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LIST OF ABBREVIATIONS

AD	Air-dry
AFM	Atomic force microscopy
AIPEA	Association Internationale pour l'Étude des Argiles
ASTM	American Society for Testing and Materials
ATR	Attenuated total reflectance
BET	Brunauer–Emmett–Teller
BNCF	Bionanocomposite films
BSE	Backscatter electrons
CCS	Central Control Standard
CEC	Cation exchange capacity
CGS	Council for Geoscience
CHN	Carbon-hydrogen-nitrogen
CMS	Clay Mineral Society
CNMMN	Commission on new minerals and mineral names
CRM	Certified reference material
CV	Coefficient of variation
DC10	N,N'-dodecyldimethylammonium chloride
DLS	Dynamic light scattering
DLVO	Derjaquin, Landau, Verwey and Overbeek theory
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
DTG	Derivative thermogravimetry
EDS	Energy-dispersive spectrometry (system)
EG	Ethylene glycol
FESEM	Field emission scanning electron microscopy
FETEM	Field emission transmission microscopy

G	Glycerol
GEV	Generalised extreme value
gMLE	Generalised maximum likelihood
FPA	Fundamental parameters approach
FTIR	Fourier transform infrared spectroscopy
HE	Hydration energy
JNCs	Joint nomenclature committees
ICDD	International centre for diffraction data
ICP-OES	Inductively coupled plasma–optical emission spectrometer
ICSD	Inorganic crystal structure database
IMA	International mineralogical association
IR	Infrared spectrometer/spectroscopy
ISO	International Organisation for Standardisation
IUCr	International Union of Crystallography
LD	Laser diffraction
LDH	Layered double hydroxides
LOI	Loss on ignition
MAS NMR	Magic angle spinning NMR
MMT	Montmorillonite
NMR	Nuclear magnetic resonance
NH ₄ -Rec/CS NCF	NH ₄ -rectorite-chitosan nanocomposite films
PCS	Photon correlation spectroscopy
PDF	Powder diffraction file
PDI	Polydispersity index
PONKCS	Phases with partial or not known crystal structures
ppm	Parts per million
PSD	Particle size distribution

pXRD	Powder X-ray diffraction
QELS	Quasi-elastic light scattering
QPA	Quantitative phase analysis
RecF	Rectorite clay films
RH	Relative humidity
SDD	Silicon drift detector
SE	Secondary electrons
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis/analyser
TEM	Transmission electron microscopy
TMS	Tetramethylsilane
TS	Tensile strength
UV-Vis	Ultraviolet-visible spectrophotometry
vol.%	Volume percentage
WDS	Wavelength-dispersive spectrometry
XRD	X-ray diffraction
XRF	X-ray fluorescence
wt.%	Weight percentage

CHAPTER 1 INTRODUCTION

1.1 Background

Natural phyllosilicate minerals, and clay minerals in particular, are among the most suitable inorganic substitutes and property enhancers in a growing array of applications (Lopes et al., 2014). Suitably modified clays can dramatically improve the physical properties of polymers, even at low concentration levels (ca. 5 vol.%). However, for best affinity it is a prerequisite that the clay is well dispersed in extensively exfoliated form. The smectite group clay minerals, e.g. montmorillonites are the most preferred reinforcement agents in nanocomposites. Because of their unique exchange capacity, reactive surface properties, lamellar crystallographic make-up and favourable particle size and aspect ratio, clay minerals can be easily modified towards target functionality (Tjong, 2006; Zhang and Evans, 2012). They are structurally analogous to some organic crystalline systems with similar lamellar arrangements, i.e. polyethylene (Ballard et al., 1980). Both organic and inorganic crystalline lamellae have comparable dimensions and due to the large aspect ratio, tend naturally to form oriented structures as coatings, membranes (Ballard and Rideal, 1983) and thin films. Clay-containing films and the hybridisation of inorganic materials is a trending topic in materials science and clay minerals research (Fernandes et al., 2014; Schoonheydt, 2014; Zhou et al., 2011). The physico-chemical properties of clay minerals, especially expandable species, define their specific behaviour in the aqueous dispersion crucial for film formation. Upon evaporation from suspensions, the dispersed clay platelets are highly susceptible to the formation of brick-like microstructures similar to that of nacre (Bennadji-Gridi et al., 2006; Sellinger et al., 1998).

While montmorillonite is the most studied and industrially utilised of the clay minerals, less attention has been given to mixed-layer clay structures such as rectorite. Illite-smectite (I/S) mixed-layer clay minerals are the most abundant and compositionally diverse in nature, and are most important in the study of diagenetic earth processes.

Generally, illite-smectites are of clay-fraction size, being dioctahedral 2:1 phyllosilicates consisting of two corner-sharing tetrahedral sheets with an octahedral sheet in-between. Regular, i.e. ordered, structures are usually given a mineral name and International Mineralogical Association (IMA) approved status, whereas random or irregularly structured sequences are generally described as I/S interstratifications. Rectorite is a regularly interstratified clay mineral with 1:1 alternating mica-like and smectite-like layers. The structure is built-up of pairs of dioctahedral 2:1 layers linked by Ca, Na or K cations. "Pure" rectorite from Beatrix Gold Mine, South Africa, features a platy-leafy morphology with translucent to transparent individual thin flakes. However, it is commonly found in layers of heterogeneous material known at the mine as "swelling clay". This clay contains between 45 % and 72 % rectorite, associated with calcite (12–14 %), quartz (8–49 %), muscovite (2–4 %), chlorite (2–6 %) and pyrophyllite (~3 %). Powdered rectorite swells in water, forming a gelatinous mass. The swelling of the structure is caused by the hydration of the exchangeable cations of the montmorillonite-like layers. The mixed-layer structure of rectorite consisting of alternating non-expandable (mica) and expandable (smectite) layers defines a set of unique properties that differ from those of mica and smectite alone. For example, the mica layer is temperature resistant and the smectite layer has cation-exchange capacity. This allows certain undesirable properties of the clay to be modified to suit specific applications, such as organoclays for polymer compatibility and the modification of thermoplastics. Rectorite dispersions facilitate the synthesis of ultralight gels that may be useful as adsorbents. Using organically modified rectorite in polymer-based nanocomposites has been found to impart desirable mechanical properties, e.g. improving the ductility of poly(lactic acid)(Li et al., 2009). However, it seems that to date no significant mechanical properties for binder-free, clay-only films have been reported.

1.2 Research objectives

This research aimed to characterise the physico-chemical, structural and material properties of rectorite clay from a local deposit, the Beatrix Gold Mine in South Africa. Preliminary characterisation based on results from XRD, electron microscopy (SEM, Field emission SEM (FESEM), and Field emission TEM (FETEM), thermal analysis (DSC/TGA), FTIR and Raman spectroscopy showed that this is an unusual material with unique and interesting properties. For instance, the ability of wet rectorite to increase in volume forming a gelatinous mass could be an effective rheological property with applications as rheological modifier and paint thickener. It was observed that the casting of slurries of fine rectorite-rich material results in the formation of relatively strong cohesive films. When subjected to direct flame, the thin clay film transforms into a silvery foil-like sheet which could be promising for use as a fire-retardant and for various specialised coatings.

The use of clay minerals to obtain hybrid multifunctional nanomaterials with new and improved properties is a prospect of growing technological interest and investigating the use of rectorite for this purpose became the main objective of this research. It was a prerequisite to use a “green” approach of a simple, energy-efficient, economical and environmentally friendly process to develop mechanically robust clay-only films and bionanocomposites with enhanced performance. The first step towards this goal was to investigate the capability of natural purified rectorite and its ion-exchanged modifications to form self-standing, mechanically strong clay films.

The ultimate research target was to explore the possibility of using rectorite clay to prepare non-isotropic (i.e. two-dimensionally oriented) nature-inspired bionanocomposites with very high clay loadings, i.e. tested over the complete compositional range of 100 - 0 % clay, i.e. 0 - 100 % chitosan respectively.

Major activities to achieve the main objectives of this research should include: development of an optimum purification procedure for maximum recovery of rectorite

from raw rectorite-rich material; ion-exchange modification of purified rectorite to prepare enough material for clay films and bionanocomposite preparation. The method development should focus on refining the process parameters and conditions for optimisation of the film preparation methodology for ultimate product performance. The film preparation process should be experimentally verified to ensure reproducibility of high performance films. The effect of texture, microstructure and other relevant parameters on the mechanical properties of the films should be considered in order to understand the mechanism of film formation and how it can be tuned towards maximum performance. Rectorite-only films and bionanocomposite films will be tested for their mechanical performance, and their light absorption and transparency. Statistical analysis of the available experimental data should be performed to determine and evaluate the limits for the ultimate mechanical performance of the films.

1.3 Research methodology

The research presented here was executed through the following major steps, determined by the set project objectives:

1.3.1 Purification, modification and characterisation of rectorite clay

- **Purification of raw material**

The aim was to remove major impurities, i.e. calcite, quartz and possibly the minor chlorite, mica and pyrophyllite. *Method:* Sieving, dispersion, sedimentation, chemical treatment. *Product:* ~2 kg high-purity rectorite-rich material to be used for further tests. *Characterisation methodology:* Electron microscopy – SEM, TEM; Structure and Crystallography – XRD, NMR; Spectroscopy – XRF, FTIR; Thermal analysis – TGA, DTA; Particle size analysis.

- **Modifications of purified rectorite**

⇒ **Inorganic cation exchange:** Li⁺, Na⁺, NH₄⁺, K⁺, Cs⁺, Mg²⁺, Ca²⁺, Sr²⁺ and Ba²⁺.

Method: Saturation with respective chloride; *Product:* Sufficient material to carry out the necessary characterisation tests.

⇒ **Organics modification:** different long-chain (carbon) organic surfactants.

Method: Intercalation. *Product:* Sufficient material for tests.

1.3.2 Rectorite clay films (RecF): preparation, characterisation and functional properties

Investigation of the effect of clay concentration, dispersion and exfoliation methodology on the microstructure and tensile strength of the clay films. *Method:* Casting aqueous dispersions and self-assembly of exfoliated purified natural clay from aqueous dispersions during slow evaporation. *Product:* RecF for characterisation and the evaluation of properties. *Characterisation methodology:* Electron microscopy – SEM, TEM; Structure and Crystallography – XRD; Spectroscopy – XRF, FTIR; UV-Vis, BET; Mechanical properties.

1.3.3 Rectorite/chitosan nanocomposite films (Rec/CS NCF): preparation, characterisation and functional properties

Investigation of the effect of clay-chitosan proportions, degree of dispersion, exfoliation, mixing methodology and pH. Parameters were to be closely controlled and tuned to achieve the best mechanical strength of the film product. *Method:* Casting and self-assembly of intercalated rectorite-chitosan composites from aqueous dispersions during slow evaporation. *Product:* Rec/CS NCF films for characterisation and testing of properties. *Characterisation methodology:* Electron microscopy – SEM; Structure and Crystallography – XRD; Elemental analysis – CHN; Spectroscopy – XRF, FTIR; UV-Vis. Mechanical properties.

CHAPTER 2 LITERATURE OVERVIEW

The following pages present a concise overview of clay science in general, and fundamental research into clays and clay minerals, with more comprehensive elaboration on the crystal chemistry of mixed-layer structures and rectorite, and mica and smectite group species as component layers in the structure of rectorite. The state of applied research on nanoclays (rectorite), biopolymers (chitosan) and nanocomposites is given, with emphasis on clay films and bionanocomposite films (NCF), specifically rectorite/chitosan composites. A literature review on all major analytical and experimental techniques relevant to this study is also presented.

2.1 Clays, clay minerals and mixed-layer structures

The study of clays and clay minerals dates back several centuries with a series of scientific and technological advances published in an impressive volume of knowledge available today. Among others, some of the fundamentals of clay science are set out in well-known books authored by (Bergaya and Lagaly, 2013; Bergaya et al., 2006; Brindley and Brown, 1984; Grim, 1962; Moore and Reynolds, 1997; Newman, 1987; Velde, 1985). It is a common belief that clays and clay minerals are the materials of the 21st century because they are environmentally friendly, naturally abundant and relatively inexpensive. Both fundamental and applied research are driven by a multi-disciplinary and multi-scale approach linking materials science and engineering with colloid science at macro-, micro- and nano-scale.

2.1.1 Definitions and terminology

The word “clays” was first assigned to fine-grained material found in geological formations by Agricola (1494–1555) almost five centuries ago in 1546 (Guggenheim and Martin, 1995), but was only identified as a mineral species at the beginning of the 19th century in the production of ceramic materials. The working bodies dealing with nomenclature and definitions of clay and clay minerals are the Joint Nomenclature

Committee (JNCs) of the Association Internationale pour l'Etude des Argiles (AIPEA) and the Clay Mineral Society (CMS). Because clay research, fundamental or applied, is such a dynamic field of science, there is an ongoing debate about and numerous revisions of clay nomenclature and definitions. These constantly evolve due to the expanding multidisciplinary approach to the study and the use of these unique materials. However, the distinction between clays and clay minerals is commonly accepted across all fields and the two terms should not be used interchangeably (Guggenheim and Martin, 1995). In essence, clay minerals are defined as naturally occurring, or synthetic, phyllosilicates or non-phyllosilicates, primarily fine-grained porous materials that impart plasticity when wet and harden upon drying and firing (Brindley, 1966; Brindley et al., 1968; Guggenheim et al., 2006; Guggenheim and Martin, 1995; Martin et al., 1991).

For clarity, the following terminology and definitions are defined here and will be applied as such throughout this document:

- *Lattice*: to be used in a strict crystallographic sense for a uniform distribution of points in space. There are 14 standard types of lattice, known as Bravais lattices. Phyllosilicates are based mainly on monoclinic and triclinic lattices.
- *Plane, sheet, layer, interlayer and structure unit*: to be used in the following manner: a *plane* of atoms, a tetrahedral or octahedral *sheet*, a 1:1 or 2:1 *layer, interlayer* space. In this order they refer to increasingly thicker arrangements, i.e. a sheet is a combination of planes and a layer is composed of sheets. Layers may be separated by *interlayer* space occupied by cations, hydrated cations, hydroxide octahedral groups or organic molecules (Brindley et al., 1968). An arrangement of a *layer* plus an *interlayer* is referred to as a *structure unit*. It may contain one or more chemical formula units (Z) (Bailey, 1984).
- *Unit cell, lattice constants and Miller indices* (usage of the terms is as agreed by the IUCr (International Union of Crystallography)): a *unit cell* is the parallelepiped

built on the vectors **a**, **b**, **c** of a crystallographic basis of the direct lattice. A *unit cell* is defined by lattice constants *a*, *b* and *c*, lattice vectors and interaxial angles α , β , and γ (always given in italic font). There are 7 different types of unit cell defined as crystal systems and 14 standard (Bravais) unit cells that describe all possible lattice networks. *Miller indices* (hkl) for crystallographic planes – these are the reciprocals of the fractional intercepts that the plane makes with the *x*, *y*, and *z* axes of the three nonparallel edges of the cubic unit cell.

- *Particles, aggregates and assembly*: clay particle is a generalised term also referred to as a crystallite, crystal or tactoid. It is defined as an assembly of layers; an assembly of particles is referred to as an aggregate (Figure 2-1). An arrangement of particles and aggregates results in different morphologies, i.e. plates, laths or fibres, and the formation of interlayer, interparticle and interaggregate spaces or pores (Bergaya and Lagaly, 2013).

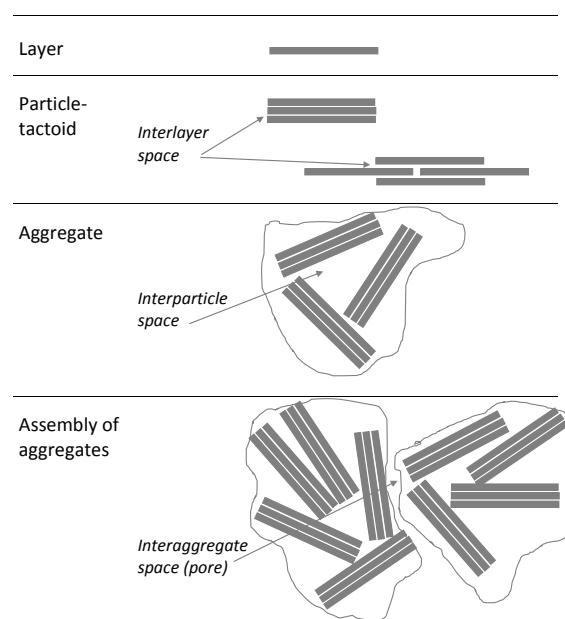


Figure 2-1. Schematic diagram showing the relationship of layer–particle-aggregate (Adapted from (Bergaya and Lagaly, 2013))

- *Delamination and exfoliation*: these occur in aqueous dispersions when intercalated water molecules cause the separation of two successive layers. When interaction

between the separating layers is sufficient enough to maintain some crystallographic integrity in the system, the separation is called *delamination*. With increasing separation no further interaction between the delaminated units is possible and eventually they cease to exist as a structure unit but become independently mobile in the liquid media, i.e. layers are completely *exfoliated* (Bergaya and Lagaly, 2013).

2.1.2 Structure and crystal chemistry of clay minerals

Clay minerals are hydrous layered silicates and belong to the larger group of phyllosilicates. The elementary structural unit is the Si-O tetrahedral linkage extending in continuous two-dimensional tetrahedral sheets (T) of composition T_2O_5 in a hexagonally symmetric network along the *a-b* crystallographic directions. All phyllosilicates contain silicate or aluminosilicate layers in which sheets of tetrahedrally coordinated cations (T – usually Si^{4+} , Al^{3+} or Fe^{3+}) link through shared oxygens to adjacent sheets of octahedrally coordinated cations (O – most commonly Al^{3+} , Fe^{3+} , Fe^{2+} or Mg^{2+}). Each tetrahedron links to adjacent tetrahedra in a lateral direction by three corner oxygens (the basal oxygens), while the fourth corner oxygen (the apical oxygen) is positioned in a direction normal to the tetrahedral basal plane and is shared with a neighbouring octahedral sheet. The Si-O bond distance is about 1.62 Å and the O-O distance about 2.64 Å. Up to half of the Si^{4+} atoms may be replaced by the larger Al^{3+} atom, causing an increase in sheet dimensions as the Al-O distance is about 1.77 Å (Moore and Reynolds, 1997). Each octahedron consists of a cation coordinated by six oxygens or hydroxyl groups and links to adjacent octahedra by sharing edges. The resulting sheets of edge-shared octahedra have a hexagonal or pseudo-hexagonal symmetry. There are two configurations of octahedra depending on the crystallographic position of the OH⁻ group, i.e. a *cis*-oriented octahedron with OH⁻ along the edge and a *trans*-oriented octahedron with OH⁻ along the diagonal. When one tetrahedral sheet (T) is linked to one octahedral sheet (O), a 1:1 (TO) layer is formed as in kaolinites. Respectively there are six

octahedral sites and four tetrahedral sites in the unit cell of a 1:1 (TO) layer structure (Figure 2-2). The 1:1 layer is approximately 0.7 nm thick.

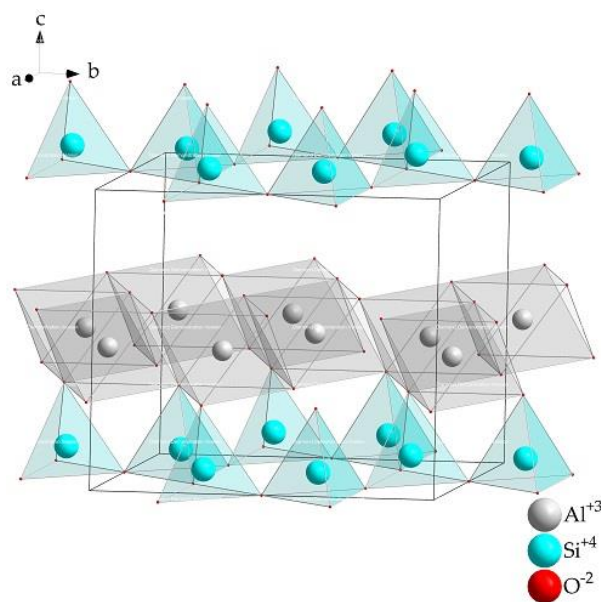


Figure 2-2. Graphical representation of the 1:1 structure of kaolinite, ICSD 31135 (Brindley and Robinson, 1946) (view down the crystallographic *a*-axis)

When one octahedral sheet (O) is linked to two tetrahedral sheets (T), i.e. one on each side, a 2:1 layer structure (TOT) is produced as in smectites and micas (Figures 2-3 and 2-4). This configuration results in six octahedral and eight (four on each side) tetrahedral sites in the 2:1 (TOT) layer unit cell. The two tetrahedral sheets are in inverted orientation to each other, i.e. they are both oriented with their apical oxygens (tips) towards the central octahedral sheet (Figures 2-3 and 2-4). Furthermore, two-thirds of the hydroxyl groups are replaced by tetrahedral apical oxygen atoms. The remaining third hydroxyl ion fits into the hole (gallery) in the hexagonal ring made by the apical oxygens of the tetrahedral sheet. Thus, the surfaces on both sides of the 2:1 layer consist of basal oxygens. The thickness of a 2:1 layer varies, depending on interlayer occupancy, from 0.91 - 0.95 nm in talc and pyrophyllite (empty interlayer space) to 1.40 - 1.45 nm in chlorite. The higher value for chlorites is ascribed to the additional octahedral interlayer sheet of cations, i.e. showing a TOTO_{int} configuration (Brindley and Brown, 1984). For

simplicity, the structural formula is usually reported based on half the unit cell content, i.e. three octahedral sites. Structures with all three octahedral sites occupied by a divalent cation (R^{2+} , usually Mg^{2+} or Fe^{2+} or Mn^{2+}) are defined as trioctahedral or brucite-like $Mg(OH)_2$, whereas those with two of the three sites filled with a trivalent cation (R^{3+} , usually Al^{3+} or Fe^{3+}) are denoted as dioctahedral or gibbsite-like $Al(OH)_3$. In these configurations structures maintain electrical neutrality until (i) substitution of Al^{3+} for Si^{4+} in tetrahedral sites occurs; (ii) substitution of Al^{3+} for Si^{4+} or other lower charge cations in octahedral sites occurs; or (iii) there are vacancies in trioctahedral species. As a result, a negative layer charge arises that is balanced by a positively charged interlayer. The most common interlayer cations are Na^+ , K^+ and Ca^{2+} as in smectites and micas, whereas Mg^{2+} , Fe^{2+} and Fe^{3+} are typical for chlorite and vermiculite. The interlayer cations can be exchangeable as in smectites or non-exchangeable ("fixed") as in mica species. Respectively interlayer cations are hydrated in the former and non-hydrated in the latter group. Ammonium ions NH_4^+ and organic molecules may replace some of the cations in the interlayer space and by electrostatic bonding neutralise the negative charge of the silicate layer. The net negative charge per layer is calculated on the basis of the structural formula, i.e. half the unit cell, and ranges from 0.2 in smectites to 2.0 in brittle micas for 2:1 clay species, whereas for 1:1 minerals the charge is close to zero. The sheets and layers can be either negatively charged as in majority of clay minerals, positively charged in the case of layered double hydroxides (LDH) or neutral or uncharged as in talc and pyrophyllite. The basic 2:1 network contains a fixed $O_{10}(OH)_2$ and the hydroxyls are uniquely in octahedral coordination. The layer charge density may have different locations in the layer depending on the origin of isomorphous substitution, e.g. octahedral or tetrahedral which affects the hydration state and the nature of the charge-balancing cation in the interlayer.

When tetrahedral and octahedral sheets join to form a 1:1 or 2:1 structural arrangement, certain adjustments and distortions take place in one or both of the sheets in order for them to combine at a common plan of oxygens. Although the O-O (oxygen-to-oxygen)

and OH-OH (hydroxyl-to-hydroxyl) ionic dimensions in the tetrahedral and octahedral sheets respectively are approximately equal at $\sim 2.64 \text{ \AA}$ for the former and $\sim 2.70 \text{ \AA}$ for the latter, the lateral dimensions of the tetrahedral sheet are usually larger than those of octahedral sheet (Brindley and Brown, 1984; Moore and Reynolds, 1997). Thus the sheets have to adjust by either rotation or tilting to accommodate a fit between them, creating a layer distortion typical of layered silicates. Stacking of the layers in the direction along the c -axis is a source of additional stacking disorder, the most extreme disorder being known as turbostratic disorder. It is manifested by displacements/rotations or translations of layers in the a - b plane and is most common in smectite minerals (Brindley and Brown, 1984; Moore and Reynolds, 1997).

Polytypism occurs when a compound exists in several different structural modifications, i.e. when structurally and compositionally identical layers are stacked in different ways. The most typical case is the mica minerals in which six theoretically possible polytypes exist; these are described in more detail in Section 2.3.

2.1.3 Mixed-layer clay minerals

Mixed-layering, interlayering and interstratification describe layered silicate structures consisting of two or more kinds of layer stacked in a vertical sequence along the c -axis, i.e. normal to (001) direction (Moore and Reynolds, 1997). The stacking sequence can be random, partially regular or regular.

Special names are assigned only to the regular interstratifications with components present in a fixed ratio (Bailey et al., 1982). The criterion for a regular sequence is to have at least ten 001 reflections of the same width with coefficient of variation $CV < 0.75$ to demonstrate adequate regularity of alternation. The coefficient of variation is defined as $CV = 100s/\bar{X}$, where the s is the standard deviation for at least ten individually observed $d(001)$ values X_i , and \bar{X} is the mean of the X_i values.

Mixed layering, where the expandable component is half or less of the mixture, is more susceptible to ordering than random stacking. Illite/smectite interstratifications are the most common mixed-layer clay minerals, even more common than the discrete end members (Reynolds, 1984). Generally, illite/smectites form in the process of transition from smectite to illite in suitable geological conditions (Hower, 1967, 1981; Srodon et al., 2000) and occur in clay-fraction size. They are dioctahedral 2:1 phyllosilicates consisting of two inverted corner-sharing tetrahedral sheets with an octahedral sheet in-between. Random or irregularly structured sequences are very common in nature and are usually designated as I/S interstratifications.

Although each layer maintains its structural and chemical identity, the sequence of layers scatters X-rays as one coherent unit (Reynolds, 1984). X-ray diffraction from a mixed-layer structure gives average values for the whole crystal, i.e. intermediate diffraction characteristics relative to the two component layer types. Stacking of two component layers A and B in a random sequence results in a disordered or irregular mixed-layer structure with irrational basal spacing that would not comply with Bragg's law. Ordered or regular stacking produces a supercell along the c-axis with diffracting basal spacing d_{00l} equal to the sum of the thicknesses of each individual layer within the superstructure, i.e. $d_{AB} = d_A + d_B$.

Structures of mixed-layer clay minerals are usually characterised by comparing experimental XRD patterns with computer-simulated mathematical models such as in the NEWMOD computer program (Reynolds, 1985). The Reichweite parameter (R) is used to characterise the range of order and the interaction between the layers (Drits, 2003; Reynolds, 1985). It is based on the probability of finding layer B after layer A or layer A after layer B and on the influence of the preceding layer has on this probability. Thus R0 describes random interstratification or lack of ordering; R1 denotes an ordered sequence where each A layer is followed by a B layer, e.g. ABABAB; R2 and R3 respectively denoting AA and AAA sequences is followed by a B layer. The R parameter is purely

statistical and can be an integer or a fraction. It describes the degree of ordering in an interstratified layer sequence using experimental *d*-values of basal reflections.

The crystallographic nature of I/S minerals is interpreted by two competing theories, both concerned with defining the mixed-layer structure unit. These are the MacEwan crystallite theory (MacEwan and Amil, 1958; MacEwan, 1956, 1957) based on Fourier transform methods, and X-ray scattering and the fundamental particles model (Nadeau et al., 1984) using transmission electron microscopy (TEM) of thin crystallites. According to the MacEwan model, one I/S unit is a sequence of illite and smectite layers stacked along the *c*-axis with individual structure units centred at the interlayer, i.e. the division between layers is through the centre of an octahedral sheet (Figure 2-8). An illite layer contains a dehydrated K-rich interlayer with an Al-rich tetrahedral sheet, whereas smectite has a hydrated Na-Ca-interlayer with a mainly Si-rich tetrahedral sheet. The stacking of such two layers is called “MacEwan crystallite”. This model was later used to calculate the XRD patterns of I/S (Reynolds and Hower, 1970) and for modelling the computer program NEWMOD (Reynolds, 1985).

The fundamental particles model of Nadeau and co-workers describes an I/S structure made of “fundamental particles” with the dimension along the *c*-axis an integral with multiples of 10 Å. The 10 Å thick particle is seen as an isolated 2:1 layer termed a “fundamental smectite particle”. Particles ≥ 20 Å are considered to be two or more 2:1 layers linked by K atoms and are termed “fundamental illite particles”.

Following NMR studies on the crystallographic characteristics of I/S, (Altaner et al., 1988; Barron et al., 1985a, b; Jakobsen et al., 1995; Lausen et al., 1999) presented evidence in support of the MacEwan’s crystallite model before the fundamental particles theory. ²⁹Si-NMR data convincingly differentiates signals of Si atoms in smectite layers from Si atoms in mica layers because relative to smectite, tetrahedral sites in illite have less Si and more Al as a result of predominantly tetrahedral Al for Si substitution in micas compared with smectite (Altaner et al., 1988).

The regular interstratification of dioctahedral mica and smectite is called **rectorite** (Bailey, 1982). The structure is built-up of pairs of dioctahedral 2:1 layers linked by Ca, Na or K cations. The alternating layers are mica-like and montmorillonite-like (Brown and Weir, 1963). Depending on the dominant cation, Ca-, Na- or K-rectorite varieties have been described. The swelling of the structure is similar to that of montmorillonites and is due to hydration of the exchangeable cations of the montmorillonite-like layers.

2.1.4 Nomenclature and classification

Based on the *charge of the interlayer content*, clay minerals are categorised into two broad classes, i.e. cationic clays which are widespread in nature, and anionic clays or mixed metal hydroxides, which are commonly synthesised.

The layer type and charge per formula unit are the classic main criteria used for the most widely accepted classification of clay minerals (Brindley et al., 1968) into the following major groups:

- Layer type 1:1
 - Serpentine-kaolin group: $x \sim 0$ (x – net layer charge)
- Layer type 2:1
 - Talc-pyrophyllite group: $x \sim 0$
 - Smectite group: $x \sim 0.2-0.6$
 - Vermiculite group: $x \sim 0.6-0.9$
 - Mica group:
 - True (flexible mica): $x \sim 0.6-1.0$
 - Brittle mica: $x \sim 1.8-2.0$

- Chlorite group: variable charge
- Sepiolite-palygorskite group: variable charge
- *Regularly interstratified 2:1 clay minerals: variable charge

*Note: It was only in 1982 when a group for Regularly Interstratified clay minerals was added to the 1:2 layered silicates (Bailey, 1982; Bailey et al., 1982) and recommendation criteria for species names were given. Among other reasons, the name “rectorite” is also justified here for a 1:1 regular interstratification of a dioctahedral mica and a dioctahedral smectite.

Species from the smectite, vermiculite, mica and chlorite groups are additionally divided into dioctahedral and trioctahedral subgroups. This basic classification remains at the core of subsequent reviews and upgrades which evolved as knowledge on clay minerals increased (Martin et al., 1991).

In summary, clay minerals can be generally categorised as: (i) 1:1 (T:O) or 2:1 (TOT) based on sheet configuration; (ii) dioctahedral or trioctahedral based on octahedral site occupancy; (iii) cationic or anionic based on the charge of the interlayer content; (iv) low ~0, medium ~0.2–0.6 and ~0.6–0.9, or high charge ~0.9–1.0 and 2.0 based on the charge per formula unit; and (v) hydrated or non-hydrated based on the hydration state of the interlayer content.

2.1.5 Properties of clay minerals

The *structural features* of clay minerals, i.e. sheet configuration or type of silicate layer and *chemical characteristics* such as magnitude of net layer charge and type of interlayer material, define the range of specific properties responsible for the growing preferential use of clays in industrial and environmental applications. On the other hand, the *fundamental properties* of clay minerals, such as layered structure with one dimension in the nanometre range, anisotropy of the layers and particles, lamellar crystallographic

make-up and favourable particle size and aspect ratio, unique exchange capacity, reactive surface properties at external (basal), internal (interlayer) and edge surfaces, allow them to be easily modified towards target functionality.

Because by definition clay minerals are fine-grained particles, generally accepted by clay mineralogists to occur in the fraction size $< 2 \mu\text{m}$, they exhibit large and variable surface areas that can significantly affect their properties. There are external and internal surface areas depending on the mean crystallite size and morphology for the former and the mineral's structural make-up and degree of dispersion/aggregation for the latter (Table 2-1). The edge surfaces contribute to the overall external surface area.

Table 2-1. Surface area of some clay minerals groups (Van Olphen and Fripiat, 1979)

	Approximate Surface Area. m²/g		
	Internal	External	Total
Smectite	750	50	800
Illite (mica)	5	25	30
Chlorite	0	15	15
Kaolinite	0	15	15

The internal surface areas include the interlayer surface area and depend on the sheet configuration, i.e. the 2:1 minerals will have some internal surfaces, whereas 1:1 structures such as kaolinite will show only external surfaces. The chlorite exception is due to the additional octahedral sheet occupying the interlayer space.

The property of ion exchange is of fundamental and practical significance for clay minerals since it has a direct effect on their physical properties. It is defined as a stoichiometric and reversible replacement by exchange of ions between two electrolytes,

or as a diffusion process between electrostatic surface ions and a solution (Grim, 1962; Harland, 1994). Cation-exchange capacity (CEC) is a measure for ion exchange usually expressed as mEq/100 g. It is defined as the average quantity of cations available for exchange, usually at pH 7. The CEC is given in range per mineral and shows significant variation within the different clay minerals. For instance, the CEC of kaolinite is in the range 1–5 mEq/100 g, for micas it is 10–40 mEq/100 g, for montmorillonite it is 70–130 mEq/100 g and for vermiculite it is 130–200 mEq/100g. It is created in two main ways: (i) by substitutions in the tetrahedral or octahedral sheets that create the charge deficit, i.e. layer charge known as permanent charge; and (ii) by adsorption or dissociation of protons at the particle edges, referred to as “broken bonds” with the charge being non-permanent or pH-dependent (Bergaya and Lagaly, 2013; Grim, 1968). The layer charge is balanced by the interlayer cations’ “counterions”, namely H^+ , Li^+ , Na^+ , K^+ , Mg^{2+} and Ca^{2+} , which are usually easily exchangeable as in smectite species. Thus the CEC is strongly dependent on the type of exchangeable cation, pH, temperature, particle size, morphology and surface area. The nature and ionic radius of the exchangeable cation defines the crucial properties of smectite minerals such as hydration state, unit cell dimensions (d-values) and rheological behaviour. For example, the most common naturally occurring Ca-montmorillonite is usually exchanged with Na^+ due to the more desirable properties of Na-montmorillonite in industrial applications.

Ionic dimensions for some of the cations relevant to the rectorite study in this work are given in Table 2-2. Ionic potential is a measure of charge density and the strength of the ionic bond. It is derived as a ratio of the ion’s electrical charge (cation valence) to its ionic radius. It is also called hydration energy (HE) or hydration power and is closely related to the hydration properties of smectite minerals (Ferrage et al., 2005a; Ferrage et al., 2005b; Ferrage et al., 2007; Morodome and Kawamura, 2011).

Another critical property of clay minerals and smectites in particular is their ability to expand in the *c*-axis direction when water and other polar molecules or certain organic

molecules enter between the layers. The hydration state and the size of the interlayer cation determine the layer thickness or spacing in the *c*-axis direction, i.e. the basal spacing. Smectite and vermiculite contain hydrated alkaline or alkaline earth cations in the interlayer space, with an average spacing around 15.5 Å. The number of water layers depends on the nature of the exchangeable cations at a given water-vapour pressure. Thus Na-exchanged montmorillonite usually has one molecular water layer and a basal spacing about 12.5 Å, whereas in the Ca-montmorillonite structure there are two molecular water layers with a spacing of about 15.5 Å. In mica and illite the non-hydrated alkaline and alkaline earth cations in the interlayer result in a periodicity of around 1.0 nm (Bergaya and Lagaly, 2013). The expansion in glycerol is considerably less than in water and similar d-spacing is usually a result of the different size and shape of the molecules in the interlayer space (Barshad, 1950). Thus the physico-chemical factors for expansion are the size and charge of the interlayered ion, the nature of the interlayered substance, i.e. water, organic matter, and the total excess negative charge per unit cell, e.g. low charge smectites are expanding and high-charge micas are non-expanding but have similar interlayer content.

The ability of clay minerals to swell/expand, or the lack of this ability, is controlled by the balance of attractive and repulsive forces between adjacent 2:1 layers. The main attractive force is the electrostatic interaction between the negatively charged layers and the balancing positively charged interlayer content of alkali or alkaline earth cations. The magnitude of this force depends on the surface charge density and the layer separation in the *c*-direction (Newman, 1987). When layers are in contact or almost in contact, there are van der Waals' attractive forces between atoms in the layer surfaces and some residual electrostatic forces between charged atoms in adjacent layers. The main repulsive force arises from the hydration of interlayer cations in natural clay minerals. In addition, repulsive forces exist between the hydrogens of the hydroxyl groups bonding to the octahedrally coordinated cations in the 2:1 layer and the interlayer cations. This

repulsive force depends on the proximity of the hydroxyl hydrogen to the interlayer cation and is largest when the O-H dipole is normal to the 2:1 layer plane.

Table 2-2. Ionic radii and derived ionic potentials for some relevant cations (compiled from (Conway and Ayranci, 1999; Shannon, 1976; Volkov et al., 1997)

Ion	Ionic Radii, nm	Hydrated Ionic Radii, nm	Ionic potential, [z/r] (-)
Li ⁺	0.09	0.38	10.64
Na ⁺	0.12	0.36	8.55
NH ₄ ⁺	0.15	0.33	6.76
K ⁺	0.15	0.33	6.71
Cs ⁺	0.19	0.33	5.38
Mg ²⁺	0.07	0.43	27.78
Ca ²⁺	0.10	0.41	20.00
Sr ²⁺	0.13	n.a.	15.87
Ba ²⁺	0.14	0.88	13.99

2.2 Smectite group

Smectite group minerals are 2:1 (TOT) clay minerals with hydrated exchangeable alkaline or alkaline earth cations in the interlayer space and a net layer charge per formula unit in the range 0.2–0.6. The species according to octahedral occupancy are (Martin et al., 1991):

- dioctahedral – beidellite, montmorillonite, nontronite, volkonskoite
- trioctahedral – hectorite, saponite, sauconite, stevensite and swinefordite

Isomorphous substitutions may occur between Si^{4+} , Al^{3+} and Fe^{3+} in tetrahedral positions and Al^{3+} , Mg^{2+} , Fe^{2+} and Fe^{3+} in octahedral sites, resulting in a negative charge between 0.2 and 0.6 per half unit cell, i.e. $\text{O}_{10}(\text{OH})_2$. For instance, montmorillonite $((\text{Al}_{3.15}\text{Mg}_{0.85})(\text{Si}_{8.00})\text{O}_{20}(\text{OH})_4\text{X}_{0.85}.n\text{H}_2\text{O})$ and beidellite $((\text{Al}_{4.00})(\text{Si}_{7.15}\text{Al}_{0.85})_{20}(\text{OH})_4\text{X}_{0.85}.n\text{H}_2\text{O})$ (Newman and Brown, 1987) (X =monovalent interlayer cation) are the aluminium-rich varieties and are distinguished on the basis of the origin of the negative charge. In montmorillonite, the charge usually arises by Mg^{2+} substitution in the octahedral position, whereas in beidellite it is due to Al^{3+} in tetrahedral occupancy.

The negative charge is balanced by the interlayer cations, most commonly Na^+ , K^+ , and Ca^{2+} and Mg^{2+} , usually hydrated and exchangeable. There is an almost linear correlation between the interlayer distance and the ionic radius of the interlayer cation (Voora et al., 2011).

Intercalation of discrete number of water layers, usually 0 - 3, can be distinguished by XRD with shifting of $d(00l)$ to lower 2θ angles (enlarged unit cell along c -axis) corresponding to 0-, 1-, 2- and 3-water layer hydrates. Dehydration is usually reversible on exposure to atmospheric humidity. Rehydration is accompanied by a rapid increase of the distance between the layers to accommodate the sorbed water molecules. Some of the main factors affecting interlayer hydration of smectites are hydration energy of the interlayer cation, polarisation of water molecules by interlayer cation, and variation of electrostatic surface potentials because of different layer charge locations. The swelling occurs in a step-wise manner in a series of phase transitions, whereby intermediate, interstratified and mixed-layer hydrates may co-exist. Based on modelling simulation of the interlayer molecular structure of swelling clay minerals, (Skipper et al., 1995) proposed that dehydrated and one-layer hydrated structures with divalent cations are more compact and rigid compared with those having monovalent cations. It is further suggested that in dehydrated structures the interlayer cation can occur both close to the tetrahedral basal oxygen atoms and symmetrically above and below the tetrahedral hole,

depending on the ionic radius. The H-bonding between water molecules and basal oxygen atoms is stronger for tetrahedral than for octahedral sheet substitutions (Sposito, 1984).

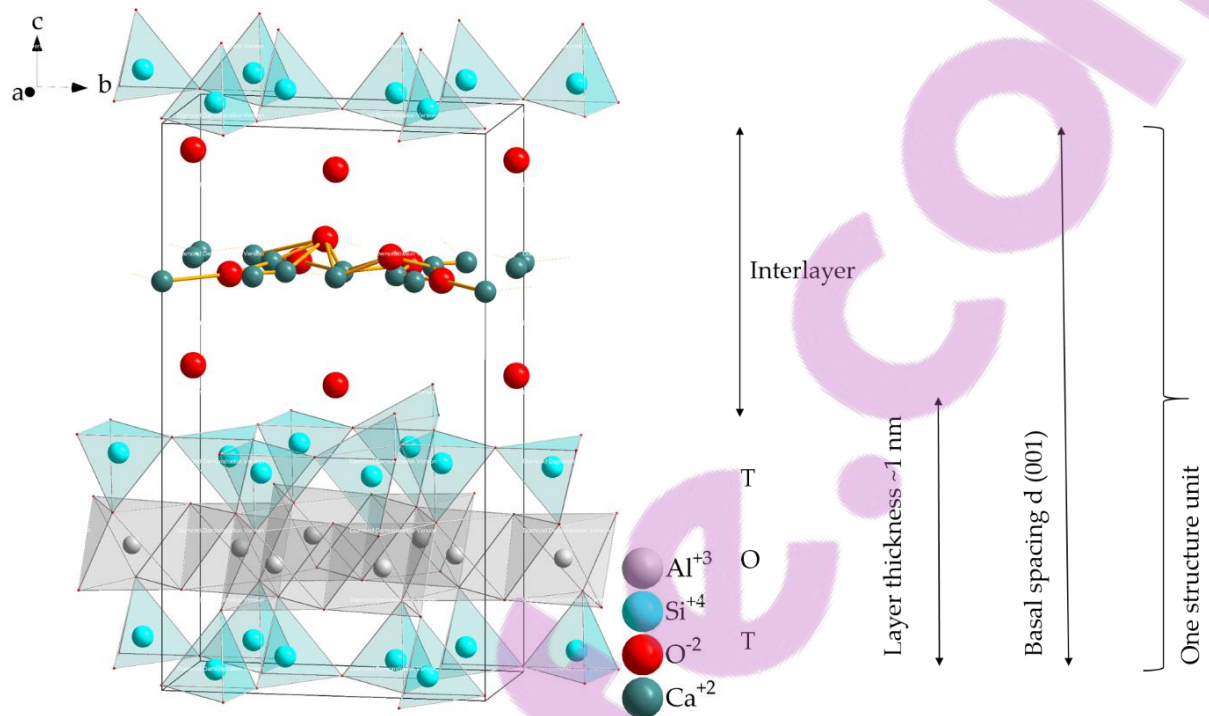


Figure 2-3. Graphical representation of the structure of montmorillonite_{Ca}, ICSD_51636 (Gualtieri et al., 2001) (view down crystallographic *a*-axis) with layer distances annotated on the right

Smectite clay minerals and specifically montmorillonite and saponite are those most commonly used in the preparation of polymer nanocomposites. They are easily available and possess the most compatible properties such as colloidal size, high specific surface area, moderate layer charge, large cation exchange capacity, variable interlayer separation depending on the ambient humidity, well-studied intercalation/exfoliation chemistry and the ability to swell in water, quite extensively for Li⁺- and Na⁺- exchanged forms. Under optimised conditions, interlayer swelling in water may eventually cause complete delamination and exfoliation of the clay particles. Interlayer reactions of smectites are the most sought-after property for technological processes and applications.

2.3 Mica group

Mica minerals are 2:1 phyllosilicates with non-hydrated alkaline or alkaline earth cations in the interlayer space and a net layer charge per formula unit in the broad range of 0.6–2.0. They are classified into two subgroups, namely *true* (flexible) micas and *brittle* micas, with the most common minerals speciation that by (Martin et al., 1991), with addition of a third subgroup by (Rieder et al., 1998)), among others not mentioned here:

- **True mica** species contain ≥ 50 % monovalent interlayer cations with net layer charge per formula unit of 0.6–1.0:
 - Dioctahedral – celadonite, glauconite, illite, muscovite, paragonite
 - Trioctahedral – biotite, lepidolite and phlogopite.
- **Brittle mica** species have ≥ 50 % divalent cations in the interlayer with net charge per formula unit of 1.8 – 2.0:
 - Dioctahedral – margarite
 - Trioctahedral – anandite, bityite, clintonite, kinoshitalite
- **Interlayer-deficient micas** are those with cation deficiency in the interlayer space. The name replaced the *hydromica* subgroup name, although previous species of it have been discarded:
 - Dioctahedral – illite, glauconite, brammalite
 - Trioctahedral – wonesite

The nomenclature of micas updated by the Mica Subcommittee of the CNMMN of the IMA (Rieder et al., 1998) is based on the chemical composition and crystal structure of mica species.

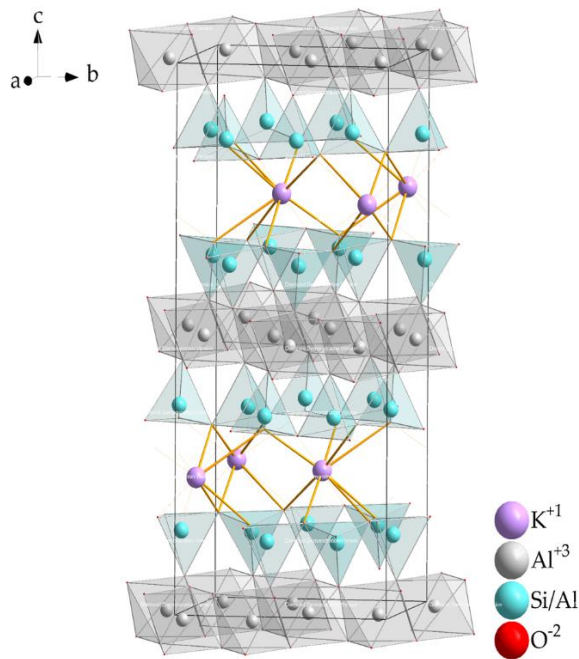


Figure 2-4. The structure of muscovite $\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$, ICSD_28553 (Gatineau, 1963) (view down *a*-axis)

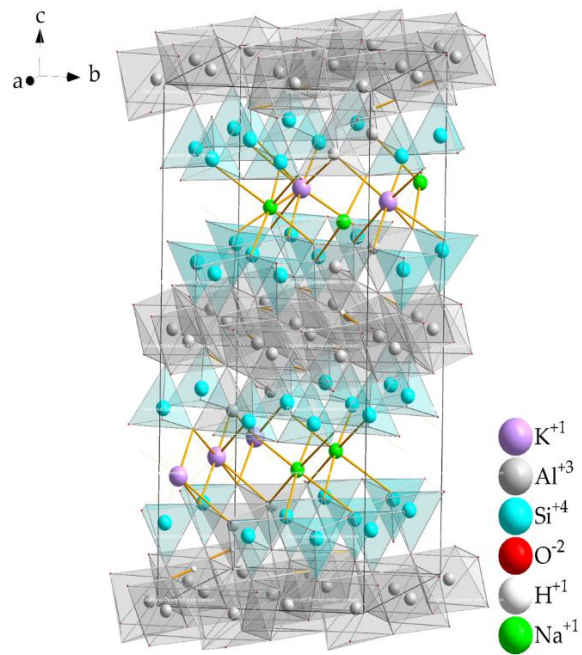


Figure 2-5. The structure of muscovite $\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$ -paragonite $\text{NaAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$ series, ICSD 187574 (Hernandez-Haro et al., 2013)

Tetrahedral sheets have composition T_2O_5 and link to the octahedral sheet in-between by the apical oxygen atoms of each tetrahedron (Figure 2-4). The structure consists of negatively charged 2:1 layers, “keyed” together by large interlayer cations (Bailey, 1984). In the true micas the interlayer cation is predominantly monovalent, whereas in the brittle micas it is divalent. The layer-charge may arise from: (i) substitution of R^{3+} (usually Al, Fe, or Cr) for Si^{4+} in tetrahedral positions; (ii) substitution of R^{1+} or R^{2+} for R^{2+} or R^{3+} in octahedral positions (primarily Al^{3+} , Mg^{2+} , Fe^{2+} and Fe^{3+}); or (iii) vacancies in octahedral positions. The resulting layer charge can be of either tetrahedral or octahedral origin, or partly from both sheets. When the tetrahedral charge exceeds unity, it is usually an indication of excess positive charge in the dioctahedral sheets, due to vacant positions. The interlayer cation is commonly monovalent K^+ and occasionally Na^+ (paragonite) in the true micas and divalent Ca^{2+} in brittle micas. Species with appreciable substitutions of Li, Cr, Ni, Mn, Ti, Zn, Co, Cu and V in octahedral positions are known. Rarely, small amounts of Sr, Ba, Rb and Cs can be present in interlayer sites.

The polytypism phenomena in micas was first demonstrated by (Hendricks and Jefferson, 1939) based on an X-ray diffraction study. There are six theoretically possible mica polytypes derived experimentally by (Smith and Yoder, 1956) from natural specimens. In the stacking of 2:1 layers in the c-direction, the tetrahedral sheets have to align so that the hexagonal rings superimpose to accommodate the interlayer cation and still maintain octahedral coordination in the structure unit. This is achieved by layer shifts in positive or negative direction of any of the three pseudo-hexagonal axes X1, X2 or X3. Two polytypes form as a result of shifts along only one axis, namely 1M and 2Or, i.e. having all the layers in the same orientation. Polytypes 2M1 and 2M2 involve shifts along two axes and, respectively, shifts along all three axes produce polytypes 3T and 6H.

In the mica structure, the 2:1 layers superimpose in such a way that the hexagonal rings of basal tetrahedral planes line up to enclose the interlayer cations. In this adjustment tetrahedral rotations reduce the size of the gallery, resulting in only six nearest oxygens instead of the twelve expected for hexagonal geometry. In dioctahedral micas the most common interlayer cation K^+ appears to be too large for this six-coordinated hole, resulting in less tetrahedral rotation and filling the gap by pushing apart the basal oxygen planes and stretching laterally the octahedral sheet (Radoslovich and Norrish, 1962). Thus the basal spacing of 10 Å is slightly larger than the actual thickness of the layer (~9.3-9.6 Å). The average distance between centres of basal oxygens in adjacent layers (also called interlayer separation/interlayer space distance) is ~3.42 Å for muscovite 2M1 (Gatineau, 1963), ~3.46 Å for muscovite 3T (Güven and Burnham, 1967), ~3.31 Å for muscovite-(Na) and ~3.08 Å for paragonite-(K) (Burnham and Radoslovich, 1964), and for margarite 2M1 between 2.83 Å (Takeuchi, 1965) and 2.87 Å (Guggenheim and Bailey, 1975). This indicates that adjacent basal oxygen planes around the interlayer K^+ (diameter ~2.76 Å) in muscovite and Na^+ (diameter ~2.04 Å) in paragonite are very close but not in contact, whereas in margarite they are almost in contact around Ca^{2+} (~2.00 Å diameter) (Bailey, 1984). In both cases the interlayer cation fills entirely the gap, i.e. it is fixed in the

gap with no space for water molecules to hydrate. As a result the 2:1 layers are held strongly together and therefore no swelling or exfoliation of the layers is possible.

In the 2:1 layer structure of mica the attractive force between the TOT layers and the interlayer cation exceeds its dehydration energy because of the high layer charge (Moore and Reynolds, 1997).

2.4 Rectorite

Rectorite was first reported by Brackett and Williams in 1891. It was found in the Blue Mountain mining district, Garland County, Arkansas, USA, and named after E.W. Rector, an attorney in Hot Springs, Arkansas.

Historic record of the first description of rectorite: Statement of ceramic manufacturer Homer Langhlin, Esq. of East Liverpool, Ohio, USA upon firing rectorite specimen from Blue Mountain mining district, Arkansas (Brackett and Williams, 1891):

“The sample of what you call kaolinite, sent to me, was duly received and carefully examined and tested under fire. The mineral is neither kaolin nor kaolinite, but just what it should be called I am unable to say, never in all my experience having seen any mineral of its kind. Unlike kaolin it will not dissolve in water. It burns a white colour and becomes very vitreous and strong. It cannot be finished with a smooth face or skin, but roughs up like a blotting pad. It is certainly a very interesting and curious mineral, but I can think of no use for it in ceramic manufacture unless it could, after careful experiments, be made into novel ornaments”.

Later, Caillere et al. (1950) described a mineral with “remarkable skin-like” appearance. They named it allevardite after the locality Allevard in France where it was found. Based on X-ray examination, Bradley (1950) suggested that the structure of rectorite from Arkansas consists of alternate stacking of pyrophyllite and vermiculite layers separated by layers of water. Brindley (1956) described it as a swelling double-layer mica mineral.

Others (Ivkin et al., 1959 and Korolev, 1961) reported a similar swelling mineral from Dagestan, Russia. Brown and Weir (1963) re-examined the two minerals for the similarity in their structure and composition. In general agreement with previous workers, they established that rectorite and allevardite are identical minerals and proposed that the name rectorite be used. The structure is built-up of pairs of dioctahedral 2:1 layers linked by Ca, Na or K cations. The alternating layers are mica-like and montmorillonite-like. Depending on the dominant cation, Ca-, Na- or K-rectorite varieties have been described. The swelling behaviour of rectorite is similar to that observed in montmorillonites. It is caused by the hydration of the exchangeable cations of the montmorillonite-like layers. Kodama (1966) used thermal analysis and infrared spectroscopy in addition to XRD and chemical analysis to study rectorite from Baluchistan, Pakistan. He described a regularly alternating sequence of Na-mica (paragonite) layers and expandable layers of montmorillonite-beidellite composition. In 1982 the Nomenclature Committee of the International Association for the Study of Clays (AIPEA) accepted the name rectorite for a 1:1 regular interstratification of dioctahedral mica and dioctahedral smectite (Bailey, 1982).

In South Africa, rectorite occurrence was first reported in 1991 at the Loraine and Beatrix Gold Mines located near Welkom (von Rahden et al., 1991). Beatrix mine is situated in the Free State Province of South Africa in the Magisterial District of Matjhabeng, at latitude 28° 15' S and longitude 26° 47' E near the towns of Welkom and Virginia, some 240 km southwest of Johannesburg (Figure 2-6).

Geologically, Beatrix Gold Mine is part of the Free State goldfields situated at the southern edge of the Witwatersrand Basin. The gold deposit is a shallow to intermediate depth type auriferous palaeoplacers (reefs), i.e. the Beatrix Reef and the underlying Kalkoenkrans Reef, both of the Kimberley Conglomerate Formation. Karoo Supergroup sediments cover the mining area underlain by the volcanic rocks of the Klipriviersberg Group (Ventersdorp Lava, Figure 2-7). The Central Rand Group that hosts the gold-

bearing conglomerates exploited by Beatrix Gold Mine follows in stratigraphy (GoldFields, 2011).

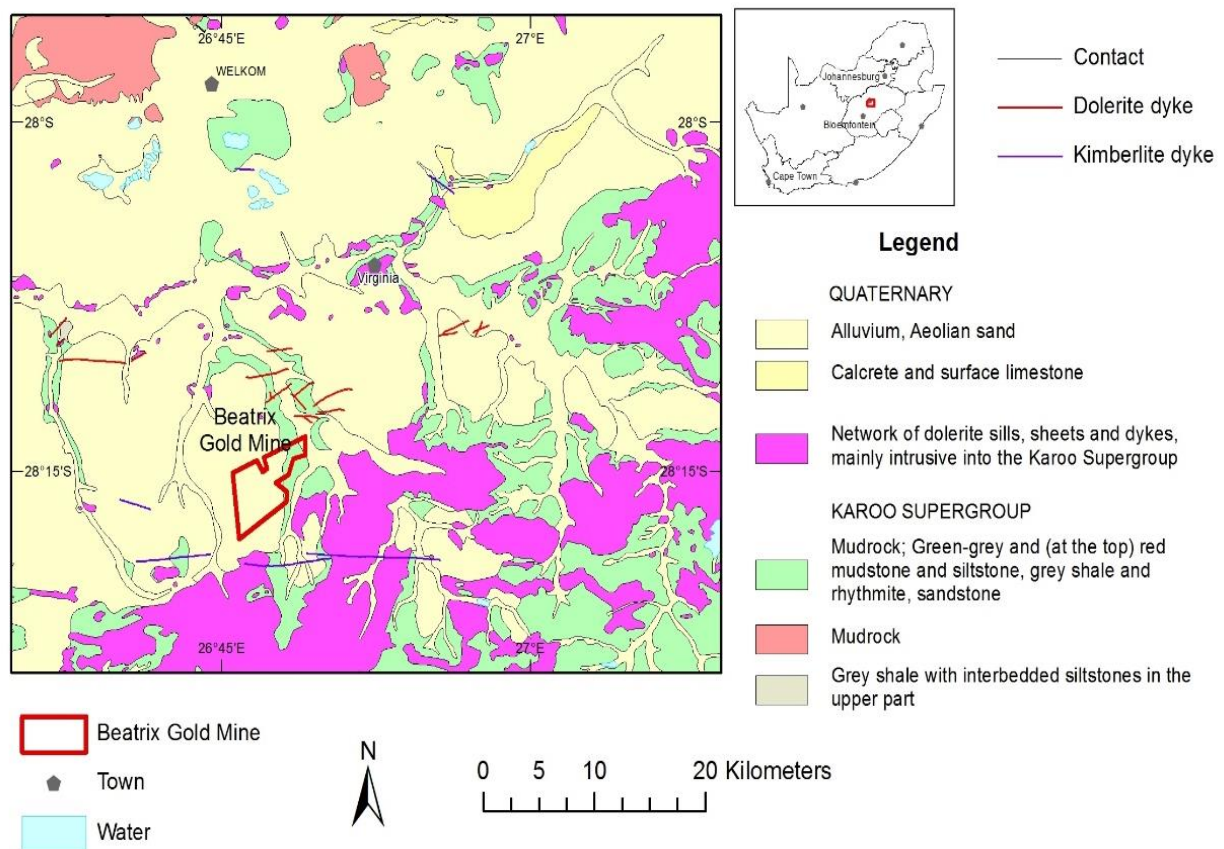


Figure 2-6. Geological map of the area around Beatrix Gold Mine

Rectorite is found in modified shale bands, up to 0.5 m thick, both in the hanging wall and footwall of the Beatrix reef (BXR in Figure 2-7) close to a major underground fault. The bands consist of low-grade metamorphic rock with mineral composition of quartz, muscovite, paragonite, chlorite, pyrophyllite, rectorite, smectite and chloritoid. The rectorite formation is associated with the alteration of other phyllosilicates, pre-existing pyrophyllite in particular, under metamorphic conditions of at least 350 °C and 250 MPa (von Rahden et al., 1991). The shale has been associated with gold losses at the mine in the process of physical and chemical extraction of the gold (Van Vuuren et al., 2000).

