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Inorganic modification of Palabora vermiculite

By

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Inorganic modification of Palabora vermiculite

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ABSTRACT

Conventional processes for the manufacture of exfoliated natural vermiculite employ temperatures exceeding 800 °C and the onset temperature is above 450 °C. In many applications, notably fire retardants, it is desirable that exfoliation of vermiculite should occur at temperatures in the range of 200 °C to 350 °C.

For this purpose, South African Palabora vermiculite was modified by ion exchange with ammonium and selected alkali metal and alkaline earth metal ions. These experiments were performed at room temperature using an orbital shaker for 15 days. Another set of experiments was performed by immersing vermiculite in saturated sodium chloride solution for periods up to six months. At the end of every month, sodium-exchanged vermiculite samples were taken for analysis.

The thermal expansion and degradation of modified vermiculites were studied using thermo-mechanical analysis (TMA) and thermogravimetric analysis (TGA) respectively. Interlayer composition was studied using cation exchange with ammonium acetate. The leached cations were quantitatively determined using inductively coupled plasma optical emission spectroscopy (ICP-OES). Scanning electron microscopy (SEM) was applied to study the

samples' morphology. X-ray diffraction (XRD), infrared (FT-IR) and Raman spectroscopy confirmed that the basic vermiculite crystal structure was left unchanged during inorganic modification in both sets of experiments.

It was confirmed that the blowing agent in the neat vermiculite was the interlayer water. In the exchanged vermiculite with ammonium ions, it was found that ammonia and water were the blowing agents and they were simultaneously released during thermal degradation. However, ammonium-vermiculite did not show a relatively better thermal expansion ratio, despite the presence of both ammonia and water in the interlayer.

In the increasing ionic potential series: Na-vermiculite, Ba-vermiculite, Ca-vermiculite and Mg-vermiculite, it was found that the onset expansion temperature also increased dramatically. Exchange with relatively low ionic potential species, namely sodium, potassium and ammonium, lowered the exfoliation onset temperature of vermiculite to below 300 °C.

Keywords: Vermiculite; Ion exchange; Exfoliation; Interstratification; Thermal analysis.

Beneficiação inorganica da vermiculita de Palabora

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SUMÁRIO (PORTUGUESE)

Processos convencionais de produção da vermiculita natural exfoliada empregam temperaturas que excedem 800 °C e a temperatura inicial de expansão está acima de 450 °C. Em muitas aplicações, particularmente em áreas onde se deseja extinção de fogo, é desejável que a exfoliação da vermiculite ocorra na região entre 200 °C e 350 °C. Assim, a vermiculita proveniente de Palabora, África do Sul, foi quimicamente modificada com cloretos de amónio, de metais alcalinos e de metais alcalino-terrosos previamente seleccionados. As experiências foram realizadas à temperatura ambiente sob agitação constante por 15 dias. Outro desenho experimental foi executado por imersão da vermiculita em solução saturada de cloreto de sódio durante 6 meses. Mensalmente foram retiradas alíquotas de vermiculita modificada para a devida análise.

A expansão e degradação térmicas das amostras da vermiculita modificada foram estudadas usando análises termo-mecânica (TMA) e termogravimétrica (TGA). O método de extracção de catiões usando acetato de amónio foi aplicado em todas as amostras e os extractos foram analisados usando plasma indutivamente acoplado ligado ao espectroscópio óptico de emissão (ICP-OES). A morfologia das amostras foi comparada usando

microscopia electronica (SEM). Difracción por raios-X (XRD), espectroscopia de infravermelho (FT-IR) e Raman, confirmaram a manutenção da estrutura cristalina da vermiculita durante a reacção de troca iónica em ambas experiências.

Na vermiculita nativa foi confirmada a libertação de água antes e durante a exfoliação. Na amostra de vermiculita-NH₄ foi detectado amoníaco, para além da água, e ambos foram libertos simultaneamente durante a degradação térmica. Entretanto, vermiculita-NH₄ não exhibe uma relativamente melhor expansão térmica apesar da presença de água e amónia entre as camadas da vermiculita.

Na seguinte série crescente the potencial iónico: vermiculita-Na, vermiculita-Ba, vermiculita-Ca e vermiculita-Mg, a temperatura inicial de exfoliação também é proporcionalmente crescente. Trocas catiónicas da vermiculita natural pelos seguintes iões de baixo potencial iónico: sódio, potássio e amónio resultaram na redução da temperatura inicial de exfoliação para temperaturas abaixo de 300 °C.

Palavras-chave: Vermiculita; Troca iónica; Exfoliação; Interstratificação; Análise térmica.

DEDICATION

To my wife Inês and daughters Keila, Flora and Inês. I highly appreciated their love, motivation and unconditional support, especially during those long periods of absence.

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And, finally, I am grateful to my parents for the opportunities they have provided for my personal growth.

DECLARATION

I, the undersigned, declare that the dissertation, which I hereby submit for the degree MSc at the University of Pretoria, is my own work and has not previously been submitted by me for the degree at this or any other tertiary institution.

.....

Hermínio Francisco Muiambo

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GLOSSARY

CEC	Cation exchange capacity
cmol	centimol
DSC	Differential scanning calorimeter
DTG	Derivative thermogravimetry
FT-IR	Fourier transform infrared spectroscopy
ICP-OES	Inductively coupled plasma optical emission spectrometer
IR	Infrared spectrometer
IUPAC	International Union of Pure and Applied Chemistry
K _{sp}	Constant of solubility product
LOI	Loss on ignition
pH	Potential hydrogen
RF	Radiofrequency
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis/analyser
TMA	Thermomechanical analysis/analyser
XRD	X-ray diffraction
XRF	X-ray fluorescence
WLHS	Water layer hydration state
0-WLHS	Zero water layers hydration state
1-WLHS	One water layer hydration state
2-WLHS	Two water layers hydration state

CHAPTER 1 INTRODUCTION

Clay minerals are attracting more and more interest in nanoscience and nanotechnology due to the huge effect that they can have on materials at low dosage levels.

Applications include nanocomposites, catalysis, adsorbents, sensors, nuclear waste storage, antibacterials, pharmaceuticals, pesticide carriers and others (Grim, 1968; Liu *et al.*, 2007; Bergaya *et al.*, 2006; Annabi-Bergaya *et al.*, 2008).

The chemical stability and mineralogical behaviour of clay minerals in saline solutions has attracted interest owing to their ability to absorb and immobilise toxic ions derived from radioactive and chemical waste. Most studies have focused on the mineralogical and chemical transformation of bentonite in saline water at elevated temperatures (Herbert and Moog, 1999; Herbert *et al.*, 2004; Suzuki *et al.*, 2008).

Due to the high cation exchange capacity (CEC) and surface area of vermiculites, research has been focused on the improvement of its surface area and porosity, the replaceability of the interlayer cations as well as its hydration/dehydration properties (Barshad 1950; Fripiat *et al.*, 1960; Saehr *et al.*, 1992; Beyer and Reichenbach, 1998; de Haro *et al.*, 2005).

According to some authors (Justo *et al.*, 1993; Marcos *et al.*, 2009), vermiculite-mica interstratification materials show larger expansion at relatively lower temperatures and the thermal effects are also observed at these temperatures. In addition, this modified and interstratified vermiculite is amenable to producing a durable exfoliated material (Frank and Edmond, 2001). In fire barrier applications, is desirable for exfoliation of vermiculite to occur at temperatures in the range of 200 °C to 350 °C.

1.1 Background

According to many authors (Grim, 1968; Anthony *et al.*, 2004b; Hindman, 2006; Bergaya *et al.*, 2006), vermiculite was first mentioned by Thomas Webb in 1824 while studying a mineral from Massachusetts (United States of America). Thomas Webb described it as a variety of talc mineral that during thermal expansion looks like small worms having the *vermicular* motion, hence its name ‘vermiculite’ (from Latin *vermiculari*, to breed worms).

Vermiculite’s remarkable exfoliation when subjected to high temperatures attracted the attention of researchers. Available relevant literature on vermiculite dates back to the 1930s. Gruner (1934) and, later on, Hendricks and Jefferson (1938) were the first to clarify the vermiculite and hydrobiotite crystal structures.

Early research on vermiculite ion exchange was done by Barshad (1950; 1954a; 1954b). Lopez-Gonzalez and Cano-Ruiz (1957) and Raman and Jackson (1963) focused on the surface morphology of both neat vermiculite and exchanged forms following exposure to alkaline salts and after thermal treatment. Recently, da Fonseca *et al.* (2005) concluded that vermiculite exhibits good adsorption capacity for divalent heavy metal ions from aqueous solutions.

The application of clay minerals in oil production, petroleum engineering and catalysis is intrinsically related to their swelling behaviour (Bougeard and Smirnov, 2007). The swelling of vermiculite solutions is the result of the insertion of relatively large particles into the interlayer space or solvation of the interlayer cation due to lack of balance of attractive and repulsive forces between adjacent 2:1 layers (Newman, 1987; de Haro *et al.* 2005).

Previous investigations dealt with the preparation of free-settling dispersions and swollen solutions of vermiculite by impregnating it with a variety of lithium salts (Ou and Yang, 1987; Ou, 1992) and found an increase on solution swelling from two to eight times in volume.

Chemical modification of vermiculite has also been done by treating it with organic cations. The majority of studies related to the intercalation of vermiculite were carried out using heat (higher than room temperature), apart from other mechanical stratagems. Alkylammonium vermiculite complexes were prepared at 70 °C in an oven (Serratosa *et al.*, 1970); at 50 °C with a shaker (Abate *et al.*, 2006); and at 70 °C in a centrifuge and dried at 40 °C (Martynková *et al.*, 2007). Zhu *et al.* (2008) stirred the suspensions at 50 °C and dried them at 80 °C.

Nevertheless, da Fonseca *et al.* (2005 and 2006) had attempted cation exchange and intercalation at room temperature. Actually, da Fonseca *et al.* (2005 and 2006) exchanged vermiculite with heavy metals at 25 ± 1 °C and intercalated cyclic aliphatic amines as well as aromatic heterocyclic amines.

Thomas and Bohor (1969), Couderc and Douillet (1973) and Justo (1989), in their studies on ion exchanged vermiculites, noticed that Mg-vermiculite retains coordinated water more powerfully at comparable elevated temperatures than other vermiculites.

On the other hand, Reichenbach and Beyer (1994) concluded that some ion exchanged vermiculite, without well-defined water layer hydration states (WLHS), are less thermally stable than Mg-vermiculite.

The Palabora mine in the Limpopo province of South Africa is a major source of commercial vermiculite. The exfoliated vermiculite is of industrial interest because it is incombustible, lightweight and shows excellent absorption and thermal insulation properties (Wada, 1973b, Schoeman, 1989; Tomanec *et al.*, 1997; Obut and Girgin, 2002; Bergaya *et al.*, 2006).

In this interstratified vermiculite from Palabora, the individual flakes are made up of elementary layers of two types: vermiculite and biotite (MacEwan *et al.* 1961, Gast and Klobe, 1971; Newman, 1987). Unlike the potassium ions in biotite, the hydrated interlayer ions (usually magnesium ions) in vermiculite are easily exchanged (Newman, 1987). Justo (1989), Justo *et al.* (1993), Ou and

Bablouzian (1994) and Marcos *et al.* (2009) have shown that, compared with pure vermiculite, vermiculite-mica interstratified materials feature higher expansion ratios, with the thermal exfoliation also commencing at lower temperatures.

In some applications, notably intumescent fire barriers, it is desirable that the exfoliation of vermiculite should occur at intermediate temperatures, i.e. in the range 200 °C to 350 °C. Flame-retardant compositions have also been proposed that rely on vermiculite expansion properties (Wada, 1973a). However, vermiculite expansion occurs at temperatures well above the melting or decomposition temperatures of common polymers.

1.2 Aims and objectives

It was the aim of the present study to lower the expansion onset temperature of Palabora vermiculite to temperatures in the range of 200 °C to 350 °C.

Since the surface morphology and the properties of vermiculites are closely related to the nature of the interlayer cation (Pérez-Maqueda *et al.*, 2004), ion exchange of original interlayer cations was performed, through room-temperature treatment of Palabora vermiculite.

The first approach consisted of long-term exposure of Palabora vermiculite to saturated brine (NaCl) at room temperature.

Ion exchange was also carried out using chloride solutions of ammonium (NH₄Cl), sodium (NaCl), potassium (KCl), magnesium (MgCl₂), calcium (CaCl₂) and barium (BaCl₂).

1.3 Dissertation outline

This dissertation is structured in six chapters.

The first chapter describes the history of vermiculite discovery and the first attempts to its characterisation as well as giving a brief summary of the relevant work done so far for the beneficiation of vermiculite. The aims and objectives of current research are also described.

Chapter 2 presents an extensive literature review. In Section 2.1, attention is briefly paid to the definition of clay minerals (due to controversy on this topic) and to phyllosilicates, namely dioctahedral and trioctahedral. In Section 2.2, a brief discussion about the structure and composition of vermiculite is provided. The geological origin, composition and physical properties of Palabora vermiculite are described in the following sections. Previous work aimed at modifying the properties of vermiculite is also discussed in this chapter, with the main focus on ion exchange and exfoliation phenomena. Special attention is paid to a discussion of interstratifications, as well as the potential applications of vermiculite. This chapter closes with a description of each characterisation technique applied in this study.

Chapter 3 reports the experimental procedures followed and briefly describes the equipment used in each analytical technique.

Chapter 4 presents details of all the experimental results achieved in this study and discusses these results.

The conclusions are summarised in Chapter 5 and the references are given in Chapter 6.

CHAPTER 2 LITERATURE SURVEY

2.1 Clay minerals

According to the charge of the interlayer cation, clays and clay minerals are classified into two broad classes: cationic clays and anionic clays. While the cationic clays are widespread in nature, the anionic clays or mixed metal hydroxides are rarely found but are relatively simple and inexpensive to synthesise (Reichle, 1986; Vaccari, 1998).

Clay minerals are defined as natural or synthetic phyllosilicate minerals and minerals that impart plasticity to clay and that harden upon drying or firing (Bergaya *et al.*, 2006).

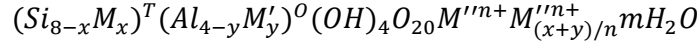
According to Bergaya *et al.* (2006), the properties of clay minerals are usually associated with those of smectites and are characterised by:

- a layered structure with one dimension in the nanometre range
- anisotropy of the layers
- different types of surface (basal, edge and interlayer)
- cation and anion exchange capacity
- relatively easy chemical, physical or thermal modification
- interlayer swelling in appropriate solvents
- plasticity.

The structures of phyllosilicates are all based on tetrahedral (T, with four sites) and octahedral (O, with six sites) sheets that may condense anisotropically in a proportion of either 1:1 (TO) or 2:1 (TOT) (Newman, 1987; Vaccari, 1998; Bergaya *et al.*, 2006).

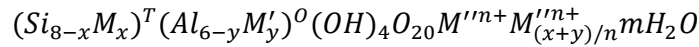
The unit cell of a 1:1 phyllosilicate layer structure is characterised by four tetrahedral sites and six octahedral sites, while a 2:1 layer unit cell is composed of eight tetrahedral sites and six octahedral sites. The oxygen atoms

are responsible for connecting the sheets (Newman, 1987; Frank, 2001; Bergaya *et al.*, 2006; da Fonseca *et al.*, 2006).



Scheme I: General formula of dioctahedral clay minerals

In dioctahedral clay minerals (Scheme I) only four of the six octahedral sites are occupied, while in trioctahedral clay minerals all the sites – either the octahedral (six) or the tetrahedral (four) sites – are occupied, as shown in Scheme II (Newman, 1987; Vaccari, 1998; Bergaya *et al.*, 2006).



Scheme II: General formula of trioctahedral clay minerals

In clay minerals the thickness of the 1:1 layer is about 0.7 nm and that of the 2:1 layer is about 1 nm (Bergaya *et al.*, 2006).

2.2 Composition of trioctahedral vermiculite

Natural vermiculite consists mainly of macroscopic and microscopic types. Macroscopic vermiculite (large plate-like morphology crystal) is trioctahedral and has a relatively narrow range of CEC, whereas microscopic or clay vermiculite may be either trioctahedral or dioctahedral (Basset, 1963; Brindley and Brown, 1980; Newman, 1987).

Vermiculite is a magnesium, iron, aluminium, silicate, hydroxide hydrate mineral. Structural water occurs between the silicate layers, depending on the interlayer cation, and non-structural water also occurs in an amount depending on the porosity and relative humidity (Brindley and Brown, 1980; Newman, 1987; Harben and Roberts, 1990; Frank, 2001; da Fonseca *et al.*, 2006).

In vermiculites, the majority of the octahedral cations are trivalent, such as Al^{3+} or Fe^{3+} . The layers carry a net negative charge owing to isomorphous

substitutions of Si in the tetrahedral sites by trivalent ions such as Al^{3+} or Fe^{3+} . However, this is partially compensated for substitution of Mg^{2+} in the octahedral sites by trivalent ions, e.g. Fe^{3+} . The excess sheet charge is neutralised by alkali metal or alkaline earth interlayer cations, e.g. Mg^{2+} , present in the interlayer space and lying in plane midway between adjacent 2:1 layers. These cations are hydrated and can be exchanged (Newman, 1987; Brindley and Brown, 1980; Pérez-Maqueda *et al.* 2003; Bergaya *et al.*, 2006).

According to Farmer (1974), the surface charge in vermiculite is concentrated on oxygens of Al-O-Si linkages and adjacent oxygens of Si-O-Si connection.

Vermiculite shows similarities in its crystalline structure and expansibility with smectites (Grim, 1968; Basset, 1963; de Haro *et al.*, 2005; Tjong, 2006). However, the electrostatic charge of the vermiculite layer is larger and more heterogenic than that of smectites due to the variations in charge density from layer to layer or within the individual layers (Grim, 1968; Tjong, 2006; de Haro *et al.*, 2005; Xu *et al.*, 2005).

Palabora vermiculite, like other commercial types, also shows considerable variability in both composition and CEC. This is attributed to differences in the composition of the original parent mica and the degree of progress in the chemical changes induced by weathering (Basset, 1963; Frank, 2001).

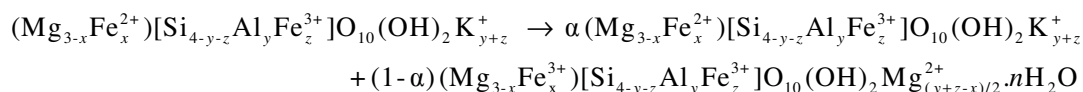
2.3 Localisation and geological origin of Palabora vermiculite

The vermiculite used in this work is from Phalaborwa, Limpopo Province, South Africa.

The Palabora mine is a major source of such commercial vermiculite. Actually, Palabora vermiculite is not pure vermiculite but rather a mixed-layer vermiculite-mica (Schwellnus, 1938; Basset, 1963; Schoeman, 1989). In fact, commerce vermiculite is a generic name for minerals with characteristics

similar to pure vermiculite (Justo, 1989; de Haro *et al.*, 2005). Schoeman (1989) proposed the name hydrophlogopite for the mineral considered presently.

Palabora vermiculite is a product of the hydration of phlogopite/biotite under the influence of percolating meteoric water at the weathering surface. During the vermiculization process there was progressive leaching of potassium ions, an increase in the total water content, a change in colour and a simultaneous loss in elasticity and transparency on the part of the mica (Basset, 1963; Schoeman, 1989).



Scheme III: Simplified representation of the partial conversion of biotite into vermiculite (Newman, 1987).

Scheme III illustrates the partial transformation of biotite to vermiculite in a decidedly simplified manner. It is assumed that Fe^{3+} is present in the tetrahedral sheets and that the Fe^{2+} in the octahedral sheets in vermiculite is completely oxidised during the vermiculisation process.

The vermiculization process entails the replacement of the interlayer potassium ions by hydrated cations (usually magnesium and, less frequently, calcium ions) and the oxidation of the octahedral Fe^{2+} ions (Newman, 1987). Thus, the net negative charge is lower than that of the parental biotite and usually falls in the range 0.6 to 0.9 per $\text{O}_{10}(\text{OH})_2$ unit. The decreased charge density facilitates the stripping of K^+ ions and their replacement by (most commonly) hydrated Mg^{2+} ions (Brindley *et al.*, 1983; Moore and Reynolds, 1989).

The co-intercalation of water increases the distance between the 2:1 layers. The hydration energy of the cation (i.e. its ionic potential, which is a function of charge density and ionic radius) attracts water. A monovalent cation has lower ionic potential than an equivalent-sized divalent cation

(discussed in detail in Section 2.5). The interlayer distance is therefore dependent on the balance of forces necessary to dehydrate the cation and the forces of attraction between the layers and the cation (Brindley and Brown, 1980; Brindley *et al.*, 1983).

During the transformation from mica to vermiculite, numerous intermediate mixed-layer phases with various compositions and ordering are formed. In general, a more ordered structure results at a higher layer charge and also when the humidity is high enough to give stable water layer hydration states (WLHS) (Brindley *et al.* 1983).

The Palabora Proterozoic igneous complex resulted from an alkaline intrusive activity. The Palabora mine is a zoned deposit with ultramafic rocks (pyroxenite) intruded by alkalic rocks, most of which are syenitic in composition (Frank, 2001).

Palabora vermiculite mining and concentration were started during 1946 by Dr Hans Merensky (Palabora Mining Company, 1976; Schoeman, 1989). At the Palabora complex there are three separate open pits (see Fig. 1). The vermiculite open-pit mine (represented by number 2 in Fig. 1) is operated by the Palabora Mining Company and since 1990 has become the world's largest producer (Evans, 1987, 1993; Hindman, 2006). This vermiculite is mined from a coarse-grained zoned ultramafic body consisting of phlogopite-serpentine rock enveloped by phlogopite-diopside rock (Palabora Mining Company, 1976; Evans, 1993).

The crude vermiculite is transported by rail from the mine in Phalaborwa to the port of Richards Bay on the Indian Ocean in KwaZulu-Natal province, South Africa. From this port it is shipped in bulk to a diversity of destinations and is also stored in the Netherlands and United Kingdom (Eaves, 2006).

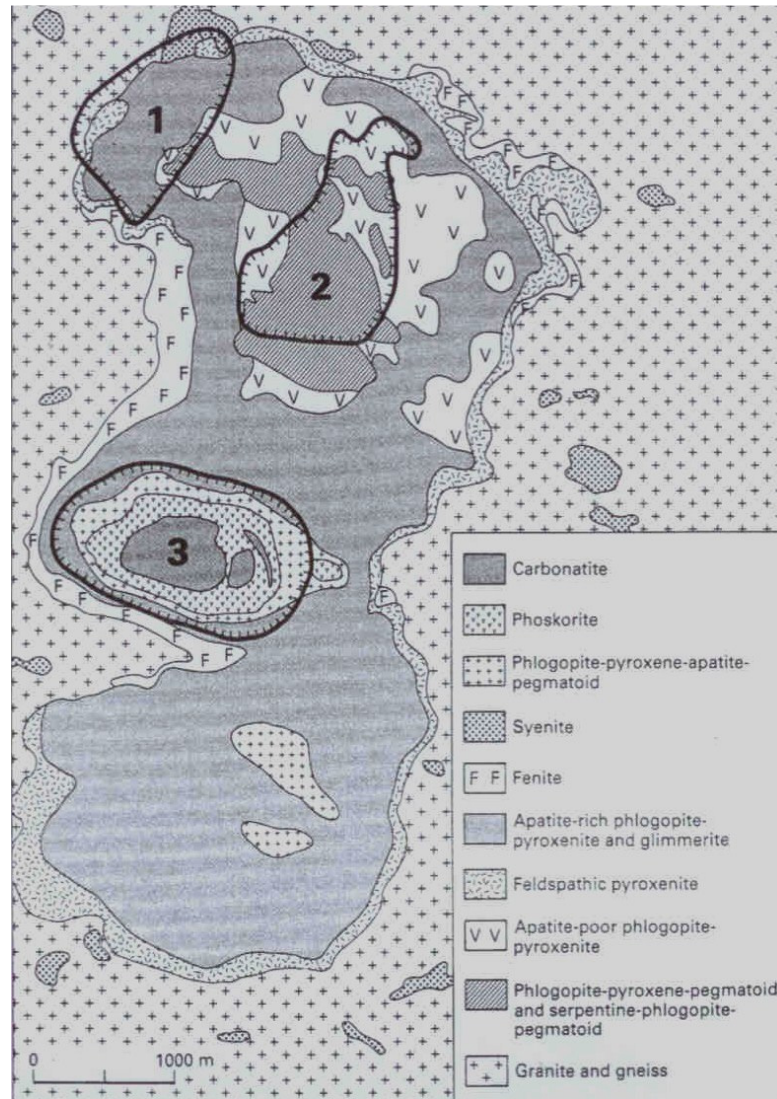


Figure 1. Simplified geological map of the Palabora igneous complex (Evans, 1993). (1) Open pit which produces phosphate; (2) Vermiculite open pit; (3) Open pit which produces basically copper and magnetite

Environmentally, Palabora vermiculite is described as essentially free of asbestiform fibres and crystalline silica (Evans, 1993; Symons, 1999; Eaves, 2006) and, by the same token, as a potential raw material for application in environmentally friendly technologies.

