A THESIS SUBMITTED IN THE FULFILMENT OF THE REQUIREMENTS FOR THE

DEGREE OF DOCTOR OF PHILOSOPHY

TEMPLATED SYNTHESIS OF TAILORED CLAYS
TO YIELD INCREASED PORE VOLUMES FOR
SORPTION AND EXCHANGE

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"The most exciting phrase to hear in science, the one that heralds new discoveries, is not 'Eureka!' but rather 'hmm.... that's funny...'

— Isaac Asimov.
DECLARATION

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**ABSTRACT**

The study aimed to enhance the textural properties of the synthetic hectorite clay Laponite RD. In the early 1990s Mobil Research and Development Corporation produced the first ordered mesoporous molecular sieves. This family of materials, M41S, were fabricated via liquid crystal templating (LCT), a technique involving the condensation and hydrolysis of a silica source around an organic template. As clays are primarily silicates, the question arises “Why not apply the same principles to enhance porosity characteristics of other silicates such as clays?”

Optimization of reagent concentrations, template choice, synthesis protocol and template removal strategy led to a maximum total pore volume of 0.95 cm$^3$ g$^{-1}$. This was achieved through templating Laponite RD with the neutral surfactant polyoxyethylene (20) sorbitan trioleate (Tween 85). This more than trebled the original total pore volume of Laponite RD, 0.27 cm$^3$ g$^{-1}$. An increase in modal pore diameter was also observed after use of this template; from 36.6 Å to 52.3 Å. Synthesis of Laponite-like compounds within the laboratory led to enhancement of porosity characteristics without templating; a total pore volume of 0.44 cm$^3$ g$^{-1}$ was observed for this synthetic hectorite (KP). Use of a template further enhanced the porosity characteristics of these samples. The cationic surfactant CTMA$^+$ (used in the original Mobil synthesis) led to a total pore volume of 0.60 cm$^3$ g$^{-1}$ for modified hectorite KP. A similar result, 0.65 cm$^3$ g$^{-1}$, was achieved through templating Laponite RD with this same surfactant.
Sorption and exchange properties of the newly modified hectorites were assessed by simple equilibrium batch testing methods using both single metal and multi-metal solutions. Hectorite KP samples removed a greater percentage of metal ions from aqueous solution than its Laponite RD analogues. For 5 mg dm$^{-3}$ single element solutions CTMA$^{+}$ modified hectorite removed > 95% of all eight metals tested. For solutions containing higher concentrations of ions the removal efficiency of all tested clays were reduced due to greater competition between ions. Partial interlayer collapse was observed during powder XRD studies, due to the acidic nature of the metal ion solutions.
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LIST OF ABBREVIATIONS

AAS       Atomic absorption spectrometry.
Brij 30   Polyoxyethylene (4) lauryl ether
Brij 35   Polyoxyethylene (23) lauryl ether
Brij 78   Polyoxyethylene (20) stearyl ether
CTMACl   Cetyltrimethyl ammonium chloride.
CTMABr   Cetyltrimethylammonium bromide
DTA       Differential thermal analysis
FT-IR     Fourier transform infrared spectroscopy.
MACl      Methylammonium chloride
MAS-NMR   Magic-angle-spinning nuclear magnetic resonance spectroscopy.
SEM       Scanning electron microscopy.
TBABr     Tetrabutylammonium bromide
TG        Thermogravimetry.
TMABr     Tetramethylammonium bromide
Tween 40  Polyoxyethylene (20) sorbitan monopalmitate
Tween 85  Polyoxyethylene (20) sorbitan trioleate
XRD       X-ray diffraction.
XRF       X-ray fluorescence analysis.
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CHAPTER 1

INTRODUCTION
The weathering and decomposition of igneous rocks results in the production of clay minerals. These earthy, fine grained materials, also known as hydrous layer silicates, form the most abundant sedimentary mineral group in the natural world.

No one knows when man first discovered clay’s potential to enhance everyday life, but the modern world would certainly be lost without argile, arcilla or lehm. Clay was, and still is a major component in the manufacture of bricks, pottery, tiles, etc., which are among the most ancient articles mankind has ever made. Indeed, the most common find at an archaeological site is a piece of clay tile or ceramic pot, which has survived many hundreds if not thousands of years. One of the first English written records of clay usage comes from the father of British printing, William Caxton (c.1421 - 1491). In 1480 he wrote “Whyte clay and reed for to make pottes, crokkes...and othir vessell” (1). Today, clay applications are much more diverse, ranging from molecular sieves to grandma’s best china, roof tiles to landfill liners, and cat litter to large pore catalysts in the petrochemical industry (2 - 4). This has resulted in clays ranking highly amongst the leading industrial minerals in terms of total monetary value and tonnage used (5).

Every gardener in Essex knows you don’t have to dig far to find bucket loads of clay, but as applications become more specialised this natural source needs modification. To this end, synthetic analogues, such as Laponite, have been developed. These compounds have fewer impurities and their properties may be tailored or enhanced to suit their intended purpose.

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1.1: Clay Classification and Structure

Clay is a generic name for many compounds (in geology the term “clay” also describes the particle size of the minerals as < 4 μm \(^{(6)}\)). The clay group may be sub-divided according to structural properties and the nature of isomorphous substitution experienced.

All clays are made from two fundamental building units: continuous 2D sheets of silica tetrahedra and layers of octahedrally co-ordinated metal oxides.

(i) Continuous 2D sheets of silica tetrahedra: these layers form a hexagonal network by sharing three basal oxygens; the fourth (apical) corner is perpendicular to the sheet. Figure 1.1.A illustrates an ideal hexagonal network of silica tetrahedra.

![Figure 1.1.A: Plan view of an ideal hexagonal network of silica tetrahedra](image)

(ii) Layers of octahedrally co-ordinated metal oxides. A sheet of metal ions (usually Al\(^{3+}\) or Mg\(^{2+}\)) is octahedrally co-ordinated by O\(^{2-}\) and/or OH\(^{-}\) ions. The individual octahedra are linked by sharing edges, as depicted in Figure 1.1.B.
There are two types of idealized octahedral layer, one which contains divalent cations (i.e. \( \text{Mg}^{2+} \)) and the other trivalent ones (i.e. \( \text{Al}^{3+} \)), as shown in Figure 1.1.C. These cations counteract the overall negative charge of the oxygens in the octahedral sheet (2- per octahedron) and form a tri- or di-octahedral layer, respectively. In the dioctahedral layer only two-thirds of the cationic positions are occupied.

The clay sheet is formed when these two layers undergo condensation - they now share the apical silicate oxygens. A 1:1 or 2:1 clay may be formed - the latter sandwiches an octahedral layer between two tetrahedral sheets, the upper layer being inverted. Figure 1.1.D shows both 1:1 and 2:1 clay layers.
As highlighted in Table 1.1.1, clays often undergo isomorphic substitution in both the tetrahedral and octahedral layers. In some cases vacant sites also occur. These factors combine to produce an overall negative charge on each layer which is balanced by interlayer cations. Stacking of clay layers occurs via electrostatic forces and sharing of cations such as Na\(^+\) or K\(^+\).

**TABLE 1.1.1: The classification of Smectite clays\(^{(9)}\).**

<table>
<thead>
<tr>
<th>Smectite Clays</th>
<th>Saponites (Trioctahedral)</th>
<th>Montmorillonites (Dioctahedral)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hectorite</td>
<td>Saponite</td>
<td>Montmorillonite</td>
</tr>
<tr>
<td>Mg(^{2+}) → Li(^+)</td>
<td>Si(^{4+}) → Al(^{3+})</td>
<td>Al(^{3+}) → Mg(^{2+})</td>
</tr>
<tr>
<td>in the octahedral...</td>
<td>in the tetrahedral...</td>
<td>in the octahedral...</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Si(^{4+}) → Al(^{3+})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>in the tetrahedral...</td>
</tr>
</tbody>
</table>

Laponites are high surface area synthetic hectorites, which belong to a sub-group of hydrous layer silicates known as smectites. Smectites consist of 2:1 type layers and contain exchangeable cations, as illustrated in Table 1.1.1.
1.2: PILLARED CLAY

A form of chemical tailoring which is commonly associated with smectite clays is pillaring \((10 \cdot 12)\). This process was developed to overcome the lack of permanent porosity which is related to this mineral class. The interlayer region is hydrophilic, addition of water leads to hydration of interlayer cations, which in turn leads to expansion of the clay interlayer volume. This swelling is, however, lost during dehydation. The use of molecular scale “pillars” to prop open and support the clay layers was adopted to resolve this problem. Porosity may, therefore, be maintained throughout the hydration-dehydration of these pillared compounds, Figure 1.2.A.

![Figure 1.2.A: Schematic diagram of the swelling of a non-pillared clay and of a rigid pillared clay](image)

Pillared clays may be prepared via an ion exchange reaction. This first step leads to direct intercalation of large (often metal-containing) cations between the clay sheets. Pillaring precursors are converted into oxide particles which bond to the clay layers, by thermal treatment (calcination) of the ion-exchanged clays, thus forming rigid pillars, Figure 1.2.B.
1.3: LAPONITE

1.3.1: SYNTHESIS

Laponite is an entirely synthetic substance. It is manufactured by combining sodium silicate solution with lithium carbonate, aqueous magnesium sulphate and sodium carbonate, under strictly controlled conditions. The first salt is dissolved in water and heated to 60°C; the latter two salts are then added slowly, while the temperature is maintained. After the slow addition of the sodium silicate solution, this precursor gel is heated to \( \approx 100^\circ C \) and left to reflux for several hours. This process yields an amorphous precipitate, which undergoes high temperature and pressure treatment in an autoclave where it becomes partially crystallised. This product is then filtered (giving “filtercake”) and may be washed, dried and milled to generate a fine white powder.
1.3.2: STRUCTURE

Laponite may be thought of as a two-dimensional inorganic polymer, whose layered structure leads to the formation of disc-shaped crystals, Figure 1.3.A, which can be dispersed in water. A typical Laponite crystal contains between 30000 and 40000 unit cells, and as such is considered a colloidal macromolecule.

![Single Laponite crystal](image)

**Figure 1.3.A: Single Laponite crystal**

Figure 1.3.B shows the idealised structure of Laponite. This idealised structure shows six octahedral magnesium ions sandwiched between two layers of four tetrahedral silicon atoms. Four hydroxyl groups and twenty oxygen atoms balance these groups. If ideal, the structure of the unit cell is neutral with a positive charge of twelve being donated by the six magnesium ions. Typically, however, some magnesium ions have been substituted by lithium ions, whilst other sites are vacant. This leads to a charge deficiency of 0.7 per formula unit and an empirical formula of $\text{Na}^{+}_{0.7} \left[ (\text{Si}_{8} \text{Mg}_{5.5} \text{Li}_{0.3})\text{O}_{20} \text{(OH)}_{4} \right]^{0.7-}$. During drying the negative charge is neutralised by the adsorption of sodium ions onto the crystals' surfaces. The crystals are held together in stacks electrostatically through sharing of sodium ions which occupy the inter particle region, Figure 1.3.C.
1.3.3: APPLICATIONS

Industrially Laponite has two key areas of use: (a) as a film former and (b) as a rheology modifier. Electrically conductive, antistatic and barrier coatings may be produced when Laponite is employed as a film forming agent, whilst this synthetic hectorite imparts shear sensitive viscosity, and improves stability and syneresis control, when added to the formulation of waterborne products such as household cleaners, personal care products and surface coatings \(^{(13)}\).

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Laponite has many other applications in a variety of industrial fields. The storage stability and flow control of paints, printing inks, varnishes, wood stains and other surface coatings are improved with the addition of this synthetic layered silicate. In agriculture, Laponite is used for rooting plant cuttings and as a medium for seed germination. It may also be employed to immobilise the aqueous phase of oil-in-water emulsions. Known to be a good proton conductor, Laponite may be used in energy storage and production i.e. in small-scale power generation and electric cars. It is also used in dielectric printing systems, as well as being a rheological additive in the construction industry. Modification of this material increases the range of applications still further i.e. fluorinated forms are used in toothpaste and pillared forms perform better as extractors because their gelling properties are reduced. A review of recent literature includes modified Laponite being used in catalysis, conductimetric microbiosensors, gas separating porous membranes, as a packing material for liquid chromatography, as a nanofiller in a direct methanol fuel cell and in the cathode of a lithium ion battery.

1.4: LIQUID CRYSTAL TEMPLATING

1.4.1: DISCOVERY

A wide variety of inorganic species are used in industry today as adsorbents, catalysts, catalytic supports and molecular sieves. By far the most investigated of these are the microporous zeolites, which have high surface areas and consequently high adsorption capacities. These crystalline materials also have narrow pore size distributions and controllable adsorption properties, allowing the nature of their pores to be tailored to specific reactions. Many chemical reactions, however, require compounds with larger pore sizes, and hence there is growing interest in the field of mesoporous inorganic solids, specifically in terms of the porosity control of these materials.
The most important development in this area of study occurred in 1992 when scientists at Mobil Research and Development Corporation produced the first ordered mesoporous molecular sieves – a family of silica based compounds known as M41S \(^{(31)}\).

### 1.4.2: MECHANISM

Mobil proposed that the mechanism of formation for these compounds involved liquid crystal templating (LCT). The synthesis involved a cationic surfactant and silica source being brought together in alkali solution, and coprecipitated to form \( S^I \) (where \( S \) = a surfactant and \( I \) = an inorganic molecular species). Shifts in surfactant molecule ordering in an aqueous environment, Figure 1.4.A, from micellar to liquid crystal phases, led to the conclusion that in the presence of silicate ions, these organic species were acting as templates for the creation of MCM-41.

![Figure 1.4.A: Effect of increasing concentration and temperature on the phase of a typical surfactant](image)

**Figure 1.4.A:** Effect of increasing concentration and temperature on the phase of a typical surfactant \(^{(34)}\).
MCM-41 is a subdivision of the M41S family, which exhibits a hexagonal array of uniform mesopores. Surfactants can have two other mesophases, cubic (MCM-48) and lamellar (MCM-50), but hexagonal liquid crystals have the most ideal morphology. In particular, templated lamellar structures are known to collapse upon template removal.

The LCT mechanism proposed by Mobil for MCM-41 synthesis begins with the aggregation of surfactant micelles to produce micellar rods, Figure 1.4.B, route 1. In solution a hexagonal array of these structures is known to exist. This configuration is then surrounded by silicate which acts as a ceramic mould. The surfactant may then be removed by heating, thereby leaving envelopes in the mould—pores.

**Figure 1.4.B:** The possible mechanisms involved in MCM-41 formation.\(^{31,35}\)
However, the mechanism proposed by Mobil researchers may not be entirely correct \(^{(35-37)}\). The formation of micelles and liquid crystal phases of surfactants requires a concentration of template significantly higher than that used in Mobil's synthesis. At concentrations below this critical micelle concentration one would not expect micelles to form. Therefore aggregation of molecules must be initiated by some other factor. Vartuli et al\(^{(35)}\) proposed that the silicate anions promote micelle formation through charge balancing interactions with the cationic surfactant, Figure 1.4.B route 2.

1.4.3: ADAPTATION

Since Mobil's initial breakthrough, research into the production of ordered mesoporous materials has become widespread. Whilst some researchers try to uncover the secrets of how the process works \(^{(28-43)}\), others have adapted the mechanism by employing anionic, amphoteric or even non-ionic surfactants \(^{(44-49)}\). Numerous research groups have also begun work to introduce catalytic activity into these inert substances by the incorporation of catalytically active atoms into the framework \(^{(50-52)}\). In addition, investigators are trying to determine whether the same mechanism may be employed to create similar frameworks with different compositions \(^{(53-58)}\), an area that may be potentially fruitful for future research \(^{(59)}\).

Investigations into improving the porosity of ordered mesoporous silicates have led to the use of a wide variety of templates. Globular quaternary templates are used to increase order within zeolite systems \(^{(28-30)}\). However, these ions act as single cavity templates which means that pore structure is limited by the size of the globular quaternary template used.

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Larger pore dimensions are created using surfactants which aggregate, thus allowing larger templates to form. The use of surfactants with long hydrophobic tails and large hydrophilic head groups has been studied. It has been noted that a balance between head size and tail length must be achieved for cylindrical micelles to form. Ryoo and co-workers proposed that a combination of two surfactants with varying head size could lead to more balanced and uniform micelle formation \(^{60}\). Figure 1.4.C illustrates this phenomenon.

**FIGURE 1.4.C:** Cross-section of surfactant micelles with (a) small head groups *e.g.* NMe\(_3\), (b) larger head groups *e.g.* NEt\(_3\) and (c) a mixture of surfactants \(^{60}\).

As well as the effect of the size and charge (cationic, anionic, non-ionic or amphoteric) of a template, the use of pore swelling agents has also been studied \(^{61}\). The use of solubilizing agents such as mesitylene (1,3,5-trimethylbenzene) \(^{39, 62}\) and straight chain alkanes \(^{63}\) have led to further increases in pore size when combined with traditional templates \(^{64}\).
Figure 1.4.D: Cross section of surfactant micelles (a) without solubilizing agent and (b) with normal alkanes as solubilizing agents \(^{(63)}\).

Figure 1.4.D demonstrates the pore swelling nature of a normal alkane. Ulagappan and Rao demonstrated that for normal alkanes with 9 to 15 carbon atoms expansion was directly related to the length of the hydrocarbon, e.g., templating with CTMABr alone leads to a \(d_{100}\) spacing of 39 Å for a mesoporous silica, whilst the addition of \(C_{14}H_{30}\) (chain length of 16.6 Å) leads to an observed \(d_{100}\) of 73.6 Å, which is very close to the predicted 72.2 Å \(^{(63)}\).

As well as the use of different templates, investigations into template removal strategy have led to numerous new fields of study. From simple calcination to remove the organic moiety \(^{(31, 65)}\) to producing organic sieves from inorganic templates \(^{(66 - 67)}\), the possibilities seem endless. One area producing a wealth of current literature involves only partial removal of the template. Instead of impregnating the inert inorganic sieve with active metal species, such as palladium \(^{(68)}\) or cobalt \(^{(69)}\) post LCT, appropriate choices of template during synthesis could lead to the production of a pre-functionalised sieve \(^{(70 - 76)}\).
The appropriate choice of template and inorganic species leads to inorganic-organic hybrids, or nanocomposites, with a wide variety of applications: as well as catalytic applications (77), a review of recent literature includes studies on fields as diverse as battery applications (78–79), removal of mercury ions (80), food packaging (81), gas sensors (82–83) and space applications (84).