Jakobsen & Nielsen (1995) and (Lausen et al., 1999) described the rectorite from Beatrix mine as being Na-Ca-rich. Based on NMR spectroscopy in combination with X-ray

diffraction and chemical analysis, they determined the composition of Beatrix rectorite as a three-component structure (Figure 2-8), made up of smectite- (Figure 2-3), paragonite- (Figure 2-10) and margarite-type layers (Figure 2-9).

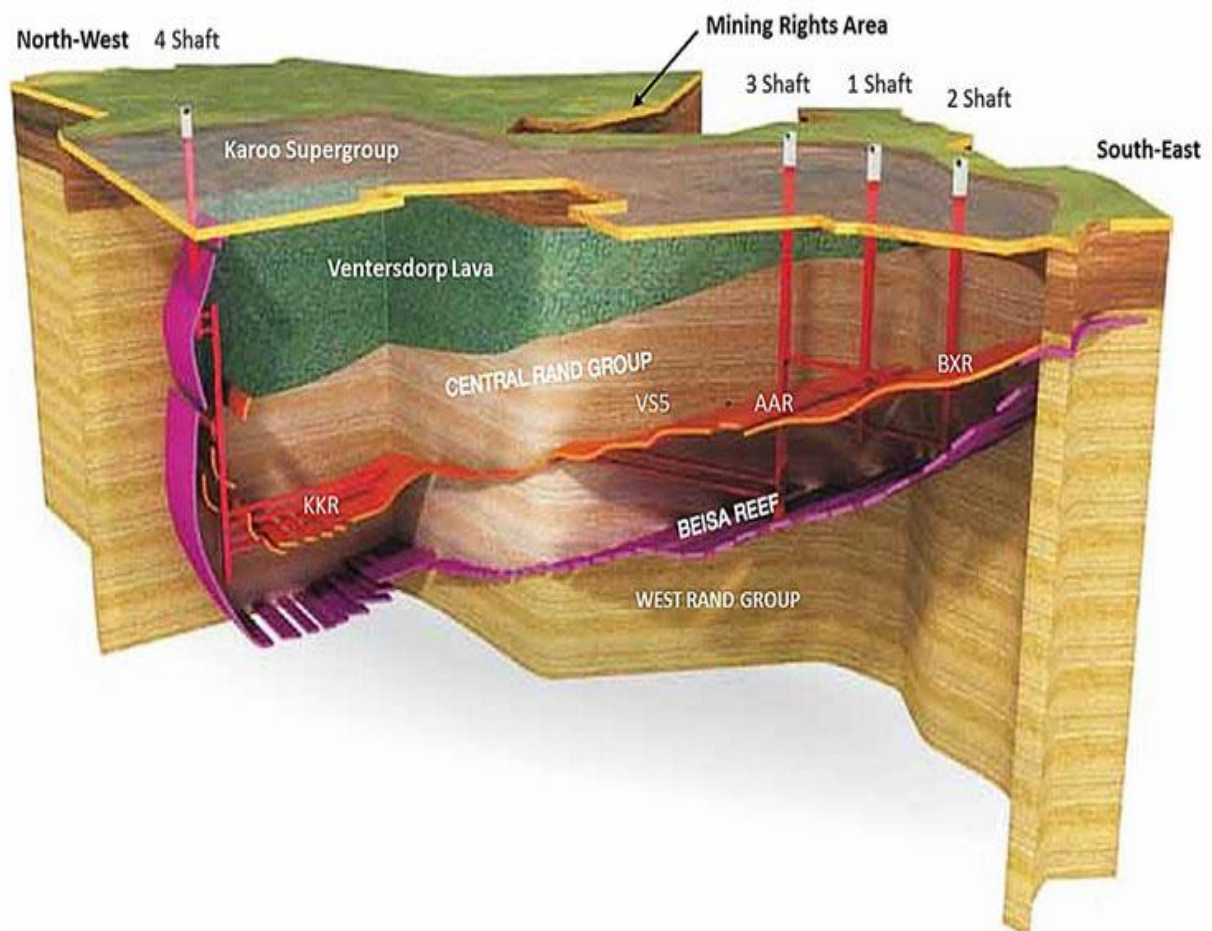


Figure 2-7. Schematic 3D section through Beatrix ore body: rectorite occurs within the modified shale bands of the Beatrix Reef indicated by BXR (Adapted from (GoldFields, 2011))

Rectorite occurrence of economic value exists in China (Hanlie et al., 2008). This large-scale deposit is hosted by Permian pelite rocks at Zhongxiang, Hubei Central China, and the rectorite is of the K-Na type.

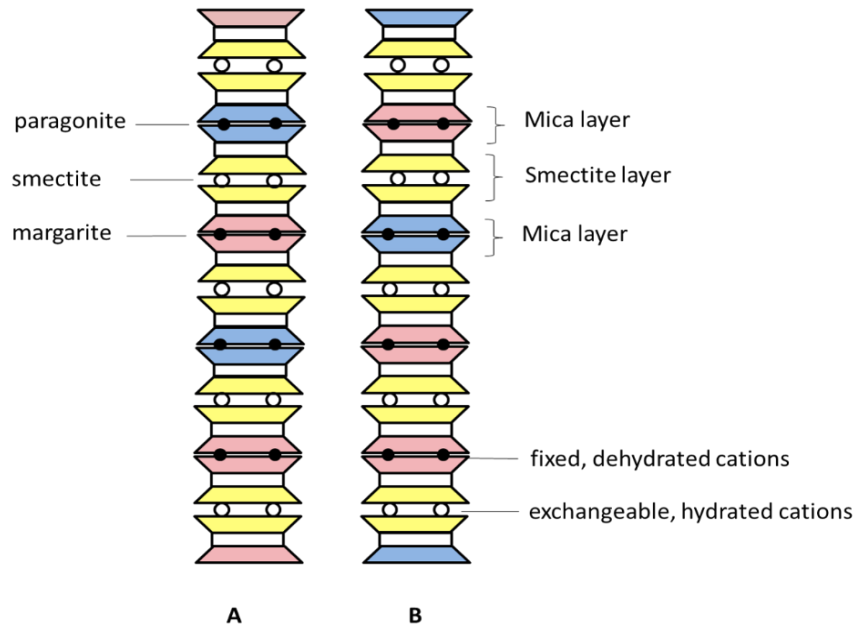


Figure 2-8. Schematic representation of the structure of rectorite adapted after (Jakobsen et al., 1995). Two configurations are shown to illustrate that the margarite and paragonite are not necessarily regularly alternating in the structure

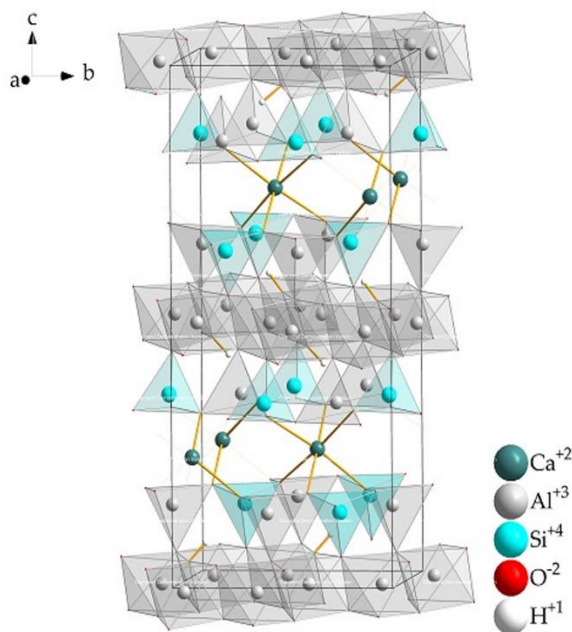


Figure 2-9. The structure of margarite $\text{CaAl}_2\text{Si}_2\text{Al}_{12}\text{O}_{10}(\text{OH})_2$, ICSD 34855 (Guggenheim and Bailey, 1975) (view down crystallographic a -axis)

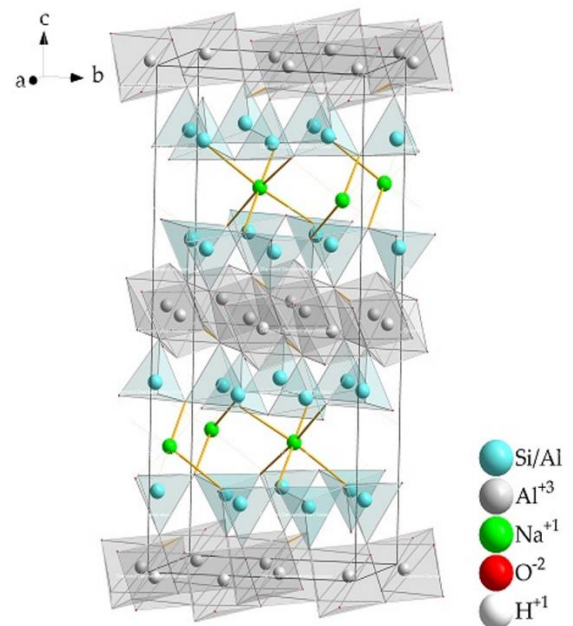


Figure 2-10. The structure of paragonite - $\text{NaAl}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$, ICSD_30663 (Lin and Bailey, 1984). Paragonite may contain $\text{K} < 0.15\%$ (Rieder et al., 1998) (view down crystallographic a -axis)

2.5 Chitosan

Chitosan is the primary derivative of chitin, the most abundant biopolymer after cellulose. Chitin is a natural polysaccharide, a long-chain poly (β -(1 \rightarrow 4)-N-acetyl-D-glucosamine), synthesised by wide range of living organisms as ordered crystalline nano-to-microfibrils and whiskers similar to isostructural cellulose. It is a major component in the exoskeleton of arthropods and the cell walls of fungi where it provides reinforcement and strength for structural components to function (Rinaudo, 2006) . The main commercial sources of chitin are crustaceans such as crab and shrimp shells. It is extracted by initial acid treatment to dissolve calcium carbonate, followed by alkaline extraction to solubilise proteins. Chitosan, a linear polysaccharide, is obtained under alkaline conditions when the degree of deacetylation of chitin reaches around 50 % (depending on the source) and it becomes soluble in aqueous acidic conditions (Figure 2-11). The solubility is enabled by protonation of the $-\text{NH}_2$ function on the C-2 position of the D-glucosamine repeat unit and the polysaccharide is converted to a polyelectrolyte in acidic solution (Rinaudo, 2006). Chitosan is characterised by its degree of deacetylation and molecular weight as these parameters have a strong effect on its solubility and solution viscosity.

There are two antiparallel chains and no water molecules in the orthorhombic unit cell of chitosan (Rinaudo, 2006). The acetyl groups are irregularly distributed along the chains due to the semi-crystalline nature of the initial polymer. In acidic solutions chitosan transforms from the random coiled structure typical of polysaccharides into extended chains due to protonation of the amine groups (Pan et al., 1999). Biopolymer intercalation in the clay interlayer space is influenced by the planar orientation of the chains and the position of the associated H-bonding network. During film formation chitosan forms arrays of parallel sheets of extended chains similar to chitin (Minke and Blackwell, 1978).

The existence of chemically active hydroxyl and amino groups facilitates modifications of chitosan to improve its properties or instil some new properties and functionality, e.g. chitosan can act as a natural electrolyte due to its ability to protonate in acidic media and become a water-soluble polycation. Chitosan is the only pseudo-natural cationic polymer and, being soluble in aqueous solutions, has proven suitable as a flocculent in protein recovery, and for the formation of gels, films and fibres in many applications. Due to its prominent biological characteristics, such as biocompatibility, biodegradability, antibacterial activity, film-forming ability and non-toxicity, chitosan has found utilisation in sectors such as biomedical and pharmaceuticals, cosmetics, food, agriculture, and water and waste treatment (Dutta, 2004; Pillai et al., 2009; Rinaudo, 2006; Wang et al., 2016). However, properties such as weak mechanical strength, and gas and water vapour permeability limit its application spectrum. For these reasons chitosan is often combined in blends with other natural polymers such as starch, alginates, collagen and gelatin, proteins from milk or soy and clays (Elsabee and Abdou, 2013).

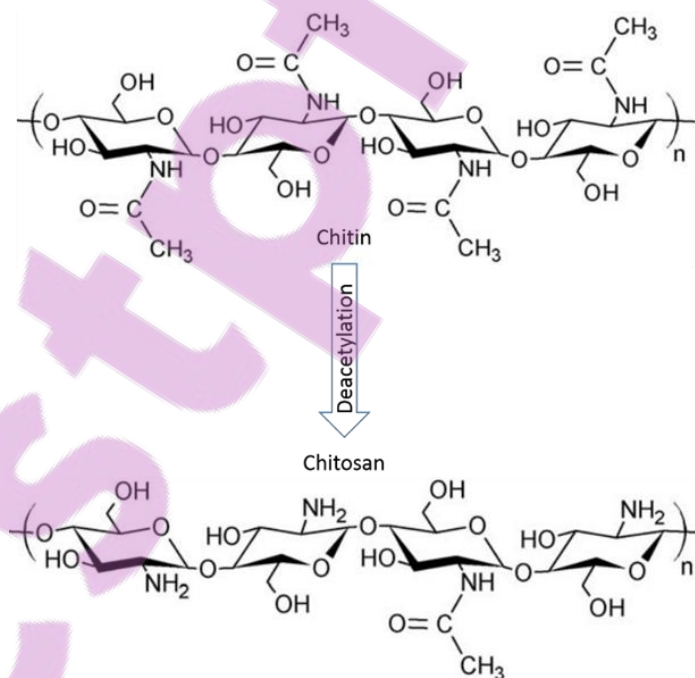


Figure 2-11. Formation of chitosan by partial deacetylation of chitin. (Adapted from (Chivrac et al., 2009))

2.6 Rectorite, nanoclays, biopolymers, bionanocomposites: state of research – fundamental and applied

2.6.1 Rectorite research

The research on rectorite during the 1950s and 1960s focused mainly on the occurrences and structural characterisation, using traditional investigative techniques such as XRD, XRF, IR spectroscopy, SEM, DTA and TGA (Brindley, 1956; Brown and Weir, 1963; Kodama, 1966; Reynolds & Hower, 1970; Korolev, 1961, 1971; Farmer and Russell, 1967). Besides the importance of interstratified clay minerals in the geological context, i.e. in the study of petroleum migration, rock permeability, and the use of smectite-to-illite transition as paleotemperature indicator in sedimentary and hydrothermally altered rocks (Hower, 1981), in recent years their properties have been increasingly investigated in search of novel materials and applications.

In the 1970s and 1980s the subject of clay-organic complexes made rapid advances in materials science, with applications in agriculture, food packaging and a variety of industries. The structures, reactions, experimental methods and applications of naturally swelling minerals have been extensively investigated by a large number of researchers and the findings have been most comprehensively summarised by (Theng, 1974, 2012).

The development of the solid-state NMR in the 1980s and 1990s added a new, highly valuable method for the structural analysis of 2:1 phyllosilicates. These studies brought more detailed insight into the nature and distribution of charged sheets in layered structures by determination of the Si/Al ratios and the ordering in tetrahedral and octahedral sites (Altaner et al., 1988; Barron et al., 1985a, b; Jakobsen et al., 1995; Lausen et al., 1999). The advancements in clay mineralogy and geochemistry allowed the development of a broad range of applications in both theoretical and practical aspects. The remarkable ability of swelling minerals to take up water and other molecules while preserving crystallographic integrity is highly advantageous for improved performance

in materials engineering. There is a growing preference for synthetic analogues where disadvantages such as stacking faults, impurities, disorders and charge heterogeneity can be controlled and tuned to attain the perfect filler with an ultra-high aspect ratio and high transparency for advanced gas-barrier applications, high water-vapour barriers, enhanced mechanical and thermal performance, and the overall increased functionality of nanocomposites (Kalo et al., 2012; Stöter et al., 2014; Stöter et al., 2013; Stöter et al., 2015; Tsurko et al., 2017).

Montmorillonite is the most widely researched and utilised clay mineral in the modification and reinforcement of polymer matrices. For the last two decades research on polymer-layered rectorite and other mixed-layer nanocomposites has been advancing notably, indicating promising prospects for organically modified rectorite (Chen et al., 2009; Huang et al., 2009; Huang et al., 2007; Yuan et al., 2007), natural rubber-rectorite nanocomposites (Wang et al., 2005) and the preparation of pillared clays (Bagshaw and Cooney, 1995; Kooli et al., 1997; Xiao et al., 2007; Zhang et al., 2010). A diverse group of investigators have evaluated the feasibility of using mixed-layer illite-smectite and clay minerals in general as caprock in CO₂ geological storage (Credoz et al., 2011; Gillman, 2011; Waldo, 2011) and for radioactive-waste disposal facilities (Phillips et al., 2011). Synthetic rectorite has also been obtained by a simple and fast method that can, in fact, be applied to any regularly interstratified composition (Möller et al., 2010). Clay-based nanostructured eco-materials in applications from energy storage to biomedical and other biodegradable materials is a fast-evolving field that could offer a relatively simple solution to a range of environmental problems of our time.

2.6.2 Clay films

The need for biodegradable alternatives to current high-performance engineering materials has focused research on sustainable resources and processes with a reduced impact on the environment. Natural phyllosilicate minerals are among the available options used for polymer property enhancement in a growing array of applications

(Lopes et al., 2014). The smectite group clay minerals, montmorillonite in particular, are commonly utilised as reinforcement agent in polymer nanocomposites. Clays are easily modified to suit specific functionalities because of their unique ion exchange capacity, reactive surface properties, lamellar morphology and favourable particle size and aspect ratio (Tjong, 2006; Zhang and Evans, 2012). Clay minerals are structurally similar to some crystalline organic systems with lamellar arrangement, e.g. polyethylene (Ballard et al., 1980). Both crystalline lamellae have comparable dimensions and large aspect ratios, with natural tendency to form oriented structures in thin films, coatings and membranes (Ballard and Rideal, 1983). Hybrid inorganic materials and clay-containing films are trending topics in materials science, especially in clay minerals research (Fernandes et al., 2014; Schoonheydt, 2014; Zhou et al., 2011).

Thanks to their platy morphology, the behaviour of clay minerals in aqueous dispersions facilitates film formation on evaporation. When clay platelets settle, they orient themselves to form brick-like microstructures analogous to that of nacre (Bennadji-Gridi et al., 2006; Sellinger et al., 1998). This natural tendency of clay platelets to assume face-to-face parallel orientation when dried from suspensions is the core principle of film formation by self-assembly (Liu et al., 2008; Walley et al., 2012).

Hauser and Le Beau (Hauser and Le Beau, 1938; Hauser and Le Beau, 1939) first demonstrated the preparation of clay films from bentonite gels. The so-called "Alsifilm" (aluminium silicate film) was developed as a replacement for mica in electrical applications, including insulation (Anon, 1939). Walley et al. (Walley et al., 2012) extended the work of Hauser and Le Beau and confirmed that the simplest way to obtain nanocomposites similar to the microstructural arrangements seen in nacre was to allow dilute clay suspensions to evaporate by slow drying. Biomimetic nanocomposites have shown that layered microstructure is critical for attaining the remarkable properties of nacre (Fernandes et al., 2014; Kawasaki et al., 2010; Liu et al., 2008; Walley et al., 2012; Walther et al., 2010).

Binder-supported composite films with high clay loading exceeding 80 wt.% (Ebina and Mizukami, 2007) displayed high temperature stability and excellent gas-barrier and flame-blocking properties (Wang et al., 2013). Binderless clay films were produced by hydrothermally pre-treating the clay to increase the particle size (Nam et al., 2009b). Due to the presence of impurities, natural clay is usually regarded as unsuitable and hence synthetic smectite clays are preferred to achieve the desired transparency of the films (Ebina and Mizukami, 2007) (Nam et al., 2009b). The effect of interlayer cations in montmorillonite on film formation and properties was also investigated (Nam et al., 2009a). Films prepared from monovalent cation-exchanged montmorillonite appeared well-ordered with thin wavy layers, while those made with polyvalent cations featured poorly ordered layers of larger particles. Bennadji-Gridi et al., (2006) reported a 120 MPa bending strength for montmorillonite films prepared with 10 wt.% sodium hexametaphosphate (NaPO_3)₆ as a binder. However, it seems that to date no significant mechanical properties for binder-free, clay-only films have been reported.

2.6.3 Bionanocomposites: polysaccharides, rectorite-chitosan nanocomposite films

Bionanocomposites are hybrid materials made from structurally combined biopolymers such as polysaccharides, proteins, lipids and nucleic acids with inorganic solids such as clays or other layered materials, phosphates or carbonates at nanometre scale (Darder et al., 2007; Ruiz-Hitzky et al., 2005). In recent years they have become the ultimate alternative to reduce human impact on the environment by the development of efficient ecological solutions for new environmentally friendly hybrid materials. As defined by ASTM Standard D 5488-94d, biopolymers are biodegradable materials capable of undergoing decomposition through microorganisms and enzyme-induced degradation (ASTM, 1994). The synergy of a biodegradable, biocompatible and non-toxic component with the mechanical and thermal properties of the inorganic counterpart produces an environmentally friendly composite material with superior performance. Most

bionanocomposites are synthesised by biomimetic or nature-inspired design and, as such, encompass the advantages of green technologies and enhanced performance. Thus these hybrid materials defeat an old common presumption that materials are either high performance or eco-friendly, but not both simultaneously.

Biobased nanoparticles are efficient building blocks for innovative materials with a diverse scope of application. The biocompatibility requirement is limited merely to specialised advanced biomedical use for tissue engineering, drug delivery and regenerative medicine (Anitha et al., 2014; Armentano et al., 2013). The non-toxic and biodegradable characteristics combined with mechanical, thermal and barrier properties in the new hybrid multifunctional materials attract user and manufacturer interest in a constantly expanding application range. This range includes food packaging and gas-diffusion barriers (Rhim et al., 2013), electrochemical devices (Darder et al., 2003, 2005; Darder et al., 2006), bioplastics and membranes, water purification and treatments, metal toxicity, controlled drug release and pesticides delivery, and energy applications (Brambilla et al., 2014; Liu et al., 2017; Reddy et al., 2013; Zafar et al., 2016; Zhao et al., 2014). Bio-sourced plastics (bioplastics) such as polylactide and plasticised starch are already in use and commercially available. However, their properties, e.g. mechanical strength and barrier property, need to be enhanced to make them really compatible with petroleum-based plastics. Natural phyllosilicate minerals are among the most suitable inorganic property enhancers for polymer applications (Lopes et al., 2014). An addition of clay (up to 5 vol.%) to the polymer matrix may dramatically improve the properties of nanocomposites. In similar manner, the dispersion of nano-sized clay in a biopolymer matrix produces a bionanocomposite with enhanced performance. Hybrid materials with functional properties based on polysaccharides (starch, chitin, chitosan, cellulose acetate, pectin) and nanoclays (smectites – montmorillonite, hectorite, saponite; fibrous clays – sepiolite, palygorskite, halloysite) are being intensively explored at present for novel multicomponent and multifunctional materials (Chivrac et al., 2009; Ruiz-Hitzky et al., 2013). Layered silicates enhance the physicochemical characteristics and mechanical

properties of biocomposite products, among others those of chitosan and its derivatives (Wang et al., 2009b; Wang et al., 2008).

A large volume of research on biomimetic or nature-inspired designs of new nanocomposite materials has been conducted and published in science literature (Fernandes et al., 2014; Kawasaki et al., 2010; Liu et al., 2008; Luz and Mano, 2009; Luz and Mano, 2010; Walley et al., 2012; Zhao et al., 2014). Research on natural and artificial nacre has pinpointed that, in fact, it is the layered microstructure that defines its remarkable properties with functionalities different from or superior to those of the primary constituents. The platelet shape and attractive interactions between clay surfaces are crucial for the formation of textured layers in the preparation of artificial nacre (Bennadji-Gridi et al., 2006). Exfoliation of montmorillonite is critical for the successful formation of clay-based nanocomposites (Kolman et al., 2012). The ability of exfoliated layered clay structures to intercalate compatible biopolymer molecules allows the formation of hybrids with functional properties. However, manufacturing large volumes of these biomimetic aligned structures with unique characteristics and remarkable performance by an effective production process has not been yet achieved.

Clay-containing films and hybridisation of inorganic materials is a hot topic in clay research, materials science and industrial research in general (Fernandes et al., 2014; Schoonheydt, 2014; Zhou et al., 2011). The physico-chemical properties of clay minerals, and especially expandable species from the smectite group, define their specific behaviour in aqueous dispersion crucial for film formation. Upon evaporation from suspensions, the dispersed clay platelets are highly susceptible to the formation of brick-like microstructures similar to that of nacre (Bennadji-Gridi et al., 2006; Sellinger et al., 1998). The natural tendency of clay platelets to assume face-to-face parallel orientation when dried from suspension is the core principle of film formation by self-assembly (Liu et al., 2008; Walley et al., 2012).

Composites and bionanocomposites with mixed-layered clay minerals and specifically ordered structures such as rectorite are not as popular as those with montmorillonite for instance, most probably because rectorite is not as easily available commercially as smectite clays. A substantial part of the research involves organically modified rectorite with the aid of thermal pre-treatments and plasticisers to improve the properties of the clay and resulting composites. Addition of up to 20 wt.% modified rectorite to thermoplastics and natural rubber has improved the glass transition temperatures and stress-strain behaviour of the nanocomposites (Ma et al., 2005; Ma et al., 2004; Wang et al., 2005) and just 2 wt.% organic rectorite positively affected the mechanical strength and thermal and ultraviolet aging in polyester resin composites (Yuan et al., 2007). Organically modified rectorite combined with various biopolymers has been found to impart desirable mechanical properties, e.g. improving the ductility of poly(lactic acid) (Li et al., 2009), enhancing ultraviolet ray resistance, and imparting mechanical and thermal stability properties in rectorite-sodium alginate bionanocomposites (Yang et al., 2009), as well as composites with plasticised starch (Chang et al., 2012) and soy protein (Yu et al., 2007).

Research on rectorite-chitosan (Rec/CS) composites has explored a variety of preparation techniques, clay pre-treatments for property enhancement and fields of applications (Deng et al., 2012; Wang et al., 2007; Wang et al., 2009b; Wang et al., 2005). Among other properties, the excellent catalytic efficiency of Rec/CS-metals has been recorded (Ling et al., 2015; Zhang et al., 2017), as well as organic Rec/CS composites in magnetic separation technology for the remediation of polluted water (Zeng et al., 2015b) and the adsorption of other metals (Zeng et al., 2015a). Rec/CS hybrid materials are highly sought-after in food packaging and preservation due to their good antibacterial activity (Deng et al., 2012; Huang et al., 2012; Wang et al., 2009b; Wang et al., 2006) for biomedical and agricultural applications in drug encapsulation for delivery and controlled release (Wang et al., 2007; Xu et al., 2012) and as a potential non-viral gene carrier (Wang et al., 2008).

2.7 Analytical and characterisation techniques

2.7.1 Brunauer–Emmett–Teller (BET)

The BET technique is used to measure the specific surface area and porosity of macro-, meso- and micro-porous materials. Because of their generally small particle size ($< 2 \mu\text{m}$), clay minerals have a large and variable surface area which has a significant effect on their properties (Table 2-2). The external surface area, which is a function of mean crystallite size and morphology, can be determined by the BET method.

The BET theory was developed in 1938 by a team consisting of Hungarian chemist Stephen Brunauer, American chemical engineer Paul Emmett and Edward Teller, a Hungarian physicist, while working on ammonia catalysts. It was named by combining the first letters of each surname of the three researchers. The theory is principally an extension of the Langmuir theory based on the physical adsorption of gas molecules on a solid surface developed by Irving Langmuir in 1916 (Langmuir, 1918). While the Langmuir theory relates to a monolayer adsorption, the BET theory assumes a multi-layer adsorption model for gas molecules on a solid surface (Brunauer et al., 1938).

Adsorption is defined as the adhesion of gas atoms or molecules to a solid surface. The BET method usually uses nitrogen gas as adsorbate because it is easily available in high purity and is known for its relatively strong interaction with solids. Helium gas is used as a blank before and after each measurement to calibrate the dead volume in the sample cell. Prior to measurements, the sample is degassed in a glass cell for 16 h in vacuum at a high temperature, chosen such that it will not destroy the structure. The solid surface is pre-cooled with liquid N_2 to enhance interaction. Known amounts of nitrogen gas are then released stepwise into the sample cell under partial vacuum to maintain relative pressures below the atmospheric pressure. Saturation pressure is achieved when adsorption has subsided, regardless of any further increase in pressure. Thereafter the sample is removed from the nitrogen atmosphere and heated to release the adsorbed gas,

which is then measured and quantified. The amount of adsorption depends on the exposed surface area as well as the temperature, gas pressure and strength of gas–solid interaction. The data is displayed in the form of a BET isotherm, which plots the amount of gas adsorbed as a function of the relative pressure.

2.7.2 Infrared and Fourier transform infrared spectroscopy (FTIR)

Infrared (IR) absorption spectroscopy is a rapid, non-destructive method applied across a broad range of applications in materials science (McKelvy et al., 1996). It is the main complementary method to X-ray diffraction for structural analysis in clay mineralogy and soil sciences (Farmer, 1968, 1974; Farmer and Russel, 1967; Madejova and Komadel, 2001; Russell, 1987). It provides information on the chemical bonds and their environment with the advantage of differentiating poorly crystalline (amorphous) materials. The technique is based on the absorption of multi-wavelength IR radiation and measures the degree of absorption of the IR spectra. Absorption is related to the molecular stretching and bending vibration modes. In inorganics it is controlled by the constraints of the total unit cell symmetry and local site symmetry of each atom, degree of crystalline order, atomic mass and interatomic bonds in the structure. The absorption of IR radiation is strongly affected by the size and shape of the mineral particles and particle orientation relative to the IR beam (Farmer and Russel, 1966). The number of potentially active internal vibrations is given by $3n-6$ where n is the number of atoms in the unit cell (Russell, 1987). Active infrared vibrations are those where a change in dipole moment occurs during the absorption. The absorption bands in the IR spectra are used to identify minerals, variations in structures and their causes, which are often not easy to identify by other methods.

The rapid development of IR spectroscopy in the 1980s to 1990s led to the replacement of the IR dispersive instruments by the more sensitive and quicker Fourier transform spectrometers (Rintoul et al., 1998). The IR dispersive instruments used transmittance mode and utilised attenuated total reflectance (ATR) as a sampling technique. They were

mostly used, and still are, in the characterisation and analysis of organic compounds. At present IR techniques such as diffuse reflectance, specular reflectance, attenuated total reflectance, photoacoustic spectrometry, infrared microscopy, long-path spectrometry, and remote fibre optic spectrometry are routinely used. They have expanded the utilisation of FTIR methods into more diverse and complex materials such as minerals, polymers, thin films, living cells and biological tissues. ATR combined with the more sensitive FTIR is routinely used in the study of clay minerals, specifically in the adsorption of organic substances. Its main advantage is that it allows IR measurements of dispersions, gels and pastes (Li et al., 2008; Shewring et al., 1995).

In a routine FTIR spectrometer, the detector monitors the full pre-set wavenumber range of radiation emitted by the IR source. The output interferogram is transformed into an absorption spectrum by a computer interface. The FTIR spectrometers are either single beam or double beam. A typical set-up includes the reflectance method (ATR) and classic transmission methods such as KBr-pellet. The ATR experiments are widely preferred as they require less sample preparation, but the method needs corrections for constant optical path to obtain spectra, and processing of the spectral data is more complex. For transmission experiments clay samples are pelletised in KBr; however, due to its hydrophilic nature this method is not suitable for studying water-absorption properties and also poses a risk of spontaneous exchange of K^+ .

Clay minerals are generally distinguished by their characteristic O-H, Si-O, Si-O-Al and Si-O-Si bands in the mid-IR region $4000\text{--}400\text{ cm}^{-1}$.

2.7.3 Characterisation of functional properties

2.7.3.1 Mechanical properties

Mechanical properties are an important measure of product quality characteristics. Testing for film mechanical properties include tensile strength (at yield or at break, MPa), strain at yield (%), elongation at break (%), Young's modulus or elastic modulus (GPa).

For a tensile test a load is applied along the longitudinal axis of a test specimen and the applied load with resulting elongation are measured. Load-deformation data obtained from tensile test do not give a direct indication of the material behaviour, because they depend on the specimen geometry. Using the relationships in equations (Eq.) (2-1) and (2-2) the obtained measurement data can be converted to stress (σ) and strain (ε) values respectively:

$$\sigma = P/A \quad (2-1)$$

$$\varepsilon = \delta/L \quad (2-2)$$

where σ is normal stress on a plane perpendicular to the longitudinal specimen axis; P is the applied load; A is the original cross sectional area; ε is the normal strain in the longitudinal direction; δ is the change in the specimen's gage length, and L is the gauge length.

The resulting stress-strain curve or diagram gives a direct indication of the material properties. For most materials used in engineering the initial section of the stress-strain diagram is a straight line. For this initial portion of the diagram, the stress σ is directly proportional to the strain ε , i.e. the case of uniaxial loading. Thus, for a specimen subjected to a uniaxial load, this relationship can be expressed by Hooke's Law in Eq. (2-3), first recorded in 1678 by Robert Hooke, an English mathematician (Ugural and Fenster, 2003).

$$\sigma = E\varepsilon \quad (2-3)$$

The slope of the straight-line portion of the stress-strain diagram is called the Modulus of Elasticity or Young's Modulus E (McNaught and Wilkinson, 1997) and is calculated by:

for normal stress-strain: $E = \sigma/\varepsilon$ (2-4)

for shear stress-strain: $G = \tau/\gamma$ (2-5)

where E is the Young's modulus or modulus of elasticity, and G is the Shear modulus or modulus of rigidity.

2.7.3.2 Optical property

Ultraviolet-visible (UV-Vis) spectrophotometry uses the principle of absorbance of light by a substance at a given wavelength to determine its concentration. The method uses the light in the ultraviolet and visible range of the electromagnetic spectrum. The electromagnetic spectrum ranges from very short wavelengths 10^{-4} nm to 1 nm (including gamma and X-rays) to very long wavelengths 10^5 – 10^{10} nm (including microwaves and broadcast radio waves). The visible spectrum constitutes only a small part of the total radiation spectrum. Most of the radiation that surrounds us cannot be seen, but can be detected by dedicated sensing instruments.

When a beam of light passes through a substance or liquid, a portion of it gets absorbed and the other part is transmitted through. The ratio between the intensity of the light entering the sample (I_0) and that exiting (I) at a particular wavelength is defined as transmittance (T). The absorbance (A) is the negative logarithm of T , i.e.:

$$A = -\log T \quad (2-6)$$

The Beer-Lambert Law relates to the attenuation of light to the properties of the material that the light is passing through within well-defined prerequisites of the law. A simplified definition states that the absorbance of a beam of collimated monochromatic radiation in a homogeneous isotropic medium at a given wavelength is proportional to

the absorptivity of the material a (constant at each wavelength) or also ε (molar absorption coefficient), the concentration of the substance c and the path length l (the distance light travels to exit the sample, i.e. thickness) (McNaught and Wilkinson, 1997). So the Beer-Lambert Law for absorbance of light is:

$$A = \varepsilon cl \quad (2-7)$$

A basic UV-Vis instrumental set-up includes: a source of radiation, usually a tungsten lamp for the visible region and either a hydrogen or deuterium lamp for the UV spectral range; a monochromator and optical geometry to ensure that a single-wavelength monochromatic light beam enters the sample compartment; a sample handler; a detector and a measurement system for light intensity; and a software interface for data processing.

2.7.4 Microscopy

2.7.4.1 Scanning electron microscopy (SEM)

SEM is used for high-magnification imaging and to obtain elemental spectra to determine mineral chemistry, provided an analytical system is available. In a principal set-up, an electron gun emits a beam of high-energy electrons under high-vacuum conditions. This beam travels through a series of magnetic lenses designed to focus the electrons on a very fine spot. Near the sample, a set of scanning coils moves the focused beam back and forth across the specimen (Goldstein et al., 1992; Wilson, 1987).

SEM images are produced by scanning the electron beam over a specimen surface and displaying the signal from an electron detector on a computer monitor by means of an amplifier.

Depending on whether secondary or backscattered electrons are used, the images provide either topographic or compositional information on the specimen. Secondary electrons (SE) are low-energy electrons ejected from the sample as a result of inelastic

collisions with beam electrons. They are produced near the surface of the sample, from a small area/volume around the beam tip (analytical volume). The resolution of the image is therefore very good and provides topographic information on the sample. Backscattered electrons (BSE) are high-energy primary electrons emitted as a result of elastic collisions with specimen electrons. BSE emission intensity is a function of the specimen's atomic number or average atomic mass, i.e. the higher the atomic number or average atomic mass, the brighter the signal, i.e. the image. BSE imaging is used to obtain qualitative compositional information from the sample.

Theoretically, SEM requires a highly polished surface for optimum imaging and X-ray microanalysis. For the imaging of clay minerals, the specimens are prepared as grain mounts, preferably freeze-dried to preserve fresh surfaces and structures. Specimens are commonly coated with gold or carbon for conductivity.

An Energy Dispersive System (EDS) linked to a SEM enables X-ray microanalysis. The process for X-ray microanalysis is as follows: when the electron beam interacts with matter, energy is released in the form of radiation over a variety of wavelengths. This energy results from beam electrons ionising the inner electron shells of an atom. When the excited atom relaxes, i.e. an outer electron fills the inner shell, radiation is released which is characteristic of the atom's electron shells' energy level. The portion of radiation in the X-ray part of the spectrum is referred to as characteristic X-rays. The generated X-rays are collected and plotted as an elemental spectrum. Each peak on the spectrum represents a transition with a characteristic energy – every element has its own “fingerprint” of peaks.

Maps of relative concentration for multiple elements can be generated using the SEM. This is achieved when an electron beam is scanned across the sample, stopping at regular intervals to count the number of X-rays arriving at the detector. The number of counts at each stop (pixel) can then be displayed as a map. By maximising the number of points at which X-rays are counted and by scanning the beam multiple times over the sample,

high-resolution maps can be produced. Element distribution maps could show concentration differences not detectable using backscattered electron imaging.

2.7.4.2 Transmission electron microscopy (TEM)

TEM and SEM are the two basic types of electron beam instruments. Usage of TEM for examination of clay minerals is not very popular due to the delicate nature of clay specimens and the risks of damaging structures of interest during sample preparation or by the electron beam during analysis. However, the high-resolution information that can be obtained at a unit cell level by imaging layered structures, with the ability to measure layer distances, can be invaluable for clay mineral studies.

In TEM the electron beam is transmitted through an ultra-thin section of the specimen under examination. The image is produced as a result of differential scattering and absorption as a function of the variation in electron density of the specimen. Areas of higher density scatter and absorb more and thus appear darker than areas of lower electron density (Flegler et al., 1993). Routinely, image resolutions of tenths of nanometres can be achieved. Proper sample preparation is crucial to provide the required electron-optically transparent specimens.

2.7.5 Nuclear magnetic resonance (NMR) spectroscopy

Solid-state NMR spectroscopy is a theoretically complex and powerful analytical technique fast becoming the preferred method for structural characterisation of powdered molecular crystals. NMR spectroscopy is the dominant method of analysis for organic compounds, but it is also increasingly gaining interest in inorganic chemistry and biochemistry for valuable structural information (Lambert and Mazzola, 2004). Nuclear magnetic resonance is a property of the nucleus of the atom known as nuclear spin (I). Although isotopes can have various spin values I including 0, the most useful for spectroscopy are those nuclei with $I = \frac{1}{2}$. A nucleus with a spin is associated with magnetic moment resembling thin atomic bar magnets. NMR spectroscopy is based on

the fact that when a population of magnetic nuclei is placed in an external magnetic field, the individual nuclei align in a finite number of orientations. The energy levels are determined by thermodynamics as described by the Boltzmann distribution, i.e. the lower energy level (nucleus aligned with the field) will contain slightly more nuclei than the higher level (aligned against the field). An NMR experiment involves electromagnetic radiation to induce the nucleus to jump to the higher energy state by absorbing energy, or by release of energy the nucleus may “relax” back to the lower energy state. Radio waves are at the very low energy end of the electromagnetic spectrum and are sufficient to induce the desired energy transition. An NMR instrument uses the Fourier transform method to apply a broad pulse of radio waves to excite all nuclei and the results are recorded and analysed by computer. In a real molecule, the effective magnetic field experienced by a nucleus (B_{eff}) includes not only the applied field (B_0), but also the magnetic effect of the surrounding nuclei and electrons. This causes interference in the absorption frequency, and is corrected for by using a standard, usually tetramethylsilane (TMS), defined as zero point. The output from the absorption experiment is plotted as a series of peaks in an NMR spectrum. The difference in ppm (parts per million) from the zero point is referred to as the chemical shift (δ). A typical range for δ is around 12 ppm for ^1H and 220 ppm for ^{13}C . It is customary to have the zero point at the right-hand side of the spectrum, with numbers growing to the left (“downfield”). Typical isotopes useful for clay mineral crystallography by means of NMR spectroscopy are ^1H , ^{27}Al , ^{23}Na and ^{29}Si analysed by solid-state magic angle spinning NMR (MAS NMR).

2.7.6 Particle size determination and ζ -potential

Particle size is a fundamental characteristic of clays and other particulate materials. Particle size distribution (PSD) may critically affect materials’ behaviour and the properties of solids, suspensions, emulsions and aerosols. Therefore its accurate determination is of the utmost importance for research and industrial quality and performance. There are many different methods to measure particle size, e.g.

sedimentation, laser diffraction, dynamic light scattering, electron microscopy and image analysis. Each technique detects size according to its own physical principle and the particle shape factor is the major cause of disagreement between analysers. It is crucial to select the most suitable technology depending on the physical and chemical attributes of the material, property scope and application. It is always beneficial, if possible, to combine at least one imaging and one direct measurement technique. Microscopy or automated image analysis are the only techniques that, besides particle size, can describe multiple parameters such as shape and morphology which are important for particles with a larger aspect ratio, such as phyllosilicates.

2.7.6.1 Particle size distribution (PSD) in submicron to millimetre size range

Laser diffraction (LD) is a well-established and widely used technique for the determination of particle sizes ranging from $< 0.02 \mu\text{m}$ to $\sim 2 \text{ mm}$ particles, depending on material and instrument sensors. The core principle of the LD method is measuring the angular variation in intensity of light scattered from a laser beam passing through a dispersed particulate sample. The angle of light scattering is inversely proportional to particle size, i.e. small particles scatter light at large angles relative to the laser beam. The measured scattering intensity data is processed and analysed by the system to calculate the size of the particles using the Mie theory of light scattering (Bowen, 2002; Lips et al., 1992). Reporting of results should define “average particle size” and always be accompanied by reference to the method of measurement or distribution base. There are different ways to define particle size. Many techniques use the assumption of spherical particles and report results as an equivalent spherical diameter. Most common is the equivalent volume spherical diameter, d_v , defined as the diameter of a sphere having the same volume as the particle. Thus, an irregular-shaped particle can be described in terms of the diameter of imaginary spherical particles that occupy the same volume as the measured irregular particle. The size distribution derived by laser diffraction technique is volume-based. For instance, if results indicate that 10 % of particles are in the size

category 20–22 μm , this means that the total volume of all particles with diameters in this range represent 10 % of the total volume of all particles in the distribution. Once the output data is analysed, the information can be displayed in different ways depending on application. A frequency curve shows the “modes” or peaks in the graph: several peaks indicate that there are distinct sizes of particles in the sample. Cumulative undersize or oversize indicates results “under” or “over” in the form of the percentage of the sample below or above a certain size of particle. The statistics of the PSD are calculated from the data using the derived diameters $d(m,n)$, which is an internationally agreed standard method for the mean and other moments of particle size BS 2955: 1993 (BSI, 1993).

2.7.6.2 Particle size distribution (PSD) in nanometre to submicron size range

Dynamic light scattering (DLS), also called photon correlation spectroscopy (PCS) or quasi-elastic light scattering (QELS), is the technique commonly used to measure the size of particles in the submicron and nanoparticle region while dispersed in liquid. It is often complemented by the atomic force microscopy (AFM) technique for its capability for 3D visualisation of morphology, surface texture and particle roughness. Some of the modern ultra-sensitive analysers can measure the size of macromolecules in solution, e.g. proteins. The theoretical principles were laid out in the earliest work on light scattering by the atmosphere by Lord Rayleigh (real name John Strutt) for particles much smaller than the wavelength of incident radiation (Rayleigh, 1881, 1899; Strutt, 1871). Later experimental research combined Rayleigh and Mie scattering theories for complete solution for spherical particles of any size and refractive index (Cox et al., 2002; Drake and Gordon, 1985; Weiner et al., 2001). DLS measures Brownian motion and relates this to particle size.

The primary results from DLS are the mean value from intensity distribution called Z-average (Z average) and polydispersity index (PDI), which describes the distribution width. Usually it is possible to convert results to a volume or number distribution for easy

comparison with other techniques. The cumulant analysis by the DLS method calculates the autocorrelation function as defined by ISO 13321 and ISO 22412 standards for particle size analysis by DLS. In order to produce comparable results, all systems should comply with the standard (ISO, 1996, 2017). The polydispersity index (PDI) is dimensionless and derived from the autocorrelation function with the assumption of a monomodal sample. It describes the width of Gaussian distribution. PDI values less than 0.05 indicate a highly monodisperse mode rarely seen in real dispersions. Values greater than 0.7 suggest an extremely broad size distribution and a sample that is not suitable for the DLS technique. Approximate guide values for dispersity parameters by DLS regard a PDI between 0.00 – 0.1 as monodisperse uniform and narrow distribution respectively, whereas a PDI in the range 0.1–0.4 and > 0.4 indicates a moderate polydisperse and a broad distribution respectively.

The Z-average is a hydrodynamic parameter and therefore only applicable for particles in dispersion or molecules in solution. Particle size derived as Z-ave (d_{nm}) will only be comparable with other techniques if the sample is monomodal, with a very narrow width of distribution, i.e. monodisperse, and particles are spherical or near-spherical in shape. In the case of a polydisperse system, particle size can be reported as d (intensity), d (volume) or d (number).

2.7.6.3 Zeta potential

Zeta potential (ζ -potential) is a physical property of any particle in suspension, macromolecule or material surface. It is a measure of the charge on a particle surface in a specific liquid. Determination of ζ -potential is useful in predicting suspension stability and understanding inter-particle interactions in suspension. The stability of colloidal systems is explained by the DLVO theory (named after Derjaguin, Landau, Verwey and Overbeek – scientists who developed the theory in 1940) (Van Olphen, 1987). It deals with the balance between two opposing forces, i.e. electrostatic repulsion and van der Waal's attraction. The ionic environment around a charged colloid particle is best

described by the electric double-layer model: the Stern layer of counter-ions directly adjacent to the charged particle surface, followed by the diffuse layer further away but still attached to the particle such that it moves together with the particle. The thickness of the double layer depends on the type and concentration of ions in solution. The boundary between the double layer and the ions in equilibrium in the solution is called the slipping plane. The potential in mV measured at the slipping plane distance from the particle surface is defined as ζ -potential and is related to the mobility of the particle (Figure 2-12).

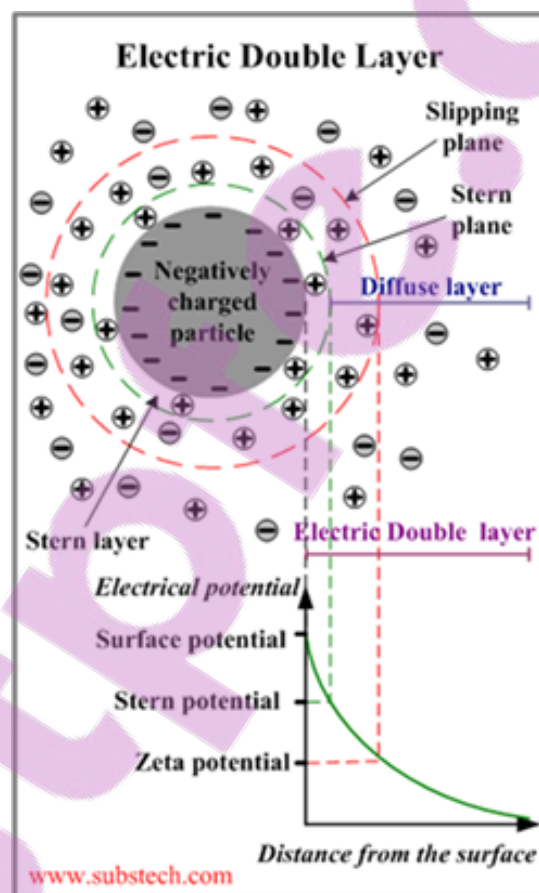


Figure 2-12. Schematic illustration of electric double layer and ζ -potential

To measure ζ -potential, a small volume of dispersed sample is injected into a cell containing two electrodes for the induced electric field. In a voltage field the particles move towards either the cathode or the anode depending on their surface charge. The direction of the motion indicates positive or negative charge respectively.

The instrumentation for ζ -potential is usually combined with that for DLS. Optical configuration for ζ -potential measurements includes a laser as a light source for incident and reference beams. The incident beam is aimed at the centre of the sample cell and the scattered light is detected. In an electric field applied to the cell, any particle moving through the measurement volume will cause fluctuation in light intensity with a frequency proportional to the particle speed. The speed of the particle motion is captured by a detector and transmitted to a digital signal processor to calculate the magnitude of the charge. The data is processed by the appropriate software to produce a frequency spectrum, from which the electrophoretic mobility and ζ -potential, respectively, are calculated.

2.7.7 Thermal analysis

Thermoanalytical methods are used complementary to the principal mineralogical tool, XRD, in the qualitative and quantitative analysis of mineral mixtures. While the XRD uses structural information to characterise and identify phases, thermal techniques study the response and change in physical properties of materials upon heating under controlled conditions. Thermal analysis is most beneficial in the study of reaction processes and their products under dynamic temperature-pressure regimes such as dehydration/hydration, interaction of clays with organic and inorganic substances, or oxidation and reduction processes (Wilson, 1987). The most useful for clay studies are differential thermal analysis (DTA) and thermogravimetric analysis (TGA). DTA analysis detects changes in thermal properties by measuring the difference ΔT in temperature between the sample and a thermally inert reference standard under a controlled temperature range up to 1 400 °C. The DTA curves show endothermic or exothermic reactions indicating the energy changes in a sample. For instance in clays, endothermic reactions result from the desorption of surface H₂O and dehydration (loss of interlayer H₂O) at temperatures < 1 000 °C or dihydroxylation and eventually melting at more elevated temperatures. Recrystallisation at high temperatures is exothermic and it may

occur concurrently with dihydroxylation and melting in this temperature range (Guggenheim and Van Gross, 2001). Alternatively, differential scanning calorimetry (DSC) can be used to monitor endothermic and exothermic reactions by measuring the energy input required to keep a sample and the standard at the same temperature over a controlled heating period. DSC is especially used for determination of enthalpy values.

The TGA curves indicate weight changes during heating. In clay minerals these changes are basically a function of water content and provide a very good indication of the mode of water present in the clay structure, i.e. surface absorbed water, interlayer bound water, hydroxyl or crystalline water. The TGA analysis produces an integral weight loss data curve that can be better interpreted using the first derivative of the weight loss curve, i.e. the derivative thermogravimetric analysis (DTG). Quantitative DTG is used mostly for poorly crystalline substances that cannot be adequately quantified by XRD due to the limitations of the technique with such materials.

2.7.8 X-ray diffraction (XRD)

X-ray diffraction (XRD) is by far the most commonly used laboratory tool for mineral/phase identification and structure characterisation. The discovery of X-rays in 1895 enabled scientists to determine crystal structure at atomic level. Because the wavelength of X-rays is comparable to the size of atoms, they are ideally suited for studying the structural arrangement of atoms and molecules in a wide range of materials. The technique provides information about the types and nature of crystalline phases, their structural make-up and degree of crystallinity, microstrain and size, and orientation of crystallites. X-rays are electromagnetic radiation with typical photon energies in the range of 100 eV–100 keV. For diffraction applications, only short-wavelength X-rays in the range of a few Angstroms to 0.1 Angstrom are used, which is about the same size as an atom. In the electromagnetic spectrum they occur between gamma rays and the ultraviolet rays.

Diffraction occurs as waves interact with a regular structure whose repeat distance is about the same as the wavelength (Moore and Reynolds, 1997). Bragg's Law (Eq. 2-8) empirically defines the conditions for diffraction in terms of the wavelength of the incident X-rays (λ), the interatomic distance between atoms planes (d), and the incidence angle of the X-ray beam to the atom planes (θ) (Figure 2-13), i.e.

$$n\lambda = 2d\sin\theta \quad (2-8)$$

If the atoms are arranged in a periodic fashion, as in crystals, the diffracted waves will consist of sharp interference maxima (peaks) with the same symmetry as in the distribution of atoms.

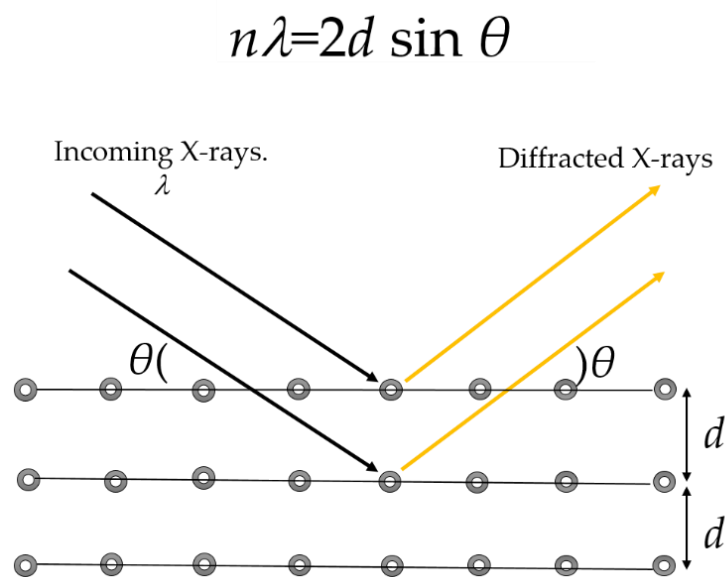


Figure 2-13. Schematic representation of Bragg's Law for X-ray diffraction

Measuring the diffraction pattern therefore allows the deduction of the distribution of atoms in a material (Figure 2-13). The peaks in XRD diffraction patterns are directly related to the atomic distances and thus allow determination of crystal structure. Each crystalline solid has its unique characteristic X-ray pattern that may be used as a "fingerprint" for its identification.

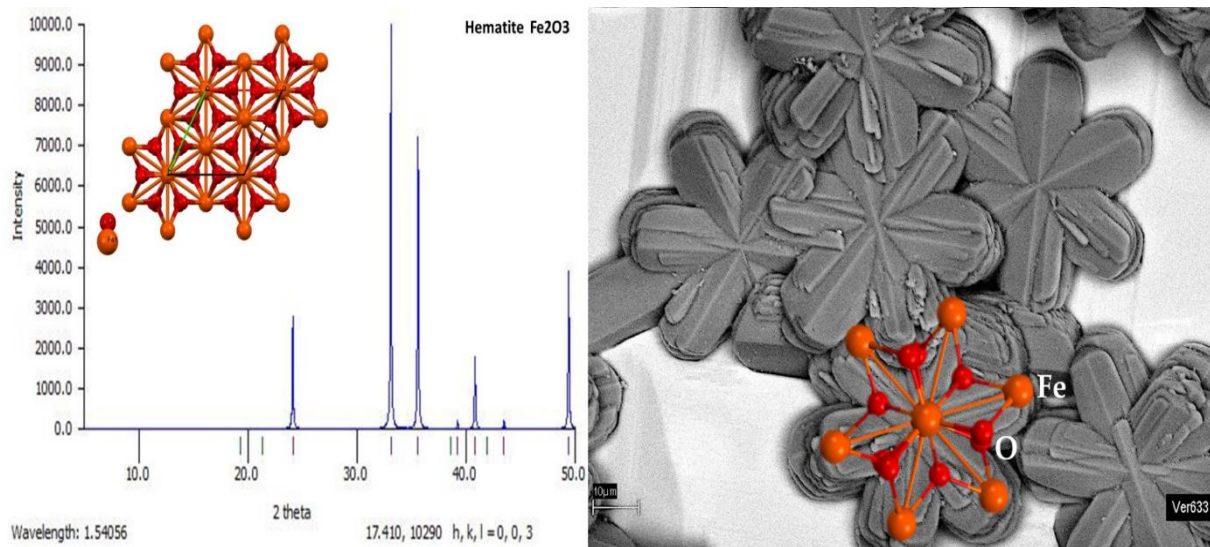


Figure 2-14. X-ray diffractogram (left) showing the peaks of hematite and insert of its structure model; (right) SEM image of a hematite crystal group with a fragment of the structure model superimposed to fit crystal morphology; FOV 137 μm

2.7.9 X-ray fluorescence (XRF) spectroscopy

The method most commonly employed for bulk chemical elemental analysis of clay materials is X-ray fluorescence spectroscopy (XRF). The technique is based on the ability of atoms constituting the matter to act as a secondary source of fluorescent X-rays when material is irradiated with primary X-rays or an electron beam source. The energy of the emitted X-rays is a function of the atomic number and concentration of each element constituent, which is the basis of quantitative elemental XRF analysis. The technique is applicable to all but the elements with a very low atomic number with sensitivities of parts per millions (ppm) (Jenkins, 1999). Fluorescent X-rays can be detected based on energy using energy-dispersive spectrometers (EDS) or their wavelength by means of wavelength-dispersive spectrometers (WDS). Modern technology offers combined EDS-WDS systems to accommodate a versatile range of materials and applications. An X-ray photon beam with enough energy to affect the electrons in the inner shells of the atoms in a sample is emitted by an X-ray tube (or an electron beam source) and focused on the sample. Upon interaction, electrons from the inner orbital shells of the atom are displaced

("kicked out"), creating vacancies and energy unbalance in the atom. Those vacancies can be filled by electrons from higher orbits that move down to a lower orbit. An electron loses energy when it drops from a higher binding electron shell to a shell closer to the nucleus (Figure 2-15). The amount of energy lost is equivalent to the difference in energy between the two electron shells, which is unique to each element. These energies can be used to identify the element from which it emanates and determine the quantity of each element present by either the instrument or by other software. Characteristic X-rays are labelled K, L, M or N, in analogy to the transitional shells from which they originate. Accordingly, the suffixes alpha (α), beta (β) or gamma (γ) indicate different subshell levels (Jenkins, 1999).