2.4 Physical properties of Palabora vermiculite

Like other clay minerals, vermiculite can exhibit different properties according to its composition which is affected by the composition of the parent mica, changes during weathering and ion exchange (Basset, 1963; Frank and Edmond, 2001; Hindman, 2006).

Table 1. Physical properties of Palabora vermiculite (Symons, 1999; Anthony *et al.*, 2004a)

Property	Characteristics
Melting point	1 315 °C
Sinter temperature	1 260 °C
Thermal conductivity	0.062–0.065 w/m°C
Colour	brownish, golden yellow
Hardness	1.5– .5 (Mohs scale)
Density	2.2–2.8 (g/cm ³)
Specific heat	0.2 J/(g ·K)
Bulk density	50–130 g/L
Cleavage	d ₀₀₁ , perfect, typically relict
Tenacity	brittle to flexible

Palabora vermiculite's main properties are summarised in Table 1. It shows properties close to those of the parental biotite: odourless, non-corrosive, non-combustible, non-allergenic and harmless if swallowed (Symons, 1999).

2.5 Ion exchange in vermiculite

Bergaya *et al.* (2006) have identified and discussed in detail different ways of modifying 2:1 clay minerals, as follows:

- (i) Adsorption

- (ii) Ion exchange with inorganic cations and cationic complexes
- (iii) Ion exchange with organic cations
- (iv) Binding of inorganic and organic cations
- (v) Grafting of organic compounds
- (vi) Reaction with acids
- (vii) Pillaring by different types of poly(hydroxo metal) cations
- (viii) Interlamellar or interparticle and interparticle polymerisation
- (ix) Dehydroxilation and calcination
- (x) Delamination and reaggregation.

Ion exchange generally consists of the stoichiometrical and reversible replacement or swapping of ions between two electrolytes in different media (Grim, 1968, Harland, 1994). Many authors (Walker, 1959; Grim, 1968; Harland, 1994; Tan, 1996) also describe ion exchange, in clay minerals, as a diffusion process of substitution of the ions held electrostatically on the surface of the ion exchanger (solid phase) and a solution phase.

According to Grim (1968) and Harland (1994), the ion exchangeability of phyllosilicates is frequently accompanied by a change in the d-spacing and is basically made by:

- *Replacement in the interlayer space:* The exchangeable cations are mostly located on cleavage surfaces and in vermiculite this region contributes approximately 80% of the total CEC. This charge results from isomorphous substitutions within the lattice structure.
- *Replacement on the edges of the platelets owing to the breaking of chemical bonds:* The availability of these exchange sites is seriously affected by the particle size, lattice distortions and crystallinity. Broken bands are responsible for up to 20% of total CEC in vermiculite.

- *Exchange of hydrogens of exposed hydroxyl groups:* Obviously, the availability of these sites during the exchange reaction is highly influenced by the pH of the medium and is of particular significance for layered minerals like vermiculite.

The ion exchange phenomenon is quantitatively measured by the CEC, which is defined as the quantity of cations available to be exchanged at a certain pH. It is traditionally expressed in (meq)/100 g of calcinated clay, which is equivalent to cmol(+)/kg, units recommended by IUPAC (Bergaya *et al.*, 2006).

Table 2. CEC of some clay minerals (Bergaya *et al.*, 2006)

Clay	CEC (meq/100g)
Vermiculite	130–210
Montmorillonite	70– 20
Illite	10–40
Kaolinite	3–15

The CEC values of selected clay minerals are presented in Table 2. It appears that the broad intervals given are due to the diverse factors that may influence the clay properties. The main aspects that affect CEC measurements are: pH, temperature, ionic strength, nature of the index cation, nature of interlayer cation(s), particle morphology and size and surface area (Raman and Jackson, 1963; Grim, 1968; Stone and Wild, 1978; Harland, 1994; Bergaya *et al.*, 2006; Peralta, 2009).

Due to its wide use in the literature, in this work the term ‘ion exchange’ is used to designate the exchange of interlayer inorganic ions adsorbed in vermiculite (Ca^{2+} and Mg^{2+}) by the following cations: ammonium (NH_4^+), alkali metals (Na^+ and K^+) and alkaline earth metals (Mg^{2+} , Ca^{2+} and Ba^{2+}). Some of their relevant properties are summarised in Table 3.

Table 3. Dehydrated and hydrated ionic radii and respective calculated ionic potentials (Grim, 1968)

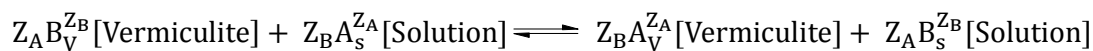
Ion	Dehydrated ionic radius (nm)	Hydrated ionic radius (nm)	Ionic potential (z/r)
NH_4^+	0.143	0.537	7.0
K^+	0.133	0.380	7.5
Na^+	0.098	0.560	10.2
Mg^{2+}	0.078	1.080	25.6
Ca^{2+}	0.106	0.960	18.9
Ba^{2+}	0.143	0.880	14.0

The ‘ionic potential’ is defined as the ratio of the ion’s electrical charge to its radius. It gives an idea of the strength of the ionic bond that can be formed by the cation and the extent of hydration. Many authors (Wild and Keay, 1964; Gier and Johns, 2000; Badreddine *et al.*, 2002a; Ferrage *et al.*, 2005; Vidal and Dubacq, 2009) have observed, in their work with clay minerals, that cations with high ionic potential possess high selectivity coefficients. As a result, they are able to create a richer interlayer hydration and consequent better enlargement of the interlayer space.

Insightful was the work done by Thomas and Bohor (1969) in their study of the surface area of ion exchanged vermiculite. They stated that “Mg-vermiculite would retain coordinated water more tenaciously at comparable elevated temperatures than would the other vermiculites studied.” According to them, this is due to three combined effects: (1) high ionic potential; (2) a stronger polarising effect; and (3) high covalent character. These results were later confirmed and augmented by Couderc and Douillet (1973), Stone and Wild (1978) and Justo (1989).

2.6 Kinetics and thermodynamics of ion exchange in vermiculite

The ion exchange reaction in vermiculite can be systematically represented by Scheme IV (Barrer and Klinowski, 1977; Inoue, 1984; Harland, 1994).



Scheme IV: Ion-exchange reaction involving vermiculite and another electrolyte

By applying mass action law to the exchange reaction (Scheme IV) between vermiculite interlayer cations $B_V^{Z_B}$ and a solution containing $A_S^{Z_A}$ cations, the equilibrium constant (K) can be determined by Scheme V (Barrer and Klinowski, 1977; Inoue, 1984):

$$K = \frac{A_V^{Z_B} (m_S^B)^{Z_A} f_A^{Z_B} \gamma_B^{Z_A}}{B_V^{Z_A} (m_S^A)^{Z_B} f_B^{Z_A} \gamma_A^{Z_B}}$$

Scheme V: Ion exchange equilibrium constant in vermiculite

Where A_V and B_V , and Z_A and Z_B are the equivalent fractions and respective charges of ions A and B in vermiculite; m_S^B , m_S^A represent the molalities in the solution; and f_A, f_B , γ_A and γ_B are the activity coefficients in vermiculite and in solution, respectively.

The standard free energy change (ΔG°) for the reaction demonstrated by Scheme VI can be determined by the expression:

$$\Delta G^\circ = -\frac{RT}{Z_A Z_B} \ln K$$

Scheme VI: ΔG° of the ion exchange reaction on vermiculite

Where R is the universal gas constant and T is the absolute temperature.

On the other hand, the standard enthalpy change (ΔH°) can be estimated by the Van't Hoff equation (Scheme VII):

$$\Delta H^\circ = -\frac{R}{Z_A Z_B} \cdot \frac{\partial(\ln K)}{\partial(1/T)}$$

Scheme VII: Van't Hoff equation for determination of ΔH°

And the standard entropy change (ΔS°) can be calculated from the following relationship (Scheme VIII):

$$\Delta S^\circ = \frac{1}{T}(\Delta H^\circ - \Delta G^\circ)$$

Scheme VIII: ΔS° that accompanies the ion exchange on vermiculite

The standard free energies (ΔG°) determined by Wild and Keay (1964) and Inoue (1984) indicate the following affinity of alkali and alkaline metal ions to vermiculite: $\text{Na}^+ < \text{Ba}^{2+} \sim \text{Ca}^{2+} < \text{Mg}^{2+} < \text{K}^+$.

According to Wild and Keay (1964) and Inoue (1984), vermiculite selectivity, in the above series, is determined mostly by the entropy increase rather than the enthalpy change since both enthalpy and entropy are positive during ion exchange. For instance, Wild and Keay (1964) found that vermiculite's preference for divalent cations is due mainly to an increase in the (configurational) entropy during the replacement of monovalent cations by corresponding half-divalent cations.

2.7 Exfoliation of vermiculite

Commercial vermiculite features the desirable property that it expands by more than eight times in volume when heated rapidly to elevated temperatures (Walker, 1961; Wada, 1973a; Wada, 1973b; Justo, 1989; Friedman *et al.*, 1994; Tomanec *et al.*, 1997; Hindman, 2006).

During exfoliation it is desirable to preserve the relevant properties for vermiculite applications. Besides its light weight, sound absorption, heat insulation and attractive appearance, properties such as its ion exchangeability, humidity control, high water-holding capacity and elimination of odours are advantageous and should be conserved.

Exfoliation of vermiculite can be achieved by means of various processes. The conventional processes for the manufacture of exfoliated vermiculite employ temperatures exceeding 800 °C. The procedure most commonly used is thermal exfoliation. This occurs as a sheet exfoliation process (i.e. normal to the basal cleavage) which is driven by an explosive release of interlayer water as steam (Baumeister and Hahn, 1976; Justo, 1989; Obut and Girgin, 2002; Pérez-Maqueda *et al.*, 2003; Bergaya *et al.*, 2006). The interlayer water is said to escape easily and explosively between the layers (pushing them apart), favouring the degree of exfoliation when the particle size is relatively small (Bergaya *et al.*, 2006).

For the application of vermiculite in intumescent fire barriers, exfoliation of vermiculite has been made to occur at relatively lower temperatures than the usual by impregnating it with a compound of urea and thiourea consisting chemical group or ammonium dihydrogen phosphate. The resulting composition is heated at temperatures (160 °C – 300 °C) not lower than the decomposition point of the urea or thiourea compound (Wada, 1973a; Wada, 1973b).

Langer and Marlor (1981) also describe the exfoliation of vermiculite via the addition of inorganic ammonium salts, such as ammonium dihydrogen phosphate, ammonium hydroxide and ammonium carbonate, as well as urea. When this inorganically treated vermiculite is heated to 400 °C, it expands by more than 200%.

Exfoliation of vermiculite also occurs by sudden decomposition on heating to 100 °C after pre-treatment and the penetration of large quantities of H₂O₂ into the interlayer space at 4 °C (Baumeister and Hahn, 1976).

Early research also focused on vermiculite expansion through irradiation of electromagnetic waves in a specific range of frequencies. This process was carried out for ore vermiculite and previously intercalated vermiculite (Wada, 1973a).

2.8 Interstratification in vermiculite

Interstratified minerals are compositions in which individual crystals are made up of elementary layers of two or more different types (MacEwan *et al.* 1961; Moore and Reynolds, 1989; Bergaya *et al.*, 2006). These minerals are structurally and chemically more complex than minerals with a one-unit structure (Newman, 1987).

Newman (1987) and Bergaya et al. (2006) classify interstratified minerals according to the stacking order or periodicity along the *c* direction as:

- Ordered or regular mixed-layer structures – if the layers arrange in an alternate order, like ...ABABAB...; ...AABAABAAB...; ...AAABAAAB...; etc.
- Disordered or irregular mixed-layer structures – when the stacking order is random, like ...ABAABA...; ...ABBAABAB...; ...AABABBABBBBA...; etc.

The literature reveals two types of interstratification in clay minerals. One form is due to the types of mineral forming the mixed layers (e.g. vermiculite/mica, vermiculite/chlorite, mica/montmorillonite) and the other is due to the difference in terms of the water layer hydration states (WLHS) of the interlayer cations (e.g. 1-WLHS mixed with 2-WLHS).

Apparently, mixed mineral layers occur naturally, while the WLHS interstratifications are usually observed during the dehydration and/or rehydration of clays (Gruner, 1934; Brindley *et al.*, 1983; Reichenbach and Beyer, 1997; Frank and Edmond, 2001; Marcos *et al.*, 2009).

Justo *et al.* (1993) and Marcos *et al.* (2009) have shown that vermiculite-mica interstratification materials have the highest expansion and the thermal effects occur at lower temperatures compared with pure vermiculite.

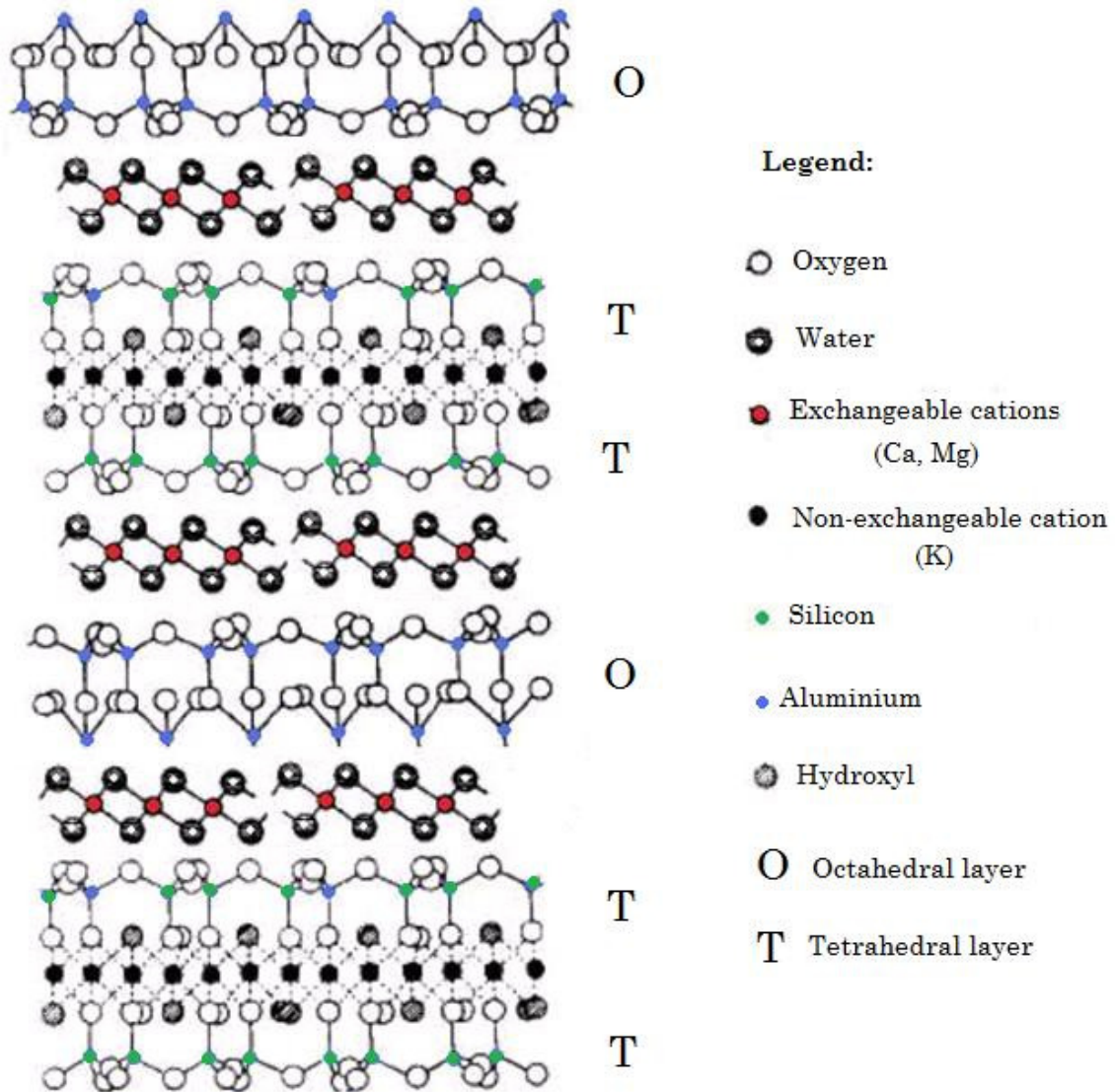
2.7.1 Mineral interstratifications in vermiculite

Hydrobiotite is a regular 1:1 interstratification of vermiculite and biotite layers (Brindley *et al.*, 1983; Newman, 1987). By the same token, hydrophlogopite is described as a regularly interstratified 1:1 mix of phlogopite/vermiculite. It has basal reflections with $d = 2.43$ nm, 1.223 nm, 0.827 nm, 0.490 nm and 0.349 nm (Gruner, 1934; Palabora Mining Company, 1976; Brindley *et al.*, 1983; Frank and Edmond, 2001).

However, the name ‘hydrobiotite’ is not internationally recognised as a valid mineral name, although it has long been used in the literature and is associated with interstratified biotite/vermiculite minerals found in commercial vermiculite deposits (Boss, 1967; Van der Marel and Beutelspacher, 1976; Brindley and Brown, 1980; Brindley *et al.*, 1983; Hudson *et al.*, 1999; Zhu *et al.*, 2008).

Mixed-layer clay minerals with any appreciable degree of randomness show a seemingly irrational series of reflections that make their identification and interpretation quite a complex exercise. However, computer programs are available for predicting the diffraction patterns of one-dimensional mixed-layer clays (Reynolds, 1985).

The presence of mixed-layer vermiculite-mica (Scheme IX) in ore vermiculite makes it more valuable, taking into account the following facts:



Scheme IX: Schematic drawing of interstratified vermiculite (adapted from Zhu, 2008)

- The interlayer spacing of hydrobiotite (2.5 nm), for instance, is largely higher than that of pure vermiculite (1.5 nm) and/or biotite (1.0 nm). In fact, this first-order reflection is close to the algebraic sum of the component interlayer spacing of the unit minerals (Ruiz-Amil *et al.*, 1992; Newman, 1987).
- Laboratory experiments by Saehr *et al.* (1990 and 1992) also showed similar results while preparing biionic Na- and K-vermiculites in

equilibrium with aqueous solutions of NaCl and KCl. Their X-ray diffraction (XRD) results showed interlayer spaces of K-vermiculite (1.08 nm), Na-vermiculite (1.41 nm) and the ordered interstratified Na/K-vermiculite (2.50 nm), and consequently the availability of two chemically different exchange sites owing to the existence of two different structural unities (Na-vermiculite and K-vermiculite).

- The interlayer space created after intercalation of interstratified vermiculite by organic surfactants is also much higher than that from pure vermiculite and biotite, as well as their exfoliated forms (Ruiz-Amil et al., 1992; Justo et al. 1993).
- Furthermore, this interstratified vermiculite is amenable to producing a durable exfoliated material (Frank and Edmond, 2001).

2.7.2 Water layer hydration states (WLHS) and dehydration of vermiculites

Water bound to the interlayer cations in clay minerals like vermiculite and montmorillonite is arranged in a series of layers, i.e. water layer hydration states (WLHS). These WLHS define the basal reflection and are intrinsically related to the interlayer cation(s), relative humidity and temperature (Barshad, 1950; Fripiat *et al.*, 1960; Marcos *et al.*, 2003).

According to Barshad (1948) and Ferrage *et al.* (2005), at room temperature and relative humidity around 35%, cations like Mg^{2+} , Ca^{2+} and H^{+} will exhibit 2-WLHS; Ba^{2+} , Li^{+} and Na^{+} only 1-WLHS; and NH_4^{+} , K^{+} , Rb^{+} and Cs^{+} 0-WLHS. In the case of the latter cations, exhibiting 0-WLHS, their relatively smaller d-spacing is caused by the size of the dehydrated interlayer cation.

In natural biotite (vermiculite parent mica) the interlayer ions are potassium and the interlayer space contains no water (0-WLHS). By contrast, pure vermiculite (Mg-vermiculite) contains the equivalent of up to two sheets of

interlayer water (2-WLHS) (Barshad, 1950; Harben and Roberts, 1990; Bergaya *et al.*, 2006).

During dehydration, initially there is release of water from external surfaces and meso-pores (unbound water), then the water of hydration (bound with the interlayer cation) and finally the water derived from dehydroxylation (combination of surface clay hydroxyl groups) (Bergaya *et al.*, 2006).

The dehydration and/or rehydration of vermiculite is, to a certain extent, a reversible process (Grim, 1968; Newman, 1987). It progresses stepwise during the elimination and/or accumulation of one or several water layer structures, with some overlap, accompanied by a change in the d-spacing (Fripiat *et al.*, 1960; Kresten and Berggren, 1978; Bergaya *et al.*, 2006).

Reichenbach and Beyer also conducted several experiments with alkaline earth exchanged vermiculites and published an interesting series on dehydration and rehydration of vermiculites (Reichenbach and Beyer, 1994, 1995 and 1997; Beyer and Reichenbach, 1998). They applied thermo-analysis and in situ XRD to study the relationship between temperature and the WLHS of homionic vermiculites. Some of their results are depicted in Table 4.

Furthermore, Reichenbach and Beyer (1994) concluded that Mg-vermiculites are more thermally stable due to the well-defined water layer hydration states (2-WLHS, 1-WLHS and 0-WLHS) compared with other ion exchanged vermiculites studied.

Several WLHS were also found by Marcos *et al.* (2003 and 2009) in their work with natural commercial vermiculites (including Palabora), supplementing preceding findings.

Table 4. Vermiculite WLHS properties (Grim, 1968; Hougardy et al., 1970; Reichenbach and Beyer, 1997)

Interlayer cation	WLHS	Thickness of water layer (nm)	d-spacing (nm)	Water content (mol/ion)
Mg ²⁺	2	0.51	1.38–1.44	4.00–4.71
	1	N/A	1.15–1.16	1.57–1.88
	0	N/A	0.93–1.00	0.00–0.51
Ca ²⁺	2	0.58	1.47–1.59	4.59–5.39
	1	N/A	1.18–1.19	1.23–1.83
	0	N/A	0.95–0.98	0.00–0.21
Ba ²⁺	1	0.34	1.24	2.36–2.53
	0	N/A	0.99–1.00	0.00–0.50
Na ⁺	2	N/A	1.48	5.6–6.0
	1	0.56	1.18	2.0
	0	N/A	N/A	N/A
NH ₄ ⁺	0	~ 0.15	1.08 (diffuse)	N/A
K ⁺	0	~ 0.13	1.06 (diffuse)	N/A

¹ N/A = data not available

In previous work a vacuum was also applied to study the dehydration and rehydration of vermiculite (Okhotnikov *et al.*, 1989; Marcos *et al.*, 2003). The results showed that during thermal dehydration of vermiculite there is no destruction of the crystals: water molecules are released by interlayer diffusion and escape through the cracks (Walker, 1959; Wild and Keay, 1964; Okhotnikov *et al.*, 1989).

Marcos *et al.* (2003) found that exposing vermiculite to a vacuum causes rapid dehydration and that below 120 °C the vacuum dehydration is arrested at 1-WLHS. They also observed that exfoliation under vacuum conditions is not dependent on the presence of water above 120 °C.

2.9 Potential applications of raw vermiculite

Clays and soils containing clays are well known in agriculture in processes such as the control of swelling, ion transport and the retention of water. Small amounts of them can have a large impact on the desired properties (Annabi-Bergaya, 2008).

The application of neat vermiculite is closely associated with its grade. However, it has been applied in lightweight insulation, aesthetic and decorative plastering, fire-resistant concrete and chimney insulation. Of some importance is its use by the breeders of chicken and some economic reptiles, and as a vitamin carrier (Mokhonoana, 1996; Horacek and Pieh, 2000).

Vermiculite has been used effectively as an absorbent in water purification due to its capacity to exchange its interlayer cations with some toxic ions like Sr, Pb, Zn and Cd (Schoeman, 1989; Das and Bandyopadhyay, 1991; Konta, 1995; Mekhamer and Assaad, 1999).

Many authors have mentioned the effectiveness of vermiculite as an adsorbent for the removal of natural and artificial organic matter, as well as for the controlled release of fertilisers and pesticides (Bailey and White, 1964; Schoeman, 1989; Abate, 2006).

2.10 Potential applications of chemically modified vermiculite

Flame-retardant compositions have been proposed that rely on vermiculite's expansion properties (Wada, 1973a). It is believed that vermiculite could impart fire resistance to polymers, provided the exfoliation temperature can be lowered sufficiently. Some patents claim that appropriately

intercalated vermiculites show lowered expansion onset temperatures (Langer and Marlor, 1981).

Acid-activated vermiculite is used as a catalyst, especially during the cracking of heavy fuels to the highest gasoline portion in the petroleum industry (Suquet *et al.*, 1994).

Organomodified vermiculite has been used in the removal of herbicides from water and in herbicide formulations for the controlled release of active components in soils (Plachá *et al.* 2008; Holešová *et al.*, 2010; Yu *et al.* 2010).