1.5: APPLICATION

1.5.1: POLLUTION

The old seafaring complaint of “water, water everywhere, but not a drop to drink” is no longer restricted to the ocean. The extent of water pollution is increasing at a worrying rate. This may be observed in litter choked canals, full of shopping trolleys and crisp packets, as well as tin cans and plastic bottles washed up on the shoreline. More worrying are the less obvious effects, unseen pollution due to modern farming methods and commercial ignorance. Even the release of industrial cooling water back into a river at a temperature higher than it was removed from the water course (thus lowering its oxygen content) can lead to devastating effects for local wildlife (85). Sometimes pollution may be adapted to (e.g. waterfowl may nest in a waterway’s crisp packets, Figure 1.5.A), but most types of pollution must be removed or dramatically reduced as quickly as possible. The main types of pollution include the over concentration of “natural” pollutants e.g. the introduction of soluble phosphate (from detergents in urban waste) can lead to algal blooms which severely reduce oxygen content and can potentially destroy all local aquatic life (except anaerobic bacteria), and the introduction of “chemicals” not known in nature (e.g. organochloro pesticides entering rivers and underground water deposits) (86).
The introduction of new chemicals into an aquatic ecosystem is further split into discreet releases such as oil spills from tankers which have run aground and releases which may be monitored and regulated e.g. industrial effluent. The Water Resources Act 1991 states that it is an offence to either cause or knowingly permit the discharge of any (i) poisonous, noxious or polluting matter, or (ii) any trade or sewage effluent, into controlled waters, whether or not it is potentially harmful (87). Urban run-off and stormwater are not discreet releases but neither can they be regulated like industrial effluent. To reduce the risk to the environment from such sources, preventative measures need to be adopted, such as detention ponds at the side of motorways which are used to trap heavy metals and hydrocarbons present in road run-off. Many heavy metals occur naturally in the environment. In fact most are essential nutrients, but only at low levels. At higher levels many metals bioaccumulate within aquatic species and can, therefore, be transferred up the food chain. The main sources of metal pollution in water are from mining and the automobile industry. Surprisingly engine emissions account for less than 5% of traffic related pollution (88); other contributors include road surface degradation, tyre wear, metal corrosion and wear, batteries and road de-icing (89).
1.5.2: REMEDIATION

Clearly for such a variety of types of water pollution there will be a wide range of remediation techniques. Gone are the days when “the solution to pollution was dilution” \(^{(90)}\). Potable water undergoes rigorous procedures to comply with drinking water standards \(^{(91)}\); these may include pre-treatment (with or without chemicals), mixing, coagulation, flocculation, settlement, filtration and sterilisation. Whether all the steps in this process are required is dependent on the nature of the source water and the quality of water required for supply. Settlement can remove up to 90% of suspended solids, so is often the key step in the water treatment process \(^{(92)}\). Filtering also removes suspended solids and microbiological treatment can remove soluble organic material, but this can lead to high carbon dioxide levels and low oxygen content. Quality standards for industrial effluents are generally defined by discharge consents issued by the Environment Agency (EA). The removal of inorganic species is achieved through precipitation, adsorption or ion-exchange. Precipitation may be achieved through an increase in pH or interactions with sulphates to produce metal sulphides. Lignite will remove cadmium, lead and other heavy metals through adsorption. Peat is capable of removing toxic metals such as mercury, cadmium and lead from wastewaters, as long as there is a low flow rate, \textit{via} ion-exchange. Natural sediment is also known to adsorb and complex with metals in the environment. The use of a combination of these processes will purify drinking water and in most cases prevent contamination of natural waterways. However, novel sorbents are still required to tackle new types of discharge and to combat pollution released through urban run-off, stormwater and discreet releases \(^{(93-101)}\).
1.6: AIMS AND OBJECTIVES

The basis of syntheses carried out by Mobil Research and Development Corporation, to produce ordered mesoporous molecular sieves, is the condensation and hydrolysis of a silica source around an organic template to form the hexagonal array of mesopores found in MCM-41\(^{62}\). As clay is primarily a metallo-silicate, the question arises “Why not apply the same principles to enhance porosity characteristics of other silicates such as clays?”

The aim of this study is to enhance the textural properties of the synthetic hectorite clay Laponite RD, relative to commercial samples provided by Rockwood Additives Ltd. In particular, increases in specific surface area, total pore volume and modal mesopore diameter are anticipated through an appropriate choice of surfactant, reagent concentrations, synthesis protocol and template removal strategy. Comparison with parent materials and alternative methods of tailoring, such as pillaring with the aluminium keggin ion ([Al\(_{13}\)O\(_4\)(OH)\(_{24}\)(H\(_2\)O)\(_{12}\)]\(^{7+}\), “Al\(_{13}^{7+}\”) will also be carried out. The characteristics of these tailored materials will be determined via nitrogen sorption porosimetry, X-ray powder diffraction, XRF analysis, FT-IR spectroscopy, elemental microanalysis, and solid state MAS-NMR. After porosity enhancement studies have taken place, investigations into the nature and efficiency of metal ion adsorption will be carried out. Atomic absorption spectrometry will be employed to determine the extent of adsorption and/or ion exchange achieved with unmodified and modified Laponite and hectorite materials.
REFERENCES


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CHAPTER 2

CHARACTERIZATION TECHNIQUES: PRINCIPLES
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CHARACTERIZATION TECHNIQUES: PRINCIPLES

To achieve the aims of this study, a wide range of characterization techniques were employed. These analyses established a variety of properties associated with the parent materials and determined the nature and extent of modification achieved through the tailoring of these synthetic hectorite systems. The analytical technique, atomic absorption spectrometry, allowed preliminary investigations into the sorption properties of these newly modified materials to take place.

This chapter introduces the relevant theory behind these techniques, whilst the particular experimental parameters used in this study are defined Chapter 3.

2.1: X-RAY METHODS

Since their accidental discovery in 1895 by Wilhelm Conrad Röntgen, X-rays have found a variety of uses in the modern world. In particular, radiography, fluorescence and crystallography may be employed for analytical purposes: the first of these allows detection of cracks and defects in solid materials, the second allows both qualitative and quantitative determination of the elemental composition of a substance, and the third gives insight into the crystal structure, particle size and, for our needs, pore periodicity in ordered porous compounds.
2.1.1: X-RAY PRODUCTION

When high speed electrons hit a solid object X-rays are generated. Therefore to produce X-rays a source of electrons, a means of accelerating the electrons and a target to stop the electrons are required \(^{(1)}\). Modern spectrometers use an X-ray tube to generate X-rays. An electrically heated tungsten filament produces electrons, which are accelerated towards a metal (normally copper) target by the application of a large potential difference (voltage) between the filament and target. A high vacuum is produced via evacuation of the X-ray tube to allow free flight of the electrons. The majority of the electrons are stopped by the target and their kinetic energy is converted into radiation energy. Other electrons, however, only have partial energy conversion and continue to collide with other target atoms, gradually converting all of their energy. This leads to a continuous range of wavelengths and hence a spectrum of “white” (or “background”) radiation. For analysis, however, a monochromatic beam (x-rays of a single wavelength) is required. Unwanted X-ray lines are removed by a crystal monochromator. The crystal, often graphite, is used as a filter; it is orientated so that it only diffracts K\(\alpha\) radiation, and not K\(\beta\) radiation \(^{(2)}\).

2.1.2: POWDER X-RAY DIFFRACTION

X-ray diffraction (XRD) was developed to determine the internal structure of solids. It is based on the German physicist Max von Laue’s theory \(^{(1)}\) that a crystal contains a regular array of atoms and that this array may act as a three dimensional diffraction grating for radiation with a wavelength comparable to the interatomic spacing.
The reflected X-ray beams experience constructive and destructive interference. When a sample is positioned between an X-ray source and a photographic plate or other detector, the resultant diffraction pattern illustrates constructive interference. When two or more reflected X-rays are in phase with each other they satisfy the Bragg condition:

\[ \lambda = 2d \sin \theta \]

where \( d \) = the interplanar spacing,
\( \theta \) = the incident angle
\( \lambda \) = the path difference, which in this case is equal to an X-ray wavelength.

This may be explained by reference to Figure 2.1.A.

**Figure 2.1.A**: Diagram representing the Bragg condition \(^{(1)}\). (CD + DE = n\lambda)

From this figure it can be seen that X-ray B travels a further distance, CDE, relative to X-ray A. \( DE = CD = d \sin \theta \). So the total extra distance = \( 2d \sin \theta \). For constructive interference between the two X-rays this path length must equal a whole number of wavelengths \((i.e. n \lambda = 2d \sin \theta)\); this is Bragg’s Law. Usually \( n \) is fixed at 1, so that \( \lambda = 2d \sin \theta \).
Following Laue’s experiments with single crystals in the early twentieth century, X-ray powder diffraction was developed almost simultaneously in Germany (Debye and Scherrer, 1916) and the USA (Hull, 1917). The nature of the sample, a fine powder, allows all the small crystallites to be orientated in all directions with respect to the incident beam, including the Bragg angle, θ. The sample may be scanned over the relevant 2θ range and information on sample purity and pore periodicity is deduced from the resulting diffraction pattern.

Powder X-ray diffraction may also be used with amorphous solids. There is no regular atomic array to act as a diffraction grating; instead ordered porous systems use the periodicity of their pores. Thus the repeat distance, $a_0$, of such a porous amorphous solid may be measured. This cannot be equated to the pore diameter, as it is the sum of this value and the thickness of the pore wall (Figure 2.1.B). The repeat distance, $a_0$, has been related to $d_{100}$ for certain compounds: e.g., $a_0 = \frac{2}{\sqrt{3}}d_{100}$ for the hexagonal array of MCM-41.

**Figure 2.1.B:** The relationship between $a_0$ and $d_{100}$ in MCM-41.
2.1.3: X-RAY FLUORESCENCE SPECTROMETRY

X-ray fluorescence spectrometry is a method of elemental analysis, which gives both qualitative and quantitative information. Electrons are ejected from the inner shells of a sample's atoms when it is bombarded with a monochromatic X-ray beam of sufficient energy. Outer shell electrons transfer to these vacant sites, during which process energy is released in the form of X-rays. The resulting fluorescent radiation is separated by an analysing crystal, which reflects the X-ray beam each time the Bragg equation is fulfilled. Due to quantised Z-dependent energy levels (where Z is atomic number), each element within the sample produces its own unique series of lines.

For qualitative analysis the technique exploits the fact that every element fluoresces at different specific wavelengths. For unknown samples a pattern is produced that can then be compared to a set of tables, hence determining the components of the material. Quantitative analysis focuses on one part of the spectrum and measures the intensity of a particular element's characteristic lines. This intensity may then be related to its concentration via standard samples of known composition. However, XRF cannot detect elements lighter than Neon, such as Lithium.

2.2: INFRARED SPECTROSCOPY

Infrared (IR) spectroscopy is based on the principle that the absorption of IR radiation by a material leads to a transition between vibrational energy levels. These vibrations must involve a changing dipole moment and may be observed as "stretches", "bends" or "deformations" of a molecule or (in extended solids) groups of atoms. Organic functional groups and inorganic constituent units each absorb the radiation at a specific wavelength and may therefore be identified on an IR spectrum.
Vibrational spectroscopies, such as infrared, are sensitive to short-range order, and therefore provide useful structural information for clay minerals. Constituent units (i.e. hydroxyl groups, the silicate anion, octahedral cations and interlayer cations) may be identified from the spectra of layered silicates. In this study the technique is mainly used as a tool to determine whether organic template removal has occurred. IR spectroscopy is routinely used as a qualitative method and should be used in conjunction with other analyses e.g. elemental CHN analysis.

Fourier transform infrared (FT-IR) spectroscopy was used in this study. The Fourier transformation is a mathematical method which allows data recorded as a time domain spectrum to be converted into the frequency domain. This process improves signal to noise ratios and decreases experimental time e.g. applying FT-IR methodology to spectrum recorded over the 4000 to 400 cm\(^{-1}\) frequency range, with a resolution of 1 cm\(^{-1}\) and the number of resolution elements, n, equal to 3600, leads to an improvement of \(n^{1/2} = 60\). Therefore, the 10 min normally taken to record a dispersive spectrum is reduced to 10 s for an FT-IR spectrum with the same signal to noise ratio.

2.3: GAS ADSORPTION STUDIES

2.3.1: PRINCIPLES

The definition of adsorption according to IUPAC is “the enrichment or depletion of one or more components in an interfacial layer”. It is a phenomenon solid surfaces experience when they are exposed to fluids (either gases or liquids). Porosity is the degree to which a solid material is permeated with pores (narrow channels or cavities) through which a liquid or gas may travel. To be labelled a pore, each cavity must be deeper than it is wide.
Figure 2.3.A illustrates a variety of different pore types. Closed pores are unlikely to contribute to measures of porosity due to their isolated nature. Ink bottle shaped pores lead to differences between measures of adsorption and desorption, by restricting and therefore slowing the latter process. The extent of porosity often leads to materials with internal surface areas far greater than their external surface areas e.g. MCM-41 can have a specific surface area in excess of 1000 m$^2$ g$^{-1}$. Porous materials, such as clays, with high or very high specific surface areas, are therefore considered to be good adsorbents.

\[ \text{Adsorption isotherms are graphical representations of the relationship between the relative gas pressure (p/p}_0) \text{ and the amount of gas adsorbed per unit mass of solid (n/mol), at a specific temperature. Solid materials which undergo physisorption while not interacting chemically (chemisorption) with gaseous substances, produce one of six types of isotherms as described by Brunauer, Deming, Deming and Teller in 1940. Figure 2.3.B illustrates these isotherms and Table 2.3.I describes the materials related to each isotherm.} \]
Figure 2.3.B: The five BDDT isotherm types (I - V) along with the rare, stepped isotherm (Type VI)\(^{(11)}\).

Table 2.3.1: The classification of materials described by the BDDT isotherms\(^{(12)}\).

<table>
<thead>
<tr>
<th>Isotherm Type</th>
<th>Characteristic of:</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Microporous solids</td>
</tr>
<tr>
<td>II</td>
<td>Non-porous solids</td>
</tr>
<tr>
<td>III</td>
<td>Weak adsorbent-adsorbate interactions in non-porous or macro porous solids</td>
</tr>
<tr>
<td>IV</td>
<td>Mesoporous solids</td>
</tr>
<tr>
<td>V</td>
<td>Weak adsorbent-adsorbate interactions in mesoporous or microporous solids</td>
</tr>
<tr>
<td>VI</td>
<td>Very rare - demonstrates stepwise layer-by-layer adsorption on a highly uniform surface(^{(13)})</td>
</tr>
</tbody>
</table>

Type IV and V isotherms both exhibit hysteresis loops, which signify differential adsorption/desorption of gas due to the different rates at which filling (capillary condensation) and emptying (capillary evaporation) of the pores occurs. Gas condensation (adsorption) may occur simultaneously along the whole length of the pore and is therefore fairly rapid, Figure 2.3.C a. In contrast, capillary evaporation (desorption) can only occur from the relatively small meniscus area, Figure 2.3.C b\(^{(14)}\). If the porosity is uniform, a single “step” in the isotherm is observed.
Type IV isotherms may be further characterised by the shape of the hysteresis loop. IUPAC have classified the loops into four types: H1, H2, H3 and H4 (15). As may be seen in Figure 2.3.D, H1 and H4 represent the two extremes; the former has a nearly vertical hysteresis with a very narrow pressure range and the latter hysteresis is nearly horizontal. H2 and H3 may be taken as intermediates between these two extremes.

Each type of loop has been associated with a characteristic pore structure. Agglomerates of spheroidal particles or solids with nearly cylindrical pores produce type H1 or H2 (and intervening) loops. Channels of uniform size and shape are associated with type H1 hysteresis loops, while more complex pore systems, usually those with interconnecting pores of varying size and shape, tend to produce isotherms with type H2 hysteresis loops.
Types H3 and H4 occur when solids with slit shaped pores or plate-like particles undergo sorption. As with type H1, type H4 hysteresis loops are associated with samples whose pores exhibit uniformity in both size and shape. For type H3, the steeper the hysteresis loop is, the greater the irregularity of the pore system will be; type H3 loops are produced by solids with non-uniform slit shaped pores.

2.3.2: ANALYSIS OF ISOTHERMS

The Micromeritics® Gemini 2375 equipment determines adsorption and desorption isotherms and calculates porosity data, such as specific surface area, pore volume and pore size distribution, of a compound. A correlation between the amount of gas adsorbed on a solid surface and the equilibrium pressure of that gas (at constant temperature) was first proposed by Langmuir in 1918\(^{(15)}\). The Langmuir Equation:

\[
\frac{n}{n_m} = \frac{Bp}{1 + Bp}
\]

where \(n\) is the amount of gas adsorbed at equilibrium pressure, \(p\);
\(n_m\) is the monolayer capacity of the adsorbent;
\((n / n_m\) is therefore the fraction of the surface covered by the adsorbate)
\(p\) is the equilibrium pressure

and \(B\) is given by the equation below:

\[
B = \frac{a_1K_1e^{q_1/RT}}{z_mV_1}
\]

where \(a_1\) is the condensation coefficient;
\(z_m\) is the number of molecules adsorbed per unit area in a completed monolayer;
\[ \nu_1 \text{ is the oscillation frequency of adsorbed molecules;} \]

\[ q_i \text{ is the isoretic heat of adsorption;} \]

\[ R \text{ is the gas constant;} \]

\[ T \text{ is the thermodynamic temperature;} \]

and \[ \kappa_1 \text{ is a constant derived from the kinetic theory of gases:} \]

\[ \kappa_1 = \frac{0.5L}{(MRT)^{1/2}} \]

where \[ L \text{ is the Avagadro number;} \]

\[ M \text{ is the molar mass;} \]

and \[ R \text{ and } T \text{ are as defined previously.} \]

The Langmuir equation is dependent on several fundamental assumptions:

1. The adsorbate behaves as an ideal gas in the bulk gaseous phase;
2. The amount of gas adsorbed is limited to a mono-molecular layer;
3. The entire surface has a constant enthalpy of adsorption;
4. No adsorbate-adsorbate interactions occur;
5. The adsorbed molecules are localised; each is attached to a specific point on the solid’s surface.

As defined by assumption 2, the Langmuir model presumes that adsorption is restricted to a monolayer of adsorbate molecules. A variety of systems are, however, known to have adsorbate-adsorbate interactions, leading to multilayer adsorption. In fact, assumptions 3 and 4 are never true. An increase in the energy of adsorption results from adsorbate-adsorbate interactions, whilst a decrease in adsorption energy occurs because of the irregularity of the solid surface. Systems appear to fit the Langmuir model when these two factors combine and cancel each other out.
Brunauer, Emmett and Teller extended the Langmuir model with further assumptions so that isotherms with multilayer adsorption could be interpreted. The two main further assumptions are:

1. Second and subsequent layers of adsorption have equal energies of adsorption ($E_i$) and this value is equivalent to the liquefication energy of the adsorptive ($E_L$);
2. The multilayer has infinite thickness at $p/p_0 = 1$ (therefore $i = \infty$; where $i$ = no of layers)\(^{(17)}\).

The BET (Brunauer, Emmett and Teller) equation\(^{(18)}\):

\[
\frac{p/p_0}{n(1 - p/p_0)} = \frac{1}{n_m c} + \frac{c - 1}{n_m c} (p/p_0)
\]

where $p_0$ is the saturation vapour pressure at measurement $T$;
$p$ is the equilibrium pressure;
$n$ is the quantity of gas adsorbed at $P_2$;
$c$ is the BET constant;
and $n_m$ is the monolayer capacity of the adsorbent.

Using this equation we must first determine the amount of adsorbent (gas) needed to cover the surface of the material with a single monolayer, this value being designated the monolayer capacity, $n_m$. A straight-line graph is achieved by plotting $(p/p_0) / n (1 - p/p_0)$ against $p/p_0$. The gradient, $m$, is $(c - 1) / n_m c$ and the intercept, $i$, is $1 / n_m c$. The monolayer capacity may then be quantified as

\[
n_m = \frac{1}{(m + i)}.
\]
The specific surface area, $S_{BET}$, may then be determined from $n_m$:

$$
S_{BET} = n_m L \sigma
$$

where $L$ is the Avagadro constant

and $\sigma$ is the average area occupied by each molecule in the completed monolayer.

$\sigma = 0.162 \text{ nm}^2$ for nitrogen at 77 K$^{(19)}$.

N.B. The normal boiling temperature of N$_2(g)$ at a pressure of 1 bar is 77.3 K.

Both Langmuir and BET specific surface areas ($S_{Lang}$ and $S_{BET}$, respectively) were calculated for all samples in this study. However, Langmuir conforms with microporous systems where monolayer adsorption is more feasible than in mesoporous networks. $S_{Lang}$ and $S_{BET}$ specific surface areas should be of the same order for microporous systems. For Laponite RD $S_{BET} = 360.0 \text{ m}^2 \text{ g}^{-1}$, whilst $S_{Lang} = 559.6 \text{ m}^2 \text{ g}^{-1}$ and for hectorite KP $S_{BET} = 612.3 \text{ m}^2 \text{ g}^{-1}$ whilst $S_{Lang} = 976.2 \text{ m}^2 \text{ g}^{-1}$. This illustrates the differences between the two models, and the inconsistencies highlight the multilayer nature of adsorption which occurs in Laponite and other hectorite systems.

### 2.3.3: GURVITSCH TOTAL PORE VOLUME

The total pore volume ($V_T$) of a porous network is another important textural property of a sample. This may be calculated from the maximum adsorption of the adsorbate by the solid ($n_p$), when the density ($\rho$) and the molecular weight ($M_w$) of the liquid adsorbate are known$^{(20)}$.

\begin{align*}
V_T &= \frac{n_p \rho}{M_w} \\
&= \frac{S_{BET}}{\sigma} \rho
\end{align*}
The maximum adsorption value for Type IV isotherms is related to the final plateau region.

2.3.4: **Pore Diameter and Size Distribution**

The Kelvin equation may be used to determine the pore diameter of a solid from the sorption isotherm\(^{(21)}\). The Kelvin equation:

\[
\ln \left( \frac{p}{p_0} \right) = \frac{2\gamma V_G}{r_kRT \cos \varphi}
\]

where \(\gamma\) is the surface tension; \\
\(r_k\) is the Kelvin radius *; \\
\(V\) is the molar volume of the adsorbate; \\
\(\varphi\) is the contact angle between the pore wall and the adsorbate (this is generally assumed to be zero).