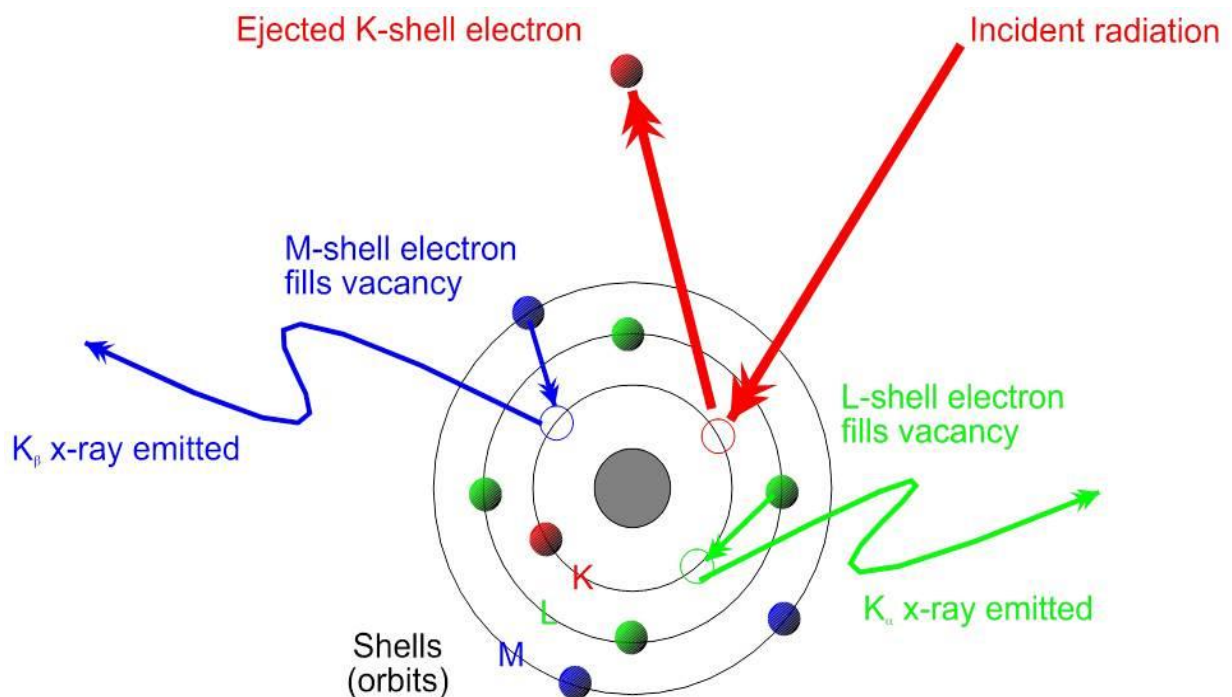


Figure 2-15. Production of a characteristic X-ray

CHAPTER 3 EXPERIMENTAL: MATERIALS, METHODOLOGY, CHARACTERISATION TECHNIQUES AND INSTRUMENTATION

3.1 Materials

Three samples of mine host-rock material containing rectorite (Figure 3-1) were obtained from Beatrix Gold Mine and marked RT1, RT2 and RT3. Sample RT1 was collected in 1995, sample RT2 in 2010 and sample RT3 in 2012. The samples differ in their visual appearance with RT1 containing large light blue-grey platy aggregates with a silky lustre, whereas RT2 and RT3 represented disintegrated host rock mine material (Figure 3-2 (A, B and C)). Note that throughout this text RT followed by a number 1, 2 or 3 denotes the sample name/number, whereas in the composites the abbreviation Rec is used for rectorite mineral proportion in the composites.



Figure 3-1. In situ rectorite-rich material in the shale footwall at Beatrix mine

All samples were purified to concentrate high-purity rectorite clay for characterisation tests and experimental work. Unless otherwise indicated, the characterisation presented here is based on purified material with a rectorite content above 90 wt.% (as determined by XRD analysis). Structurally and chemically, the purified materials from the three samples are very similar and are categorised as rectorite, except where applicable specifics are highlighted. For rectorite characterisation mostly material from sample RT1 was used, whereas for cation-exchanged modifications and nanocomposite films purified rectorite from sample RT3 was used because of its abundance.

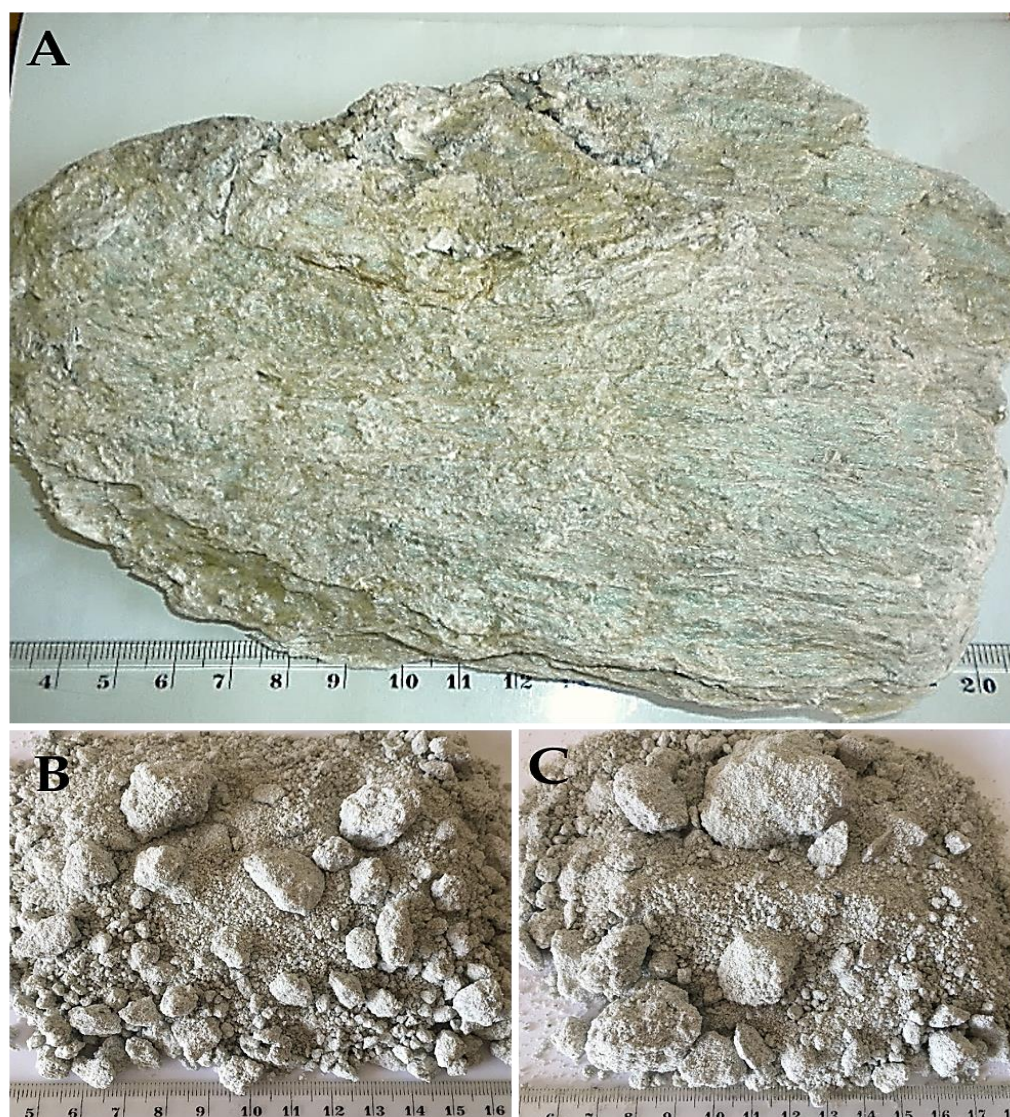


Figure 3-2. Macroscopic view of Beatrix rectorite from: (A) sample RT1 with rectorite content ~72 %; (B) disintegrated mine material from sample RT2 with rectorite content ~60 %; and (C) sample RT3 containing ~46 % rectorite

Organic surfactants, i.e. long-chain dodecyl-dimethyl ammonium chloride (DCC10), dialkylmethylammonium chloride (DCC18) and hexadecyltrimethyl-ammonium chloride (SCC16), as well as the metal chlorides of Li, Na, NH₄, K, Cs, Mg, Ca, Sr and Ba for cation exchange, were sourced from Merck Chemicals, SA. Chitosan (CS) of average molecular weight, i.e. viscosity of 150 mPas (1.0 wt.% solution in 1 % acetic acid at 25 °C) and degree of deacetylation 86.7 %, was obtained from G.T.C. Bio Corporation, China.

Other chemicals used in the laboratory experimental work such as acetic acid (CH₃COOH), silver nitrate (AgNO₃), calcium nitrate tetrahydrate (Ca(NO₃)₂·4H₂O) and other supplementary laboratory consumables were supplied by either Merck Chemicals, SA or Sigma Aldrich, SA (since 2014 Sigma Aldrich has been a subsidiary of Merck KGaA). High-purity corundum (Al₂O₃) and zincite (ZnO) used for calibration and/or as internal XRD standards for structure modelling were purchased from Sigma–Aldrich, SA.

3.2 Primary processing of rectorite clay material

Primary processing of raw clay material and sample preparation were done as carefully as possible to prevent any physical distortion of the clay structure that may affect its behaviour, properties and the respective experimental results. The general guidelines on sample preparation for clay minerals outlined by Brindley and Brown (1984) and Moore and Reynolds (1997) were followed, with slight adaptations to accommodate specifics encountered in the preparation process. All pre-treatments were kept to a minimum and as mild as possible, both physically and chemically.

The method and degree of primary sample processing were determined by the physical appearance and aggregate size of the raw material of the three samples. Where applicable, the material containing raw rectorite was first disaggregated with a laboratory jaw crusher (sample RT1) to break down large platy aggregates to around 1 – 2 mm, followed by further size reduction in a swing mill, coffee-grinder, kitchen blender,

or McCrone micronising mill (McCrone Research Associates Ltd., London). Samples RT2 and RT3 were first sieved and the < 75 μm fraction used for further purification. As needed, vibrating mill (Retsch GmbH, MM30401, 80W) was utilised to prevent lump formation and aggregation of milled material.

3.3 Purification of rectorite

Structural identification and characterisation of clay minerals is usually performed on a concentrated clay fraction extracted from the bulk. In most cases the extraction of a small portion of < 2 μm clay fraction by gravity separation is sufficient for analytical purposes. However, for the characterisation of the engineering properties of rectorite products in this study a more efficient purification process was required to obtain larger quantities of concentrated pure material. The design and extent of the purification procedure was based on bulk mineral composition and mineral associations determined by a preliminary XRD and SEM investigation of the starting material. These observations suggested that impurities could be liberated through ultrasonic dispersion and separated by gravity sedimentation which served as the basis for the design of the purification procedure. In this way it was possible to remove the larger-than-clay fraction components such as quartz and other lump-sized clay minerals from the bulk.

Different methods including sieving, a Wilfley table for gravity separation by shaking, chemical treatment and gravity sedimentation were experimentally tested and evaluated to optimise the final process. It was established that the most efficient and successful method/procedure for best rectorite recovery involved primary disaggregation as needed, dispersion by ultrasound, gravity separation through sedimentation and recovery by centrifugation.

3.3.1 Removal of calcium carbonate

Calcite impurity in sample RT1 was removed using 0.3 M acetic acid following a standard method (Ostrom, 1961). The separation was performed at room temperature and the

process was closely monitored by measuring the pH after each cycle. The samples were repeatedly washed after effervescence had subsided. X-ray diffractograms were compared before and after exposure to acid to ensure that calcite had been removed and no damage to the rectorite structure had occurred. In the process some quartz and clinocllore were also washed out.

3.3.2 Removal of quartz, clinocllore, mica and pyrophyllite

This procedure was applied to samples RT2 and RT3 using the < 75 µm fraction of the bulk disintegrated mine material. The method was carefully designed and experimentally refined according to the mode of occurrence of rectorite in the Beatrix material with optimal utilisation of the available laboratory equipment. The aim was to find the most efficient, fast and economical process for maximum recovery of high-purity rectorite clay.

For the development and optimisation of the rectorite purification method, a Malvern Mastersizer 2000 instrument was utilised. The analyser bath was used to mimic the process of particle disaggregation and dispersion. Values for solid/liquid ratio, ultrasound settings, obscuration and dispersion time were monitored, measured, evaluated and adjusted for optimal performance. The concentration of particles in suspension during a measurement in a particle size analyser was monitored by the obscuration of the laser beam caused by the sample. It is a measure of the fraction of light “lost “when the incident laser beam passes through the sample in suspension due to scattering or absorption.

The intensity and duration of ultrasound dispersion was derived from the outcomes of two experiments: (i) three runs were performed at different ultrasound (US) settings, namely 70 %, 30 % and 0 % US over a duration of 2 h, measuring obscuration every 5 min; (ii) the particle sizer was run overnight at 30 % US, measuring obscuration every 5 min. The plots in Figure 3-3 show that the obscuration increased quickly in the first 30

min, then slowed down and became almost a straight line before increasing again after 60 min, best evident in the 30 % experiment. This ultrasound setting also provided obscuration within 10–20 % for up to 60 min, which is the optimal range recommended by the particle analyser.

The experiment run overnight for 15 h at 30 % US in the particle sizer showed a similar trend for a slow but steady increase in particle concentration over time. However, particle distribution curves indicated that after the second hour an additional population of intermediate particle size starting to form, most possibly due to the re-aggregation and formation of lumps or measurement artefacts caused by particle orientation with respect to the laser beam during prolonged measurement. Based on these two experiments, dispersion for 30 min at 30 % ultrasound intensity proved to achieve fast production and is at the point before the obscuration curve begins to flatten out. This conclusion was also supported by measurements of derived diameters $d(m,n)$, suggesting that after 30 min of dispersion the mean particle size almost reaches a plateau (Figure 3-4).

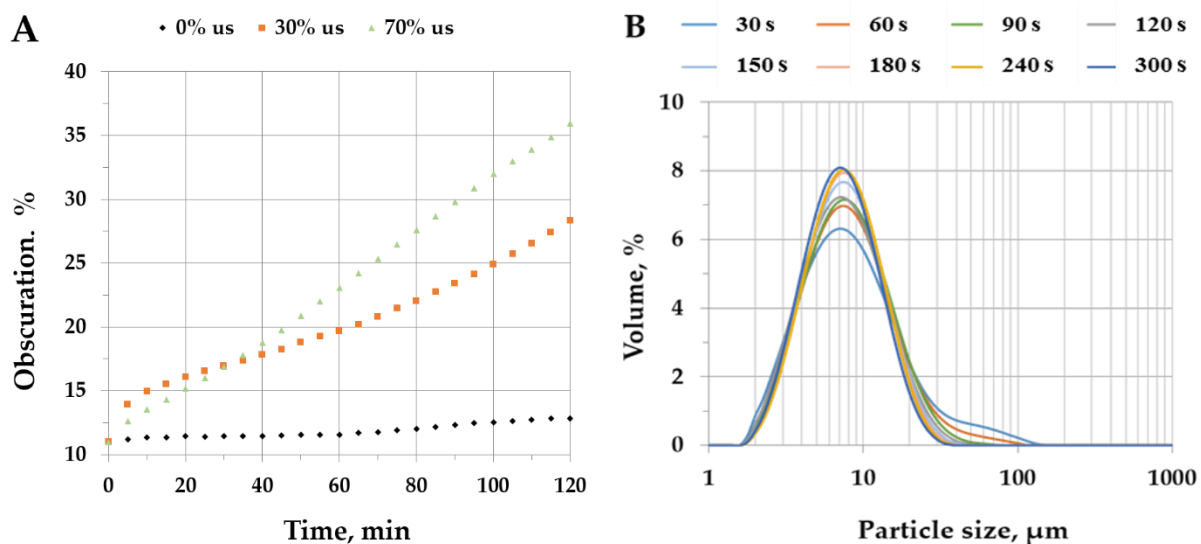


Figure 3-3. Obscuration vs. time: (A) 0.6 g dispersed over 2 h at different ultrasound settings; (B) particle distribution for 0.6 g sample over 5 min at 30 % ultrasound

The experiments in the method development stage conducted in the particle analyser bath were performed with a 0.6 g of sample. This amount was calibrated as optimal for

the rectorite material to maintain obscuration in the ideal recommended range of 10–20 % and prevent blockage of and damage to the equipment. To optimise the process for large volums production, this mass was extrapolated by experimentally monitoring the particle size distribution at the already established obscuration-ultrasound-time settings (Figure 3-3). Careful account was taken of process artefacts such as heat generation and lump formation during sonication step and size measurements. The capacity of the available stand-alone ultrasound bath (LABOTEC SCIENTECH 702, 50Hz, 5.7 l) and glassware was also considered to achieve the highest production rate with the least loss of material and efficiency. Thus it was decided that 50 g of starting material would be mixed with 250 ml of ultrapure water and subjected to ultrasound treatment for 30 min. Five 400 ml glass beakers were placed in the ultrasound bath at a time at optimised settings for frequency, power and temperature, i.e. high frequency equivalent to 30 % ultrasound as discussed above, power set to 4, temperature set to ambient and timer set to 30 min.

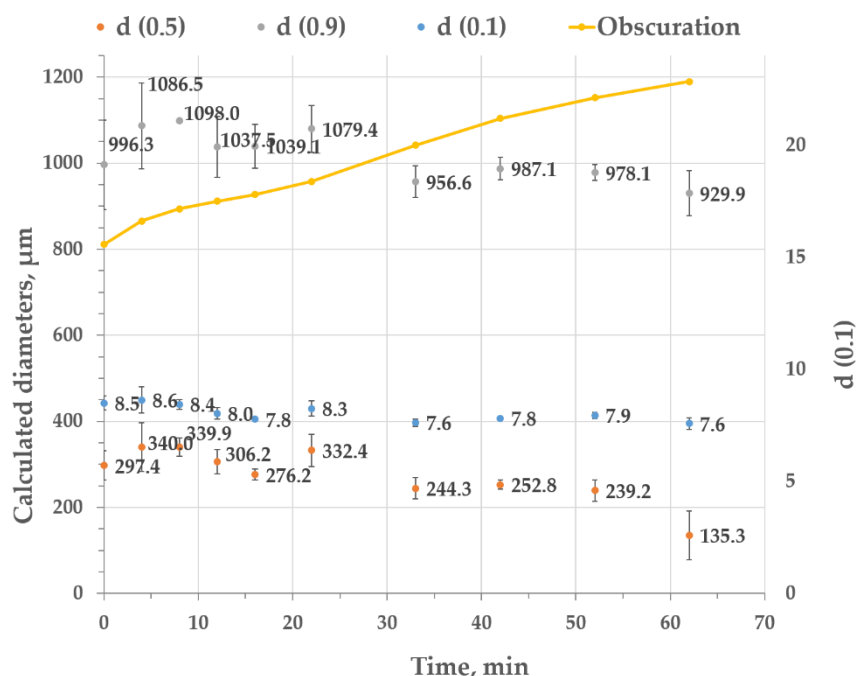


Figure 3-4. Obscuration and derived diameters vs. time: 0.6 g dispersed over 60 min at 30 % ultrasound

To determine the optimum settling time, two experiments were undertaken: (i) five beakers containing 50 g of rectorite material were treated for 30 min in the ultrasound bath. Each beaker was decanted every 30 s in sequence and the particle size measured. The particle size distribution curves are shown in Figure 3-5(A); (ii) the same experiment was carried out in time steps 120 s, 300 s, 900 s, 1200s and 1800 s and the results are plotted in Figure 3-5(B). These results and the XRD quantification on the purified material showed that settling for 5 min gave good particle distribution, good recovery (> 5 g) and high purity of rectorite clay (90–95 %). The results of the second run (2) showed the narrowest particle size distribution after settling for 15–20 min with good purity (> 90 % rectorite), but a lower recovery rate (< 3 g per 50 g), suggesting that due to the longer settling time some of the rectorite clay particles also settled down with the impurities. The 5 min settling time was chosen and applied throughout all the recycling steps of the final process as it is the optimum with least loss and gave the best recovery rate during the first run. As would be expected, recovery progressively decreased with every recycle run.

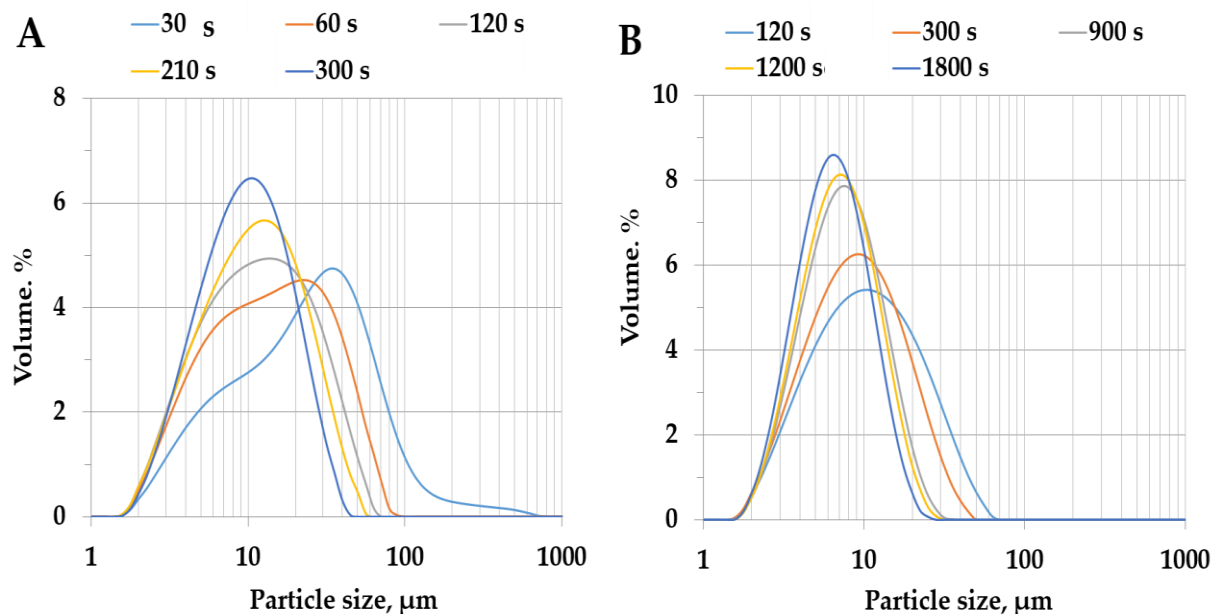


Figure 3-5. Particle size distribution of 50 g sample after settling time of (A) 5 min and (B) 30 min

During the method development stage, process optimisation and mass purification particle size (Malvern Mastersizer) and mineral composition (XRD D8 Advance) were interactively monitored at each step. The final purified product was collected by centrifugation (Hettich ROTIXA 50S), followed by oven drying at 40 °C. The sequence of steps and processes in the optimised final method is schematically presented in Figure 3-6. Approximately 50 g of < 75 µm sieved rectorite-containing material was dispersed ultrasonically in ultrapure water (~250 ml) for 30 min to allow disaggregation and the formation of suspension. A settling time of 5 min was established for optimal recovery of the clay fraction. The supernatant (Top 1) containing the clay fraction was carefully decanted from the bottom (Bottom 1) where the denser impurity particles had settled. The suspension (Top 1) was subjected to centrifugation at 2000 rpm for 30 min to separate the solid clay particles from the water. The coarse remainder (Bottom 1) was recycled up to four times by adding ultrapure water (~250 ml) and repeating the above procedure. After each cycle quantitative XRD analysis was conducted on the top and bottom solid fractions until optimal extraction of rectorite clay was achieved.

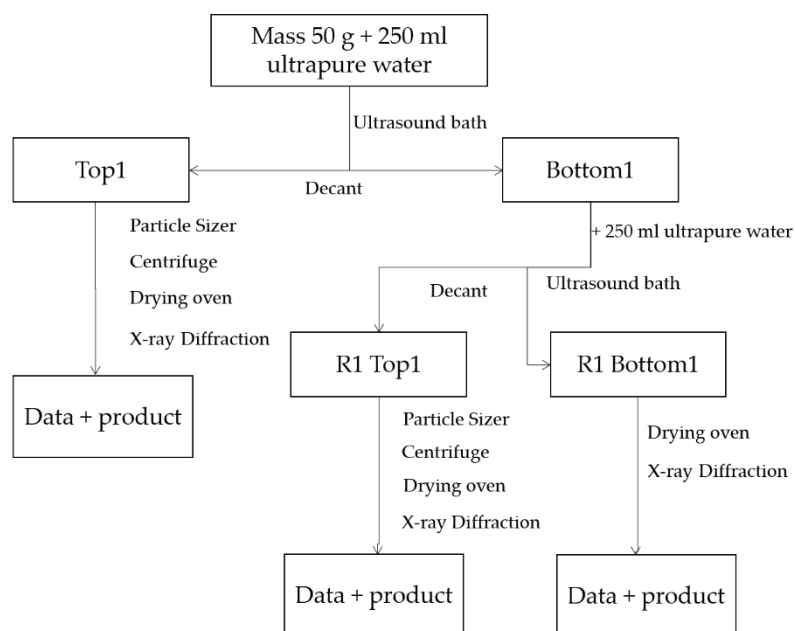


Figure 3-6. Flow chart of the rectorite purification process designed and used in this study. R1 denotes the first recycle and usually up to four recycles were performed per starting mass of 50 g.

The final solid product containing mainly rectorite clay particles was then dried and gently ground to produce powdered high-purity rectorite clay for use in further experiments. The particle size distribution of rectorite-rich material from samples RT1, RT2 and RT3 at various stages of disaggregating pre-treatments is shown in Figure 4-2 (A, B and C) and their respective XRD diffractograms are displayed in Figure 4-1.

3.4 Modifications of purified rectorite

3.4.1 Inorganic cation exchange

Inorganic cation exchange of purified rectorite was achieved by saturation with a metal chloride. Ion-exchanged Li^+ , Na^+ , NH_4^+ , K^+ , Cs^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} rectorite modifications were used for rectorite structural characterisation and in the preparation of clay films and nanocomposite films. The saturation process involved treating about 20 g of sample with a 1 M solution of the respective chlorides. The exchange procedure was carried out using a shaker (LABOTEC Shaker 202) for three days at room temperature. The frequency of the shaker was adjusted to 225 rpm. The saturation was repeated three times per day, replacing the liquid each time with fresh solution containing an excess of the exchanging cation. The last round was completed by multiple washing with ultrapure water through three shaking sessions to remove excess chloride. To ensure that all chloride ions had been removed a test was performed by reaction of an aliquot of supernatant solution with 0.1 M AgNO_3 . The washed clay was separated by centrifugation in acetone for 30 min at a speed of 2000 rpm.

3.4.2 Organic modification

Modification of rectorite with organic surfactants followed a procedure similar to that above. Intercalation was achieved via the ion exchange mechanism by which inorganic interlayer cations are replaced by organic molecules. Three different organic surfactants in liquid form, i.e. dodecyldimethyl ammonium chloride (DCC10), dialkylmethyl ammonium chloride (DCC18) and hexadecyltrimethyl ammonium chloride (SCC16),

were used. Mixtures were prepared from 30 g clay with a sufficient amount of surfactant solution so that there would be a 50 % excess of ions based on a CEC of 45 mEq/100 g. Ultrapure water was added to make solutions of 250 ml. The intercalation reaction took place over 20 days under constant shaking at room temperature. The frequency of the shaker was adjusted to 200 rpm. After the elapse of time, the organically modified rectorite was repeatedly washed with ultrapure water until all excess surfactant had been quantitatively removed. The test was performed by reaction of supernatant solution with 0.1 M AgNO₃ until the mixtures were free of chloride ions. The moist solid material was recovered by centrifugation for 30 min and dried under ambient temperature. Sufficient material was produced to carry out the necessary characterisation tests, including SEM, XRD, TGA, FTIR and chemical composition by XRF.

3.5 Preparation of rectorite clay films (RecF)

Rectorite clay films (RecF) were prepared by a solution casting process. The aqueous clay dispersions were poured into shallow pans and allowed to evaporate and dry slowly at ambient conditions. Aqueous suspensions of neat purified rectorite clay and its ion-exchanged Li⁺, Na⁺, NH₄⁺, K⁺, Cs⁺, Mg²⁺, Ca²⁺, Sr²⁺ and Ba²⁺ modifications were prepared in the concentration range between 1 and 5.8 wt.%. Parameters such as concentration, sonication time, stirring time and type of casting pan were varied to tune the method for optimum mechanical performance of the films.

Prior to film casting, all suspensions were ultrasonically dispersed in ultrapure water for either 5 or 30 min using a LABSONIC 2000U/ B. Braun sonicator fitted with a generator, transducer and a 2000U titanium probe of 19 mm tip. The operating output frequency was 20 kHz. The instrument settings were optimised experimentally by the interactive measurements of the degree of dispersion, i.e. obscuration in a particle sizer. In order to prevent overheating, low power-output settings were selected, i.e. the instrument amplitude dial was set close to the minimum and a duty cycle of 1 was chosen. After sonication the suspensions were cast immediately or subjected to further agitation by

stirring for either 4 or 24 h before casting. The particle size (proxy for the degree of exfoliation) and the intrinsic stability of each suspension were monitored by ζ -potential measurements. Suspensions were cast into shallow pans (glass or teflon) and dried at room temperature. The casts were left undisturbed to evaporate at a slow rate over 3–4 days until completely dry films could be peeled off the surface.

3.6 Preparation of NH₄⁺-rectorite-chitosan nanocomposite films

(Rec/CSNCF)

Rec/CS NCF films were produced by self-assembly of intercalated ammonia-exchanged rectorite-chitosan composites during slow evaporation from aqueous dispersions. Parameters such as clay-chitosan concentration, degree of dispersion, exfoliation and mixing methodology, and pH were experimentally determined, closely controlled and tuned to achieve the best mechanical strength of the final film product.

Rectorite clay of > 90 % purity from sample RT3 was cation-exchanged to obtain NH₄⁺-rectorite used in the preparation of the composite films. Mixtures of ion-exchanged ammonium rectorite (NH₄-Rec) and chitosan (CS) were prepared in NH₄-Rec/CS proportions in the range 100–0 wt.% clay-chitosan (wt.% based on chitosan mass) in increments of 5 wt.%. In the following text, the nanocomposites are denoted by the initial clay/chitosan ratio, given as NH₄-Rec/CS, used for their preparation, e.g. 100/0 means neat NH₄-Rec film, 80/20 stands for 80 % NH₄-Rec and 20 % CS and so forth.

Each weighted clay portion was dispersed in ultrapure water by ultrasonication for 30 min, followed by stirring for 4 h. Simultaneously, a powdered CS portion (0–100 wt.%) was dissolved in 2 % (v/v) aqueous acetic acid while continuously stirring. The latter solution was added very slowly to the stirring NH₄-Rec clay solution and the resulting mixtures were stirred for another 24 h. Thereafter, the NH₄-Rec/CS suspensions were cast on glass Petri dishes (145 mm internal diameter) and dried at room temperature over 3–

4 days until completely dry films could be peeled off the flat surface. The stability of each suspension was monitored by ζ -potential measurements.

3.7 Sample preparation and treatments for XRD analysis

For rectorite characterisation X-ray diffraction measurements were performed on random powder preparations (pXRD), thin flakes of raw rectorite (sample RT1) and oriented slides.

Random powder diffraction tests on micronised material (by McCrone micronizing mill) were carried out for bulk qualitative and quantitative analysis. For Rietveld quantitative analysis, modelling of the rectorite structure was required because there were no structure files for rectorite in the commercially available databases or other open access online sources at the time. Modelling by the Rietveld method was performed (as detailed further below) and the resulting structure file was then used for quantification to determine the proportion of impurities and the respective concentrations of rectorite in the mixtures.

Diffraction data from oriented slides in air-dry state and after various treatments was used for identification of the clay species and characterisation of the rectorite structure and its swelling properties. There are considerable limitations to a phyllosilicate analysis based only on the data of basal reflections from oriented air-dry samples because of overlapping reflections of clay minerals as they frequently occur together. It is therefore beneficial to examine air-dry oriented clay specimens after various treatments that alter the diffraction patterns of the components due to their structural properties. To enable this, four air-dry orientated preparations per sample were produced and X-rayed before and after treatment. Generally, treatment with ethylene glycol (EG) and/or glycerol (G) is performed to aid the identification of smectite species, vermiculites and interstratifications (Brindley and Brown (1984), Moore and Reynolds (1997)). Heat treatment at 500 °C collapses swelling minerals by dehydrating the interlayer content

and destroys or transforms minerals such as kaolinites and chlorites respectively. X-ray diffraction on clay films and bionanocomposite films was done to study the orientation of the particles and the microstructure of the films.

3.7.1 Sample preparation for powder XRD analysis (pXRD)

A McCrone micronising mill with corundum grinding elements was utilised to reduce the mean particle size of the milled sample (by laboratory swing mill) and ensure homogeneous size distribution for X-ray diffraction. About 4 g of milled sample was ground with 10 ml ethanol for 8 min and each sample was prepared in duplicate. Calibration mixtures, prepared by adding ZnO (or corundum) as an internal standard, were ground and homogenised following the same procedure. Slurries were air-dried and homogenised in a vibrating mill (VM) with steel balls prior to XRD measurements. Powder was pressed in a shallow sample holder against filter paper to ensure random particle orientation.

3.7.2 Oriented clay preparations and treatments

Purified clay was dispersed in ultrapure water by means of ultrasound probe. Small volume of the supernatant containing $< 2 \mu\text{m}$ clay particles was deposited onto glass slides by a pipette and air-dried (AD) for XRD analysis. Glycerol (G) and ethylene glycol (EG) saturation was achieved by the vapour method. The AD oriented mounts were placed in a desiccator with G or EG for 16–18 h at a temperature of 80 °C and analysed again on the X-ray diffractometer. The nature of the expandable component in the mixed-layer structure of rectorite was determined by the Greene-Kelly test. It entails X-ray diffraction of Li-saturated oriented specimens after heating at 300 °C, followed by G saturation (Greene-Kelly, 1952). The test was duplicated with high repeatability of the results. Relative humidity in the laboratory was maintained at between 50 % RH and 60 % RH.

3.7.3 Heat treatment

Heating experiments were carried out in a high-temperature muffle furnace (LABOTEC LABCON RM4, 50 Hz, Max Temp. 1200 °C) with a pre-calibrated and thermocouple-monitored temperature regime. Heating from 25 °C–1 200 °C was done on oriented specimens in increments of 50 °C for 1 h. Heated specimens were transferred to a desiccator and as rapidly as possible scanned in the diffractometer through an angular range of 2 – 36 °2θ where the major basal clay reflections occur. XRD measurements on heated rectorite specimens were performed under controlled relative humidity to prevent possible rehydration of the clay specimens.

3.8 Rectorite structure refinement, modelling and quantitative phase analysis

The Rietveld method (Rietveld, 1969) is widely accepted and utilised as the most accurate method for quantitative phase analysis (QPA) from diffraction data of powdered mixtures. The Rietveld quantification method generally requires that all phases in a mixture are crystalline and their structures are well described. The method performs full pattern fitting and needs input of crystal structure data for each constituent.

Disordered layer structures such as clay minerals present a real challenge when their phase concentrations and associated impurities in a mixture need to be determined. The compositional and structural variations due to turbostratic disorders, hydration state, easily exchangeable cations, degree of ordering and anisotropic peak broadening may cause deviations of the observed diffraction patterns from published structure information. Discrepancies in relative intensities are also common as basal reflections could be preferentially enhanced due to platelet orientation during sample preparation.

Mixed-layer clay minerals are very common in nature, and the most common of these contain expandable layers, i.e. mica-smectite (I/S) interstratifications. The sequence of expandable and non-expandable layers can be irregular (random) or regular as in the

case of rectorite structure. Very often no structure information or only partial information (space group and cell parameters, but no atomic positions) is available and in these cases the traditional Rietveld method cannot be used for quantification. The application of the Rietveld method for quantification of phases in a mixture requires structure models for each phase. Refinement of the structure parameters of clay minerals, including mixed-layer minerals, is further complicated due to the cis-vacant and trans-vacant configurations of the dioctahedral 2:1 layers, random rotations and translations of the layers relative to each other, and the frequent occurrence of stacking faults in these structures. Upon X-ray diffraction these structural specifics and defects modify the intensity distribution (Drits and Tchoubar, 1990), rendering structure refinement by Rietveld code meaningless. Various software packages and modelling approaches exist for elucidating the nature of the stacking order in clay minerals (Drits and Sakharov, 1976);(Ufer et al., 2008; Ufer et al., 2012a, b). However, their use for routine QPA is often restricted by specialised software codes, proprietary regulations and limited structure models for clay mineral structures. Furthermore, for mixed-layer structures, including rectorite, there are no published structure files. A method for the quantification of phases with Partial or Not Known Crystal Structures (PONKCS) (Scarlett and Madsen, 2006) offers an alternative approach that overcomes some of these obstacles. It uses a calibrated method to derive empirical “structure factors” by measuring peak intensities from the diffraction pattern of a pure material of the “unknown”.

In the present study the rectorite structure was empirically modelled based on a monoclinic unit cell with primitive lattice using the Rietveld method and DIFFRAC.TOPAS V4.2 software from BRUKER AXS (BrukerAXS, 2009). Diffraction data collected from purified material (rectorite content above 91 %) was used for modelling and calibration.

3.8.1 Derivation of unit cell parameters and instrument function

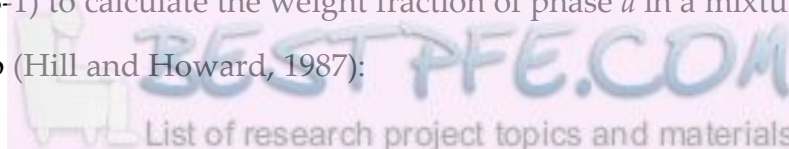
Combined indexing information, i.e. unit cell parameters from published partial structural information for rectorite (Brindley, 1977; Korolev, 1971) (Bayliss, 1989), served to generate an *hkl* phase file by the Le Bail method (Le Bail et al., 1988). This approach uses the space group and cell parameters to constrain the peak positions while permitting the intensities to vary until the best fit to the observed diffraction data is achieved. After the refinement, a peaks file was generated with calculated *hkl* values, multiplicity information, peak positions and intensities. This input file can then be used as a rectorite structure file in the refinement of raw data and for quantitative Rietveld analysis.

The instrument function was modelled using the fundamental parameters approach (FPA) (Cheary and Coelho, 1992a) for peak profile modelling adopted by TOPAS software. The instrument parameters were defined by refinement of the LaB₆ diffraction data obtained with the same diffractometer set-up as the experimental data. Background function was modelled by a Chebychev polynomial of order 1–6 and 1/X Bkg correction was applied to account for possible air scattering at low angles.

The *a*, *b* and *c* lattice parameters of the modelled *rt_hkl* (i.e. rectorite_*hkl*) phase were refined within reasonably set limits to accommodate the variation in cell parameters from an expanded to a dehydrated state of rectorite. From the angular parameters only beta (β) was set to refine. Crystallite size and microstrain were always refined with the limits set to achieve the best fit, i.e. the minimum level for crystallite size was set to 12 nm and microstrain was set within limits of 0–1.

3.8.2 Generation of a calibration model

Calibration mixtures were prepared using zincite (ZnO) as internal standard following the procedure described in Scarlett and Madsen (2006). The Rietveld-based method uses an algorithm (Eq.3-1) to calculate the weight fraction of phase *a* in a mixture of *n* phases by the relationship (Hill and Howard, 1987):



$$W_a = \frac{S_a(ZMV)_a}{\sum_{k=1}^n S_k(ZMV)_k} \quad (3-1)$$

where W_a is the weight fraction of phase a ; Z is the number of formula units in the unit cell; M is the molecular mass of the formula unit; V is the unit cell volume; and S is the Rietveld scale factor. In TOPAS code the phase constant ZMV is defined as mass M , which represents $Z \times M$ and the volume V .

Calibration mixtures of 50 % purified rectorite sample and 50 % zincite (ZnO) were prepared and homogenised. Some impurities of quartz, calcite, muscovite and chlinochlore in the rectorite samples were quantified from the same standard mixture before the calibration of ZMV for rectorite. The total of impurities was then used to calculate by difference the exact amount of rectorite in the mixture. The refinement of the calibration mixture by TOPAS provided the scale factor and the volume of the rectorite unit cell needed to calculate the “phase constant ZMV” in the equation:

$$(ZM)_{RT} = \left(\frac{W_{RT}}{W_{ZnO}} \right) \left(\frac{S_{ZnO}}{S_{RT}} \right) \left(\frac{ZMV_{ZnO}}{V_{RT}} \right) \quad (3-2)$$

where ZM , W , S and V are the mass, weight, scale factor and volume for phase RT -rectorite and the zincite standard respectively.

3.8.3 Quantitative phase analysis (QPA) of rectorite mixtures

The PONKCS method for quantitative analysis of phases described above (Scarlett and Madsen, 2006) allows the accurate quantification of compounds where the traditional Rietveld method or other classic quantification methods fail. Disordered phases or phases with unknown or partial crystal structures (e.g. mixed-layer structures, new polymorphs) can be quantified with the same or even higher accuracy as for well-defined crystalline phases.

Quantification of mixtures by the Rietveld method requires knowledge of the crystal structure of each component in the mixture. The structure information comprises the

lattice parameters, crystal system and starting parameters of site occupancies; for well-known structures this is usually found in the literature. The calibrated rectorite model *rt_hkl* generated by the procedure explained above contains measured intensities from a pure rectorite flake reference sample and is used here in place of crystal structure information for rectorite. The structural data on the additional minerals, namely quartz (Gualtieri, 2000.), calcite (Effenberger et al., 1981), muscovite (Gatineau, 1963), chlinochlore (Guggenheim and Zhan, 1999), pyrophyllite (Gruner, 1934), gypsum (Wooster, 1977) and zincite (Albertsson et al., 1989) was taken from the ICSD structure database (Table 3-1). The peak list file *rt_hkl* (Appendix I) resulting from this calibration was then applied to the raw samples containing rectorite.

Table 3-1. Sources of crystal structure data used in the quantification of rectorite mixtures by the Rietveld method

Mineral	Structural formula	Source of crystal structure data
Rectorite	$(\text{Na}_{0.76}\text{Ca}_{0.44}\text{K}_{0.13})[\text{Al}_{4.03}\text{Ti}_{0.03}(\text{Fe.Mg})_{0.006}](\text{Si}_6\text{Al}_2)\text{O}_{20}(\text{OH})_4.n\text{H}_2\text{O}$	<i>rt_hkl</i> model this study
Quartz	SiO_2	Gualtieri (2000)
Muscovite	$\text{KAl}_2(\text{AlSi}_3\text{O}_{10}) (\text{O H})_2$	Gatineau (1963)
Chlorite	$\text{Mg}_3(\text{Mg}_2\text{Al})((\text{Si}_3\text{Al})\text{O}_{10})(\text{OH})_2\text{O}_3$	Guggenheim and Zhan (1999)
Pyrophyllite	$\text{Al}_2(\text{Si}_4\text{O}_{10}) (\text{OH})_2$	Gruner (1934)
Calcite	$\text{Ca}(\text{CO}_3)$	Effenberger <i>et al.</i> (1981)
Gypsum	$\text{Ca} (\text{SO}_4) (\text{H}_2\text{O})_2$	Wooster (1977)
Zincite	ZnO	Albertsson <i>et al.</i> (1989)

The precision of the method was tested by in-laboratory replicate sample preparation and analysis. The consistency between phase analysis by the Rietveld method and bulk chemical analysis for the purified rectorite samples was evaluated and verified to estimate the degree of confidence in the model and method applied. The modal abundance of minerals in a mixture can be expressed as chemical oxide compositions for direct comparison with XRF-derived compositions (Monecke et al., 2001; Ward and Gómez-Fernández, 2003). For the rectorite samples, chemical compositions implied by the Rietveld analysis were calculated assuming ideal stoichiometric compositions from the literature for all minor impurity minerals. Due to the variability of published rectorite compositions caused by the exchangeable interlayer cations and layer substitutions, an

individual chemistry for Beatrix rectorite of this study was considered. Rectorite material of highest purity was analysed by XRF, and the results were recalculated adjusting for mineral impurities and used as a basis to calculate the mean structural formula (Atanasova et al., 2016) (Table 4-7). For reasons of comparison, published compositions for rectorite samples with similar interlayer content were also used (Gaines et al., 1997; Nishiyama and Shimoda, 1981).

Another source of uncertainty in the comparison of calculated and observed chemical compositions is the estimate of volatile components, i.e. LOI. These include non-structural water or pore water, structural OH⁻ in hydroxyls and hydroxides or CO₃²⁻ in carbonates. To overcome complications with differentiation between structural and non-structural components, and correct for their influence on the accuracy of the method, the LOI component was ignored in the calculations. Thus, the normative compositions were only calculated from the oxide forms for all minerals.

3.9 Characterisation techniques

3.9.1 Microscopy

Optical microscopy was used for preliminary visual description and colour imaging with a Leica Wild10 binocular microscope and a Leica DVM6 digital microscope. The latter is equipped with a tilting stand, a combined motorised precision XY-stage with manual coarse positioning, and a motorised focus for automatic 3D image-stacking. With a PlanAPO FOV 12.55 objective and a 10 MP camera with a focus resolution of 0.5 µm and a 16:1 zoom range, sharp multi-focus images, 3D-analysis and high-resolution scans on larger areas are allowed.

SEM was used for morphological and structural observations and imaging, and X-ray microanalysis by EDS. **SEM/EDS analysis** was carried out on a Leica Stereoscan 440 SEM linked to an OXFORD INCA EDS at an acceleration voltage of 5 kV. The system is equipped with an Oxford X-Max SDD detector with 20 mm² active area and a resolution

of ca. 128 eV for Mn K α (5895 eV). Examination was performed on polished specimens and grain mounts, coated with carbon for conductivity. SEM imaging was obtained by ultrahigh-resolution field emission SEM (FESEM) Zeiss Ultra Plus 55 with an In Lens detector at acceleration voltages of 0.6 kV to ensure maximum resolution of surface detail.

For TEM imaging a JEOL-JEM 2100F field emission transmission microscopy (FETEM) was utilised operated at 100 kV. Rectorite platelets were dispersed in ethanol using ultrasound, deposited on a Cu grid and left to air-dry.

3.9.2 Nuclear magnetic resonance (NMR) spectroscopy

Purified rectorite clay was characterised by ^1H , ^{27}Al , ^{23}Na and ^{29}Si solid-state MAS NMR. All NMR measurements were performed on a 11.7 T Bruker Avance 500 spectrometer operating at the resonance frequencies of 500.13 MHz for ^1H , 130.34 MHz for ^{27}Al , 132.31 MHz for ^{23}Na and 99.36 MHz for ^{29}Si using a Bruker BL4 HXY 4 mm MAS and a BL 2.5 mm MAS probe-head. All spectra were fitted using Dmfit (Massiot et al., 2002).

^{27}Al MAS NMR spectra were acquired at a spinning frequency of 14 kHz. A single pulse of 2 μs pulse duration ($< \pi/3$ for 30 kHz rf-amplitude) was applied to ensure a quantitative excitation of the central transition. High-power two-pulse phase modulation (TPPM) ^1H decoupling of 80 kHz rf field strength was applied. A recycle delay of 1 s and 256 repetitions were used. ^{27}Al chemical shifts were referenced externally to 1M AlCl_3 aqueous solution at 0 ppm.

The ^{29}Si solid-state NMR spectra were acquired at a spinning frequency of 5 kHz with direct ^{29}Si polarisation with ^1H decoupling (cw field strength 50 kHz), a single 90° pulse of 3 μs duration, recycle delays of 60 s (for higher signal-to-noise ratio) and 600 s (for a quantitative excitation) and 1 024 repetitions. The ^{29}Si chemical shifts were referenced relative to TMS using Q8M8 as an external standard, which gives an $\text{Si}(-\text{CH}_3)_3$ signal at 12.6 ppm.

^1H MAS NMR spectra were measured at a recycle delay of 5 s employing a single 90° rf-pulse of 3 μs duration. The ^1H NMR spectra were referenced to TMS at 0 ppm using an NH_4 signal of ammonium dihydrogen phosphate at 6.7 ppm as an external reference.

For ^{23}Na MAS NMR measurements, a single $\pi/2$ pulse of 2.5 μs was applied, ensuring a quantitative excitation of the central transition. High-power two-pulse phase modulation (TPPM) ^1H decoupling of 80 kHz was applied. A recycle delay of 5 s and 2 048 repetitions were used. ^{23}Na chemical shifts were referenced externally to 1M NaCl aqueous solution at 0 ppm.

3.9.3 X-ray diffraction analysis (XRD)

X-ray data was recorded on a Bruker D8 Advance diffractometer with 2.2 kW Cu $K\alpha$ radiation ($\lambda=1.54060$ nm), a LynxEye detector with an active area of 3.7° and Ni filter. The beam path included 0.2 mm (0.1°) Fixed Divergence Slit (FDS), 0.1 mm Receiving Slit (RS) and Soller slits of 2.5° on the primary and secondary sides. Scans from $2 - 70^\circ 2\theta$ for random powder preparations (pXRD) and $2 - 36^\circ 2\theta$ for oriented specimens and films were recorded in step scan mode at a speed of $0.02^\circ 2\theta$ steps, size/5 s and generator settings of 40 kV and 40 mA. A sample spinner was on for all powder measurements for representative particle statistics. Qualitative phase analysis was performed by the conventional search/match procedure using the BRUKER DIFFRAC. EVA software program and the ICDD PDF database. Rietveld refinements and quantification were done with DIFFRAC.TOPAS V4.2 software using the fundamental parameters approach (FPA) (Cheary and Coelho, 1992).

The NEWMOD (Reynolds, 1985) computer program for modelling one-dimensional X-ray diffraction patterns of mixed-layer structures was used to compare the experimental XRD data with calculated patterns.

3.9.4 Chemical analysis by X-ray fluorescence (XRF) spectroscopy

For major element analysis a milled sample (< 75 μm) of the neat, purified or exchanged material was roasted at 1 000 °C for at least 3 h to oxidise Fe^{2+} and S and to determine the loss of ignition (LOI). Glass discs were prepared by fusing 1 g of roasted sample and 8 g 12–22 flux consisting of 35 wt.% LiBO_2 and 64.71 wt.% $\text{Li}_2\text{B}_4\text{O}_7$ at 1 050 °C. For trace element analysis 12 g of milled sample and 3 g of Lico wax were mixed and pressed into a powder briquette by a hydraulic press with the applied pressure at 344 MPa. The glass discs and wax pellets were analysed by a PANalytical wavelength dispersive Axios X-ray fluorescence spectrometer equipped with a 4 kW Rh tube.

3.9.5 Carbon and sulphur (C&S) analysis

Quantitative carbon and sulphur analyses were performed on an Eltra CS 800 double dual range carbon-sulphur analyser. An amount of 0.2 g of milled or sieved to < 75 μm sample material was weighed and homogenised by slow rotation into a ceramic crucible with iron and tungsten chips. Method detection limits for carbon and sulphur of 0.017 and 0.009 g/100 g respectively were achieved by repeat analyses of blank samples. The instrument was calibrated using the Euronorm-CRM 484-1 Whiteheart malleable iron, Euronorm-CRM 058-2 sulphur steel and Euronorm-CRM 086-1 carbon steel standards, while instrument stability was monitored using in-house reference standards.

3.9.6 Carbon-hydrogen-nitrogen (CHN) elemental analysis

CHN analyses were performed using LECO CHN628 instrumentation. Samples of 0.1 - 0.2 g in the fraction below 212 μm were weighed and homogenised. The material was combusted in oxygen at 950 °C, converting elemental carbon, hydrogen, and nitrogen into CO_2 , H_2O , N_2 and NO_x . These gases pass through infrared cells that determine the carbon and hydrogen content, and a thermal conductivity cell that determines N_2 . Method detection limits were achieved by repeat analyses of blank samples. The instrument was calibrated using the LECO EDTA CRM 2015, while instrument stability

was monitored by the Central Control Standard (CCS) analysed in duplicate for each batch of samples. CCS data is recorded in a quality control chart and monitored within the upper and lower warning ($\pm 2\sigma$) and control limits ($\pm 3\sigma$) of the charts.

3.9.7 Fourier transform infrared spectroscopy (FTIR)

Infrared spectra were recorded using a diamond ATR cell, which fitted in the macro sample compartment of a Bruker Optics Vertex 70v spectrometer. Small amount of powdered sample (enough to cover the crystal area) was placed onto the ATR crystal and the spectrum was collected under pressure of up to 70 psi. The spectra were acquired in the range $400 - 4000 \text{ cm}^{-1}$ wavelength in 32 acquisitions at a resolution of 4.0 cm^{-1} . The sample compartment was evacuated during acquisitions and the contact area between the sample and the diamond ATR crystal was 2 mm in diameter.

FT-IR spectra by the KBr method were recorded using a Perkin Elmer Spectrum RX FT-IR with a scan resolution of 2.0 cm^{-1} . Applying single-beam radiation, a total of 32 interferograms were collected for each sample. KBr compressed pellets were prepared using a mortar and pestle to disperse fine powdered sample with 100 mg of dehydrated KBr.

3.9.8 Thermogravimetric analysis (TGA)

TGA was performed using the dynamic method on a Mettler Toledo A851 TGA/SDTA instrument. About 15 mg of sample powder was placed in an open $70 \mu\text{l}$ alumina pan. The temperature was scanned from $25 - 1200 \text{ }^\circ\text{C}$ at a rate of $10 \text{ }^\circ\text{C}/\text{min}^{-1}$ with an air flowing rate of $50 \text{ ml}/\text{min}^{-1}$.

DSC scans were recorded on a Mettler Toledo DSC instrument. Samples of about 5 mg were placed in aluminium pans with a small hole in the lid. The samples were heated (and cooled) from $-40 \text{ }^\circ\text{C}$ to $220 \text{ }^\circ\text{C}$ at a scan rate of $10 \text{ }^\circ\text{C}/\text{min}^{-1}$. The heating and cooling runs were carried out under nitrogen flowing at $50 \text{ ml}/\text{min}^{-1}$.

3.9.9 Brunauer–Emmett–Teller (BET) analysis

Specific surface area determinations by BET analysis were performed on powdered rectorite clay and rectorite clay films. The instrumentation used was a Micromeritics Flowsorb II 2300 and a Nova 1000e BET instrument in N₂ at 77 K.

3.9.10 Particle size distribution and ζ -potential measurements

Particle size distribution was determined by laser diffraction technique using a Malvern Mastersizer 2000 equipped with a Hydro 2000G dispersion unit (Malvern Instruments Ltd, Malvern, UK). Scattered light data was recorded from 2 000 - 5 000 snapshots of 10 μ s. A polydispersity mode of analysis and a refractive index of 1.533 with an adsorption of 0.1 were chosen. Size data collection was performed at a constant obscuration in the range 10–20 %, and the built-in ultrasonic bath was set at 30 % before and during measurements to achieve adequate disintegration of aggregates and proper dispersion of primary particles. The method is volume-based and assumes that all particles are spherical. In the case of phyllosilicates such as clays and other platy materials, the results are usually overestimated due to their aspect ratio and represent equivalent spherical diameter (Bowen, 2002).. The results therefore describe the volume concentration of irregular-shaped particles contained in the sample in terms of the diameter of imaginary spherical particles that occupy the same volume. For these reasons the results do not represent absolute particle sizes, although they provide very useful information for comparative purposes between various treatments.

Electrophoretic mobility measurements of colloidal rectorite particles present in aqueous suspensions were carried out in an electric field using the Malvern Zetasizer Nano ZS system (Malvern Instruments Ltd, Malvern, UK). The ζ -potential was then calculated from the electrophoretic mobility (u_c) of the rectorite particles using the Smoluchowski equation. All measurements were performed at 25.0 ± 0.1 °C, with an attenuation in the range 5–6. Each reported value of ζ -potential is an average of three measurements. The

pH of the suspensions was also recorded. The size of the dispersed particles in the sub-micron region below 0.02 μm was determined by the Dynamic Light Scattering (DLS) technique using the same instrument; the reported values represent mean size distribution by number (polydispersity index (PDI) was > 0.1 , i.e. the system has moderate to broad polydispersity, in which case size distribution by volume is meaningless).

3.10 Characterisation of functional properties

Rectorite clay films and bionanocomposite films were tested for their mechanical properties and UV-Vis characteristics.