Organovermiculite polymer nanocomposites with improved mechanical properties, as well as good fire-retardant and intumescent properties, are also discussed in the literature, although less frequently than other clay minerals (montmorillonite, hectorite and saponite) which are relatively less abundant and much more expensive (Connell *et al.*, 1994; Connell *et al.*, 2000; Liu *et al.*, 2005; Gomes *et al.*, 2009; Qiu *et al.*, 2009).

2.11 Potential applications of exfoliated vermiculite

The lightweight (low bulk density) vermiculite produced by thermal expansion finds use in a variety of areas, according to the particle size and mechanical disintegration (Konta, 1995).

Exfoliated vermiculite is of industrial interest because it is incombustible, lightweight and shows excellent absorption and thermal insulation properties (Wada, 1973b, Schoeman, 1989; Tomanec *et al.*, 1997; Obut and Girgin, 2002; Bergaya *et al.*, 2006). It is used as lightweight aggregate in concretes and plasters (Wada, 1973b; Konta, 1995; da Silva *et al.*, 2003).

Expanded vermiculite is used in commercial and residential construction for fire protection to prevent warping, bending or collapse of the reinforced-concrete or steel-beam framework. Due to its inertness with respect to heat and fire, expanded vermiculite is also used as a high-temperature insulator, as well

as for ambient-temperature refrigeration and sound dissipation (Schoeman, 1989; Evans, 1993; The Vermiculite Association, 2000; Bergaya *et al.*, 2006). It is also used as thermal protection and shock-proof filling material for glass containers and vessels in the packaging industry (Konta, 1995; Bergaya *et al.*, 2006).

Since expanded vermiculite is able to retain liquids and gases better than natural soils, it is used in agriculture and animal feeds as an absorbent of water, air and other fluid plant and animal nutrients, and as a filler and carrier for powdered fertilisers and animal nutrients (Schoeman, 1989; Evans, 1993; Konta, 1995; The Vermiculite Association, 2000).

A mixture of exfoliated vermiculite, modified bentonite and peat is currently applied as a deodorising agent in the protection of the environment. Exfoliated vermiculite is also recommended as a bio-remediate aid to clean contaminated soils and sites, as an absorbent or filter in water purification and beverages, and for the controlled release of fertilisers and pesticides (Schoeman, 1989; Konta, 1995; The Vermiculite Association, 2000).

Exfoliated vermiculite is used in the friction brake linings market, for high-temperature insulation, loft insulation, various construction products, animal feeds, horticulture and many other industrial applications. Vermiculite, with its layered structure and surface characteristics, is utilised in products such as intumescent coatings and gaskets, for the treatment of toxic waste and in air-freight packaging of hazardous goods (Konta, 1995)

2.12 Commercial value of vermiculite

Fig. 2 shows world production of vermiculite from 1994 to 2009. During this period, the average South African production was about 200 000 tons per year.

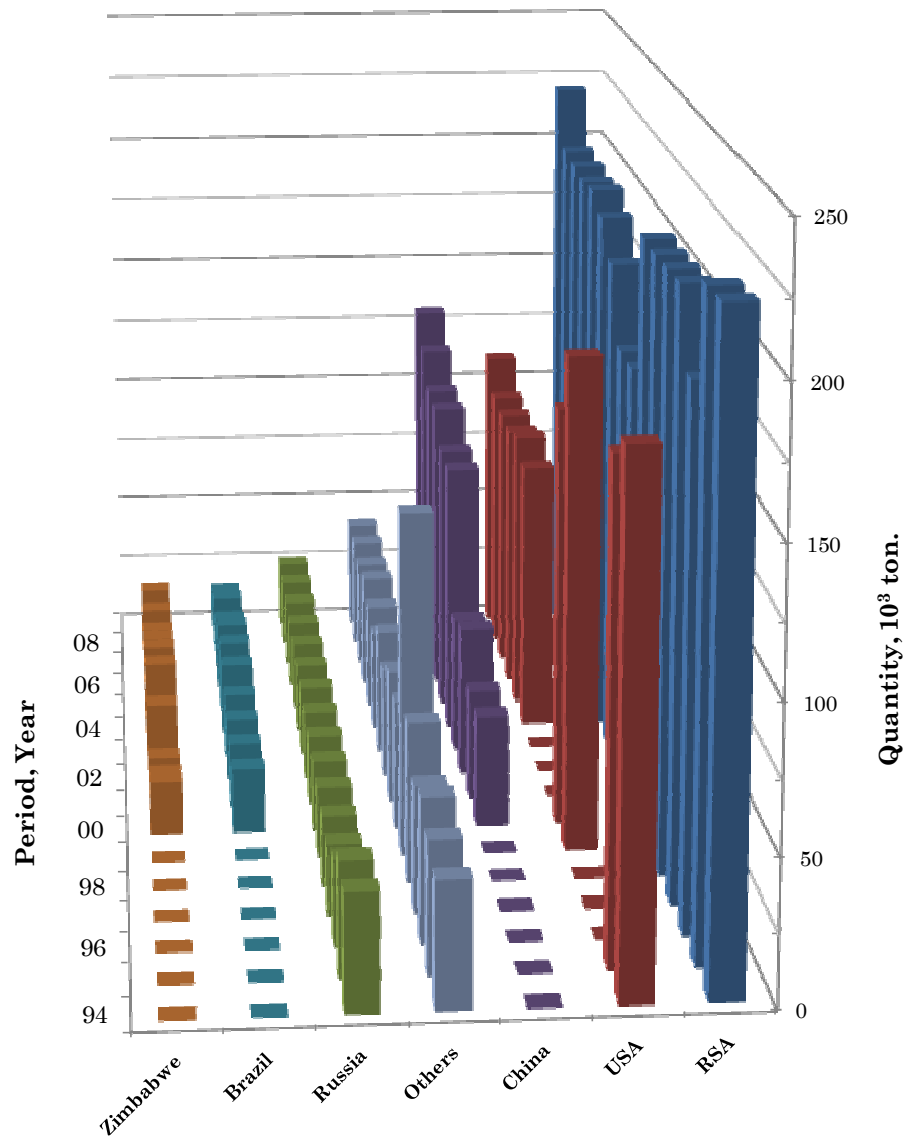


Figure 2. Worldwide production of vermiculite, from 1994 to 2009 (Potter, 1996 to 2009; and Cordier, 2010)

According to Potter (1996), from 1991 to 1995 South Africa was the main exporter of vermiculite to the USA (about 99%), while during the period 2005 to 2008 the country was responsible for around 59% of such exports (Potter, 2002; Cordier, 2010). This apparent decrease in exports is due to the emergence of new suppliers such as Australia, Brazil, China and Zimbabwe. Even with the appearance of these new suppliers, as shown above, the price of vermiculite

remained at approx. US\$143 per ton, and production remained relatively stable during the last decade (Potter, 2005; Cordier, 2010).

2.13 Characterisation techniques

2.13.1 X-ray Fluorescence (XRF)

The XRF technique is widely used in various areas since this method is fast, non-destructive and, usually, does not require laborious sample preparation.

Absorbed energy from a primary X-ray source (X-ray tube or radioactive source) can eject sample electrons from inner shells, creating vacancies. So, to re-establish the stable condition the outer shell electrons have to move into the inner shells, producing characteristic XRF patterns (Fig. 3) (Jenkins, 1988; Wilson, 1994).

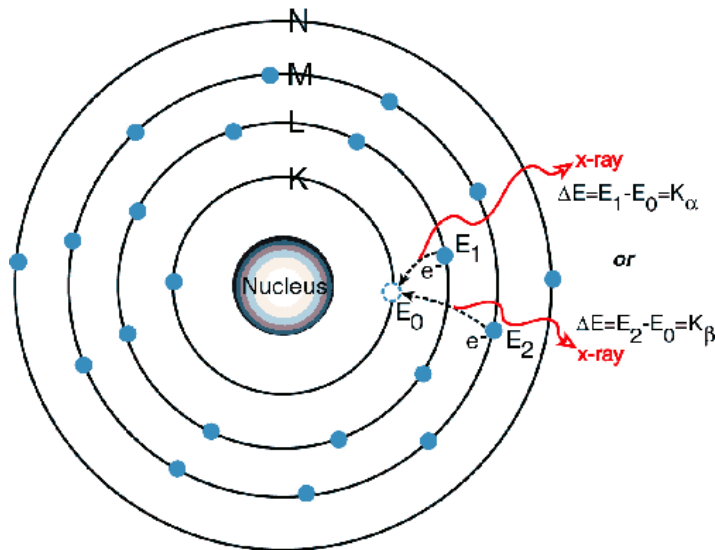


Figure 3. X-ray fluorescence after photoelectric effect with respective production of K_α and K_β X-rays

X-rays possess energy (E) that is a sinusoidal waveform with a typical wavelength (λ). These parameters and the frequency (ν), speed of light (c) and Planck's constant (h) are related by the equation represented by Scheme X:

$$E = h\nu = \frac{hc}{\lambda}$$

Scheme X: Planck's energy quantisation law

X-rays are labelled K, L, M or N, according to the destination shell. The suffixes alpha (α), beta (β) or gamma (γ) are added to distinguish X-rays originating from electrons from the different shell levels (Jenkins, 1988; Wilson, 1994).

2.13.2 Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) and ammonium acetate method

Several techniques are disclosed in the literature regarding the determination of CEC and exchangeable cations in clays and clay minerals.

The most commonly applied techniques are based on the exchange and saturation of interlayer cations using an mono-ionic 'index' cation in solution (theoretically not present in the sample) in a known quantity (Bergaya *et al.*, 2006, Aran, *et al.*, 2008). Various analytical techniques (atomic absorption, spectrophotometry, ICP-MS, ICP-OES, UV-Vis, titration, etc.) are then used to quantify the index cation and the displaced cations.

The basic ICP-OES instrument has the following components: (i) light path to optical system; (ii) excitation zone; (iii) emission zone; (iv) water-cooled plasma interface; (v) argon supply; (vi) plume; (vii) analytical zone; (viii) radiofrequency (RF) coil; (ix) plasma torch; and (x) a sample flow compartment (Ametek, 2009).

In the excitation zone, the temperature of the air-acetylene flame reaches values between 1 700 °C and 2 700 °C. Inert argon in the plasma is heated to high temperatures which efficiently excite many elements and prevent interference from oxides and nitrides (Ametek, 2009).

The current ICP-OES instrument records the entire spectrum between 175 and 777 nm, enabling simultaneous determination of more than 70 elements (Ametek, 2009).

The most relevant CEC determination methods are usually called by the name of the chemical compound used to extract the interlayer cations (index cation) and comprise:

- Ammonium acetate (Schollenberger, and Simon, 1945; Barshad, 1954a; Barshad, 1954b; Tan, 1996)
- Barium chloride (Bascomb, 1964; Hendershot and Duquette, 1986)
- Cobaltihexamine chloride (Ciesielski *et al.*, 1997; Aran *et al.*, 2008)
- Methylene blue (MB) (Carter and Wilde, 1972; Kahr and Madsen, 1995)
- Silver-thiourea (Dohrmann, 2006a; Dohrmann, 2006b).

The interlayer CEC of vermiculites and other 2:1 clay minerals can also be estimated from the layer charge density as shown in Scheme XI (Lagaly, 1979 and 1982; Ghabru *et al.*, 1989; Mermut and Lagaly, 2001).

$$\text{Interlayer CEC } \left(\text{cmol/Kg} \right) = 10^5 \frac{\xi}{\bar{M}}$$

Scheme XI: Calculation of interlayer CEC from interlayer charge

Where $\bar{M}$ is the mean relative molar mass and ξ is the layer charge, which can be determined by measuring the interlayer spacing after intercalation with alkylammonium cations ($C_nH_{2n+1}NH_3^+$) of varying carbon chain lengths.

2.13.3 Thermogravimetry (TG)

TG is an analytical technique that measures the mass change of the analyte as a function of temperature, independent of bonding mode. TG results

are evaluated and interpreted by thermogravimetric analysis (TGA) and/or by evaluating the respective derivative against temperature (dm/dT), known as derivative thermogravimetry (DTG). DTG also shows the rate at which the mass changes (Brown, 2001; Haines, 2002; Bergaya *et al.*, 2006; Gabbott, 2008).

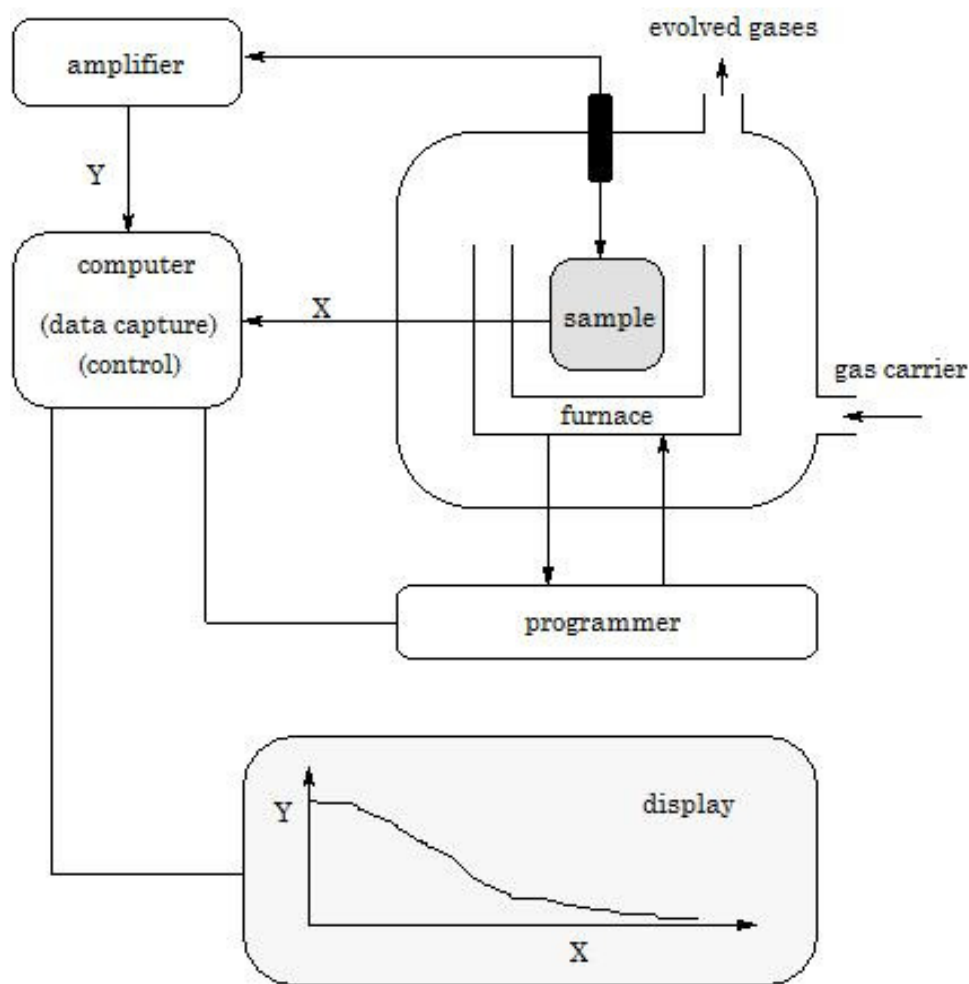


Figure 4. Basic TGA instrument (adapted from Brown, 2001)

Modern thermal instruments (TG, DT, TMA, DSC, etc.) comprise basically an electronic balance, furnace, atmosphere control, sample holder, thermocouples, temperature control and a data collection device (Brown, 2001; Haines, 2002; Bergaya *et al.*, 2006). A schematic representation of a TG instrument is shown in Fig. 4.

2.13.4 Thermomechanical Analysis (TMA)

TMA or static force-TMA (sf-TMA) is a technique that derives from thermomechanometry. It is a very important tool for studying materials that are to be subjected to a wide variation in temperature during their usage. An illustrative example is food packaging which has to undergo thermal processes such as heating, pasteurisation, freezing, etc. (Brown, 2001; Haines, 2002).

In TMA the sample's dimension or length is measured as a function of temperature while it is under constant mechanical stress. Usually the results are evaluated by examining the changes in the thermal expansion coefficients with temperature and/or time (Haines, 2002; Gabbott, 2008).

Modern TMA instruments are designed to measure: (i) penetration; (ii) extension; (iii) flexure; and (iv) torsion (Brown, 2001). For extension measurements, a flat-ended probe is inserted and rested on the top surface of the sample, and a static force is applied. A sensor then measures the movement of the probe (Haines, 2002).

2.13.5 X-ray Diffraction (XRD)

The XRD technique has been extensively used to identify and distinguish vermiculite from other clay minerals (e.g. chlorite and smectites) and, in fact, the definition of vermiculite is based on its ca. 1.45 nm basal spacing for Mg-vermiculite treated with glycerol and on the characteristic 1.0 nm spacing for the K-vermiculite form on heating at 300 °C (Brindley and Brown, 1980; Bergaya *et al.*, 2006). XRD is also used to distinguish the dioctahedral ($d_{060} = 0.149\text{--}0.150$ nm) from the trioctahedral ($d_{060} = 0.151\text{--}0.153$ nm) clay minerals (Brindley and Brown, 1980).

XRD is a versatile and also non-destructive technique that reveals detailed information about the phases contained, as well as their crystallographic features (Cullity, 1978; Moore and Reynolds Jr., 1989).

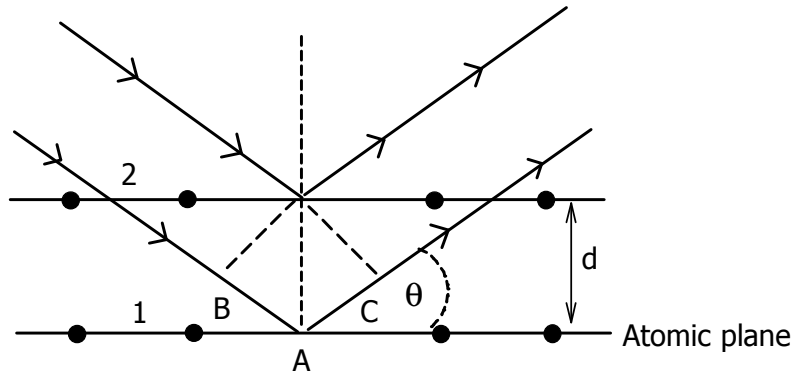


Figure 5. X-ray diffraction by a crystal according to Bragg's law

X-rays are a radiation of short wavelength, from 10^{-3} nm to 10 nm. They are generally produced during the collision of a high-energy electron with a metal target (Cullity, 1978; Moore and Reynolds, 1989).

When the incident wavelength (λ) is of the same order of magnitude as the repeated distance (d) between scattering centres, diffraction can occur. This diffraction phenomenon, known as Bragg's law and represented in Fig. 5, is mathematically described by Scheme XII.

$$n \lambda = 2 d \sin \theta$$

Scheme XII: Bragg's law

Where:

n is an integer ($n = 1, 2, \dots$)

d is the interlayer spacing

θ is the diffraction angle or Bragg's angle

λ is the wavelength of the incident X-rays

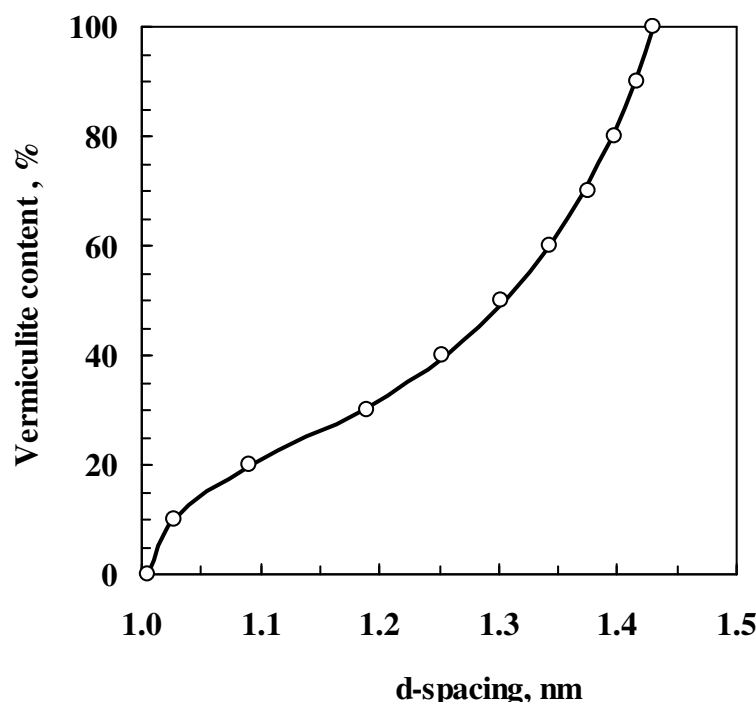


Figure 6. Determination of vermiculite content from d-spacing (according to Moore and Reynolds, 1989)

By knowing λ and measuring θ , d can be calculated using the relationship shown in Scheme XI. Furthermore, vermiculite content can be determined by applying the d-spacing determined using Bragg's law, as shown in Fig. 6 (Moore and Reynolds, 1989).

2.13.6 Scanning Electron Microscopy (SEM)

Nowadays SEM (along with TEM) is one of the most important characterisation techniques as a result of the huge technological improvements made since its invention and the relatively easy interpretation of data. This technique has also been used by some researchers to study the surface changes in vermiculite resulting from physical or chemical modification.

SEM apparatus basically consists of (Lawes, 1987): (i) electron-optical column (principally an electron gun, lens and detector); (ii) vacuum system (to

prevent scattering of electrons by collision with gas molecules); and (iii) electronics and a display system (mainly an amplifier, cathode-ray tubes and a control system).

In a SEM, the electron gun bombards the sample with electrons of a specific wavelength. Deflected electrons, commonly elastically scattered electrons, are collected as signals for imaging. Different topographies and different chemical compositions bring about different signal intensities, thereby giving different contrasts on the SEM screen (Lawes, 1987).

2.13.7 Other characterisation techniques

Other relevant techniques have been being applied to characterise vermiculite and other clay minerals. Techniques such as particle size analysis, IR spectroscopy (Farmer, 1971; Farmer, 1974; Van der Marel and Beutelspacher, 1976; Raupach, 1988; Badreddine *et al.* 2002c), as well as Raman spectroscopy (Okui *et al.*, 1998; Arab *et al.*, 2002; Rinaudo *et al.*, 2004), have been shown to be useful for the characterisation of vermiculite and its exchanged forms.

CHAPTER 3 EXPERIMENTAL

3.1 Starting materials and suppliers

Mandoval Vermiculite supplied the superfine (1 mm) and micron (0.5 mm) samples of Palabora material.

All metal chlorides and ammonium salts were obtained from Merck Chemicals. The orbital shaker (SPO-MP15) used to run the experiment was supplied by LABEX.

For these experiments, a long-term approach and/or the use of a shaker were applied due to the high layer charge of vermiculite. Previous kinetic studies have already shown a very slow rate of exchange in similar vermiculites due to the high layer charge density (Inoue, 1984; Skipper *et al.*, 1991; Kodama and Komarneni, 1999).

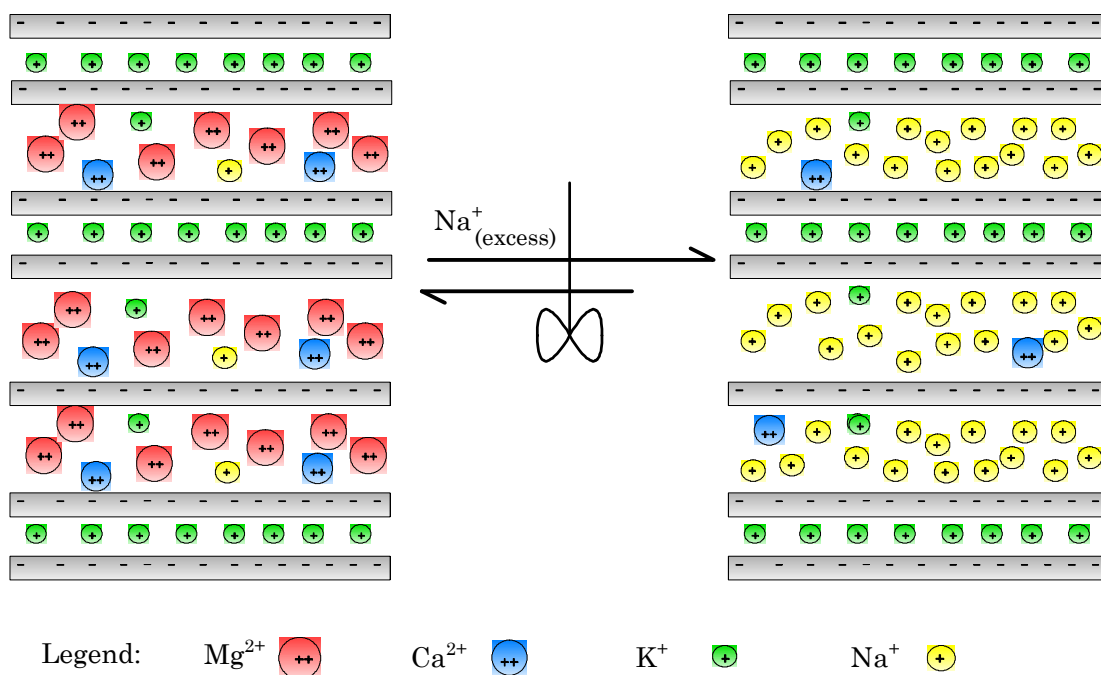
All experiments were run at the pH of the salt solution and it was not controlled accurately since the exchange rate is not affected by the pH in the range of 4 to 9 (Wild and Keay, 1964).