* The Kelvin radius is not the actual radius of the pore; it is the pore radius minus the thickness of the adsorbed monolayer.

There are a variety of methods in use for the determination of pore size distribution (pore size versus pore volume) in mesoporous solids. The BJH (Barrett, Joyner and Halenda) method is the most commonly used\(^{(22)}\). The basis of this method is that the thickness of the adsorbate layer on the surface of the pore will increase with increasing pressure. The BJH method is an extension of the Kelvin equation\(^{(21)}\), with a few added assumptions:
1. The Kelvin equation is applicable over the entire mesoporous range;
2. The pores are rigid and of well defined shape;
3. The meniscus curvature is controlled by the pore size and shape;
4. The pore distribution is confined to the mesopore range;
5. The filling/emptying of each pore is not dependent upon its location in the structure;
6. Adsorption on the pore walls occurs by the same mechanism as adsorption onto the external surface.

Desorption or adsorption data may be used to obtain pore size distribution plots and hence modal mesopore diameters. Desorption data were used in this study.

2.4: THERMAL METHODS

Thermal methods of analysis are many and varied. Each technique measures a change in physical property of a substance as a function of temperature as the substance is subjected to a controlled temperature programme (23). The two methods used in this study were thermogravimetry (TG) and differential thermal analysis (DTA); the former measures changes in mass with respect to temperature and the latter is concerned with differential changes in temperature between a standard and a sample during heating. All mass changes are accompanied by a gain or loss in energy, which may be detected by DTA, but not all energy changes are associated with a change in mass (e.g. phase changes) as detected by TG. Therefore, the coupling of TG and DTA illustrates all chemical and physical changes (phase changes and reactions leading to mass loss) of a compound within a given temperature range and can distinguish between these two phenomena.
2.4.1: THERMOGRAVIMETRY

The two main components required for TG analysis are a sensitive analytical balance and a furnace. Most modern instruments also have a purge gas system capable of providing an inert or reactive atmosphere and a microcomputer for instrument control and data acquisition. As with all analytical apparatus, accuracy, sensitivity and reproducibility are the main requirements of a good balance. Two types of balance are available: the null point balance and the deflection balance. Null point balances are favoured because the sample is kept in the same temperature zone of the furnace throughout the analysis. A null point balance operates by detecting a change in weight and using a restoring force to return the balance to its null point, Figure 2.4.A. A null point balance was used in this study and the restoring force was recorded as a voltage difference, which is proportional to the change in weight.

**Figure 2.4.A:** Schematic diagram of a null point balance (24).

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2.4.2: Differential Thermal Analysis

DTA measures the difference in temperature between the sample and a reference material, as both are subjected to an identical heating regime. A plot of the difference in temperature between the sample and reference against the programmed temperature shows transition temperatures and whether each transition is endo- or exo-thermic. The DTA reference material requires the following characteristics:

- Thermal stability over operating temperature range
- Inert with respect to the sample holder and thermocouple
- Similar thermal conductivity and heat capacity to those of the sample

α-Al₂O₃ and SiC are often used as references for inorganic compounds, whilst octyl phthalate and silicone oil are used for organic substances. Calcined α-alumina was used as a reference in this study.

2.4.3: Optimisation

For both TG and DTA, the following factors must be optimised to ensure homogeneous heating of the sample:

- Sample amount
- Particle size
- Layer thickness (i.e. thin)
- Packing density (i.e. even and loose)
- Ease of escape of volatile products (achieved through loose packing)
- Thermal conductivity of sample
- Heat capacity
- Surrounding atmosphere (i.e. gaseous products should be removed from the vicinity of the residue to prevent side reactions)
2.5: MAGIC ANGLE SPINNING NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

The Oxford Dictionary of Chemistry defines NMR as the “absorption of electromagnetic radiation at a precise frequency by a nucleus with non-zero magnetic moment in an external magnetic field” (26). Applying a static magnetic field, $B_0$, to a compound leads to different resonant frequencies for similar nuclei in different environments; it is this difference, chemical shift (in ppm from a reference), which allows NMR to be used to study a compound’s structure.

This section aims to describe the fundamental background to nuclear magnetic resonance (NMR) in relation to the solid state, paying particular attention to processes leading to improved resolution in spectra. $^7$Li and $^{29}$Si species were identified within the clay structure of “natural” and modified Laponite and hectorite, whilst $^{13}$C and $^{27}$Al were observed for species in the interlayer regions of templated and pillared samples, respectively.

2.5.1: INTRODUCTION

There is at least one naturally occurring magnetic isotope for most elements. When a magnetic field is applied each nucleus adopts one of a number, $m$, of allowed orientations. The permitted orientations, or spin states, are defined as

$$m = I, I - 1, I - 2, ..., -I = 2I + 1$$

where $I$ equals the nuclear spin quantum number. Transitions between these states are permitted for $\Delta m = \pm 1$. Figure 2.5.A shows the two spins states of a nucleus with $I = \frac{1}{2}$. Of these two spin states one is aligned to the field and has low energy, whilst that with high energy is opposed to the external field. The energy gap between these two states is $\Delta E$, where $\Delta E = \hbar \nu$ from the Planck equation.
Unlike bar magnets, magnetic nuclei do not align themselves with an external magnetic field when it is applied. Instead, due to angular momentum, nuclei precess about the field with a frequency, \( v_p \), Figure 2.5.B. This frequency is given by the equation

\[
    v_p = -\gamma B_0 / 2\pi
\]

or in terms of angular frequency \( \omega_p = -\gamma B_0 \) since \( \omega = 2\pi v \)

where \( \gamma \) is the gyromagnetic ratio, which is a constant specific to each individual nuclide (27).

There are three key steps in an NMR experiment: preparation, perturbation and detection. The system is prepared by the application of a constant external magnetic field, which leads to a quantisation of the energies of spins, Figure 2.5.A. The perturbation of the system is achieved by the application of a continuous or pulsed irradiation with a radio frequency magnetic field, which leads to transitions between spin states/energy levels. The detection of energy changes (\( \Delta E \)), as spins return to their ground state, leads to the production of characteristic spectra.

2.5.2: LINE BROADENING

Solid state NMR spectra are very different in appearance than those for liquid samples. Due to the relatively static nature of a solid's atoms, spectra tend to be broad and, without enhancement, difficult to interpret. The three main factors which effect line broadening are chemical shift anisotropy (CSA), and heteronuclear and homonuclear dipolar coupling within and between molecules. Techniques used to reduce these effects include magic angle spinning, cross polarisation and dipolar decoupling.
**Figure 2.5.A:** Non degenerate energy levels for an $I = \frac{1}{2}$ nucleus arising from the application of a magnetic field, $B_0$.  

**Figure 2.5.B:** Precession of a magnetic moment, $\mu$, about an applied field, $B_0$, with precessing angular velocity, $\omega_0$.  

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Chemical shift anisotropy

Chemical shift is a tensor property with two principle components, one that is orientation-dependent (anisotropic) and one that is not (isotropic). The anisotropic factor is due to electron distribution clouds that surround magnetic nuclei. When an atom is exposed to a magnetic field not only is there an effect on its nucleus, but also on the electrons surrounding this central core. Magnetic fields are created by the disturbance of the electron cloud, although small (approximately a million times smaller than $B_0$) this magnetic field affects the nucleus by adding to or subtracting from the external field.

In liquids, anisotropy may be averaged to zero due to the random tumbling motion of the molecules, but in more viscous or “rigid” media it leads to a range of chemical shifts and hence a broad spectrum. This phenomenon is particularly problematic for polycrystalline materials where a wide range of orientations is possible. Creating liquid-like motion in solids is somewhat impractical; therefore the anisotropic factor, which is proportional to $(3\cos^2\theta - 1)$, is averaged to zero by rotating the sample at $54.7^\circ$ (or $54^\circ 44''$) with respect to $B_0$. This is the so called magic angle; when applied to NMR the technique is known as magic angle spinning (MAS)\(^{(29)}\).

Dipole-dipole interactions

Dipole-dipole interactions may be homonuclear ($^1H - ^1H$), heteronuclear ($^1H - ^29Si$), intramolecular or intermolecular. Dipolar coupling results from the magnetic fields of two neighbouring nuclei interacting. Three factors affect the extent of dipolar coupling: the strength of the nuclei’s magnetic moments, their orientation with respect to the external magnetic field and the internuclear distance (the closer the nuclei are, the stronger the interaction between them). Dipolar coupling leads to highly broadened spectra due to the splitting of resultant signals.
Quadrupole moments

In addition to dipole-dipole interactions and chemical shift anisotropy, nuclei with $I > \frac{1}{2}$ may also be affected by electric quadrupole moments. This phenomenon is caused by an ellipsoidal charge distribution within the nucleus; which leads to non-equal energy gaps for the $2I + 1$ energy levels. First order quadrupole interactions effect all transitions except those between $m = \frac{1}{2}$ and $m = -\frac{1}{2}$ for nuclei with half integral spins, such as $^{27}$Al ($\frac{5}{2}$) and $^7$Li ($\frac{3}{2}$). The orientation of the sample in the applied magnetic field is key to the extent of first order interactions experienced, consequently the random nature of a powdered sample leads to particularly broad lines. Fortunately for this study, only transitions between $m = \frac{1}{2}$ and $m = -\frac{1}{2}$ are observable in the spectra of polycrystalline samples. These energy transfers only experience the less powerful second order quadrupole interactions, which may be minimised with the application of high external magnetic fields.

Cross-polarisation

Elements with low natural abundances suffer from long spin-lattice relaxation times, leading to low intensity spectra and broad line widths. Cross-polarisation transfers the magnetization (polarisation) of highly abundant nuclei (i.e. protons) to elements with limited magnetic nuclei. Very simply the process shortens relaxation times by allowing the less abundant nuclei to relax via the protons, thus increasing the intensity of the spectra. This multipulse technique is analogous to heat transfer between hot and cold objects (30).

2.5.3: Study Specific Parameters

Each element responds differently to NMR spectroscopy, depending on their individual characteristics. Table 2.5.I highlights relevant properties of the four elements analysed by NMR in this study.

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Table 2.5.1: Relevant properties of nuclei to be studied by solid state MAS-NMR.

<table>
<thead>
<tr>
<th></th>
<th>$^{27}$Al</th>
<th>$^{13}$C</th>
<th>$^{7}$Li</th>
<th>$^{29}$Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>5/2</td>
<td>1/2</td>
<td>3/2</td>
<td>1/2</td>
</tr>
<tr>
<td>Natural abundance / %</td>
<td></td>
<td>100</td>
<td>1.1</td>
<td>93</td>
</tr>
<tr>
<td>Reference</td>
<td>AlCl$_3$ (aq)</td>
<td>(CH$_3$)$_4$Si</td>
<td>LiCl$_2$ (aq)</td>
<td>(CH$_3$)$_4$Si</td>
</tr>
</tbody>
</table>

$^{29}$Si NMR
There are three main reasons for line broadening in $^{29}$Si NMR: CSA, and in clays, structural disorder, and also heteronuclear dipole interactions with $^1$H (and where present $^{27}$Al). These broadening effects can be reduced with the use of MAS and proton dipolar decoupling, respectively. Due to their low natural abundances homonuclear ($^{29}$Si -- $^{29}$Si) and heteronuclear $^{29}$Si -- $^{17}$O interactions (abundance of $^{17}$O is 0.037%) can be ignored.

$^{29}$Si MAS-NMR is very sensitive to the environment of the $^{29}$Si nucleus. Chemical shifts are therefore particularly pertinent in determining aspects of a compound’s structure. A high field shift occurs when polymerisation is increased. Figure 2.5.C illustrates shifts associated with different levels of Si-O-Si condensation. Further shifts take place if the tetrahedrally co-ordinated atom, Si-O-T is not another Si, e.g. if T is Al a significant low field shift occurs.

$^7$Li NMR
Line broadening in $^7$Li NMR is a result of second order quadrupole effects and CSA from low symmetry $^7$Li nuclei. If aluminium is present heteronuclear dipolar coupling can also occur. The use of a high magnetic field will minimise the effects of second order quadrupole interactions, whilst MAS will reduce line broadening caused by CSA.
**Figure 2.5.C:** Chemical shifts [(CH$_3$)$_4$Si as a reference] observed in $^{29}$Si solid state MAS-NMR spectra of siloxane species, as a function of the different number of neighbouring Si nuclei attached to a central SiO$_4$ unit (adapted from Englehardt and Michel, 1987 $^{31}$).

**$^{27}$Al NMR**

The 100% natural abundance of $^{27}$Al leads to fast relaxation times and, when coupled with its low quadrupole moment, this leads to relatively high intensity spectra. Line broadening that does occur can be decreased with the use of high magnetic fields and fast spin rates, which minimise the effect of second order quadrupole interactions.

The chemical shift of $^{27}$Al is not as sensitive to polymerisation as that of $^{29}$Si, but tetrahedral and octahedral environments may be distinguished between quite easily. Tetrahedral AlO$_4$ is observed as a peak at $50 > \delta > 80$, whilst a peak shift of $-10 > \delta > 20$ (with respect to the standard AlCl$_3$ (aq)) indicates the presence of octahedral AlO$_6$. 
**13C NMR**

Solid state NMR of $^{13}$C is hampered by low natural abundance (1.1%), which leads to long relaxation times and low intensity spectra. Cross polarisation (CP) with highly abundant protons leads to shorter relaxation times and higher intensity spectra. Low abundance is, however, an advantage with respect to line broadening as homonuclear and heteronuclear couplings with Si or O are less significant. The use of CP techniques does, however, lead to spectra in which intensity is not directly related to the abundance of individual environments.

**2.6: SCANNING ELECTRON MICROSCOPY**

The use of glass lenses to magnify small objects is probably as old as glass itself. Scientists have refined this technique and created microscopes which allow the observer to examine the fine detail of small items and to view objects which are "invisible" to the naked eye. Compound light microscopes use a series of lenses to examine smaller and smaller objects, however, these instruments are ultimately restricted by the wavelength of light and subsequent diffraction interferences. The minimum resolution for a typical light microscope is 0.3 μm; this is approximately 1000 times better than the human eye, which can just about resolve two points separated by 0.1 mm $^{(32)}$. However, science is currently exploring the world of nanotechnology ($10^{-7}$ to $10^{-9}$ m), which requires images of objects 1000 times smaller still.

Electron microscopes use beams of electrons instead of beams of light to focus on sub-micrometer objects. Electron wavelengths are much shorter than that of light and beams of electrons may be focused with the use of magnetic or electrostatic fields. The basic structure of an SEM is outlined in Figure 2.6A.
Figure 2.6.A: Simplified diagram of a scanning electron microscope (33). Scanning electron microscopes consist of an electron “gun” (A), two condenser lenses (B), an objective lens (C) and an electron collection system (D). The entire system, including the specimen chamber and stage (E), is kept under vacuum (F).

The beam of electrons fired from the electron “gun” (traditionally a tungsten filament) is focused on the surface of the sample, where a range of interactions take place. The SEM scans across the surface of a sample in a “raster” or pattern of parallel lines collecting information from these interactions numerous times, thus building an image of the sample’s surface (34).
2.7: ATOMIC ABSORPTION SPECTROMETRY

Atomic absorption spectrometry (AAS) was used in this study to quantitatively determine the concentrations of metal ions in aqueous solution, both pre- and post- batch equilibrium testing and hence the efficiency of Laponite and hectorite samples as novel sorbents. The absorption of radiation at certain wavelengths allowed the determination of concentrations of individual analytes in solution when compared to calibration curves for the respective element.

The basic process of flame AAS starts with the introduction of the sample, as a solution, which is then broken down into small droplets (an aerosol) via nebulization. The droplet stream is "filtered" by a series of baffles allowing only the smallest droplets through, which are then atomized in the flame. The stream of free atoms contained within the flame is then exposed to external radiation via a hollow cathode lamp of element specific wavelength. Absorption of this radiation converts the atoms from the stable ground state to various excited states. The strongest absorption is observed for the first excited state.

![Diagram of Atomic Absorption Spectrometer](image)

**Figure 2.7.A:** Schematic diagram of an atomic absorption spectrometer (adapted from 35).
AAS is a single element technique. Hollow-cathode lamps emit radiation at a wavelength specific to each element, therefore a high throughput of samples may be achieved but only for individual elements.

**Calibration**

Absorption, $A$, is related to concentration, $C$, via the Beer-Lambert law:

$$A = \varepsilon / C$$

where $\varepsilon$ is the molar absorptivity and $l$ is pathlength.

Plotting a graph of absorption versus known concentration gives a straight line graph over a specified range. Thus the concentrations of unknown analytes may be calculated from observed absorbencies within the calibration range. Table 3.4.1 in Chapter 3 shows the wavelengths and calibration ranges of the specific elements analysed in this study.

N.B. Some machines record transmittance rather than absorbance; the relationship between the two is:

$$A = \log (1 / T) = - \log T$$
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CHAPTER 3

EXPERIMENTAL
CHAPTER 3: EXPERIMENTAL

3.1: SAMPLE PREPARATION AND SYNTHESIS

3.1.1: CHEMICAL ACQUISITION

Water used in syntheses was deionised using an Elga option 3 water purifying system (reverse osmosis), whilst that used in batch testing was purified for a second time using an Elga UHQ PS system. All chemicals were used as supplied. Laponite RD powder and Laponite RD filtercake were kindly provided by Rockwood Additives Ltd, Widnes, UK. Lithium carbonate and sodium carbonate, as well as the surfactants polyoxyethylene (4) lauryl ether (Brij 30), polyoxyethylene (23) lauryl ether (Brij 35), polyoxyethylene (20) stearyl ether (Brij 78), polyoxyethylene (20) sorbitan monopalmitate (Tween 40) and polyoxyethylene (20) sorbitan trioleate (Tween 85), were obtained from Acros Organics (for each surfactant the number in the first bracket refers to the number of polyoxyethylene units contained within the system, the second bracket giving the brand name of the chemical). The templates cetyltrimethylammonium bromide, methylammonium chloride and tetrabutylammonium bromide were acquired from Lancaster, FSA Laboratory Supplies and Janssen respectively. The templates cetyltrimethylammonium chloride (25%) and tetramethylammonium bromide were purchased from Aldrich, as was the surfactant pore swelling-agent mesitylene (98%). Hydrated magnesium sulphate and nitric acid (70%) were obtained from Fisher Chemicals. Sodium silicate (Na$_2$Si$_3$O$_7$) solution was purchased from Sigma.
3.1.2: LAPONITE RD

Laponite RD was provided by Rockwood Additives Ltd, Widnes, both as a powder and in filtercake form. The former was analysed as provided, whilst the latter was analysed both after oven drying at 70°C and after calcination (of the dried compound) at 450°C.

3.1.3: SYNTHETIC HECTORITE KP (AUTOCLAVE OR OVEN)

Li$_2$CO$_3$ (1.338 g, 0.018 mol) was dispersed in deionised water (100 g, 5.58 mol) and agitated by rapid magnetic stirring for one hour at ambient temperature. A second quantity of deionised water (150 g, 8.24 mol) and MgSO$_4$.7H$_2$O (103 g, 0.42 mol) were then added to the vessel. Once the magnesium sulphate had dissolved, the mixture was heated to 60°C. In a separate vessel, Na$_2$CO$_3$ (32.65 g, 0.31 mol) was dissolved in deionised water (130 g, 7.25 mol). This solution was added slowly (over a thirty-minute period), to the first vessel. Maintaining the temperature at 60°C, aqueous sodium silicate solution (135 g of a solution containing $≈ 27\%$ SiO$_2$ and $≈ 14\%$ NaOH; 0.60 mol SiO$_2$) was added over a thirty-minute period to the resultant solution and the mixture was then heated to boiling, where it was held for two hours under reflux. A sealed Parr autoclave* (or a PTFE airtight container in an oven) was charged with the reaction mixture and heated at 200°C for 6 h. The masses of reaction mixture charged and discharged from the container were noted. After overnight cooling, the produced slurry was reheated to 70°C and the solid was recovered by filtration. The white filtercake was washed with deionised water (total washing volume = twice the initial volume of slurry) and then left to dry in an oven at 110°C for 14 h. The dried white solid was ground prior to analysis.

*N.B. The autoclave is enclosed in its own heating system with in-built thermocouple. The autoclave has a one litre capacity, is made of type 316 stainless steel and has an internal stirring mechanism. Care must be taken when filling the reactor and expansion of the sample, due to changes in pressure, should be taken into consideration.