3.10.1 Characterisation of mechanical properties

Tensile measurements were performed on an Ametek Lloyd Instrument LRX Plus single-column tensile tester fitted with a 50 N load cell. Film thickness was measured using a Mitutoyo Digimatic micrometer with a measurement accuracy of $\pm 0.2 \mu\text{m}$ and the average of multiple measurements along the strip was used. Film strips with dimensions 100 mm long and 10 mm wide were cut and conditioned in a desiccator at room temperature for at least 48 h prior to measurements (ASTM, 2012, 2013a, b). Controlled humidity in the desiccator was maintained around 55 % using a saturated calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) solution at room temperature. The ends of the strips were sandwiched with masking tape before being fastened in the clamps of the tester, with the gauge length (grip separation) set at 75 mm. The tensile tests were conducted at a draw speed of $20 \text{ mm}/\text{min}^{-1}$. At least three measurements per film were made and the maximum value is reported together with the overall standard deviation. This approach was followed as the objective was to determine the ultimate strength of the clay films. In the case of bionanocomposites, films of each composition were replicated at least three times.

3.10.2 Visible and ultraviolet spectroscopy (UV-Vis)

UV-Vis transmission spectra of rectorite and composite films were recorded on a PerkinElmer Lambda 750S spectrophotometer.

3.11 Statistical analysis

Statistical analysis of the available experimental data was carried out in two steps. First, a global fit of the tensile strength (or the Young's modulus) of the films was modelled and analysed using extreme value analysis (EVA) by means of the generalised extreme value (GEV) distribution (Beirlant et al., 2005; Reiss and Thomas, 2007). Parameter estimation was carried out using the generalised maximum likelihood (gMLE) (Gilleland and Katz, 2016). The location and scale parameters of the GEV distribution were considered to be linear combinations of possible additional variables. Based on the outcomes, the data was split into three groups. Permutational multivariate analysis of variance (MANOVA), using distance matrices (Anderson, 2001; McArdle and Anderson, 2001), was performed to check whether the data split into these three sets according to the interlayer charge variables can be justified from a statistical point of view. The resultant p -value from this test was 0.007, which signifies an overall effect. This was followed by the Kruskal-Wallis rank sum test (Hollander and Wolfe, 1973) for testing the individual effects, the results of which indicated that this was indeed the case for both tensile strength (p -value = 0.0019) and Young's modulus (p -value = 0.0004) as dependent variables, and with the interlayer charge as independent variable. Secondly, a peak-over-threshold (POT) model was fitted to each of the six possible permutations for determining the maximum potentially attainable values for tensile strength and Young's modulus. Maximum likelihood estimation (MLE) was used to fit the exponential distribution to all the cases. The parametric bootstrap (Efron and Tibshirani, 1993) was then used in each case in deriving 95 % upper confidence limits.

CHAPTER 4 RESULTS

4.1 Characterisation of neat and cation-exchanged rectorite

4.1.1 Primary materials processing, disintegration and particle size statistics

Due to the platy morphology and sensitivity to relative humidity, the rectorite material was fairly resistant to crushing and milling using routine laboratory techniques. The pXRD data plotted in Figure 4-1 demonstrate the effect of various size-reduction treatments on the relative intensities, preferred orientation and peak profile resolution, shape and broadening.

The particle size distribution of the rectorite-rich material from samples RT1, RT2 and RT3 at various stages of disaggregation is shown in Figures 4-2, 4-3 and 4-4 respectively. The frequency curves display an apparent bimodal distribution for the crushed and blender-treated material with maxima around 1.2 mm. With the use of a coffee grinder, ball mill and McCrone micronising mill, followed by a short vibrating mill spin, a much finer and more homogeneous product was achieved. The crushing and the blender reduced the size of the raw material below 1 mm with 35 % and 18 % of the particles being smaller than 100 μm . At this stage only 10 % and 5 % of the sample were smaller than 20 μm after crushing and using the blender respectively. The vibrating mill reduced the particle size of lumpy crushed material further, with the samples now containing 90 % of sub-100 μm particles and *ca.* 40 % of sub-20 μm particles. The milling process produced a more homogeneous distribution with 90 % of sub-20 μm particles. Surprisingly, the population represented by the shoulder at around 500 μm (ranging from 280 μm to 700 μm) was not affected by the use of the vibrating mill as would have been expected if it represents larger lumps and aggregates.

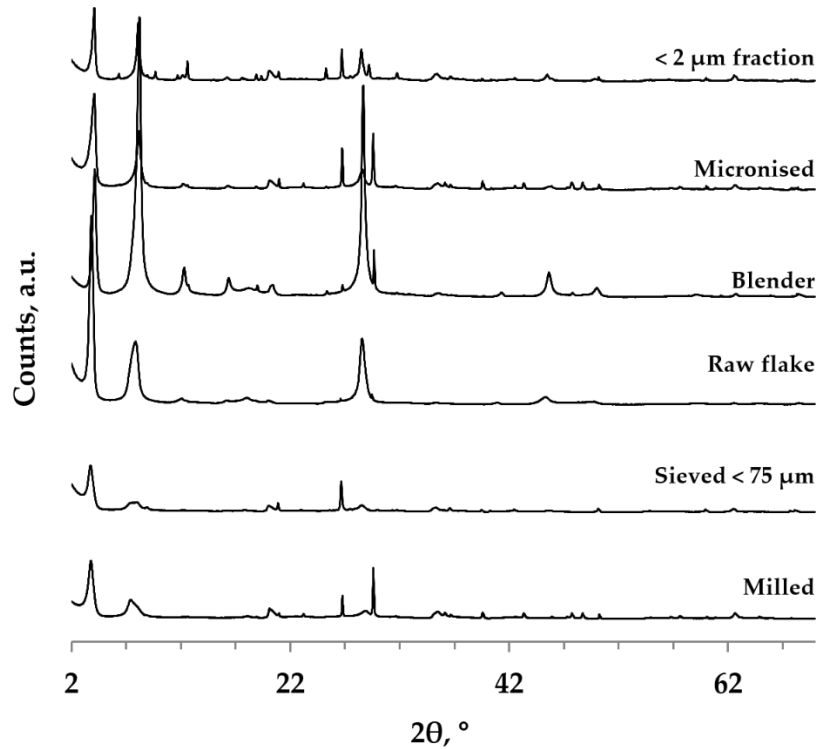


Figure 4-1. Powder diffraction patterns of rectorite-rich material (RT1) after various processing treatments

Wet grinding in the McCrone micronising mill produced the most narrow grain-size distribution; it decreased the particle size of milled samples further (95 % $\leq 20 \mu\text{m}$) and eliminated the shoulder formed by the population of larger particles. Only about 50 % of the particles were below 5–7 μm in size, i.e. the ideal particle size for random powder diffraction.

The observed bimodal distribution is indicative of two characteristic aspects of clay particles: firstly, differences in the dispersion properties of complex particles; and secondly, the high aspect ratio of the clay particles which tend to orient preferentially as they traverse the measuring cell of the instrument and refract the incident light during measurement. It is generally expected that mixed-layer assemblages will show relatively good dispersability, particularly when one of the component layers is non-expandable. The mixing would cause weakening of the bonds between particles which would enhance the ease of splitting into thinner units and consequently lead to dispersion.

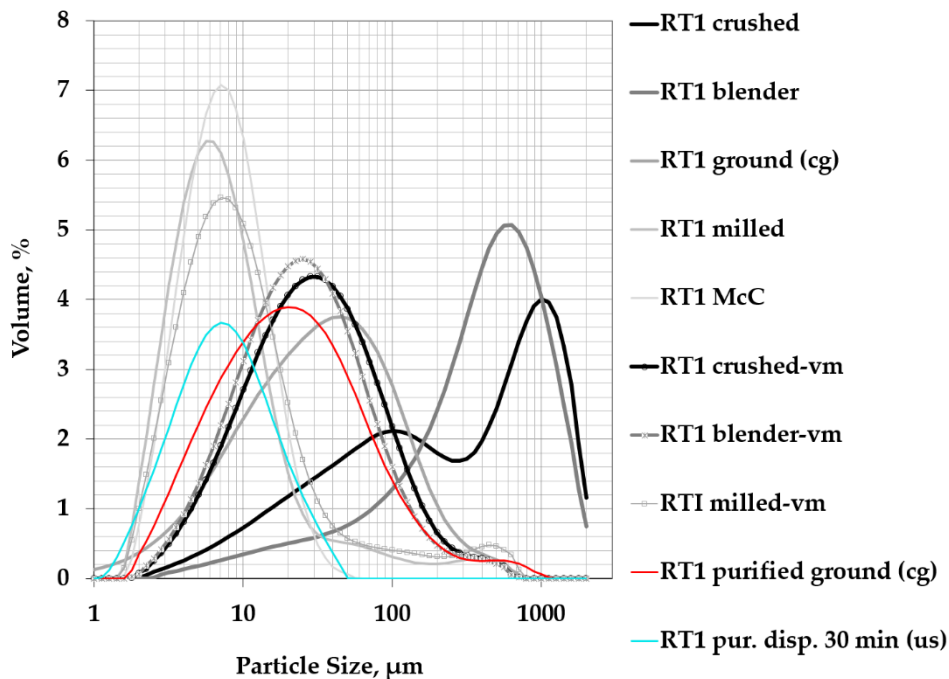


Figure 4-2. Particle size distribution of Beatrix rectorite from sample RT1, after various disintegrating pre-treatments: purified (pur.); coffee grinder (cg); dispersion (disp.); vibrating mill (vm); micronising mill (McC); and ultrasound(us)

However, the effect of particles' aspect ratio at this size range seems to remain vital, irrespective of the degree of dispersion. As a consequence, the sample preparation induced preferred orientation is almost unavoidable when performing pXRD on clay minerals, despite the various preparation techniques used to prevent it.

Theoretically, the method of fractionation by sedimentation is based on Stokes's Law, which generally applies to spherical particles. In the case of platy clay particles, it is assumed that Stokes's Law would approximately apply below a particle size of about 20 μm (Moore and Reynolds, 1997). Particle size analysis of sample RT1 after various disaggregating pre-treatments showed that the sequential use of jaw crushing and blender processing, followed by use of the vibrating mill produced the largest (~ 50 %) size fraction below 25 μm .

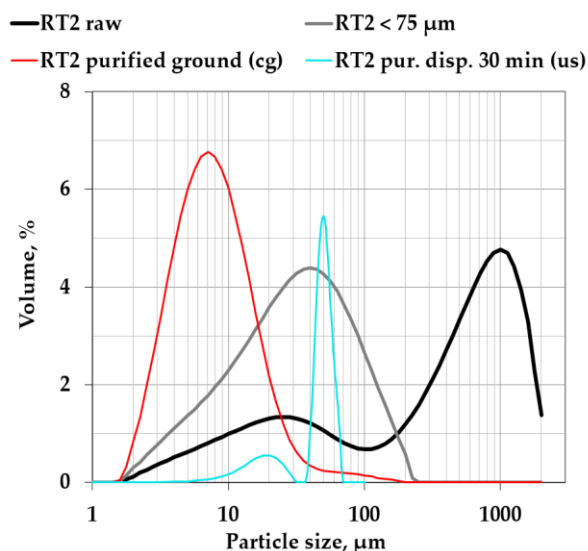


Figure 4-3. PSD frequency curves of Beatrix rectorite sample RT2 after various disintegrating procedures: purified (pur.); coffee grinder (cg); dispersion (disp.); and ultrasound (us)

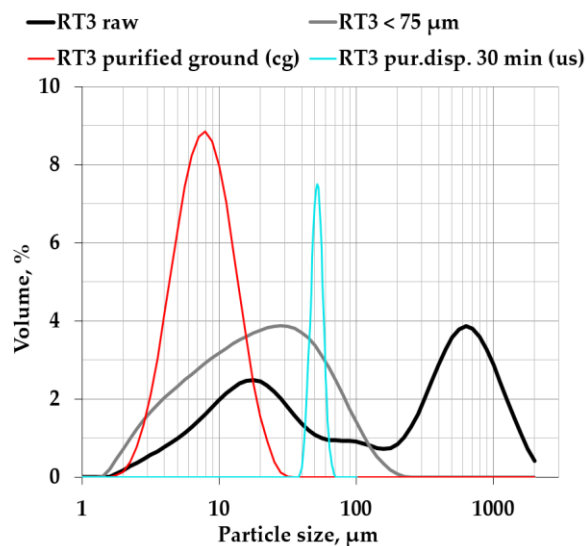


Figure 4-4. PSD frequency curves of Beatrix rectorite sample RT3 after various disintegrating treatments: coffee grinder (cg); dispersion (disp.); and ultrasound (us)

A portion of this material was dispersed ultrasonically under high frequency in ultrapure water (~250 ml) to allow disaggregation and the formation of a suspension. The material of samples RT2 and RT3 was sieved and the < 75 μm fraction was dispersed ultrasonically under the same settings. Based on interactive particle distribution measurements, a settling time of 5 min was established as optimal for best clay fraction recovery. By that time the settling of the remaining clay aggregates and impurities larger than 2 μm is theoretically complete and the cloudy supernatant should contain only the clay fraction with individual particles < 2 μm.

4.1.2 Purification and recovery

Preliminary XRD analysis of the bulk material from Beatrix mine showed that the material was very heterogeneous. After purification the rectorite content increased by almost 30 % for sample RT1, around 40 % for sample RT2 and doubled in the case of sample RT3. The mineral quantities in the bulk and purified material are presented in

Table 4-1 with standard deviations (e.s.d), in terms of the least-significant figure to the left (Hill and Howard, 1987).

Table 4-1. XRD-derived proportions of rectorite and associated impurities in bulk and purified samples (wt.%)

Sample	RT1		RT2		RT3	
	Raw	Purified	Raw	Purified	Raw	Purified
Rectorite	72.37 (74)	91.27 (33)	60.66 (66)	86.32 (65)	45.69 (33)	91.45 (71)
Quartz	7.78 (19)	3.21 (10)	28.83 (45)	5.64 (17)	48.81 (20)	5.95 (48)
Calcite	13.42 (35)	0.66 (15)	n.d.	n.d.	n.d.	n.d.
Muscovite	n.d.	n.d.	1.63 (27)	2.93 (35)	3.74 (55)	1.66 (20)
Chlorite	6.45 (64)	4.86 (30)	3.94 (35)	2.44 (47)	1.77 (29)	1.52 (27)
Pyrophyllite	n.d.	n.d.	3.40 (37)	2.66 (37)	n.d.	n.d.
Gypsum	n.d.	n.d.	1.55 (14)	n.d.	n.d.	n.d.

* Figures in parenthesis represent the e.s.d, in terms of the least-significant figure to the left (Hill, R.J. and Howard, C.J., 1987).

The three samples collected at Beatrix mine differ in macroscopic and microscopic appearance and in the mode of occurrence of rectorite, as well as mineral associations (Figure 3-2). Larger platy rectorite fragments in sample RT1 appear to have calcite and quartz particles trapped between sheets, as seen on the SEM micrographs in Figure 4-5.

In samples RT2 and RT3 a visibly disintegrated mix of fine and coarse material (Figure 3-2) is seen by SEM to contain complex particles of mainly quartz grains coated by rectorite or fine rectorite clay binding quartz and other impurities to form larger aggregates and lumps (Figures 4-5 and 4-6). These observations informed the purification procedure described above (Figure 3-6), in which, once liberated, the various mineral grains could be separated by gravity, removing the larger-than-clay fraction components such as quartz and other lump-sized clay minerals of the bulk, and concentrating the rectorite as the main component of the clay fraction.

The method for purification and mass production was developed step by step with careful evaluation of every parameter to achieve the most efficient and productive process for highest purity rectorite clay.

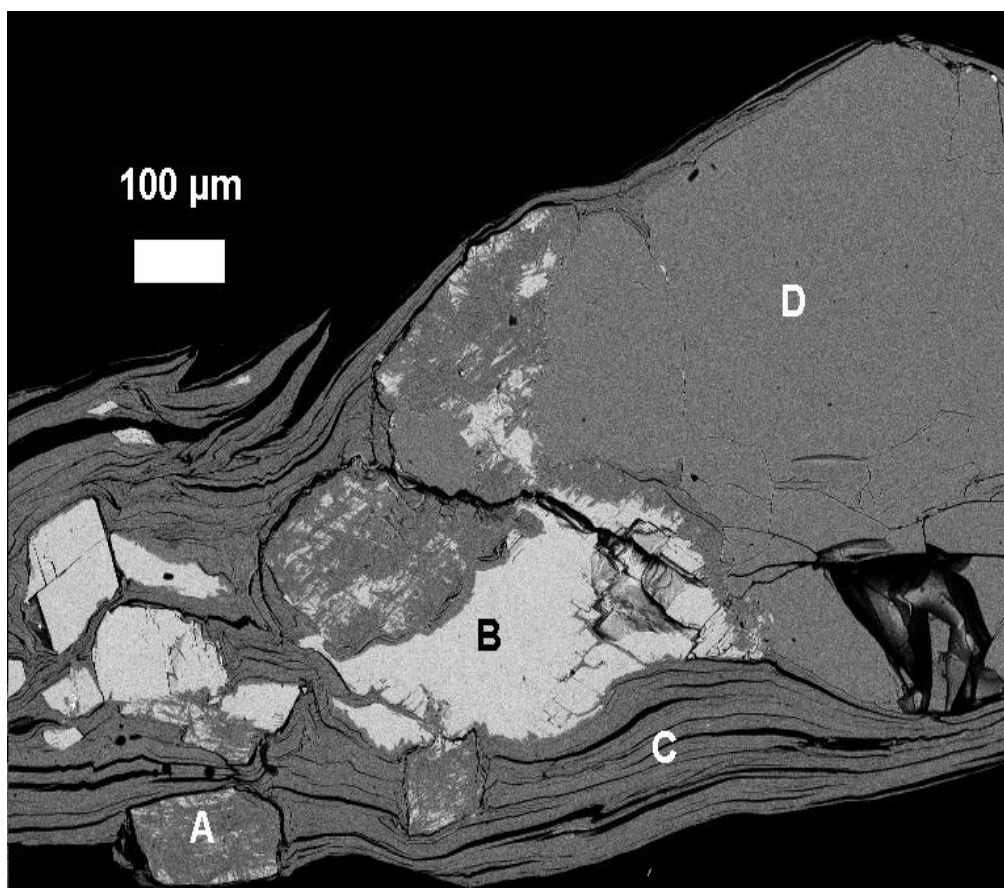


Figure 4-5. SEM image of raw material from sample RT1 showing the distribution of (A) clinochlore (light-grey solid and finely mixed); (B) calcite; (C) rectorite (grey layered); and (D) quartz (grey solid)

Although optimised, it is a tedious process as only 250 g could be processed at a time, from which about 40 g of pure material was recovered. With the available centrifuge, it took two centrifuge runs to process a batch, which also hampered the process with respect to time. If a scale-up process for a more efficient production rate is sought, it is recommended to increase the batch volume starting material by using a larger ultrasound bath and centrifuge. This should, however, also ensure that the negative effects of upscaling on expected losses in recovery and purity of the final product are kept to a minimum.

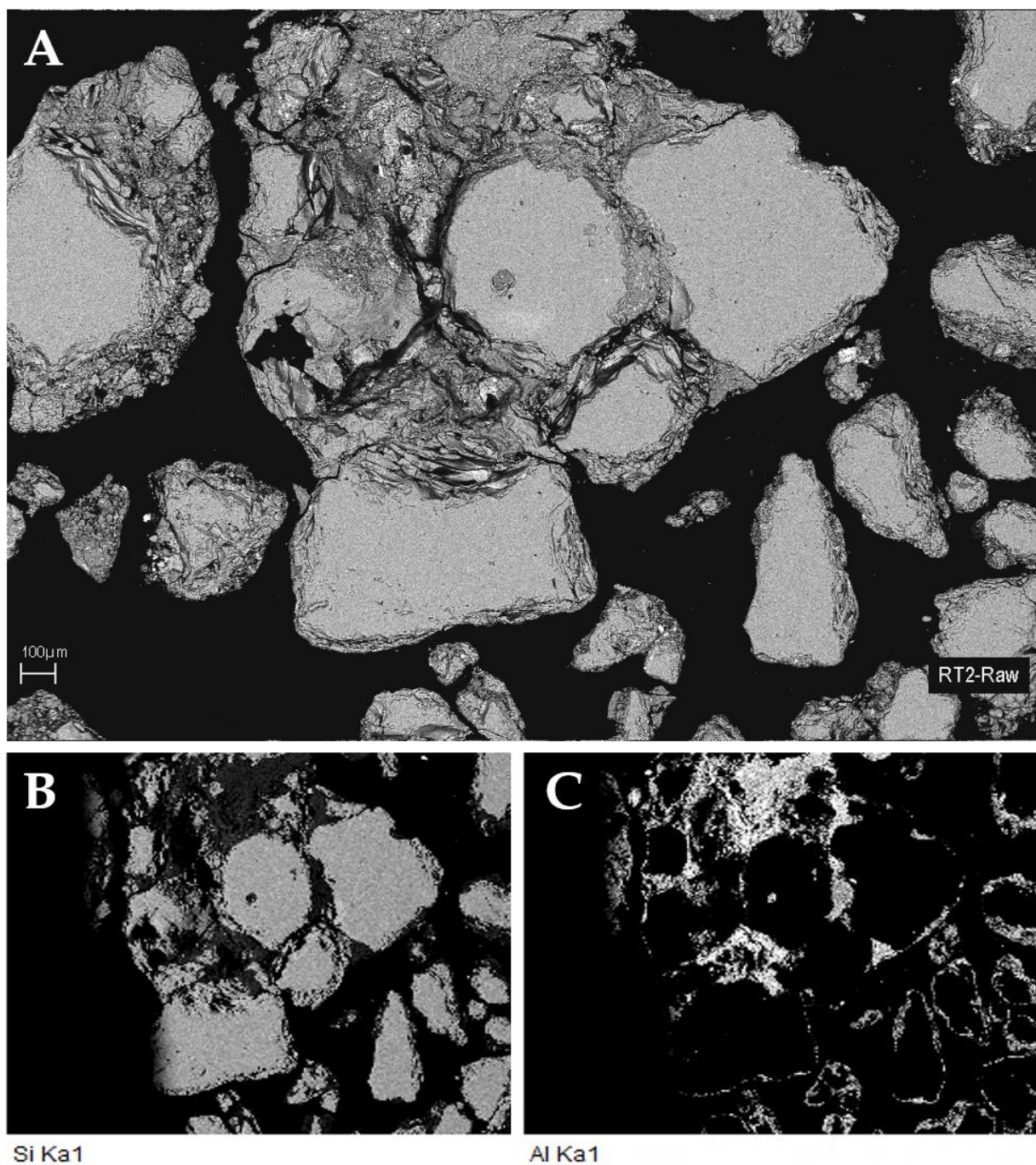


Figure 4-6. (A) Low-magnification backscatter electron (BE) SEM images and element distribution maps for (B) Si and (C) Al from raw material (sample RT2), showing the natural occurrence and spatial relationship between rectorite, quartz and other minor impurities

4.1.3 Microscopy

Natural “pure” rectorite from Beatrix mine features a platy-leafy morphology with a pale blue-grey colour and brown pigmentation along cracks and folds, probably caused by iron contamination. Aggregates of stacked ultrafine flakes have a pearly lustre with an earthy appearance and a soft soapy feel to the touch. Individual flakes are translucent to transparent (Figure 3-2 and Figure 4-8) with thin, sharp edges. SEM showed typical layered morphology. Platy and folded aggregates of compact parallel layers are either stacked continuously or thinly curled at the edges, as seen in Figure 4-7. High-resolution FETEM imaging performed on raw rectorite platelets shows continuous silicate layers in parallel to sub-parallel orientation. Ultra-thin edges display unambiguously regular periodicity of well-distinguished light and dark layers of about 2.0 nm and domains of higher thickness. Within the domains, alternating contrast layers of spacing 1.00, 1.30 and 2.20 nm are visible at high magnification (Figure 4-9), identical with the basal spacing of mica and smectite or complete rectorite crystallite.

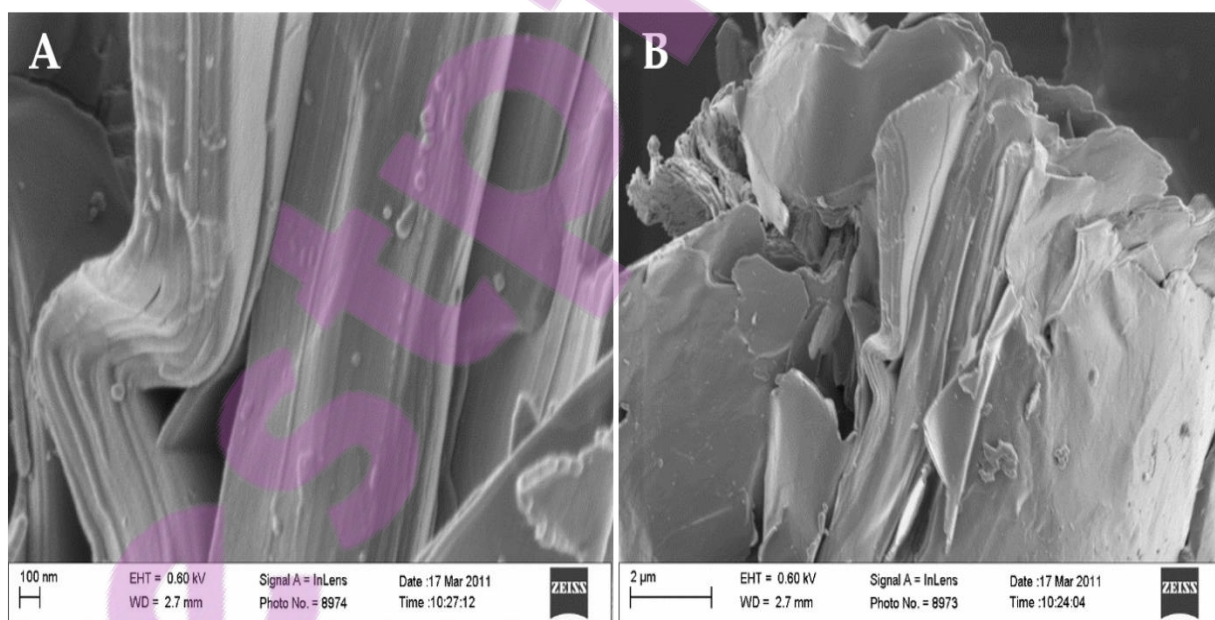


Figure 4-7. SEM images of rectorite (RT1) displaying typical layered textures

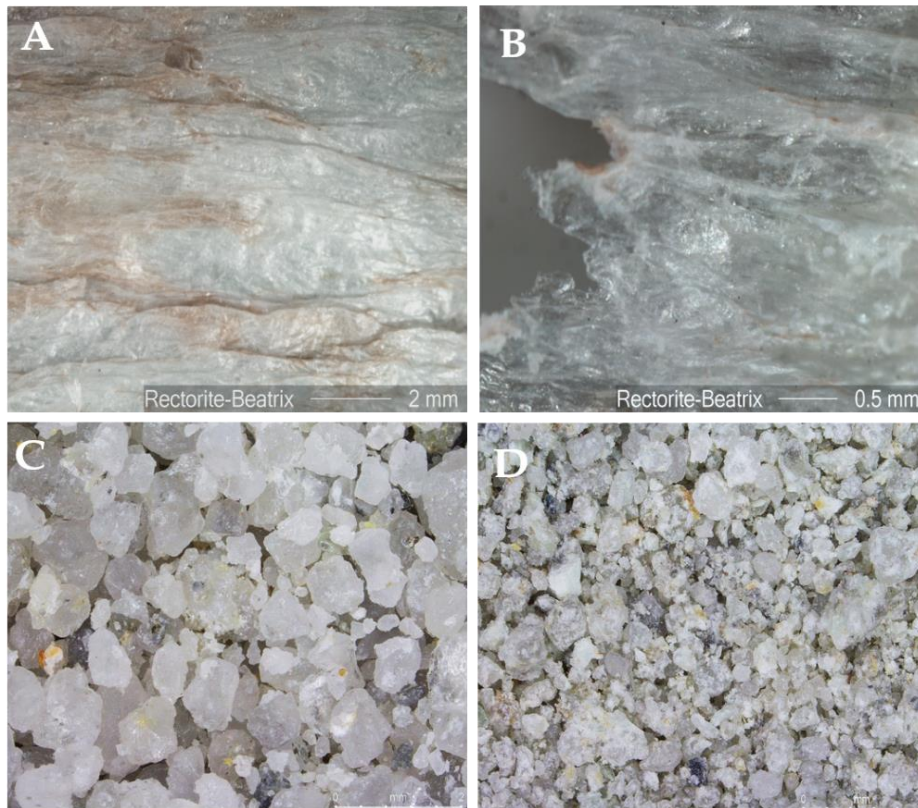


Figure 4-8. Microscope photographs of rectorite sample RT1: (A) compact aggregate; (B) thin flake fragment with translucent to transparent at sharp edges. Disintegrated mine material containing rectorite: (C) sample RT2 and (D) sample RT3

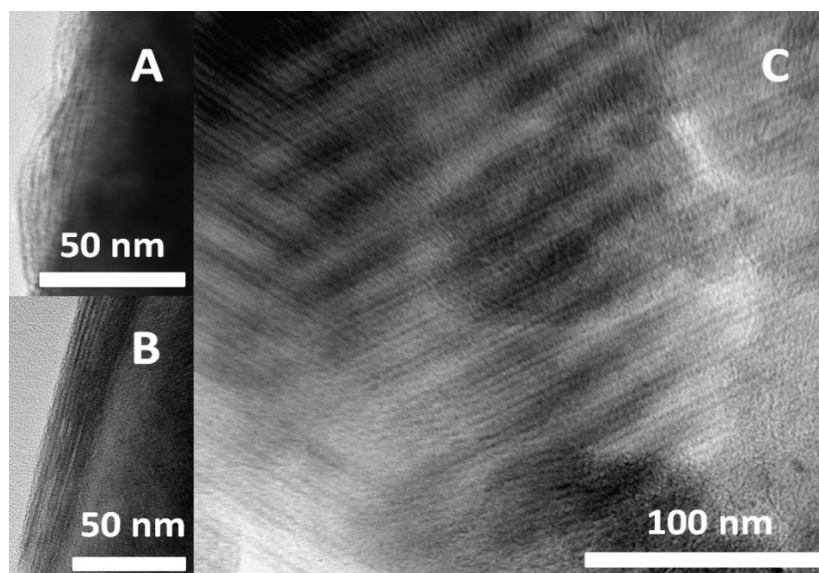


Figure 4-9. FETEM images of sample RT1 showing the typical layer arrangement of rectorite. The thickness of the light and dark domains is ~ 2.2 nm. The distances between the alternating contrast fringes within the domains are ~ 1 and ~ 1.3 nm, corresponding to the basal spacing of mica and smectite respectively.

4.1.4 X-ray diffraction and thermal analysis: neat and cation-exchanged rectorite

Typical pXRD diffractograms for a raw and a highly purified sample are presented in Figure 4-10. Quantitative pXRD analysis of bulk material from the three samples showed heterogeneous mineral assemblage with a rectorite content between 45 wt.% and 72 wt.% associated with quartz (7–49 wt.%) and chlorite (1–6 wt.%) in all three samples, calcite (12–14wt.%) in sample RT1, muscovite (1–4 wt.%) in samples RT2 and RT3, pyrophyllite (2–4 wt.%) and gypsum (ca. 2 wt.%) detected only in sample RT2 (Table 4-1).

The diffraction data of powdered raw rectorite obtained at room temperature and humidity showed variations in basal spacing with average d_{001} values ranging from 22.00 Å to 23.73 Å within the three samples. Exposure to controlled 55 % relative humidity (RH) in a desiccator showed that absorption of moisture is a function of time, with full expansion achieved after 90 h. The rectorite lattice expanded to 23.64 Å, 23.48 Å and 23.66 Å for RT1, RT2 and RT3 respectively.

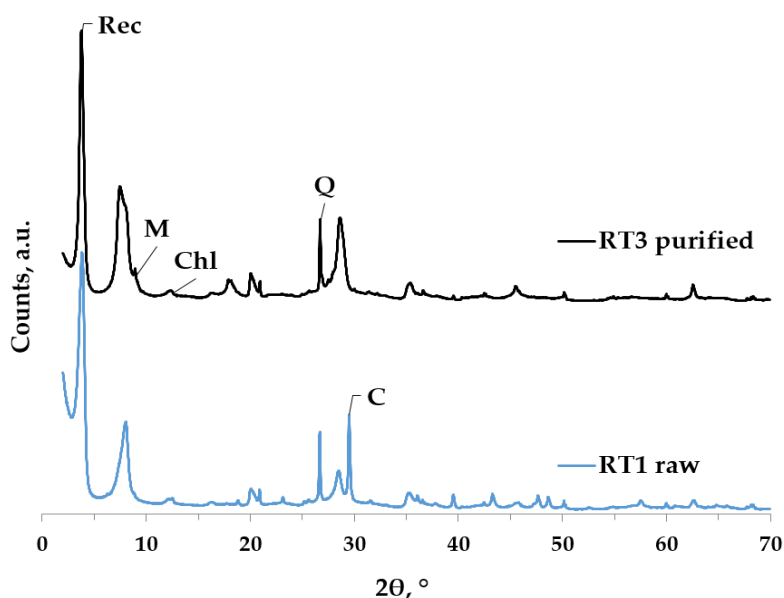


Figure 4-10. Representative powder diffraction patterns of a raw and a purified rectorite sample: rectorite (Rec), muscovite (M), chlorite (Chl), calcite (C), quartz (Q)

Besides being directly related to the layer charge, interlayer cation radius, degree of saturation and hydration state, the basal spacing of expandable materials is also a function of ambient humidity (Moore and Hower, 1986). Therefore, the peak positions from air-dried specimens in Figure 4-11 may vary slightly and should serve only as a baseline to observe diagnostic structural changes upon various organic and cation saturations.

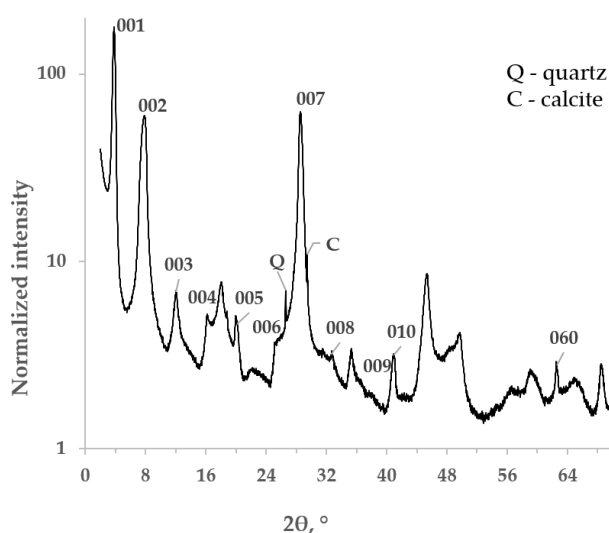


Figure 4-11. XRD diffractogram of purified rectorite in oriented slide at air-dried state (sample RT1)

Diffraction data from oriented air-dry and glycolated specimens show a good integral sequence of basal reflections with an average coefficient of variation (CV) of 0.12 (Bailey, 1982). The 060 reflection at 1.48 Å (2θ 62.40 °) indicates the dioctahedral character of the 2:1 structure. The average d_{001} spacing is between 22.07 Å and 22.20 Å, and the periodicity of smaller order d_{001} is consistent with a well-ordered 1:1 layered structure.

Upon saturation for 24 h, the mixed-layer structure expanded to d_{001} 26.75 Å when exposed to ethylene glycol (EG) and to 27.32 Å after exposure to glycerol (G) (Figure 4-12(A)). Mg^{2+} -exchanged specimens showed cell dimensions of 24.60 Å and d_{001} at 27.49 Å after glycerol exposure. Rectorite exchanged with Li^+ has d_{001} at 22.48 Å and exchanged with Na^+ at 22.16 Å in air-dry state (Figure 4-12(B)). The latter expanded to 27.24 Å–27.67 Å and 26.80 Å–28.69 Å after exposure to EG and G respectively for 24 h.

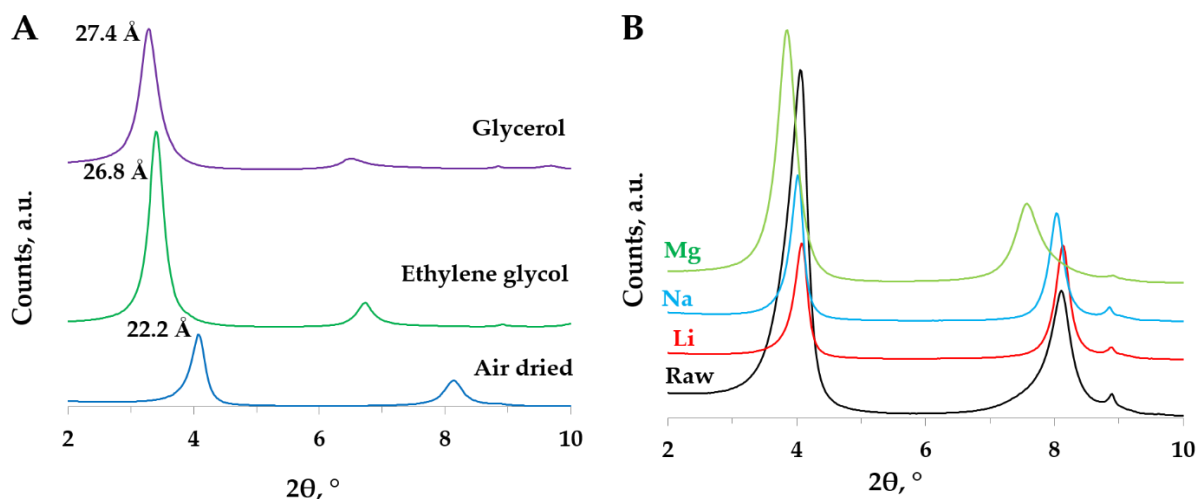


Figure 4-12. Diffraction data: (A) neat rectorite oriented specimens in air-dry state and after saturation with ethylene glycol (EG) and glycerol (G); (B) overlay of Li-, Na- and Mg-exchanged rectorite compared to neat rectorite in air-dry state

The almost identical values observed for the raw and Na-exchanged specimens suggest that Na^+ is a major exchangeable cation or is the cation most susceptible to exchange in the smectite interlayer component of rectorite. These values are consistent with the 1:1 stacking sequence of the smectite-mica interstratification of an expanding single water layer: Na-smectite at 1.24 nm alternating with a non-expanding layer of Na-mica (paragonite) at around 0.96 nm, producing a “superstructure” with a basal spacing above 2.2 nm. A similar spatial relationship is observed with glycolated specimens at 1.72 nm or 1.77 nm: glycerol-expanded smectite layers alternated in regular manner with a 0.96 nm mica layer not affected by the organic intercalation. Pattern simulation for glycolated specimens using NEWMOD indicate compositions of 50 % dioctahedral mica and 50 % dioctahedral smectite with R1 ordering.

The Greene-Kelly test (Greene-Kelly, 1951) suggested that the expandable smectite layer is of montmorillonite-beidellite composition. Partial collapse of the rectorite structure was observed, which produced reflections around 1.96 nm and 0.96 nm indicative of montmorillonite. The remaining strong reflection at around 2.76 nm, identical with that of Li-saturated glycerol expanded rectorite, serves as evidence for the beidellite component of the smectite layer. The basal 00l reflections move upon organic saturation

or cation replacement in a manner much similar to montmorillonite. Consequently, the type of exchangeable interlayer cation and its hydration energy will ultimately determine the swelling behaviour of rectorite.

The results of TGA/DSC thermal analysis (Figure 4-13) supplemented by XRD examination of heated specimens demonstrate the response of rectorite to heating. Overlays of XRD diffractograms recorded from rectorite specimens heated to 1 200 °C in steps of 50 °C are presented in Figure 4-14.

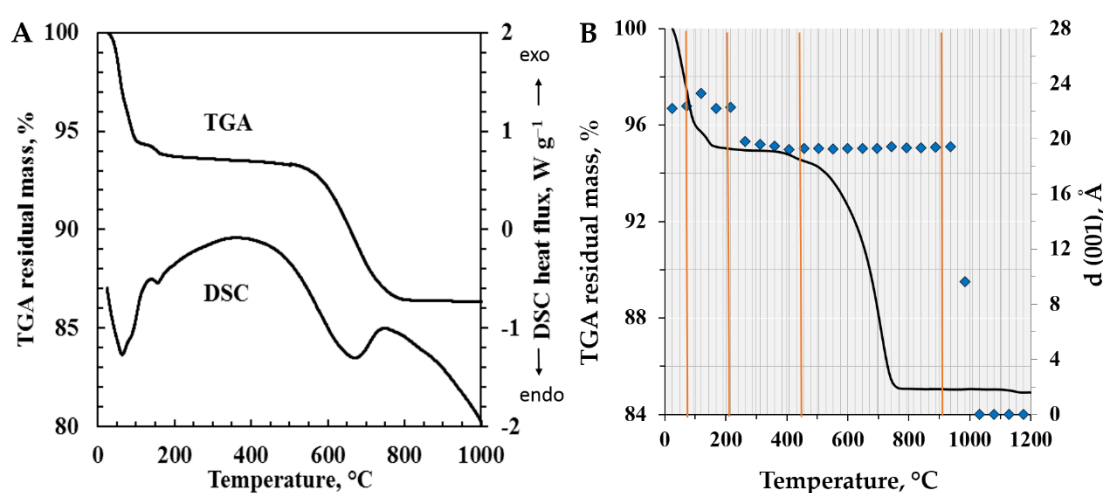


Figure 4-13. (A) TGA/DSC curves for rectorite from the Beatrix mine recorded at a scan rate of 10 °C min⁻¹ with air flowing at 30 mL min⁻¹. The sample was equilibrated at 55 % RH in a desiccator for more than 90 h; (B) d_{001} values (Å) for heated rectorite versus residual mass (%) as a function of increasing temperature.

The two methods generally agreed that full decomposition of rectorite occurred in three major steps with a total weight loss of 15.2 %. A fast, steep drop below 150 °C is followed by slow and continuous mass loss between 200 and 470 °C and a significant decrease in mass between 470 and 800 °C (Figure 4-13(A)). Initially, the structure expands slightly between 50 °C and 100 °C, possibly due to the formation of steam in the interlayer region on heating. At the start, 50 °C to 100 °C basal reflections fluctuate with d_{001} from 22.20 Å through 22.37 Å to 23.29 Å and then revert to the initial 22.29 Å at 150 °C–200 °C (Figure 4-13(B)).

The DSC patterns feature three endothermic peaks at 53 °C, 73 °C and 140 °C associated with progressive TGA mass loss of 5.9 wt.% completed at 150 °C. This mass loss is consistent with the desorption of surface water and loss of the interlayer water (Kodama, 1966). The two endothermic peaks at low temperatures indicate dehydration from the smectite layer with a divalent cation, i.e. beidellite where Ca^{2+} is the interlayer cation. The IR spectra support this observation by the disappearance of OH stretching bands at 3420 cm^{-1} and 1640 cm^{-1} (Figure 4-15). A downshift and a significant drop in intensity of d_{001} to 19.79 \AA , accompanied by increased d_{002} now at 9.89 \AA , marks the loss of regularity and the collapse of the clay structure at 250 °C .

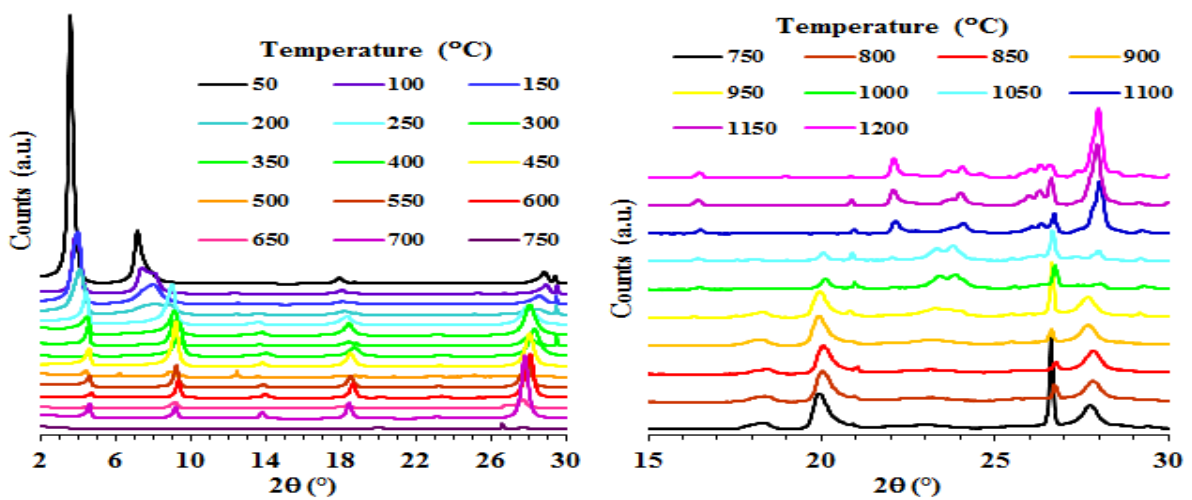


Figure 4-14. Overlay of the X-ray diffraction patterns of rectorite heated at 50 °C intervals: temperature range is 50 °C to 1200 °C

A further increase in temperature results in a change of profile intensity ratios, i.e. a very weak 001, enhancement of intensity around the mica region and adjusting positions to those consistent with paragonite d_{002} at 0.965 nm , d_{004} at 0.48 nm and d_{006} at 0.32 nm around $450 - 500\text{ °C}$. From this point up to around 750 °C the 001 reflection is very weak and gradually disappears. The loss of intensity at the first basal reflection indicates the end of dehydroxylation with the complete breakdown of the interlayer, i.e. the periodicity along the c -direction has ceased to exist. On the TG/DSC plots a weak, broad peak at around 470 °C and a more intense one at 715 °C are attributed to dehydroxylation (Kodama, 1966). At 950 °C the formation of mullite commences, followed by cristobalite

at 1 050 °C and albite at 1 100 °C. By 1 000 °C the clay structure is completely destroyed. The TGA curve indicated a mass loss of 7.7 wt.% between 500 °C and 820 °C related to dehydroxylation of structural hydroxyl groups.

4.1.5 FTIR

An IR vibration spectrum of untreated rectorite is in general agreement with published data for rectorite, montmorillonite and beidellite (Farmer and Russel, 1967; Kloprogge et al., 1999; Kodama, 1966b; Madejova and Komadel, 2001; Shimoda and Brydon, 1971).

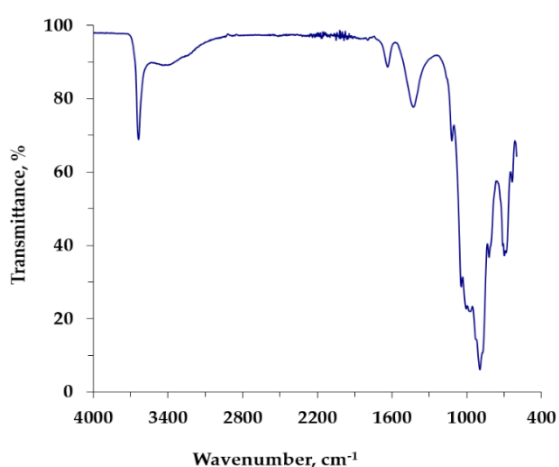


Figure 4-15. FTIR spectrum for purified rectorite (sample RT1)

Although the spectrum of raw rectorite generally resembles a mixture of muscovite-paragonite and montmorillonite-beidellite spectra, it also contains unique bands and exhibits spectral sharpness not seen in either of the individual components or other interstratified clay mineral. Such bands at 1120 cm^{-1} , 993 cm^{-1} and 710 cm^{-1} could be ascribed to Si-O stretching, while the vibration observed at 925 cm^{-1} can be associated with the Al-Al-OH deformation. A group of well-resolved sharp bands in the low-frequency range from 450 cm^{-1} to 1200 cm^{-1} , typically characteristic of a phyllosilicate structure, are present in both the raw and modified rectorite spectra.

Apart from the relatively minor shifts in peak positions, the modified forms feature considerable broadening of the absorption bands compared to those of the neat sample.

This is due to structural imperfections and reduced order arising from organic substitution. Two sharp bands at 1045 cm^{-1} and 1006 cm^{-1} assigned to the Si-O-Si group are in close proximity to Si-O stretching in the tetrahedral sheet of beidellite at 1041 cm^{-1} and montmorillonite at 1010 cm^{-1} (Farmer and Russel, 1967). Two bands at 820 cm^{-1} and 698 cm^{-1} closely resemble Al-O out-of-plane vibrations in beidellite at 819 cm^{-1} and Si-O-Al bending at 693 cm^{-1} . These originate from Al for Si substitutions in the tetrahedral sheet of beidellite and are analogous to similar vibrations in muscovite (Farmer, 1974). The absorption peak at 892 cm^{-1} represents the OH deformation band in either the Al-OH-Al or Al (Fe^{3+})-OH groups described for Wyoming-type montmorillonite with high iron content (Russell et al., 1970) and results from the substitution of Fe^{3+} for Al^{3+} in the octahedral sheet. However, this vibration has also been reported for montmorillonites with very low iron content (Farmer and Russell, 1967) and could therefore also be ascribed to the Al-OH band of rectorite.

The OH absorption spectra in the high-frequency region above 3500 cm^{-1} are generally similar for raw and modified rectorite, with slight broadening and intensity progressively decreasing from double- to single-chain surfactant intercalation. The sharp intense absorption band at 3638 cm^{-1} corresponds to the structural H bonding vibrations in the Si-O-Si linkage of rectorite (Kloprogge et al., 1999). Two less pronounced broad peaks at 3420 cm^{-1} and 1638 cm^{-1} are assigned to OH stretching and bending respectively in the H-O-H group of molecular water. Kodama (1966b) attributed the latter two to absorbed and interlayer water molecules as both peaks disappeared upon heating at $200\text{ }^{\circ}\text{C}$. The band at 3638 cm^{-1} disappears at $900\text{ }^{\circ}\text{C}$ following complete dehydroxylation of the structure. Where a very weak and broad band appears in the spectra of raw samples at around 1375 cm^{-1} , it is due to trace amounts of absorbed NH_4^+ .

Table 4-2. Band positions (cm⁻¹) and assignments for the IR absorption maxima of neat purified rectorite from Beatrix mine with the literature data for comparison as indicated

Band Assignment	Rectorite	Rectorite	Modified rectorite	Modified rectorite	Modified rectorite	Rectorite	Rectorite	Synthetic mica-montmorillonite	Synthetic beidellite	Paragonite	Swy-2, Wyoming montmorillonite	Rectorite
	This study: Untreated KBr	This study: Untreated ATR	This study: Hexadecyltrimethyl Ammonium Chloride-(SCC16) KBr	This study: Didecyltrimethyl Ammonium Chloride-(DCC10) KBr	This study: Dialkyltrimethyl Ammonium Chloride-(DCC18) KBr	Li et al., 2008. ATR	Kloprogge et al, 1999. KBr	Kloprogge et al, 1999. KBr	Kloprogge et al, 1999. KBr	Kloprogge et al, 1999. KBr	Madejova and Komadel, 2001 KBr	Kodama, 1966. KBr
Si-O bending		481				479	478	471	473	481		
Si-O-Al bending		523				523	545	536	535	542	524	
Si-O-Al deformation	638	636				635	615	620	625	625	620	
Si-O-Al bending	699	694				699	693	699	694	694		
Si-O-Al bending	710	710										
Al-O-Si in-plane	732	732					726	732				730
Al-O-Si in-plane	760	760					758	756	753		778	
Al-O-H libration	815	815					804	819	812	805		810
Al-O-out-of-plane	820	821				823	822			832	842	823
Al-O-H libration	875	877					875	888	884	883	885	875
Al-O-H libration	897	896				895						
Al-O-H libration	925	928					914	936	928	935	917	920
Si-O-Si stretching	993											995
Si-O-Si stretching	1006	1006				1004						
In-plane Si-O-Si stretching		1034					1021	1030	1028	1009		1023
In-plane Si-O-Si stretching	1046	1046				1048	1058	1053			1041	1050
Si-O stretching		1088					1082					1080
Si-O stretching	1121	1120				1120	1123	1126	1124	1125		1125
NH4	1375							1401				1388
C-H bending vibration			1448	1434	1442max			1441				
C-H bending vibration			1470max	1468max	1466	1469						
H2O bending (OH deformation of H2O)	1640	1645	1648	1655	1644	1634	1639	1637	1634		1634	1640
C-H symmetric stretching vibrations			2851	2856	2855	2850						
CH2 asymmetric stretching			2924	2927	2929							
C-H asymmetric stretching vibrations			2954	2959	2962	2919						
Chemically bonded interlayer H2O	3240	3240		3282	3246		3240	3266	3230			
H2O stretching or H-bonding vibrations in Si-O-Al linkage	3420	3420	3410	3421	3442	3390	3433	3478	3453	3420	3422	3420
H bonding vibrations in Si-O-Si linkage	3640	3640	3644	3644	3640	3639	3638	3651	3659	3620	3632 (3627)	3645

4.1.6 Rectorite structure refinement, modelling and quantitative analysis

4.1.6.1 Structure refinement and modelling

Similarly to other mixed-layer structures, only partial indexing information for rectorite is available in the two PDF files in the ICDD database. This data contains 001 reflections only and describes a 2-dimensional crystal structure characteristic of clay minerals where layers are stacked along the third dimension. The observed diffraction data from the Beatrix mine rectorite fits a structure intermediate between those of PDF 025-0781 (Korolev, 1971) and PDF 029-1495 (Brindley, 1977). Based on the empirically modelled *rt_hkl* phase (Figure 4-16), the cell parameters of purified raw Beatrix rectorite refined to $a = 5.177(13) \text{ \AA}$; $b = 8.980(33) \text{ \AA}$; $c = 22.489(20) \text{ \AA}$ and $\beta = 97.335(44)^\circ$. The calculated volume weighted mean crystallite size was around 14 nm and the cell volume was $1045.41(16) \text{ \AA}^3$.

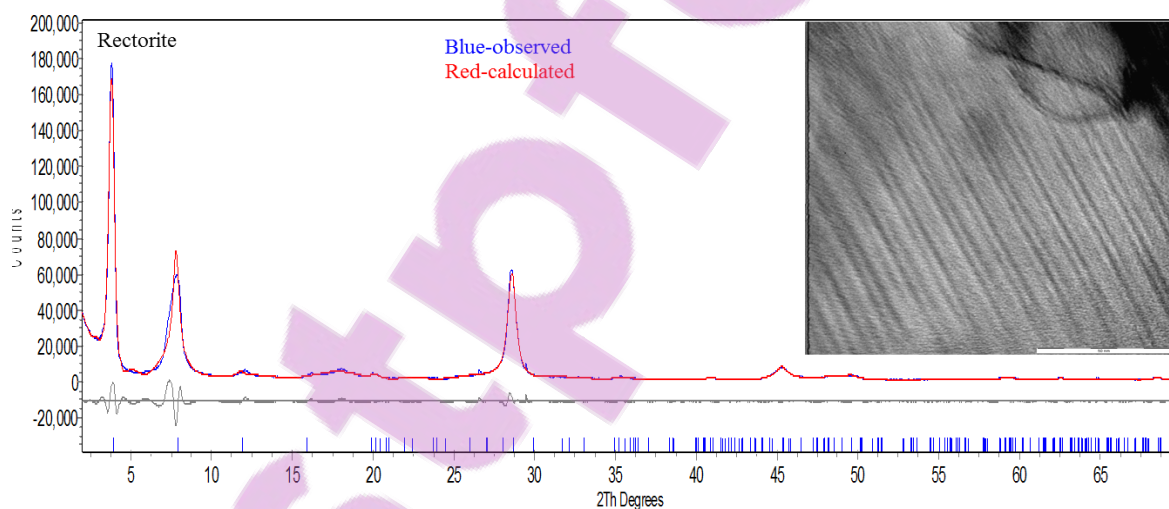


Figure 4-16. Observed (blue), calculated (red) and difference curve (grey) patterns after refinement using the modelled rectorite phase in place of a structure file. The TEM image (FOV 150 nm) displays layer periodicity; the approximate thickness of a set of light/dark fringes is below 15 nm, i.e. in the range of calculated crystallite size.

The refinement data from Na-exchanged rectorite was $a = 5.090(11) \text{ \AA}$; $b = 9.026(30) \text{ \AA}$; $c = 22.200(66) \text{ \AA}$ and $\beta = 98.836(23)^\circ$ with V of $1008.06(50) \text{ \AA}^3$ and the Mg-exchanged

structure showing unit cell parameters $a = 5.138(17) \text{ \AA}$; $b = 9.001(47) \text{ \AA}$; $c = 24.349(26) \text{ \AA}$, $\beta = 97.52(44)^\circ$ and cell volume $1094.60(41) \text{ \AA}^3$.

The quality of the Rietveld refinement was assessed by inspection of the difference curve between the measured and calculated XRD patterns and the numerical quality criteria Rwp (weighted residual). Figure 4-10 shows a typical refinement plot to demonstrate the goodness of fit for rectorite refinement using the modelled *rt_hkl* structure file. The weighted residual errors Rwp ranged from 5.3 % to 15 %, indicating a very good agreement between observed and simulated XRD patterns.

4.1.6.2 Quantitative phase analysis (QPA): accuracy and validation

The closeness of the qualitative and quantitative determinations of the replicate samples was comparatively small within laboratory errors. The QPA percentage, inferred by the Rietveld method, of major oxides for rectorite in each sample was compared to the respective oxide proportions determined by XRF and the results are plotted against each other in Figure 4-17. RecBea indicates the unique chemistry for Beatrix rectorite determined in this study (Table 4-7). This chemistry is used as a basis to calculate the mean structural formula, and here for the calculation of normative compositions. Calculations were also done based on chemical compositions for rectorite from the literature data (Gaines et al., 1997; Nishiyama and Shimoda, 1981). These calculations were used to assess the accuracy of rectorite modelling, QPA and mineral chemistry determined in this study. Linear regression lines are shown for each oxide plot, together with the respective equation ($y = ax + b$) and the relevant correlation coefficient R^2 . The diagonal line on each plot is drawn to visualise statistical fit: in the case of exact agreement, the points would fall on the diagonal line. Points below this line would indicate underestimation and points above it, an overestimation by the Rietveld phase quantification. For SiO_2 and Al_2O_3 all samples show good agreement between the values from the XRD and XRF results (Figure 4-17(A, B and D)). The slight deviations shown on plots (B) and (C) by empty circles all belong to recalculation data

based on rectorite compositions from published sources. This is confirmed in plots (D) and (E) by the improved correlation coefficient R^2 after removal of the literature-based recalculated data, i.e. where only RecBea compositions are used. The comparison of CaO, Na₂O and K₂O shows greater dispersion, more pronounced in the lower values range. These elements comprise the interlayer content of rectorite with Ca²⁺ and Na⁺ present in the exchangeable and fixed interlayer, and minor K⁺ in the fixed interlayer only and also in the free-standing muscovite. In sample RT1 some Ca²⁺ is also related to the calcite occurrence that carries a substantial LOI component and may explain the underestimation of CaO by Rietveld at a higher concentration range (Figure 4-17(C and E)). The wide spread in the K₂O population is most probably due to the low concentrations and greater degree of variation of its occurrence, confirmed by the drastic improvement of correlation R^2 when local RecBea composition was used for normative calculation. The latter also applies to the CaO and Na₂O correlation trends (Figure 4-17 (C and E)).