3.2 Ion exchange of vermiculite

For the first set of reactions it was attempted to replace the magnesium ions with sodium ions using concentrated brine, since vermiculite selectivity rises with an increase in the preferred ion loading (Wild and Keay, 1964; Gast and Klobe, 1971) (Scheme XIII). The sodium exchange reaction was performed over a period of six months in closed containers, having the vermiculite submerged in a large volume of saturated sodium chloride solution. The suspension was agitated daily. Every fortnight approximately 1 000 ml of the supernatant liquid was exchanged with fresh saturated brine. At the end of every month, vermiculite samples were taken for analysis. They were rinsed with distilled water and allowed to air-dry at ambient conditions.

The exchange process was therefore controlled by monthly extraction of aliquots by taking out Na-exchanged vermiculite samples after first month up to the sixth month.

The second approach of ion exchange by ammonium, alkali metal and alkaline earth metal ions was carried out using a shaker for exactly 360 hours (15 days) at room temperature. The frequency of the shaker was adjusted to 200 rpm (rotations per minute).

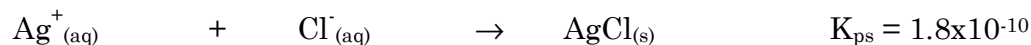


Scheme XIII: Schematic representation of ion exchange in interstratified vermiculite. It is assumed that the biotite layers (containing K as interlayer cation) remain intact after treatment

For these experiments, 50 g of vermiculite were weighed off for each sample and enough salt was added to prepare 250 ml of saturated solution (for the reasons mentioned above).

For both sets of experiments, the ion exchanged vermiculites were then washed thoroughly with distilled water until all chloride anions had been

removed quantitatively. This test was performed by reaction of an aliquot of supernatant solution with 0.1M AgNO₃ (Scheme XIV).



Scheme XIV: Reaction of Ag⁺ and Cl⁻ ions with formation of a white precipitate of silver chloride

3.3 Characterisation of chemically modified vermiculites

3.3.1 *X-ray Fluorescence (XRF)*

The chemical composition of neat and long-term Na-exchanged vermiculites was determined by XRF. For major element analysis a milled sample (< 75 µm) of the neat or ion exchanged material was calcined at 1 000 °C for at least 3 h to oxidise Fe²⁺ and S and to determine the loss on ignition (LOI). Glass disks were prepared by fusing 1 g of roasted sample and 8 g of 12–22 flux consisting of 35% LiBO₂ and 64.71% Li₂B₄O₇ at 1 050 °C. The glass disks were analysed by a PANalytical Axios X-ray fluorescence spectrometer equipped with a 4 kW Rh tube.

Ammonium, alkali metal and alkaline earth metal ion exchanged vermiculites were analysed using an ARL9400XL+ spectrometer. One gram of sample was then placed together with 6 g of Li₂B₄O₇ into a Pt/Au crucible and fused into a glass bead. The samples were roasted at 1 000 °C to determine the LOI. The analyses were done using Quantas software. The results were also monitored and filtered to eliminate the presence of some of the flux – the elements of the wetting and oxidising agents.

3.3.2 *Interlayer composition*

With the ammonium acetate extraction method it was attempted to quantify the interlayer cations regardless of the compositional (interstitial or

structural) cations, which in some cases are definitely present in higher quantities.

The extracted Na^+ , K^+ , Mg^{2+} and Ca^{2+} ions were quantitatively determined using an ICP-OES Spectro Genesis spectrometer, equipped with Smart Analyzer Vision software and a 27 MHz free-running generator for constant plasma power output.

3.3.3 Particle size

The particle size distribution (PSD) was obtained by laser diffraction using a Malvern Mastersizer 2000 fitted with a Hydro 2000G dispersion unit. Samples were prepared in duplicate and three runs were made per replicate.

3.3.4 Thermogravimetry (TG)

Thermogravimetry (TG) was performed by the dynamic method on a Mettler Toledo A851 TGA/SDTA instrument. For TG analysis, a sample of about 15 mg was placed in an open 150 μl alumina pan. The temperature was scanned from 25 to 1 000 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C}/\text{min}$ with air flowing at a rate of 50 ml/min.

3.3.5 Thermomechanical Analysis (TMA)

Thermal expansion measurements were conducted with a TA Instruments Q400 Thermo Mechanical Analyzer. The thickness of the micron-grade flakes tested ranged from 91 μm to 231 μm and their cross-sectional surface area varied from ca. 1.66 mm^2 to about 4.2 mm^2 . In each experiment, a single flake was sandwiched between the flat surface probe and the bottom surface of an alumina pan. The flake's expansion behaviour was measured under a suitably chosen applied force.

In the dynamic scan experiments, the temperature was scanned from 30 °C to 1 000 °C in argon at a scan rate of 10 °C/min. Since the objective was to follow the free expansion of the flakes, the lowest possible force (0.001 N) was applied. The expansion relative to the original flake dimension was reported.

Additional TMA experiments were limited to the sodium vermiculite obtained after six months of brine exposure. The effect of the magnitude of the applied force was investigated using settings of 0.05, 0.20 and 1.0 N. Finally, the expansion behaviour of the flakes subjected to a stepwise increasing temperature-change protocol was investigated. In these experiments the temperature was scanned at 10 °C/min to an isothermal hold temperature at which the sample was kept for 10 minutes before the temperature scan was continued. The first hold temperature was 270 °C and the subsequent hold temperatures were set at 10 °C increments, with the final isothermal halt at 340 °C.

3.3.6 X-Ray Diffraction (XRD)

For X-ray diffraction (XRD) analysis, samples of neat and ion exchanged vermiculite were split and a sub-sample of each was homogenised and milled to a fine powder.

Due to the layered structure of vermiculites, careful sample preparation was essential for meaningful and accurate results. Special precautions were taken to prevent preferred orientation when it was not needed. Samples were split and representative portions were milled and homogenised to a fine powder of approximately 15–20 µm in size. Prior to analysis, a sub-sample was lightly ground in a mortar and pestle, and pressed into a shallow sample holder against a rough filter paper in order to ensure random orientation.

The evaluation was done on both random and oriented preparations. The neat vermiculite was saturated with Mg prior to the various treatments. All

oriented preparations were analysed in an air-dried state (AD), after ethylene glycol (EG) solvation and heating to 550 °C, for additional information.

X-ray diffraction data were obtained on a BRUKER D8 Advance diffractometer instrument with CuK α radiation ($\lambda=1.5406$), a Johansson crystal primary monochromator and a LynxEye detector with an active area of 3.7°. Scans from 2 to 70° 2 θ for random powder preparations and 2 to 28° 2 θ for the oriented slides were recorded in step-scan mode at a speed of 0.01° 2 θ step size/4 s and generator settings of 40 kV and 40 mA.

Mineral identification was done by means of the BRUKER DIFFRAC^{Plus} – EVA evaluation program using the International Centre for Diffraction Data (ICDD) Inorganic/Organic Database. Phase concentrations were determined by the Rietveld quantitative method using the DIFFRAC^{Plus} – TOPAS software at an estimated accuracy of $\pm 1\%$. Refinement of diffraction data was done using the same program.

3.3.7 Scanning Electron Microscopy (SEM)

Images of neat and Na-exchanged vermiculite were obtained on a JSM-840 scanning electron microscope equipped with Orion 6.60.4 software. For these studies the vermiculite flakes were mounted on adhesive carbon tape.

The temperature-driven dynamic exfoliation process was also studied under a scanning electron microscope (FEI QUANTA 200 ESEM) fitted with a heating stage. The samples were placed inside a crucible and mounted in the heating stage. They were viewed at 200x magnification. The pressure was 0.5 kPa, voltage 20 kV, spot size 6–7 and a working distance of 16–20 mm was used. The temperature was ramped at 20 °C/min.

3.3.8 Fourier Transform–Infrared (FT-IR) Spectroscopy

Fourier Transform–Infrared Spectroscopy (FT-IR) spectra were recorded using a PerkinElmer Spectrum RX FT-IR, coupled with a computer using

Spectrum v5.0.1 software, with a scan resolution of 2.0 cm^{-1} . A total of 32 interferograms were collected for each sample, applying single-beam radiation.

KBr compressed pellets were prepared from a fine powder that was obtained by grinding a mixture of 3–5 mg of sample with 100 mg of dehydrated KBr using a mortar and pestle.

CHAPTER 4 RESULTS AND DISCUSSION

The superfine (1 mm) and micron (0.5 mm) grades of vermiculite ostensibly differed in flake size only.

A backscattered SEM image (Fig. 7) of the neat material showed the flaky nature of vermiculite. Granular impurities were observed in between the flakes and on the surface of the aggregates.

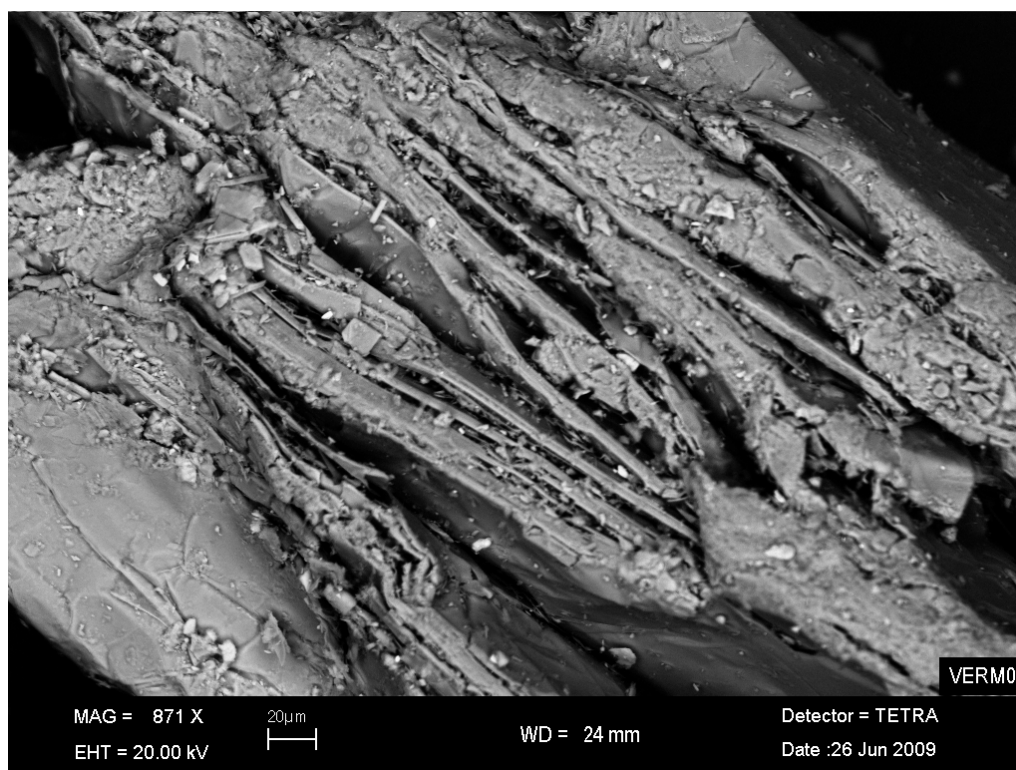


Figure 7. SEM image of neat superfine vermiculite

4.1 X-ray Fluorescence (XRF)

4.1.1 *Neat and long-term Na-exchanged vermiculites*

The XRF-derived chemical compositions are presented in Table 5. The sodium content showed a step change from effectively zero (0.01 mass %) to an average value of ca. 1.67 ± 0.11 mass % after one month's exposure and

thereafter. The presence of calcium and phosphorus is attributed to apatite and dolomite contamination.

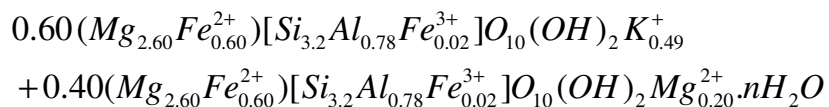
These XRF results also emphasise the fact that Palabora vermiculite is not pure because the content of potassium oxide (K_2O) is higher than 0.35% (Justo *et al.* 1986). This is in accordance with previous findings (Inoue, 1984; Marcos *et al.*, 2009).

Table 5. XRF (%) composition analysis of long-term Na-exchanged samples

Month	0	1	2	3	4	5	6
SiO ₂	39.74	40.27	40.01	39.73	39.72	40.28	40.41
MgO	22.70	22.23	21.60	22.75	21.73	22.40	22.12
Al ₂ O ₃	8.36	8.62	8.35	8.76	8.33	8.74	8.61
Fe ₂ O ₃ (t)	7.06	7.30	7.10	7.58	7.12	7.42	7.27
CaO	5.72	5.03	6.46	4.28	6.27	4.71	5.37
K ₂ O	4.81	4.97	4.85	5.30	4.84	5.08	4.87
P ₂ O ₅	2.81	2.40	3.29	1.95	3.15	2.32	2.66
Na ₂ O	0.01	1.50	1.44	1.64	1.59	1.71	1.51
TiO ₂	0.88	0.90	0.86	0.92	0.87	0.90	0.90
MnO	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Cr ₂ O ₃	0.02	0.02	0.02	0.02	0.02	0.02	0.02
LOI	7.83	6.66	5.83	6.59	6.21	6.22	6.20
Total	99.94	99.95	99.86	99.57	99.91	99.86	99.99

Cardille and Slade (1987), Schoeman (1989), Badreddine *et al.* (2002a), Marcos *et al.* (2009) and Marcos and Rodríguez (2010) also found that Palabora vermiculite has, comparatively, an unusually high level of iron. These iron ions (and also aluminium ions) are the main magnesium isomorphous substitutes in

the octahedral sites, and there are also considerable silica replacements in the tetrahedral sites, in agreement with the findings of Cardille and Slade (1987).



Scheme XV: Structural formula of neat vermiculite consistent with the XRF data

The unknown quantities in Scheme XV were determined by fitting the formulae to the XRF data for the other elements using atom balances. In this calculation it was assumed that titanium and manganese occupied the tetrahedral and octahedral positions respectively. However, neglecting the existence of these impurities made little difference to the calculations.

The composition estimated from the XRF data suggests about 60% biotite and 40 % vermiculite with a CEC value of about 98 meq/100 g.

4.1.2 Ammonium, alkali metal and alkaline earth metal ion exchanged vermiculites

The modified vermiculites showed an expected increase in the exchanged cations, confirming the success of the ion exchange process under the conditions considered.

As can be seen from Table 6, barium vermiculite (BaVER) shows the most noticeable change in chemical composition – it increased by almost 4% (described in terms of BaO) compared with neat vermiculite. This is in agreement with previous findings that refer to the high affinity of barium ions for the surface of clay minerals (del Rey-Perez-Caballero and Poncelet, 2000; Shahwan and Erten, 2004).

Table 6. XRF (%) composition analysis of ammonium, alkali metal and alkaline earth metal ion exchanged vermiculite samples

Sample	NaVER	KVER	MgVER	CaVER	BaVER	NH₄VER
SiO ₂	38.76	35.64	39.54	39.45	39.38	40.29
MgO	23.42	23.81	24.21	22.44	22.49	22.74
Al ₂ O ₃	9.47	9.24	10.16	9.60	9.69	10.11
Fe ₂ O ₃	8.27	10.09	8.12	8.17	8.24	8.21
CaO	3.87	5.40	3.42	5.06	3.40	3.76
K ₂ O	5.10	6.77	5.07	5.36	4.89	5.18
P ₂ O ₅	0.88	1.19	1.17	0.98	1.12	0.99
Na ₂ O	1.69	<0.01	<0.01	<0.01	<0.01	<0.01
TiO ₂	0.94	1.10	1.05	1.00	1.02	1.01
MnO	0.04	0.06	0.06	0.06	0.07	0.06
Cr ₂ O ₃	0.03	0.03	0.03	0.03	0.04	0.04
NiO	0.03	0.03	0.03	0.03	0.04	0.03
V ₂ O ₅	<0.01	<0.01	0.01	0.02	<0.01	<0.01
SO ₃	<0.01	<0.01	<0.01	0.04	<0.01	<0.01
BaO	<0.01	<0.01	<0.01	<0.01	4.00	<0.01
Cl	<0.01	<0.01	<0.01	0.03	<0.01	<0.01
CuO	0.01	0.03	0.02	0.02	0.02	0.02
ZnO	0.02	<0.01	0.02	0.02	0.01	0.01
Rb ₂ O	0.05	0.09	0.05	0.05	0.04	0.05
SrO	0.02	0.07	0.02	0.01	0.01	0.02
LOI	7.39	6.43	7.02	7.64	5.50	7.49
Total	100.00	100.00	100.00	100.00	100.00	100.00

By contrast, magnesium vermiculite (MgVER) did not show substantial compositional changes. This was expected due to the fact that neat vermiculite is composed mainly of magnesium ions as exchangeable cations.

4.2 Interlayer composition and extractable cations

To determine whether the exchangeable cations in the neat vermiculite have been successfully exchanged, the interlayer composition of the neat vermiculite and the ion exchanged vermiculites were determined by the ammonium acetate method. This procedure showed tangible results compared with the XRF results. For instance, the exchangeable Mg^{2+} ions are negligible in comparison with the structural Mg^{2+} and thus the difference after exchange is not easily detectable by XRF. However, after extraction with ammonium acetate it was possible to differentiate between them.

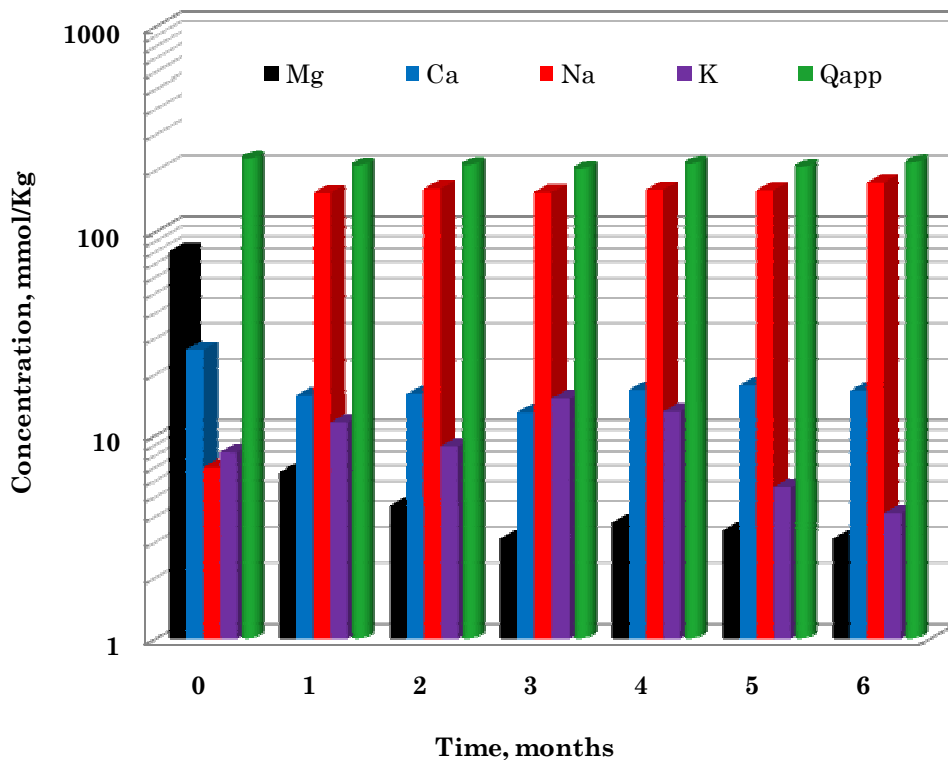


Figure 8. Change in interlayer composition of vermiculite during long-term treatment with NaCl

According to the ICP-OES results (Fig. 8), the vermiculite interlayer spaces initially contained both Mg^{2+} and Ca^{2+} ions, in addition to some K^+ ions.

The extraction data indicate almost quantitative replacement of the exchangeable Mg^{2+} and Ca^{2+} ions, in the vermiculite phase, by Na^+ ions. The Ca^{2+} ions that were not replaced by Na^+ ions but were extractable by ammonium acetate are attributed to the presence of the apatite $[Ca_3(PO_4)_2]$. Baddredine *et al.* (2002b) ascribed this to calcite impurities, although they could not detect it using XRD techniques.

The majority of the K^+ ions, i.e. those associated with the mica phase (located in the hexagonal cavities of the O^{2-} ion sheets of the layer surface), were not exchanged by sodium, consistent with previous reports (Barshad, 1948; MacEwan *et al.* 1961, Newman, 1987).

The apparent total metal charge adsorbed into the vermiculite (Q_{app}) was determined using Scheme XVI. According to Fig. 8, Q_{app} is not affected during long-term brine treatment.

$$Q_{app} = \sum z_i n_i$$

Scheme XVI: Determination of apparent total metal charge

Where:

Q_{app} is the apparent total metal charge

Z is the ionic charge

n is the number of mol

4.3 Thermogravimetry (TG)

4.3.1 Long-term Na-exchanged vermiculites

The thermogravimetric (TG) curves for the unaltered materials and the Na-exchanged forms are shown in Fig. 9. Mass loss commenced below 100 °C

and occurred in several steps for all the samples. As shown in Fig. 10, the total mass loss was 7–9 mass % for all samples. This compares with a total expected mass loss of 10.5 mass %, with interlayer water contributing 6.5 mass %, for the structure indicated in Scheme XV with the assumption that $n = 4$.

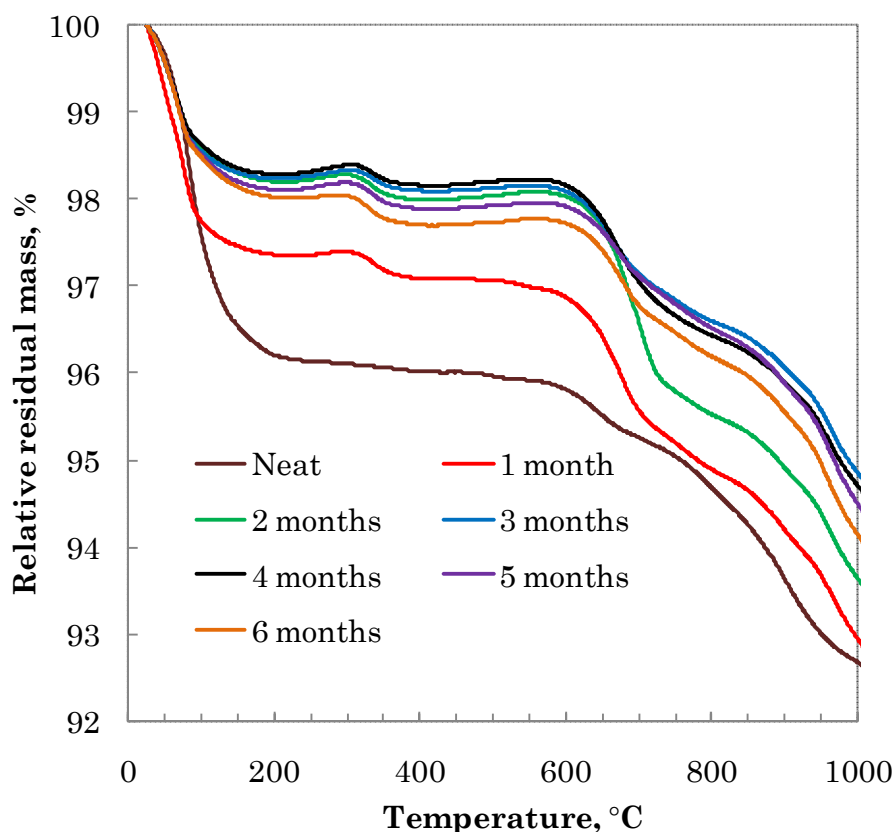


Figure 9. TG plots of micron vermiculite and its Na-exchanged forms

Fig. 10 reports the overall mass loss and percentages for the temperature regions < 250 °C, 250–520 °C and 520–1 000 °C. Most of the mass loss occurred in the first and final temperature ranges.

As shown below, most of the vermiculite exfoliation occurred in the temperature range 250–520 °C. Surprisingly, the explosive exfoliation corresponded to the release of less than 0.5 mass % water.