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3.1.4: ALUMINIUM-KEGGIN-ION-EXCHANGED LAPONITE

Aluminium-Keggin-Ion-Exchanged Laponite or “Pillared” Laponite was prepared in two stages: (1) Synthesis of the aluminium-Keggin-ion solution and (2) the pillaring of Laponite RD.

Synthesis of Aluminium Keggin Ion Solution

An aqueous solution of aluminium-Keggin-ion, \([\text{Al}_{13}\text{O}_{4}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}\) ("\(\text{Al}^{7+}\)"), was prepared by very slow addition of sodium hydroxide solution (0.8 mol dm\(^{-3}\), 32 g dm\(^{-3}\)) to vigorously stirred aqueous aluminium chloride solution (0.4 mol dm\(^{-3}\), prepared from solid \(\text{AlCl}_3 \cdot 6\text{H}_2\text{O}\)) at room temperature. The optimised Keggin-ion concentration was obtained when the resultant solution had reached a pH of \(\approx 4.2\) (verified with a calibrated CD70 combination electrode). Once the pH was stabilised, the solution was refluxed at 80°C for at least 12 h. An aliquot was taken for \(^{27}\text{Al}\) NMR analysis to determine the environment of the aluminium nuclei. A dominance of tetrahedrally co-ordinated aluminium (50 < \(\delta\) < 80 \(^{(1)}\)) over octahedrally co-ordinated aluminium (-10 < \(\delta\) < 20 \(^{(1)}\)) sites is expected when the \(\text{Al}^{7+}\) concentration is optimised. This analysis was kindly carried out by Mr Jim Bloxsidge in Chemistry at the University of Surrey, using a Brüker AC300 spectrometer (\(^{1}\text{H}\) resonant frequency 300 MHz) at 298 K.

“Pillaring”

Laponite RD (40 g, in filtercake form) was added to a Keggin-ion solution (prepared with 250 cm\(^3\) of 0.4 mol dm\(^{-3}\) \(\text{AlCl}_3 \cdot 6\text{H}_2\text{O}_{(aq)}\)) and stirred vigorously for 24 h. The resultant slurry was separated, and the clay recovered using a Centurion 1000 series centrifuge (3000 rpm). The final product was washed thoroughly in de-ionised water until the washings were free of chloride ions (standard silver nitrate test). The pillared clay was then dried in an oven at 40°C for at least 24 h. A portion was taken for later analysis, while the rest of the clay was calcined in a muffle furnace at 450°C for at least 4 h.
3.1.5: Restructured or ‘Templated’ Laponite RD

The surfactant cetyltrimethylammonium chloride (CTMACl [25%, aq], 13.2 g (0.01 mol)) was added to deionised water (180 g, 10 mol) and stirred vigorously for 5 mins. A quantity of Laponite RD filtercake(s) (I: 7.1 g, II: 14.2 g, III: 21.3 g), was added and stirred for one week. The resultant slurry was separated, and the clay recovered, using a Centurion 1000 series centrifuge (3000 rpm). The final product was washed in de-ionised water three times and dried in an oven at 40°C for at least 24 h. A portion was collected for analysis, while removal of the template was investigated for the rest of this clay (Section 3.1.11).

This synthesis was repeated with a variety of templates. Each sample was prepared using 0.01 mol of organic surfactant compound and 21.3 g of Laponite RD filtercake. Separate samples were prepared using cetyltrimethylammonium bromide (CTMABr), methylammonium chloride (MACl), tetrabutylammonium bromide (TBABr), tetramethylammonium bromide (TMABr), polyoxyethylene (4) lauryl ether (Brij 30), polyoxyethylene (23) lauryl ether (Brij 35), polyoxyethylene (20) stearyl ether (Brij 78), polyoxyethylene (20) sorbitan monopalmitate (Tween 40) and polyoxyethylene (20) sorbitan trioleate (Tween 85). For the structures of these template molecules please see Appendix I.

3.1.6: Templated Synthetic Hectorite KP (Autoclave)

Method 3.1.3 was repeated with the addition of cetyltrimethylammonium chloride (CTMACl [25% aq], ≈76.8 g (0.06 mol); Si:surfactant mole ratio 10:1) during the initial agitation step with lithium carbonate. After drying at 110°C for 14 h, a portion of the resultant powder was taken for analysis, whilst template removal was carried out for the remainder of the sample (Section 3.1.11).
3.1.7: TEMPLATE-EXPANDED AND SWOLLEN LAPONITE RD

Synthesis 3.1.5 was repeated with the addition of CTMACl and a known quantity of mesitylene (surfactant:mesitylene mole ratio = 1:1 and 1:1.5) to the reaction mixture. This process was repeated with the use of n-octane in place of mesitylene. Both modifiers were later removed with the template (Section 3.1.11).

3.1.8: TEMPLATE-EXPANDED AND SWOLLEN SYNTHETIC HECTORITE KP (AUToclave)

Method 3.1.6 was repeated with the addition of the template CTMACl and of mesitylene as a pore modifier (surfactant:mesitylene mole ratio = 1:1 and 1:1.5) to the reaction mixture. The template and the modifier were removed with the template (Section 3.1.11).

3.1.9: SYNTHETIC HECTORITE KP WITH VARIED SI\textsubscript{2}O\textsubscript{5} CONCENTRATION

Procedure 3.1.3 was repeated with both an increased and decreased quantity of sodium silicate solution (168.4 g, an increase of 25% in SiO\textsubscript{2} and 101.0 g, a decrease of 25% in SiO\textsubscript{2}).

3.1.10: TEMPLATED SYNTHETIC HECTORITE KP WITH VARIED SI\textsubscript{2}O\textsubscript{5} CONCENTRATION

Procedure 3.1.6 was repeated with both an increased and decreased quantity of sodium silicate solution (168.4 g, an increase of 25% in SiO\textsubscript{2} and 101.0 g, a decrease of 25% in SiO\textsubscript{2}). The Si:surfactant mole ratio of 10:1 was maintained.
3.1.11: **Template Removal**

During the course of this study, a variety of methods of template removal were employed. Calcination of the samples at 450°C was the principal method of template elimination. The use of various temperatures and extraction media were also explored.

**Calcination**

Several methods of calcination were investigated to remove the template from the clay: (1) calcination in a tube furnace under flowing nitrogen, (2) calcination in a tube furnace under flowing oxygen, and (3) calcination in a muffle furnace in static (no forced flow) air. All calcinations were at 450°C for at least 12 h.

Different calcination temperatures were also investigated in the muffle furnace. A range of samples were calcined for at least 12 h in static (no forced flow) air at 450, 500, 550 and 600°C.
3.2: MATERIALS CHARACTERIZATION

3.2.1: X-RAY METHODS

Characterization of samples was carried out using both X-ray powder diffraction, for phase identification, and X-ray fluorescence, for quantitative analysis.

Powder X-Ray Diffraction

Powder X-ray diffraction studies were carried out with a Seifert 3003 TT X-ray diffractometer, with copper radiation of wavelength $\lambda = 1.5418 \ \text{Å}$ (a 2:1 intensity weighted average of Cu K$_{\alpha 1}$ $\lambda = 1.5405 \ \text{Å}$ and of Cu K$_{\alpha 2}$ $\lambda = 1.5442 \ \text{Å}$). Data were collected every 0.025° of 2θ with a scan dwell time of 9 s between 1.5° and 8.0° and of 1 s between 8.0° and 50.0°.

X-Ray Fluorescence Spectroscopy

X-ray fluorescence spectroscopy was carried out by Debbie McCarthy at Rockwood Additives Ltd, using a Philips PW2400 spectrometer. This machine employs a sequential X-ray spectrometer system. The first step of sample preparation was calcination for 1h at 700°C. Subsequently, samples were mixed with Spectroflux 100B (80% LiBO$_2$ and 20% Li$_2$B$_4$O$_7$) in a 1:5 weight ratio (usually 1.5000 g sample to 7.5000 g Spectroflux 100B). This mixture was then fused at high temperature (up to a maximum of 1200°C); this process destroys the sample’s mineralogical and particulate composition and converts the elements present into their respective oxides. Following homogenisation, the resultant melt was cast into a glass bead. The bead was introduced into the X-ray spectrometer for analytical measurements to take place. Intensities of the fluorescent X-rays were recorded and the chemical composition of the sample was established by reference to a previously determined calibration from standards of known composition.
3.2.2: INFRARED SPECTROSCOPY

Infrared spectra were recorded, over a range of 400 – 4000 cm\(^{-1}\), using a Perkin Elmer System 2000 Fourier-transform infrared spectrometer and a Nicolet 512P FT-IR spectrometer. Finely ground solid samples were mixed with dry potassium bromide and pressed into discs of 13 mm in diameter and with a thickness of \(\approx 0.6\) mm.

3.2.3: GAS ADSORPTION STUDIES

Textural properties of a compound, such as the specific surface area, pore volume and pore size distribution, may be determined by the adsorption and desorption of nitrogen at 77 K. To obtain an adsorption/desorption isotherm one must first outgas the material. A Micromeritics Flowprep 060 with flowing nitrogen gas was used to purge the samples (ca. 0.3 g) of physisorbed vapour. This was carried out at 150°C for at least 6 h (usually overnight). This temperature was chosen as it is considered low enough not to denature the samples in any way. Once the sample had cooled to room temperature, its mass (accurate to 0.1 mg) was recorded. Outgassed samples were then analysed on an automated Micromeritics Gemini 2375 surface area and porosimetry analyser, using nitrogen at 77 K as the adsorptive. The sample tube and a reference tube (with identical internal volume) were immersed in a liquid nitrogen bath; this allows isothermal conditions to be maintained. Using a flowing gas technique, nitrogen gas was introduced concurrently to both the sample and reference tubes. Hence, any volume changes observed may be solely attributed to the adsorption of N\(_2\)\(_{(g)}\). The gas delivery rate is decreed by the rate at which physisorption of the vapour onto the sample’s surface occurs. As the gas is adsorbed the pressure in the sample tube decreases; this imbalance is corrected by the continual introduction of the adsorptive. A differential pressure transducer records these changes and an isotherm is produced.
A small number of samples were kindly also run by Rockwood Additives Limited using a Micromeritics ASAP 2400 analyser. Samples of Laponite RD and hectorite KP produced near identical results on both sets of apparatus e.g. for a sample of Laponite RD $S_{BET} = 360 \text{ m}^2 \text{ g}^{-1}$ Micromeritics Gemini 2375 analyser at the University of Surrey and $S_{BET} = 356 \text{ m}^2 \text{ g}^{-1}$ using Micromeritics ASAP 2400 analyser at Rockwood Additives Limited.

3.2.4: ELEMENTAL ANALYSIS

Carbon, hydrogen and nitrogen (CHN) analyses of samples were carried out by Ms Nicola Walker and Mrs Judith Peters in Chemistry at the University of Surrey, using a Leemans CE 440 Elemental Analyser. Samples were accurately weighed into consumable tin capsules, introduced into a combustion furnace and heated to 960°C. Helium, the carrier gas, passed the resulting products, carbon dioxide (CO$_2$), water (H$_2$O), nitrogen (N$_2$) and oxides of nitrogen, through the combustion tube, where scrubbing reagents removed halogens, sulphur and phosphorus. The combustion products then passed through a reduction tube, which contained copper wires. Here any unburnt O$_2$ was removed and the oxides of nitrogen were reduced to N$_2$. The products of combustion are then passed into the mixing chamber where they are thoroughly homogenised at a precise volume, temperature and pressure. This mixture is released through the sample volume into a high precision thermal conductivity detector. These detectors determined the carbon, hydrogen and nitrogen concentrations of the sample, $\pm$ 0.3%. All analyses were carried out in duplicate and the accuracy and precision of the results were verified against known standards throughout the procedure (acetonilide (C$_9$H$_{10}$NHCOCH$_3$) was used as the calibration standard). This analytical technique was used in conjunction with IR spectroscopy in monitoring template removal.
3.2.5: MAGIC-ANGLE-SPINNING NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Magic-Angle-Spinning Nuclear Magnetic Resonance (MAS-NMR) spectroscopy was carried out by Dr David Apperley at the EPSRC Solid State NMR Service (University of Durham) using a Varian Unity Inova 300 MHz spectrometer.

- Carbon-13 ($^{13}$C) spectra were recorded using a 7 mm (outside diameter) rotor; at a frequency of 75.43 MHz, combined with spin rates $\approx 4.1$ kHz, which were compared with shifts relative to an external (CH$_3$)$_4$Si standard (TMS);
- Lithium-7 ($^7$Li) spectra were recorded using a 7 mm (outside diameter) rotor; at 116.57 MHz with spins rates of $\approx 4.5$ kHz with shifts relative to a LiCl(aq) (1 mol dm$^{-3}$) standard.
- Silicon-29 ($^{29}$Si) spectra were recorded using a 7 mm (outside diameter) rotor; at a frequency of 59.58 MHz, with spin rates $\approx 4.5$ kHz and shifts relative to an external TMS standard;
- Aluminium-27 ($^{27}$Al) spectra* were recorded using a 5 mm rotor; at a Larmor frequency of 78.16 MHz, with spin rates $\approx 10.8$ kHz and shifts relative to a AlCl$_3$(aq) (1 mol dm$^{-3}$) standard.

*N.B. Background signals were subtracted from $^{27}$Al spectra, because of background interferences caused by aluminium within components of the spectrometer.
3.2.6: THERMOGRAVIMETRY

Thermogravimetry was carried out using a Stanton Redcroft STA-780 thermal analyser. 10 - 20 mg of sample was weighed into a platinum crucible, then heated to 1200°C at a heating rate of 10°C min⁻¹. α-Al₂O₃ was used as a reference. Analyses were carried out in either flowing O₂(g) or flowing N₂(g), with flow rates of 60 cm³ min⁻¹; comparisons showed that the chemical nature of the gas had minimal effects on the data acquired. Figure 3.2.A highlights this minimal effect when using different gases with a non-templated hectorite KP sample; whilst figure 3.2.B shows that, although a difference in slope, due to combustion is observed for templated samples, the end result with the same total mass loss is achieved.

![Thermogravimetry analysis](image)

**Figure 3.2.A:** Thermogravimetry analysis of non-templated hectorite KP comparing the use of flowing O₂ and N₂ gases during analysis.
Figure 3.2.B: Thermogravimetry analysis of templated hectorite KP comparing the use of flowing O\textsubscript{2} and N\textsubscript{2} gases during analysis.

3.2.7: Scanning Electron Microscopy

Samples were prepared by being placed on a sticky carbon pad and mounted on an aluminium sample holder. They were then vacuum sputtered with a fine layer of gold to increase their conductivity and thus improve the clarity of the electron micrographs. The gold-coated samples were then viewed under vacuum in a Hitachi 3200M scanning electron microscope.
Chapter 3: Experimental

3.3: SHAKING EXPERIMENTS

3.3.1: SAMPLE PREPARATION

Five samples were chosen for metal sorption testing and potential pollutant removal: Laponite RD (LP); Laponite RD templated with the surfactant CTMACl, Ratio III (LS); synthetic hectorite KP (KP); synthetic hectorite KP templated with the surfactant CTMACl (KS) and the natural montmorillonite IKO-MONT Ca Weiss (KCW) from IKO-Minerals, Marl. All samples were calcined at 450°C in static air (no forced flow) prior to use.

3.3.2: SOLUTION PREPARATION

For initial batch testing, 5 mg dm$^{-3}$ solutions of manganese, iron, cobalt, nickel, copper, zinc, cadmium and lead, both individually and as a mixture, were produced. All solutions were prepared by dilution of Aristar™ stock solutions, as detailed in Table 3.3.1, with deionised water. 5, 10 and 20 mg dm$^{-3}$, of each metal, mixed metal solutions were also tested. These solutions contained vanadium, chromium, tin and mercury, as well as the eight metals previously mentioned.

**Table 3.3.1:** Details of Aristar™ elemental stock solutions.

<table>
<thead>
<tr>
<th>Element</th>
<th>Solute</th>
<th>Matrix</th>
<th>Mass content / mg dm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manganese</td>
<td>Mn(C$_2$H$_3$O$_2$)$_2$</td>
<td>2% HNO$_3$</td>
<td>10 000</td>
</tr>
<tr>
<td>Iron</td>
<td>Fe</td>
<td>5% HNO$_3$</td>
<td>10 000</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Co</td>
<td>2% HNO$_3$</td>
<td>1 000</td>
</tr>
<tr>
<td>Nickel</td>
<td>Ni</td>
<td>2% HNO$_3$</td>
<td>10 000</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu</td>
<td>2% HNO$_3$</td>
<td>10 000</td>
</tr>
<tr>
<td>Zinc</td>
<td>Zn</td>
<td>2% HNO$_3$</td>
<td>10 000</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Cd</td>
<td>2% HNO$_3$</td>
<td>10 000</td>
</tr>
<tr>
<td>Lead</td>
<td>Pb(NO$_3$)$_2$</td>
<td>2% HNO$_3$</td>
<td>10 000</td>
</tr>
<tr>
<td>Chromium</td>
<td>(NH$_4$)$_2$Cr$_2$O$_7$</td>
<td>1% HNO$_3$</td>
<td>10 000</td>
</tr>
<tr>
<td>Vanadium</td>
<td>V$_2$O$_5$</td>
<td>2% HNO$_3$</td>
<td>1 000</td>
</tr>
<tr>
<td>Mercury</td>
<td>Hg(NO$_3$)$_2$</td>
<td>0.5 mol dm$^{-3}$ HNO$_3$</td>
<td>1 000</td>
</tr>
<tr>
<td>Tin</td>
<td>Sn</td>
<td>0.5 mol dm$^{-3}$ HCl</td>
<td>1 000</td>
</tr>
<tr>
<td>Sodium</td>
<td>NaNO$_3$</td>
<td>2% HNO$_3$</td>
<td>10 000</td>
</tr>
</tbody>
</table>
3.3.3: CONTAMINATED WATER PREPARATION

Synthetic contaminated water solutions were prepared from “metallic” waste from the laboratory. This was mixed together with concentrated HNO₃ (aq) (70%) and tap water. Once this mixture had partially dissolved, it was divided in two (LA and LB) and mixed with water from the University of Surrey lakes to add further unknowns to the solutions including organic species. The laboratory waste included a lead acetate battery, several rechargeable nickel-cadmium batteries (all of which were sawn apart so that the plastic casing could be removed), staples, copper wire, a piece of brass, zinc pellets, aluminium foil and a hacksaw blade. The samples were shaken for a week and then left to “mature” for a month. A simple gravity filtration was carried out before the solutions were tested, thus removing suspended solids and reducing changes in elemental concentrations via leaching from the solid waste.

Due to high concentrations of certain elements, solution LA was further diluted with water from the University of Surrey lakes. The solution was once again shaken for a week and left to “mature” before use in sorption testing.

3.3.4: SORPTION TESTING

Initial batch testing was carried out using a ratio of x g of solid sample and 100x cm³ of solution e.g. if x = 0.5: 0.5 g LP and 50 cm³ 5 mg dm⁻³ Co II solution would be tested. The mixture was shaken for ten minutes on an IKA LABORTECHNIK, HS250 basic shaker at 240 osc min⁻¹. The mixture was then separated by centrifugation using an MSE Mistral 2000 at 3000 rpm for 5 min. The solutions were then stored at 4°C prior to elemental analysis, whilst the solid matter was oven dried at 80°C. All procedures were carried out in duplicate. This process was repeated with multi-element metal ion solutions and then synthetic contaminated water solutions.
The parameters for equilibrium batch testing were optimised in a study by Pitcher in 2002 (2). Pitcher investigated the efficiency of heavy metal removal from motorway storm water using a variety of inorganic materials including clays. During the course of this study batch testing was optimised to include short contact times and an appropriate solid to water ratio. Pitcher also noted that column packing was difficult with fine grained materials; as hectorites have very small particle sizes, column ion-exchange was not carried out in this study.

3.4: ANALYTICAL TECHNIQUE INSTRUMENTATION

Atomic adsorption spectroscopy (AAS) was employed to determine selectivity and efficiency of metal ion removal by Laponite-related materials. This technique determined concentrations of heavy metals in synthetic solutions, as well as the levels of these metals removed from such solutions after batch testing and the sodium content released from the sorption materials. Powder XRD was used to assess the structure of chosen clay samples post equilibrium batch testing. Comparison with powder XRD profiles produced when characterizing clay structure illustrated the occurrence of structural changes.