Despite some individual outliers, comparison of the major oxide percentages of the theoretical and measured compositions shows a generally high level of agreement. All data points, including those based on published rectorite compositions, plot close to the equality line with slight deviations indicating under- or overestimation of the Rietveld QPA (Figure 4-17(A)). The best agreement is achieved when the mineral chemistry of RecBea is used for calculation. This is a good indication that the proposed quantification method for rectorite-containing samples provides a quantitative estimation of mineral percentages that are consistent with independent chemical determinations, in this case by XRF. This further confirms the accuracy of the *rt_hkl* model proposed here, the calibrated QPA method generated with the modelled rectorite structure file, and the chemical determinations by XRF.

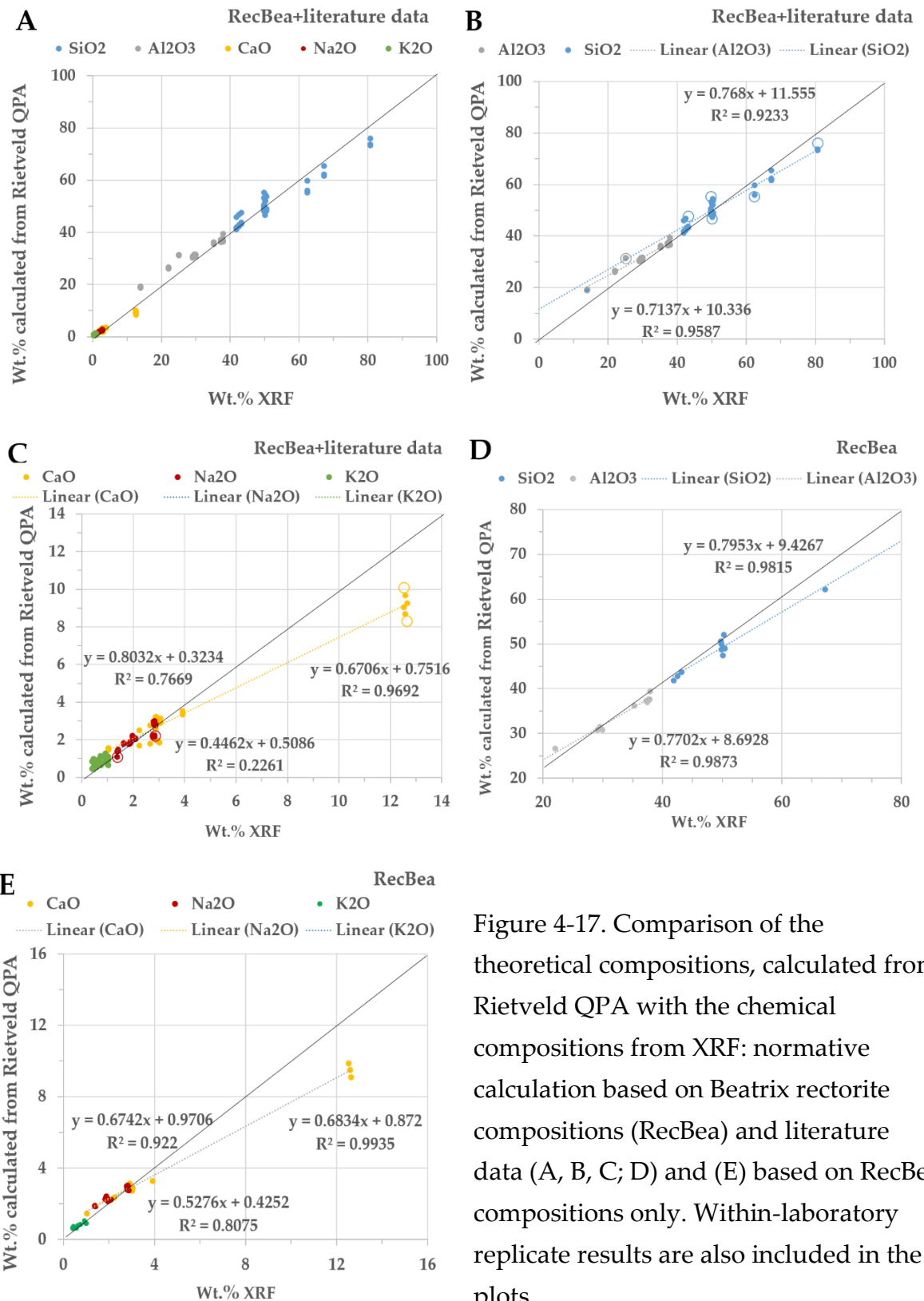


Figure 4-17. Comparison of the theoretical compositions, calculated from Rietveld QPA with the chemical compositions from XRF: normative calculation based on Beatrix rectorite compositions (RecBea) and literature data (A, B, C; D) and (E) based on RecBea compositions only. Within-laboratory replicate results are also included in the plots.

4.1.7 NMR

NMR probes the local environment of the nucleus under study and thus it focuses on the short-range order. It is therefore ideally suited for disordered materials or materials exhibiting short-range order only. The NMR spectra provide quantitative information complementary to the scattering experiments on the relative content of various species. NMR inherently gives an ensemble average. For this reason the solid-state NMR spectra of all NMR-active nuclei in the sample were recorded.

4.1.7.1 ^{27}Al MAS NMR

The ^{27}Al MAS (14 kHz) NMR spectra of all samples showed two signals with spinning side-bands (ssb) (Figure 4-18 (a) and (b)). The central transitions of the lines featured characteristic second-order quadrupolar broadened line shapes. The dominating line at *ca.* 5 ppm is attributed to six-coordinated (or octahedral or AlO_6 or Al-VI) Al sites, while the second peak at *ca.* 70 ppm is known to arise from Al sites in the tetrahedral coordination (four-coordinated AlO_4 or Al-IV) (Vyalikh et al., 2009). The relative ratio of AlO_4 (Al-IV) to AlO_6 (Al-VI) is 1:2 and remained constant across all samples. Deviation from the characteristic second-order quadrupolar line shape due to inhomogeneous broadening indicates a distribution of Al environments. The fit parameters changed only slightly within the uncertainty limits, pointing to the fact that the local structure around Al was not affected by purification and ion substitutions. Similar spectral parameters and the invariance of the ^{27}Al NMR spectra on modification of the local environment in interlayers were previously reported for synthetic beidellite (Kloprogge et al., 1992). Slight deviations of the fit parameters for RT2 and its remarkable line broadening reflect a more disordered and less symmetric environment as compared to other samples (Table 4-3).

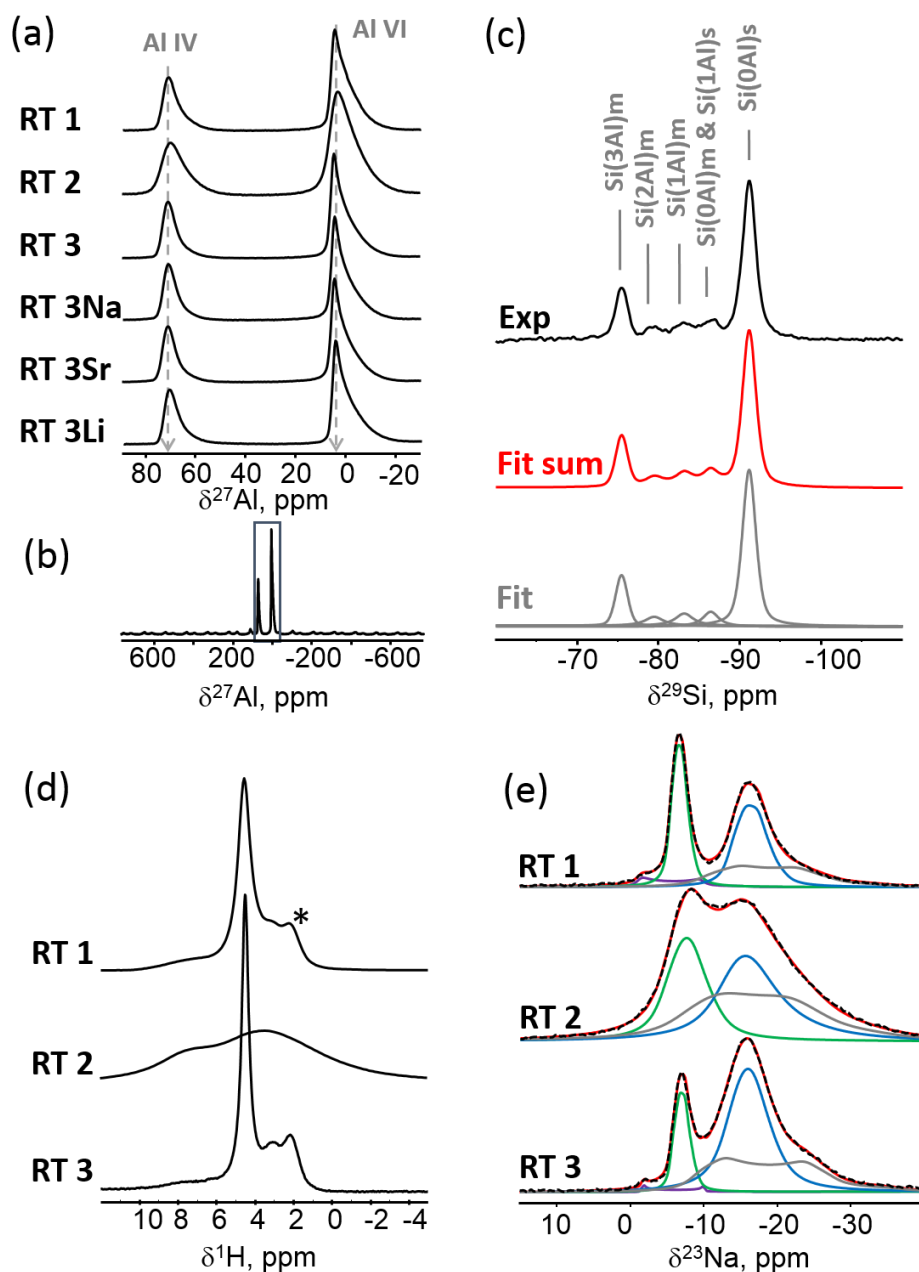


Figure 4-18. (a) ^{27}Al MAS NMR spectra of rectorite samples; (b) broad width ^{27}Al MAS NMR spectrum of RT1 with spinning sidebands. The frame shows the spectral region expanded in (a). (c) ^{29}Si MAS NMR spectrum of RT1 (Exp) with spectral deconvolution (Fit) and a sum of fit components (Fit sum). (d) ^1H MAS NMR spectra at 20 kHz spinning speed of the three rectorite samples. The spectra are normalised at the high-field peak shown by the asterisk. (e) ^{23}Na MAS NMR spectra of the three rectorite materials (black dotted lines) with their deconvolution, including the sum of fit components (red line). Site I is green, Site II is grey, Site III is blue and Site IV is lilac.

Table 4-3. Fit data for ^{27}Al NMR spectra, where $^{27}\delta$ is the isotropic chemical shift (± 0.2 ppm) and C_Q is the quadrupolar coupling constant (± 0.2 MHz). The relative intensities ($\pm 1\%$) for the two components are calculated from central transitions and spinning sidebands.

Sample	$^{27}\delta$, ppm		C_Q , MHz		Relative intensities, %	
	Al-IV	Al-VI	Al-IV	Al-VI	Al-IV	Al-VI
RT1	74.3	6.6	3.4	3.6	33	67
RT2	74.5	6.8	4.0	4.2	32	68
RT3	74.0	6.5	3.1	3.5	33	67
RT3 Na	74.2	6.6	3.2	3.5	33	67
RT3 Sr	74.2	6.6	3.2	3.5	33	67
RT3 Li	74.1	6.5	3.3	3.6	33	67

4.1.7.2 ^{29}Si MAS (5 kHz) NMR

Since T_1 relaxation times can be different for various ^{29}Si sites, the repetition time had to be adjusted according to the longest T_1 in the sample in order to obtain quantitative spectra. Due to the very long ^{29}Si T_1 relaxation times in these materials, ^{29}Si MAS NMR spectra were measured at two repetition time values in order (i) to obtain a sufficient signal-to-noise ratio for signal assignment, and (ii) to obtain quantitative information from fully relaxed spectra. Five lines are found in all ^{29}Si spectra, which are attributed to silicon tetrahedra surrounded by aluminium atoms located in either the mica (m) or the smectite (s) layers (Figure 4-17(c)). The nomenclature Si ($n\text{Al}$) designates a Si atom bonded via oxygen bridges to n Al atoms in tetrahedral sheets ($n = 0-3$). Due to their similar positions, $\text{Si}(0\text{Al})_m$ and $\text{Si}(1\text{Al})_s$ cannot be distinguished in the present experiment. The Si ($n\text{Al}$) intensity distribution presented in Table 4-4 shows a deviation from the expected binomial intensity distribution in mica, pointing to a high degree of Al substitution (high fraction of the $\text{Si}(3\text{Al})_m$ component).

Table 4-4. Fit data for ^{29}Si NMR spectra, where $^{29}\delta$ is isotropic chemical shift (± 0.1 ppm). Relative intensities ($\pm 5\%$) are calculated from the fully relaxed spectra (at a repetition time of 600 s).

Sample	^{29}Si chemical shifts					Relative intensities
RT1	-75.5	-79.5	-83.2	-86.3	-91.1	20 : 6 : 7 : 7 : 60
RT3	-75.5	-79.5	-82.7	-86.7	-91.0	13 : 10 : 10 : 15 : 52
RT3 Na	-75.5	-79.3	-82.8	-85.7	-91.0	11 : 8 : 16 : 17 : 48
RT3 Sr	-75.5	-79.3	-83.6	-86.3	-91.1	12 : 12 : 14 : 12 : 50
RT3 Li	-75.5	-79.3	-83.2	-86.1	-91.0	11 : 13 : 12 : 15 : 49
Assignment	Si(3Al)m	Si(2Al)m	Si(1Al)m	Si(0Al)m	Si(1Al)s	Si(0Al)s

4.1.7.3 ^1H MAS (20 kHz) NMR

High-resolution MAS NMR spectra (Figure 4-17(d)) show sharp signals at 2.1 ppm, 3.1 ppm, and 4.6 ppm and a broad background signal at ca. 8 ppm for the samples RT1 and RT3, while only two broad peaks are seen for RT2 (Table 4-5). The broadening can arise from structural disorder and/or the presence of minor paramagnetic impurities (e.g. the presence of iron oxide or iron substitution in the octahedral sheets of the rectorite itself) and is consistent with the ^{27}Al and ^{23}Na data for RT2. The peaks at 2.1 ppm and 3.1 ppm are assigned to the hydroxide groups of hydrated Al_2O_3 and SiO_2 in the mineral structure, while the peak at 4.6 ppm is attributed to water physically adsorbed on the mineral surface. Similar peaks have been noted in a study on aluminium layered hydroxides (Wang et al., 2009a). In contrast with the latter study, the narrower line width and Lorentzian line shape in the present study point to weak residual dipolar interactions and thus higher mobility of water, because the proton dipolar coupling is the major source of broadening. The broad peak at ca. 8 ppm can arise from interlayer water surrounding the Na^+ in the interlayer space of the smectite layers. In general, the presence of water and hydroxide signals is in a good agreement with the FTIR data reported above.

Table 4-5. Fit data for ^1H NMR (14 kHz MAS) spectra, where $^1\delta$ is isotropic chemical shift (± 0.1 ppm)

	Exp. No:	^1H chemical shifts				Relative intensities, %
RT1	30	-	-	2.55	-	
RT3	31	4.5	4.2	3.1	2.1	25:33:19:23
RT3 Na	32	-	-	3.2	2.0	68:32
RT3 Sr	33	4.5	4.2	3.2	2.0	30:31:15:24
RT3 Li	34	-	4.2	3.0	2.0	55:20:25

4.1.7.4 ^{23}Na MAS (20 kHz) NMR

The ^{23}Na NMR spectra of RT1 and RT3 exhibit at least three major components, while in the spectrum of RT2, only two components are resolved due to the very strong line broadening (Figure 4-17(e) and Table 4-6. The well-resolved signal at the low-field side (positive ppm values) characterised by a $\delta(^{23}\text{Na})$ value of ca. -5 ppm, a C_Q value of 1 MHz, η of 0.5 and narrow line broadening is attributed to Na^+ fixed in-between the margarite tetrahedral sheets according to the literature data (Site I, green line in Figure 4-17(e)) (Jakobsen et al., 1995). The deviations in both $\delta(^{23}\text{Na})$ and C_Q for RT2 point to changes in the local electron environment around the sodium atom in RT2 the margarite sheets, while the increase of its line width (EM) indicates greater disorder in comparison to the other samples.

The high-field broad line represents a superposition of the components with more pronounced quadrupolar characteristics, in which the strength and distribution of quadrupolar interactions point to symmetry and ordering in the local sodium environment. Site II at ca. $\delta(^{23}\text{Na}) = -7$ ppm possesses a large C_Q of ca. 2.8 MHz (grey line in Figure 4-17(e)), indicating even larger deviations from the spherical symmetry around a sodium atom in RT2 and RT3. The higher EM value informs about structural inhomogeneity and disorder, which has been significantly improved in Sample RT3. Site III (blue line in Figure 4-17(e)) is characterised, in general, by a $\delta(^{23}\text{Na})$ value of ca.

-13 ppm and a C_Q value of 1.2 - 1.5 MHz. According to the data reported for Beatrix rectorite (Jakobsen et al., 1995), the high-field broad line giving rise to Sites II and III may result from overlap between Na^+ fixed between the paragonite tetrahedral sheets and exchangeable Na^+ . In addition, a very weak signal (lilac line in Figure 4-16(e)) at ca. 1 ppm and a C_Q of 2.2 MHz (up to 5 % of total intensity) is visible in RT1 and RT3.

Table 4-6. Major components in the ^{23}Na MAS NMR spectra with their relative integral intensities ($\pm 2\%$) and assignment

Sample	Spectral intensity, %				Ratio Site I: Site II
	Site I $^{23}\delta = -5.1$ ppm	Site II $^{23}\delta = -7.9$ ppm	Site III $^{23}\delta = -13.1$ ppm	Site IV $^{23}\delta = 1.2$ ppm	
RT1	31	26	37	5	1:0.8
RT2	27	37	36	-	1:1.4
RT3	15	32	51	2	1:2.2
Assignment	Mica interlayer Na^+ fixed between margarite sheets	Na^+ fixed between paragonite sheets	Smectite interlayer Na^+ exchangeable in smectite interlayer	n.a.	

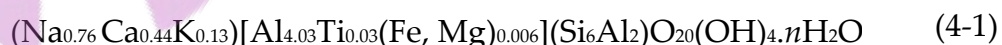
In the literature, the narrow ^{23}Na peak at ca. 0 ppm is attributed to trapped Na^+ ions in symmetric cavities created by a mica-type stacking or to the non-exchangeable part of the sodium interlayer cations (Möller et al., 2010). In contrast to that work, the quadrupolar interactions for this peak are not averaged out, and they can tentatively be assigned to a variety of Na-containing mica in the samples under study. Although for accurate assignment additional experiments are required, the assumption is that Site III with smaller quadrupole parameters results from more mobile exchangeable Na^+ in the smectite interlayer. This allows estimation of the ratios of Na^+ fixed between the margarite and paragonite tetrahedral sheets, which are found to be 1:0.8, 1:1.4 and 1:2.2 for RT1, RT2 and RT3, respectively. Exact quantification for RT2 is impossible at this stage due to strong signal overlapping. The effect of interlayer composition on the distribution of Na^+ for various exchanged forms of rectorite is beyond the scope of the present study.

In summary, the NMR results indicate that two Al sites are present in all rectorites (Al-VI and Al-IV). The local structure around Al does not vary upon modification and a high degree of Al substitution is indicated. Structural inhomogeneity and disorder are indicated for RT2 rectorite. The relative concentrations of Na⁺ fixed between the margarite and paragonite layers differ in the three rectorite samples.

4.1.8 XRF

The average chemical composition of purified rectorite (RT3) determined by XRF analysis is listed in Table 4-7. The components in the samples with the highest rectorite content were recalculated, adjusting for mineral impurities, and used as a basis to calculate the mean structural formula. Trace concentrations of P₂O₅, Cr₂O₃, ZnO and BaO were considered to be due to matrix contamination and omitted from further calculations. The CEC, estimated from the XRF-determined compositions of the purified and the various RT3 cation-exchanged samples, was 45 ± 7 mEq/100 g. Such a value is expected if alternate interlayers are of the montmorillonite type. The compositions of the fixed and exchangeable interlayers were determined from the Na⁺ and K⁺ cation-exchanged rectorite forms under the assumption that all exchangeable cations reside in the swelling interlayer region. The exchangeable interlayer composition is (Na_{0.10} Ca_{0.13}) with a layer charge of -0.36 per O₂₀(OH)₄, and the fixed interlayer contains (Na_{0.66} Ca_{0.31} K_{0.13}) with a total charge of -1.41.

The summarised formula derived from the ignited composition (dry basis) based on O₂₀(OH)₄ is:



The structural formula indicates that monovalent Na⁺, K⁺ and divalent Ca²⁺ cations are available in the interlayer of natural rectorite. The fixed interlayer space (mica interlayer space) contains proportionally dominant Na⁺ and Ca²⁺ and minor K⁺. The exchangeable smectite interlayer contains almost equal Na⁺ and Ca²⁺ ions. This

elemental distribution implies that the mica layer is represented by paragonite (Na-mica)-margarite (Ca-mica with minor Na) series, rather than muscovite (K-mica). Potassium is most probably contributed by paragonite which may contain up to 0.15 % K (Rieder et al., 1998). Furthermore, this composition suggests a 1:2.5 margarite-to-paragonite distribution. This agrees well with the margarite-to-paragonite distribution of 1:2.2 in RT3 estimated from the ^{23}Na NMR data.

Table 4-7. Major element concentrations of rectorite determined by X-ray fluorescence spectroscopy, recalculated for concentrations of impurities compared to published data (von Rahden, 1994). The reported chemical compositions represent the mean values for five purified rectorite samples (RT3).

Oxide	Composition, wt.%		
	Average	Recalculated ^a	Literature ^b
SiO ₂	50.09 ± 0.38	49.56	51.02
TiO ₂	0.27 ± 0.01	0.310	
Al ₂ O ₃	37.57 ± 0.36	42.27	40.69
Fe ₂ O ₃ (t)	0.04 ± 0.02	0.049	0.40
MgO	0.01 ± 0.00	0.012	0.57
CaO	2.94 ± 0.07	3.388	5.33
Na ₂ O	2.81 ± 0.03	3.25	1.68
K ₂ O	0.95 ± 0.07	0.87	0.31
P ₂ O ₅	0.02 ± 0.00	0.023	
Cr ₂ O ₃	0.05 ± 0.05	0.058	
V ₂ O ₅	0.02 ± 0.00	0.021	
BaO	0.05 ± 0.01	0.059	
ZnO	0.02 ± 0.01	0.024	
ZrO ₂	0.01 ± 0.00	0.010	
SrO	0.08 ± 0.01	0.096	
LOI	5.40 ± 0.04		
Dry basis	94.95 ± 0.61		
Total	100.14 ± 0.62		100.00

^a Recalculated (ignited basis) adjusting for impurities based on XRD mineral composition: rectorite 91.45 wt.%; quartz 5.95 wt.%, mica 1.66 wt.% and chlorite 1.52 wt.%.

^b Ignited-weight basis, (von Rahden, 1994).

The expandable layer charge of -0.36 is predominantly due to tetrahedral substitution; this is characteristic of beidellite rather than montmorillonite in which the net layer charge arises from octahedral substitutions. In the dioctahedral 2:1 structure, the four octahedral sites are dominantly occupied by Al^{3+} with minor Ti^{4+} , Fe^{3+} and Mg^{2+} . Based on chemical data, the distribution of tetrahedral and octahedral Al is proportionally 1:2. These conclusions support the XRD identification of beidellite by the Greene-Kelly test (Greene-Kelly, 1952) and the identification of paragonite by the thickness of the mica layer of 9.65 \AA as opposed to the muscovite layer thickness of 10.00 \AA . Hence, Beatrix rectorite identifies with Na-Ca-rectorite, which conforms well with previously reported XRF data for rectorite (Jakobsen et al., 1995; Lausen et al., 1999; von Rahden, 1994).

Smectites and other 2:1 layered structures commonly exhibit heterogeneous charge distribution among the different layers (Lagaly and Beneke, 1991). In mixed-layer structures heterogeneity is further emphasised by the existence of two types of 2:1 layer. Therefore the structural formulae derived from the major element concentrations as given above represent average compositions of the layers.

4.2 Characterisation of organically modified rectorite

Modified complexes of rectorite with long-chain dodecyldimethyl-ammonium chloride (DCC10), dialkyldimethylammonium chloride (DCC18) and hexadecyltrimethylammonium chloride (SCC16) were characterised by XRD, FTIR spectroscopy and TGA. The surfactant loading of 50 % excess was based on a CEC of 45 mEq/100 g . The XRD patterns (Figure 4-19) show well-defined peaks as the surfactant was homogeneously intercalated between the rectorite layers. The expansion of the interlayer with the double-chain surfactants was 3.60 nm and 3.70 nm for DCC10 and DCC18 respectively, while the d-spacing corresponding to single-chain intercalation with SCC16 was 3.20 nm . The shift of the basal spacing is due to the exchange and adsorption of larger organic molecules into the smectite layer in the

rectorite structure. Homogeneous intercalation implies an increase in the organophilic properties of rectorite at the expense of its hydrophilic nature, and suggests that adsorption is feasible and can be used as a precursor step to the subsequent adsorption of non-polar organic compounds.

The FTIR spectra of raw rectorite and rectorite modified by SCC16, DCC10 and DCC18 in the middle IR region 400–4000 cm^{-1} are plotted in Figure 4-20. Table 4-2 lists the band positions and assignments together with some relevant published data for comparison. Expected similarities in the spectra are well displayed in the regions typical of neat rectorite. The well-resolved bands in the low-frequency range from 450 cm^{-1} to 1 200 cm^{-1} , typically characteristic of a phyllosilicate structure, are present in both the raw and modified rectorite spectra.

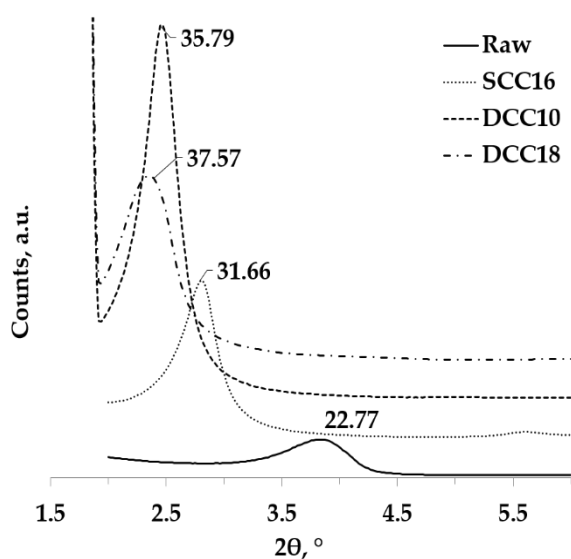


Figure 4-19. Basal spacing d_{001} , Å of the rectorite-organic complexes with reference to raw rectorite

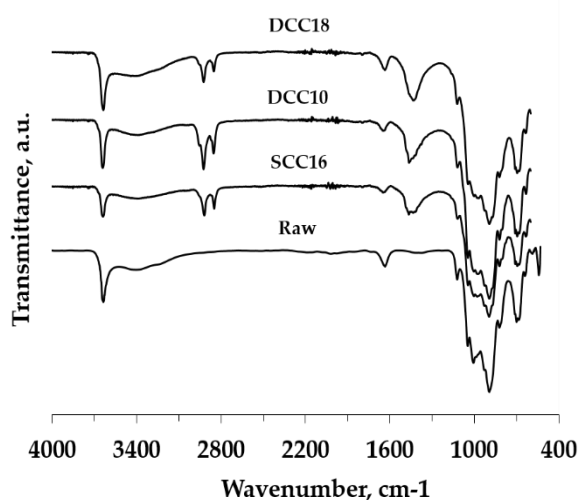


Figure 4-20. FTIR spectra of raw rectorite and the DCC10, DCC18 and SCC16 intercalated forms

The FTIR spectra of the organically modified rectorite contain additional absorbance peaks characteristic of the infrared active vibrations of the main functional groups of the surfactant. A pair of sharp bands between 2820 cm^{-1} and 2970 cm^{-1} is ascribed to the symmetric and asymmetric stretching vibrations of CH_2 groups of the alkyl chains,

of which the bending vibrations are visible around 1460 cm^{-1} (Table 4-2). The former two were stronger with the DCC10 chain and proportionally weakened for DCC18, being the weakest for the single-chain SCC16 intercalated rectorite. The maxima of CH_2 bending vibrations in the range $1440\text{--}1480\text{ cm}^{-1}$ gradually shifted towards higher frequencies from 1442 cm^{-1} for DCC18 through DCC10 (1468 cm^{-1}) to 1470 cm^{-1} for SCC16 intercalated rectorite. There is also slight movement of the O-H stretching band in the region between 3800 and 3200 cm^{-1} in the SCC16 and DCC10 spectra to 3644 cm^{-1} compared to 3640 cm^{-1} of the raw and DCC18 modified rectorite. Higher frequency usually reflects a higher energy state of the OH groups and an increase of 1 cm^{-1} corresponds to an energy increase of 2.859 cal/mol (Kodama, 1966).

Generally, the thermal behaviour of alkyl ammonium-modified rectorite resembles the decomposition pattern of neat material (Figure 4-21). The deviations are strongly affected by the surfactant chain length and initial loading. Peak shifts and variations in relative intensity proportions reflect the effect of modification on the structure and consequently its influence on the water-loss reactions.

With 50 % excess loading of DCC10 and DCC18 ions, the TG/DTG results of the double alkyl chain organorectorite show a small peak at $53\text{ }^\circ\text{C}$ identical to that in the neat rectorite and assigned to the removal of loose water. The first mass loss calculated at $150\text{ }^\circ\text{C}$ was 1.30 % for DCC10 and 1.44 % for DCC18. This is lower compared to the raw material and reflects the change of surface properties from hydrophilic to hydrophobic as a result of the exchange. These values are slightly lower than observations reported in the literature (Li and Jiang, 2009) for a higher surfactant loading of 1.56 CEC and a mass loss of 2.1 %. The TG curve of DCC10-intercalated rectorite shows three additional peaks at $253\text{ }^\circ\text{C}$, $293\text{ }^\circ\text{C}$ and $427\text{ }^\circ\text{C}$. For DCC18-modified material, corresponding peaks occurred at $250\text{ }^\circ\text{C}$ and $421\text{ }^\circ\text{C}$.

The second mass loss in the range of $258\text{--}431\text{ }^\circ\text{C}$ for DCC10 and $295\text{--}454\text{ }^\circ\text{C}$ for DCC18 is attributed to the combustion of the adsorbed surfactants. At more elevated

temperatures the last weight change is a result of the loss of structural OH groups leading to full dehydroxylation. The DTG patterns of both double alkyl chain organorectorites confirmed this change with a peak at 730 °C. Proportionally, this peak is less intense here than in the single-chain form and the neat rectorite.

The derivative curve of rectorite intercalated with a single alkyl chain (SCC16) shows two small peaks at 46 °C and 122 °C, accounting for a mass loss of 2.19 % due to the removal of adsorbed water. This value is intermediate compared to 3.0 % at 1.25 CEC and 1.8 % at 1.75 CEC for single-chain modifications reported previously (Li and Jiang, 2009). The mass loss due to decomposition of the surfactant was recorded between 331 and 531°C, which is confirmed in the DTG plot by the peak at 425 °C. The dehydration peak at 717 °C is as strong as in the neat sample, marking the release of the structural OH groups and the associated mass loss.

The two-step decomposition of alkylammonium intercalated in the rectorite interlayer at 50 % excess loading, irrespective of surfactant configuration, indicates the existence of two types of bonding mechanism of intercalation (Li and Jiang, 2009). The larger mass loss in the temperature range 200 °C–350 °C and the smaller loss in the range 350 °C–500 °C suggest that the intercalation occurred mainly by hydrophobic interactions and to lesser extent by cation exchange. The FTIR results support these observations with the location and shifts of the CH₂ stretching bands at around 2850 cm⁻¹ and 2930 cm⁻¹. This conforms to previous findings (Lee and Kim, 2002) for the expansion of smectite by hexadecyltrimethylammonium with loading above CEC of the smectite, where adsorption via hydrophobic bonding dominates the cation exchange.

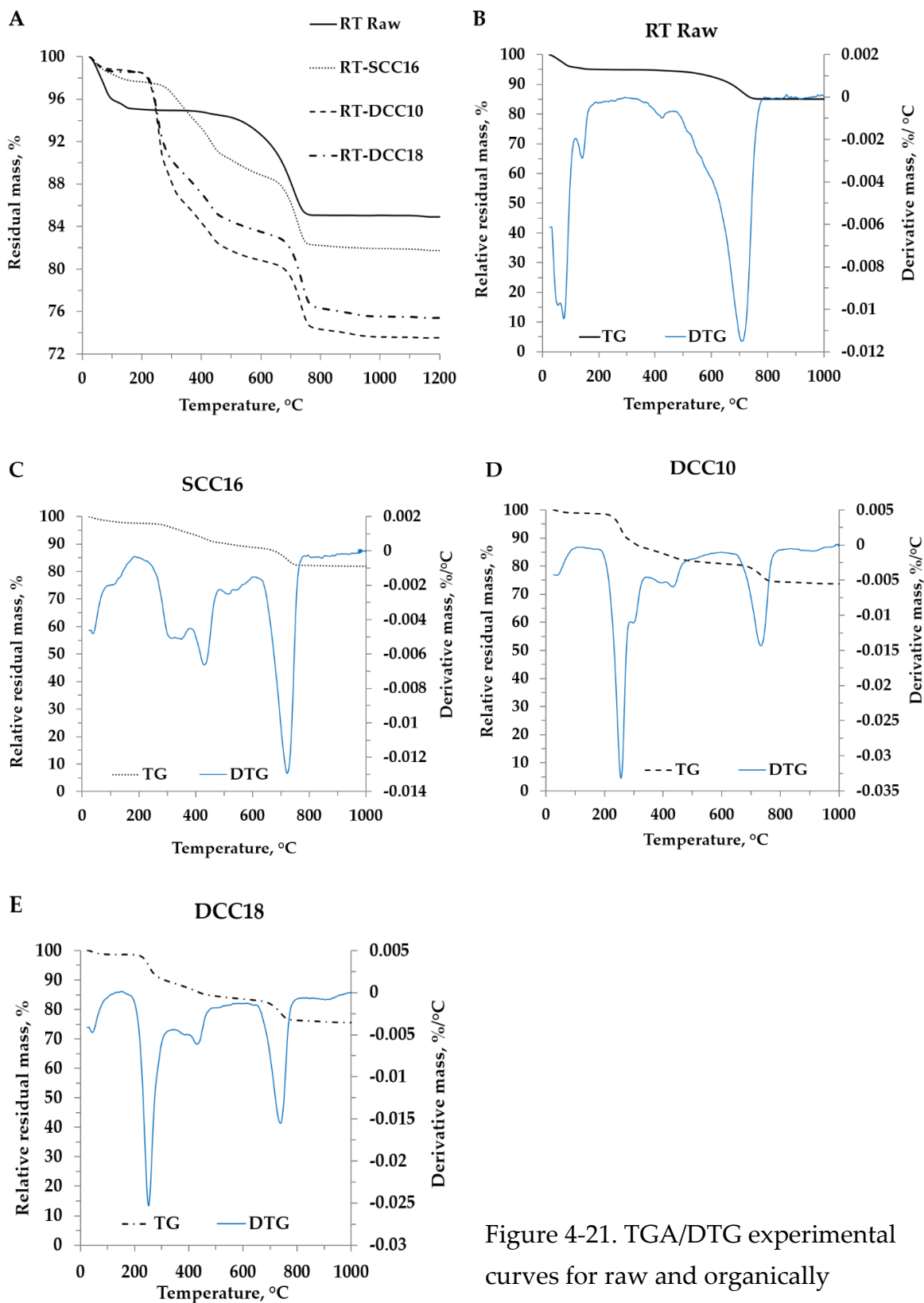


Figure 4-21. TGA/DTG experimental curves for raw and organically modified rectorite

4.3 Rectorite clay films (RecF)

The primary aim of this study was to find the best rectorite clay derivative (via ion exchange) and to optimise the preparation method (slurry-solids content, ultrasonication conditions, etc.) for maximum strength or stiffness of the cast inorganic films. In this process a large number of experiments (246) were conducted. The experimental conditions, and the properties of the resultant films, are provided as Appendix III (Tables: Rectorite-only films dataset). This dataset lists the physical properties of the particle suspensions employed, the processing conditions and the tensile properties of the cast films that were obtained.

4.3.1 Processing conditions and properties of the clay suspensions

For each ion-exchanged clay sample, the film that featured the best mechanical properties, and the procedures that were used to prepare it, were identified. Additional measurements were performed on the parent slurry as well as the resultant films. Table 4-8 shows the processing conditions and the physical properties of the corresponding clay suspensions, together with the pH, ζ -potential and number mean particle size. An attempt is made to link the film with the best mechanical properties to the process conditions that made them possible.

Upon casting, the divalent suspensions settled relatively quickly and at similar rates. However, those from the purified neat material and the monovalent-exchanged samples formed more-or-less viscous gels at the higher solids loadings. The particle size distributions of all the suspensions featured moderate to broad polydispersity indices ($PDI > 0.1$) for which the number mean particle diameter (d) is reported in Table 4-8.

The neat and monovalent rectorite suspensions produced stable colloidal systems with ζ -potential values below -30 mV. Lithium- and sodium-containing dispersions with ζ -potential values of -52 mV and -48 mV respectively did not settle before full

evaporation. These films also took a longer time to dry. The divalent suspensions showed electric potential shifts towards less negative values, i.e. above -30 mV where agglomeration typically commences. This is supported by the larger mean particle sizes listed in Table 4-8, and the experimental observation that they had a higher tendency to flocculate. The size of the exchangeable interlayer cation also had an effect on the suspensions' flocculation rate. Cations larger than Na^+ exhibited a progressively more unstable suspension which readily re-aggregated after dispersion. The neat rectorite suspensions with mixed Na-Ca-ion interlayers showed stability similar to that of the monovalent rectorite modifications. The RT1 suspension featured a lower ζ -potential, probably due to the higher pH of 8.85 caused by the presence of calcite as impurity.

Table 4-8. Processing conditions and physical properties of slurries that yielded rectorite films with the highest mechanical performance. In all cases the solids content was 1.0 g clay/100 ml and sonication time was 30 min (except for RT1 where it was 5 min).

Cation	Stirring time	pH	ζ -potential	d (Number mean)
	h		mV	mm
Li	0	9.62	-52.3 ± 0.9	0.31 ± 0.16
Na	4	8.58	-48.5 ± 0.3	0.23 ± 0.01
NH_4	4	7.10	-38.7 ± 1.8	0.62 ± 0.17
K	4	8.8	-43.7 ± 0.3	0.66 ± 0.02
Cs	0	5.50	-31.4 ± 1.6	0.70 ± 0.04
RT1	24	8.85	-34.8 ± 0.4	0.57 ± 0.23
RT2	24	6.80	-46.5 ± 1.7	0.19 ± 0.01
RT3	4	6.85	-47.6 ± 0.2	0.21 ± 0.05
Mg	24	8.22	-20.6 ± 2.5	1.12 ± 0.60
Ca	4	6.30	-25.9 ± 0.9	1.09 ± 0.07
Sr	0	6.20	-27.2 ± 0.3	0.89 ± 0.13
Ba	0	6.80	-30.8 ± 0.8	1.17 ± 0.09

There is a distinct positive correlation for the monovalent rectorite modifications, i.e. the ζ -potential increased with increases in pH. However, the Mg-rectorite, with pH 8.2, dropped towards lower negative values. These results indicate a strong

dependence of the electrostatic behaviour of rectorite colloidal systems on the ionic composition and is in agreement with previous reports for Na- and Ca-forms of smectite (Chorom and Rengasamy, 1995; Kaya and Yukselen, 2005). It is interesting to note how the largest ions of both groups, i.e. monovalent Cs^+ and divalent Ca^{2+} , Sr^{2+} and Ba^{2+} , had ζ -potentials approaching the critical system stability boundary value, bordering the lowest values for the former and the highest values for the latter at the same clay concentrations and pH below 7.0. These results suggest that the net negative charge is affected by the pH of the suspensions and that it plays a role in the behaviour and stability of rectorite dispersions.

4.3.2 Characterisation and properties of the clay films

The tensile properties of the clay films from neat rectorite and ion-exchanged rectorite modifications are presented in Figures 4-22 and 4-23, and Table 4-9. Figure 4-22 shows examples of the stress-strain curves for the stronger monovalent, divalent and mixed valence rectorite films. In all cases the strain at break was very small, seldom exceeding 2 %. Noteworthy (from visual observations) is the fact that many samples failed by developing tears that started either at an edge defect or right at the end where the sample was gripped. This means that the intrinsic mechanical properties were not achieved. Rather, the measured values were notably influenced by the numerous defects present in the cast films, by handling during testing, and perhaps even by small alignment errors when they were clamped into the tester. Nevertheless, the measured values for tensile strength and Young's modulus compare quite favourably with the values featured by polymer films.

Among the large set of films with thickness ranging up to 150 μm , those with a tensile strength exceeding 5 MPa were less than 65 μm thick. The films that featured the highest strengths invariably had a thickness less than 30 μm . For neat rectorite films the maximum measured tensile strength varied from 12 - 34 MPa and the modulus values from 19 - 50 GPa. Those from the ion-exchanged modifications ranged from 8

- 44 MPa with modulus 18–56 GPa. The films obtained from monovalent cation forms performed notably better, ranging from 13 - 44 MPa and 43 - 56 GPa, than those made with rectorite modified with divalent ions (tensile strength 8 - 23 MPa and modulus 18–25 GPa) (Table 4-9). The films made from the NH₄-Rec also showed excellent tensile properties, with strength and modulus values reaching 44 MPa and 47 GPa respectively.

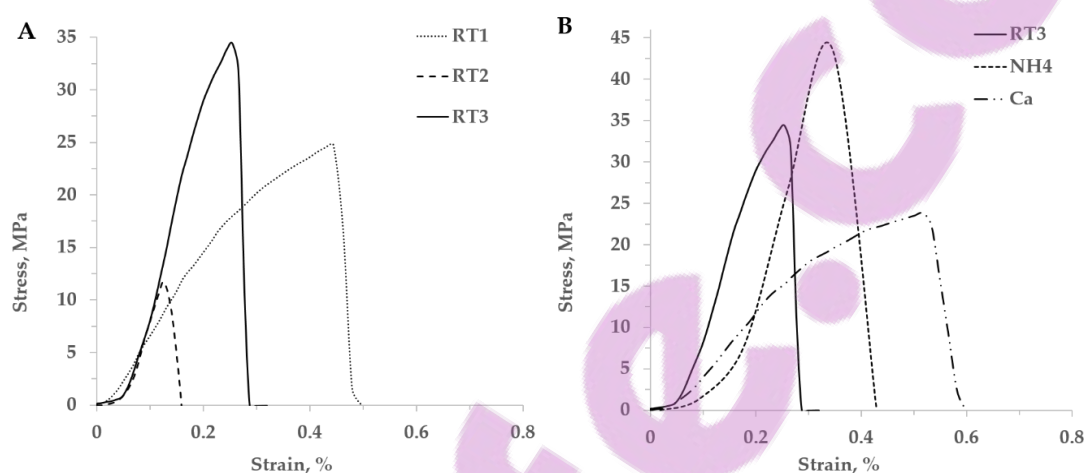


Figure 4-22. Representative stress-strain curves for rectorite films prepared from (A) the three purified rectorite samples, and (B) a comparison of the films with the highest performance from neat, monovalent and divalent exchanged rectorite

The films with the best tensile properties did not necessarily originate from suspensions prepared under the same dispersion conditions. However, the dispersion regime of sonicating for 30 min with subsequent stirring for 4 h proved most effective for producing strong films from each of the three groups – monovalent, divalent and neat rectorite. The exceptions are RT1 where 5 min sonication followed by 24 h stirring, and RT2 and Mg²⁺-films where 30 min sonication followed by 24 h stirring, yielded the best results. Dispersions of Li⁺- and Cs⁺-based films and divalent Sr²⁺ and Ba²⁺ proved more suited to casting after 30 min sonication without stirring.

The data in Figures 4-23 and 4-24 and Table 4-9 show considerable scatter in both the strength and the modulus characteristics of the rectorite films. There is variation not only between films from different rectorite modifications, but also within ion-

exchanged samples, despite all the attempts made to exercise strict control over the processing parameters used in the preparation.

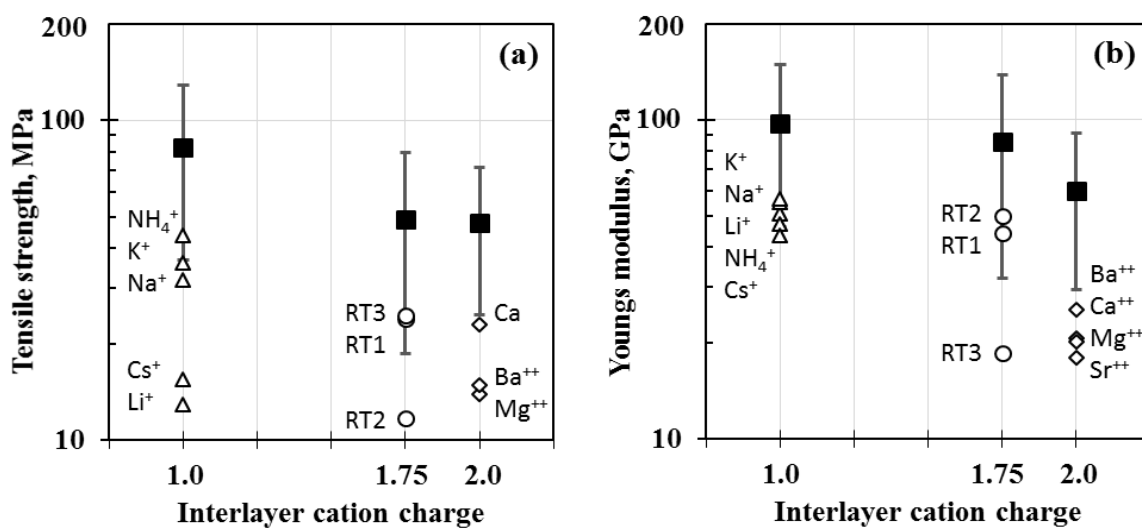


Figure 4-23. Tensile strength and Young's modulus of films from neat and cation-exchanged rectorite. The black square symbols indicate the projected maximum values possible, with the error bars show the 95 % confidence intervals. The open symbols indicate actual maximum values measured.

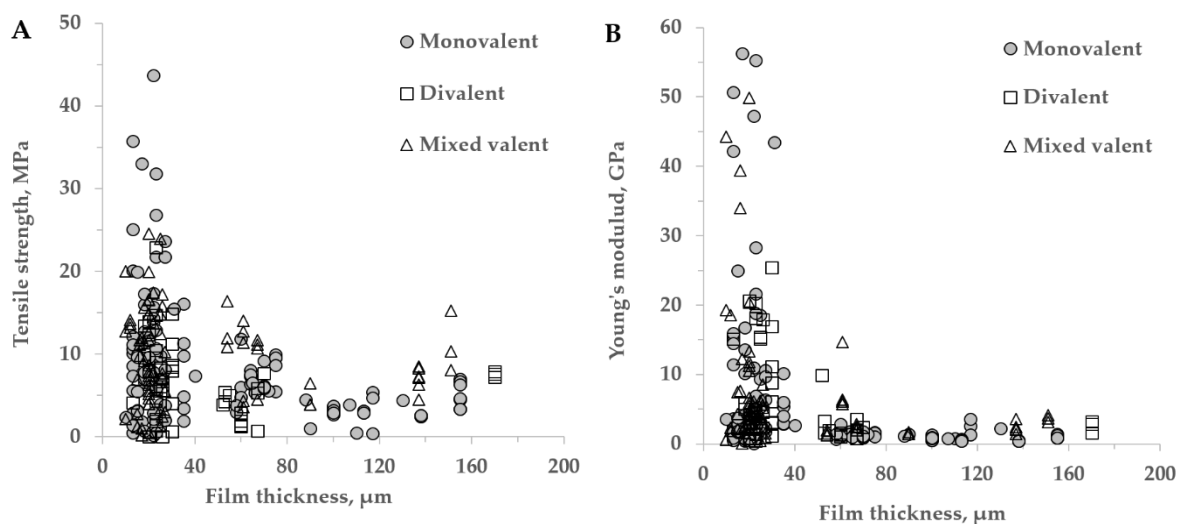


Figure 4-24. Film thickness and the mechanical performance of rectorite films (based on 246 measurements)

Table 4-9. Mechanical and physical properties of the best rectorite-derived clay films. The maximum tensile properties (instead of average values), together with the standard deviation based on all samples measured, are indicated.

Cation	Film thickness	d-spacing	Crystallite size	BET	Tensile strength	Young's modulus
	μm	nm	nm	m^2g^{-1}	MPa	GPa
Li	23	2.23	6.8	259	12.9 ± 4.9	50.7 ± 11.7
Na	23	2.19	10.8	163	31.8 ± 7.1	55.3 ± 10.1
NH₄	22	2.15	13.7	354	43.7 ± 8.3	47.3 ± 18.0
K	17	2.1	6.5	251	35.7 ± 10.9	56.3 ± 16.3
Cs	25	2.16	12.6	139	15.5 ± 5.3	43.4 ± 15.3
RT1	18	2.16	8.1	259	23.9 ± 5.7	44.3 ± 10.0
RT2	20	2.34	6.9	115	11.7 ± 3.4	49.8 ± 17.3
RT3	23	2.28	5.7	208	34.4 ± 7.9	18.6 ± 4.0
Mg	20	2.37	9	184	13.9 ± 4.6	20.6 ± 6.0
Ca	22	2.38	8.6	128	22.9 ± 6.8	20.2 ± 7.9
Sr	30	2.32	9.2	169	8.0 ± 2.9	18.0 ± 8.3
Ba	30	2.16	11.2	176	14.9 ± 2.5	25.4 ± 4.5

Figure 4-25A illustrates the translucence of the clay films obtained from neat rectorite. The UV-Vis spectra of a 28 μm ammonium-exchanged rectorite film is compared to that of an 8 μm raw rectorite film in Figure 4-26. All films had an off-white colour with a subtle blue-grey tint and pearly lustre on the smooth underside. The films also displayed a noteworthy flexibility, allowing folding and bending. It was even possible to crease the thinner films that were made from raw and monovalent-exchanged rectorite (Figure 4-25(B)).

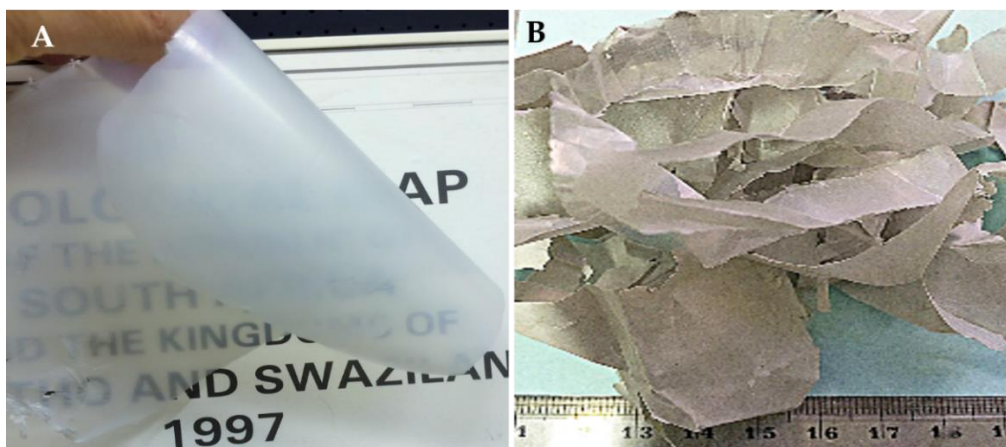


Figure 4-25. (A) Illustrates the transparency of translucent flexible films made from purified rectorite clay without the use of additives or binders, and (B) shows the flexing, bending and creasing of ribbon offcuts. The film thickness was 8.0 μm in both cases.

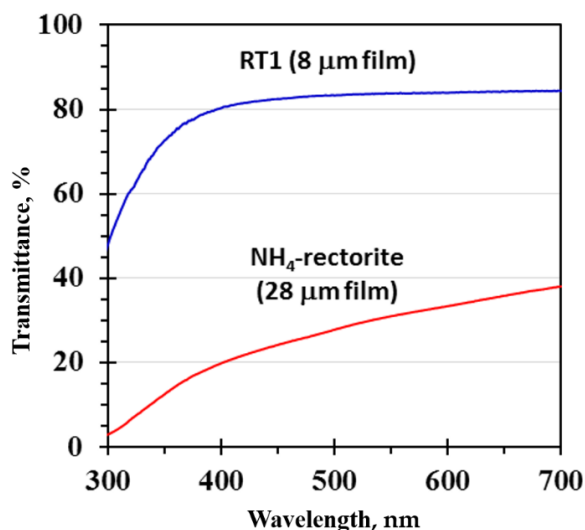


Figure 4-26. UV-Vis spectrum of an ammonium ion-exchanged film with a thickness of 28 μm and a raw (purified) rectorite film with a thickness of 8 μm

SEM micrographs of multilayer textured rectorite films are shown in Figures 4-27 and 4-28. The microstructure of the films is defined by more-or-less planar orientations of the flakes. Clay platelets are arranged in continuous layers with faces aligned sub-parallel to parallel to each other (face-to-face orientation) and to the casting surface. Figure 4-27 (A) and (B) shows polygonal clay platelets, with frayed edges that smoothly interconnect laterally in continuous layers. The platelets bend randomly and join neighbouring layers through edge-to-face contacts resulting in structured coherent sheets, flexible enough to withstand ripple formation (Figure 4-27 (C) and

(D). This geometrical model produces a random but somewhat complex network of cavities of variable shape and size. Nanoscale porosity is clearly observed in the high-resolution SEM micrographs of Figure 4-27 and 4-28. The high surface areas of the films, reported in Table 4-9, are also consistent with the presence of nanoporosity.

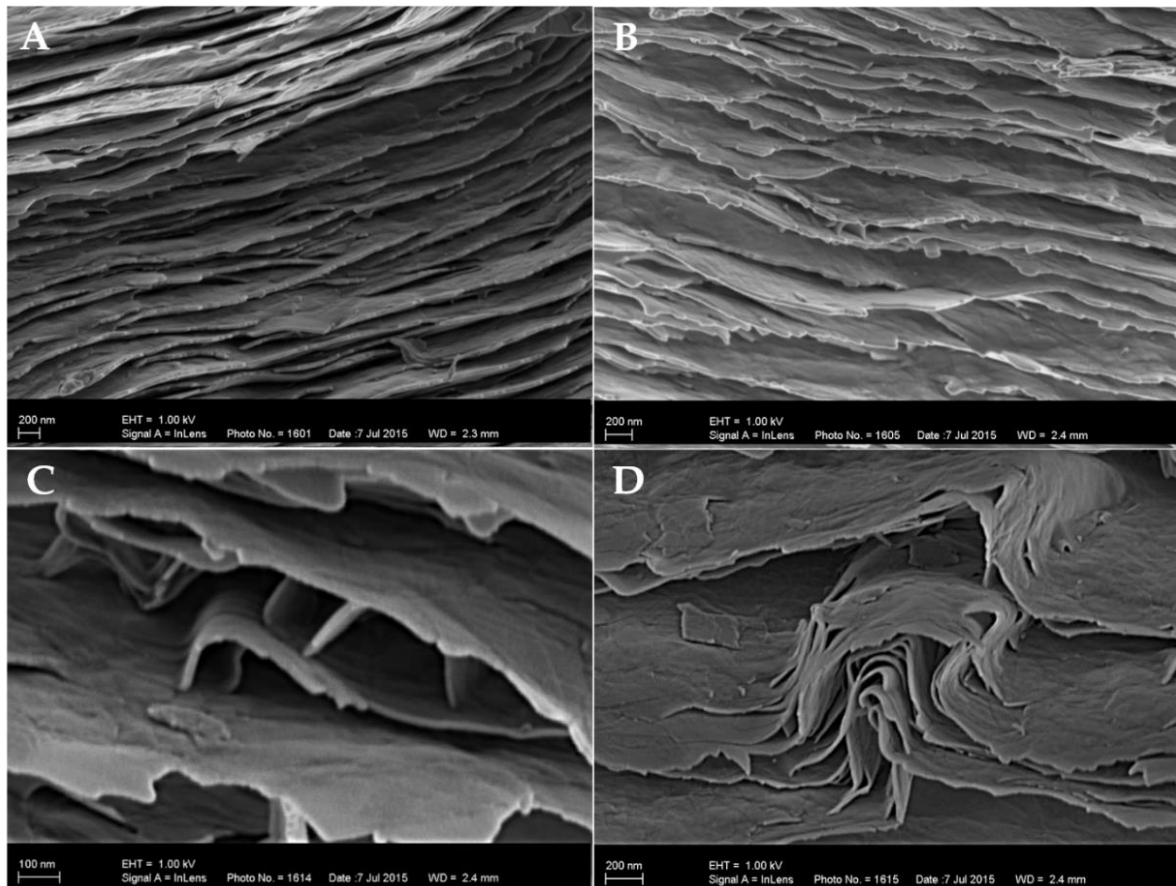


Figure 4-27. SEM micrographs of cross-sectional views of rectorite films from raw purified clay, showing the microstructures of (A&B) parallel layering and layer overlap; (A&B) face-to-face and (C) edge-to-face relationships, and (D) ripple formation

All films exhibit unevenly frayed fracture surfaces with a rather curved profile pattern. The upper sections of the films are usually made of lightly waved, finely layered parallel clay sheets which appear to be much more tightly stacked compared to the more ruggedly textured middle and base sections. This is an apparent artefact of size segregation that occurs during the gravity-driven settling of clay particles on drying.