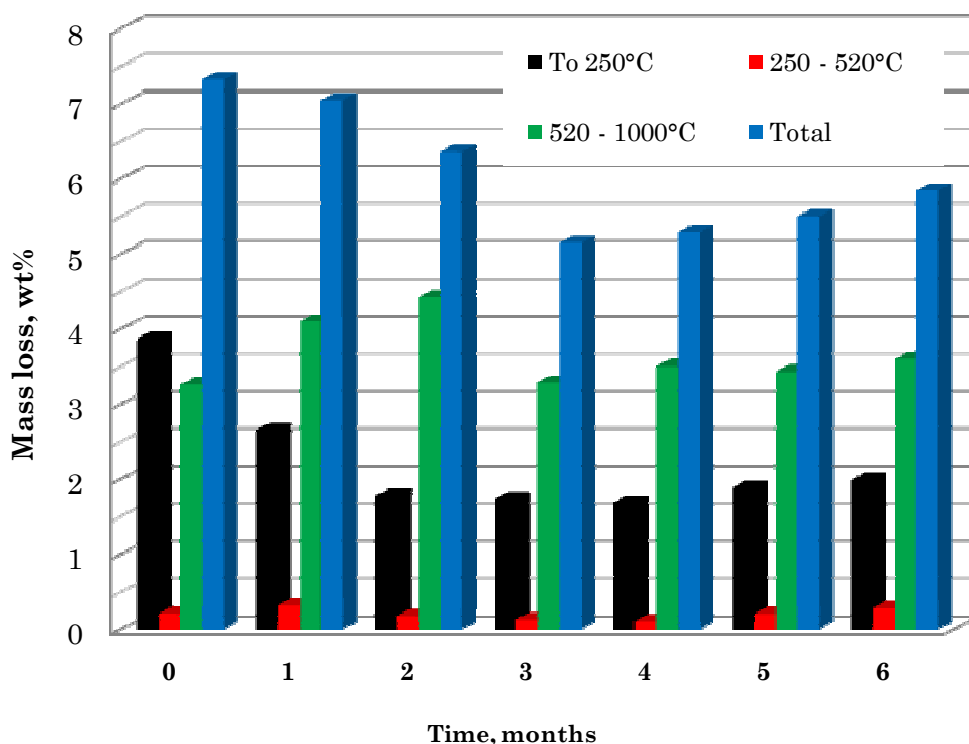


Figure 10. Mass loss for neat vermiculite and its Na-exchanged forms

4.3.2 Ammonium, alkali metal and alkaline earth metal ion exchanged vermiculites

According to Fig. 11, ion exchanged vermiculites show a multi-stage decomposition. Mg-vermiculite (MgVER) exhibits relatively (well known) stable intermediates, while NH_4 -vermiculite (NH_4VER) shows extensive dehydration in the second stage.

NH_4VER shows a decomposition that resembles the recoil effect (Gabbott, 2008) and an overall total mass loss close to 18%, whereas the other ion exchanged vermiculites show losses below 10%. The higher mass loss in NH_4VER is a result of the release of both water and ammonia ($\text{NH}_3(\text{g})$) (Stone and Wild, 1978; Pérez-Maqueda *et al.*, 2004; Pérez-Rodríguez *et al.*, 2004).

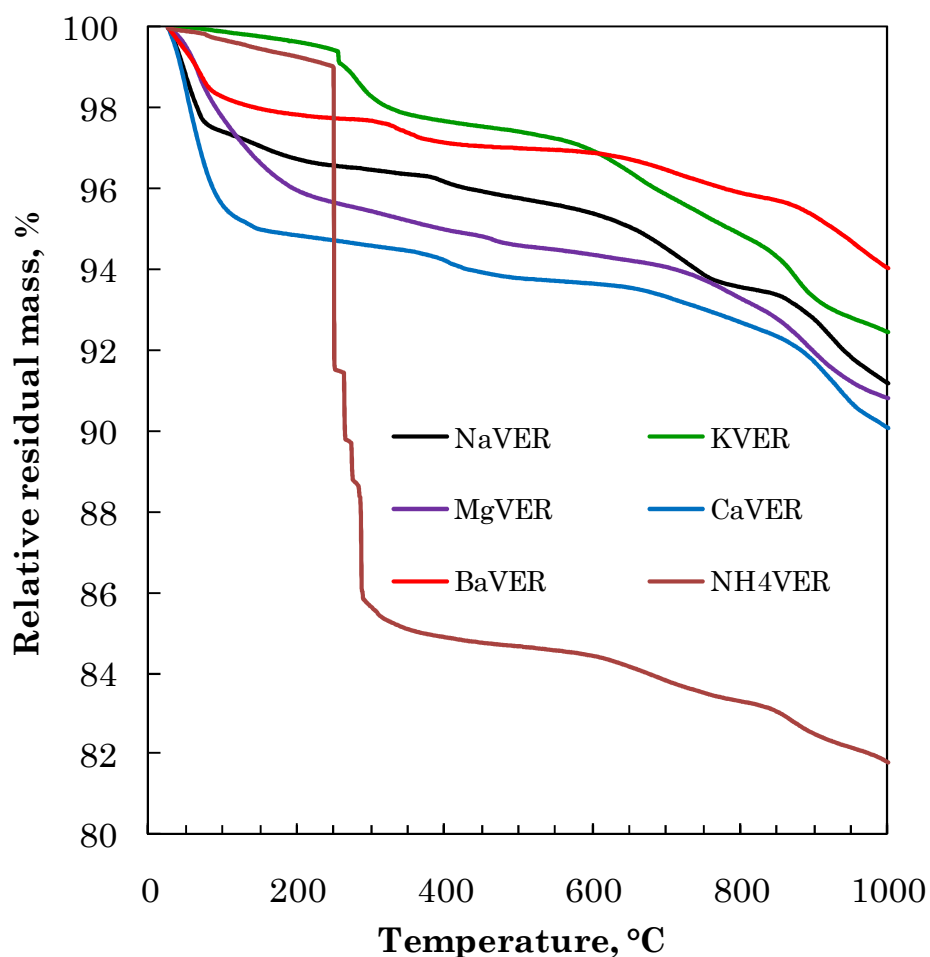


Figure 11. TG plots of metal ion exchanged vermiculites

In the range of 250–520 °C, which is the expansion temperature of vermiculites, only around 1.0% of mass is lost for all vermiculites ion exchanged with metal ions. However, in the same interval, NH₄VER shows mass losses of around 7.1%, for the same reasons mentioned above (Fig. 12).

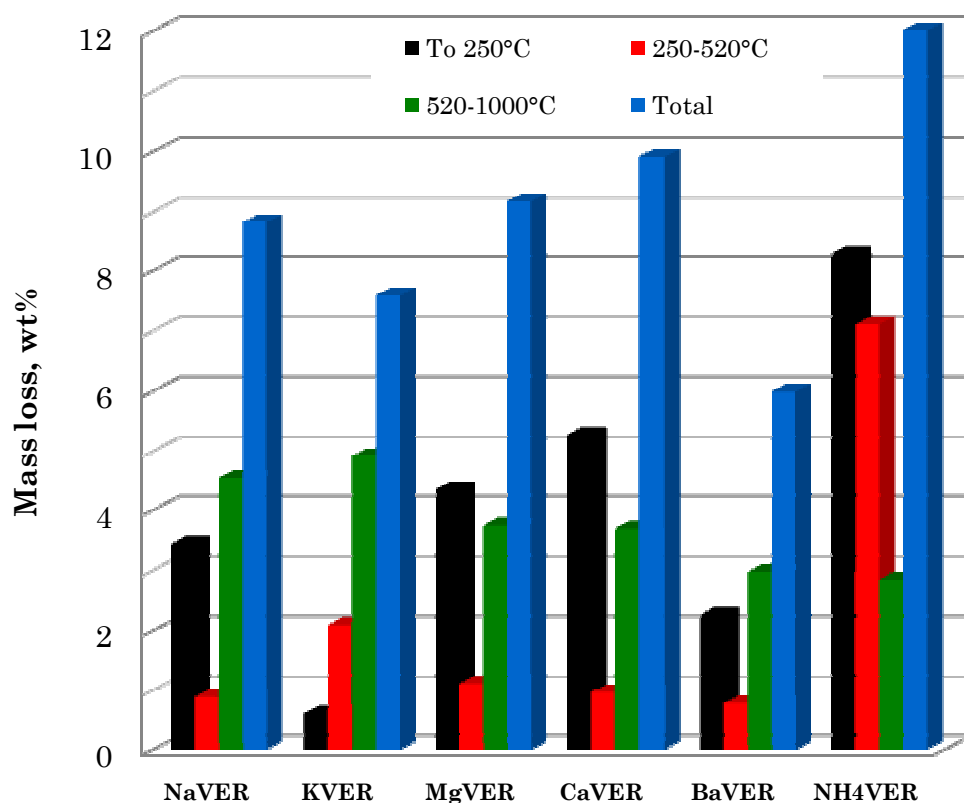
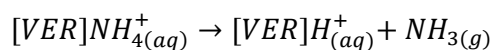
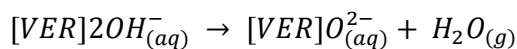


Figure 12. Mass loss of ion exchanged vermiculites

Between 520 and 1 000 °C dehydroxylation of all samples occurs. Again NH₄VER shows comparatively high mass losses. This behaviour is attributed to the release of both ammonia (Scheme XVII) and water due to expected vermiculite dehydroxylation (Scheme XVIII) (Stone and Wild, 1978; Pérez-Maqueda *et al.*, 2004; Pérez-Rodríguez *et al.*, 2004).



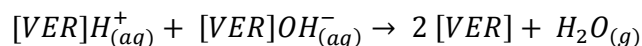
Scheme XVII: Thermal decomposition of ammonium ions in vermiculite



Scheme XVIII: Dehydroxylation of vermiculite

A supplementary water quantity, resulting from the combination of hydrogen ions released during ammonia liberation and hydroxyl groups from

the vermiculite surface (Scheme XIX), is also expected to contribute, as observed by Pérez-Maqueda *et al.* (2004) and Pérez-Rodríguez *et al.* (2004) during thermal decomposition of NH_4VER .



Scheme XIX: Dehydroxylation of vermiculite aided by hydrogen ions

4.4 Thermo-Mechanical Analysis (TMA)

The free expansion curves, obtained at an initial force of 0.02 N and with constant temperature ramping (Fig. 14 and Fig. 16), showed a rather abrupt rise at the expansion onset temperature, followed by a more gradual expansion over a temperature range of several hundred degrees Celsius.

The initial steep rise leads to linear expansions equivalent to three to six times the initial flake thickness at rates ranging from 3%/s to 16%/s. The maximum expansion was attained at around 700 °C. Above this temperature some sample contraction was observed.

4.4.1 Long-term Na-exchanged vermiculites

The exfoliation onset temperature of the neat material exceeded 450 °C. All the long-term sodium-exchanged samples had similar exfoliation onset temperatures between 260 °C and 300 °C (Fig. 13).

Irregular variation in the initial stages of expansion of different flakes from the same sample was detected during the experiments. This could obviously be attributed to the variability of the properties of those individual flakes.

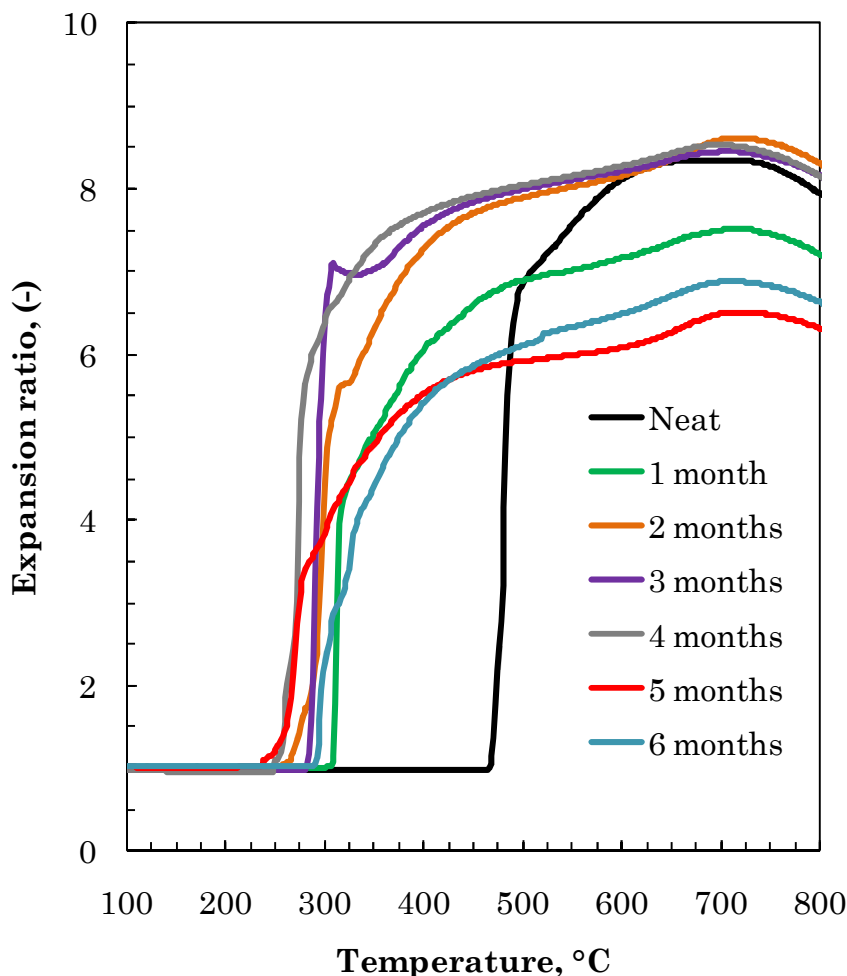


Figure 13. TMA expansion of vermiculite and its Na-exchanged forms

Fig. 14 shows the effect of the applied force on the expansion behaviour of the six-month sodium-exchanged vermiculite. The observed variation in the expansion onset temperature was attributed to the variability of the properties of individual flakes rather than to the change in the applied force.

The smallest flake tested had a cross-sectional area of 1.66 mm². At an applied force of 1 N, this corresponds to a pressure of only 0.6 MPa. The lowest onset temperature exceeded 250 °C, and at this point the vapour pressure of water is already 3.92 MPa. Thus, it is unlikely that the TMA applied force would have affected the expansion onset temperature.

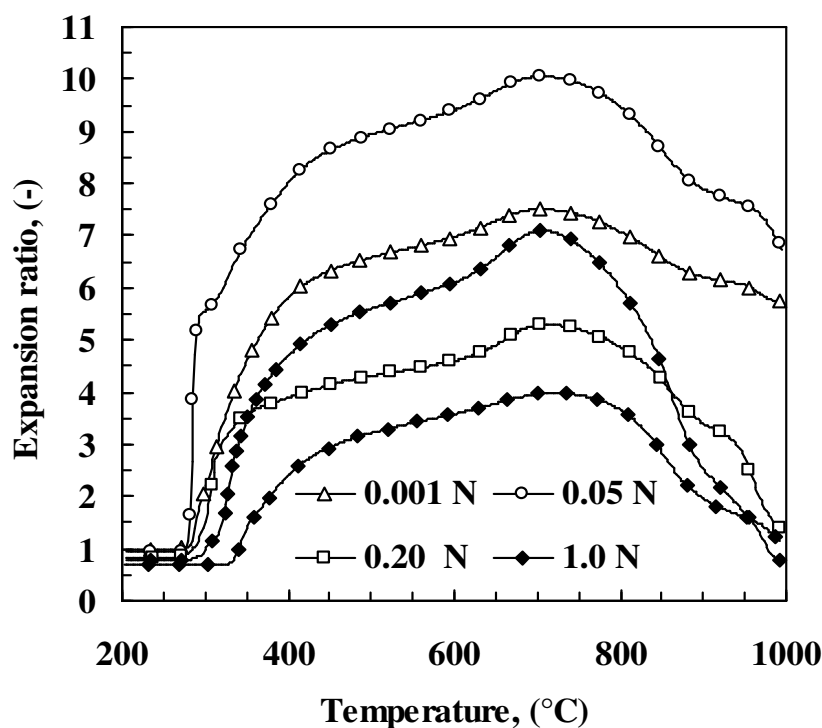


Figure 14. Effect of the TMA applied force on the expansion behaviour of vermiculite flakes reacted for 6 months with saturated brine

Fig. 15 shows the effect of the stepped-temperature-increase protocol on the expansion behaviour of six-month sodium-exchanged vermiculite. Again it reveals considerable variability in the behaviour of the individual flakes. Notably, significant expansion occurred during the isothermal periods. This is indicated by the staircase-like expansion as a function of time.

The expansion of Flake A commenced at the first isothermal hold temperature of 270 °C. The temporal evolution of this isothermal expansion is shown in Fig. 16, together with the isothermal expansion results for other flakes proceeding at different hold temperatures.

Remarkably, in at least two of these curves, the expansion was characterised by an induction time before a sigmoidal expansion occurred. It is assumed that water is continuously lost as time proceeds during the isothermal

period. The observed time delay then suggests that expansion was triggered when a critical water content level was reached inside the interlayer space.

The expansion of Flake A, at the hold temperature of 270 °C, actually took place in two distinct steps. This can be explained by assuming that the composition of the flakes is not homogeneous along the c-axis, i.e. that the vermiculite content varies with distance along the flake thickness.

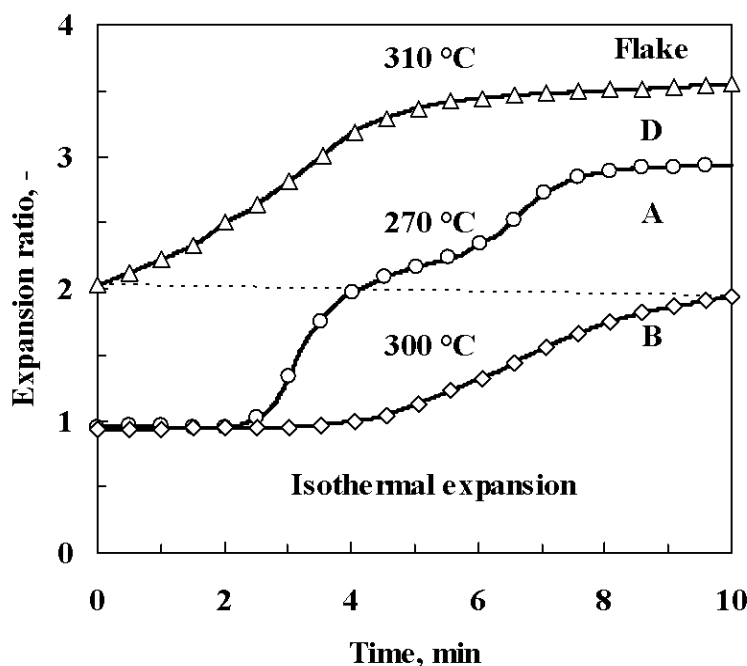


Figure 15. TMA characterisation of the isothermal expansion of long-term Na-exchanged vermiculite, at selected temperatures

4.4.2 *Ammonium, alkali metal and alkaline earth metal ion exchanged vermiculites*

It is evident from Fig. 16 that the sodium, potassium and ammonium ion exchanges lowered the exfoliation onset temperature of vermiculite to temperatures below 300 °C. Among these, sodium vermiculite (NaVER) shows a comparably better expansion ratio, while magnesium vermiculite (MgVER) shows a thermal behaviour similar to that of neat vermiculite (with the majority of magnesium ions as interlayer cations). This latter fact

demonstrates the great contribution of the interlayer cations to the expansion behaviour of vermiculites.

In the increasing ionic potential series of Na-, Ba-, Ca-, Mg-exchanged vermiculites, the expansion onset temperature seems to increase dramatically. Hence these TMA results also provide evidence that cations with lower ionic potential (see Table 3) produce ion exchanged vermiculites with comparatively low expansion onset temperatures.

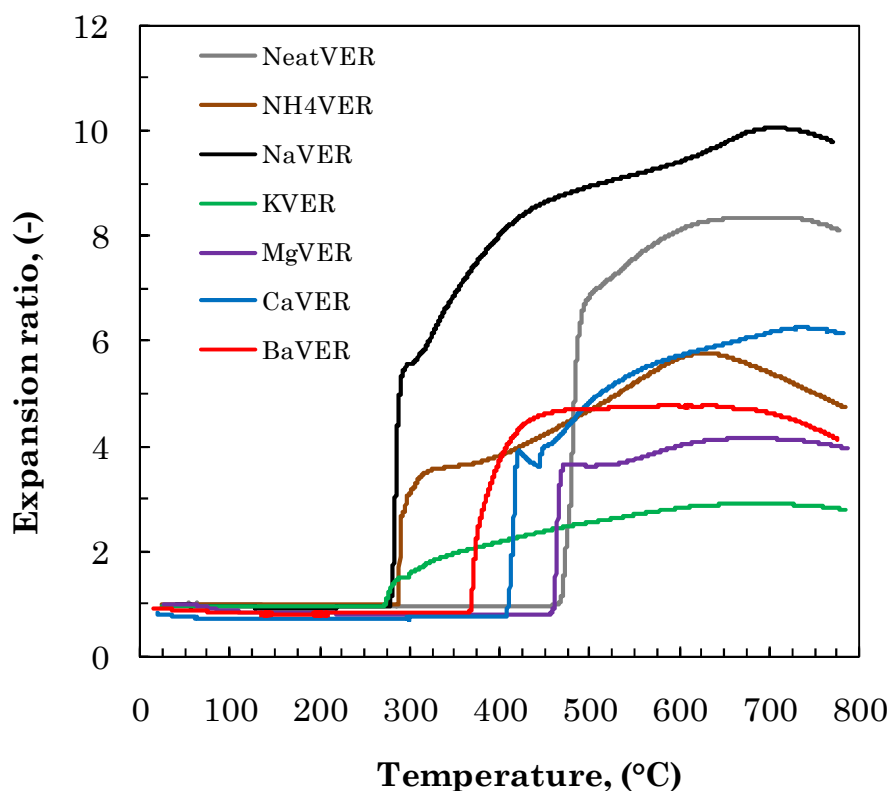


Figure 16. TMA expansion of ion exchanged vermiculites

The second step of expansion of NH₄VER occurs at slightly lower temperatures. This is also due to the release of ammonia and water resulting from the combination of hydrogen ions from ammonium ions and hydroxyl groups from the vermiculite surface. This is in agreement with the results of Pérez-Maqueda *et al.* (2004) who also observed that the quantity of water released was more than expected from the dehydroxylation of vermiculite itself.

The stages involved in this process are demonstrated above in Schemes XVII and XVIII.

4.5 X-Ray Diffraction (XRD)

4.5.1 Long-term Na-exchanged vermiculites

The main mineral impurities found via XRD analysis were dolomite and apatite. Fig. 17 depicts the evolution of the XRD spectra with time of brine treatment.

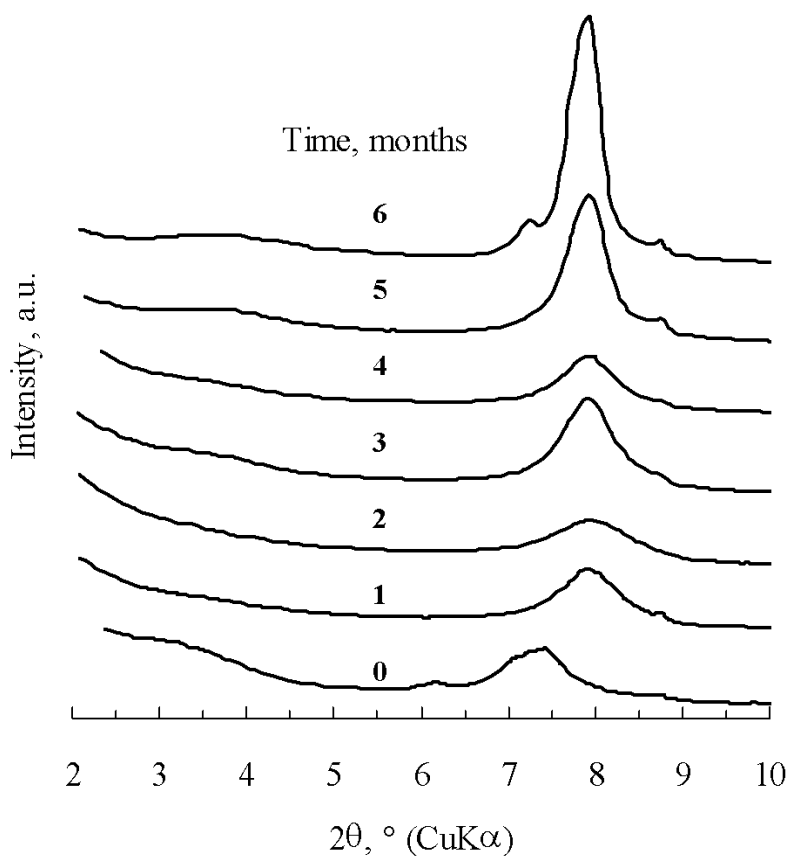


Figure 17. Evolution of the XRD spectra as a function of brine exposure time

The neat material featured a strong, broad reflection at $2\theta = 7.43^\circ$ (1.19 nm) and weaker reflections at $2\theta = 6.17^\circ$ (1.43 nm) and $2\theta = 8.77^\circ$

(1.02 nm). The 1.43 nm reflection is consistent with the Mg-vermiculite phase with two (slightly incomplete) water bilayers (Mathieson, 1958; Pérez-Maqueda *et al.*, 2003). The 1.02 nm reflection is from the mica (biotite/phlogopite).

Perfectly alternating 50/50 mixed-layer vermiculite, i.e. 'hydrobiotite', features reflections at 2.44 nm (001) and 1.22 nm (002) (Newman, 1987; Ruiz-Amil *et al.*, 1992). In the present sample the main reflection is located at higher 2θ angles. This and the extensive line broadening are indicative of a random distribution of the vermiculite layers.