3.4.1: ATOMIC ABSORPTION SPECTROMETRY

A Perkin Elmer 5000 atomic adsorption spectrophotometer and, later (due to replacement of the former instrument), a Perkin Elmer Analyst 400 atomic adsorption spectrophotometer were used with an ethyne/air flame. Analyte concentrations were determined with the use of hollow cathode lamps; the highest possible detected energy readings, at a fixed current, were generated by manually adjusting the lamps' positions (P.E. 5000 AAS).
**TABLE 3.4.1:** Study specific AAS operational parameters.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength / nm</th>
<th>Lamp current* / mA</th>
<th>Calibration range / mg dm(^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>279.5</td>
<td>10</td>
<td>0.1 – 5</td>
</tr>
<tr>
<td>Fe</td>
<td>248.3</td>
<td>15</td>
<td>0.5 – 10</td>
</tr>
<tr>
<td>Co</td>
<td>240.7</td>
<td>15</td>
<td>0.5 – 10</td>
</tr>
<tr>
<td>Ni</td>
<td>232.0</td>
<td>12</td>
<td>0.5 – 10</td>
</tr>
<tr>
<td>Cu</td>
<td>324.8</td>
<td>7</td>
<td>0.5 – 10</td>
</tr>
<tr>
<td>Zn</td>
<td>213.9</td>
<td>10</td>
<td>0.1 – 5</td>
</tr>
<tr>
<td>Cd</td>
<td>228.8</td>
<td>8</td>
<td>0.1 – 5</td>
</tr>
<tr>
<td>Pb</td>
<td>217.0 283.3*</td>
<td>10 10</td>
<td>0.5 – 20 0.5 – 20</td>
</tr>
<tr>
<td>Na(^#)</td>
<td>589.0 330.2</td>
<td>8 8</td>
<td>0.1 – 5 20 – 100</td>
</tr>
</tbody>
</table>

* Lamp currents were required to set up the Perkin Elmer 5000 AAS. The Perkin Elmer Analyst 400 AAS is automated.

* Second Pb wavelength used on Perkin Elmer Analyst 400 AAS.

\(^\#\) Two wavelengths used for Na to increase the calibration range of the instrument.
REFERENCES


CHAPTER 4
RESULTS AND DISCUSSION:
CHARACTERIZATION STUDIES
CHAPTER 4: RESULTS AND DISCUSSION OF

CHARACTERIZATION STUDIES

Characterization is a key phase in establishing the structure and nature of each sample. In this study, investigating the similarities and differences between compounds prepared from restructuring Laponite RD filtercake and those synthesized from the component salts (synthetic hectorite KP) is fundamental. Before modification began, reference points were determined via analysis of the parent material, Laponite RD, in both powdered and filtercake forms. This was followed by investigating how the method of synthesis, without templating, has affected the porosity of synthetic hectorite KP relative to Laponite RD. Comparisons with alternative methods of tailoring, such as "pillaring", were also carried out.

The characteristics of these tailored materials were determined via nitrogen sorption porosimetry, X-ray powder diffraction (XRD), X-ray fluorescence analysis (XRF), Fourier transform infrared spectroscopy (FT-IR), elemental microanalysis, thermogravimetry (TG), scanning electron microscopy (SEM), and solid-state magic angle spinning nuclear magnetic resonance spectroscopy (MAS-NMR).

4.1: LAPONITE RD: POWDER VERSUS FILTERCAKE

Before modification began and enhancement could be determined, analyses were first carried out on powdered Laponite RD, and Laponite RD filtercake (both dried and calcined), to create reference points for subsequent samples. Both forms of Laponite RD were provided by Rockwood Additives Ltd, Widnes, UK.
4.1.1: X-RAY FLUORESCENCE

According to Rockwood Additives Ltd. the typical chemical composition of Laponite RD (dry basis by mass) is 59.5% SiO₂, 27.5% MgO, 0.8% Li₂O and 2.8% Na₂O with 8.2% loss on ignition. Table 4.1.1 presents the chemical compositions of Laponite samples used in this study. As expected all compounds had similar compositions. Dehydration to give calcined filtercake led to higher individual contents of each component, but the silica to magnesium oxide ratio remained the same, indicating similar composition. The drying of Laponite RD filtercake at 70°C led to a 32 ±2% loss of mass.

Table 4.1.1: Chemical compositions of Laponite samples determined by XRF analysis.

<table>
<thead>
<tr>
<th>CHEMICAL COMPOSITION</th>
<th>NATURE OF LAPONITE RD SAMPLE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Powdered</td>
</tr>
<tr>
<td>%SiO₂</td>
<td>63.38</td>
</tr>
<tr>
<td>%MgO</td>
<td>29.32</td>
</tr>
<tr>
<td>%Na₂O</td>
<td>2.86</td>
</tr>
<tr>
<td>%CaO</td>
<td>0.20</td>
</tr>
<tr>
<td>%Total</td>
<td>95.76</td>
</tr>
<tr>
<td>SiO₂:MgO</td>
<td>2.16</td>
</tr>
<tr>
<td>Li g/kg *</td>
<td>3.12</td>
</tr>
</tbody>
</table>

* Determined by AAS at Rockwood Additives Ltd, Widnes, UK.

4.1.2: X-RAY POWDER DIFFRACTION

X-ray powder diffraction (XRD) patterns for small particle turbostratic clays are not rich in detail. However, low angle peaks relate to a compound’s stacking (layer repeat) distance and higher angles indicate hk0 reflections which arise from within the layers themselves. A move to lower angles for the 001 peak will indicate either an increased d-spacing, and hence greater separation of the layers, or an increase in a₀, the pore periodicity repeat distance (pore diameter plus thickness of the pore wall; see Section 2.1.2). Shifts in hk0 peaks indicate structural changes to constituent clay layers.
**Figure 4.1.A:** Powder XRD profile of powdered Laponite RD, showing major peaks and their assignments. NaCl was used as an internal standard.

**Figure 4.1.B:** Powder XRD profiles for (a) powdered Laponite RD, (b) Laponite RD filtercake (dried at 70°C) and (c) Laponite RD filtercake (calcined at 450°C in static air). NaCl was used as an internal standard.
Figure 4.1.A shows the component peaks for Laponite RD. The pattern has broad peaks due to the low crystallinity nature of the sample. Assignments were made in relation to typical hectorite peaks \(^{(2)}\). Broad reflections at \(2\theta \approx 13^\circ\) and \(27^\circ\) were initially assigned to incomplete filling of the sample holder (broad peaks are observed in this region when the empty sample holder was analysed). However, a clear peak was observed at \(2\theta \approx 28^\circ\) for some of the samples, such as c in Figure 4.1.B. Literature assigns a peak in this area to a \(d_{004}\) peak for hectorite \(^{(3)}\). The second peak that was previously assigned to the sample holder was also located in the same region as another hectorite peak. The \(d_{002}\) was less intense than the \(d_{004}\), therefore sample holder reflections could be masking this peak in some patterns.

In order to ensure precise peak position measurements, a small amount of \(\text{NaCl}(s)\) was added to act as an internal standard. The 200 and 220 peaks for this compound are clearly observed at \(2\theta = 31.6^\circ\) and \(45.4^\circ\) (d spacings of 2.84 and \(2.00\) Å respectively) \(^{(4)}\). The intense signal at very low angles (\(2\theta < 3^\circ\)) observed in Figures 4.1.A and 4.1.B is the trailing edge from the incident X-ray beam.

The powder XRD pattern of the dried filtercake sample differed only in signal intensity relative to powdered Laponite RD. The calcined sample was essentially the same except for the 001 peak which shifted to higher angles, indicating that the drying process led to partial internal collapse within the interlayer region. This is illustrated by Figure 4.1.B.
4.1.3: Textural Studies

Porosity data for Laponite RD (Rockwood Additives Ltd. data) gives the compound a BET multipoint specific surface area of $S_{\text{BET}} = 370 \, \text{m}^2 \, \text{g}^{-1}$. Gas adsorption data achieved in this study are summarized in Table 4.1.II.

**Table 4.1.II**: Porosity data for Laponite RD samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET Specific Surface Area / m$^2$ g$^{-1}$</th>
<th>Total Pore Volume / cm$^3$ g$^{-1}$</th>
<th>Modal Mesopore Diameter / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder Laponite RD</td>
<td>360</td>
<td>0.27</td>
<td>42</td>
</tr>
<tr>
<td>Dried filtercake</td>
<td>310</td>
<td>0.22</td>
<td>38</td>
</tr>
<tr>
<td>Calcined* filtercake</td>
<td>270</td>
<td>0.23</td>
<td>37</td>
</tr>
</tbody>
</table>

* Calcined at 450°C in static air.

The values achieved for powdered Laponite RD are close (within 3%) to those quoted by Rockwood Additives Ltd. Values for the dried and calcined filtercake are slightly lower; reported studies indicate that this is dependent on drying techniques. The sheet structure of clay aggregates, such as montmorillonites, become randomly orientated when dispersed in water. A slow drying procedure, such as air-drying, results in individual clay particles settling into a nearly homogeneous parallel orientation. As shown in Figure 4.1.C, this leads to microporosity as opposed to mesoporosity. Fast drying (e.g. freeze drying) permits the random distribution of the clay layers to be retained; porosity and specific surface area are therefore increased, whereas crystallinity (as detected via XRD peak width) decreases.

Oven-drying is a faster process than air-drying, but slower than freeze-drying. This is reflected in the porosity data reported above. The decrease in specific surface area indicated that some of the mesoporous structure had collapsed, but also shows that a significant amount of mesoporosity was retained.
This is supported by examining the N₂ gas adsorption/desorption isotherms, as shown in Figure 4.1.D. Isotherms of the powdered and calcined Laponite samples are very similar (both have classic type IV hysteresis loops), supporting the proposition that the samples are mesoporous. The slightly downward shift of the isotherm for the calcined sample reflects the lower pore volume of this sample.

4.1.4: FOURIER-TRANSFORM INFRARED SPECTROSCOPY

Fourier-transform infrared spectroscopy (FT-IR) data was used in this study to monitor template removal and to contrast “as-synthesized” samples to calcined ones. However, inorganic structural data were also obtained. The identification of features assigned to constituent units of layered silicates (i.e. hydroxyl groups, the silicate anion, and octahedral cations) was achieved. The main structural bands observed for Laponite RD in powder, dried and calcined filtercake forms are highlighted in Figure 4.1.E and Table 4.1.III.
CHAPTER 4: CHARACTERIZATION STUDIES

**FIGURE 4.1.D:** $\text{N}_2$ gas adsorption/desorption isotherms comparing powdered Laponite RD and calcined * Laponite RD filtercake (* calcined at 450°C in a static air environment).

**FIGURE 4.1.E:** FT-IR spectra comparing powdered Laponite RD to Laponite RD filtercake calcined at 450°C in static air.
TABLE 4.1.III: Main peaks featured in FT-IR spectra of Laponite RD.

<table>
<thead>
<tr>
<th>LAPONITE SAMPLE</th>
<th>Wavenumber / cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(SH)</td>
</tr>
<tr>
<td>LAPONITE RD</td>
<td>3608</td>
</tr>
<tr>
<td></td>
<td>(S/B)</td>
</tr>
<tr>
<td></td>
<td>3430</td>
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<td></td>
<td>(M/B)</td>
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<td></td>
<td>1646</td>
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<td></td>
<td>(S/B)</td>
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<tr>
<td></td>
<td>1011</td>
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<tr>
<td></td>
<td>(M)</td>
</tr>
<tr>
<td></td>
<td>653</td>
</tr>
<tr>
<td></td>
<td>(M)</td>
</tr>
<tr>
<td></td>
<td>460</td>
</tr>
<tr>
<td></td>
<td>(M)</td>
</tr>
<tr>
<td>FILTERCAKE, DRIED</td>
<td>3600</td>
</tr>
<tr>
<td></td>
<td>(SH)</td>
</tr>
<tr>
<td></td>
<td>3460</td>
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<td>(S/B)</td>
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<td>1640</td>
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<td></td>
<td>1007</td>
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<td></td>
<td>(S/B)</td>
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<tr>
<td></td>
<td>653</td>
</tr>
<tr>
<td></td>
<td>(M)</td>
</tr>
<tr>
<td></td>
<td>460</td>
</tr>
<tr>
<td></td>
<td>(S)</td>
</tr>
<tr>
<td>FILTERCAKE, CALCINED</td>
<td>3610</td>
</tr>
<tr>
<td></td>
<td>(SH)</td>
</tr>
<tr>
<td></td>
<td>3464</td>
</tr>
<tr>
<td></td>
<td>(M/B)</td>
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<td></td>
<td>1639</td>
</tr>
<tr>
<td></td>
<td>(M)</td>
</tr>
<tr>
<td></td>
<td>1007</td>
</tr>
<tr>
<td></td>
<td>(S/B)</td>
</tr>
<tr>
<td></td>
<td>669</td>
</tr>
<tr>
<td></td>
<td>(M)</td>
</tr>
<tr>
<td></td>
<td>448</td>
</tr>
<tr>
<td></td>
<td>(S/B)</td>
</tr>
</tbody>
</table>

Assignments:

- ~3670 - 3630 cm⁻¹ O-H stretching of clay lattice (octahedral layer) (6, 7)
- ~3620 - 3430 cm⁻¹ O-H stretching of water in interlayer region (6, 7)
- ~1635 cm⁻¹ H-O-H deformation (scissoring) (6)
- ~1010 cm⁻¹ Si-O stretching (6)
- ~660 - 650 cm⁻¹ O-H bend or wag (6)
- ~470 - 460 cm⁻¹ O-Si-O bend and deformation (6)

FT-IR vibrational intensities: s - strong; m - medium; w - weak; vw - very weak; sh - shoulder; b - broad.

N.B. A small double peak at ca. 2350 cm⁻¹ is observed in all spectra; this is assigned to CO₂(g) in the atmosphere being at different concentrations during background and sample scans.

4.1.5: SOLID STATE MAS-NMR

²⁹Si MAS-NMR (direct polarization) is very sensitive to the environment of the ²⁹Si nucleus. Chemical shifts are therefore particularly pertinent in determining aspects of a compound’s structure. Figure 4.1.F illustrates shifts (with respect to a TMS standard) associated with different levels of Si-O-Si condensation.
CHAPTER 4: CHARACTERIZATION STUDIES

FIGURE 4.1.F: Chemical shifts [(CH$_3$)$_4$Si as a reference] observed in $^{29}$Si solid state MAS-NMR spectra of siloxane species, as a function of the different number of neighbouring Si nuclei attached to a central silicate unit (adapted from Englehardt and Michel, 1987 (8)).

FIGURE 4.1.G: $^{29}$Si solid state MAS-NMR (direct polarization) of (a) Laponite RD, (b) dried Laponite RD filtercake and (c) Laponite RD filtercake calcined in static air at 450°C.


$^{29}$Si MAS-NMR spectra of Laponite RD and dried Laponite RD filtercake, as highlighted in Figure 4.1.G, show two signals: a weak one at $\delta = -85.0$ and a strong one at $\delta = -94.5$. These indicate a $Q^2$ resonance from the edges of the layers and $Q^3$ within the layers, respectively. However, the $Q^3$ signal of the calcined filtercake was skewed with the apex now at $\delta = -97.8$, while the $Q^2$ signal lost intensity. Data from Engelhardt and Michel assign hectorite [(Mg, Li)$_3$Si$_4$O$_{10}$(OH)$_2$.4H$_2$O, from Hector, California] a $Q^3$ peak of $\delta = -95.3$, whilst the non-lithium substituted magnesium silicate, talc [Mg$_3$Si$_4$O$_{10}$(OH)$_2$, from The Urals, Russia], has a $Q^3$ peak of $\delta = -98.1$. This indicates a high field shift occurs as lithium concentration decreases. The calcined sample does indeed have a lower lithium content, whilst the asymmetry of its $Q^3$ peak may be explained by disorder with slight changes in geometry within the structure. Appendix II gives better resolution of $Q^2$ peaks.

$^7$Li MAS-NMR (direct polarization) data for Laponite RD in Figure 4.1.H show one signal at $\delta = -0.46$, which is consistent with one structural environment for this species. However, closer inspection of the sideband bandshapes illustrate the possible presence of a second environment (two signals of different linewidths overlapping). A second environment was obvious in the calcined sample, where a shoulder to the main band was observed. As previously reported, a signal at $-0.4 \geq \delta \geq -0.5$ is expected, which corresponds to an octahedral LiO$_6$ environment in the system. As the larger of the two signals occurred in this region, it was concluded that the majority of the lithium nuclei were present in this octahedral environment. It is likely that the secondary peak arose from disorder within the Laponite RD structure; a possible interpretation is that an increase in lithium sites and defects near the surface which are due to a decrease in particle size. As the anomaly is asymmetric the cause could be from quadrupolar effects on lineshape.
Figure 4.1.H: $^7$Li solid state MAS-NMR (direct polarization) of (a) Laponite RD, (b) Laponite RD filtercake oven-dried at 70°C and (c) Laponite RD filtercake calcined in static air at 450°C.

Overview

Comparison of Laponite RD in both powdered and filtercake forms has shown that analysis carried out on powdered samples may be directly compared to dried filtercake data, and hence that of samples produced from adaptation or modification of filtercake. Calcination led to some degradation of the samples i.e. XRD profiles show some internal collapse had occurred; this was confirmed by N$_2$ gas adsorption studies, which showed decreases in pore volume and specific surface area after calcination. Solid-state MAS-NMR also shows the presence of some changed silicate and lithium environments after calcination.
Chapter 4: Characterization Studies

4.2: Methods of Synthesis

One of the main aims of this study was to improve the textural and adsorptive properties of Laponite RD via modification or tailoring techniques. Initially verification that our synthesis product was similar to that of Rockwood Additives Ltd was undertaken. To this end, samples were produced following Rockwood’s standard synthesis procedure from the component salts with the aim of producing a laponite with SiO₂:MgO ratio of 2.16. Typically the reaction mixture was subjected to hydrothermal conditions in an autoclave as part of the synthesis, but due to technical difficulties at the beginning of this study the samples were simply heated in a PTFE sealed container in an oven to the required temperature. This permitted a study of the effects of different synthetic methodologies to be carried out.

4.2.1: X-Ray Fluorescence

Table 4.2.1: Chemical compositions of laponite samples determined in this study by XRF analysis.

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>Nature of Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Powdered Laponite RD</td>
</tr>
<tr>
<td>%SiO₂</td>
<td>63.38</td>
</tr>
<tr>
<td>%MgO</td>
<td>29.32</td>
</tr>
<tr>
<td>%Na₂O</td>
<td>2.86</td>
</tr>
<tr>
<td>%CaO</td>
<td>0.20</td>
</tr>
<tr>
<td>%Total</td>
<td>95.76</td>
</tr>
<tr>
<td>SiO₂:MgO</td>
<td>2.16</td>
</tr>
<tr>
<td>Li g/kg *</td>
<td>3.12</td>
</tr>
</tbody>
</table>

* Determined by AAS at Rockwood Additives Ltd, Widnes, UK.
XRF analyses of oven and autoclave synthesized samples were carried out at Rockwood Additives Ltd. As illustrated in Table 4.2.1 the SiO$_2$ and MgO concentrations were similar, but, the SiO$_2$:MgO ratio for both synthetic hectorite KPs were higher than that of Laponite RD, 2.30 compared to 2.16. The most significant difference was the change in Na$_2$O concentration; that of the synthesized samples was considerably lower than that of the Rockwood sample. Although not introduced during the synthesis, a small amount of CaO was also present in all samples – the Rockwood samples had twenty fold the concentration (0.2%). It is hypothesised that the CaO content was due to either an impurity within the magnesium source used by Rockwood Additives Ltd during Laponite RD production or to the use of local tap water in factory synthesis.

**4.2.2: Powder X-Ray Diffraction**

Differences highlighted in the XRF data were clearly seen in the comparison of powder XRD profiles of Laponite RD versus hectorite KP samples. Figure 4.2.A shows that upon calcination at 1000°C powdered Laponite RD and its filtercake analogues were inherently the same. The synthetic hectorite KP samples, however, differed both from each other and the Laponite RD materials.

