 2 × 1.6 cm², 1.5 × 0.8 cm² and 1.2 × 2 cm² expanded completely within 100 s (Fig. 1). Flakes of 1–3 mm² did not expand.

The process of expansion started in the centre of the flakes, and proceeded towards the edges. The vermiculite sample absorbed microwaves through the adsorbed water which increases the temperature. The water dipoles were aligned and re-oriented with the alternating applied field. This generated internal friction, causing the vermiculite to heat up, and many water molecules were vaporized. This expanded the particles (Fig. 2). When the water steam could not escape, the water molecules kept on boiling, pressure and temperature increased until packets of vermiculite layers opened and expanded (Fig. 3). Some particles of vermiculite irradiated with microwave for a short time, and showed an uneven expansion (Fig. 4). This might be partly due to the uneven distribution of microwave energy inside the oven, and partly due to the different rates of energy absorption in different parts of the sample. Other particles assumed fan-like shapes (Fig. 5), revealing incomplete exfoliation. Therefore, the thermal equilibrium was neither established nor maintained during irradiation.

The XRD pattern of Santa Olalla (Fig. 6) corresponded to the pattern of vermiculite, although the intensity of reflections of the expanded sample was reduced, indicating loss of crystallinity and structural order. The 002 reflection was centred 2θ = 6.3° (d = 14.0 Å) but very broadened because of different hydration states. The decreasing of the intensity of the (002) reflection and the increasing intensity of the (060), (0,0,10) and (0,0,12) reflections indicated the collapse of the structure and the formation of enstatite, a phase which was obtained after calcining the sample at 1000 °C for 1 min. The XRD pattern indicated that expansion of the vermiculite particles by microwave heating was slower than under vacuum or with abrupt heating at 1000 °C. As a consequence the phase with d = 13.8 Å could not be observed.

CHE vermiculite showed also an XRD pattern (Fig. 7) with very broadened reflections of low intensity. Transformation, probably into...
mica through interstratified phases centred at 15.0 Å and 12.5 Å, was more evident than for CHG which revealed interstratified phases at 12.5–12.0 Å and a reflection at 10.0 Å (Fig. 8), indicating a similar transformation similar as by heating to 1000 °C (Marcos et al., 2009).

In the CHW sample (Fig. 9) the reflection corresponding to a dehydrated phase with $d = 10.1$ Å coexisted with an interstratified phase ($d = 12.1$ Å) and it could indicate the transformation into the mica phase, as it occurred at 1000 °C (Marcos et al., 2009).

Microwave heating vermiculite particles in a similar way as heating at 1000 °C, although the reaction was slower, microwave heating inhibited the dehydration–rehydration more strongly than dehydration in vacuum (Marcos et al., 2003). Microwave irradiation of Santa Olalla seemed to restrict dehydration to the formation of the water-bilayer state, and of the China vermiculites to the water-monolayer state. Complete dehydration was not observed, even at a longer time. In vacuum, the vermiculites did not expand, probably because the edge regions of the particles were dehydrated and closed and the external layers of the sample could dehydrate but became a barrier between the outer atmosphere and the internal regions, thus inhibiting further dehydration and expansion.
The XRD results agreed with the thermogravimetric data (Table 1). Microwave heating of the samples shifted the endothermic peaks moving towards higher temperatures by about 20 °C. The water content of the samples after microwave heating was only slightly smaller than the untreated samples. The expansibility values (K) obtained under microwave treatment during 20 s for the vermiculites from China were 7.3 (CHG), 5.4 (CHW) and 5.0 (CHE). These values indicated that these vermiculites, especially CHG yielded well expanded products as compared with the results obtained by Justo et al. (1989). CHG had the highest apparent density before and after the irradiation. Justo et al. (1989) argued that this could be due to the small size of the flakes, which would result in a more compacted product. In the present case, the China samples had the same flake size and they were treated under the same experimental conditions, so the cause must be different. On the other hand, Obut and Yörükoğlu (2003) concluded that microwave expansion was mainly related to the state of interlayer water, and other factors seemed to be of little importance. If a direct correlation between expansion and water content existed the vermiculite with a larger water content such as Santa Olalla vermiculite should better expand. However, this was not observed, neither by microwave irradiation nor by abruptly heating or heated to high temperatures (Marcos et al., 2009). On the other hand, the calculated Pearson correlation for the Chinese samples was −0.73564, 25% lower than obtained by Obut and Yörükoğlu (2003) and indicated that the exfoliation was mainly related to the water loss. This effect would be related to the composition and distribution of the cations. It seemed that Fe²⁺ ions would facilitate the fixing of the K⁺ ions (Marcos and Rodríguez, 2010), which was responsible of a larger exfoliation after heating at elevated temperatures (Marcos et al., 2009). In fact, CHW and CHE samples with a lower content of K⁺ than the CHG (Table 2) gave lower exfoliation values after microwave heating.

### 4. Conclusions

Microwave irradiation of vermiculite samples caused structural changes such as loss of crystallinity and disorder, as revealed in the XRD patterns. Microwave heating did not generally lead to complete dehydration as in vacuum. The outflow of water molecules escaping from the particles was significantly smaller than during heating to 1000 °C, with the advantage of saving energy and time. The expanded material was produced at low temperature (ca. 100 °C), important in some applications, such as intumescent fire barriers. The materials should also be found in application of adsorption as adsorbent such as oil and aromatics (benzene, toluene, chlorobenzene, nitrobenzene, etc.) or heavy metal ions from aqueous solutions, without the need of hydrophobic modification. Reasons to push this possible application were good expansibility, low loss of water (<2%) and negligible absorption of water at the external surfaces (Reichenbach and Beyer, 1993). In addition high availability, easy handling and low-cost are advantageous.

### Acknowledgements

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### References


### Table 1

Water contents (mass %) derived from TG.

<table>
<thead>
<tr>
<th>Water content (%)</th>
<th>Conventional*</th>
<th>Microwave</th>
<th>1000 °C for 1 min</th>
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<tr>
<td>Santa Olalla</td>
<td>25.6</td>
<td>24.9</td>
<td>4.9</td>
</tr>
<tr>
<td>CHE</td>
<td>13.1</td>
<td>12.4</td>
<td>6.6</td>
</tr>
<tr>
<td>CHG</td>
<td>12.3</td>
<td>10.4</td>
<td>7.0</td>
</tr>
<tr>
<td>CHW</td>
<td>12.0</td>
<td>10.7</td>
<td>6.0</td>
</tr>
</tbody>
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* Taken from Marcos et al. (2009).

### Table 2

Cation content of the vermiculites (Marcos et al., 2009).

<table>
<thead>
<tr>
<th></th>
<th>CHE</th>
<th>CHG</th>
<th>CHW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe²⁺</td>
<td>0.083</td>
<td>0.109</td>
<td>0.119</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>1.492</td>
<td>1.572</td>
<td>1.301</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.000</td>
<td>1.047</td>
<td>0.000</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.903</td>
<td>1.205</td>
<td>1.175</td>
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