While the sodium uptake reached a plateau by the end of the first month, the XRD pattern (Fig. 17) suggested continued evolution up to month six. The intensity of the main reflection increased with time but had settled at its ultimate d-spacing of 1.12 nm already by the end of the first month.

After six months of brine exposure, reflections were found at ca. 2.44 nm, 1.22 nm; 1.12 nm and 1.01 nm. The broad reflection at ca. 2.44 nm and the well-resolved 1.12 nm reflections are diagnostic for the formation of a more ordered structure, similar to 'hydrobiotite'. However, pattern simulations using NEWMOD software indicated a composition of ca. 45 % vermiculite.

4.5.2 Alkali metal and alkaline earth metal ion exchanged vermiculites

According to the results shown in Fig. 18, Mg-vermiculite (MgVER) showed similarities with the blank vermiculite, i.e. neat vermiculite subjected to the same physical treatment as the other samples. The main reflections were almost in the same positions and the main Mg-vermiculite peak was present in both samples at ca. $2\theta = 6.17^\circ$ (1.43 nm). However, the blank vermiculite showed more well-defined interstratification peaks, at $2\theta = 3.26^\circ$ (2.7 nm), $2\theta = 7.13^\circ$ (1.24 nm) and $2\theta = 7.41^\circ$ (1.19 nm), due to the presence of other interlayer cations (mainly K). This resemblance supports the fact that Palabora vermiculite is mainly of the Mg-type.

Rietveld quantitative analysis of blank vermiculite showed the following mineralogical composition (Table 7):

Table 7. Mineralogical composition of blank vermiculite

Mineral phase	Mass (%)	Assigned reflections (nm)
Vermiculite	15.88	1.43
Mica/Vermiculite interstratifications	72.10	2.71, 1.24, 1.19
Mica (biotite/phlogopite)	6.13	1.01
Apatite	2.73	
Dolomite	2.61	

In K-vermiculite (KVER), all typical vermiculite features had disappeared and the lattice had drastically collapsed (Gast and Klobe, 1971). By the same token, the typical well-ordered mica-like structure reflection at $2\theta = 8.74^\circ$ (10.10 nm) was mostly observed (Fig. 18).

Ca-vermiculite (CaVER) and Ba-vermiculite (BaVER) showed similar characteristics. The expected regular interstratification reflections at lower 2θ angles (long-spacing reflections) were not clearly observed, although it was seen that K^+ ions were still present in those samples. They both showed a distinctive and intense (002) reflection and a typical mica reflection at ca. $2\theta = 8.7^\circ$ (10.10 nm).

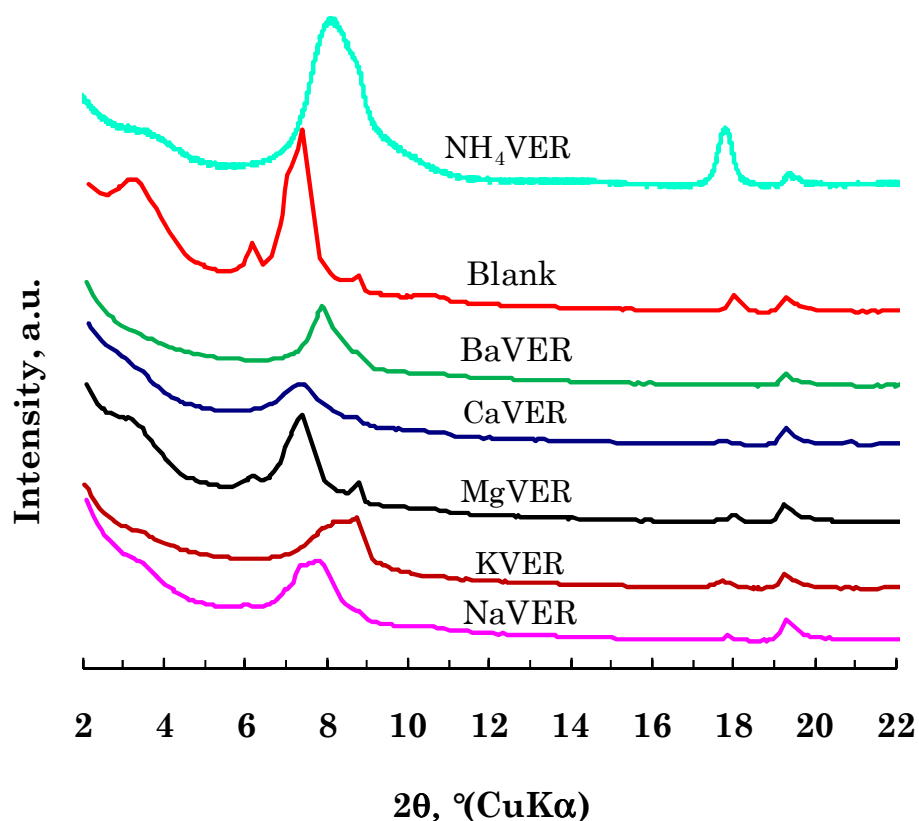


Figure 18. XRD patterns of blank, alkali metal and alkaline metal treated vermiculites

All samples, prepared with different salts, showed the d_{060} reflection at 1.53 nm, confirming the preservation of the trioctahedral mineral structure.

A comparison of the XRD results of neat and blank vermiculites is presented in Fig. 19. It shows the effect of applying the shaker during vermiculite treatment. Blank vermiculite showed well-resolved reflection peaks, especially at small 2θ angles, and no reflection shift was observed. This result should be attributed to the effect of washing and the removal of soluble impurities and small powdered vermiculite produced during milling process, as well as the shaking process.

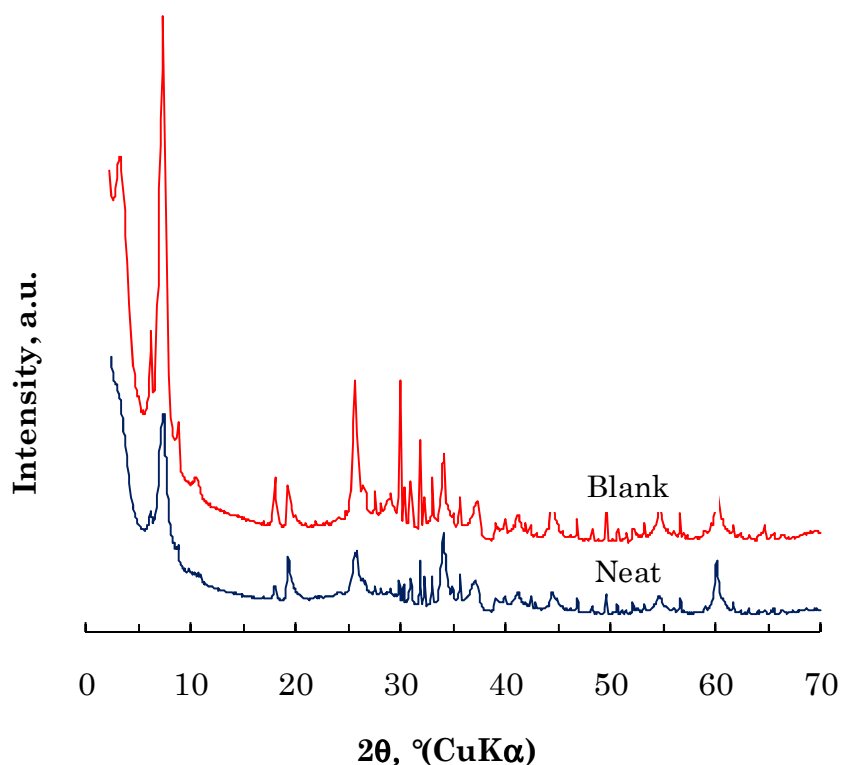


Figure 19. XRD patterns of neat vermiculite and blank vermiculite (the latter subjected to similar physical treatment given to all ion exchanged samples)

Characteristic interstratified vermiculite reflection peaks were noticeable in both samples at $2\theta = 3.30^\circ$ (2.68 nm) and $2\theta = 7.41^\circ$ (1.19 nm). Typical Mg-vermiculite and mica reflection peaks were located at $2\theta = 6.18^\circ$ (1.43 nm) and $2\theta = 8.78^\circ$ (1.01 nm) respectively.

4.6 Scanning Electron Microscopy (SEM)

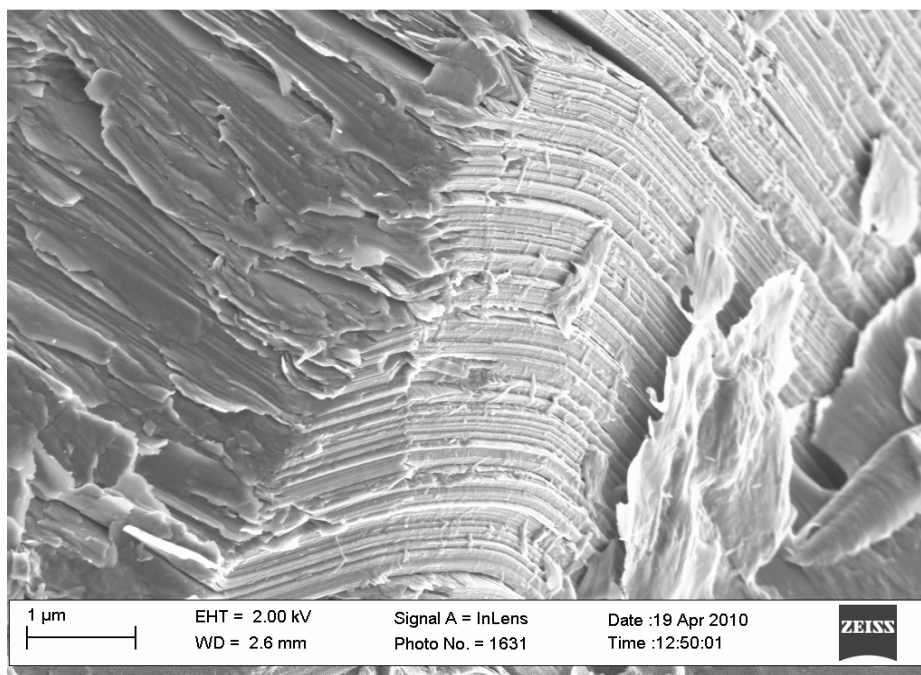


Figure 20. SEM image of vermiculite flakes reacted for 6 months with saturated brine

Generally, the vermiculite particles are flake-like with striations, humps and folds on the surface. The brine treatment did not affect the macroscopic appearance of the Palabora material.

Fig. 20 shows a SEM surface topographic image of flakes that were exposed to brine for six months. The damage caused by the milling process is manifested by the folded and lacerated edges.

The expansion process of sodium-exchanged vermiculite was studied as a function of time and temperature in an ESEM (Appendix V). Careful study of the full video clearly shows heterogeneous exfoliation of a single flake.

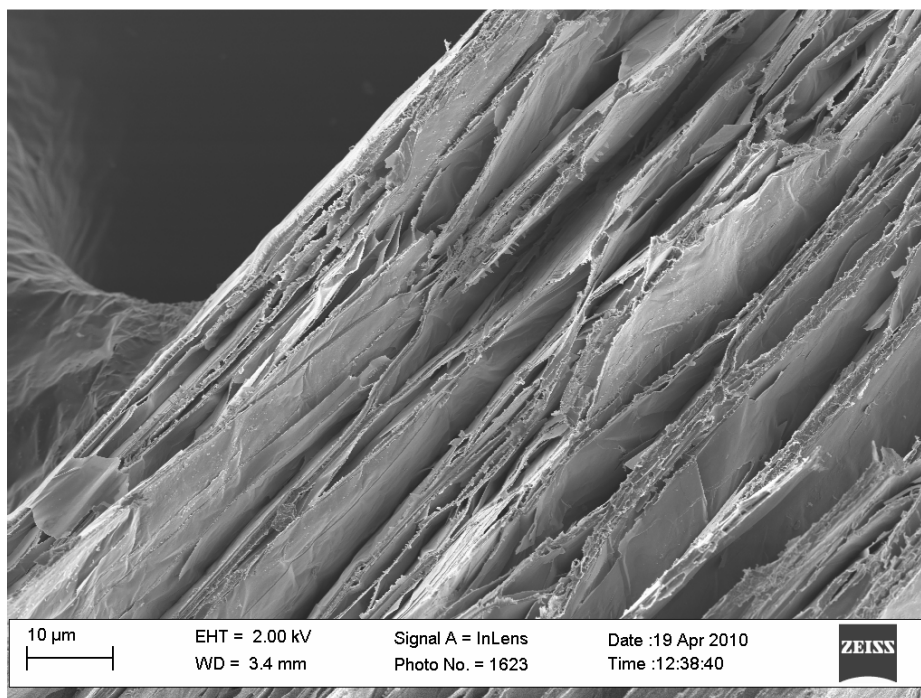


Figure 21. SEM image of heat-expanded Na-vermiculite

The expansions of sodium-exchanged vermiculite occurred in stages at different positions along the flake thickness (Fig. 21). It is remarkable that significant expansion still occurred despite the low pressure of only 0.5 kPa in the ESEM chamber.

4.7 Particle size distribution

The particle size distribution for the micron-grade vermiculite showed an apparent bimodal distribution (Fig. 22) and was not materially affected by exposure to the concentrated brine.

The lower peaks range from ca. 5 μm to just above 200 μm . Since the material consisted essentially of high-aspect-ratio flakes, the lower hump is indicative of the variation in flake thickness.

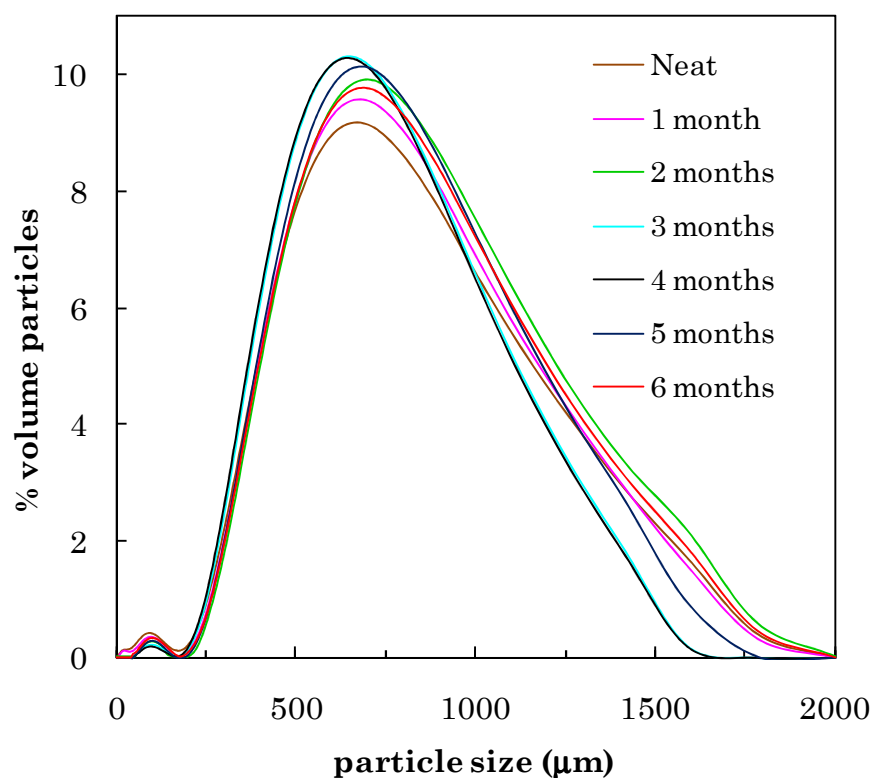


Figure 22. Particle size distribution of the neat and long-term Na-exchanged vermiculites

Fig. 23 shows the particle size distribution for blank vermiculite and its ion exchanged forms. After ion exchange, the particle size distribution of vermiculites is relatively broadened. All ion exchanged samples show also more than 2% of particles with dimensions greater than 2000 μm . Alkaline earth ion exchanged vermiculites have a size of ca. 1 002 μm , while alkali metals ion exchanged vermiculites have a size of ca. 893 μm .

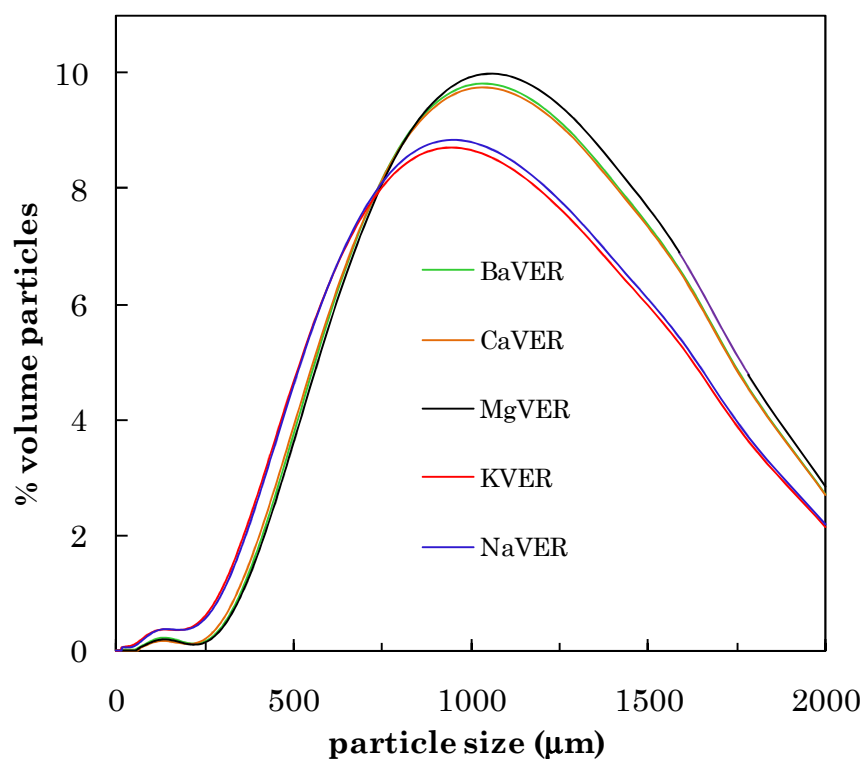


Figure 23. Particle size distribution of vermiculite and its ion exchanged forms

4.8 Fourier Transform–Infrared (FT-IR) and Raman Spectroscopy

4.8.1 Long-term Na-exchanged vermiculites

According to Fig. 24, the FT-IR spectra of the Na-exchanged forms were almost identical to that of the neat vermiculite. All the IR spectra showed a strong band at 3420–3446 cm^{-1} , ascribed to the characteristic O–H stretching vibration of the hydration water and bound silanol groups (Hougardy *et al.*, 1970; Farmer, 1974).

Other strong bands were observed at around 1641–1646 cm^{-1} . They are due to the O–H bending vibrations of the hydration water molecules (Hougardy *et al.*, 1970; Farmer, 1974; Van der Marel and Beutelspacher, 1976).

At 995–999 cm^{-1} there is a strong band attributed to the Si–O–Si and Si–O–Al stretching vibrations (Farmer, 1974; Van der Marel and Beutelspacher, 1976).

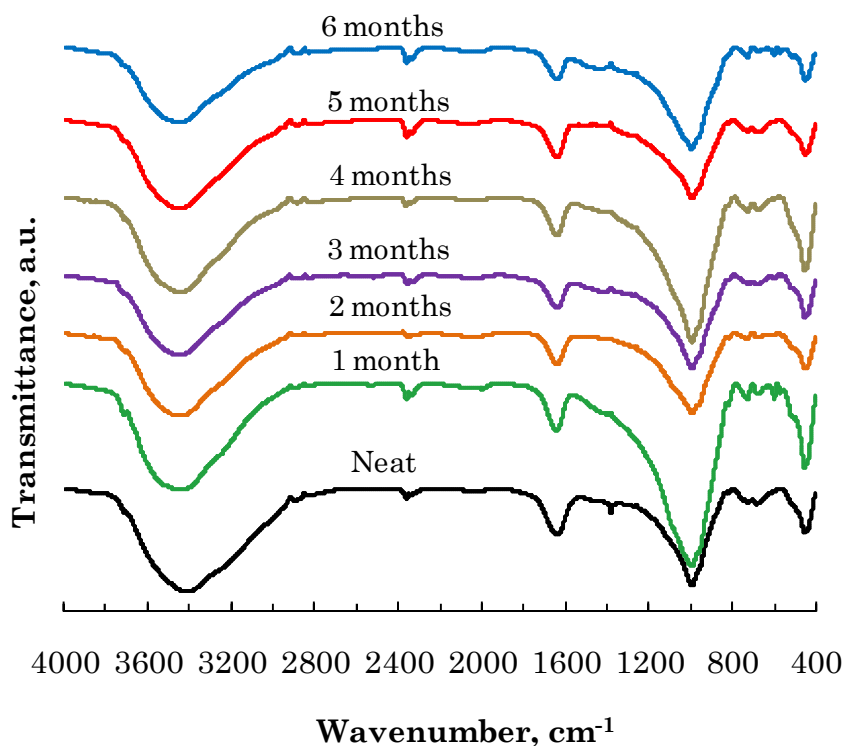


Figure 24. FT-IR plots of neat vermiculite and all its Na-exchanged forms, obtained after immersion in saturated brine

4.8.2 *Ammonium, alkali metal and alkaline earth metal ion exchanged vermiculites*

All FT-IR spectra of the neat, alkali and alkaline metal ion exchanged vermiculites showed the structural O–H group’s stretching vibrations at 3709 cm^{-1} . The ammonium vermiculite (NH_4VER) O–H stretching vibrations were shifted to 3697 cm^{-1} since the position of this peak maximum is a function of the nature of the interlayer cation (Bradley and Serratosa, 1960; Hougardy *et al.*, 1970; Farmer, 1974).

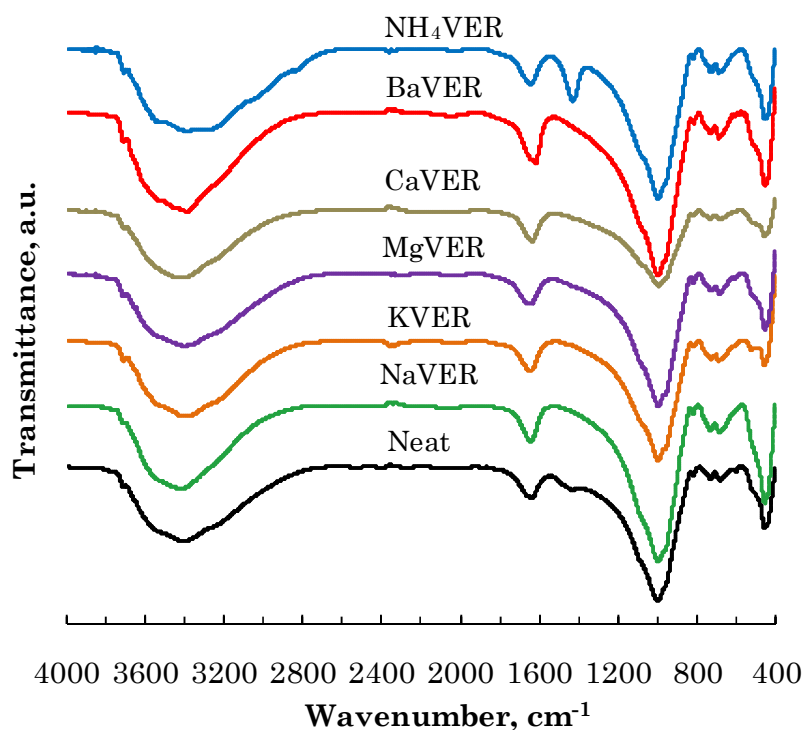


Figure 25. FT-IR spectra of neat vermiculite, ammonium, alkali metal and alkaline metal ion exchanged vermiculites

Characteristic vermiculite absorption bands were also observed in the results depicted in Fig. 25. Strong hydration H_2O bands are noticeable at $3409\text{--}3424\text{ cm}^{-1}$ (O–H stretching vibrations and also bound silanol groups) and at $1638\text{--}1646\text{ cm}^{-1}$ (O–H bending vibrations) (Hougardy *et al.*, 1970; Farmer, 1974; Van der Marel and Beutelspacher, 1976).

Well-defined Si–O–Si and Si–O–Al stretching vibrations are present at $996\text{--}997\text{ cm}^{-1}$, as well as a medium-intensity band at ca. 456 cm^{-1} attributed to the Si–O–Mg structural bending vibration (Farmer, 1974; Van der Marel and Beutelspacher, 1976).

In addition, NH_4VER presents bands at 3529 cm^{-1} , 3283 cm^{-1} , 3064 cm^{-1} and 2835 cm^{-1} , as well as a well-resolved band at 1430 cm^{-1} attributed to NH_4^+ vibration (Stone and Wild, 1978; Pérez-Rodríguez *et al.*, 2004, Petit *et al.*, 2006).