Comparisons, using a Seifert data search-match program, with the JCPDS powder XRD database show degradation of Laponite RD, at 1000°C, produced either Na$_2$Mg$_5$Si$_{12}$O$_{30}$ \(^{(11)}\) and/or Na$_2$Mg$_4$LiSi$_{12}$O$_{30}$ \(^{(12)}\). However, the reflection in Laponite RD with a peak of $2\theta = 28.08$, which is not attributable to either of these materials, was assigned to $d_{101}$ in quartz \(^{(13)}\). The less complicated profiles of the synthetic hectorite KP materials were closely related to those of enstatite (MgSiO$_3$)\(^{(14, 15)}\) and crystalline SiO$_2$ (such as quartz, cristoballite and/or tridymite \(^{(13, 16, 17)}\)).
**Figure 4.2.A:** Powder XRD profiles comparing (a) powdered Laponite RD, (b) Laponite RD filtercake (dried at 70°C), (c) Laponite RD filtercake (calcined at 450°C in static air), (d) synthetic hectorite KP (oven) and (e) synthetic hectorite KP (autoclave) all calcined at 1000°C in static air. s and e indicate reflections due to SiO₂ and enstatite. NaCl was used as an internal standard, and * denotes the positions of the $d_{200}$ and $d_{220}$ NaCl peaks.
Despite the clear differences between Laponite RD and synthetic hectorite KP that have been highlighted by XRF and powder XRD of the samples when calcined at 1000°C, Figure 4.2.B illustrates some notable similarities between these materials. Peaks for $hk\theta$ and the internal standard, NaCl$(s)$, were clearly in the same positions for all samples, indicating hectorite phases were produced. Comparison with the XRD profile of a Californian hectorite further supports this proposal. Brindley compared the XRD profiles of a number of smectites to highlight similarities in their 2D diffraction bands. The profile of a Californian hectorite shows $d_{001}$ with $2\theta \approx 7^\circ$, $d_{020, 110}$ with $2\theta \approx 20^\circ$ and $d_{130, 200}$ with $2\theta \approx 35^\circ$. The clear $d_{001}$ peak observed with Laponite RD was present in both the autoclave and oven synthesised samples, but it was not well defined and assigning $d_{001}$ values was problematic.
4.2.3: THERMOGRAVIMETRY AND DIFFERENTIAL THERMAL ANALYSIS

The dehydration and dehydroxylation of Laponite RD and hectorite KP results in production of enstatite (MgSiO₃) and crystalline SiO₂ such as quartz, cristoballite and/or tridymite and can be probed using thermogravimetric (TG) and differential thermal analysis (DTA). The relatively steep initial slope was due to the loss of water from the surface and the interlayer regions of the samples, whilst the dehydroxylation of the clay layers was a more gradual process. Broad endotherms, like those observed at T ≈ 150°C in the DTA curves in Figures 4.2.C and 4.2.D, were related to dehydration. The narrow exotherm at T ≈ 800°C was due to chemical changes in the system and was likely to be a result of crystallization and the formation of enstatite. Although the general shape of the TG and DTA graphs appeared very similar for Laponite RD and hectorite KP, differences were observed. Laponite RD had a greater overall mass loss than hectorite KP (17.7% as opposed to 13.5% at 1000°C), although the drying of Laponite RD filtercake at 70°C led to a 32% mass loss, and so this difference may be due to different levels of hydration before analysis. More significantly, Laponite RD had a smaller temperature range between initial dehydration and final dehydroxylation. The dehydration endotherm occurred 70°C higher for Laponite RD than for hectorite KP (183°C as opposed to 124°C) and there was a 90°C difference between the sharp crystallization exotherms (777°C for Laponite RD and 865°C for hectorite KP). These results reflect the chemical differences observed in XRD and XRF analyses.
CHAPTER 4: CHARACTERIZATION STUDIES

**FIGURE 4.2.C:** Thermogravimetric and DTA analysis of Laponite RD.

**FIGURE 4.2.D:** Thermogravimetric and DTA analysis of hectorite KP (autoclave).
4.2.4: **Fourier Transform Infrared Spectroscopy**

Comparison of the FT-IR spectra for Laponite RD and hectorite KP, showed very little difference between the two dry samples. All peaks assigned from Table 4.1.111 to Laponite RD were present in hectorite KP in the same positions. Figures 4.2.E and 4.2.F support the previous evidence that calcination changes the structure of both compounds and that this process highlights differences between the two clays. The most obvious changes, due to calcination, were the loss of peaks due to dehydration and dehydroxylation of the clays. Peaks due to O-H stretches, both from within the clay lattice ($\approx 3650 \text{ cm}^{-1}$) and from interlayer water ($\approx 3620 - 3430 \text{ cm}^{-1}$), as well as H-O-H scissoring ($\approx 1635 \text{ cm}^{-1}$) disappeared. The fingerprint region below 1000 cm$^{-1}$ split into a wide variety of peaks. As with the powder XRD profiles, this increase in detail was a result of increased crystallinity. These peaks are difficult to assign, but are due to stretching and bending of bonds within enstatite and/or crystalline SiO$_2$ (quartz, cristoballite and/or tridymite (21)). Differences between the spectra of the two calcined samples were expected from previous data. Differences were observable within the FT-IR data but were not as pronounced as with other techniques, such as powder XRD. A greater number of peaks were observed in the fingerprint region of the FT-IR spectra of calcined Laponite RD than for its hectorite KP analogue; this could be due to the former sample's higher degree of crystallinity in its calcined form, as evident in powder XRD, Figure 4.2.A.
**Figure 4.2.E:** FT-IR spectra comparing powdered Laponite RD with Laponite RD filtercake calcined at 1000°C.

**Figure 4.2.F:** FT-IR spectra comparing hectorite KP samples when dried at 110°C and when calcined at 1000°C.
4.2.5: Scanning Electron Microscopy

One difference between these samples, which may be observed with the naked eye, was their physical appearance. After the drying process was complete, Laponite RD required grinding to produce a talc-like powder, whereas synthetic hectorite KP was held together by static electricity and required just the lightest touch to be reduced to a very fine powder. Upon closer inspection, with the use of SEM the smaller particle size of hectorite KP, with respect to Laponte RD, was observed, as shown in Figures 4.2.G and 4.2.H.

Figures 4.2.G: SEM image of Laponite RD.

Figure 4.2.H: SEM image of hectorite KP.
4.2.6: Textural Studies

The pore volumes and surface areas for the hectorite KP samples were surprisingly high. Indeed, Table 4.2.I shows both parameters almost doubled in value compared to those found for the parent Laponite RD. Modal pore diameter values were lower than those of Laponite RD, but were similar to those of the dried filtercake. This indicates that the drying procedure reduced the extent of mesoporosity within the system.

**Table 4.2.II: Porosity data of Laponite RD and hectorite KP samples.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET Specific Surface Area / m² g⁻¹</th>
<th>Total Pore Volume / cm³ g⁻¹</th>
<th>Modal Mesopore Diameter / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder Laponite RD</td>
<td>360</td>
<td>0.27</td>
<td>42</td>
</tr>
<tr>
<td>Hectorite KP (autoclave)</td>
<td>610</td>
<td>0.44</td>
<td>36</td>
</tr>
<tr>
<td>Hectorite KP (oven)</td>
<td>550</td>
<td>0.40</td>
<td>38</td>
</tr>
</tbody>
</table>

Closer inspection of the gas adsorption isotherms in Figure 4.2.I showed significant differences between the three samples. All may be considered as Type IV isotherms, with obvious hysteresis loops, but the loops were of differing shapes. The shape of the isotherm is thought to indicate the shape of the pores present in the system. Laponite RD presents a classic H₂ hysteresis loop indicating near-cylindrical pore channels which were interconnected and of various sizes and shapes. Hectorite KP (oven) appeared to have a H₃ loop, a lot narrower than Laponite RD; non-uniform slit-shaped pores were likely to be present. Finally, the sample produced in the autoclave seemed to be intermediate between the two other samples. It had a fairly open hysteresis, but there was no “step” when the loop closed. It was likely that either a mixture of cylindrical and slit-shaped pores were present in this sample, or the pore shape could have been intermediate between these two forms (i.e. they were rounded slits).
FIGURE 4.2.I: \( N_2 \) gas adsorption/desorption isotherms comparing the effect different methods of synthesis produce on the textural properties of Laponite-like samples.

FIGURE 4.2.J: The effect of different methods of synthesis on pore size distribution data.
Analysis of pore size distribution data, Figure 4.2.J, showed that all three methods of synthesis lead to monomodal mesoporosity. However, the hectorite samples had a higher degree of microporosity than the Laponite RD analogue, which explains the higher specific surface area and pore volumes observed, as well as the decreases in modal pore diameter size.

4.2.7: SOLID STATE MAS-NMR:
Contrary to Laponite RD (Section 4.1.5), the hectorite KP samples appeared to only contain octahedral lithium present in their structure; a single signal was observed in the $^7$Li spectra at $\delta = -0.52$. The narrower line width and larger signal to noise ratio (hence smaller area under the peak), as observed in Figure 4.2.K, and supporting XRF data confirmed that the sample prepared in the autoclave had less lithium present than the Laponite RD analogue.

$^{29}$Si MAS-NMR (direct polarisation) spectra for the hectorite KP samples are very complex in Figure 4.2.L. Strong $Q^3$ signals were observed at $\delta = -96.9$ for the sample produced in the autoclave and at $\delta = -95.2$ for the oven synthesised one. Both have shifted to higher fields than the signal for Laponite RD at $\delta = -94.5$. This follows the trend in Section 4.1.5, where a decrease in lithium content leads to a high field shift of the $Q^4$ peak $^{(9)}$. A medium intensity $Q^2$ signal was observed at $\delta = -85.3$ for both samples, which was very similar to that of Laponite RD at $\delta = -85.0$. In contrast to Laponite RD, a third signal was also apparent in the spectra. This weak signal at $\delta = -112.0$ implied that some Si species were present in a $Q^4$ environment. Closer inspection presented an even more complex system with the $Q^2$ and $Q^3$ signals appearing to mask others; this was likely to be due to disorder within the system. In Figure 4.2.L some of the peaks appear no greater than the background noise; larger spectra are provided in Appendix II which show better resolution of these peaks.
**CHAPTER 4: CHARACTERIZATION STUDIES**

**FIGURE 4.2.K:** $^7$Li solid state MAS-NMR (direct polarisation) spectra of (a) Laponite RD, (b) hectorite KP (oven) and (c) hectorite KP (autoclave).

**FIGURE 4.2.L:** $^{29}$Si solid state MAS-NMR (direct polarisation) spectra of (a) Laponite RD, (b) hectorite KP (oven) and (c) hectorite KP (autoclave).
OVERVIEW

Although significant decreases in sodium and lithium contents, relative to Laponite RD, were observed for the hectorite KP samples, the porosity of these compounds was greatly enhanced. A possible scale-down dependent effect led to an increase of over 200 m² g⁻¹ in specific surface area and the pore volume almost doubled with respect to Laponite RD. Both similarities and differences in the compounds were observed by powder XRD. Analysis of dried and calcined compounds gave similar profiles up to 450°C, but at 1000°C Laponite RD showed a tendency to greater crystallinity. Pore size distribution data indicated that greater porosity was due to a higher percentage of micropores in these systems compared with the analogous Laponite RD samples. N₂ gas adsorption isotherms supported the hypothesis of a different network of pores being present. Although both samples gave Type IV isotherms, the hysteresis loops of the hectorite KP samples were less vertical than that of Laponite RD indicating slit shaped pores rather than cylindrical ones.

A possible consequence of the decrease in Na₂O content is its effect on the proposed templating of hectorite KP. It is thought that the ejection of Na⁺ ions from the interlayer spaces allows the incorporation of CTMA⁺ ions into the clay interlayer via ion exchange. With such a low sodium content, such templating may be hindered.

N.B. Due to the enhanced porosity characteristics of the products of autoclave synthesis with respect to oven synthesis, all other hectorite KP samples produced in this study were synthesised with the aid of an autoclave.
4.3: Pillaring of Laponite RD

Clays lack permanent porosity; interlayer regions expand during hydration and collapse during dehydration (Figure 1.2.E). The most common process employed to overcome this problem is known as pillaring, which “props” open the pores while stopping swelling and contracting of the interlayer region (Section 1.2). To determine whether liquid crystal templating of clay is a feasible method of porosity enhancement, it was compared to samples that have undergone pillaring with the aluminium keggin ion \( [\text{Al}_{13}\text{O}_{4}(\text{OH})_{24}(\text{H}_{2}\text{O})_{12}]^{7+} \) or “\( \text{Al}_{13}^{7+} \)”. As described in Chapter 3, a polyoxoaluminium (III) ion-exchanged sample was produced and then calcined at 450°C to give a pillared one.

4.3.1: Powder X-Ray Diffraction

The ion-exchanged sample gave an XRD pattern related to that of Laponite RD, Figure 4.3.A. The \( h\k\ell \) and NaCl peaks were present in the same positions, however, the \( d_{001} \) peak shifted to a slightly lower angle and hence increased \( d \)-spacing, from 13.5 Å to 17.3 Å. This was due to the “\( \text{Al}_{13}^{7+} \)” ion been much bulkier than Na⁺ ions.

The pillared sample also showed that \( h\k\ell \) and NaCl peaks were similar to those found for Laponite RD. However, the \( d_{001} \) peak has moved to higher angles but was badly defined. This indicated that internal contraction occurred during calcination, due to dehydration and condensation. It was difficult to observe the extent of contraction as the trailing edge of the X-ray beam masked the detail, Figure 4.3.A.
Figure 4.3.A: Powder XRD profiles for (a) powdered Laponite RD, (b) Keggin-ion exchanged Laponite RD and (c) pillared Laponite RD. NaCl(s) was used as an internal standard.

4.3.2: Textural Studies

The pillaring of Laponite RD reduced the specific surface area and modal mesopore diameter of the sample. However, an increase in pore volume was observed in Table 4.3.1.

Table 4.3.1: Porosity data of Laponite-like samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET specific surface area / m² g⁻¹</th>
<th>Total pore volume / cm³ g⁻¹</th>
<th>Modal mesopore diameter / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder Laponite RD</td>
<td>360</td>
<td>0.27</td>
<td>42</td>
</tr>
<tr>
<td>Laponite RD, dried* filtercake</td>
<td>310</td>
<td>0.22</td>
<td>38</td>
</tr>
<tr>
<td>Laponite RD, calcined# filtercake</td>
<td>270</td>
<td>0.23</td>
<td>37</td>
</tr>
<tr>
<td>Ion exchanged Laponite</td>
<td>400</td>
<td>0.37</td>
<td>37</td>
</tr>
<tr>
<td>Pillared Laponite</td>
<td>310</td>
<td>0.32</td>
<td>37</td>
</tr>
</tbody>
</table>

* Dried in static air at 70°C.  # Calcined at 450°C.
The pillared sample was produced from filtercake and then calcined; a comparison with filtercake calcined at 450°C gave a slightly elevated surface area, a significantly increased pore volume and no change in modal mesopore diameter. Figure 4.3.B shows that pillared Laponite produced an H2, type IV isotherm, confirming mesoporosity. Contrary to hectorite KP, pillared samples produced similar shaped hystereses to that of untreated Laponite RD. Hence, similar shaped pores were likely, although they were possibly more uniform as a more vertical H2 loop was produced. This was not unexpected; pillaring should regulate order between clay platelets.

**Figure 4.3.B:** N2 gas adsorption/desorption isotherms comparing Laponite RD to a “Al137+” pillared Laponite RD.
4.3.3: SOLID STATE MAS-NMR:

Solid state MAS-NMR data were recorded for $^7$Li, $^{29}$Si and $^{27}$Al nuclei for both the ion-exchanged and pillared samples, Figures 4.3.C, 4.3.D and 4.3.E, respectively. Both exhibited single octahedral signals at $\delta = -0.46$ and $\delta = -0.41$, respectively, in the $^7$Li spectra. In $^{29}$Si MAS-NMR spectra, $Q^3$ signals were clearly present at $\delta = -94.5$ and $\delta = -97.3$, for the ion-exchanged and pillared samples, respectively. Both signals were slightly skewed, but the $Q^2$ signal had all but disappeared. The high field shift, observed for pillared Laponite RD, could have been caused by the formation of Si-O-Al bonds on condensation between the layers and the Keggin ion.

![Figure 4.3.C: $^7$Li solid state MAS-NMR (direct polarisation) spectra of (a) Laponite RD, (b) Keggin ion-exchanged Laponite RD and (c) pillared Laponite RD.](image-url)
Figure 4.3.D: $^{29}$Si solid state MAS-NMR (direct polarisation) spectra of (a) Laponite RD, (b) Keggin ion-exchanged Laponite RD and (c) pillared Laponite RD.

Figure 4.3.E: $^{27}$Al solid state MAS-NMR (direct polarisation) spectra of (a) Keggin ion-exchanged Laponite RD and (b) pillared Laponite RD.
The $^{27}$Al spectra of these two samples showed two main signals; the major one at $\delta = 2.3$ for the ion-exchanged sample shifted slightly to $\delta = 5.4$ for the pillared sample. Al nuclei are considered to be in an octahedral environment in this $\delta$ range. The second signal at $\delta = 59.8$ and $\delta = 56.6$ for the ion-exchanged and pillared samples, respectively, indicated that a proportion of the aluminium nuclei were present in tetrahedral form. This dominance by the octahedral sites was in contrast to the tetrahedral dominance found in solution NMR of the Keggin ion solution. This change was likely due to change in internal geometry of the Keggin ion in moving from solution to the solid state.

**OVERVIEW**

The $^{27}$Al solid state MAS-NMR data showed that pillaring of Laponite RD was achieved using the aluminium Keggin ion. Compared to powdered Laponite RD, pillaring in this sample led to relatively small improvements in its porosity; minor changes in specific surface area occurred, whilst the pore volume improved. The main advantage of pillaring was the increased order of the porous network, as demonstrated by the more vertical H2 hysteresis loop in the N$_2$ adsorption/desorption isotherm.
4.4: CHANGE IN SiO₂ CONCENTRATION

Liquid crystal templating methods are based on the condensation of silica and a surfactant (Section 1.4)\(^{22-23}\). Therefore, a change in the silica content of the solid matrix might lead to a change in textural properties of the Laponite system, such as increased specific surface area and pore volume when the silica content is increased.

4.4.1: X-RAY FLUORESCENCE

For this part of the study, samples were produced using the standard synthesis procedure as provided by Rockwood Additives Ltd. A combination of salts designed to give a SiO₂:MgO ratio of 2.16 was used to obtain hectorite KP. Subsequent samples were made using a 25% change in SiO₂ content of the starting materials; viz. a 25% increase or decrease in sodium silicate solution was added to the reaction mixture.

**Table 4.4.1:** Chemical compositions of synthetic hectorite systems, with varying SiO₂ contents, contrasted with Laponite RD, as determined by XRF analysis.

<table>
<thead>
<tr>
<th><strong>CHEMICAL COMPOSITION</strong></th>
<th><strong>NATURE OF SAMPLE</strong></th>
<th><strong>Powdered Laponite RD</strong></th>
<th><strong>Hectorite KP</strong></th>
<th><strong>Hectorite KP with an increase in SiO₂ content</strong></th>
<th><strong>Hectorite KP with a decrease in SiO₂ content</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>%SiO₂</td>
<td>63.38</td>
<td>66.01</td>
<td>65.71</td>
<td>66.02</td>
<td></td>
</tr>
<tr>
<td>%MgO</td>
<td>29.32</td>
<td>28.72</td>
<td>25.74</td>
<td>32.11</td>
<td></td>
</tr>
<tr>
<td>%Na₂O</td>
<td>2.86</td>
<td>0.01</td>
<td>0.43</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>%CaO</td>
<td>0.20</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>%Total</td>
<td>95.76</td>
<td>94.75</td>
<td>91.89</td>
<td>98.14</td>
<td></td>
</tr>
<tr>
<td>Li g/kg *</td>
<td>3.12</td>
<td>0.16</td>
<td>0.27</td>
<td>nd</td>
<td></td>
</tr>
<tr>
<td>SiO₂:MgO</td>
<td>2.16</td>
<td>2.30</td>
<td>2.55</td>
<td>2.06</td>
<td></td>
</tr>
<tr>
<td>Change in SiO₂:MgO / %</td>
<td>-</td>
<td>0</td>
<td>+10.9</td>
<td>-10.4</td>
<td></td>
</tr>
</tbody>
</table>

**nd** = not determined.  * Determined by AAS at Rockwood Additives Ltd, Widnes, UK.
As noted in Section 4.2, the synthesis of hectorite KP did not lead to a SiO₂:MgO ratio of 2.16 and the samples had low sodium and lithium contents with respect to the Laponite RD analogue. Table 4.4.1 shows that a 25% change in the quantity of silicon dioxide added to the reaction mixture led to a ~10% change in the SiO₂:MgO ratio compared to hectorite KP. The 10% increase in silica to magnesium oxide ratio led to an increase in the sodium and lithium contents, although these values were still small with respect to that of Laponite RD.