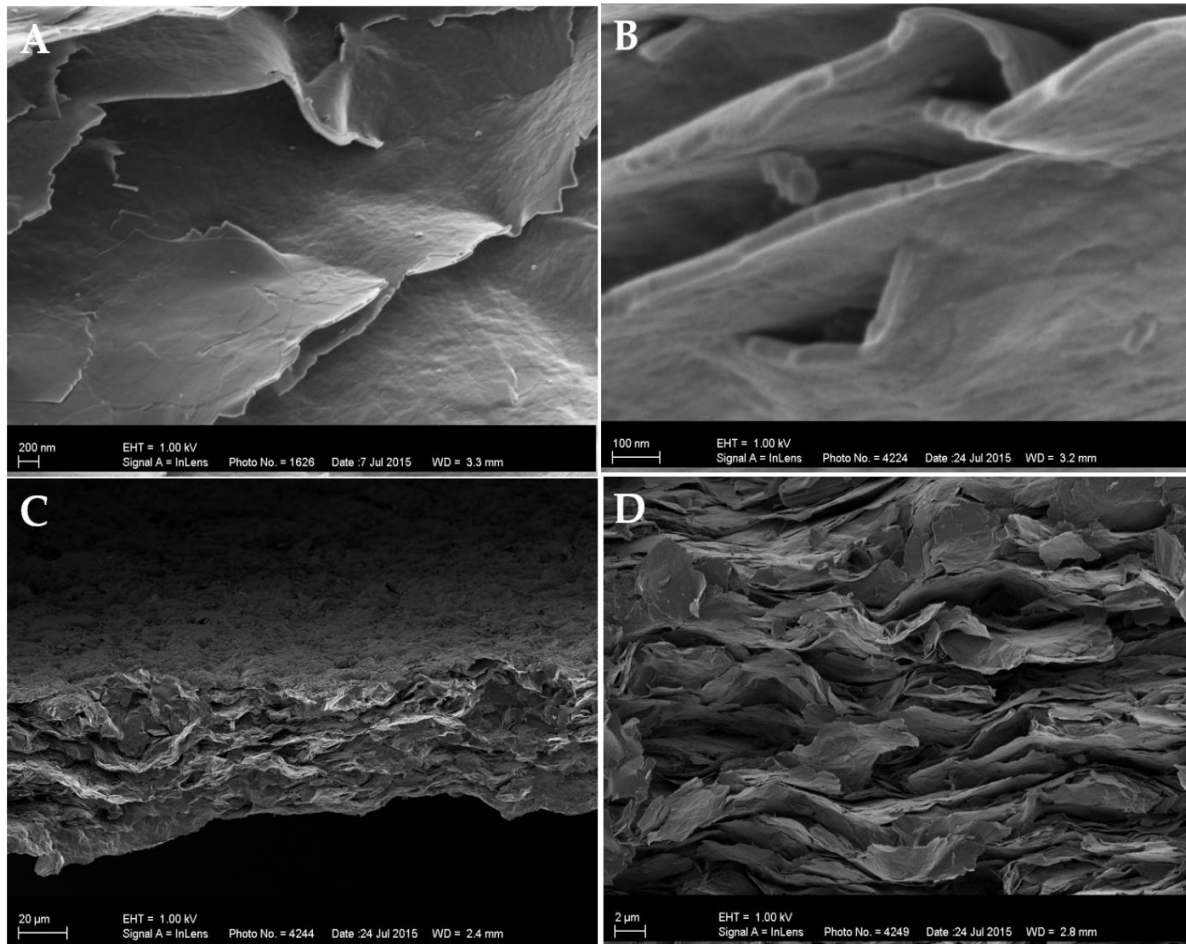


Figure 4-28. SEM micrographs showing a cross-section view of rectorite films from exchanged rectorite clay: (A) Li⁺; (B) Na⁺; (C) Mg²⁺ and (D) Ba²⁺

The top section is layered by nano-sized particles which are the last to assemble during evaporation. These flakes have the most favourable aspect ratio to align into compact sheets with the highest surface-to-volume ratio. This anisotropic texture is less pronounced in the raw and monovalent clay films, whereas the films from divalent rectorite feature large undulations throughout the profile with visibly more loosely assembled sheets (Figure 4-28 (C) and (D)). Similar effects of the interlayer content on the microstructure of clay films has been observed previously (Nam et al., 2009a) and is attributed to differences in the tendency of the ion modifications to delaminate and aggregate in aqueous suspensions. The texture of an anisotropic film has a direct effect on the performance characteristics, especially the damage tolerance. For instance, rectorite films with a thickness exceeding 20 μm drastically lose flexibility on bending

(Figure 4-24). Folding distorts the orientation of the sheets; this is typically initiated at the weakly textured base of the films made up of larger, loosely connected particles. Eventually this results in facile crack propagation and ultimately in mechanical failure (Figure 4-29).

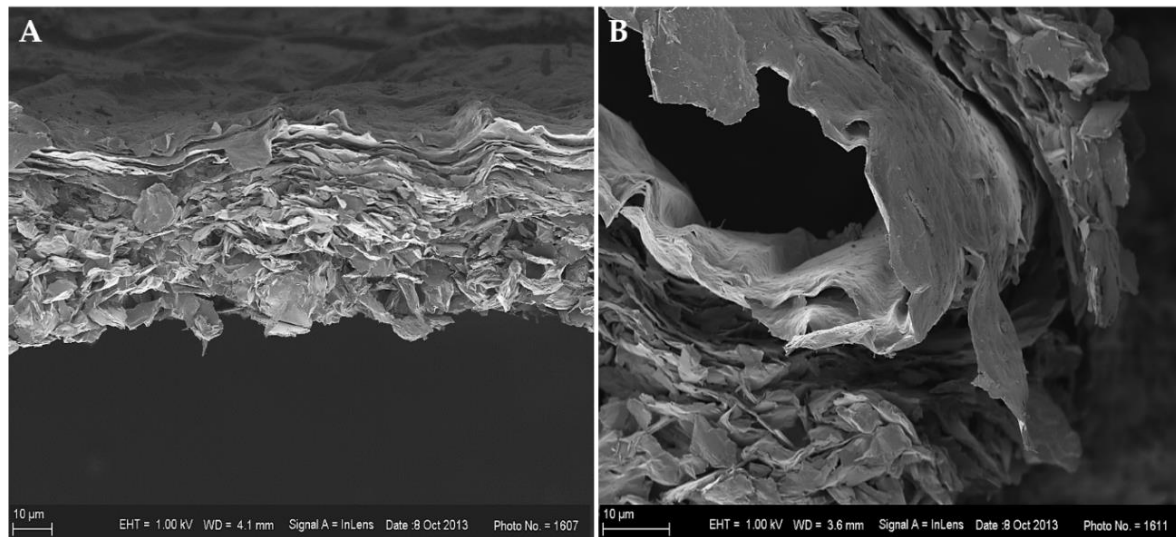


Figure 4-29. SEM micrographs of ammonia-modified rectorite film: (A) cross-section view of a film about 40 μm thick showing a finely layered top of about 10 μm and a random sheet arrangement through the rest of the profile; (B) continuous top layer of parallel clay platelets withstanding the banding of the film as opposed to the bottom layer, which is seen to be in the process of fracturing

The XRD plots of the films presented in Figure 4-30 provide further information on the microstructural organisation of the clay films. The strong first-order basal reflections indicate well-ordered laminated structures that complement well the SEM observations of oriented multi-layer films (Figure 4-27). Furthermore, evidence of preferred orientation is provided not only by the enhanced intensity, but also the second- and third-order peaks are prominent in the diffractograms of the films which is usually not possible for clay powders. Beatrix rectorite is a Na-Ca smectite-mica interstratified structure with a d-spacing between 2.18 and 2.22 nm, a mean crystallite size in the range 14–21 nm and 6–10 2:1 layers per tactoid (Atanasova et al., 2016). Basal spacing $d(001)$ of 2.22 nm for neat Na-Ca-rectorite corresponds to one water-layer structure with an $\text{Na}^+\text{-Ca}^{2+}$ expandable interlayer content in the ratio of 3:4. A

reverse trend in the $d(001)/d(002)$ intensity ratio is clearly observed in the diffractograms of the films, with transition from monovalent to divalent rectorite forms (Figure 4-30).

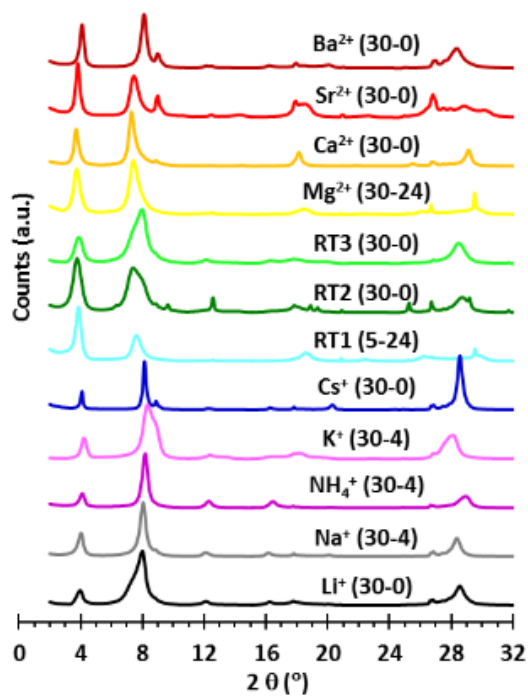


Figure 4-30. XRD profiles of films from purified neat Na-Ca-rectorite and exchanged rectorite modifications. Numbers in brackets behind the cation indicate the dispersion regime.

This is due to differences in the scattering efficiency of the monovalent and divalent atoms which is dependent on their electron configurations (Moore and Reynolds, 1997). The phenomenon has been used to determine the Na:Ca ratio in bi-ionic interlayer structures or other substitutions common in clay minerals using XRD data (Kodama, 1966b). One 2:1 layer of rectorite is about 2.20 nm thick, consisting of 0.96 nm and 1.30 nm mica- and smectite-type layers respectively stacked along the c -direction. The primary tactoids in the natural rectorite consist of up to ten 2:1 silicate layers and have a thickness of about 200 nm (Atanasova et al., 2016). The tactoid thickness in the films from neat rectorite and its exchanged modifications was estimated to range from two to six layers, suggesting the successful exfoliation and increased aspect ratio of the rectorite platelets. This is also supported by the very high

BET surface areas measured for the films (Table 4-9). A large surface area provides for enhanced inter-lamellar interaction, largely attributable to the nature of the interlayer cation.

4.3.3 Estimating the ultimate mechanical property values for rectorite films

The presently reported mechanical property measurements do not represent the intrinsic values that can potentially be attained. This is because of the many flaws and defects in the films caused by limitations in the preparation methods. The measurement process itself was flawed, including the way the samples were clamped. It was of interest to estimate limits for the ultimate material properties. This was attempted via a statistical analysis of the available experimental data as described in some detail in the Experimental Chapter (Chapter 3). First, a global fit of the tensile strength (or the Young's modulus) of the films was modelled and analysed using extreme value analysis (EVA) by means of the generalised extreme value (GEV) distribution (Beirlant et al., 2005; Reiss and Thomas, 2007). Parameter estimation was carried out using generalised maximum likelihood (gMLE) (Gilleland and Katz, 2016). The location and scale parameters of the GEV distribution were considered to be linear combinations of possible additional variables. In both cases, it was found that a significant improvement was observed when the interlayer cation was included as a variable in the model. The p -values corresponding to the significant categories for interlayer cation of the location and scale parameters of the fitted distributions were location = (0.0025371, 0.0025370) and scale = (0.0166080, 0.0448101), for tensile strength, and with location = 0.0235088 and scale = 0.0065562 for Young's modulus. The nature of the interlayer cation determines the interlayer charge. The data was therefore split into groups that contained monovalent cations (122 samples; dummy variable assigned = 0), divalent cations (48 samples; dummy variable assigned unity), and the mixed cation situation for the RT samples (77 samples; dummy variable = 0.75).

Table 4-10. Best values for tensile strength and Young's modulus obtained experimentally compared to projected values based on a statistical analysis of the data

Cation type	Experimental[#]	Estimate[†]	95 % lower CI	95 % upper CI
Tensile strength (MPa)				
Monovalent	44	83	37	129
Divalent	23	48	25	71
Mixed valent	25	49	19	79
Young's modulus (GPa)				
Monovalent	56	97	46	149
Divalent	25	60	29	91
Mixed valent	50	85	32	139

[#]Highest value actually measured. [†]Statistical projection for maximum attainable value.

Permutational multivariate analysis of variance (MANOVA), using distance matrices (Anderson, 2001; McArdle and Anderson, 2001), was performed to check whether the data split into these three sets according to the Interlayer Charge variables can be justified from a statistical point of view. The resultant *p*-value from this test was 0.007, which signifies an overall effect. This was followed up by the Kruskal-Wallis rank sum test (Hollander and Wolfe, 1973), for testing the individual effects, for which the results indicated that this was indeed the case for both tensile strength (*p*-value = 0.0019) and Young's modulus (*p*-value = 0.0004) as dependent variables, and with interlayer charge as independent variable. Secondly, a peak-over-threshold (POT) model was fitted to each of the six possible permutations in determining the maximum potentially attainable values for tensile strength and Young's modulus. Maximum likelihood estimation (MLE) was used to fit the exponential distribution to all the cases. The parametric bootstrap (Efron and Tibshirani, 1993) was then used in each case in deriving the 95 % upper confidence limits, which are listed in Table 4-10. The highest value actually measured in each case is also listed.

4.4 NH₄-rectorite-chitosan bionanocomposite films (NH₄-Rec/CS NCF)

The NH₄-Rec/CS suspensions produced stable colloidal mixtures with ζ -potential values above 44 mV in the pH range 2.6–4.0. X-ray diffraction of oriented slurries showed that the clay structure was successfully exfoliated and intercalated by the polymer using the applied preparation methodology (Figure 4-31).

The X-ray diffraction data of the neat starting components NH₄-Rec and CS and selected composites is displayed in Figures 4-31 and 4-32. The neat NH₄-rectorite has a strong and sharp d(001) reflection at $2\theta=4.12^\circ$ ($d=2.15$ nm) and d(002) at $2\theta=8.25^\circ$ ($d=1.07$ nm). The XRD patterns of powdered chitosan featured two broad peaks around $2\theta=10.65^\circ$ ($d=0.840$ nm) and $2\theta=20.06^\circ$ ($d=0.444$ nm). Interestingly, the diffraction data obtained from the chitosan films showed more crystalline regions around $2\theta=8.47^\circ$ ($d=1.042$ nm), $2\theta=11.55^\circ$ ($d=0.765$ nm), $2\theta=16.26^\circ$ ($d=0.544$ nm), $2\theta=18.30^\circ$ ($d=0.484$ nm) and $2\theta=23.04^\circ$ ($d=0.386$ nm), suggesting sheet-like orientation in the films, attributed to parallel sheets of chains similar to chitin (Darder et al., 2003; Minke and Blackwell, 1978).

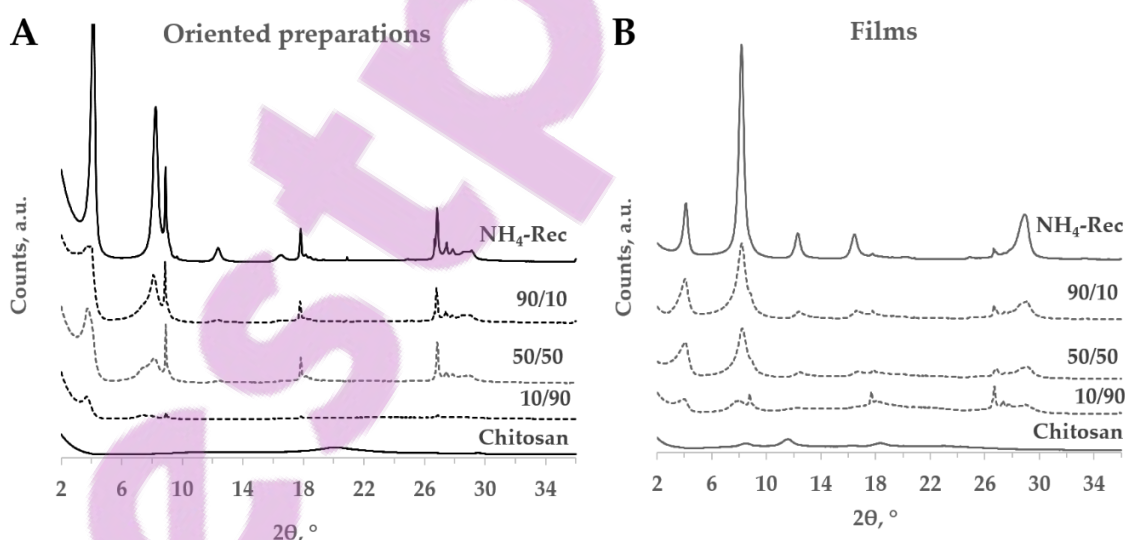


Figure 4-31. X-ray diffraction data for neat NH₄-Rec and chitosan (CS) and their derivative composites 90/10, 50/50 and 10/90 (Rec/CS); (A) glass slides; (B) films

With the addition of chitosan, the spacing of the NH₄-Rec/CS composites moved to lower angles, indicating continuous enlargement of the rectorite unit cell. The *d*-values between 2.15 and 2.19 nm for the NH₄-Rec/CS nanocomposites are consistent with the intercalation of a monolayer of chitosan in the interlayer space (Darder et al., 2003). Diffraction peaks from the expanding composite structure became broader and asymmetric (Figure 4-32), suggesting loss of regularity and layer orientation in the initial rectorite structure. However, even in compositions 10/90 NH₄-Rec/CS some of the original reflections of rectorite, although very broad, were still visible around the respective basal spacings (Figure 4-31B). The original structure of chitosan disappeared completely in the composite diffraction patterns from oriented slides of the dispersions and the films (Figure 4-31). These changes indicate that the rectorite sheets have been exfoliated and chitosan has intercalated into the interlayer space of rectorite with the increase of chitosan content and the corresponding decrease of clay. It also indicates that the presence of the rectorite interferes with the crystallisation of the bulk chitosan.

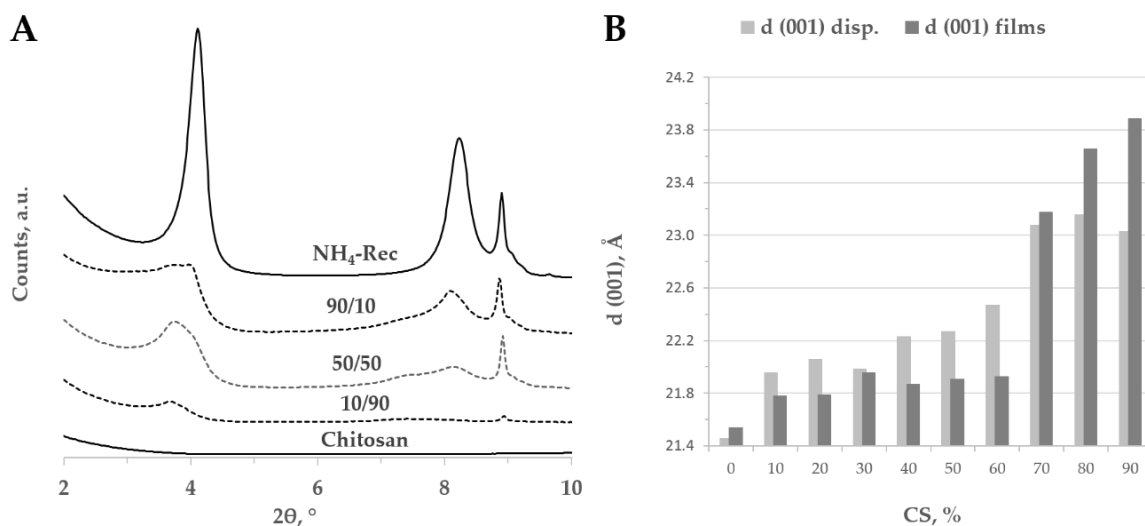


Figure 4-32. (A) X-ray diffraction data of neat NH₄-Rec and chitosan and their composite derivatives 90/10, 50/50 and 10/90 (Rec/CS); (B) migration of d(001) with increasing proportion of chitosan for dispersions and their respective films

The swelling of rectorite occurs at the smectite-type layer in its structure (Atanasova et al., 2016) and therefore defines similar exchange properties. The interlayer NH_4^+ ions in the smectite layer of rectorite are easily exchanged with the protonated $-\text{NH}_3^+$ cations from chitosan, resulting in partial to almost complete chitosan intercalation into the rectorite layers.

The FTIR spectra of neat NH_4 -rectorite, chitosan and their derivative composites (range 90 % to 10 % in increments of 10 %) are presented in Figure 4-33. The FTIR spectra of purified rectorite and organically modified rectorite have been discussed in a previous communication on rectorite from this deposit (Atanasova et al., 2016). The composites' spectra resemble a combination of peaks featured in the spectra of the clay and chitosan. Characteristic peak maxima for both end-components appear to be drastically decreased at intermediate composition. As the proportion of rectorite/chitosan decreases, the composite spectra feature progressive broadening of the absorption bands, with relatively minor shifts in the peak positions attributed to reduced structural ordering and imperfections arising from organic interaction.

Apart from the vibrational bands of Si-O-Si and Si-O-Al in the low-frequency range from 500 cm^{-1} to 1200 cm^{-1} , which are characteristic of phyllosilicates, unique bands for rectorite at 1120 cm^{-1} , 976 cm^{-1} and 707 cm^{-1} were ascribed to Si-O stretching, while the vibration at 926 cm^{-1} can be associated with the Al-OH deformation. In this frequency range chitosan spectra also have overlapping resonance bands. Bands between 1039 cm^{-1} and 1155 cm^{-1} are characteristic for primary and secondary hydroxyl in chitosan (Wang et al., 2010). The band at 1080 cm^{-1} is ascribed to C-O-C vibrations (Darder et al., 2003). The two sharp bands in the spectra of neat NH_4 -Rec at 1440 cm^{-1} and 1640 cm^{-1} result from the NH_4^+ deformation band in the interlayer space of rectorite and from OH stretching and bending in the H-O-H group of molecular water respectively (Kloprogge et al., 1999; Russel and White, 1968).

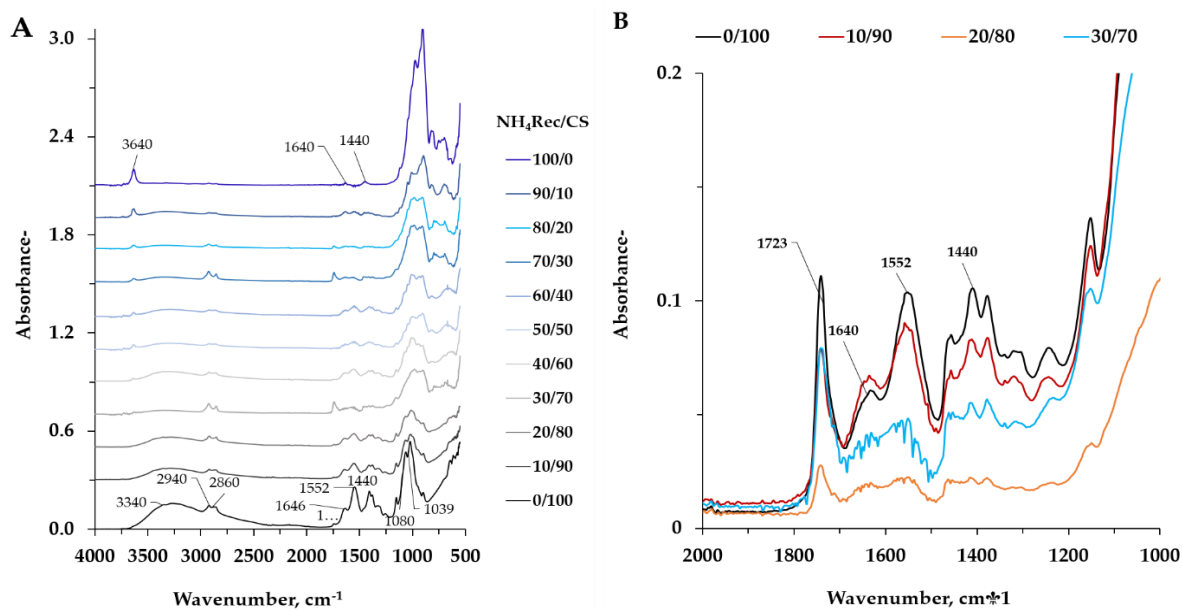


Figure 4-33. (A) FTIR spectra of neat $\text{NH}_4\text{-Rec}$ and chitosan films and their derivative composite films; (B) enlarged segment of the IR spectra for the three highest CS composites where 1723 cm^{-1} and 1553 cm^{-1} bands occur

In the chitosan spectra, deformation vibration of the protonated amine group NH_3^+ appears at 1552 cm^{-1} whereas the band at around 1646 cm^{-1} is ascribed to the stretching of amide I ($\text{C}=\text{O}$). In the composite spectra the former shifts slightly towards the lower frequency with a decrease in the amount of CS, whereas the latter disappears or is assimilated into the broader band, now 1640 cm^{-1} , of the H-O-H group in the clay spectra. The shift has been explained as being caused by the electrostatic interaction between the protonated amine groups and the negatively charged clay surfaces in montmorillonite-chitosan composites (Darder et al., 2003, 2005). An additional stretching band at 1723 cm^{-1} appears in the spectra of one of the two film surfaces (all films were analysed on both sides) for each of the composite films, including chitosan, but not in the neat $\text{NH}_4\text{-Rec}$ films. The band has been previously attributed to acetate salt ions and associated with a double layer of chitosan in the intercalated composite structure (Darder et al., 2003, 2005), or to the $\text{C}=\text{N}$ from cross-linking of chitosan by glutaraldehyde (Lu et al., 2015). As the XRD data of the Rec/CS composites reported above do not indicate a double layer spacing and no

cross-linking reagents were used in the preparation of the films, the observed acetate band most probably indicates the presence of acetate salts in the bulk of the chitosan phase. A pair of sharp bands at 2860 cm^{-1} and 2940 cm^{-1} is ascribed to the symmetric and asymmetric stretching vibrations of the $-\text{CH}_2$ and $-\text{CH}_3$ groups of the alkyl chains, the bending vibrations of which are visible in the region around $1440\text{--}1430\text{ cm}^{-1}$ (Atanasova et al., 2016; Li et al., 2008; Wang et al., 2006). The presence of these two bands in all the composite FTIR spectra confirms the presence of chitosan in the interlayer space of $\text{NH}_4\text{-Rec}$. In the high-frequency region above 3000 cm^{-1} , characteristic H_2O and H-O-H resonance bands for silicates and chitosan broadly overlap. The hydroxyl stretching typical of silicates is seen as a sharp, intense absorption band at 3640 cm^{-1} in the spectra of neat $\text{NH}_4\text{-Rec}$ and indicates H-bonded Si-O-Si linkages (Kloprogge et al., 1999). In the composite spectra the peak progressively drops intensity and broadens with the decrease of rectorite proportion until it becomes completely invisible below compositions of 30/70 with the advancement of chitosan intercalation. At this frequency the vibration of N-H bonded to O-H in chitosan around 3340 cm^{-1} broadened over the lower wavenumber region centred between 3300 cm^{-1} and 3000 cm^{-1} in all composites, indicative of hydrogen bonding between rectorite and chitosan (Wang et al., 2006). The intensity of the broad peak is higher with the increase of chitosan proportions, suggesting an increase of hydrogen bonding between the hydroxyl and amine groups during film formation (Park et al., 2002).

The microstructural characteristics of the composite films are demonstrated by the SEM micrographs in Figure 4-34 in parallel to the neat $\text{NH}_4\text{-Rec}$ and CS films (Figure 4-35). The upper surfaces of both neat films appear almost identical; however, the cross-section views show distinct differences. Although at first sight layering is observed in both film types, the $\text{NH}_4\text{-Rec}$ films display more-or-less planar orientation of the flakes arranged in continuous thin clay layers parallel to each other. The CS films show a semi-layered fracture surface with unclear layer boundaries and dim,

smear sections due to the poorly crystalline nature of chitosan also demonstrated on the XRD patterns. It can be observed how the parallel layering of the neat rectorite clay films slowly becomes ruggedly open and more widely spaced-out with the increase of chitosan proportion (and corresponding decrease of clay) in the composite mixture. The rectorite flake structure opens to accommodate the chitosan phase and becomes more irregular, affecting the layer orientation within the microstructure of the films. This is illustrated on the image of composite film 20/80 (Figure 4-35(D)) where the view is almost identical to that of neat chitosan film (Figure 4-34(A-2)), although in this compositional range even at 10/90 the XRD image still shows some of the original rectorite reflections. This indicates that chitosan is intercalated into rectorite preserving the clay structure, and also acting as a binder to produce a more compact film.

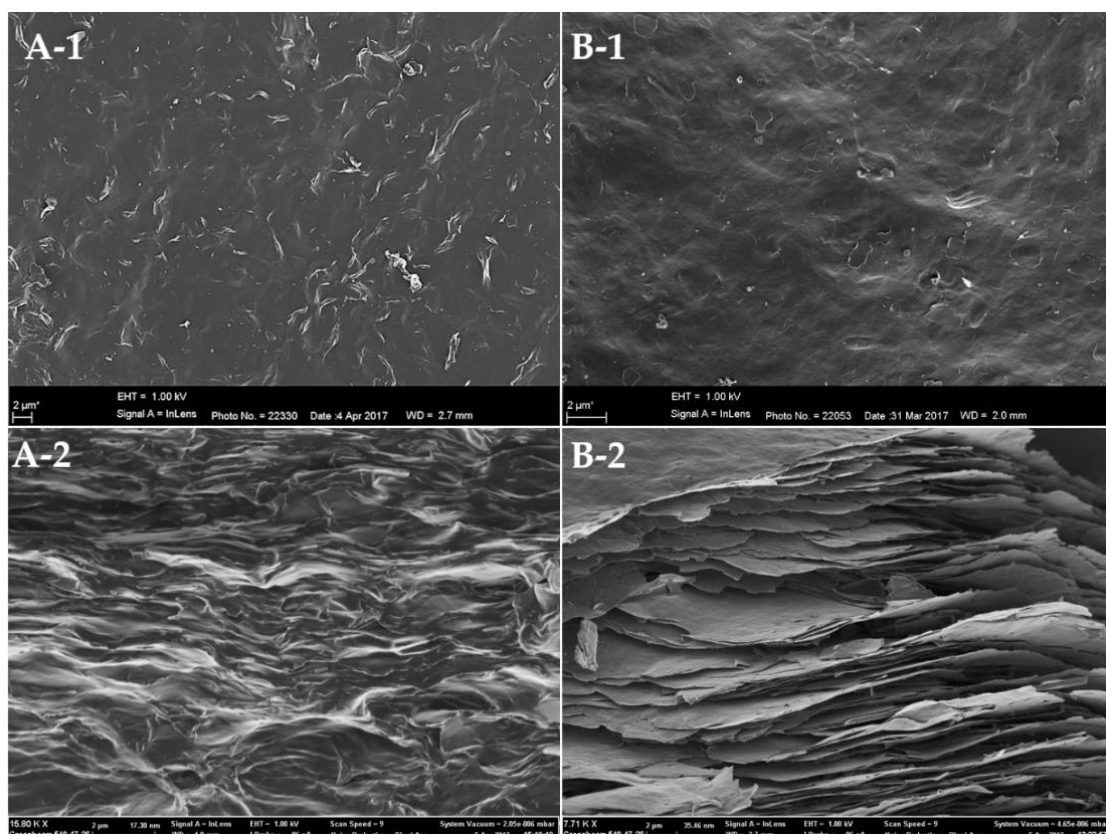


Figure 4-34. SEM micrographs of chitosan (CS) only and NH₄-Rec only films: (A-1) CS top surface and (A-2) CS cross-section view; (B-1) NH₄-Rec clay film top surface and (B-2) cross-section view

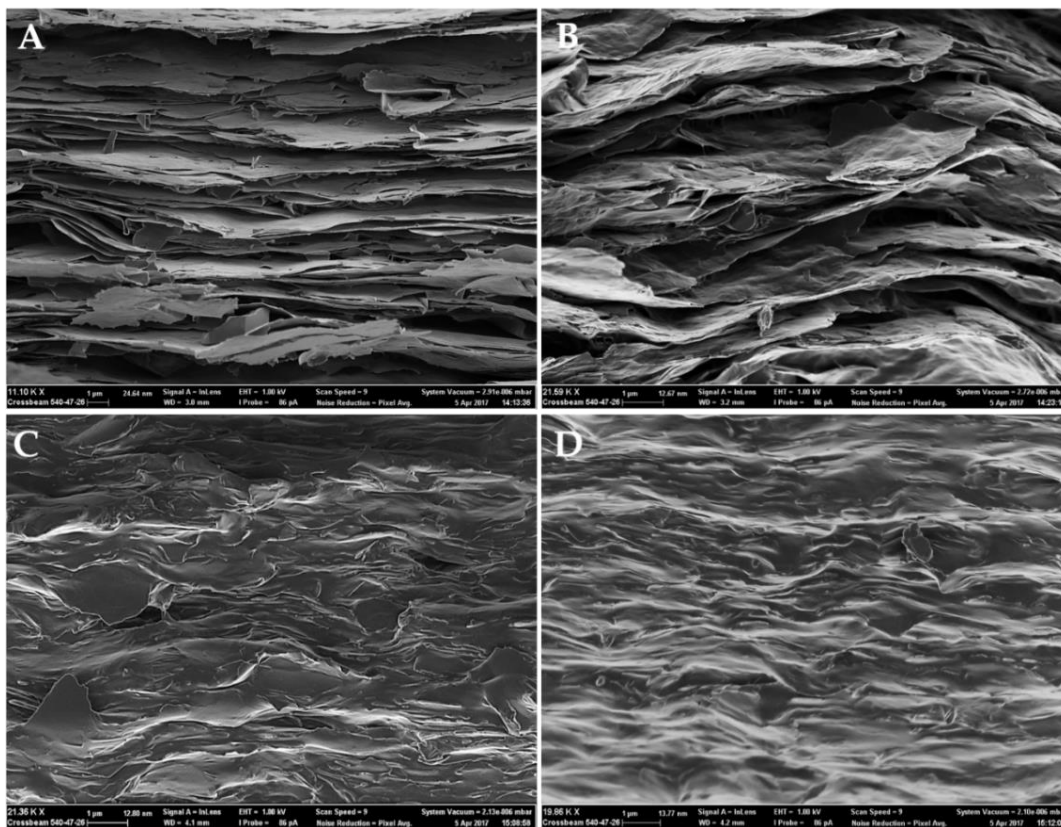


Figure 4-35. SEM images of fractured profile surface of composite films with compositions NH₄-Rec/CS (A) 80/20, (B) 60/40, (C) 40/60, and (D) 20/80

A compact film structure, though less ordered, might be the decisive factor for enhanced tensile strength of the composites at the expense of a decrease in the elongation at break compared to neat chitosan films (Figure 4-37).

The chemical composition of the rectorite from the Beatrix mine used to produce the bionanocomposites has been discussed in a previous communication (Atanasova et al., 2016). The CEC was estimated at 45 ± 7 mEq/100 g. Such a value is expected for mixed-layer structures where alternate interlayers are of the montmorillonite type. The exchangeable smectitic interlayer contains almost equal Na⁺ and Ca²⁺ ions. The fixed interlayer space (mica interlayer) contains proportionally dominant Na⁺ and Ca²⁺ and minor K⁺. Major element concentrations determined by XRF, for the batch of purified neat and NH₄⁺-exchanged rectorite used for preparing the bionanocomposites, are presented in Table 4-11.

Table 4-11. XRF analyses of the NH₄-Rec and purified rectorite (RT3) used for exchange. The value for N is derived by difference from LOI estimations.

Sample	Purified Rec	NH ₄ -Rec
SiO ₂	49.61	49.57
TiO ₂	0.28	0.28
Al ₂ O ₃	37.02	37.72
Fe ₂ O ₃ ^(t)	0.07	0.04
MnO	< 0.001	0.001
MgO	< 0.01	< 0.01
CaO	2.97	2.10
Na ₂ O	2.78	2.51
K ₂ O	0.86	0.85
P ₂ O ₅	0.022	0.019
CoO	< 0.001	< 0.001
Cr ₂ O ₃	0.062	0.046
CuO	< 0.001	< 0.001
NiO	0.002	< 0.001
PbO	< 0.001	< 0.001
SO ₃	< 0.001	< 0.001
V ₂ O ₅	0.019	0.018
BaO	0.061	0.042
ZnO	0.010	0.012
ZrO ₂	< 0.001	0.012
SrO	0.094	0.070
N		1.86
LOI	5.38	7.23
Total	99.24	100.27
H ₂ O-	5.08	3.19

The higher LOI in the ion-exchanged rectorite is consistent with the amount of ammonia ions introduced into the rectorite structure during the exchange. The amount of ammonia calculated by difference from these results is in good agreement with the carbon-hydrogen-nitrogen (CHN) determinations presented in Table 4-12.

Elemental analyses for the CHN content in the chitosan and bionanocomposite films are plotted in Figure 4-36. The carbon content of the chitosan used was 41.5 %, and therefore the expected slope of the line in Figure 4-36 is 0.415. This compares favourably with the experimental slope of 0.434. The results therefore indicate a good correlation with the theoretical clay/chitosan proportions.

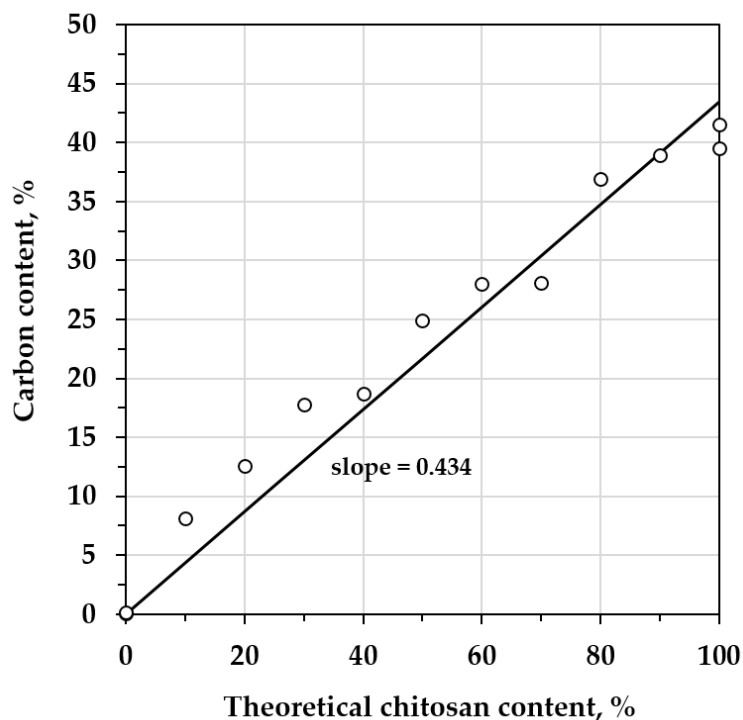


Figure 4-36. Correlation between experimental proportions of clay/chitosan and analytical estimations of CHN concentrations

Table 4-12. Elemental carbon-hydrogen-nitrogen content of neat NH₄-rectorite and chitosan powders, films and bionanocomposite films

Sample	Carbon %	Hydrogen %	Nitrogen %
NH ₄ -Rec powder	0.04	2.98	1.78
100/0F	0.19	2.43	1.46
90/10F	8.10	3.86	2.47
80/20F	12.60	7.08	4.57
70/30F	17.80	4.56	4.48
60/40F	18.70	6.62	4.71
50/50F	24.90	8.12	5.90
40/60F	28.00	5.57	6.55
30/70F	28.10	8.30	6.52
20/80F	36.90	6.43	7.33
10/90F	38.90	9.14	7.84
0/100F	39.50	9.82	7.67
CS powder	41.50	7.45	7.93

Tensile measurements, including tensile strength (TS), Young's modulus and Elongation at break are presented in Table 4-13 and Figure 4-37. Films of each composition were replicated at least three times and a minimum of three measurements per film was performed. The summarised results Figure 4-37B and in Table 4-13 represent the maximum tensile properties (instead of average values), together with the standard deviation based on all samples measured.

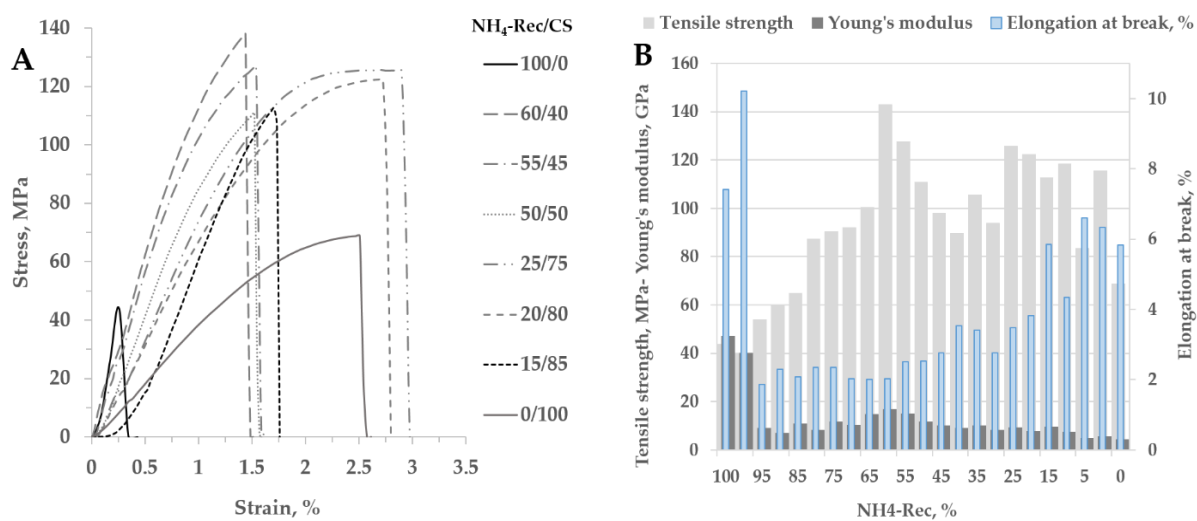


Figure 4-37. Tensile properties of the NH₄-Rec/CS composites: (A) stress-strain curves of end members and selected composites; (B) mechanical properties in the compositional range 100–0 %

The addition of chitosan (in increments of 5 %) to NH₄-Rec clay resulted in a consistent increase in the tensile strength (TS) of the composite films. The strength values at compositions 80/20 already exceeded the maximum values for neat clay films and chitosan films. Films in the mid-compositional range showed a tensile strength increase of up to 227 % and 108 % relative to the neat clay films and chitosan films respectively, with the maximum measured for the 60/40 composition. The Young's modulus followed a similar trend after the sudden drop at the two highest clay compositions. The maximum values occurred over a broad compositional range (80/20 to 30/70) and thereafter gradually decreased with a decrease of clay proportion in the mix. A similar model from Verbeek and Focke, (2002) has been attributed to composite

porosity being highly dependent on the particle aspect ratio. Their model predicted significantly lower values for Young's modulus as proportions of high-aspect-ratio filler particles in a composite decrease, i.e. towards the CS-rich end. The sudden drop in Young's modulus of the neat NH₄-Rec films from 95/5 - 70/30 can be explained by the loss of compact layering in the clay as a result of chitosan entering the interlayer spaces, expressed in an increase in film porosity. In the range 75/25–45/55 the two components seem to be in equilibrium, producing compacted-enough films with experimentally the best modulus and strength (Figure 4-37). In composite 40/60, further addition of chitosan results in insufficient high-aspect-ratio particles to maintain a compact film microstructure.

Table 4-13. Mechanical and physical properties of the composite films (compositions are listed as proportions of NH₄-Rec/CS)

Composition	Thickness	d-spacing	pH	Tensile strength	Young's modulus	Elongation at break
NH ₄ -Rec/CS	μm	nm		MPa	GPa	%
100/0	22	2.15	7.10	43.7 ± 10.4	47.3 ± 13.1	7.4 ± 2.1
98/2	20	2.16	3.98	40.2 ± 13.2	40.1 ± 14.7	10.2 ± 4.6
95/5	32		3.88	53.9 ± 15.4	9.5 ± 6.3	1.9 ± 0.4
90/10	32	2.16	3.95	59.8 ± 3.4	9.2 ± 1.1	2.3 ± 0.3
85/25	33		3.68	65.0 ± 8.8	10.8 ± 0.9	2.1 ± 0.3
80/20	33	2.14	3.77	87.5 ± 15.2	11.7 ± 1.2	2.3 ± 0.4
75/25	35		3.78	90.6 ± 17.9	11.6 ± 1.8	2.3 ± 0.4
70/30	32	2.16	3.92	92.2 ± 16.2	10.3 ± 1.1	2.0 ± 0.2
65/45	28		3.56	100.5 ± 22.3	14.8 ± 2.6	2.0 ± 0.3
60/40	30	2.15	3.85	143.5 ± 26.4	17.0 ± 3.3	2.0 ± 0.3
55/45	25		3.88	127.5 ± 21.9	15.3 ± 2.8	2.5 ± 0.4
50/50	30	2.16	3.78	111.0 ± 18.3	11.8 ± 1.6	2.5 ± 0.3
45/55	38		3.65	98.3 ± 14.1	10.3 ± 1.5	2.8 ± 0.3
40/60	34	2.17	3.58	89.8 ± 9.4	9.0 ± 1.2	3.5 ± 0.6
35/75	33		3.50	105.7 ± 12.8	10.2 ± 1.2	3.4 ± 0.5
30/70	37	2.19	3.50	93.9 ± 14.3	8.4 ± 0.7	2.8 ± 0.3
25/75	35		3.75	125.7 ± 19.0	9.4 ± 1.2	3.5 ± 0.6
20/80	42	2.26	3.60	122.4 ± 19.5	7.7 ± 1.3	3.8 ± 0.6
15/85	25		2.90	112.9 ± 16.7	9.7 ± 1.3	5.8 ± 1.2
10/90	37	2.31	2.98	118.6 ± 16.6	7.4 ± 0.8	4.4 ± 0.6
5/95	38		2.90	83.6 ± 11.1	5.5 ± 0.8	6.6 ± 0.9
2/98	36	2.41	2.70	115.5 ± 21.9	5.8 ± 0.9	6.3 ± 1.3
0/100	45		2.60	68.9 ± 12.7	4.3 ± 1.0	5.8 ± 1.1

The measured values for elongation at break (Table 4-13, Figure 4-37) were significantly affected by the surface flaws in the films. Nevertheless, overall it appeared that the increase of TS was accompanied by a decrease in the elongation at break (ϵ) and this was more pronounced in the compositional range 90/10 - 30/70. Similar inverse relation has been attributed to nanofillers/chitosan interactions enhancing the stress transfer at the interface (Luo et al., 2003; Xu et al., 2006; Chivrac et al., 2009). The property enhancements indicate that film microstructure have become more compact as a result of good interaction of the two end-components, also observed by Ruiz-Hitzky et al., 2005, Darder et al., 2005, Darder et al., 2006, Chivrac et al., 2009.

The UV-Vis absorption spectra of the NH_4 -rectorite and chitosan films and their derivative composite films are presented in Figure 4-38. They show a gradual improvement of transparency with the decrease in clay content. The films from the two end-components differ visually in colour and surface topography (Figure 4-39).

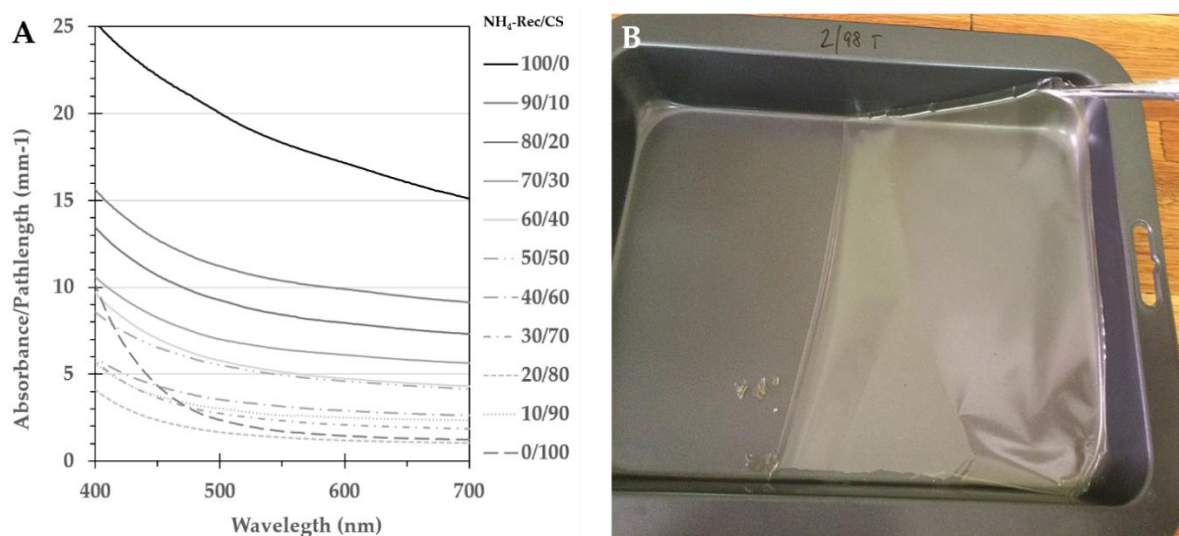


Figure 4-38. (A) UV-Vis spectra of ammonium ion-exchanged film, chitosan film and films of derivative composites; (B) peeling off of a 2/98 composite film

The rectorite films had an off-white colour with a subtle blue-grey tint and pearly lustre on the smooth underside, whereas the chitosan films showed a smoky brown-yellow appearance often with a wavy top surface after drying (Figure 4-39). The neat

clay films were translucent to transparent when the thickness was below 25 μm , whereas the chitosan films were transparent even at a thickness of 40 μm and above. The composite films appeared generally dull yellow-grey with the yellow tint becoming more intense with an increase of chitosan proportion (Figure 4-39).

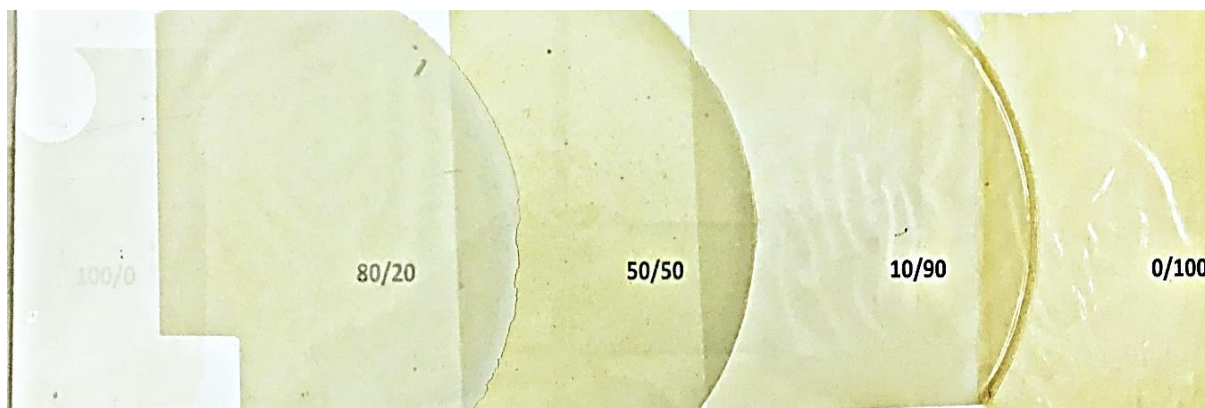


Figure 4-39. Visual comparison of transparency: at left $\text{NH}_4\text{-Rec}$ film (100/0) 22 μm thick (top left corner has a round cut to visually discriminate the film from the white background of a similar shade); and composites as indicated: thickness from left to right 22 μm , 33 μm , 25 μm , 37 μm and chitosan film (0/100) of thickness 45 μm

The $\text{NH}_4\text{-Rec/CS}$ nanocomposite films were highly solvent-resistant even in water, despite the fact that both starting components are water-dispersible under suitable pH conditions. Figure 4-40 shows fragments of composite films that remained fully intact even after being immersed in water for 277 days.

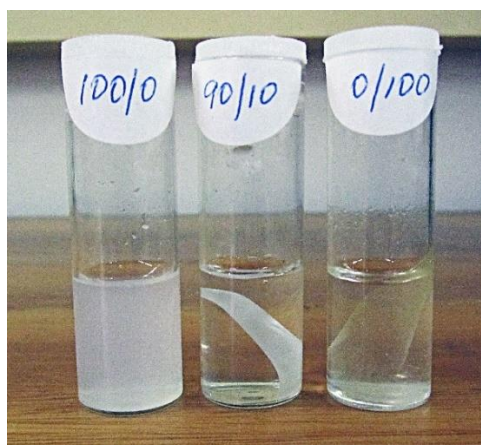


Figure 4-40. Film fragments of the two starting components and composite film 90/10 immersed in water for 277 days

CHAPTER 5 KEY FINDINGS AND DISCUSSION

5.1 Characterisation of rectorite

Three rectorite-rich samples from the Beatrix Gold Mine, South Africa, were characterised. The samples differed in their visual appearance with RT1 containing large, light blue-grey platy aggregates with a silky lustre, while RT2 and RT3 represented disintegrated host rock mine material. All samples were subjected to various purification procedures aimed at producing high-purity material. The characterisation presented in this document is based on purified material with a rectorite content above 90 wt.% (XRD analysis). Structurally and chemically, the purified materials from the three samples were very similar and were categorised as rectorite, except where applicable specifics are highlighted.

SEM of the rectorite clay particles revealed a layered morphology. High-resolution TEM showed well-distinguished light and dark layers of about 2.20 nm, consistent with the 1:1 interstratified mica-smectite nature. XRD measurements confirmed the basal spacing d_{001} of 2.20 nm, indicating a one-water-layer structure. Unit cell parameters, for a monoclinic unit cell with primitive lattice, refined to $a = 5.177 \text{ \AA}$; $b = 8.980 \text{ \AA}$; $c = 22.489 \text{ \AA}$ and $\beta = 97.335^\circ$, with a mean crystallite size around 14 nm and a calculated cell volume of 1045 \AA^3 . The Greene-Kelly test suggested that the expandable smectite layers have montmorillonite-beidellite composition. Nuclear magnetic resonance (NMR) spectroscopy indicated a high degree of Al substitution and the presence of two different Al sites corresponding to six- and four-fold octahedral and tetrahedral aluminium respectively. The chemical composition and diffraction data suggest that the mica is Na-Ca-rich, i.e. of paragonite-margarite series. The fixed interlayer regions (mica interlayers) contain proportionally dominant Na^+ and Ca^{2+} and minor amounts of K^+ . The exchangeable smectitic interlayers contain almost equal amounts of Na^+ and Ca^{2+} ions. The distribution of the interlayer Na^+ ions was quantified by ^{23}Na solid-state NMR spectroscopy. These results point to a three-

component mixed-layer structure with considerable variation in the composition of the mica layer of the different samples.

Organically modified layered silicates such as clay minerals are the commonly preferred property modifier in materials processing and manufacture. Modification complexes of rectorite with long-chain dodecyldimethylammonium chloride (DCC10), dialkyldimethylammonium chloride (DCC18) and hexadecyltrimethylammonium chloride (SCC16) were characterised by XRD, FTIR spectroscopy and TGA. The XRD data showed well-defined peaks as the surfactant was homogeneously intercalated between the rectorite layers. The expansion of the interlayer with the double-chain surfactants was 3.60 nm and 3.70 nm for DCC10 and DCC18 respectively, while the d-spacing corresponding to single-chain intercalation with SCC16 was 3.20 nm. The shift of the basal spacing of the rectorite indicates the exchange and adsorption of the larger organic molecules into the smectite layer in the rectorite structure. The FTIR analysis confirmed the presence of organic surfactants in the rectorite, showing absorbance peaks at 2840 cm^{-1} and 2913 cm^{-1} . Homogeneous intercalation implies an increase in the organophilic properties of rectorite at the expense of its hydrophilic nature, and suggests that the adsorption is feasible and can be used as a precursor step to the subsequent adsorption of non-polar organic compounds.