CHAPTER 5 CONCLUSIONS

The effect of inorganic modification on the properties of Palabora vermiculite was studied by scanning electron microscopy (SEM), X-ray fluorescence (XRF) spectroscopy, Fourier transform–infrared (FT-IR) spectroscopy, inductively coupled plasma – optical emission spectroscopy (ICP-OES), X-ray diffraction (XRD) analysis and thermo-mechanical analysis (TMA).

Modification of Palabora vermiculite was achieved by ion exchanging with ammonium and selected alkali metal and alkaline earth metal chlorides and by submerging the macroscopic flakes in saturated brine for periods of several months.

In the long-term treated vermiculite, the sodium content reached a plateau value by the end of month one, but the XRD pattern continued to change, reaching a final form only after an exposure period of six months. The final XRD pattern indicated the presence of at least two distinct interstratified phases containing different amounts of vermiculite.

All samples, prepared with different salts and/or by different methods, showed the typical d_{060} clay mineral reflection at 1.53 nm, confirming the preservation of the trioctahedral unit cell structure.

Barium ions showed relatively high affinity to the vermiculite surface and ammonium ions were able to exchange potassium ions from biotite layers.

Thermal expansion of the neat vermiculite commenced at temperatures above 450 °C and reached levels exceeding an eight-fold expansion at ca. 700 °C. Beyond this temperature a slight contraction occurred.

It was confirmed that the blowing agent was the interlayer water in the neat, alkali metal and alkaline earth metal ion exchanged vermiculite samples. In the ammonium ion exchanged vermiculite, it was found that ammonia and water were the blowing agents and that they were simultaneously released during thermal degradation. However, ammonium-vermiculite did not show a

relatively better thermal expansion ratio, despite the presence of both ammonia and water in the interlayer.

In the increasing ionic potential series: sodium-vermiculite, barium-vermiculite, calcium-vermiculite and magnesium-vermiculite, the expansion onset temperature also increased dramatically. So, sodium, potassium and ammonium ion exchange lowered the expansion onset temperature to below 300 °C. It was the aim of this study to lower the expansion onset temperature of Palabora vermiculite to temperatures in the range of 200 °C to 350 °C and therefore this aim has been achieved.

The simple process of exchanging the interlayer magnesium ions with the aforementioned ions of relatively low ionic potential lowered the exfoliation onset temperature to a range that may have technological significance, for instance in applications like intumescent fire barriers.

CHAPTER 6 REFERENCES

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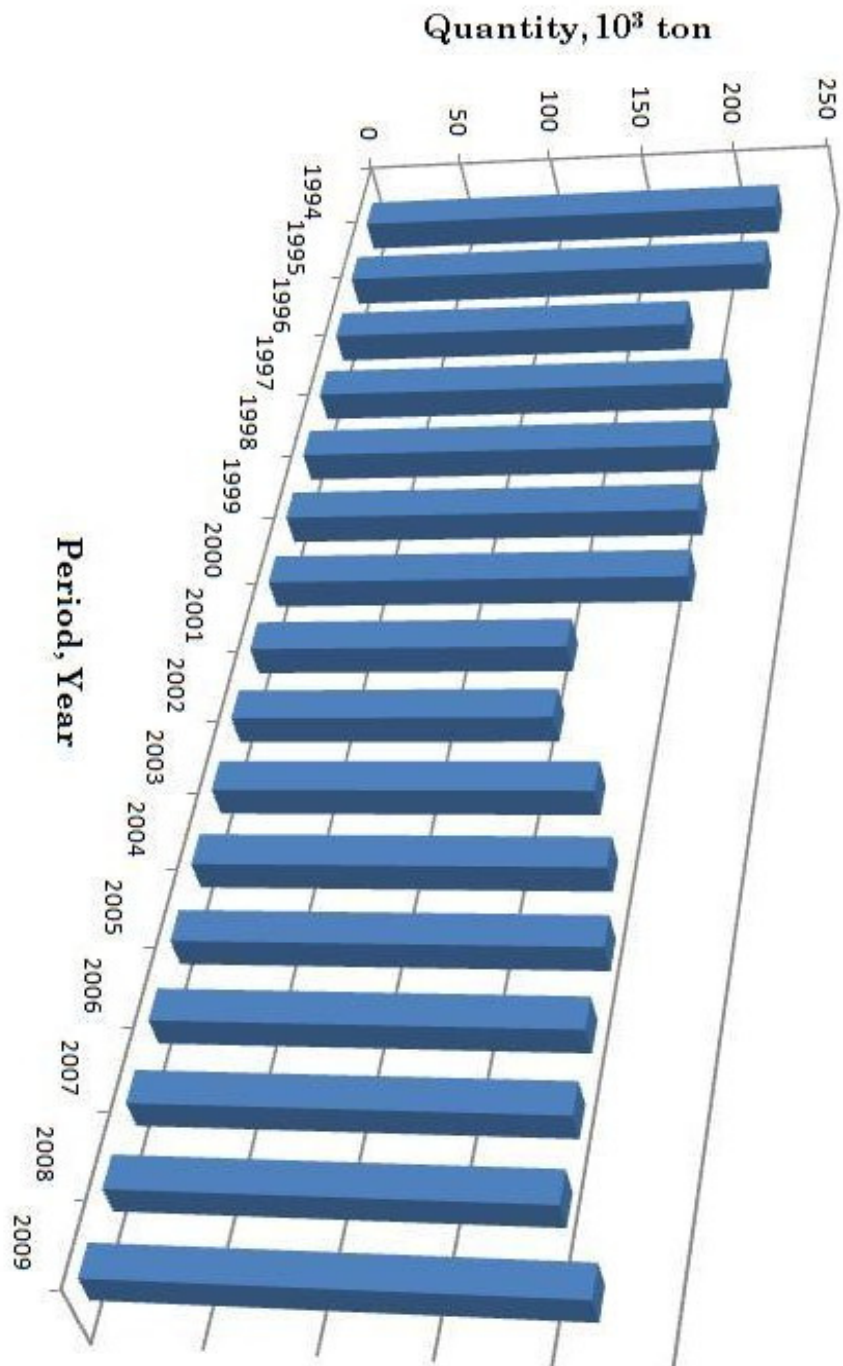
APPENDICES

Appendix I. Salts used to prepare ion exchanged vermiculites

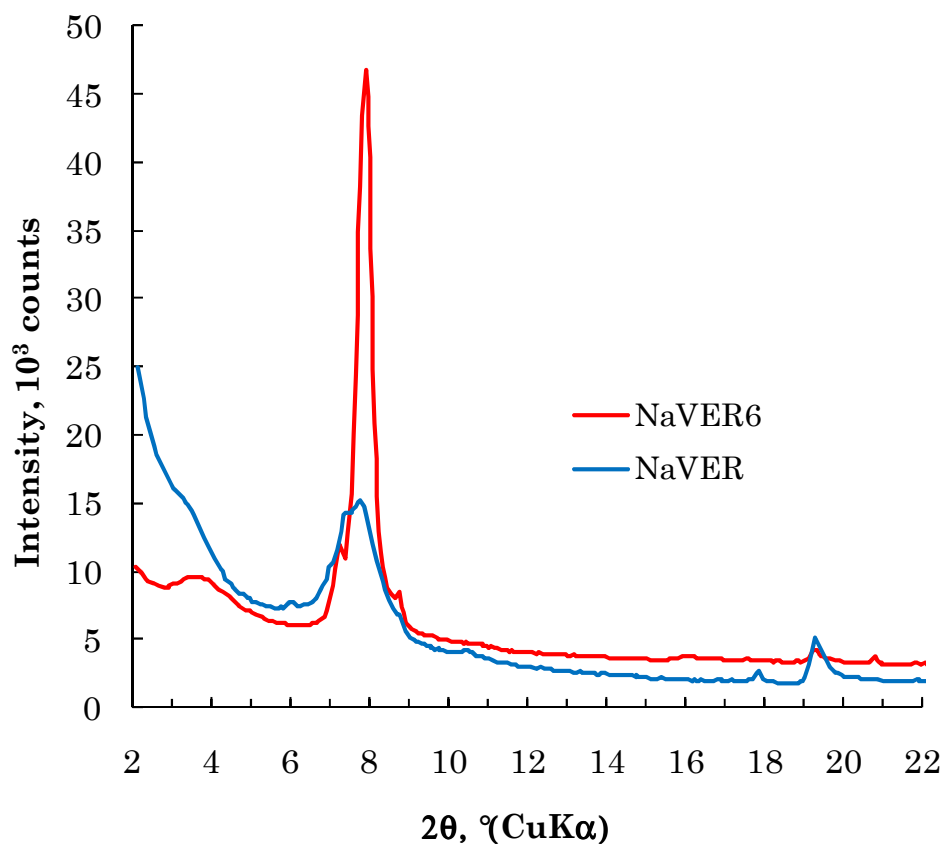
Salt	Molecular formula	Molar Mass (g/mol)	Solubility (g/L)	Quantity used (g)
Sodium chloride	NaCl	58.44	35.9	53.85
Potassium chloride	KCl	74.55	34.4	51.6
Magnesium chloride	MgCl ₂	95.21	54.3	81.45
Calcium chloride	CaCl ₂	110.98	74.5	111.75
Barium chloride	BaCl ₂	208.23	35.8	53.7
Ammonium chloride	NH ₄ Cl	53.49	37.2	55.8

Saturated solutions of the respective chlorides were preferred and prepared since the vermiculite selectivity coefficient rises with an increase in the selected ion loading. All experiments were run at the pH of the salt solution since the rate of exchange is not affected by the pH in the range of 4 to 9 (Wild and Keay, 1964; Gast and Klobe, 1971).

Appendix II. Vermiculite production in South Africa from 1994 to 2009 (Potter, 1996–2009 and Cordier, 2010)



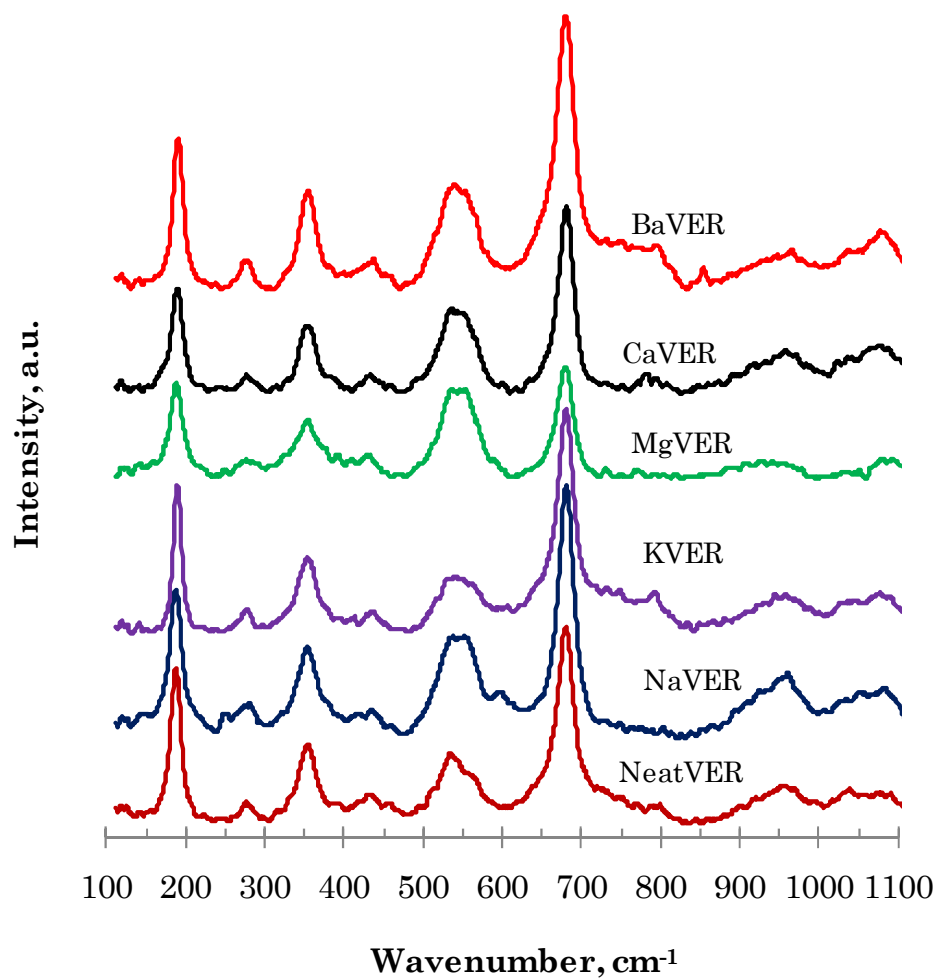
Appendix III. Comparison of XRD patterns of ion exchanged Na-vermiculite, prepared in different conditions



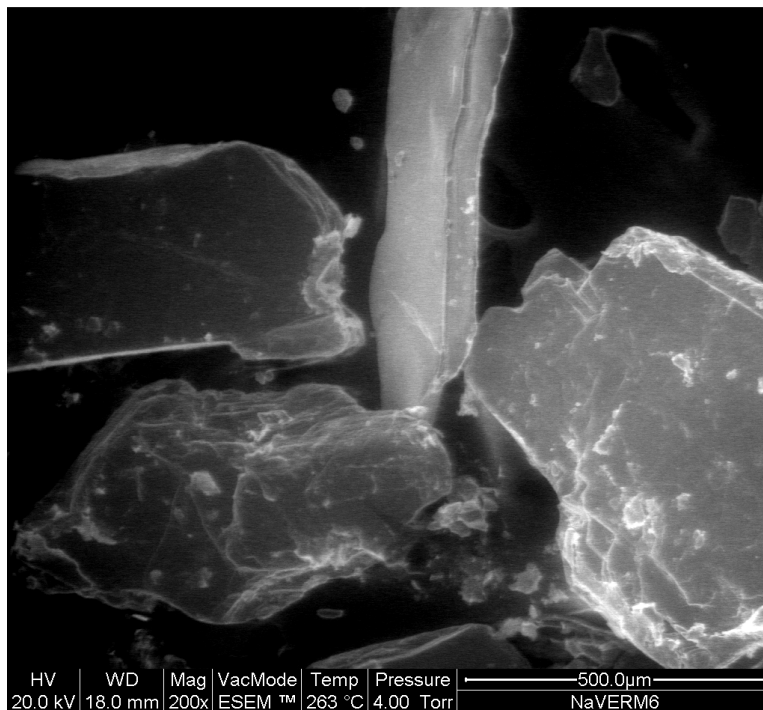
NaVER6 is the sample prepared by long-term treatment for up to six months. This reaction was performed in closed plastic boxes containing vermiculite submerged in a large volume of saturated sodium chloride solution. The solution was agitated daily and every fortnight approximately 1 000 ml of the supernatant liquid was exchanged with fresh saturated brine.

NaVER was prepared in 14 days using an orbital shaker. The reaction was performed in a closed glass container with saturated sodium chloride solution.

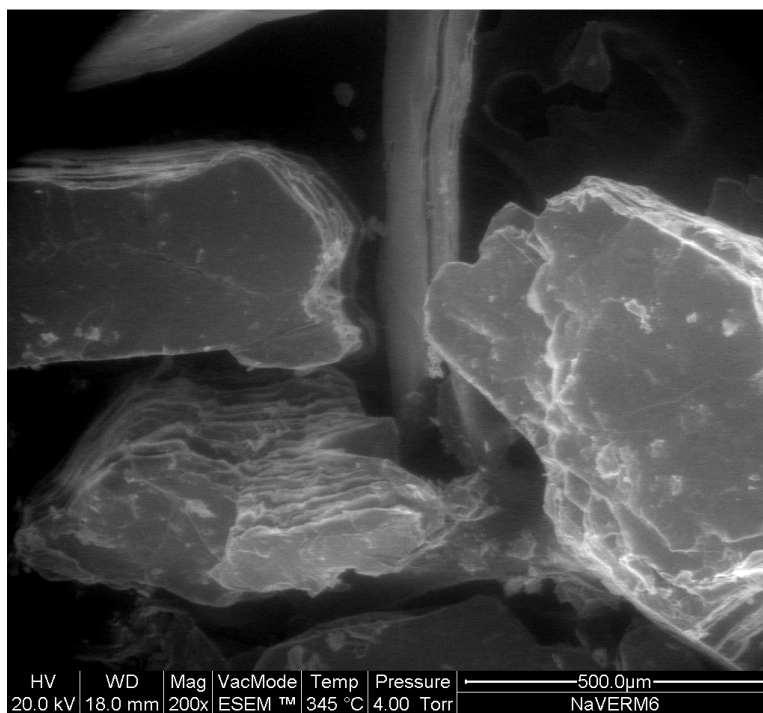
Appendix IV. Raman spectra of alkali and alkaline metal ion exchanged vermiculites



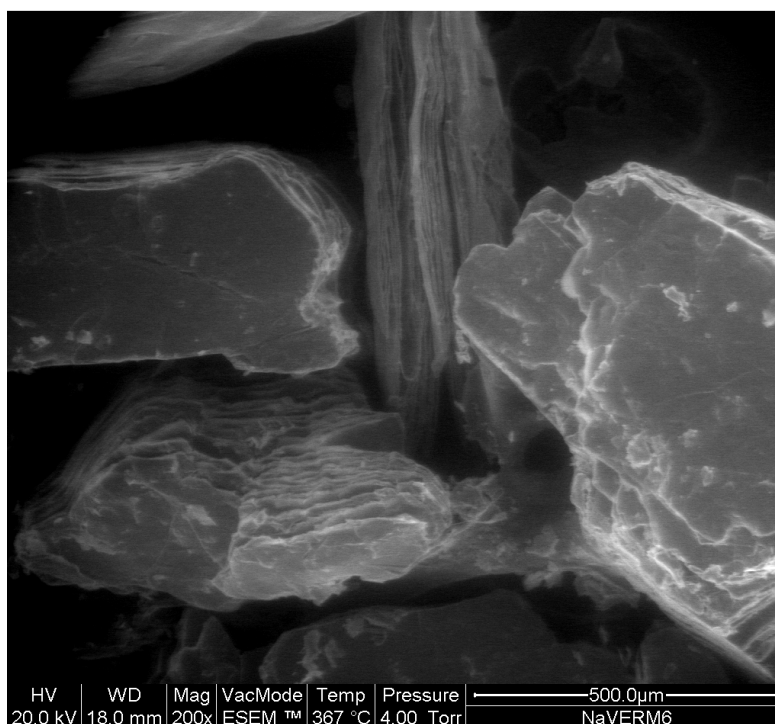
Appendix V. ESEM micrographs of the expansion of superfine-grade vermiculite reacted for six months with brine



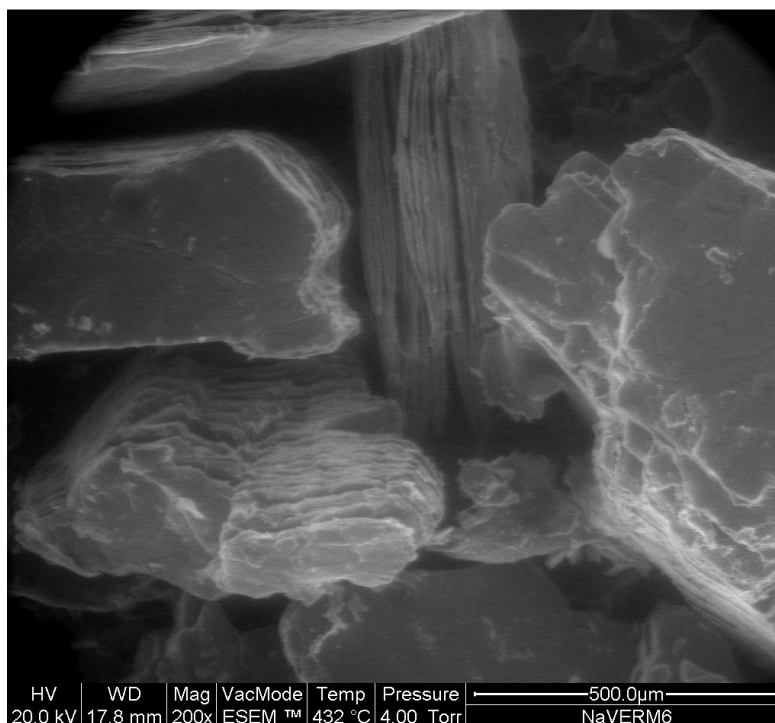
Appendix V-a) Just before exfoliation, which commenced at 263 °C



Appendix V-b) During exfoliation at 345 °C



Appendix V-c) During exfoliation at 367 °C



Appendix V-d) After exfoliation at 432 °C

Appendix VI. Mandoval Vermiculite technical data sheet

MANDOVAL VERMICULITE

TECHNICAL DATA

TO: _____

FAX NO: _____

Raw Vermiculite

Vermiculite is a micaceous mineral. Mandoval's vermiculite consists of golden/brown flakes carefully classified into 5 grade each having a specified range of particle size.

Exfoliation of Vermiculite

Exfoliation occurs at right angles to the cleavage planes, causing the flakes to expand into concertina-shaped granules.

Commercial exfoliation of vermiculite is achieved by passing the crude vermiculite in a controlled manner through a furnace chamber at elevated temperatures. Vermiculite reabsorbs some moisture after exfoliation.

Sintering Temperature

About 1,260°C.

Melting Point

About 1,315°C.

Specific Heat

0.2.

Specific Gravity

2.6.

pH Value

8-8.6 owing to the presence of associated carbonaceous rock, the reaction is normally alkaline as these break down into alkali oxides/hydroxides.

Thermal Conductivity

Vermiculite has low thermal capacity and high thermal insulation properties. Thermal conductivity at normal atmospheric temperatures:
 $k = 0.062 - 0.065 \text{ W/m}^2\text{C}$

Incombustibility
 Vermiculite is incombustible.

Water Holding Capacity

Exfoliated vermiculite will readily hold water within the interlamellar voids. The water retained as a percentage of the air dry weight is 240%.

Cation Exchange Properties

The exchangeable cation normally present in vermiculite is magnesium. The cation exchange capacity is 90-100 milliequivalents per 100 grams.

Vermiculite is clean to handle, non-abrasive, reflective, rot-proof, odourless, mouldable, non-irritant.

Typical Chemical Analysis

The chemical analysis of raw and exfoliated vermiculite is identical. The major elements are:

SiO ₂	39.37%*
TiO ₂	1.25%
Al ₂ O ₃	12.08%
Fe ₂ O ₃	5.45%
FeO	1.17%
MnO	0.30%
MgO	23.37%
CaO	1.46%
Na ₂ O	0.80%
K ₂ O	2.46%
H ₂ O + 105°C	5.17%
H ₂ O - 105°C	6.02%
CO ₂	0.60%
P ₂ O ₅	0.15%
Li ₂ O	0.03%
* Free silica content	<1.0%



Insolubility
 Vermiculite is insoluble in water and organic solvents

Sizes and Densities of the standard grades as packed per 100 litre bag.