4.4.2: POWDER X-RAY DIFFRACTION

The XRD profiles of materials calcined at 1000°C in static air, highlighted in Figure 4.4.A, show that very similar materials were produced. Hectorite KP and the sample synthesized with a decreased amount of sodium silicate solution provided almost identical profiles. As discussed in Section 4.2.2 hectorite KP, and hence the sample with a 10% reduction in SiO₂:MgO, gave very similar XRD profiles to that for enstatite (MgSiO₃) (14-15). Other crystalline phases may also be present, particularly crystalline SiO₂ as quartz, cristoballite and/or tridymite (13, 16-17). This is particularly noticeable when the SiO₂ content was increased; a peak appears at 2θ = 21.8° which is not present in enstatite but can be assigned to the reflection from the d₁₀₁ plane in cristoballite (16). This peak was more pronounced for the sample with increased SiO₂ content than it was in the XRD profile of Laponite RD. Upon calcination at 1000°C, Laponite RD gives a more complex powder XRD pattern, consistent with greater long range order than that of the calcined synthetic hectorite KP samples.
FIGURE 4.4.A: Powder XRD profiles of hectorite KP with varying levels of SiO₂ content. (a) increased (b) synthesised according to Rockwood Additives protocol and (c) decreased. All samples calcined at 1000°C. NaCl was used as an internal standard.

FIGURE 4.4.B: Powder XRD profiles of hectorite KP with varying levels of SiO₂ content. (a) increased (b) synthesised according to Rockwood Additives protocol and (c) decreased. All samples uncalcined. NaCl was used as an internal standard.
Figure 4.4.B illustrates patterns produced by powder XRD for these samples, when uncalcined. These highlight that the materials were indeed hectorites. Although intensity was low when the silica content was decreased, all three samples gave NaCl (2θ = 31.6° and 45.4°, d_200 and d_220 respectively) and hk0 peaks which appear in the same regions, both with respect to each other and to Laponite RD. These similarities and a comparison with the XRD profile of a Californian hectorite indicate that hectorite structures are still being formed. Detail of the d_001 peak was masked by the trailing edge of the X-ray beam.

4.4.3: Textural Studies

Although there were no significant changes in specific surface area or modal mesopore diameter on variation of SiO_2 content, differences were observed in total pore volume. As may be seen in Chapter 5, this was not as significant as that achieved by templating alone, it is nonetheless an improvement. This could be enhanced by the addition of a surfactant during synthesis (Section 5.4).

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>BET SPECIFIC SURFACE AREA / m^2 g^-1</th>
<th>TOTAL PORE VOLUME / cm^3 g^-1</th>
<th>MODAL MESOPORE DIAMETER / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder Laponite RD</td>
<td>360</td>
<td>0.27</td>
<td>42</td>
</tr>
<tr>
<td>Hectorite KP</td>
<td>610</td>
<td>0.44</td>
<td>36</td>
</tr>
<tr>
<td>Hectorite KP with an increase in SiO_2 content</td>
<td>670</td>
<td>0.52</td>
<td>35</td>
</tr>
<tr>
<td>Hectorite KP with a decrease in SiO_2 content</td>
<td>610</td>
<td>0.39</td>
<td>37</td>
</tr>
</tbody>
</table>

Table 4.4.II: Porosity data of synthetic hectorite KP samples with varying SiO_2 contents.
Figure 4.4.C shows hysteresis loops observed in the N$_2$ gas adsorption isotherms, confirming the mesoporous nature of all three materials. In section 4.2.3 we established that hectorite KP displayed a hysteresis intermediate between the H2 and H3 loops, relating either to a mixture of cylindrical and slit-shape pores or an intermediate between the two forms, such as rounded slits. The sample with increased silica content exhibited a similar isotherm, but the sample with a lower SiO$_2$ content displayed a much narrower hysteresis. This H4 type loop indicates that uniform slit-shaped pores are formed from plate-like particles \textsuperscript{(21)}.

**Figure 4.4.C:** N$_2$ gas adsorption/desorption isotherms of synthetic hectorite KP samples with varying SiO$_2$ content.

**OVERVIEW**

As expected, a decrease in SiO$_2$ content led to a reduction in the desirable textural properties of hectorite KP. An increase in silica led to improvements in pore volume, to a level almost double that of Laponite RD. The next step is to examine whether this marked improvement can be enhanced when combined with liquid crystal templating.
4.5: SUMMARY

The standard properties of Laponite RD were determined through characterization of powdered and filtercake samples. Once these reference points were established the nature and extent of modification through the tailoring of filtercake samples and synthesis of new samples could be examined. These characteristics were determined via nitrogen sorption porosimetry, powder X-ray diffraction, XRF analysis, FT-IR spectroscopy, solid state MAS-NMR, TG analysis and SEM.

The synthesis of Laponite RD, following the Rockwood protocol, led to the production of a hectorite (hectorite KP) with decreased sodium and lithium contents. Although no changes were made to the procedure, increased specific surface area and total pore volume were achieved. Powder XRD of dried and calcined samples showed that these samples were synthetic hectorites. However, calcination at 1000°C highlighted differences between the chemistry, crystallinity and long-range order of these clays and the analogous Laponite RD.

The production of hectorite KP led to improvements in porosity characteristics with respect to Laponite RD; these changes are possibly due to scale-down errors between laboratory synthesis and Rockwood's multi-tonne manufacture of Laponite RD. A 70% increase in BET multipoint specific surface area was achieved; $S_{BET} = 360 \text{ m}^2 \text{ g}^{-1}$ for Laponite RD and $S_{BET} = 610 \text{ m}^2 \text{ g}^{-1}$ for hectorite KP. While the total pore volume rose from $0.27 \text{ cm}^3 \text{ g}^{-1}$ for Laponite RD to $0.44 \text{ cm}^3 \text{ g}^{-1}$ for hectorite KP.
Comparison with alternative methods of tailoring, such as pillaring with the aluminium keggin ion ([Al$_{13}$O$_4$(OH)$_{24}$(H$_2$O)$_{12}$]$^{7+}$) were also carried out. $^{27}$Al solid state MAS-NMR confirmed that pillaring with the aluminium keggin ion had been achieved. Compared to powdered Laponite RD, pillaring led to relatively minor changes in porosity. The main advantage of pillaring was the increased order of the porous network, as demonstrated by the more vertical H2 hysteresis loop in the N$_2$ adsorption/desorption isotherm.

Changes in the silica content of hectorite KP led to changes in its porosity. A 25% change in the amount of silica introduced during synthesis of hectorite KP led to a 10% change in silica:magnesium oxide ratio of the product. Increased silica content during this synthesis led to increased total pore volume and specific surface area. A 10% increase in SiO$_2$ content led to an 18% increase in pore volume for these samples; from 0.44 cm$^3$ g$^{-1}$ to 0.52 cm$^3$ g$^{-1}$, nearly double that of Laponite RD (0.27 cm$^3$ g$^{-1}$).

Reference points and standard parameters have been established in this chapter. Significant rises in porosity parameters have also been observed during laboratory synthesis of hectorite KP. The next step is to examine whether further improvements can be achieved when combined with liquid crystal templating.
REFERENCES

4. JCPDS file No. 77-2064 NaCl
11. JCPDS file No. 73-929 Na₂Mg₅Si₁₂O₃₀
12. JCPDS file No.73-934 Na₃Mg₄LiSi₁₂O₃₀
13. JCPDS file No. 79-1913 Quartz
14. JCPDS file No. 83-2057 or 19-768 Enstatite
15. JCPDS file No. 11-273 MgSiO₃
16. JCPDS file No. 76-941 Cristoballite, India
17. JCPDS file No. 83-2299 Tridymite


CHAPTER 5
RESULTS AND DISCUSSION:
POROSITY ENHANCEMENT STUDIES
CHAPTER 5: RESULTS AND DISCUSSION OF

POROSITY ENHANCEMENT STUDIES

The most significant development in the field of ordered mesoporous materials occurred in 1992 when the first ordered mesoporous molecular sieves, a family of silica-based compounds known as M41S, were produced by researchers at Mobil Research and Development Corporation. The basis of their synthesis was the liquid crystal templating of a silica source (Section 1.4). As clay is primarily a silicate, the question arises “Why not apply the same principles to enhancing the textural properties of Laponite RD?”

In Chapter 4, reference points were determined via characterization of parent materials. Analysis of Laponite RD, in both powdered and filtercake forms, and hectorite KP is key in establishing the structure and nature of each sample. The extent of modification and its effect on the porosity of Laponite RD and synthetic hectorite KP will now be discussed. The appropriate choices of template, reagent concentrations, synthesis protocol and template removal strategy, to give maximum porosity enhancement, were determined.

The characteristics of these tailored materials were determined via nitrogen sorption porosimetry, X-ray diffraction (XRD), X-ray fluorescence analysis (XRF), Fourier transform infrared spectroscopy (FT-IR), elemental microanalysis, thermogravimetry (TG), and solid-state magic-angle-spinning nuclear magnetic resonance spectroscopy (MAS-NMR).

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5.1: Different Ratios of Clay to Template

The main template used in this study was the surfactant cetyltrimethylammonium chloride (CTMACl). It was chosen because of its previous use in MCM synthesis (2) and its cationic nature; Laponite RD has a negative charge of 0.7, which is balanced by interlayer sodium cations. Three different ratios of clay to surfactant were employed in this study: I: 7.1 g, II: 14.2 g, III: 21.3 g of Laponite RD filtercake to 0.01 mol surfactant (see Section 3.1.5).

5.1.1: Powder X-Ray Diffraction

The powder XRD patterns of the three uncalcined templated compounds were very similar to previous samples in this study. NaCl and hko peaks were consistent with non-templated systems, whilst d001 was visible for all samples. It is possible to see that this latter peak shifted to lower angles and therefore higher d-spacing, but as it is characteristically masked by the trailing edge of the X-ray beam, precise spacings cannot be determined. Figure 5.1.A (c) shows a clear d001 signal. Upon removal of the template NaCl and hko peaks remained constant, but dehydration (and thus contraction of the interlayer spacing) occurred for calcined samples, as indicated in Figure 5.1.B by the shift to higher angles of the d001 peak.

5.1.2: Textural Studies

As illustrated in Table 5.1.1 the introduction of a template to the Laponite RD system leads to a significant increase in pore volume. That synthesised with the greatest proportion of surfactant introduced (Ratio I) almost doubled in pore volume, whilst the other samples with lower surfactant:clay ratios (Ratio II and III) increased the pore volume by two and a half fold. The specific surface areas of these two latter samples were very similar, but the sample templated with the lowest ratio (III) has a greater modal pore diameter. All samples were calcined prior to N2 gas absorption analyses.

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**Figure 5.1.A:** Powder XRD profiles of Laponite RD templated with CTMACl (a) III, (b) II, (c) I and (d) untemplated. All samples were uncalcined. NaCl was used as an internal standard; the $d_{200}$ and $d_{220}$ peaks are highlighted.

**Figure 5.1.B:** Powder XRD profiles of Laponite RD templated with CTMACl (a) III, (b) II, (c) I and (d) untemplated. All samples were calcined at 450°C. NaCl was used as an internal standard; the $d_{200}$ and $d_{220}$ peaks are highlighted.
TABLE 5.1.1: Porosity data of Laponite RD samples templated with the surfactant CTMACl. Each sample (except powder Laponite RD) was calcined at 450°C before N₂ gas adsorption studies.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>BET SPECIFIC SURFACE AREA / m² g⁻¹</th>
<th>TOTAL PORE VOLUME / cm³ g⁻¹</th>
<th>MODAL MESOPORE DIAMETER / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder Laponite RD</td>
<td>360</td>
<td>0.27</td>
<td>42</td>
</tr>
<tr>
<td>Laponite RD filtercake</td>
<td>270</td>
<td>0.23</td>
<td>37</td>
</tr>
<tr>
<td>0</td>
<td>320</td>
<td>0.28</td>
<td>39</td>
</tr>
<tr>
<td>I</td>
<td>310</td>
<td>0.47</td>
<td>43</td>
</tr>
<tr>
<td>II</td>
<td>460</td>
<td>0.66</td>
<td>37</td>
</tr>
<tr>
<td>III</td>
<td>450</td>
<td>0.65</td>
<td>39</td>
</tr>
</tbody>
</table>

Although in comparison to the original powdered Laponite RD the specific surface area decreased, for Ratio I, an increase was achieved relative to calcined Laponite RD filtercake. The use of lower surfactant:clay ratios has led to increases in specific surface area of approximately 100 m² g⁻¹. These relatively small changes were dramatically outweighed by the large increases in pore volume. Comparison of the N₂ sorption isotherms of Laponite RD and a sample templated with CTMACl (Ratio III) provided evidence that order within the system improved through restructuring. Figure 5.1.C shows that templated Laponite RD filtercake yielded an H2 hysteresis loop, which was more vertical than the non-templated Laponite RD, indicating more uniform pores.
Chapter 5: Porosity Enhancement

Figure 5.1.C: N\textsubscript{2} gas adsorption/desorption isotherms comparing Laponite RD and Laponite RD filtercake templated with CTMACl (Ratio III) and calcined at 450\textdegree C in flowing oxygen.

Comparison with a sample of filtercake that had experienced the same processing but without the addition of a template (Ratio 0), showed that the change in textural properties is indeed related to the addition of CTMACl, as opposed to the mixing process. Previous studies\textsuperscript{(3)} have reported that interlayer sodium ions undergo ion-exchange with pillaring or templating species. Analysis of water removed by centrifugation after templating, but before washing and drying of the samples, revealed that 260 mg dm\textsuperscript{-3} of sodium was released from a templated sample, whilst only 20 mg dm\textsuperscript{-3} of sodium was present in the water of a non-templated sample. This apparent exchange of bulky CTMA\textsuperscript{+} ions for small Na\textsuperscript{+} ions in the clay interlayer, may explain the increases in \textit{d}-spacing and total pore volume found within these systems.

* The release of sodium ions without the presence of templating ions indicates a small degree of hydrolysis occurred.
5.1.3: ELEMENTAL CHN ANALYSIS

Elemental analysis of the samples provided interesting information. All uncalcined samples contained approximately 30% carbon (Table 5.1.II). This suggested that an optimum amount of surfactant may have been incorporated into the system. However, as the porosity data illustrated, although the same proportion of surfactant was present, different textural effects were ultimately observed for each sample.

**Table 5.1.II:** Elemental CHN data for restructured Laponite RD samples with varying clay to template ratios.

<table>
<thead>
<tr>
<th>CLAY: SURFACANT RATIO</th>
<th>DETERMINED MASS %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>I</td>
<td>30.50</td>
</tr>
<tr>
<td>II</td>
<td>30.60</td>
</tr>
<tr>
<td>III</td>
<td>30.00</td>
</tr>
</tbody>
</table>

**Overview**

The use of a surfactant led to dramatic changes in the textural properties of the synthetic hectorite Laponite RD. Pore volume increased by two and a half fold and specific surface area increased by around 100 m² g⁻¹. The lowest surfactant-to-clay ratio gave the most significant increases, which will reduce the financial and environmental impact of this process. Release of Na⁺ ions during templating indicates that surfactant cations are exchanged with these interlayer ions. The size difference between these ions may explain the increases observed in clay porosity characteristics.
5.2: DIFFERENT TEMPLATES
A variety of parameters were investigated in this part of the study. Firstly, a sample was produced with the surfactant cetyltrimethylammonium bromide (CTMABr) and contrasted to one synthesized with CTMACl to determine whether the anion has any effect on the resultant porosity. A selection of samples was also produced using alternative templates, such as the globular quaternary template tetrabutylammonium bromide (TBABr) and the non-ionic block co-polymers Brij 30 and Tween 85. These templates were chosen to illustrate the effect of the size of the templating species, the charge on the template and the number of polyoxyethylene units within each block co-polymer system.

5.2.1: POWDER X-RAY DIFFRACTION
Calcination of the samples, to remove the template, led to dehydration and thus contraction of the layers and a decrease in d-spacing. This is illustrated in Figure 5.2.A, where the NaCl and hko peaks remained constant, but the d001 peak moved to higher angles.

The effect of the anion on the powder XRD profiles was minimal, as illustrated by Figure 5.2.A. Peak positions remained constant, but the d001 peak of the CTMABr modified sample was more defined than for the sample tailored with CTMACl, but remained quite broad and was still masked by the trailing edge of the X-ray beam.

There was a dramatic difference in the patterns of the samples templated with globular quaternary ions, as observed in Figure 5.2.B. Although NaCl and hko peaks remain constant, the d001 peak was more clearly defined. Tetrabutylammonium bromide (TBABr), tetramethylammonium bromide (TMABr) and methylammonium chloride (MACl) are globular quaternary ions, not surfactants. Unlike surfactants, these compounds do not aggregate but act as single cavity templates. As expected, the sample templated with the largest diameter globular quaternary ion exhibited a d001 peak with the lowest 2θ value and hence greatest d-spacing.
**FIGURE 5.2.A:** Powder XRD profiles comparing the effect of templating with CTMACl and CTMABr. Both before and after calcination at 450°C. NaCl was used as an internal standard.

**FIGURE 5.2.B:** Powder XRD profiles of Laponite RD uncalcined and templated with (a) TBABr, (b) TMABr, (c) MACl and (d) CTMABr. NaCl was used as an internal standard.
When contrasted to the pattern of the sample templated with CTMABr, Figure 5.2.B (d), the $d_{001}$ peak was observed to have shifted to an even lower $\theta$ value, for the surfactant. However, it was difficult to assign a precise $d$-spacing due to the effects of the trailing edge of the X-ray beam. As expected, the increase of $d$-spacing within the XRD patterns indicates that micelles formed by CTMABr are greater in diameter than the quaternary ions TBA$^+$, TMA$^+$ and MA$^+$. 

**Figure 5.2.C:** Powder XRD profiles of Laponite RD uncalcined and templated with (a) Tween 40, (b) Brij 78 and (c) Brij 30. NaCl was used as an internal standard.

Powder XRD profiles of samples templated with non-ionic block co-polymers are illustrated in Figure 5.2.C. Contrary to expectations, the $d$-spacings appear to have decreased for these larger templates. Due to their bulkiness (see Appendix I), it is possible that they were too large to be incorporated into the clay interlayers in optimal micellar form. An increase in $d$-spacing in comparison to the untemplated Laponite RD suggests that a “smaller” configuration has been adopted, *i.e.* the surfactant CTMACl may have adopted a hexagonal array of micelles, whilst Tween 40 aggregated in lamellar form, giving the larger template a smaller thickness within the interlayer region.
Table 5.2.1: Powder XRD data for templated Laponite RD samples.

<table>
<thead>
<tr>
<th>Template</th>
<th>2θ / Degrees</th>
<th>d_{001} / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>No template</td>
<td>6.53</td>
<td>13.5</td>
</tr>
<tr>
<td>MACl</td>
<td>7.08</td>
<td>12.5</td>
</tr>
<tr>
<td>TMABr</td>
<td>6.28</td>
<td>14.1</td>
</tr>
<tr>
<td>TBABr</td>
<td>6.03</td>
<td>14.7</td>
</tr>
<tr>
<td>CTMABr</td>
<td>4.21</td>
<td>21.0</td>
</tr>
<tr>
<td>CTMACl</td>
<td>4.30</td>
<td>20.5</td>
</tr>
<tr>
<td>Brij 30</td>
<td>5.00</td>
<td>17.7</td>
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<tr>
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<td>5.03</td>
<td>17.6</td>
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<tr>
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<td>18.7</td>
</tr>
<tr>
<td>Tween 40</td>
<td>4.78</td>
<td>18.5</td>
</tr>
<tr>
<td>Tween 85</td>
<td>5.53</td>
<td>16.0</td>
</tr>
</tbody>
</table>

N.B. All values are for uncalcined samples: corrected by internal standard, assuming NaCl gives a d<sub>200</sub> reflection at 2θ = 31.6°<sup>(4)</sup>.