5.2 Rectorite clay films

The behaviour of a rectorite particle in aqueous suspension is defined by its mixed-layer structure and in particular by the exchangeable interlayer in the smectite component. The physico-chemical dynamics in the interlayer space of a clay structure in suspension eventually result in swelling and subsequent delamination of the clay tactoids into smaller entities. The interlayer cations diffuse into the double layers around the separated silicate layers in a state of "osmotic swelling" (Lagaly, 2006). The mixed-layer structure of rectorite comprises alternating interlayer spaces with

different cation densities, i.e. non-expandable (mica-like) and expandable (smectite-like) layers in a 1:1 ratio with an average CEC of 45 mEq/100 g (Atanasova et al., 2016). The expandable smectite layer is of montmorillonite-beidellite composition and the mica component is of the brittle mica species paragonite-margarite. Previous NMR and XRD studies of Beatrix rectorite (Atanasova et al., 2016; Jakobsen et al., 1995; Lausen et al., 1999) reported a high degree of regularity in the layered structure (coefficient of variation for d_{001} of 0.12). A high degree of Al substitution in the mica tetrahedral sheet was established, resulting in the pairing of high-charge top and bottom tetrahedral sheets in a MacEwan crystallite model (MacEwan and Amil, 1958; MacEwan, 1956, 1957). The mica component layer carries a charge density solely of tetrahedral origin almost four-fold higher than that of the alternating smectite layer where the charge is of a dual nature, i.e. partially octahedral from isomorphous substitutions in montmorillonite and partially tetrahedral substitutions in beidellite. The tetrahedral charge is more localised (on three surface oxygens) than the octahedral charge, resulting in stronger H-bonding of adsorbed H₂O as in micas and vermiculites (Schoonheydt and Johnston, 2006). Hence, the bonding strength between silicate layers in the stacking direction of rectorite tactoids is stronger at the mica component layers, inflicting stronger rectorite lamellae as opposed to smectite-only lamellae. Reportedly, this has significant effects on the elastic constant of micas and mica-containing products, and ultimately on their mechanical properties (Kunz et al., 2009; Moller et al., 2010). In suspension, rectorite crystallite will swell only in half of the layers, i.e. at the smectite interlayer. It is also known that monovalent ions cause more extensive swelling of the interlayer than divalent ions (Norrish, 1954) and that micas do not swell at all (Grim, 1968). Consequently, during delamination the mixed-layer rectorite tactoids will separate only at the low-charged interlayer space, i.e. that of smectite. Theoretically, this process could produce a suspension of “fundamental particles” consisting of a single or just a few mica layers (Nadeau et al., 1985; Srodon et al., 2000) with separation distances in the range of 1 nm, short enough for van der

Waals' attraction forces to preserve elementary particle integrity. Furthermore, upon drying and re-assembling, the high tetrahedral charge of the outer rectorite layers would promote strong forces bonding the phyllosilicate layers back together. The X-ray diffraction profiles of the dried films (Figure 4-30) showed peak positions and ordering identical to the rectorite source material. This provides additional confirmation that the delaminated layers re-assembled in an orderly and regular manner and not as random physical mixtures. The primary tactoids in the raw rectorite consisted of up to ten 2:1 silicate layers and had a thickness of about 220 nm, whereas after delamination and re-assembling into coherent films, the stacks contained an average of two to six 2:1 silicate layers. This confirms that delamination occurred and that an increased aspect ratio of the rectorite platelets was achieved, resulting in the generation of a large surface area in the films, as confirmed by the BET results. These results also suggest that dual ordering was attained during the film formation process: at structure level the ordering of 2:1 rectorite layers after delamination and at film microstructure level the two-dimensional organisation of the clay sheets.

The role of heterogeneous layer charge: The physico-chemical properties of rectorite are defined by the regular alternation of low-charge (smectite) and high-charge (mica) layers and their respective interlayer spaces. The expandable smectite layer controls the thickness and the mica layer serves to maintain the structural integrity of the rectorite platelet. Within a tactoid unit, the former layer acts as a shear-labile and the latter as a shear-stiff reinforcement of the rectorite nanoplatelets (Moller et al., 2010). This functional distribution at a structure level resembles other natural mineralised structures such as bone and nacre where ordered arrangements of "soft" and "stiff" phases act synergistically to promote superior mechanical performance tantamount to advanced engineering materials. The hierarchical arrangement of such layered nanostructures has a dramatic effect on the stress and strain propagation in materials and their derivatives (Dimas and Buehler, 2012). The Coulomb attractions between

silicate layers and interlayers along the stacking direction are stronger for micas compared to smectites (Kunz et al., 2009) and have a strong impact on the mechanical properties of materials containing mica. Hence, when rectorite platelets self-assemble from aqueous suspension, the bonding strength along the lamellar stacking and corresponding layer stacking in the film organisation is stronger than would be expected in smectite suspensions and films.

5.3 NH₄-rectorite-chitosan bionanocomposite films (NH₄-Rec/CS NCF)

NH₄-Rec/CS NCF were produced over the full compositional range (100 - 0 % clay, i.e. 0 - 100 % chitosan respectively). Precursor dispersions were prepared by combining partially exfoliated ammonia-exchanged rectorite with a solution of protonated chitosan. The films formed at slow evaporation of the aqueous phase. In this process composites were obtained via re-assembly of chitosan-intercalated rectorite. The intercalation occurred through electrostatic interaction as cation exchange between the NH₄ cations in the interlayers of rectorite and the protonated amino groups of chitosan. At high chitosan content the tactoids were uniformly dispersed in the bulk matrix. Parameters such as clay-chitosan proportions, degree of dispersion, exfoliation and mixing methodology and pH were experimentally determined, closely controlled and tuned to achieve optimal mechanical strength of the final film product. Consistent increase of tensile strength of the composite films was observed with the addition of chitosan to NH₄-Rec clay. At 80/20 compositions, values already exceeded the maximum values for neat clay films and chitosan films. Films in the mid-compositional range showed a tensile strength increase of up to 227 % and 108 % relative to the neat clay films and chitosan films respectively, with the maximum measured for composition 60/40. The Young's modulus followed a similar trend after the sudden drop at the highest clay composition, with the maximum values occurring over a broader compositional range (80/20 - 30/70) and gradually decreasing with the decrease of clay proportion in the mix. It overall appeared that the increase of tensile

strength was correlated to a decrease in the elongation at break (ϵ), more pronounced in the compositional range 90/10 - 30/70. Such inverse relation has been attributed to nanofillers/chitosan interactions resulting in enhancement of stress transfer at the interface (Luo et al., 2003; Xu et al., 2006; Chivrac et al., 2009). The enhancement of the properties indicates an effective interaction between the clay and the biopolymer also observed by Ruiz-Hitzky et al., 2005, Darder et al., 2005, Darder et al., 2006 and Chivrac et al., 2009.

The composite films showed a gradual improvement in transparency with the decrease of clay content. The rectorite films have an off-white colour with a subtle blue-grey tint and pearly lustre on the smooth underside, whereas the chitosan films have a smoky yellow-gray appearance often with a wavy top surface.

The NH₄-Rec/CS nanocomposite films proved to be extremely solvent-resistant even in water, despite the fact that both starting components are water-dispersible under suitable pH conditions. Film fragments remained fully intact after being immersed in water for 277 days.

CHAPTER 6 CONCLUSIONS

Both starting materials, i.e. clay and biopolymer, can be obtained as waste materials. The rectorite occurs as a host rock alteration and could be recovered from mine tailings. Similarly, chitosan is derived from chitin produced from shellfish waste from the seafood industry.

6.1 Characterisation of rectorite

Based on major element concentrations from XRF, X-ray diffraction (XRD) and nuclear magnetic resonance (NMR) evidence, rectorite from Beatrix mine identifies with Na-Ca-rectorite, a dioctahedral regular interstratification of mica-smectite type. The dioctahedral character of the interstratified structure was confirmed by d_{060} at 1.48 Å.

The structure of rectorite was empirically modelled by refinement of high-resolution XRD data collected from a single “pure” rectorite flake. Unit cell parameters, for a monoclinic unit cell with primitive lattice, refined to $a = 5.177 \text{ \AA}$; $b = 8.980 \text{ \AA}$; $c = 22.489 \text{ \AA}$ and $\beta = 97.335^\circ$ with a mean crystallite size around 14 nm and a calculated cell volume of 1045 \AA^3 . The Greene-Kelly test suggested that the expandable smectite layers have montmorillonite-beidellite composition.

Scanning electron microscopy (SEM) of rectorite clay particles revealed a layered morphology. High-resolution transmission microscopy (TEM) showed well-distinguished light and dark layers of about 2.20 nm, consistent with the 1:1 interstratified mica-smectite nature.

There are Na^+ , Ca^{2+} and K^+ cations in the fixed interlayer region (mica interlayer) in a ratio of approximately 15:7:3, and the cationic presence of the exchangeable smectite interlayer comprises Na^+ and Ca^{2+} ions in a ratio of about a 3:4. The distribution of the interlayer Na^+ ions was quantified by ^{23}Na solid-state NMR spectroscopy. It points to a three-component mixed-layer structure with considerable variation in the composition of the mica layer in the different samples. These compositions indicate that the mica layer is represented by paragonite (Na-mica) -margarite (Ca-mica) series, rather than muscovite (K-mica). The structural formula also indicates relatively high tetrahedral substitution, resulting in an expandable layer charge of -0.36 which is characteristic of beidellite rather than montmorillonite in which the net layer charge arises from octahedral substitutions. Furthermore, the chemical data and derived structural formula of Beatrix rectorite suggest an Al-IV:Al-VI ratio of 1:2. The four octahedral sites are dominantly occupied by Al^{3+} with minor Ti^{4+} , Fe^{3+} and Mg^{2+} . Variable interlayer composition of the mica component among the samples is also indicated by NMR and chemically by the XRF data. NMR spectroscopy confirmed a high degree of Al substitution and the presence of two different Al sites corresponding to six- and four-fold octahedral and tetrahedral aluminium respectively. These

findings conform to previous reports on paragonite-margarite-type mica layers alternating with an Na-montmorillonite-beidellite swelling component in rectorite from this locality (Jakobsen et al., 1995). In addition, the ^1H MAS (20 kHz) NMR data reported in the present work contributed to the understanding of the nature and position of the metal hydroxide groups in the mineral structure and the physically adsorbed water and metal-bound OH-groups in the rectorite studied here. A previous study on aluminium layered hydroxides (Wang et al., 2009a) reported similar peak positions, but the peak characteristics observed in the present work point to weak residual dipolar interactions and thus higher mobility of water.

Although the bulk “in situ” occurrence of rectorite in the three samples from Beatrix mine shows rather heterogeneous mineral associations and physical appearance, mineralogically, structurally and chemically all purified rectorite samples were identified as Na-Ca-rectorite. Thus the Beatrix rectorite appears to be compositionally different from the (K, Na, Ca)-rectorite from the Zhongxiang deposit in Hubei, China (Hanlie et al., 2008), the Na-rich rectorite from Arkansas, USA (Jakobsen et al., 1995) and the (Na, K, Mg, Ca, Sr)-rectorite specimens from Baluchistan, Pakistan (Kodama, 1966).

6.2 Rectorite clay films

The capability of rectorite to form strong, flexible self-standing clay films without binders and property enhancers was investigated and the limits of their ultimate material properties evaluated. Clay-only films were prepared by casting aqueous dispersions of exfoliated neat and ion-exchanged rectorite clay through self-assembly during slow evaporation.

The clay films consisted of continuous layers of well-aligned clay platelets parallel to the casting surface. Layers overlapped face to face in the lateral direction and joined vertically in an irregular manner by face-to-face and edge-to-face bridging to form

coherent multi-layer nanostructured films with a platelet-void microstructure. All films showed good mechanical properties with some comparing favourably to values featured by polymer films. Rectorite clay films with monovalent interlayer content exhibit higher strength and stiffness compared to films with divalent modifications and neat Na-Ca-rectorite films. Of all the modifications, only NH₄-Rec films showed enhancement of both tensile properties compared to films from the neat material used for the exchange. Statistical projection for the maximum attainable values for mechanical properties indicates that defect-free films could offer significantly better performance.

The results presented highlighted the lamellar crystal morphology along with the hybrid layer charge of the mixed-layer structure as the most relevant and unique characteristics of rectorite with regard to its potential to produce strong cohesive films. The large surface area of the clay particles is critical for efficient particle interactions during self-assembly. The increase in the particle aspect ratio was achieved through exfoliation and delamination of the clay tactoids in aqueous suspensions. This is largely dependent on the physico-chemical dynamics in the interlayer space and the nature of the exchangeable interlayer cation in the smectite component of the rectorite structure. XRD of the films confirmed that the delaminated layers re-assembled in a regular and orderly manner and not as random physical mixtures, i.e. maintaining the original configuration of pairing the high tetrahedral charge of the outer rectorite layers originating from the mica component of the mixed-layer structure. Average tactoid thickness in the films was two to six layers as opposed to ca. ten 2:1 silicate layers in the primary tactoids. During self-assembly, the thinner tactoids were able to compact better into textured layered structures due to the stronger forces bonding the phyllosilicate layers back together.

Hypothetically, the alternating hybrid layer functionality and charge density distribution in rectorite domains at the structural level could synergistically translate

at the level of re-assembly of the rectorite clay layers into sheets to form nanostructured hierarchical films, imparting property reinforcement to the nanoplatelets and ultimately rendering films with strong mechanical performance.

6.3 NH₄-rectorite-chitosan bionanocomposite films (NH₄-Rec/CS NCF)

Bionanocomposite films with enhanced mechanical strength and optical transparency were successfully prepared from rectorite clay and chitosan without organic pre-modifications, binders, plasticisers, thermal pre-treatments or other property enhancers. NH₄-rectorite-chitosan nanocomposites were prepared over the complete compositional range (100 - 0 % clay, i.e. 0 - 100 % chitosan respectively). Partially exfoliated and intercalated ammonia-exchanged rectorite-chitosan composites were directly mixed in aqueous acetic dispersions and cast for self-assembly during slow evaporation.

The enhancement of the mechanical and optical properties of the NH₄-rectorite-chitosan nanocomposite films indicates good compatibility of the two end-components and feasibility of the ion-exchange method for the preparation of strong clay-chitosan nanocomposite films with high clay loading. The partially exfoliated and intercalated rectorite structure was confirmed by XRD and FTIR analysis, and SEM imaging. Chemical analysis suggested that all chitosan in solution has been incorporated into the clay and film structure. Composite films became compact as a result of structural interaction between the clay and the biopolymer, also acting as a binder during film formation.

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APPENDICES

Appendix I: Chitosan Certificate of Analysis

威東銘生物科技有限公司

G.T.C. Bio Corporation

分析报告单

CERTIFICATE OF ANALYSIS

品名 (product):壳聚糖 (CHITOSAN) 批号 (Batch No.) :GC130430G

生产日期 (Manufacturing Date) : 20130430 数量 (Quantities) :1000KGS

项目 (Items)	标准参数 (Specifications)	测试结果 (Results)
脱乙酰基度 (D.A.C) % Deacetylation degree	85	86.7
粘度 (Viscosity) cps	200-600	150cps
不溶物 (Insolubles) %	≤1	0.45
灰份 (Ash) %	≤1	1.07
水分 (Moisture) %	≤10	9.2
重金属 (Heavy metals) ppm	≤10	Qualified
砷 (Arsenic) ppm	≤1	Qualified
目数 (Particle size) Mesh	80 (95 % Pass)	Qualified
外观 (Appearance)	White Powder	Qualified

分析员 (Analyst):WangZunhua 复核员 (Verification) :ZhangXueling

Appendix II. Refinement data for modelled *rt_hkl* phase used for QPA

Table AII. Refinement data for modelled *rt_hkl* phase used for QPA in this study

<u>h</u>	<u>k</u>	<u>l</u>	<u>m</u>	<u>d</u>	<u>Th2</u>	<u>I</u>
0	0	1	2	21.70973	4.06676	32.5
0	0	2	2	10.85487	8.13865	90.8
0	1	0	2	8.90950	9.91975	2.59
0	-1	1	2	8.24240	10.72487	1.06
0	1	1	2	8.24240	10.72487	1.06
0	0	3	2	7.23658	12.22086	17.1
0	1	2	2	6.88678	12.84414	2.11
0	-1	2	2	6.88678	12.84414	2.11
0	-1	3	2	5.61715	15.76400	2.57e-028
0	1	3	2	5.61715	15.76400	4.87e-014
0	0	4	2	5.42743	16.31871	15
1	0	0	2	5.06812	17.48442	0.41
1	0	-1	2	4.96423	17.85328	0.936
1	0	1	2	4.90710	18.06287	0.184
1	0	-2	2	4.63896	19.11645	0.00469
0	-1	4	2	4.63512	19.13242	1.28e-015
0	1	4	2	4.63512	19.13242	4e-017
1	0	2	2	4.54689	19.50725	3.22e-075
0	2	0	2	4.45475	19.91482	2.09e-016
1	-1	0	2	4.40525	20.14090	35.8
1	1	0	2	4.40525	20.14090	0.00039
0	-2	1	2	4.36383	20.33412	50.5
0	2	1	2	4.36383	20.33412	6.93
0	0	5	2	4.34195	20.43769	0.602
1	1	-1	2	4.33652	20.46356	3.6
1	-1	-1	2	4.33652	20.46356	0.00484
1	1	1	2	4.29827	20.64761	0.000562
1	-1	1	2	4.29827	20.64761	0.00971
1	0	-3	2	4.20324	21.11975	5.06
0	-2	2	2	4.12120	21.54515	1.31e-007
0	2	2	2	4.12120	21.54515	1.31e-007
1	-1	-2	2	4.11462	21.58000	7.04e-020
1	1	-2	2	4.11462	21.58000	1.12e-009
1	0	3	2	4.10121	21.65141	1.55e-020

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1	3	15	2	1.25311	75.86177	5.43e-006
2	-3	13	2	1.24996	76.08646	2.01e-005
2	3	13	2	1.24996	76.08646	8.46e-006
1	-2	16	2	1.24991	76.09026	3e-007
1	2	16	2	1.24991	76.09026	2.52e-007
1	0	-17	2	1.24608	76.36640	1.08e-005
2	0	15	2	1.24286	76.59992	3.46e-007
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1	-1	-17	2	1.23407	77.24621	1.19e-005
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2	1	15	2	1.23094	77.47890	6.03e-005
1	0	17	2	1.23074	77.49419	6.04e-005
0	-2	17	2	1.22760	77.72955	2.61e-005
0	2	17	2	1.22760	77.72955	0.000471
1	-1	17	2	1.21916	78.37013	0.000308
1	1	17	2	1.21916	78.37013	0.000353
0	0	18	2	1.20610	79.38551	0.000369
0	-1	18	2	1.19519	80.25578	0.000133
0	1	18	2	1.19519	80.25578	0.000133

Appendix III. Rectorite-only films dataset

Table AIII-1. Sample ID and mechanical properties

		Clay	Interlayer	Film		Tensile properties	
Test	Sample name	Cation	Charge index	Thickness	BET	Tensile strength	Young's modulus
#			Na=0/Ca=1	mm	m ² /g	MPa	GPa
602	F3191015-Ba 30OU 4h-2	Ba	1.00	18		13.4	5.8
601	F3191015-Ba 30OU4h-1	Ba	1.00	18		9.6	5.1
600	F3191015-Sr 30OU 4h-2	Sr	1.00	23		0.7	0.4
599	F3191015-Sr 30OU 4h -1	Sr	1.00	23		1.9	1.5
598	F3191015-Mg 30OU 4h-4	Mg	1.00	23		4.4	3.0
597	F3191015-Mg 30OU 4h-3	Mg	1.00	23		9.6	3.9
596	F3191015-Mg 30OU 4h-2	Mg	1.00	23		10.4	4.4
595	F3191015-Mg 30OU 4h-1	Mg	1.00	23		4.7	2.4
594	F3191015-K 30OU 4h -2	K	0.00	17	251	33.0	56.3
593	F3191015-K 30OU 4h-1	K	0.00	17		1.8	3.2
592	F3191015-NH 30OU 4h-3	NH	0.00	22		7.8	4.4
591	F3191015-NH 30OU 4h-2	NH	0.00	22		2.1	1.9
590	F3191015-NH 30OU 4h-1	NH	0.00	22	354	43.7	47.3
589	F1021115-RT1b 30OU NS-3	RT1b	0.75	20		16.5	5.9
588	F1021115-RT1b 30OU NS-2	RT1b	0.75	20		12.6	2.2
587	F1021115-RT1b 30OU NS-1	RT1b	0.75	20		4.0	2.1
586	F3021115-Ba 30OU NS top-3	Ba	1.00	30	176	14.9	25.4
585	F3021115-Ba 30OU NS top-2	Ba	1.00	30		11.2	8.8
584	F3021115-Ba 30OU NS top-1	Ba	1.00	30		8.4	16.9
583	F3021115-Sr 30OU NS-3	Sr	1.00	23		6.1	5.0
582	F3021115-Sr 30OU NS-2	Sr	1.00	23		2.1	2.2
581	F3021115-Sr 30OU NS-1	Sr	1.00	23		0.7	0.8
580	F3021115-AAf 30OU NS-2	RT3-AAf	0.75	18		11.3	1.5
579	F3021115-AAf 30OU NS-1	RT3-AAf	0.75	18	208	15.6	2.3
578	F3021115-AAf 30OU NS-1	RT3-AAf	0.75	18		9.2	2.5
577	F2021115-TH70 30OU NS-2	RT2	0.75	26		2.4	3.1
576	F2021115-TH70 30OU NS-1	RT2	0.75	26	115	7.7	8.5
575	F3021115-AA13 30OU NS-3	RT3-AA13	0.75	20		24.6	13.3
574	F3021115-AA13 30OU NS-2	RT3-AA13	0.75	20		7.4	11.8
573	F3021115-AA13 30OU NS-1	RT3-AA13	0.75	20		5.5	4.2
572	F3191015-Na 30OU 4h-3	Na	0.00	23	163	31.8	55.3
571	F3191015-Na 30OU 4h-2	Na	0.00	23		21.8	21.6
570	F3191015-Na 30OU 4h-1	Na	0.00	23		26.8	28.3

		Clay	Interlayer	Film		Tensile properties	
Test	Sample name	Cation	Charge index	Thickness	BET	Tensile strength	Young's modulus
#			Na=0/Ca=1	mm	m ² /g	MPa	GPa
569	F3191015-Li 30OU 4h-3	Li	0.00	13		8.6	3.4
568	F3191015-Li 30OU 4h-2	Li	0.00	13		10.1	3.6
567	F3191015-Li 30OU 4h-1	Li	0.00	13		2.5	1.6
566	F3021115-Ca 5OU 4h-3	Ca	1.00	23		14.7	20.2
565	F3021115-Ca 5OU 4h-2	Ca	1.00	23		22.9	18.1
564	F3021115-Ca 5OU 4h-1	Ca	1.00	23		1.4	0.9
563	F3021115-Ca 30OU 4h-3	Ca	1.00	25		6.1	2.6
562	F3021115-Ca 30OU 4h-2	Ca	1.00	25		5.5	15.1
561	F3021115-Ca 30OU 4h-1	Ca	1.00	25		8.3	15.4
560	F3021115-Ca 30OU NS-3	Ca	1.00	30		0.6	1.1
559	F3021115-Ca 30OU NS-2	Ca	1.00	30		8.7	6.1
558	F3021115-Ca 30OU NS-1	Ca	1.00	30	128	8.0	3.0
557	F3021115-Mg 30OU NS-1	Mg	1.00	13		4.1	15.2
556	F3021115-Cs 30OU NS-3	Cs	0.00	25		4.0	9.4
555	F3021115-Cs 30OU NS-2	Cs	0.00	25	139	9.8	5.3
554	F3021115-Cs 30OU NS-1	Cs	0.00	25		6.9	18.5
553	F3021115-K 30OU NS-4	K	0.00	13		35.7	11.4
552	F3021115-K 30OU NS-3	K	0.00	13		25.1	14.8
551	F3021115-K 30OU NS-2	K	0.00	13		20.1	42.2
550	F3021115-K 30OU NS-1	K	0.00	13		12.1	3.6
549	F3021115-NH 30OU NS-3	NH	0.00	22		13.8	3.5
548	F3021115-NH 30OU NS-2	NH	0.00	22		0.2	0.1
547	F3021115-NH 30OU NS-1	NH	0.00	22		15.7	4.2
546	F3021115-Na 30OU NS-3	Na	0.00	22		17.4	2.8
545	F3021115-Na 30OU NS-2	Na	0.00	22		14.3	4.6
544	F3021115-Na 30OU NS-1	Na	0.00	22		2.9	11.0
543	F3021115-Li 30OU NS-2	Li	0.00	23	259	12.9	18.8
542	F3021115-Li 30OU NS-1	Li	0.00	23		5.7	5.6
541	F3201213-Sr-3	Sr	1.00	26		0.0	4.6
540	F3201213-Sr-2	Sr	1.00	26	169	5.6	2.3
539	F3201213-Sr-1	Sr	1.00	26		6.7	18.0
350	F1250615DE-MgRT-NU30-3	Mg	1.00	20		13.9	20.6
349	F1250615DE-MgRT-NU30-3	Mg	1.00	20		0.0	0.8
348	F1250615DE-MgRT-NU30-2	Mg	1.00	20	184	12.3	3.7
347	F1250615DE-MgRT-NU30-1	Mg	1.00	20		8.0	3.2
346	F3250615DE-NH-NU5-2	NH	0.00	23		0.5	0.8

		Clay	Interlayer	Film		Tensile properties	
Test	Sample name	Cation	Charge index	Thickness	BET	Tensile strength	Young's modulus
#			Na=0/Ca=1	mm	m ² /g	MPa	GPa
345	F3250615DE-NH-NU5-1	NH	0.00	23		10.7	6.9
344	F3230615DE-RT3Na-NU30-3	Na	0.00	35		11.3	5.4
343	F3230615DE-RT3Na-NU30-2	Na	0.00	35		9.8	2.9
342	F3230615DE-RT3Na-NU30-1	Na	0.00	35		16.1	6.0
341	F3230615DE-RT3Na-NU5-3	Na	0.00	35		1.9	10.2
340	F3230615DE-RT3Na-NU5-2	Na	0.00	35		4.9	3.0
339	F3230615DE-RT3Na-NU5-1	Na	0.00	35		3.4	4.1
338	F3240615DE-RT3Li-NU5-3	Li	0.00	13		7.3	2.5
337	F3240615DE-RT3Li-NU5-2	Li	0.00	13		2.9	1.7
336	F3240615DE-RT3Li-NU5-1	Li	0.00	13		10.6	50.7
335	F3240615DE-AA13-NU5-3	RT3-AA13	0.75	20		14.8	6.6
334	F3240615DE-AA13-NU5-2	RT3-AA13	0.75	20		0.5	0.4
333	F3240615DE-AA13-NU5-1	RT3-AA13	0.75	20		4.6	1.5
332	F3240615DE-RT3NH-OU30-3	NH	0.00	27		21.7	10.6
331	F1240615DE-RT1b-NU5s-3	RT1b	0.75	20	259	19.9	3.0
330	F1240615DE-RT1b-NU5s-2	RT1b	0.75	20		14.9	5.5
329	F1240615DE-RT1b-NU5s-1	RT1b	0.75	20		8.7	4.8
328	F3240615DE-RT3Na-OU30-2	Na	0.00	13		0.5	0.5
327	F3240615DE-RT3NH-OU30-2	NH	0.00	27		3.8	6.3
326	F3240615DE-RT3NH-OU30-1	NH	0.00	27		23.7	9.7
325	F3240615DE-RT3NH-OU5-3	NH	0.00	27		8.1	1.7
324	F3240615DE-RT3NH-OU5-2	NH	0.00	27		1.9	2.3
323	F3230615DE-RT3Na-OU5-3	Na	0.00	18		16.0	4.2
322	F3240615DE-RT3NH-OU5-1	NH	0.00	10		2.4	3.5
321	F3230615DE-RT3Na-OU5-2	Na	0.00	18		0.7	0.5
320	F3240615DE-RT3Li-OU5-3	Li	0.00	13		5.6	15.9
319	F3240615DE-RT3Li-OU5-2	Li	0.00	13		1.4	0.8
318	F3240615DE-RT3Li-OU5-1	Li	0.00	13		11.1	14.5
317	F3240615DE-AAfOU5-3	RT3-AAf	0.75	12		13.2	18.6
316	F3240615DE-AAfOU5-2	RT3-AAf	0.75	12		14.1	1.9
315	F3240615DE-AAfOU5-1	RT3-AAf	0.75	12		13.6	2.3
314	F3230615DE-AA13OU30-3	RT3-AA13	0.75	17		0.2	0.0
313	F3230615DE-AA13OU30-2	RT3-AA13	0.75	17		12.0	12.2
312	F3230615DE-AA13OU30-1	RT3-AA13	0.75	17		1.0	2.3
311	F3230615DE-AA13OU5-3	RT3-AA13	0.75	15		2.7	4.3
310	F3230615DE-AA13OU5-2	RT3-AA13	0.75	15		1.2	2.1

		Clay	Interlayer	Film		Tensile properties	
Test	Sample name	Cation	Charge index	Thickness	BET	Tensile strength	Young's modulus
#			Na=0/Ca=1	mm	m ² /g	MPa	GPa
309	F3230615DE-AA13OU5-1	RT3-AA13	0.75	15		6.9	7.5
308	F1-061113-RT1b-P-3	RT1b	0.75	10		2.1	0.6
307	F1-061113-RT1b-P-2	RT1b	0.75	10		20.0	44.3
306	F1-061113-RT1b-P-1	RT1b	0.75	10		12.7	19.3
304	F2-121113-RT2pur-P-1	RT2	0.75	20		6.3	20.4
301	F1-260415-RT1Li-2	Li	0.00	18		6.6	0.7
300	F1-260415-RT1Li-1	Li	0.00	18		7.8	0.8
299	F3-260415-RT3Li-1	Li	0.00	18		7.0	10.2
298	F3-260415-RT3NH4-15-3	NH	0.00	18		11.5	1.6
297	F3-260415-RT3NH4-15-2	NH	0.00	18		17.3	2.8
296	F3-260415-RT3NH4-15-1	NH	0.00	18		12.8	16.8
295	F3-260415-RT3Na-3	Na	0.00	18		7.8	13.6
294	F3-260415-RT3K-3	K	0.00	20		8.9	1.2
293	F3-260415-RT3K-2	K	0.00	20		11.6	1.2
292	F3-260415-RT3K-1	K	0.00	20		9.6	0.8
291	F3-230415-RT3AA13wT-2	RT3-AA13	0.75	25		1.2	0.4
290	F3-230415-RT3AA13wT-1	RT3-AA13	0.75	25		3.3	6.2
289	F2-230415-RT2TH70 wT-3	RT2	0.75	20		4.0	11.2
288	F2-230415-RT2TH70 wT-2	RT2	0.75	20		7.8	49.8
287	F2-230415-RT2TH70 wT-1	RT2	0.75	20		11.7	3.2
286	F1-230415-RT1b wT-3	RT1b	0.75	25		14.8	3.6
285	F1-230415-RT1b wT-2	RT1b	0.75	25		23.9	4.3
284	F1-230415-RT1b wT-1	RT1b	0.75	25		12.4	4.3
283	F3-270115-NH4-14-3	NH	0.00	15		9.8	1.7
282	F3-270115-NH4-14-2	NH	0.00	15		5.5	1.7
281	F3-270115-NH4-14-1	NH	0.00	15		19.9	2.8
280	F3-200114-NH4-14-3	NH	0.00	100		3.6	0.5
279	F3-200114-NH4-14-2	NH	0.00	100		3.4	1.1
278	F3-200114-NH4-14-1	NH	0.00	100		3.7	1.3
277	F3-200114-Li13-3	Li	0.00	15		3.2	1.9
276	F3-200114-Li13-2	Li	0.00	15		3.1	24.9
275	F3-200114-Li13-1	Li	0.00	15		9.7	3.8
274	F3-070414AAf4-3	RT3-AAf	0.75	54		16.4	1.5
273	F3-070414AAf4-2	RT3-AAf	0.75	54		10.8	1.3
272	F3-070414AAf4-1	RT3-AAf	0.75	54		11.9	1.9
271	F3-070414AAf3-3	RT3-AAf	0.75	67		4.5	2.4

		Clay	Interlayer	Film		Tensile properties	
Test	Sample name	Cation	Charge index	Thickness	BET	Tensile strength	Young's modulus
#			Na=0/Ca=1	mm	m ² /g	MPa	GPa
270	F3-070414AAf3-2b	RT3-AAf	0.75	67		11.7	2.5
269	F3-070414AAf3-2	RT3-AAf	0.75	67		11.1	2.0
268	F3-070414AAf3-1	RT3-AAf	0.75	67		10.7	2.9
267	F3-070414AAf2-2	RT3-AAf	0.75	90		3.9	1.4
266	F3-070414AAf2-2	RT3-AAf	0.75	90		3.9	1.4
265	F3-070414AAf2-1	RT3-AAf	0.75	90		6.4	1.7
264	F3-070414AAf1-3	RT3-AAf	0.75	27		3.0	0.9
263	F3-070414AAf1-2	RT3-AAf	0.75	27		10.2	2.5
262	F3-070414AAf1-1	RT3-AAf	0.75	27		5.5	1.5
261	F3-201213-Cs-last1	Cs	0.00	31		15.5	43.4
260	F3-201213-NH4-13-2-3	NH	0.00	155		4.5	0.9
259	F3-201213-NH4-13-2-2b	NH	0.00	155		7.0	1.4
258	F3-201213-NH4-13-2-2	NH	0.00	155		6.7	1.0
257	F3-201213-NH4-13-2-1	NH	0.00	155		6.3	1.3
256	F3-201213-NH4-13-1-3	NH	0.00	155		4.6	0.9
253	F3-201213-NH4-13-1-2	NH	0.00	155		3.3	0.9
252	F3-201213-NH4-13-1	NH	0.00	155		3.3	0.9
251	F3-201213-Sr3-last2	Sr	1.00	30		8.0	11.1
250	F3-201213-Sr3-last1	Sr	1.00	30		4.0	3.1
249	F3201213-43-K-last3	K	0.00	117		5.4	2.6
248	F3201213-43-K-last2	K	0.00	117		0.4	3.6
247	F3201213-43-K-last1	K	0.00	117		4.7	1.3
246	F3201213-42-NH4-12last3	NH	0.00	70		9.2	1.6
245	F3201213-42-NH4-12last2	NH	0.00	60		6.0	1.6
244	F3201213-42-NH4-12last1	NH	0.00	60		11.8	2.9
243	F3201213-41-2-Na2last3	Na	0.00	75		9.6	1.5
242	F3201213-41-2-Na2last2	Na	0.00	75		9.9	1.7
241	F3201213-41-2-Na2last1	Na	0.00	75		9.5	1.3
240	F3201213-41-Na2last3	Na	0.00	75		5.5	1.6
239	F3201213-41-Na2last2	Na	0.00	75		8.7	1.0
238	F3201213-40-Na1last1	Na	0.00	64		8.1	1.4
237	F3201213-40-Na1last3	Na	0.00	64		7.3	1.7
236	F3201213-40-Na1last2	Na	0.00	64		6.4	1.2
235	F3201213-40-Na1last	Na	0.00	64		7.5	1.4
215	F2121113RT2TH70-3	RT2	0.75	16		11.1	34.0
214	F2121113RT2TH70-2	RT2	0.75	16		9.8	7.7

		Clay	Interlayer	Film		Tensile properties	
Test	Sample name	Cation	Charge index	Thickness	BET	Tensile strength	Young's modulus
#			Na=0/Ca=1	mm	m ² /g	MPa	GPa
213	F2121113RT2TH70-1	RT2	0.75	16		11.7	39.4
209	F1061113RT1m-3	RT1m	0.75	22		7.8	6.1
208	F1061113RT1m-2	RT1m	0.75	22		13.7	4.6
207	F1061113RT1m-1	RT1m	0.75	22		17.4	5.1
202	F1061113RT1b-3	RT1b	0.75	26		17.2	6.4
201	F1061113RT1b-2	RT1b	0.75	26		7.1	5.2
200	F1061113RT1b-1	RT1b	0.75	26		15.7	5.7
182	F3180913RT3 100-3	RT3-OWE	0.75	20		6.8	4.0
181	F3180913RT3 100-2	RT3-OWE	0.75	20		16.6	10.5
180	F3180913RT3 100	RT3-OWE	0.75	20		5.2	3.7
179	F3-49-OWF-P3	RT3-OWF	0.75	151		8.0	3.6
178	F3-49-OWF-P2	RT3-OWF	0.75	151		15.2	4.1
177	F3-49-OWF-P1	RT3-OWF	0.75	151		10.3	3.1
176	F3-48-Sr-P3	Sr	1.00	70		7.7	2.4
175	F3-48-Sr-P2	Sr	1.00	55		5.0	2.0
174	F3-48-Sr-P1	Sr	1.00	52		3.9	9.9
173	F3-41-Na2-P4	Na	0.00	66		5.9	1.4
172	F3-41-Na2-P3	Na	0.00	66		5.3	1.3
171	F3-41-Na2-P2	Na	0.00	65		6.5	0.9
170	F3-41-Na2-P1	Na	0.00	60		4.8	1.0
97	F3-49-OWF 2i3	RT3-OWF	0.75	137		8.3	2.4
96	F3-49-OWF 2 i2	RT3-OWF	0.75	137		7.3	2.4
95	F3-49-OWF 2 i1	RT3-OWF	0.75	137		8.5	3.6
94	F3-49-OWF i3	RT3-OWF	0.75	137		4.5	1.4
93	F3-49-OWF i2	RT3-OWF	0.75	137		6.3	2.0
92	F3-49-OWF i1	RT3-OWF	0.75	137		7.1	2.2
91	F3-48-Sr-i3	Sr	1.00	67		5.9	2.0
90	F3-48-Sr-i2	Sr	1.00	67		5.3	3.6
89	F3-48-Sr-i1	Sr	1.00	67		0.7	0.8
88	F3-46-Ba-i3	Ba	1.00	170		7.2	1.6
86	F3-46-Ba-i2	Ba	1.00	170		7.9	3.2
85	F3-46-Ba-i1	Ba	1.00	170		7.6	2.9
84	F3-45-Cs-i3	Cs	0.00	130		4.4	2.3
83	F3-45-Cs-i2	Cs	0.00	110		0.5	0.8
82	F3-45-Cs-i1	Cs	0.00	90		1.0	1.4
58	F3-32-Na1-i7	Na	0.00	100		3.0	0.5

		Clay	Interlayer	Film		Tensile properties	
Test	Sample name	Cation	Charge index	Thickness	BET	Tensile strength	Young's modulus
#			Na=0/Ca=1	mm	m ² /g	MPa	GPa
57	F3-31-Li-i7	Li	0.00	58		3.0	0.7
56	F3-31-Li-i8	Li	0.00	58		3.8	1.4
55	F3-47-Sr-i4	Sr	1.00	53		4.3	3.3
54	F3-47-Sr-i2	Sr	1.00	53		5.4	1.6
53	F3-44-Mg-i4	Mg	1.00	60		1.9	1.6
52	F3-44-Mg-i3	Mg	1.00	60		1.4	1.1
51	F3-44-Mg-i2	Mg	1.00	60		2.9	1.4
50	F3-44-Mg-i1	Mg	1.00	60		1.2	1.3
49	F3-43-K-i4	K	0.00	72		5.6	1.4
48	F3-43-K-i3	K	0.00	40		7.4	2.7
47	F3-43-K-i2	K	0.00	88		4.5	1.1
46	F3-43-K-i1	K	0.00	107		3.8	0.8
45	F3-38-OWE i9	RT3-OWE	0.75	61		14.0	6.1
44	F3-38-OWE i8	RT3-OWE	0.75	61		12.7	6.4
43	F3-38-OWE i7	RT3-OWE	0.75	61		11.4	5.8
42	F3-38-OWE i6	RT3-OWE	0.75	61		3.6	14.6
40	F3-38-OWE i6	RT3-OWE	0.75	61		4.3	6.1
39	F3-42 NH4 4i	NH	0.00	70		5.9	1.8
38	F3-42 NH4 3i	NH	0.00	70		6.0	0.9
37	F3-42 NH4 2i	NH	0.00	70		6.1	1.0
36	F3-42 NH4 1i	NH	0.00	70		6.0	1.2
35	F3-41 Na2 4i	Na	0.00	100		2.8	0.8
34	F3-41 Na2 3i	Na	0.00	100		2.7	0.8
33	F3-41 Na2 2i	Na	0.00	100		3.2	1.0
32	F3-41 Na2 1i	Na	0.00	100		2.9	0.9
31	F3-40 Na1 5i	Na	0.00	138		2.5	0.5
30	F3-40 Na1 4i	Na	0.00	138		2.4	0.4
29	F3-40 Na1 3i	Na	0.00	138		2.6	0.4
28	F3-40 Na1 2i	Na	0.00	138		2.4	0.5
27	F3-40 Na1 1i	Na	0.00	138		2.6	0.4
17	F3-Li-39o6	Li	0.00	113		2.9	0.7
16	F3-Li-39i5	Li	0.00	113		3.1	0.5
15	F3-Li-39i4	Li	0.00	113		3.1	0.6
14	F3-Li-39i3	Li	0.00	113		2.9	0.4

Table AIII-2. Slurry processing conditions

Test	Sample name	Clay	Slurry processing conditions			
		Cation	Concentration	Sonication time	Stirring time	pH
#			clay g/100 ml UPW	min	h	
602	F3191015-Ba 30OU 4h-2	Ba	1.00	30	4	6.80
601	F3191015-Ba 30OU4h-1	Ba	1.00	30	4	6.80
600	F3191015-Sr 30OU 4h-2	Sr	1.00	30	4	6.20
599	F3191015-Sr 30OU 4h -1	Sr	1.00	30	4	6.20
598	F3191015-Mg 30OU 4h-4	Mg	1.00	30	4	7.06
597	F3191015-Mg 30OU 4h-3	Mg	1.00	30	4	7.06
596	F3191015-Mg 30OU 4h-2	Mg	1.00	30	4	7.06
595	F3191015-Mg 30OU 4h-1	Mg	1.00	30	4	7.06
594	F3191015-K 30OU 4h -2	K	1.00	30	4	8.80
593	F3191015-K 30OU 4h-1	K	1.00	30	4	8.80
592	F3191015-NH 30OU 4h-3	NH	1.00	30	4	7.10
591	F3191015-NH 30OU 4h-2	NH	1.00	30	4	7.10
590	F3191015-NH 30OU 4h-1	NH	1.00	30	4	7.10
589	F1021115-RT1b 30OU NS-3	RT1b	1.00	30	0	8.23
588	F1021115-RT1b 30OU NS-2	RT1b	1.00	30	0	8.23
587	F1021115-RT1b 30OU NS-1	RT1b	1.00	30	0	8.23
586	F3021115-Ba 30OU NS top-3	Ba	1.00	30	0	6.80
585	F3021115-Ba 30OU NS top-2	Ba	1.00	30	0	6.80
584	F3021115-Ba 30OU NS top-1	Ba	1.00	30	0	6.80
583	F3021115-Sr 30OU NS-3	Sr	1.00	30	0	6.20
582	F3021115-Sr 30OU NS-2	Sr	1.00	30	0	6.20
581	F3021115-Sr 30OU NS-1	Sr	1.00	30	0	6.20
580	F3021115-AAf 30OU NS-2	RT3-AAf	1.00	30	0	6.85
579	F3021115-AAf 30OU NS-1	RT3-AAf	1.00	30	0	6.85
578	F3021115-AAf 30OU NS-1	RT3-AAf	1.00	30	0	6.85
577	F2021115-TH70 30OU NS-2	RT2	1.00	30	0	6.80
576	F2021115-TH70 30OU NS-1	RT2	1.00	30	0	6.80
575	F3021115-AA13 30OU NS-3	RT3-AA13	1.00	30	0	7.00
574	F3021115-AA13 30OU NS-2	RT3-AA13	1.00	30	0	7.00
573	F3021115-AA13 30OU NS-1	RT3-AA13	1.00	30	0	7.00
572	F3191015-Na 30OU 4h-3	Na	1.00	30	4	8.58
571	F3191015-Na 30OU 4h-2	Na	1.00	30	4	8.58
570	F3191015-Na 30OU 4h-1	Na	1.00	30	4	8.58
569	F3191015-Li 30OU 4h-3	Li	1.00	30	4	9.62
568	F3191015-Li 30OU 4h-2	Li	1.00	30	4	9.62

Test	Sample name	Clay	Slurry processing conditions			
		Cation	Concentration	Sonication time	Stirring time	pH
			clay g/100 ml UPW	min	h	
567	F3191015-Li 30OU 4h-1	Li	1.00	30	4	9.62
566	F3021115-Ca 5OU 4h-3	Ca	1.00	30	4	6.10
565	F3021115-Ca 5OU 4h-2	Ca	1.00	30	4	6.10
564	F3021115-Ca 5OU 4h-1	Ca	1.00	30	4	6.10
563	F3021115-Ca 30OU 4h-3	Ca	1.00	30	4	6.30
562	F3021115-Ca 30OU 4h-2	Ca	1.00	30	4	6.30
561	F3021115-Ca 30OU 4h-1	Ca	1.00	30	4	6.30
560	F3021115-Ca 30OU NS-3	Ca	1.00	30	0	6.30
559	F3021115-Ca 30OU NS-2	Ca	1.00	30	0	6.30
558	F3021115-Ca 30OU NS-1	Ca	1.00	30	0	6.30
557	F3021115-Mg 30OU NS-1	Mg	1.00	30	0	7.06
556	F3021115-Cs 30OU NS-3	Cs	1.00	30	0	5.50
555	F3021115-Cs 30OU NS-2	Cs	1.00	30	0	5.50
554	F3021115-Cs 30OU NS-1	Cs	1.00	30	0	5.50
553	F3021115-K 30OU NS-4	K	1.00	30	0	8.80
552	F3021115-K 30OU NS-3	K	1.00	30	0	8.80
551	F3021115-K 30OU NS-2	K	1.00	30	0	8.80
550	F3021115-K 30OU NS-1	K	1.00	30	0	8.80
549	F3021115-NH 30OU NS-3	NH	1.00	30	0	7.10
548	F3021115-NH 30OU NS-2	NH	1.00	30	0	7.10
547	F3021115-NH 30OU NS-1	NH	1.00	30	0	7.10
546	F3021115-Na 30OU NS-3	Na	1.00	30	0	8.58
545	F3021115-Na 30OU NS-2	Na	1.00	30	0	8.58
544	F3021115-Na 30OU NS -1	Na	1.00	30	0	8.58
543	F3021115-Li 30OU NS-2	Li	1.00	30	0	9.62
542	F3021115-Li 30OU NS-1	Li	1.00	30	0	9.62
541	F3201213-Sr-3	Sr	1.00	30	0	6.20
540	F3201213-Sr-2	Sr	1.00	30	0	6.20
539	F3201213-Sr-1	Sr	1.00	30	0	6.20
350	F1250615DE-MgRT-NU30-3	Mg	1.00	30	24	8.22
349	F1250615DE-MgRT-NU30-3	Mg	1.00	30	24	8.22
348	F1250615DE-MgRT-NU30-2	Mg	1.00	30	24	8.22
347	F1250615DE-MgRT-NU30-1	Mg	1.00	30	24	8.22
346	F3250615DE-NH-NU5-2	NH	1.00	5	24	7.10
345	F3250615DE-NH-NU5-1	NH	1.00	5	24	7.10
344	F3230615DE-RT3Na-NU30-3	Na	1.00	30	24	8.58

Test	Sample name	Clay	Slurry processing conditions			
		Cation	Concentration	Sonication time	Stirring time	pH
			clay g/100 ml UPW	min	h	
343	F3230615DE-RT3Na-NU30-2	Na	1.00	30	24	8.58
342	F3230615DE-RT3Na-NU30-1	Na	1.00	30	24	8.58
341	F3230615DE-RT3Na-NU5-3	Na	1.00	5	24	8.58
340	F3230615DE-RT3Na-NU5-2	Na	1.00	5	24	8.58
339	F3230615DE-RT3Na-NU5-1	Na	1.00	5	24	8.58
338	F3240615DE-RT3Li-NU5-3	Li	1.00	5	24	9.62
337	F3240615DE-RT3Li-NU5-2	Li	1.00	5	24	9.62
336	F3240615DE-RT3Li-NU5-1	Li	1.00	5	24	9.62
335	F3240615DE-AA13-NU5-3	RT3-AA13	1.00	5	24	7.00
334	F3240615DE-AA13-NU5-2	RT3-AA13	1.00	5	24	7.00
333	F3240615DE-AA13-NU5-1	RT3-AA13	1.00	5	24	7.00
332	F3240615DE-RT3NH-OU30-3	NH	1.00	30	24	7.10
331	F1240615DE-RT1b-NU5s-3	RT1b	1.00	5	24	8.85
330	F1240615DE-RT1b-NU5s-2	RT1b	1.00	5	24	8.85
329	F1240615DE-RT1b-NU5s-1	RT1b	1.00	5	24	8.85
328	F3240615DE-RT3Na-OU30-2	Na	1.00	30	24	8.58
327	F3240615DE-RT3NH-OU30-2	NH	1.00	30	24	7.10
326	F3240615DE-RT3NH-OU30-1	NH	1.00	30	24	7.10
325	F3240615DE-RT3NH-OU5-3	NH	1.00	5	24	7.10
324	F3240615DE-RT3NH-OU5-2	NH	1.00	5	24	7.10
323	F3230615DE-RT3Na-OU5-3	Na	1.00	5	24	8.58
322	F3240615DE-RT3NH-OU5-1	NH	1.00	5	24	7.10
321	F3230615DE-RT3Na-OU5-2	Na	1.00	5	24	8.58
320	F3240615DE-RT3Li-OU5-3	Li	1.00	5	24	9.62
319	F3240615DE-RT3Li-OU5-2	Li	1.00	5	24	9.62
318	F3240615DE-RT3Li-OU5-1	Li	1.00	5	24	9.62
317	F3240615DE-AAfOU5-3	RT3-AAf	1.00	5	24	6.85
316	F3240615DE-AAfOU5-2	RT3-AAf	1.00	5	24	6.85
315	F3240615DE-AAfOU5-1	RT3-AAf	1.00	5	24	6.85
314	F3230615DE-AA13OU30-3	RT3-AA13	1.00	30	24	7.00
313	F3230615DE-AA13OU30-2	RT3-AA13	1.00	30	24	7.00
312	F3230615DE-AA13OU30-1	RT3-AA13	1.00	30	24	7.00
311	F3230615DE-AA13OU5-3	RT3-AA13	1.00	5	24	7.00
310	F3230615DE-AA13OU5-2	RT3-AA13	1.00	5	24	7.00
309	F3230615DE-AA13OU5-1	RT3-AA13	1.00	5	24	7.00
308	F1-061113-RT1b-P-3	RT1b	1.00	5	24	8.50

Test	Sample name	Clay	Slurry processing conditions			
		Cation	Concentration	Sonication time	Stirring time	pH
#			clay g/100 ml UPW	min	h	
307	F1-061113-RT1b-P-2	RT1b	1.00	5	24	8.50
306	F1-061113-RT1b-P-1	RT1b	1.00	5	24	8.50
304	F2-121113-RT2pur-P-1	RT2	1.00	5	24	6.70
301	F1-260415-RT1Li-2	Li	1.00	30	24	9.62
300	F1-260415-RT1Li-1	Li	1.00	30	24	9.62
299	F3-260415-RT3Li-1	Li	1.00	30	24	9.62
298	F3-260415-RT3NH4-15-3	NH	1.00	30	24	7.10
297	F3-260415-RT3NH4-15-2	NH	1.00	30	24	7.10
296	F3-260415-RT3NH4-15-1	NH	1.00	30	24	7.10
295	F3-260415-RT3Na-3	Na	1.00	30	24	8.58
294	F3-260415-RT3K-3	K	1.00	30	24	8.80
293	F3-260415-RT3K-2	K	1.00	30	24	8.80
292	F3-260415-RT3K-1	K	1.00	30	24	8.80
291	F3-230415-RT3AA13wT-2	RT3-AA13	1.00	30	24	7.00
290	F3-230415-RT3AA13wT-1	RT3-AA13	1.00	30	24	7.00
289	F2-230415-RT2TH70 wT-3	RT2	1.00	30	24	6.70
288	F2-230415-RT2TH70 wT-2	RT2	1.00	30	24	6.70
287	F2-230415-RT2TH70 wT-1	RT2	1.00	30	24	6.70
286	F1-230415-RT1b wT-3	RT1b	1.00	30	24	8.50
285	F1-230415-RT1b wT-2	RT1b	1.00	30	24	8.50
284	F1-230415-RT1b wT-1	RT1b	1.00	30	24	8.50
283	F3-270115-NH4-14-3	NH	1.00	30	24	7.10
282	F3-270115-NH4-14-2	NH	1.00	30	24	7.10
281	F3-270115-NH4-14-1	NH	1.00	30	24	7.10
280	F3-200114-NH4-14-3	NH	1.00	30	0	7.10
279	F3-200114-NH4-14-2	NH	1.00	30	0	7.10
278	F3-200114-NH4-14-1	NH	1.00	30	0	7.10
277	F3-200114-Li13-3	Li	1.00	30	0	9.62
276	F3-200114-Li13-2	Li	1.00	30	0	9.62
275	F3-200114-Li13-1	Li	1.00	30	0	9.62
274	F3-070414AAf4-3	RT3-AAf	1.00	5	0	6.85
273	F3-070414AAf4-2	RT3-AAf	1.00	5	0	6.85
272	F3-070414AAf4-1	RT3-AAf	1.00	5	0	6.85
271	F3-070414AAf3-3	RT3-AAf	1.00	5	0	6.85
270	F3-070414AAf3-2b	RT3-AAf	3.03	5	0	6.85
269	F3-070414AAf3-2	RT3-AAf	3.03	5	0	6.85

Test	Sample name	Clay	Slurry processing conditions			
		Cation	Concentration	Sonication time	Stirring time	pH
			clay g/100 ml UPW	min	h	
268	F3-070414AAf3-1	RT3-AAf	3.03	5	0	6.85
267	F3-070414AAf2-2	RT3-AAf	2.92	5	0	6.85
266	F3-070414AAf2-2	RT3-AAf	2.92	5	0	6.85
265	F3-070414AAf2-1	RT3-AAf	2.92	5	0	6.85
264	F3-070414AAf1-3	RT3-AAf	2.04	5	0	6.85
263	F3-070414AAf1-2	RT3-AAf	2.04	5	0	6.85
262	F3-070414AAf1-1	RT3-AAf	2.04	5	0	6.85
261	F3-201213-Cs-last1	Cs	1.00	30	0	5.50
260	F3-201213-NH4-13-2-3	NH	1.00	30	0	7.10
259	F3-201213-NH4-13-2-2b	NH	1.00	30	0	7.10
258	F3-201213-NH4-13-2-2	NH	1.00	30	0	7.10
257	F3-201213-NH4-13-2-1	NH	1.00	30	0	7.10
256	F3-201213-NH4-13-1-3	NH	1.00	30	0	7.10
253	F3-201213-NH4-13-1-2	NH	1.00	30	0	7.10
252	F3-201213-NH4-13-1	NH	1.00	30	0	7.10
251	F3-201213-Sr3-last2	Sr	1.00	30	0	6.20
250	F3-201213-Sr3-last1	Sr	1.00	30	0	6.20
249	F3201213-43-K-last3	K	3.67	30	0	8.80
248	F3201213-43-K-last2	K	3.67	30	0	8.80
247	F3201213-43-K-last1	K	3.67	30	0	8.80
246	F3201213-42-NH4-12last3	NH	3.43	5	0	7.10
245	F3201213-42-NH4-12last2	NH	3.43	5	0	7.10
244	F3201213-42-NH4-12last1	NH	3.43	5	0	7.10
243	F3201213-41-2-Na2last3	Na	2.60	5	0	8.58
242	F3201213-41-2-Na2last2	Na	2.60	5	0	8.58
241	F3201213-41-2-Na2last1	Na	2.60	5	0	8.58
240	F3201213-41-Na2last3	Na	2.04	5	0	8.58
239	F3201213-41-Na2last2	Na	2.04	5	0	8.58
238	F3201213-40-Na1last1	Na	4.05	5	0	8.58
237	F3201213-40-Na1last3	Na	4.05	5	0	8.58
236	F3201213-40-Na1last2	Na	4.05	5	0	8.58
235	F3201213-40-Na1last	Na	4.05	5	0	8.58
215	F2121113RT2TH70-3	RT2	1.00	5	24	6.70
214	F2121113RT2TH70-2	RT2	1.00	5	24	6.70
213	F2121113RT2TH70-1	RT2	1.00	5	24	6.70
209	F1061113RT1m-3	RT1m	1.00	5	24	8.50

		Clay	Slurry processing conditions			
Test	Sample name	Cation	Concentration	Sonication time	Stirring time	pH
#			clay g/100 ml UPW	min	h	
208	F1061113RT1m-2	RT1m	1.00	5	24	8.50
207	F1061113RT1m-1	RT1m	1.00	5	24	8.50
202	F1061113RT1b-3	RT1b	1.00	5	24	8.50
201	F1061113RT1b-2	RT1b	1.00	5	24	8.50
200	F1061113RT1b-1	RT1b	1.00	5	24	8.50
182	F3180913RT3 100-3	RT3-OWE	2.30	5	0	6.60
181	F3180913RT3 100-2	RT3-OWE	2.30	5	0	6.60
180	F3180913RT3 100	RT3-OWE	2.30	5	0	6.60
179	F3-49-OWF-P3	RT3-OWF	4.00	5	0	6.60
178	F3-49-OWF-P2	RT3-OWF	4.00	5	0	6.60
177	F3-49-OWF-P1	RT3-OWF	4.00	5	0	6.60
176	F3-48-Sr-P3	Sr	2.22	30	0	6.20
175	F3-48-Sr-P2	Sr	2.22	30	0	6.20
174	F3-48-Sr-P1	Sr	2.22	30	0	6.20
173	F3-41-Na2-P4	Na	3.70	5	0	8.58
172	F3-41-Na2-P3	Na	3.70	5	0	8.58
171	F3-41-Na2-P2	Na	3.70	5	0	8.58
170	F3-41-Na2-P1	Na	3.70	5	0	8.58
97	F3-49-OWF 2i3	RT3-OWF	4.00	5	0	6.60
96	F3-49-OWF 2 i2	RT3-OWF	4.00	5	0	6.60
95	F3-49-OWF 2 i1	RT3-OWF	4.00	5	0	6.60
94	F3-49-OWF i3	RT3-OWF	4.00	5	0	6.60
93	F3-49-OWF i2	RT3-OWF	4.00	5	0	6.60
92	F3-49-OWF i1	RT3-OWF	4.00	5	0	6.60
91	F3-48-Sr-i3	Sr	2.22	30	0	6.20
90	F3-48-Sr-i2	Sr	2.22	30	0	6.20
89	F3-48-Sr-i1	Sr	2.22	30	0	6.20
88	F3-46-Ba-i3	Ba	5.82	30	0	6.80
86	F3-46-Ba-i2	Ba	5.82	30	0	6.80
85	F3-46-Ba-i1	Ba	5.82	30	0	6.80
84	F3-45-Cs-i3	Cs	4.76	30	0	5.50
83	F3-45-Cs-i2	Cs	4.76	30	0	5.50
82	F3-45-Cs-i1	Cs	4.76	30	0	5.50
58	F3-32-Na1-i7	Na	3.12	5	0	8.58
57	F3-31-Li-i7	Li	3.28	5	0	9.62
56	F3-31-Li-i8	Li	3.28	5	0	9.62