Grade	Approx Size of Granule	Bag Mass	*kg/m ³ *g/litre
Large	8mm & smaller	7kg	Max. 80
Medium	4mm & smaller	8kg	Max. 90
Fine	2mm & smaller	9kg	Max. 112
Superfine	1mm & smaller	10kg	Max. 125
Micron	0.5mm & smaller	10kg	Max. 125

Prices on request
 Prices quoted are exclusive of VAT

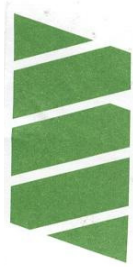
(Prices are subject to change without notice)

MANDOVAL VERMICULITE CC

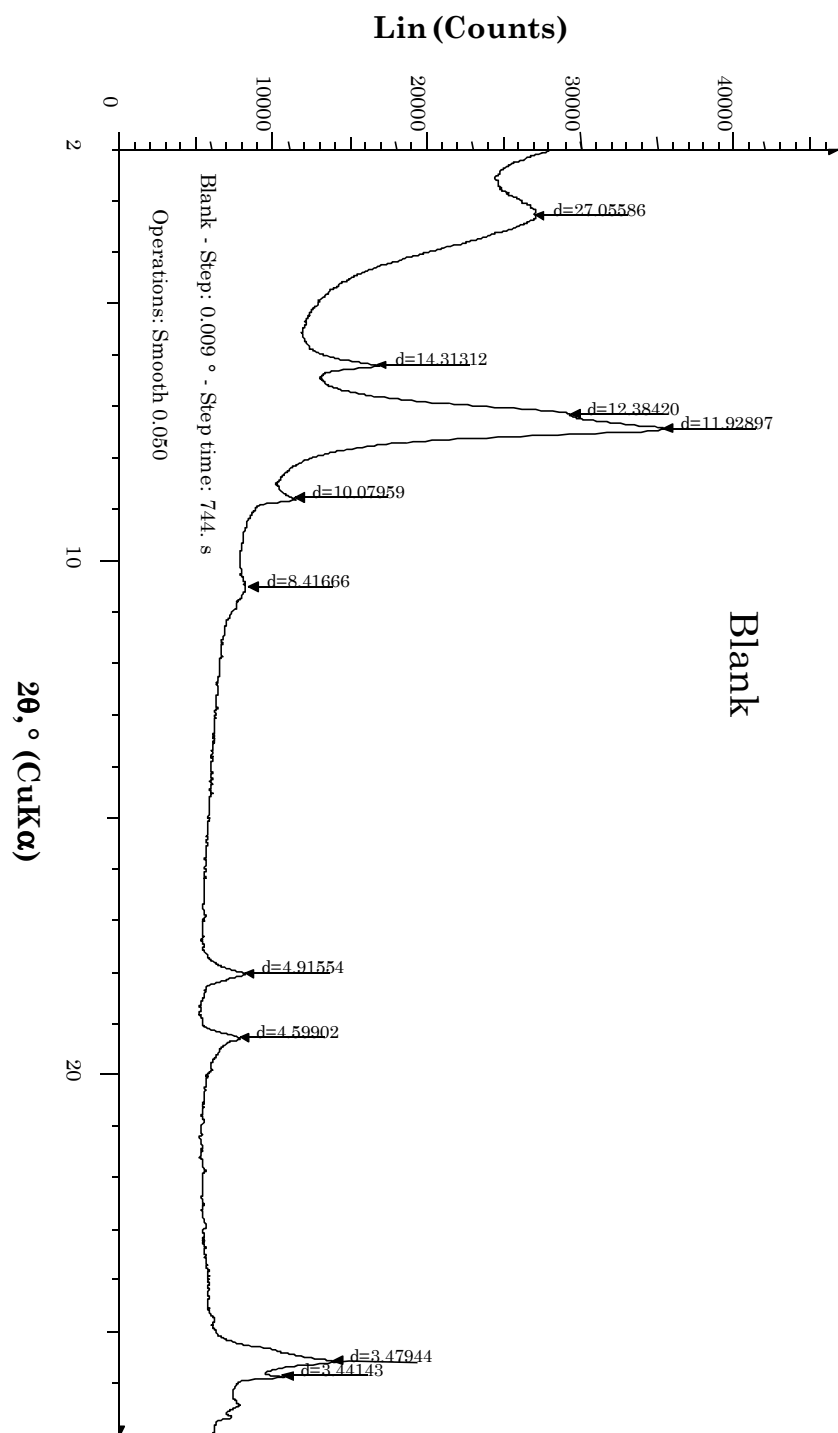
Reg. No. CK2000/045769/23

2 Johnson Street, Alrode
 P.O. Box 124114, Alrode
 Tel: (011) 864-5205
 Fax: (011) 908-3049

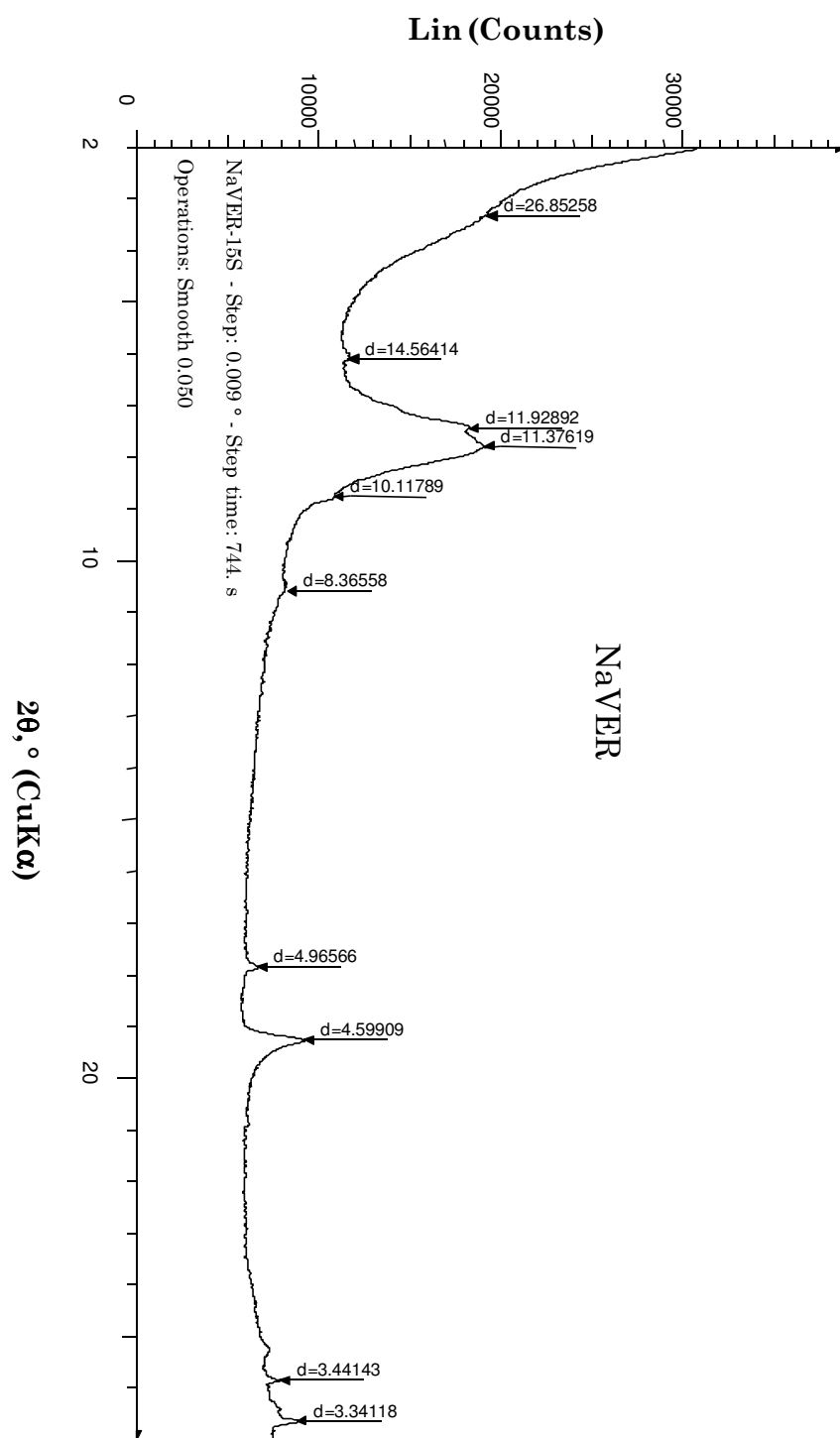
E-Mail: mandoval@mandoval.co.za



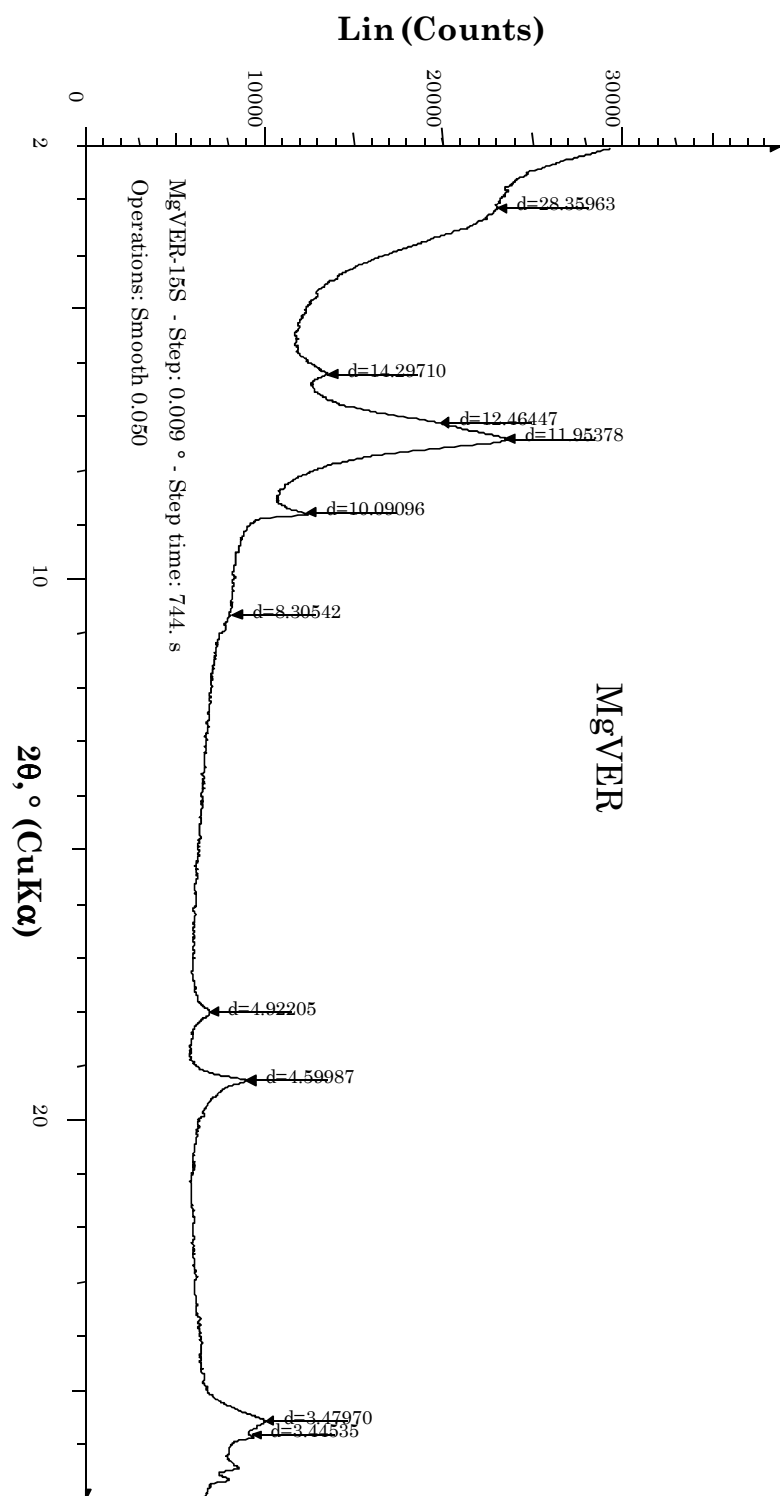
Appendix VII. Original XRD data of alkali metal and alkaline metal exchanged vermiculites



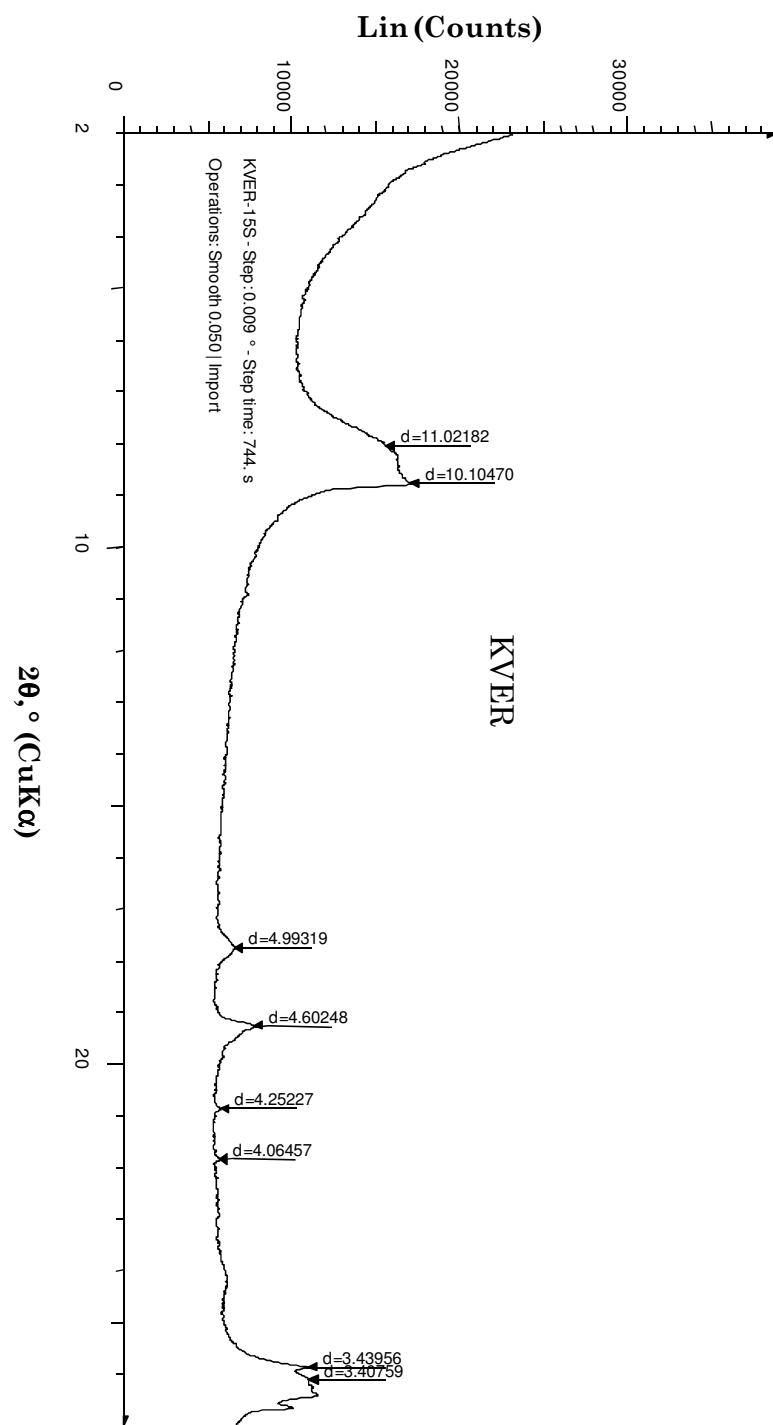
Appendix VII-a) XRD pattern of blank vermiculite



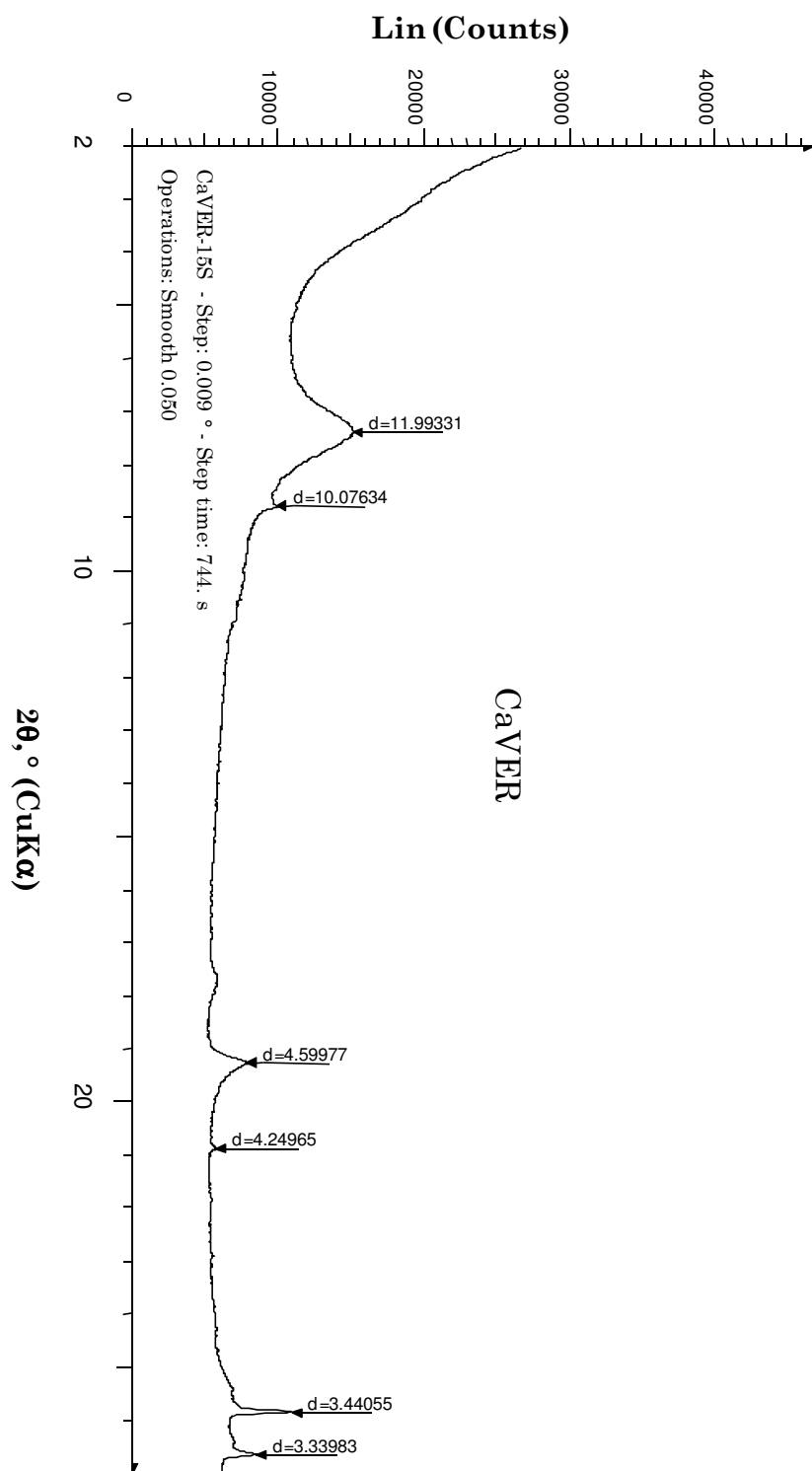
Appendix VII-b) XRD pattern of Na-vermiculite



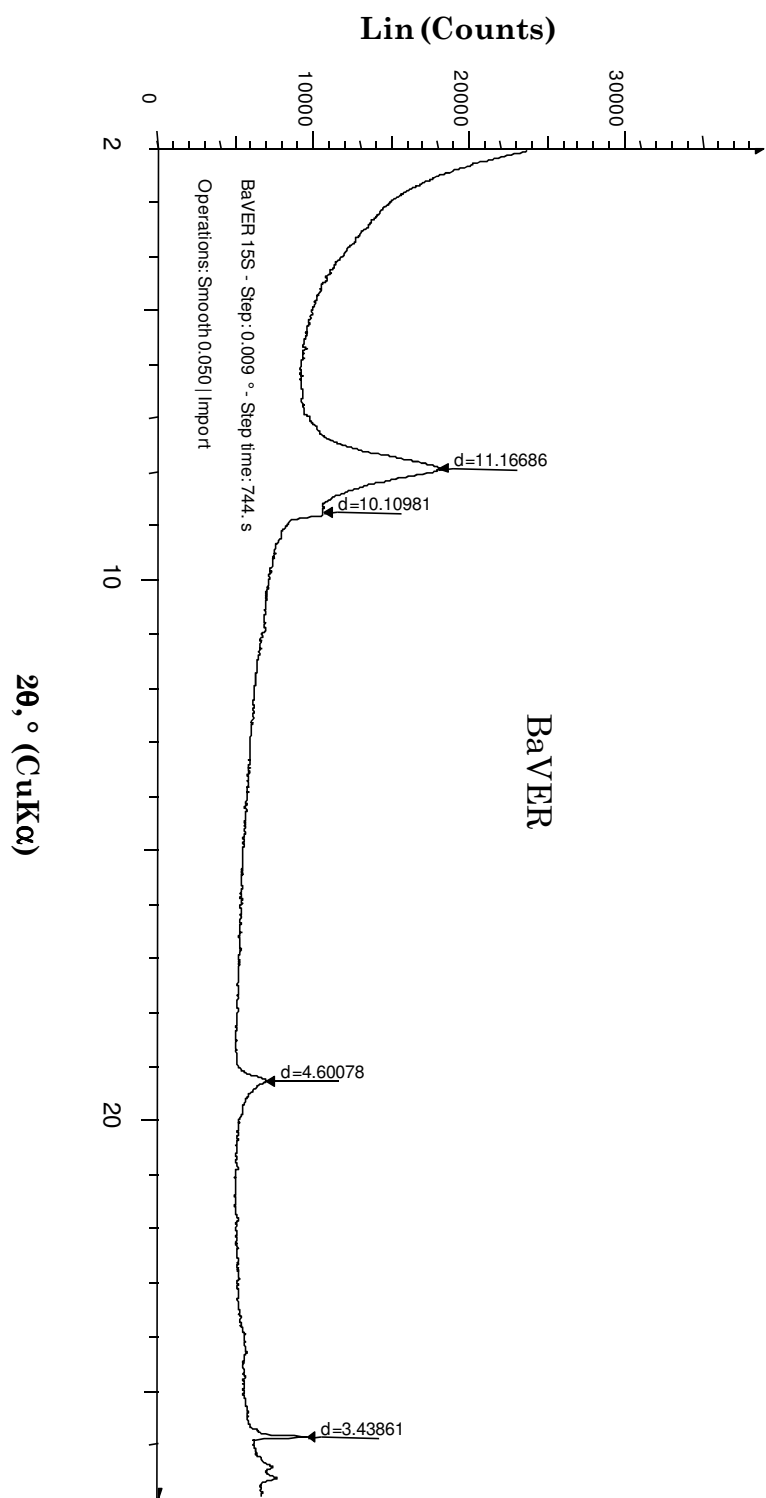
Appendix VII-c) XRD pattern of Mg-vermiculite



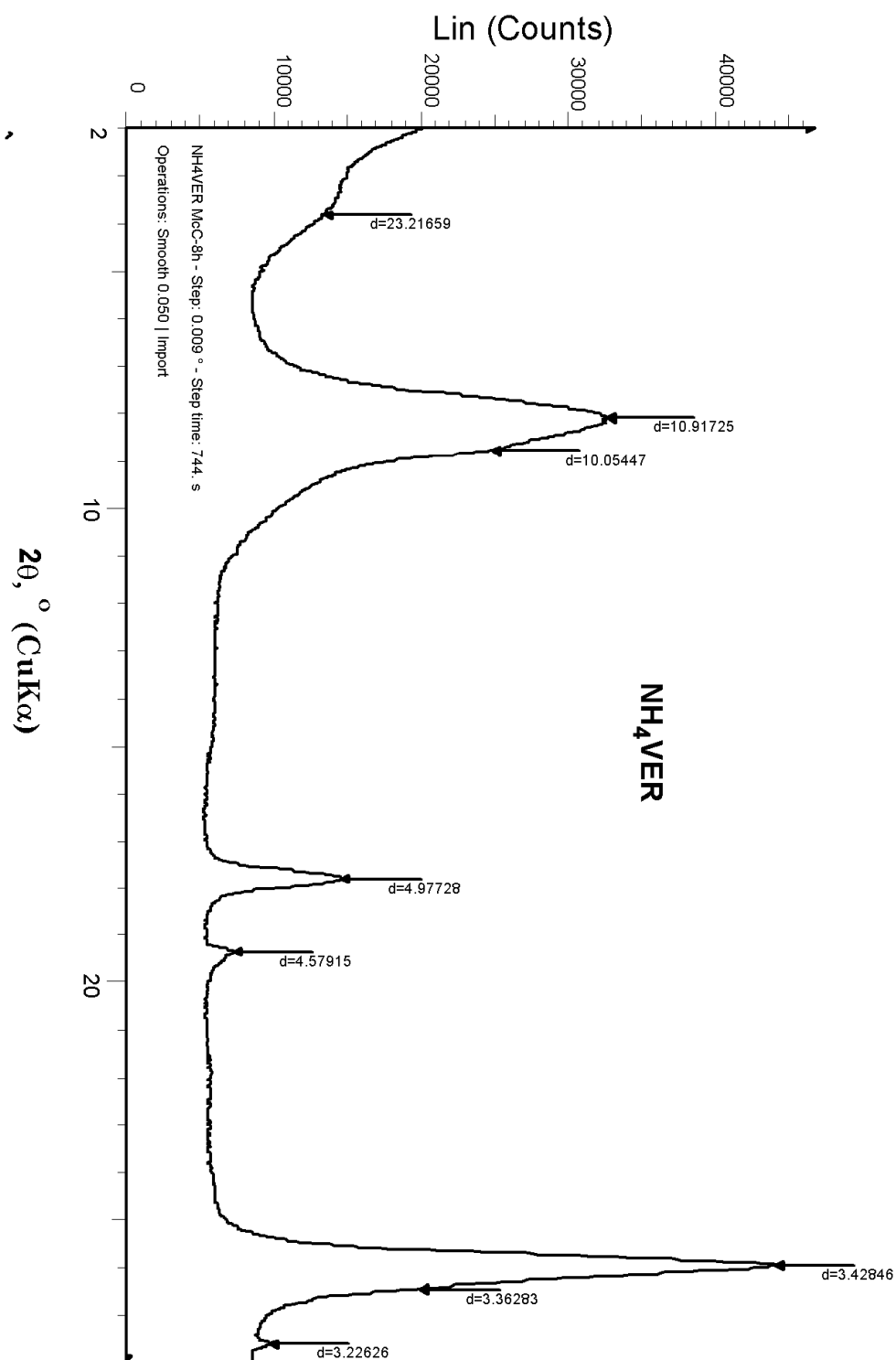
Appendix VII-d) XRD pattern of K-vermiculite



Appendix VII-e) XRD pattern of Ca-vermiculite



Appendix VII-f) XRD pattern of Ba-vermiculite



Appendix VII-f) XRD pattern of NH₄-vermiculite

Appendix VIII. Publication resulting from this research

Muiambo, H.F., Focke, W.W., Atanasova, M., Van der Westhuizen, I., Tiedt, L.,
2010. Thermal properties of sodium-exchanged Palabora vermiculite.
Appl. Clay Sci. 50, 51–57.