		Clay	Slurry processing conditions			
Test	Sample name	Cation	Concentration	Sonication time	Stirring time	pH
#			clay g/100 ml UPW	min	h	
55	F3-47-Sr-i4	Sr	3.82	5	0	6.20
54	F3-47-Sr-i2	Sr	3.82	5	0	6.20
53	F3-44-Mg-i4	Mg	2.70	5	0	7.06
52	F3-44-Mg-i3	Mg	2.70	5	0	7.06
51	F3-44-Mg-i2	Mg	2.70	5	0	7.06
50	F3-44-Mg-i1	Mg	2.70	5	0	7.06
49	F3-43-K-i4	K	3.34	30	0	8.80
48	F3-43-K-i3	K	3.34	30	0	8.80
47	F3-43-K-i2	K	3.34	30	0	8.80
46	F3-43-K-i1	K	3.34	30	0	8.80
45	F3-38-OWE i9	RT3-OWE	4.24	5	0	6.60
44	F3-38-OWE i8	RT3-OWE	4.24	5	0	6.60
43	F3-38-OWE i7	RT3-OWE	4.24	5	0	6.60
42	F3-38-OWE i6	RT3-OWE	4.24	5	0	6.60
40	F3-38-OWE i6	RT3-OWE	4.24	5	0	6.60
39	F3-42 NH4 4i	NH	3.10	5	0	7.10
38	F3-42 NH4 3i	NH	3.10	5	0	7.10
37	F3-42 NH4 2i	NH	3.10	5	0	7.10
36	F3-42 NH4 1i	NH	3.10	5	0	7.10
35	F3-41 Na2 4i	Na	3.70	5	0	8.58
34	F3-41 Na2 3i	Na	3.70	5	0	8.58
33	F3-41 Na2 2i	Na	3.70	5	0	8.58
32	F3-41 Na2 1i	Na	3.70	5	0	8.58
31	F3-40 Na1 5i	Na	3.12	5	0	8.58
30	F3-40 Na1 4i	Na	3.12	5	0	8.58
29	F3-40 Na1 3i	Na	3.12	5	0	8.58
28	F3-40 Na1 2i	Na	3.12	5	0	8.58
27	F3-40 Na1 1i	Na	3.12	5	0	8.58
17	F3-Li-39i6	Li	3.12	5	0	9.62
16	F3-Li-39i5	Li	3.28	5	0	9.62
15	F3-Li-39i4	Li	3.28	5	0	9.62
14	F3-Li-39i3	Li	3.28	5	0	9.62

Table AIII-3. Slurry characterisation

		Clay	Slurry characterisation in Zetasizer							
Test	Sample name	Cation	ζ - potenti al	ζ - potential st. dev.	Number Mean (d)	Numb er Mean st. dev.	Z-average (d)	Z- average st. dev.	Polydi spersit y Index	Polydis persity Index st. dev.
#			mV	mV	nm	nm	nm	nm		
602	F3191015-Ba 30OU 4h-2	Ba	-27.1	0.4	2176	84	2194	44	0.16	0.10
601	F3191015-Ba 30OU4h-1	Ba	-27.1	0.4	2176	84	2194	44	0.16	0.10
600	F3191015-Sr 30OU 4h-2	Sr	-25.0	0.8	481	19	1636	14	0.25	0.03
599	F3191015-Sr 30OU 4h -1	Sr	-25.0	0.8	481	19	1636	14	0.25	0.03
598	F3191015-Mg 30OU 4h-4	Mg	-13.6	0.6	1184	123	1539	33	0.15	0.02
597	F3191015-Mg 30OU 4h-3	Mg	-13.6	0.6	1184	123	1539	33	0.15	0.02
596	F3191015-Mg 30OU 4h-2	Mg	-13.6	0.6	1184	123	1539	33	0.15	0.02
595	F3191015-Mg 30OU 4h-1	Mg	-13.6	0.6	1184	123	1539	33	0.15	0.02
594	F3191015-K 30OU 4h -2	K	-43.7	0.3	662	23	818	20	0.17	0.07
593	F3191015-K 30OU 4h-1	K	-43.7	0.3	662	23	818	20	0.17	0.07
592	F3191015-NH 30OU 4h-3	NH	-38.7	1.8	622	172	1069	20	0.18	0.03
591	F3191015-NH 30OU 4h-2	NH	-38.7	1.8	622	172	1069	20	0.18	0.03
590	F3191015-NH 30OU 4h-1	NH	-38.7	1.8	622	172	1069	20	0.18	0.03
589	F1021115-RT1b 30OU NS-3	RT1b	-42.7	0.7	597	107	983	25	0.22	0.04
588	F1021115-RT1b 30OU NS-2	RT1b	-42.7	0.7	597	107	983	25	0.22	0.04
587	F1021115-RT1b 30OU NS-1	RT1b	-42.7	0.7	597	107	983	25	0.22	0.04
586	F3021115-Ba 30OU NS top-3	Ba	-30.8	0.8	1165	93	1413	49	0.83	0.24
585	F3021115-Ba 30OU NS top-2	Ba	-30.8	0.8	1165	93	1413	49	0.83	0.24
584	F3021115-Ba 30OU NS top-1	Ba	-30.8	0.8	1165	93	1413	49	0.83	0.24
583	F3021115-Sr 30OU NS-3	Sr	-27.2	0.3	886	129	1153	75	0.80	0.29
582	F3021115-Sr 30OU NS-2	Sr	-27.2	0.3	886	129	1153	75	0.80	0.29
581	F3021115-Sr 30OU NS-1	Sr	-27.2	0.3	886	129	1153	75	0.80	0.29
580	F3021115-AAf 30OU NS-2	RT3-AAf	-47.6	0.2	211	49	624	13	0.42	0.01
579	F3021115-AAf 30OU NS-1	RT3-AAf	-47.6	0.2	211	49	624	13	0.42	0.01
578	F3021115-AAf 30OU NS-1	RT3-AAf	-47.6	0.2	211	49	624	13	0.42	0.01
577	F2021115-TH70 30OU NS-2	RT2	-46.5	1.7	189	13	627	7	0.30	0.01
576	F2021115-TH70 30OU NS-1	RT2	-46.5	1.7	189	13	627	7	0.30	0.01
575	F3021115-AA13 30OU NS-3	RT3-AA13	-32.7	0.9	778	19	1043	33	0.12	0.06
574	F3021115-AA13 30OU NS-2	RT3-AA13	-32.7	0.9	778	19	1043	33	0.12	0.06
573	F3021115-AA13 30OU NS-1	RT3-AA13	-32.7	0.9	778	19	1043	33	0.12	0.06
572	F3191015-Na 30OU 4h-3	Na	-48.5	0.3	230	9	900	59	0.52	0.05
571	F3191015-Na 30OU 4h-2	Na	-48.5	0.3	230	9	900	59	0.52	0.05
570	F3191015-Na 30OU 4h-1	Na	-48.5	0.3	230	9	900	59	0.52	0.05
569	F3191015-Li 30OU 4h-3	Li	-52.3	0.9	306	159	628	10	0.45	0.09
568	F3191015-Li 30OU 4h-2	Li	-52.3	0.9	306	159	628	10	0.45	0.09

		Clay	Slurry characterisation in Zetasizer							
Test	Sample name	Cation	ζ - potenti al	ζ - potential st. dev.	Number Mean (d)	Numb er Mean st. dev.	Z-average (d)	Z- average st. dev.	Polydi spersit y Index	Polydis persity Index st. dev.
#			mV	mV	nm	nm	nm	nm		
567	F3191015-Li 30OU 4h-1	Li	-52.3	0.9	306	159	628	10	0.45	0.09
566	F3021115-Ca 5OU 4h-3	Ca	-25.2	0.2	2010	73	2096	81	0.06	0.01
565	F3021115-Ca 5OU 4h-2	Ca	-25.2	0.2	2010	73	2096	81	0.06	0.01
564	F3021115-Ca 5OU 4h-1	Ca	-25.2	0.2	2010	73	2096	81	0.06	0.01
563	F3021115-Ca 30OU 4h-3	Ca	-24.4	0.1	894	158	1471	15	0.17	0.00
562	F3021115-Ca 30OU 4h-2	Ca	-24.4	0.1	894	158	1471	15	0.17	0.00
561	F3021115-Ca 30OU 4h-1	Ca	-24.4	0.1	894	158	1471	15	0.17	0.00
560	F3021115-Ca 30OU NS-3	Ca	-25.9	0.9	1089	65	1344	37	0.87	0.19
559	F3021115-Ca 30OU NS-2	Ca	-25.9	0.9	1089	65	1344	37	0.87	0.19
558	F3021115-Ca 30OU NS-1	Ca	-25.9	0.9	1089	65	1344	37	0.87	0.19
557	F3021115-Mg 30OU NS-1	Mg	-20.8	0.1	1365	157	1468	91	0.25	0.07
556	F3021115-Cs 30OU NS-3	Cs	-31.4	1.6	699	37	1159	15	0.17	0.02
555	F3021115-Cs 30OU NS-2	Cs	-31.4	1.6	699	37	1159	15	0.17	0.02
554	F3021115-Cs 30OU NS-1	Cs	-31.4	1.6	699	37	1159	15	0.17	0.02
553	F3021115-K 30OU NS-4	K	-49.6	1.5	663	10	804	11	0.09	0.02
552	F3021115-K 30OU NS-3	K	-49.6	1.5	663	10	804	11	0.09	0.02
551	F3021115-K 30OU NS-2	K	-49.6	1.5	663	10	804	11	0.09	0.02
550	F3021115-K 30OU NS-1	K	-49.6	1.5	663	10	804	11	0.09	0.02
549	F3021115-NH 30OU NS-3	NH	-37.4	0.6	677	160	1028	78	0.21	0.17
548	F3021115-NH 30OU NS-2	NH	-37.4	0.6	677	160	1028	78	0.21	0.17
547	F3021115-NH 30OU NS-1	NH	-37.4	0.6	677	160	1028	78	0.21	0.17
546	F3021115-Na 30OU NS-3	Na	-46.2	0.8	219	62	876	27	0.54	0.03
545	F3021115-Na 30OU NS-2	Na	-46.2	0.8	219	62	876	27	0.54	0.03
544	F3021115-Na 30OU NS -1	Na	-46.2	0.8	219	62	876	27	0.54	0.03
543	F3021115-Li 30OU NS-2	Li	-52.3	0.9	306	159	628	10	0.45	0.09
542	F3021115-Li 30OU NS-1	Li	-52.3	0.9	306	159	628	10	0.45	0.09
541	F3201213-Sr-3	Sr	-27.2	0.3	886	129	1153	75	0.80	0.29
540	F3201213-Sr-2	Sr	-27.2	0.3	886	129	1153	75	0.80	0.29
539	F3201213-Sr-1	Sr	-27.2	0.3	886	129	1153	75	0.80	0.29
350	F1250615DE-MgRT-NU30-3	Mg	-20.6	2.5	1125	601	1728	137	0.30	0.09
349	F1250615DE-MgRT-NU30-3	Mg	-20.6	2.5	1125	601	1728	137	0.30	0.09
348	F1250615DE-MgRT-NU30-2	Mg	-20.6	2.5	1125	601	1728	137	0.30	0.09
347	F1250615DE-MgRT-NU30-1	Mg	-20.6	2.5	1125	601	1728	137	0.30	0.09
346	F3250615DE-NH-NU5-2	NH	-38.2	0.2	1126	76	2650	199	1.00	0.00
345	F3250615DE-NH-NU5-1	NH	-38.2	0.2	1126	76	2650	199	1.00	0.00
344	F3230615DE-RT3Na-NU30-3	Na	-41.4	1.8	202	24	819	108	0.68	0.07
343	F3230615DE-RT3Na-NU30-2	Na	-41.4	1.8	202	24	819	108	0.68	0.07

		Clay	Slurry characterisation in Zetasizer							
Test	Sample name	Cation	ζ - potenti al	ζ - potential st. dev.	Number Mean (d)	Numb er Mean st. dev.	Z-average (d)	Z- average st. dev.	Polydi spersit y Index	Polydis persity Index st. dev.
#			mV	mV	nm	nm	nm	nm		
342	F3230615DE-RT3Na-NU30-1	Na	-41.4	1.8	202	24	819	108	0.68	0.07
341	F3230615DE-RT3Na-NU5-3	Na	-39.5	0.6	290	31	1080	54	0.63	0.03
340	F3230615DE-RT3Na-NU5-2	Na	-39.5	0.6	290	31	1080	54	0.63	0.03
339	F3230615DE-RT3Na-NU5-1	Na	-39.5	0.6	290	31	1080	54	0.63	0.03
338	F3240615DE-RT3Li-NU5-3	Li	-39.2	1.1	710	45	1235	50	0.33	0.18
337	F3240615DE-RT3Li-NU5-2	Li	-39.2	1.1	710	45	1235	50	0.33	0.18
336	F3240615DE-RT3Li-NU5-1	Li	-39.2	1.1	710	45	1235	50	0.33	0.18
335	F3240615DE-AA13-NU5-3	RT3-AA13	-45.0	1.3	1064	88	2280	44	1.00	0.00
334	F3240615DE-AA13-NU5-2	RT3-AA13	-45.0	1.3	1064	88	2280	44	1.00	0.00
333	F3240615DE-AA13-NU5-1	RT3-AA13	-45.0	1.3	1064	88	2280	44	1.00	0.00
332	F3240615DE-RT3NH-OU30-3	NH	-41.3	0.2	886	157	1214	54	0.22	0.14
331	F1240615DE-RT1b-NU5s-3	RT1b	-34.8	0.4	566	230	1249	26	0.26	0.01
330	F1240615DE-RT1b-NU5s-2	RT1b	-34.8	0.4	566	230	1249	26	0.26	0.01
329	F1240615DE-RT1b-NU5s-1	RT1b	-34.8	0.4	566	230	1249	26	0.26	0.01
328	F3240615DE-RT3Na-OU30-2	Na	-46.2	1.6	236	20	868	101	0.64	0.04
327	F3240615DE-RT3NH-OU30-2	NH	-41.3	0.2	886	157	1214	54	0.22	0.14
326	F3240615DE-RT3NH-OU30-1	NH	-41.3	0.2	886	157	1214	54	0.22	0.14
325	F3240615DE-RT3NH-OU5-3	NH	-37.7	1.3	1344	216	1764	178	0.38	0.13
324	F3240615DE-RT3NH-OU5-2	NH	-37.7	1.3	1344	216	1764	178	0.38	0.13
323	F3230615DE-RT3Na-OU5-3	Na	-39.2	1.6	275	24	1337	111	0.69	0.02
322	F3240615DE-RT3NH-OU5-1	NH	-37.7	1.3	1344	216	1764	178	0.38	0.13
321	F3230615DE-RT3Na-OU5-2	Na	-39.2	1.6	275	24	1337	111	0.69	0.02
320	F3240615DE-RT3Li-OU5-3	Li	-39.2	1.1	238	44	1078	101	0.58	0.04
319	F3240615DE-RT3Li-OU5-2	Li	-39.2	1.1	238	44	1078	101	0.58	0.04
318	F3240615DE-RT3Li-OU5-1	Li	-39.2	1.1	238	44	1078	101	0.58	0.04
317	F3240615DE-AAfOU5-3	RT3-AAf	-45.1	2.4	523	12	785	18	0.27	0.02
316	F3240615DE-AAfOU5-2	RT3-AAf	-45.1	2.4	523	12	785	18	0.27	0.02
315	F3240615DE-AAfOU5-1	RT3-AAf	-45.1	2.4	523	12	785	18	0.27	0.02
314	F3230615DE-AA13OU30-3	RT3-AA13	-39.3	0.6	812	148	1310	88	0.42	0.16
313	F3230615DE-AA13OU30-2	RT3-AA13	-39.3	0.6	812	148	1310	88	0.42	0.16
312	F3230615DE-AA13OU30-1	RT3-AA13	-39.3	0.6	812	148	1310	88	0.42	0.16
311	F3230615DE-AA13OU5-3	RT3-AA13	-45.2	2.3	1169	101	2060	126	0.36	0.10
310	F3230615DE-AA13OU5-2	RT3-AA13	-45.2	2.3	1169	101	2060	126	0.36	0.10
309	F3230615DE-AA13OU5-1	RT3-AA13	-45.2	2.3	1169	101	2060	126	0.36	0.10
308	F1-061113-RT1b-P-3	RT1b	-38.3	1.5	440	122	1244	67	0.24	0.02
307	F1-061113-RT1b-P-2	RT1b	-38.3	1.5	440	122	1244	67	0.24	0.02
306	F1-061113-RT1b-P-1	RT1b	-38.3	1.5	440	122	1244	67	0.24	0.02

		Clay	Slurry characterisation in Zetasizer							
Test	Sample name	Cation	ζ -potential	ζ -potential st. dev.	Number Mean (d)	Number Mean st. dev.	Z-average (d)	Z-average st. dev.	Polydispersity Index	Polydispersity Index st. dev.
#			mV	mV	nm	nm	nm	nm		
304	F2-121113-RT2pur-P-1	RT2								
301	F1-260415-RT1Li-2	Li	-47.2	1.5	204	11	850	28	0.56	0.04
300	F1-260415-RT1Li-1	Li	-47.2	1.5	204	11	850	28	0.56	0.04
299	F3-260415-RT3Li-1	Li	-47.2	1.5	204	11	850	28	0.56	0.04
298	F3-260415-RT3NH4-15-3	NH	-41.3	0.2	886	157	1214	54	0.22	0.14
297	F3-260415-RT3NH4-15-2	NH	-41.3	0.2	886	157	1214	54	0.22	0.14
296	F3-260415-RT3NH4-15-1	NH	-41.3	0.2	886	157	1214	54	0.22	0.14
295	F3-260415-RT3Na-3	Na	-46.2	1.6	236	20	868	101	0.64	0.04
294	F3-260415-RT3K-3	K								
293	F3-260415-RT3K-2	K								
292	F3-260415-RT3K-1	K								
291	F3-230415-RT3AA13wT-2	RT3-AA13	-39.3	0.6	812	148	1310	88	0.42	0.16
290	F3-230415-RT3AA13wT-1	RT3-AA13	-39.3	0.6	812	148	1310	88	0.42	0.16
289	F2-230415-RT2TH70 wT-3	RT2								
288	F2-230415-RT2TH70 wT-2	RT2								
287	F2-230415-RT2TH70 wT-1	RT2								
286	F1-230415-RT1b wT-3	RT1b	-31.7	1.3	470	91	881	18	0.28	0.01
285	F1-230415-RT1b wT-2	RT1b	-31.7	1.3	470	91	881	18	0.28	0.01
284	F1-230415-RT1b wT-1	RT1b	-31.7	1.3	470	91	881	18	0.28	0.01
283	F3-270115-NH4-14-3	NH	-41.3	0.2	886	157	1214	54	0.22	0.14
282	F3-270115-NH4-14-2	NH	-41.3	0.2	886	157	1214	54	0.22	0.14
281	F3-270115-NH4-14-1	NH	-41.3	0.2	886	157	1214	54	0.22	0.14
280	F3-200114-NH4-14-3	NH	-37.4	0.6	677	160	1028	78	0.21	0.17
279	F3-200114-NH4-14-2	NH	-37.4	0.6	677	160	1028	78	0.21	0.17
278	F3-200114-NH4-14-1	NH	-37.4	0.6	677	160	1028	78	0.21	0.17
277	F3-200114-Li13-3	Li	-42.2	1.2	721	36	826	31	0.14	0.08
276	F3-200114-Li13-2	Li	-42.2	1.2	721	36	826	31	0.14	0.08
275	F3-200114-Li13-1	Li	-42.2	1.2	721	36	826	31	0.14	0.08
274	F3-070414AAf4-3	RT3-AAf	-49.0	0.6	444	177	908	16	0.28	0.02
273	F3-070414AAf4-2	RT3-AAf	-49.0	0.6	444	177	908	16	0.28	0.02
272	F3-070414AAf4-1	RT3-AAf	-49.0	0.6	444	177	908	16	0.28	0.02
271	F3-070414AAf3-3	RT3-AAf	-49.0	0.6	444	177	908	16	0.28	0.02
270	F3-070414AAf3-2b	RT3-AAf	-49.0	0.6	444	177	908	16	0.28	0.02
269	F3-070414AAf3-2	RT3-AAf	-49.0	0.6	444	177	908	16	0.28	0.02
268	F3-070414AAf3-1	RT3-AAf	-49.0	0.6	444	177	908	16	0.28	0.02
267	F3-070414AAf2-2	RT3-AAf	-49.0	0.6	444	177	908	16	0.28	0.02
266	F3-070414AAf2-2	RT3-AAf	-49.0	0.6	444	177	908	16	0.28	0.02

		Clay	Slurry characterisation in Zetasizer							
Test	Sample name	Cation	ζ -potential	ζ -potential st. dev.	Number Mean (d)	Number Mean st. dev.	Z-average (d)	Z-average st. dev.	Polydispersity Index	Polydispersity Index st. dev.
#			mV	mV	nm	nm	nm	nm		
265	F3-070414AAf2-1	RT3-AAf	-49.0	0.6	444	177	908	16	0.28	0.02
264	F3-070414AAf1-3	RT3-AAf	-49.0	0.6	444	177	908	16	0.28	0.02
263	F3-070414AAf1-2	RT3-AAf	-49.0	0.6	444	177	908	16	0.28	0.02
262	F3-070414AAf1-1	RT3-AAf	-49.0	0.6	444	177	908	16	0.28	0.02
261	F3-201213-Cs-last1	Cs	-31.4	1.6	699	37	1159	15	0.17	0.02
260	F3-201213-NH4-13-2-3	NH	-37.4	0.6	677	160	1028	78	0.21	0.17
259	F3-201213-NH4-13-2-2b	NH	-37.4	0.6	677	160	1028	78	0.21	0.17
258	F3-201213-NH4-13-2-2	NH	-37.4	0.6	677	160	1028	78	0.21	0.17
257	F3-201213-NH4-13-2-1	NH	-37.4	0.6	677	160	1028	78	0.21	0.17
256	F3-201213-NH4-13-1-3	NH	-37.4	0.6	677	160	1028	78	0.21	0.17
253	F3-201213-NH4-13-1-2	NH	-37.4	0.6	677	160	1028	78	0.21	0.17
252	F3-201213-NH4-13-1	NH	-37.4	0.6	677	160	1028	78	0.21	0.17
251	F3-201213-Sr3-last2	Sr	-27.2	0.3	886	129	1153	75	0.80	0.29
250	F3-201213-Sr3-last1	Sr	-27.2	0.3	886	129	1153	75	0.80	0.29
249	F3201213-43-K-last3	K	-49.6	1.5	663	10	804	11	0.09	0.02
248	F3201213-43-K-last2	K	-49.6	1.5	663	10	804	11	0.09	0.02
247	F3201213-43-K-last1	K	-49.6	1.5	663	10	804	11	0.09	0.02
246	F3201213-42-NH4-12last3	NH	-39.1	0.2	1223	53	1459	89	0.66	0.30
245	F3201213-42-NH4-12last2	NH	-39.1	0.2	1223	53	1459	89	0.66	0.30
244	F3201213-42-NH4-12last1	NH	-39.1	0.2	1223	53	1459	89	0.66	0.30
243	F3201213-41-2-Na2last3	Na	-37.7	0.3	381	364	1375	90	0.51	0.07
242	F3201213-41-2-Na2last2	Na	-37.7	0.3	381	364	1375	90	0.51	0.07
241	F3201213-41-2-Na2last1	Na	-37.7	0.3	381	364	1375	90	0.51	0.07
240	F3201213-41-Na2last3	Na	-37.7	0.3	381	364	1375	90	0.51	0.07
239	F3201213-41-Na2last2	Na	-37.7	0.3	381	364	1375	90	0.51	0.07
238	F3201213-40-Na1last1	Na	-37.7	0.3	381	364	1375	90	0.51	0.07
237	F3201213-40-Na1last3	Na	-37.7	0.3	381	364	1375	90	0.51	0.07
236	F3201213-40-Na1last2	Na	-37.7	0.3	381	364	1375	90	0.51	0.07
235	F3201213-40-Na1last	Na	-37.7	0.3	381	364	1375	90	0.51	0.07
215	F2121113RT2TH70-3	RT2								
214	F2121113RT2TH70-2	RT2								
213	F2121113RT2TH70-1	RT2								
209	F1061113RT1m-3	RT1m	-5.3	1.2	440	122	1197	17	0.26	0.03
208	F1061113RT1m-2	RT1m	-5.3	1.2	440	122	1197	17	0.26	0.03
207	F1061113RT1m-1	RT1m	-5.3	1.2	440	122	1197	17	0.26	0.03
202	F1061113RT1b-3	RT1b	-38.3	1.5	440	122	1244	67	0.24	0.02
201	F1061113RT1b-2	RT1b	-38.3	1.5	440	122	1244	67	0.24	0.02

		Clay	Slurry characterisation in Zetasizer							
Test	Sample name	Cation	ζ -potential	ζ -potential st. dev.	Number Mean (d)	Number Mean st. dev.	Z-average (d)	Z-average st. dev.	Polydispersity Index	Polydispersity Index st. dev.
#			mV	mV	nm	nm	nm	nm		
200	F1061113RT1b-1	RT1b	-38.3	1.5	440	122	1244	67	0.24	0.02
182	F3180913RT3 100-3	RT3-OWE	-44.7	0.7	1271	164	1631	61	0.19	0.16
181	F3180913RT3 100-2	RT3-OWE	-44.7	0.7	1271	164	1631	61	0.19	0.16
180	F3180913RT3 100	RT3-OWE	-44.7	0.7	1271	164	1631	61	0.19	0.16
179	F3-49-OWF-P3	RT3-OWF	-44.7	0.7	1271	164	1631	61	0.19	0.16
178	F3-49-OWF-P2	RT3-OWF	-44.7	0.7	1271	164	1631	61	0.19	0.16
177	F3-49-OWF-P1	RT3-OWF	-44.7	0.7	1271	164	1631	61	0.19	0.16
176	F3-48-Sr-P3	Sr	-27.2	0.3	886	129	1153	75	0.80	0.29
175	F3-48-Sr-P2	Sr	-27.2	0.3	886	129	1153	75	0.80	0.29
174	F3-48-Sr-P1	Sr	-27.2	0.3	886	129	1153	75	0.80	0.29
173	F3-41-Na2-P4	Na	-37.7	0.3	381	364	1375	90	0.51	0.07
172	F3-41-Na2-P3	Na	-37.7	0.3	381	364	1375	90	0.51	0.07
171	F3-41-Na2-P2	Na	-37.7	0.3	381	364	1375	90	0.51	0.07
170	F3-41-Na2-P1	Na	-37.7	0.3	381	364	1375	90	0.51	0.07
97	F3-49-OWF 2i3	RT3-OWF	-44.7	0.7	1271	164	1631	61	0.19	0.16
96	F3-49-OWF 2 i2	RT3-OWF	-44.7	0.7	1271	164	1631	61	0.19	0.16
95	F3-49-OWF 2 i1	RT3-OWF	-44.7	0.7	1271	164	1631	61	0.19	0.16
94	F3-49-OWF i3	RT3-OWF	-44.7	0.7	1271	164	1631	61	0.19	0.16
93	F3-49-OWF i2	RT3-OWF	-44.7	0.7	1271	164	1631	61	0.19	0.16
92	F3-49-OWF i1	RT3-OWF	-44.7	0.7	1271	164	1631	61	0.19	0.16
91	F3-48-Sr-i3	Sr	-27.2	0.3	886	129	1153	75	0.80	0.29
90	F3-48-Sr-i2	Sr	-27.2	0.3	886	129	1153	75	0.80	0.29
89	F3-48-Sr-i1	Sr	-27.2	0.3	886	129	1153	75	0.80	0.29
88	F3-46-Ba-i3	Ba	-30.8	0.8	1165	93	1413	49	0.83	0.24
86	F3-46-Ba-i2	Ba	-30.8	0.8	1165	93	1413	49	0.83	0.24
85	F3-46-Ba-i1	Ba	-30.8	0.8	1165	93	1413	49	0.83	0.24
84	F3-45-Cs-i3	Cs	-31.4	1.6	699	37	1159	15	0.17	0.02
83	F3-45-Cs-i2	Cs	-31.4	1.6	699	37	1159	15	0.17	0.02
82	F3-45-Cs-i1	Cs	-31.4	1.6	699	37	1159	15	0.17	0.02
58	F3-32-Na1-i7	Na	-37.7	0.3	381	364	1375	90	0.51	0.07
57	F3-31-Li-i7	Li	-38.7	1.2	388	256	1191	46	0.62	0.02
56	F3-31-Li-i8	Li	-38.7	1.2	388	256	1191	46	0.62	0.02
55	F3-47-Sr-i4	Sr	-27.2	0.3	886	129	1153	75	0.80	0.29
54	F3-47-Sr-i2	Sr	-27.2	0.3	886	129	1153	75	0.80	0.29
53	F3-44-Mg-i4	Mg	-20.3	0.6	431	74	1436	36	0.35	0.06
52	F3-44-Mg-i3	Mg	-20.3	0.6	431	74	1436	36	0.35	0.06
51	F3-44-Mg-i2	Mg	-20.3	0.6	431	74	1436	36	0.35	0.06

		Clay	Slurry characterisation in Zetasizer							
Test	Sample name	Cation	ζ -potential	ζ -potential st. dev.	Number Mean (d)	Number Mean st. dev.	Z-average (d)	Z-average st. dev.	Polydispersity Index	Polydispersity Index st. dev.
#			mV	mV	nm	nm	nm	nm		
50	F3-44-Mg-i1	Mg	-20.3	0.6	431	74	1436	36	0.35	0.06
49	F3-43-K-i4	K	-49.6	1.5	663	10	804	11	0.09	0.02
48	F3-43-K-i3	K	-49.6	1.5	663	10	804	11	0.09	0.02
47	F3-43-K-i2	K	-49.6	1.5	663	10	804	11	0.09	0.02
46	F3-43-K-i1	K	-49.6	1.5	663	10	804	11	0.09	0.02
45	F3-38-OWE i9	RT3-OWE	-44.7	0.7	1271	164	1631	61	0.19	0.16
44	F3-38-OWE i8	RT3-OWE	-44.7	0.7	1271	164	1631	61	0.19	0.16
43	F3-38-OWE i7	RT3-OWE	-44.7	0.7	1271	164	1631	61	0.19	0.16
42	F3-38-OWE i6	RT3-OWE	-44.7	0.7	1271	164	1631	61	0.19	0.16
40	F3-38-OWE i6	RT3-OWE	-44.7	0.7	1271	164	1631	61	0.19	0.16
39	F3-42 NH4 4i	NH	-39.1	0.2	1223	53	1459	89	0.66	0.30
38	F3-42 NH4 3i	NH	-39.1	0.2	1223	53	1459	89	0.66	0.30
37	F3-42 NH4 2i	NH	-39.1	0.2	1223	53	1459	89	0.66	0.30
36	F3-42 NH4 1i	NH	-39.1	0.2	1223	53	1459	89	0.66	0.30
35	F3-41 Na2 4i	Na	-37.7	0.3	381	364	1375	90	0.51	0.07
34	F3-41 Na2 3i	Na	-37.7	0.3	381	364	1375	90	0.51	0.07
33	F3-41 Na2 2i	Na	-37.7	0.3	381	364	1375	90	0.51	0.07
32	F3-41 Na2 1i	Na	-37.7	0.3	381	364	1375	90	0.51	0.07
31	F3-40 Na1 5i	Na	-37.7	0.3	381	364	1375	90	0.51	0.07
30	F3-40 Na1 4i	Na	-37.7	0.3	381	364	1375	90	0.51	0.07
29	F3-40 Na1 3i	Na	-37.7	0.3	381	364	1375	90	0.51	0.07
28	F3-40 Na1 2i	Na	-37.7	0.3	381	364	1375	90	0.51	0.07
27	F3-40 Na1 1i	Na	-37.7	0.3	381	364	1375	90	0.51	0.07
17	F3-Li-39o6	Li	-42.6	6.8	388	256	1191	46	0.62	0.02
16	F3-Li-39i5	Li	-42.6	6.8	388	256	1191	46	0.62	0.02
15	F3-Li-39i4	Li	-42.6	6.8	388	256	1191	46	0.62	0.02
14	F3-Li-39i3	Li	-42.6	6.8	388	256	1191	46	0.62	0.02

Table AIII-4. Slurry characterisation in Malvern particle size analyser

Test	Sample name	Clay	Slurry characterisation in Malvern particle size analyser				
		Cation	Particle Size (μm)			Surface weighted mean	Volume weighted mean
			d (0.1)	d (0.5)	d (0.9)	d (3, 2)	d (4, 3)
#							
602	F3191015-Ba 30OU 4h-2	Ba	2.74	5.71	14.35	5.07	43.99
601	F3191015-Ba 30OU4h-1	Ba	2.74	5.71	14.35	5.07	43.99
600	F3191015-Sr 30OU 4h-2	Sr	2.88	6.27	761.02	5.63	145.51
599	F3191015-Sr 30OU 4h -1	Sr	2.88	6.27	761.02	5.63	145.51
598	F3191015-Mg 30OU 4h-4	Mg	2.80	5.72	12.01	4.98	6.72
597	F3191015-Mg 30OU 4h-3	Mg	2.80	5.72	12.01	4.98	6.72
596	F3191015-Mg 30OU 4h-2	Mg	2.80	5.72	12.01	4.98	6.72
595	F3191015-Mg 30OU 4h-1	Mg	2.80	5.72	12.01	4.98	6.72
594	F3191015-K 30OU 4h -2	K	3.62	9.98	969.60	8.34	257.45
593	F3191015-K 30OU 4h-1	K	3.62	9.98	969.60	8.34	257.45
592	F3191015-NH 30OU 4h-3	NH	3.56	8.91	546.61	7.37	116.60
591	F3191015-NH 30OU 4h-2	NH	3.56	8.91	546.61	7.37	116.60
590	F3191015-NH 30OU 4h-1	NH	3.56	8.91	546.61	7.37	116.60
589	F1021115-RT1b 30OU NS-3	RT1b	0.13	20.96	1324.14	0.50	478.46
588	F1021115-RT1b 30OU NS-2	RT1b	0.13	20.96	1324.14	0.50	478.46
587	F1021115-RT1b 30OU NS-1	RT1b	0.13	20.96	1324.14	0.50	478.46
586	F3021115-Ba 30OU NS top-3	Ba	2.73	5.70	13.79	5.03	28.92
585	F3021115-Ba 30OU NS top-2	Ba	2.73	5.70	13.79	5.03	28.92
584	F3021115-Ba 30OU NS top-1	Ba	2.73	5.70	13.79	5.03	28.92
583	F3021115-Sr 30OU NS-3	Sr	2.76	5.66	11.97	4.92	6.67
582	F3021115-Sr 30OU NS-2	Sr	2.76	5.66	11.97	4.92	6.67
581	F3021115-Sr 30OU NS-1	Sr	2.76	5.66	11.97	4.92	6.67
580	F3021115-AAf 30OU NS-2	RT3-AAf	0.12	556.21	1074.91	0.44	482.18
579	F3021115-AAf 30OU NS-1	RT3-AAf	0.12	556.21	1074.91	0.44	482.18
578	F3021115-AAf 30OU NS-1	RT3-AAf	0.12	556.21	1074.91	0.44	482.18
577	F2021115-TH70 30OU NS-2	RT2	1.78	5.70	18.50	1.16	8.15
576	F2021115-TH70 30OU NS-1	RT2	1.78	5.70	18.50	1.16	8.15
575	F3021115-AA13 30OU NS-3	RT3-AA13	3.30	6.96	15.50	5.98	8.55
574	F3021115-AA13 30OU NS-2	RT3-AA13	3.295	6.96	15.499	5.975	8.547
573	F3021115-AA13 30OU NS-1	RT3-AA13	3.295	6.96	15.499	5.975	8.547
572	F3191015-Na 30OU 4h-3	Na	2.705	5.825	17.903	5.147	47.267
571	F3191015-Na 30OU 4h-2	Na	2.705	5.825	17.903	5.147	47.267
570	F3191015-Na 30OU 4h-1	Na	2.705	5.825	17.903	5.147	47.267
569	F3191015-Li 30OU 4h-3	Li	4.171	18.278	1078.051	10.98	291.418
568	F3191015-Li 30OU 4h-2	Li	4.171	18.278	1078.051	10.98	291.418
567	F3191015-Li 30OU 4h-1	Li	4.171	18.278	1078.051	10.98	291.418

		Clay	Slurry characterisation in Malvern particle size analyser				
Test	Sample name	Cation	Particle Size (µm)			Surface weighted mean	Volume weighted mean
#			d (0.1)	d (0.5)	d (0.9)	d (3, 2)	d (4, 3)
566	F3021115-Ca 5OU 4h-3	Ca	3.238	7.267	17.404	6.106	9.149
565	F3021115-Ca 5OU 4h-2	Ca	3.238	7.267	17.404	6.106	9.149
564	F3021115-Ca 5OU 4h-1	Ca	3.238	7.267	17.404	6.106	9.149
563	F3021115-Ca 30OU 4h-3	Ca	2.964	6.35	14.663	5.452	7.906
562	F3021115-Ca 30OU 4h-2	Ca	2.964	6.35	14.663	5.452	7.906
561	F3021115-Ca 30OU 4h-1	Ca	2.964	6.35	14.663	5.452	7.906
560	F3021115-Ca 30OU NS-3	Ca	2.84	6.421	16.188	5.415	8.634
559	F3021115-Ca 30OU NS-2	Ca	2.84	6.421	16.188	5.415	8.634
558	F3021115-Ca 30OU NS-1	Ca	2.84	6.421	16.188	5.415	8.634
557	F3021115-Mg 30OU NS-1	Mg	2.815	5.862	14.064	5.172	28.267
556	F3021115-Cs 30OU NS-3	Cs	2.964	5.416	9.969	4.885	6.029
555	F3021115-Cs 30OU NS-2	Cs	2.964	5.416	9.969	4.885	6.029
554	F3021115-Cs 30OU NS-1	Cs	2.96	5.42	9.97	4.89	6.03
553	F3021115-K 30OU NS-4	K	3.04	6.41	13.37	5.48	7.42
552	F3021115-K 30OU NS-3	K	3.04	6.41	13.37	5.48	7.42
551	F3021115-K 30OU NS-2	K	3.04	6.41	13.37	5.48	7.42
550	F3021115-K 30OU NS-1	K	3.04	6.41	13.37	5.48	7.42
549	F3021115-NH 30OU NS-3	NH	3.52	8.69	346.14	7.18	83.06
548	F3021115-NH 30OU NS-2	NH	3.52	8.69	346.14	7.18	83.06
547	F3021115-NH 30OU NS-1	NH	3.52	8.69	346.14	7.18	83.06
546	F3021115-Na 30OU NS-3	Na	2.86	6.79	800.99	6.00	176.61
545	F3021115-Na 30OU NS-2	Na	2.86	6.79	800.99	6.00	176.61
544	F3021115-Na 30OU NS-1	Na	2.86	6.79	800.99	6.00	176.61
543	F3021115-Li 30OU NS-2	Li	7.58	80.24	1156.30	22.45	372.24
542	F3021115-Li 30OU NS-1	Li	7.58	80.24	1156.30	22.45	372.24
541	F3201213-Sr-3	Sr	2.763	5.657	11.969	4.923	6.672
540	F3201213-Sr-2	Sr	2.763	5.657	11.969	4.923	6.672
539	F3201213-Sr-1	Sr	2.763	5.657	11.969	4.923	6.672
350	F1250615DE-MgRT-NU30-3	Mg	0.11	3.21	20.42	0.34	13.92
349	F1250615DE-MgRT-NU30-3	Mg	0.11	3.21	20.42	0.34	13.92
348	F1250615DE-MgRT-NU30-2	Mg	0.11	3.214	20.424	0.344	13.917
347	F1250615DE-MgRT-NU30-1	Mg	0.11	3.21	20.42	0.34	13.92
346	F3250615DE-NH-NU5-2	NH	3.47	8.09	18.77	6.63	9.91
345	F3250615DE-NH-NU5-1	NH	3.47	8.09	18.77	6.63	9.91
344	F3230615DE-RT3Na-NU30-3	Na	2.66	6.40	40.29	5.42	45.83
343	F3230615DE-RT3Na-NU30-2	Na	2.66	6.40	40.29	5.42	45.83
342	F3230615DE-RT3Na-NU30-1	Na	2.66	6.40	40.29	5.42	45.83

Test	Sample name	Clay	Slurry characterisation in Malvern particle size analyser				
		Cation	Particle Size (µm)			Surface weighted mean	Volume weighted mean
			d (0.1)	d (0.5)	d (0.9)	d (3, 2)	d (4, 3)
#							
341	F3230615DE-RT3Na-NU5-3	Na	3.46	11.70	36.93	7.90	18.61
340	F3230615DE-RT3Na-NU5-2	Na	3.46	11.70	36.93	7.90	18.61
339	F3230615DE-RT3Na-NU5-1	Na	3.46	11.70	36.93	7.90	18.61
338	F3240615DE-RT3Li-NU5-3	Li	3.17	7.29	18.53	6.11	27.27
337	F3240615DE-RT3Li-NU5-2	Li	3.17	7.29	18.53	6.11	27.27
336	F3240615DE-RT3Li-NU5-1	Li	3.17	7.29	18.53	6.11	27.27
335	F3240615DE-AA13-NU5-3	RT3-AA13	3.43	7.96	19.36	6.57	10.09
334	F3240615DE-AA13-NU5-2	RT3-AA13	3.43	7.96	19.36	6.57	10.09
333	F3240615DE-AA13-NU5-1	RT3-AA13	3.43	7.96	19.36	6.57	10.09
332	F3240615DE-RT3NH-OU30-3	NH	3.51	8.45	26.62	7.00	78.55
331	F1240615DE-RT1b-NU5s-3	RT1b	0.16	17.98	1177.76	0.71	347.35
330	F1240615DE-RT1b-NU5s-2	RT1b	0.16	17.98	1177.76	0.71	347.35
329	F1240615DE-RT1b-NU5s-1	RT1b	0.16	17.98	1177.76	0.71	347.35
328	F3240615DE-RT3Na-OU30-2	Na	2.73	6.99	814.91	5.92	171.81
327	F3240615DE-RT3NH-OU30-2	NH	3.51	8.45	26.62	7.00	78.55
326	F3240615DE-RT3NH-OU30-1	NH	3.51	8.45	26.62	7.00	78.55
325	F3240615DE-RT3NH-OU5-3	NH	3.50	8.48	25.14	6.99	66.26
324	F3240615DE-RT3NH-OU5-2	NH	3.50	8.48	25.14	6.99	66.26
323	F3230615DE-RT3Na-OU5-3	Na	3.30	11.43	66.25	7.81	77.81
322	F3240615DE-RT3NH-OU5-1	NH	3.38	6.98	14.85	6.07	26.74
321	F3230615DE-RT3Na-OU5-2	Na	3.30	11.43	66.25	7.81	77.81
320	F3240615DE-RT3Li-OU5-3	Li	3.07	8.41	774.63	6.82	163.20
319	F3240615DE-RT3Li-OU5-2	Li	3.07	8.41	774.63	6.82	163.20
318	F3240615DE-RT3Li-OU5-1	Li	3.07	8.41	774.63	6.82	163.20
317	F3240615DE-AAfOU5-3	RT3-AAf	0.12	6.27	1136.00	0.39	325.26
316	F3240615DE-AAfOU5-2	RT3-AAf	0.12	6.27	1136.00	0.39	325.26
315	F3240615DE-AAfOU5-1	RT3-AAf	0.12	6.27	1136.00	0.39	325.26
314	F3230615DE-AA13OU30-3	RT3-AA13	3.37	8.25	31.55	6.84	86.04
313	F3230615DE-AA13OU30-2	RT3-AA13	3.37	8.25	31.55	6.84	86.04
312	F3230615DE-AA13OU30-1	RT3-AA13	3.37	8.25	31.55	6.84	86.04
311	F3230615DE-AA13OU5-3	RT3-AA13	3.27	7.99	21.59	6.50	22.39
310	F3230615DE-AA13OU5-2	RT3-AA13	3.27	7.99	21.59	6.50	22.39
309	F3230615DE-AA13OU5-1	RT3-AA13	3.27	7.99	21.59	6.50	22.39
308	F1-061113-RT1b-P-3	RT1b	0.15	16.14	1183.63	0.65	355.05
307	F1-061113-RT1b-P-2	RT1b	0.15	16.14	1183.63	0.65	355.05
306	F1-061113-RT1b-P-1	RT1b	0.15	16.14	1183.63	0.65	355.05
304	F2-121113-RT2pur-P-1	RT2	3.11	6.99	17.25	5.90	9.83

		Clay	Slurry characterisation in Malvern particle size analyser				
Test	Sample name	Cation	Particle Size (µm)			Surface weighted mean	Volume weighted mean
#			d (0.1)	d (0.5)	d (0.9)	d (3, 2)	d (4, 3)
301	F1-260415-RT1Li-2	Li	3.10	7.68	811.42	6.55	167.09
300	F1-260415-RT1Li-1	Li	3.10	7.68	811.42	6.55	167.09
299	F3-260415-RT3Li-1	Li	3.10	7.68	811.42	6.55	167.09
298	F3-260415-RT3NH4-15-3	NH	3.51	8.45	26.62	7.00	78.55
297	F3-260415-RT3NH4-15-2	NH	3.51	8.45	26.62	7.00	78.55
296	F3-260415-RT3NH4-15-1	NH	3.51	8.45	26.62	7.00	78.55
295	F3-260415-RT3Na-3	Na	2.73	6.99	814.91	5.92	171.81
294	F3-260415-RT3K-3	K					
293	F3-260415-RT3K-2	K					
292	F3-260415-RT3K-1	K					
291	F3-230415-RT3AA13wT-2	RT3-AA13	3.37	8.25	31.55	6.84	86.04
290	F3-230415-RT3AA13wT-1	RT3-AA13	3.37	8.25	31.55	6.84	86.04
289	F2-230415-RT2TH70 wT-3	RT2	3.11	6.99	17.25	5.90	9.83
288	F2-230415-RT2TH70 wT-2	RT2	3.11	6.99	17.25	5.90	9.83
287	F2-230415-RT2TH70 wT-1	RT2	3.11	6.99	17.25	5.90	9.83
286	F1-230415-RT1b wT-3	RT1b	0.12	10.83	1044.89	0.44	308.23
285	F1-230415-RT1b wT-2	RT1b	0.12	10.83	1044.89	0.44	308.23
284	F1-230415-RT1b wT-1	RT1b	0.12	10.83	1044.89	0.44	308.23
283	F3-270115-NH4-14-3	NH	3.51	8.45	26.62	7.00	78.55
282	F3-270115-NH4-14-2	NH	3.51	8.45	26.62	7.00	78.55
281	F3-270115-NH4-14-1	NH	3.51	8.45	26.62	7.00	78.55
280	F3-200114-NH4-14-3	NH	3.10	7.16	468.39	6.19	96.24
279	F3-200114-NH4-14-2	NH	3.10	7.16	468.39	6.19	96.24
278	F3-200114-NH4-14-1	NH	3.10	7.16	468.39	6.19	96.24
277	F3-200114-Li13-3	Li	2.98	7.32	881.61	6.37	195.52
276	F3-200114-Li13-2	Li	2.98	7.32	881.61	6.37	195.52
275	F3-200114-Li13-1	Li	2.98	7.32	881.61	6.37	195.52
274	F3-070414AAf4-3	RT3-AAf	0.11	6.70	912.29	0.37	200.44
273	F3-070414AAf4-2	RT3-AAf	0.11	6.70	912.29	0.37	200.44
272	F3-070414AAf4-1	RT3-AAf	0.11	6.70	912.29	0.37	200.44
271	F3-070414AAf3-3	RT3-AAf	0.11	6.70	912.29	0.37	200.44
270	F3-070414AAf3-2b	RT3-AAf	0.11	6.70	912.29	0.37	200.44
269	F3-070414AAf3-2	RT3-AAf	0.11	6.70	912.29	0.37	200.44
268	F3-070414AAf3-1	RT3-AAf	0.11	6.70	912.29	0.37	200.44
267	F3-070414AAf2-2	RT3-AAf	0.11	6.70	912.29	0.37	200.44
266	F3-070414AAf2-2	RT3-AAf	0.11	6.70	912.29	0.37	200.44
265	F3-070414AAf2-1	RT3-AAf	0.11	6.70	912.29	0.37	200.44

Test	Sample name	Clay	Slurry characterisation in Malvern particle size analyser				
		Cation	Particle Size (µm)			Surface weighted mean	Volume weighted mean
			d (0.1)	d (0.5)	d (0.9)	d (3, 2)	d (4, 3)
#							
264	F3-070414AAf1-3	RT3-AAf	0.11	6.70	912.29	0.37	200.44
263	F3-070414AAf1-2	RT3-AAf	0.11	6.70	912.29	0.37	200.44
262	F3-070414AAf1-1	RT3-AAf	0.11	6.70	912.29	0.37	200.44
261	F3-201213-Cs-last1	Cs	2.96	5.42	9.97	4.89	6.03
260	F3-201213-NH4-13-2-3	NH	3.10	7.16	468.39	6.19	96.24
259	F3-201213-NH4-13-2-2b	NH	3.10	7.16	468.39	6.19	96.24
258	F3-201213-NH4-13-2-2	NH	3.10	7.16	468.39	6.19	96.24
257	F3-201213-NH4-13-2-1	NH	3.10	7.16	468.39	6.19	96.24
256	F3-201213-NH4-13-1-3	NH	3.10	7.16	468.39	6.19	96.24
253	F3-201213-NH4-13-1-2	NH	3.10	7.16	468.39	6.19	96.24
252	F3-201213-NH4-13-1	NH	3.10	7.16	468.39	6.19	96.24
251	F3-201213-Sr3-last2	Sr	2.76	5.66	11.97	4.92	6.67
250	F3-201213-Sr3-last1	Sr	2.76	5.66	11.97	4.92	6.67
249	F3201213-43-K-last3	K	3.04	6.41	13.37	5.48	7.42
248	F3201213-43-K-last2	K	3.04	6.41	13.37	5.48	7.42
247	F3201213-43-K-last1	K	3.04	6.41	13.37	5.48	7.42
246	F3201213-42-NH4-12last3	NH	3.38	6.981	14.851	6.074	26.743
245	F3201213-42-NH4-12last2	NH	3.38	6.981	14.851	6.074	26.743
244	F3201213-42-NH4-12last1	NH	3.38	6.981	14.851	6.074	26.743
243	F3201213-41-2-Na2last3	Na	3.91	17.626	55.709	9.843	36.919
242	F3201213-41-2-Na2last2	Na	3.91	17.626	55.709	9.843	36.919
241	F3201213-41-2-Na2last1	Na	3.91	17.626	55.709	9.843	36.919
240	F3201213-41-Na2last3	Na	3.91	17.626	55.709	9.843	36.919
239	F3201213-41-Na2last2	Na	3.91	17.626	55.709	9.843	36.919
238	F3201213-40-Na1last1	Na	3.91	17.626	55.709	9.843	36.919
237	F3201213-40-Na1last3	Na	3.91	17.626	55.709	9.843	36.919
236	F3201213-40-Na1last2	Na	3.91	17.626	55.709	9.843	36.919
235	F3201213-40-Na1last	Na	3.91	17.626	55.709	9.843	36.919
215	F2121113RT2TH70-3	RT2	3.11	6.99	17.25	5.90	9.83
214	F2121113RT2TH70-2	RT2	3.11	6.99	17.25	5.90	9.83
213	F2121113RT2TH70-1	RT2	3.11	6.99	17.25	5.90	9.83
209	F1061113RT1m-3	RT1m	2.70	6.19	23.23	5.32	16.74
208	F1061113RT1m-2	RT1m	2.70	6.19	23.23	5.32	16.74
207	F1061113RT1m-1	RT1m	2.70	6.19	23.23	5.32	16.74
202	F1061113RT1b-3	RT1b	0.15	16.14	1183.63	0.65	355.05
201	F1061113RT1b-2	RT1b	0.15	16.14	1183.63	0.65	355.05
200	F1061113RT1b-1	RT1b	0.15	16.14	1183.63	0.65	355.05

Test	Sample name	Clay	Slurry characterisation in Malvern particle size analyser				
		Cation	Particle Size (µm)			Surface weighted mean	Volume weighted mean
			d (0.1)	d (0.5)	d (0.9)	d (3, 2)	d (4, 3)
182	F3180913RT3 100-3	RT3-OWE	11.52	6.97	3.53	8.69	23.12
181	F3180913RT3 100-2	RT3-OWE	11.52	6.97	3.53	8.69	23.12
180	F3180913RT3 100	RT3-OWE	11.52	6.97	3.53	8.69	23.12
179	F3-49-OWF-P3	RT3-OWF	3.41	7.81	18.24	6.47	9.64
178	F3-49-OWF-P2	RT3-OWF	3.41	7.81	18.24	6.47	9.64
177	F3-49-OWF-P1	RT3-OWF	3.41	7.81	18.24	6.47	9.64
176	F3-48-Sr-P3	Sr	2.76	5.66	11.97	4.92	6.67
175	F3-48-Sr-P2	Sr	2.76	5.66	11.97	4.92	6.67
174	F3-48-Sr-P1	Sr	2.76	5.66	11.97	4.92	6.67
173	F3-41-Na2-P4	Na	3.91	17.626	55.709	9.843	36.919
172	F3-41-Na2-P3	Na	3.91	17.626	55.709	9.843	36.919
171	F3-41-Na2-P2	Na	3.91	17.626	55.709	9.843	36.919
170	F3-41-Na2-P1	Na	3.91	17.626	55.709	9.843	36.919
97	F3-49-OWF 2i3	RT3-OWF	3.41	7.81	18.24	6.47	9.64
96	F3-49-OWF 2 i2	RT3-OWF	3.41	7.81	18.24	6.47	9.64
95	F3-49-OWF 2 i1	RT3-OWF	3.41	7.81	18.24	6.47	9.64
94	F3-49-OWF i3	RT3-OWF	3.41	7.81	18.24	6.47	9.64
93	F3-49-OWF i2	RT3-OWF	3.41	7.81	18.24	6.47	9.64
92	F3-49-OWF i1	RT3-OWF	3.41	7.81	18.24	6.47	9.64
91	F3-48-Sr-i3	Sr	2.76	5.66	11.97	4.92	6.67
90	F3-48-Sr-i2	Sr	2.76	5.66	11.97	4.92	6.67
89	F3-48-Sr-i1	Sr	2.76	5.66	11.97	4.92	6.67
88	F3-46-Ba-i3	Ba	2.73	5.70	13.79	5.03	28.92
86	F3-46-Ba-i2	Ba	2.73	5.70	13.79	5.03	28.92
85	F3-46-Ba-i1	Ba	2.73	5.70	13.79	5.03	28.92
84	F3-45-Cs-i3	Cs	2.96	5.42	9.97	4.89	6.03
83	F3-45-Cs-i2	Cs	2.96	5.42	9.97	4.89	6.03
82	F3-45-Cs-i1	Cs	2.96	5.42	9.97	4.89	6.03
58	F3-32-Na1-i7	Na	3.91	17.626	55.709	9.843	36.919
57	F3-31-Li-i7	Li	3.16	7.81	896.64	6.70	188.86
56	F3-31-Li-i8	Li	3.16	7.81	896.64	6.70	188.86
55	F3-47-Sr-i4	Sr	2.76	5.66	11.97	4.92	6.67
54	F3-47-Sr-i2	Sr	2.76	5.66	11.97	4.92	6.67
53	F3-44-Mg-i4	Mg	0.11	2.73	31.12	0.33	19.64
52	F3-44-Mg-i3	Mg	0.11	2.73	31.12	0.33	19.64
51	F3-44-Mg-i2	Mg	0.11	2.73	31.12	0.33	19.64
50	F3-44-Mg-i1	Mg	0.11	2.73	31.12	0.33	19.64

Test	Sample name	Clay	Slurry characterisation in Malvern particle size analyser				
		Cation	Particle Size (μm)			Surface weighted mean	Volume weighted mean
			d (0.1)	d (0.5)	d (0.9)	d (3, 2)	d (4, 3)
#							
49	F3-43-K-i4	K	3.04	6.41	13.37	5.48	7.42
48	F3-43-K-i3	K	3.04	6.41	13.37	5.48	7.42
47	F3-43-K-i2	K	3.04	6.41	13.37	5.48	7.42
46	F3-43-K-i1	K	3.04	6.41	13.37	5.48	7.42
45	F3-38-OWE i9	RT3-OWE	11.52	6.97	3.53	8.69	23.12
44	F3-38-OWE i8	RT3-OWE	11.52	6.97	3.53	8.69	23.12
43	F3-38-OWE i7	RT3-OWE	11.52	6.97	3.53	8.69	23.12
42	F3-38-OWE i6	RT3-OWE	11.52	6.97	3.53	8.69	23.12
40	F3-38-OWE i6	RT3-OWE	11.52	6.97	3.53	8.69	23.12
39	F3-42 NH4 4i	NH	3.38	6.98	14.85	6.07	26.74
38	F3-42 NH4 3i	NH	3.38	6.98	14.85	6.07	26.74
37	F3-42 NH4 2i	NH	3.38	6.98	14.85	6.07	26.74
36	F3-42 NH4 1i	NH	3.38	6.98	14.85	6.07	26.74
35	F3-41 Na2 4i	Na	3.91	17.63	55.71	9.84	36.92
34	F3-41 Na2 3i	Na	3.91	17.63	55.71	9.84	36.92
33	F3-41 Na2 2i	Na	3.91	17.63	55.71	9.84	36.92
32	F3-41 Na2 1i	Na	3.91	17.63	55.71	9.84	36.92
31	F3-40 Na1 5i	Na	3.91	17.63	55.71	9.84	36.92
30	F3-40 Na1 4i	Na	3.91	17.63	55.71	9.84	36.92
29	F3-40 Na1 3i	Na	3.91	17.63	55.71	9.84	36.92
28	F3-40 Na1 2i	Na	3.91	17.63	55.71	9.84	36.92
27	F3-40 Na1 1i	Na	3.91	17.63	55.71	9.84	36.92
17	F3-Li-39o6	Li	3.16	7.81	896.64	6.70	188.86
16	F3-Li-39i5	Li	3.16	7.81	896.64	6.70	188.86
15	F3-Li-39i4	Li	3.16	7.81	896.64	6.70	188.86
14	F3-Li-39i3	Li	3.16	7.81	896.64	6.70	188.86

Appendix IV. Publications emanating from this research

Atanasova, M.T., Vyalikh, A., Scheler, U., Focke, W.W., 2016. Characterisation of rectorite from the Beatrix Gold Mine in South Africa. *Applied Clay Science* 126, 7-16.

Atanasova, M.T., Focke, W.W., Loots, T., 2018. Self-assembled rectorite films with remarkable mechanical performance: preparation, structural characterisation and properties. Submitted for publication to *Applied Clay Science*, January 2018.

Atanasova, M.T., Focke, W.W., 2018. Flexible NH_4 -rectorite-chitosan bionanocomposite films with enhanced mechanical performance. In preparation for publication, January 2018.