### 5.2.2: Textural Studies

All compounds were calcined at 450°C in flowing oxygen to remove the organic template. In comparison to a filtercake RD sample calcined in similar conditions, the use of all templates led to increases in specific surface area and total pore volume. Contrasting the use of CTMACl and CTMABr showed that only negligible changes in porosity data occurred when using different anions. Due to the single cavity templating nature of the globular templates, a lower degree of porosity was expected in samples restructured with these compounds, compared with the use of a surfactant. The data reported in Table 5.2.11 support this hypothesis; the samples templated with cationic surfactants had higher specific surface areas and modal pore diameters, whilst total pore volumes more than doubled compared to those templated with globular quaternary ions. Despite the decrease in d-spacing observed in powder XRD profiles, the use of non-ionic surfactants led to even greater increases in specific surface area and total pore volume for restructured Laponite RD. The “largest” (highest RMM and most branched polymer) template, Tween 85, increased the total pore volume by more than four fold the original value.
Observation of the $N_2$ gas adsorption/desorption isotherms for samples modified with these templates showed an increase in the order and uniformity of the pores within Laponite RD as the size of the template increased. Figures 5.2.D and 5.2.E show the isotherms of a selection of samples. The use of templates led to isotherms with Type IV hysteresis loops, confirming mesoporosity. All samples had H2 hystereses, which became more vertical with increased (greater RMM) template size. This indicates that pore shape becomes more cylindrical and, as the loop approaches type H1, improved uniformity is inferred. An anomaly in this data is for the block co-polymer Brij 35. Although it has a greater RMM than Brij 30 it has significantly lower specific surface area and pore volume. Ryoo and co-workers suggest this may be due to inefficient micellar packing caused by the alkyl chain being too short for its large hydrophilic head group (23 PEO units).

**Table 5.2.2:** Porosity data of templated Laponite RD samples. All samples calcined at 450$^\circ$C in flowing oxygen.

<table>
<thead>
<tr>
<th>Template</th>
<th>BET Specific Surface Area / m² g⁻¹</th>
<th>Total Pore Volume / cm³ g⁻¹</th>
<th>Modal Mesopore Diameter / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>No template</td>
<td>270</td>
<td>0.23</td>
<td>37</td>
</tr>
<tr>
<td>MACl</td>
<td>320</td>
<td>0.26</td>
<td>36</td>
</tr>
<tr>
<td>TMABr</td>
<td>370</td>
<td>0.30</td>
<td>40</td>
</tr>
<tr>
<td>TBABr</td>
<td>340</td>
<td>0.30</td>
<td>35</td>
</tr>
<tr>
<td>CTMACl</td>
<td>450</td>
<td>0.65</td>
<td>39</td>
</tr>
<tr>
<td>CTMABr</td>
<td>450</td>
<td>0.66</td>
<td>36*</td>
</tr>
<tr>
<td>Brij 30</td>
<td>450</td>
<td>0.66</td>
<td>39</td>
</tr>
<tr>
<td>Brij 35</td>
<td>400</td>
<td>0.52</td>
<td>37</td>
</tr>
<tr>
<td>Brij 78</td>
<td>460</td>
<td>0.75</td>
<td>43</td>
</tr>
<tr>
<td>Tween 40</td>
<td>490</td>
<td>0.90</td>
<td>54</td>
</tr>
<tr>
<td>Tween 85</td>
<td>490</td>
<td>0.94</td>
<td>52</td>
</tr>
</tbody>
</table>

* Insufficient liquid $N_2$ for accurate data.
FIGURE 5.2.D: N₂ gas adsorption/desorption isotherms comparing Laponite RD samples restructured with globular quaternary and surfactant templates.

FIGURE 5.2.E: N₂ gas adsorption/desorption isotherms of Laponite RD samples comparing restructuring with a cationic surfactant and a non-ionic block co-polymer.

CHAPTER 5: POROSITY ENHANCEMENT
Figure 5.2.F shows the pore size distribution data for a selection of templated samples. The use of templates led to monomodal distributions in the mesoporous range.

**Figure 5.2.F:** Pore size distribution data for Laponite RD samples, comparing restructuring with a cationic surfactant and a non-ionic block co-polymer.

### 5.2.3: Elemental CHN Analysis

Comparing the percentage of carbon in the template to that determined by elemental analysis of the modified clay, the percentage of template in the system can be calculated. As expected, the nature of the anion had very little effect on the percentage of organic moiety involved in the templating process. It is, in general, the size of the template that affects its interaction with the clay. The larger (greater RMM) the template becomes the greater is its incorporation into the system and the greater is the porosity of the resultant clay.
TABLE 5.2.III: Elemental CHN microanalytical data for a variety of uncalcined, templated Laponite RD samples.

<table>
<thead>
<tr>
<th>TEMPLATE</th>
<th>DETERMINED MASS %</th>
<th>CALCULATED MASS % OF TEMPLATE #</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>MACl</td>
<td>0.62</td>
<td>1.63</td>
</tr>
<tr>
<td>TMABr</td>
<td>3.10</td>
<td>2.20</td>
</tr>
<tr>
<td>TBABr</td>
<td>13.59</td>
<td>3.30</td>
</tr>
<tr>
<td>CTMACl</td>
<td>30.00</td>
<td>6.41</td>
</tr>
<tr>
<td>CTMABr</td>
<td>29.32</td>
<td>6.15</td>
</tr>
<tr>
<td>Brij 30</td>
<td>24.94</td>
<td>4.86</td>
</tr>
<tr>
<td>Brij 35</td>
<td>19.25</td>
<td>3.74</td>
</tr>
<tr>
<td>Brij 78</td>
<td>26.32</td>
<td>4.87</td>
</tr>
<tr>
<td>Tween 40</td>
<td>31.04</td>
<td>5.48</td>
</tr>
<tr>
<td>Tween 85</td>
<td>37.68</td>
<td>6.09</td>
</tr>
</tbody>
</table>

# based on % carbon present in template.

Overview

By comparing the results of using the cationic surfactant CTMABr with its chloride analogue, it was concluded that the choice of anion (for cationic templates) had no effect on the templating of Laponite RD. Due to the low crystallinity of the samples, many of the $d_{001}$ peaks in the powder XRD profiles were difficult to assign with any precision, but qualitative shifts to lower angles and hence higher $d$-spacings were observed. The profiles of samples modified with globular quaternary templates showed decreasing $2\theta$ values on increasing cation size. This trend continued with the larger cationic surfactants, although the $d$-spacings were difficult to assign. In contrast, the $d_{001}$ peaks of Laponite RD templated with block co-polymers of even larger size resulted in reduced $d$-spacings. N$_2$ gas adsorption data showed a general trend of an increase in total pore volume and specific surface area with an increase in template RMM.
A maximum pore volume of 0.94 cm\(^3\) g\(^{-1}\) was achieved when Laponite RD filtercake was templated with the block co-polymer Tween 85, an increase of over four fold relative to the untemplated value, 0.23 cm\(^3\) g\(^{-1}\). The difference obtained when using different analysis techniques for samples modified by block co-polymers was due to one of two reasons, both related to template size. The first explanation regards orientation of the template molecules and the second is associated with positioning. The surfactant CTMACl may adopt a hexagonal array of micelles, whilst Tween 40 aggregates into lamellar form, giving the larger template a smaller thickness within the interlayer region, \textit{i.e.} there is a bigger overall internal volume but it is smaller per channel. Alternatively, due to their bulkiness, the block co-polymers may be restricted to interactions between packets of layers \textit{i.e.} main interactions may occur in mesoporous regions as shown in Figure 5.2.G.

\textbf{FIGURE 5.2.G:} Mesoporous and microporous regions created by tactoid layer stacking.
5.3: **One-Pot Synthesis in an Autoclave versus Restructuring of Laponite RD**

The mixing of templates and Laponite RD filtercake provided significant changes in textural properties particularly pore volume. Significant differences were also observed when hectorite KP was synthesised from its component salts (see Chapter 4). It is proposed that a combined use of a templating surfactant and synthesis from component salts would further increase porosity.

5.3.1: **Powder X-Ray Diffraction**

The powder XRD patterns of samples were similar in terms of $hk0$ and NaCl peaks in Figure 5.3.A, but differences were apparent in the low angle $d_{001}$ region. High signal/noise ratio and proximity to the trailing edge of the X-ray beam makes it difficult to define the exact location of the $d_{001}$ peaks. However, for the restructured Laponite RD the peaks are more defined than the profile of templated hectorite KP, indicating less disorder in the Laponite system.

![Figure 5.3.A](image)

**Figure 5.3.A:** Powder XRD profiles of (a) Laponite RD and (b) hectorite KP both templated with the surfactant CTMACl and uncalcined. NaCl was used as an internal standard.
5.3.2: Textural Studies

The incorporation of a surfactant into both Laponite RD and hectorite KP provided significant improvements in pore volume to both systems. As shown in Table 5.3.1, specific surface areas were increased, although a decrease in modal mesopore diameter was observed.

Table 5.3.1: Porosity data of Laponite RD and hectorite KP samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET Specific Surface Area / m² g⁻¹</th>
<th>Total Pore Volume / cm³ g⁻¹</th>
<th>Modal Mesopore Diameter / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder Laponite RD</td>
<td>360</td>
<td>0.27</td>
<td>42</td>
</tr>
<tr>
<td>Laponite RD filtercake *</td>
<td>270</td>
<td>0.23</td>
<td>37</td>
</tr>
<tr>
<td>Laponite RD templated with CTMACl *</td>
<td>450</td>
<td>0.65</td>
<td>39</td>
</tr>
<tr>
<td>H Hectorite KP</td>
<td>610</td>
<td>0.44</td>
<td>36</td>
</tr>
<tr>
<td>H Hectorite KP templated with CTMACl*</td>
<td>660</td>
<td>0.60</td>
<td>30</td>
</tr>
</tbody>
</table>

* Calcined at 450°C in flowing oxygen.

Although improvements were observed for both systems, the restructuring of Laponite RD gave the most significant changes. Both had similar pore volumes, which were high compared to unmodified Laponite RD. The restructured Laponite RD sample had a lower specific surface area, but higher modal mesopore diameter, than the hectorite KP analogue. This was highlighted by the adsorption/desorption isotherms which were both Type IV, but with different shaped hysteresis loops. Figure 5.3.B shows that restructured Laponite RD, with an H2 hysteresis, had more cylindrical pores when templated with CTMACl than its hectorite KP analogue, whose H3 hysteresis inferred slit shaped pores. Both pore systems were likely to be irregular and highly interconnected.
FIGURE 5.3.B: N₂ gas adsorption/desorption isotherms comparing templating of Laponite RD to that of hectorite KP. Both samples templated with CTMACl and calcined at 450°C in flowing oxygen.

FIGURE 5.3.C: Pore size distribution data comparing templating of Laponite RD to that of hectorite KP. Both samples templated with CTMACl and calcined at 450°C in flowing oxygen.
Contrasting the pore size distributions of non-templated samples, Figures 4.2.J, to those templated with CTMACl, Figure 5.3.C, the latter process appeared to reduce the microporosity of both systems. Non-templated systems displayed a tendency to a bimodal system with an incomplete, but apparent, second peak with an average pore diameter below 30 Å; templated systems, however, clearly showed monomodal distributions in the mesoporous range.

5.3.3: SOLID STATE MAS-NMR

$^{13}$C MAS-NMR (cross polarisation) spectra of the templated uncalcined Laponite RD and hectorite KP samples were identical, Figure 5.3.D, and show signals assigned to the cation of the CTMACl [CH$_3$(CH$_2$)$_3$N(CH$_3$)$_3$] template. A broad intense signal at $\delta = 31$ and a smaller narrower signal at $\delta = 24$ represent the CH$_2$ nuclei. Three other less intense signals present at $\delta = 67$, $\delta = 54$ and $\delta = 15$ were attributed to the CH$_2$N carbons, N(CH$_3$)$_3$ carbons and CH$_3$ carbons respectively. As expected, no trace of carbon was found in calcined samples, confirming complete removal of the template.

$^7$Li MAS-NMR (direct polarisation) spectra highlight differences between Laponite RD and hectorite KP, Figure 5.3.E. The spectra for non-templated samples exhibited reduced integrated intensity for hectorite KP compared with Laponite RD, which on assumption of similar acquisition conditions, is consistent with less lithium content. This was corroborated by XRF data. For Laponite RD, the uncalcined spectra had a single sharp signal, whilst the calcined analogue (Figure 4.1.H c) appeared to have either superimposed signals of different line widths or slightly different chemical shifts, both of which suggests more than one environment (morphological or chemical respectively), i.e. more disorder. The uncalcined templated hectorite KP had a small shoulder on the $\delta = -0.52$ signal, whilst the calcined sample had a single symmetrical peak at $\delta = -0.41$. 

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**Figure 5.3.D:** $^{13}$C solid state MAS-NMR (cross polarisation) of (a) uncalcined templated Laponite RD and (b) uncalcined templated hectorite KP.

**Figure 5.3.E:** $^7$Li solid state MAS-NMR (direct polarisation) of (a) Laponite RD, (b) uncalcined templated Laponite RD, (c) calcined templated Laponite RD, (d) hectorite KP, (e) uncalcined templated hectorite KP and (f) calcined templated hectorite KP.
Figure 5.3.F: $^{29}$Si solid state MAS-NMR (direct polarisation) of (a) Laponite RD, (b) uncalcined templated Laponite RD, (c) calcined templated Laponite RD, (d) hectorite KP, (e) uncalcined templated hectorite KP and (f) calcined templated hectorite KP.

$^{29}$Si MAS-NMR (direct polarisation) spectra were complex for the hectorite KP samples, Figure 5.3.F. The uncalcined templated sample was similar to the uncalcined untemplated sample with signals located at $\delta = -109.7$ ($Q^4$), -96.0 ($Q^3$) and -84.8 ($Q^2$). Shoulders were clearly visible for the uncalcined untemplated sample. After calcination, the spectra of the templated sample changed: the $Q^4$ signal ($\delta = -112.2$) was diminished in intensity, while the $Q^3$ signal ($\delta = -97.6$) was more symmetrical than that found with the uncalcined untemplated hectorite KP. The greatest change occurs in the $Q^2$ region of the spectra: instead of a medium intensity peak with a shoulder, two weak peaks at $\delta = -87.3$ and $\delta = -88.9$ were visible. Larger spectra in Appendix II show better resolution of $Q^2$ peaks.
When contrasted to the analogous Laponite RD spectra, both similarities and differences may be observed. Calcination causes an upfield shift of the Q² signal in both cases, as well as causing a greater splitting of this signal (in Laponite RD a more pronounced shoulder and the appearance of a second signal for hectorite KP). In Figure 5.3.F some of the weaker signals appear no greater than the background noise; larger spectra in Appendix II show better resolution of peaks.

5.3.4: ELEMENTAL CHN ANALYSIS

Elemental CHN analysis of templated Laponite RD and hectorite KP both before and after calcination monitored the extent of template removal. This analysis highlighted a further difference between the two compounds: templated uncalkined Laponite RD included ca. 38% surfactant in its system, whilst the analogous hectorite KP incorporated ca. 26%.

| TABLE 5.3.II: Elemental CHN data for Laponite RD and hectorite KP, both templated with CTMACl and uncalcined. |

<table>
<thead>
<tr>
<th>TEMPLATED SAMPLE</th>
<th>C</th>
<th>H</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laponite RD</td>
<td>30.00</td>
<td>6.41</td>
<td>1.63</td>
</tr>
<tr>
<td>Hectorite KP</td>
<td>20.36</td>
<td>4.73</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Overview

XRF data, determined by Rockwood Additives Ltd, determined that hectorite KP had a lower Na₂O content than Laponite RD (Section 4.2.4). This indicated that hectorite KP had lower polarity than Laponite RD. Polarity is the key to micelle formation; fewer micelles will be formed and incorporated into a network with lower polarity. However, despite a dramatic reduction in sodium content, a significant amount of templating was still achieved with hectorite KP. The total pore volume of hectorite KP increased from 0.44 m² g⁻¹ to 0.60 m² g⁻¹ with the aid of templating.
5.4: CHANGE IN SiO₂ CONCENTRATION AND INCORPORATION OF A TEMPLATE.

In Chapter 4 a significant improvement in the porosity of hectorite KP was achieved with an increase in the amount of sodium silicate added during its synthesis. This section aimed to combine this improvement with that seen through the templating of hectorite KP with CTMACl, Section 5.3.

5.4.1: POWDER X-RAY DIFFRACTION

Powder XRD profiles of uncalcined templated hectorite KP samples with altered SiO₂ content, Figure 5.4.A, were similar to the uncalcined untemplated analogues, Figure 4.4.B. The hkl peaks were clearly visible for all samples, although to a lesser extent for the sample with reduced SiO₂ content, indicating that production of hectorite phases occurred. The profiles of hectorite KP and the sample with reduced SiO₂ content yielded little information in the d₀₀₁ region, but the sample with increased SiO₂ content exhibited a defined low angle peak. It was difficult to assign a d-spacing because of the trailing edge of the incident X-ray beam but modification of the interlayer space was evident.

5.4.2: TEXTURAL STUDIES

Analysis of the data presented in Table 5.4.I showed that templating led to increases in total porosity. The most significant changes occurred for the sample with reduced SiO₂ content, whose pore volume increased one and a half fold and whose specific surface area improved by approximately 200 m² g⁻¹. The highest total pore volume was produced when the hectorite KP sample with increased SiO₂ content was templated but the reduced SiO₂ content analogue shows the greatest change.
**Figure 5.4.A:** Powder XRD profiles of hectorite KP with varying levels of SiO₂ content (a) increased (b) synthesised according to Rockwood Additives protocol (c) decreased. All samples templated with CTMACl and uncalcined.

**Figure 5.4.B:** N₂ gas adsorption/desorption isotherms of hectorite KP with varying levels of SiO₂ content. All samples templated with CTMACl and calcined at 450°C.
When compared to modification of Laponite RD, the differences between untemplated samples, which showed hectorite KP to have better porosity, were not repeated after templating with CTMACl. An improvement of 18% in pore volume was achieved when synthesis was carried out with increased silica content, but the difference between templated samples was only 5%. Templated Laponite RD had a higher total pore volume (0.65 cm$^3$ g$^{-1}$) than its hectorite KP analogue, even when the silica content was increased.

**Table 5.4.1: Porosity data of hectorite KP samples with varying levels of SiO$_2$ content.**

<table>
<thead>
<tr>
<th>Method of Modification</th>
<th>BET Specific Surface Area / m$^2$ g$^{-1}$</th>
<th>Total Pore Volume / cm$^3$ g$^{-1}$</th>
<th>Modal Mesopore Diameter / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>No modification</td>
<td>610</td>
<td>0.44</td>
<td>36</td>
</tr>
<tr>
<td>Templation with CTMACl *</td>
<td>660</td>
<td>0.60</td>
<td>30</td>
</tr>
<tr>
<td>Increased SiO$_2$ content</td>
<td>670</td>
<td>0.52</td>
<td>35</td>
</tr>
<tr>
<td>Increased SiO$_2$ content and templation with CTMACl *</td>
<td>650</td>
<td>0.63</td>
<td>30</td>
</tr>
<tr>
<td>Decreased SiO$_2$ content</td>
<td>550</td>
<td>0.36</td>
<td>35</td>
</tr>
<tr>
<td>Decreased SiO$_2$ content and templation with CTMACl *</td>
<td>740</td>
<td>0.57</td>
<td>35</td>
</tr>
</tbody>
</table>

* Calcined at 450°C in flowing oxygen.

The differences between N$_2$ gas adsorption/desorption isotherms of the templated hectorite KP sample and the analogous sample with a 10% increase in silica content were less marked than those between the related untemplated samples. Figure 4.4.C shows three distinct hystereses, whilst Figure 5.4.B shows two very similar Type IV isotherms with H3 hysteresis loops and a very narrow H4 loop for the sample with decreased silica content. The H3 loops were both larger and more vertical than for their untemplated analogues, consistent with greater irregularity within the pore networks of the templated clays.
5.4.3: ELEMENTAL CHN ANALYSIS

As expected, CHN elemental analysis showed only small differences in template content of the samples, as the surfactant to silica ratio was kept the same.

<table>
<thead>
<tr>
<th>TEMPLATED SAMPLE</th>
<th>DETERMINED MASS %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Hectorite KP</td>
<td>20.36</td>
</tr>
<tr>
<td>Increased SiO₂ content</td>
<td>20.97</td>
</tr>
<tr>
<td>Decreased SiO₂ content</td>
<td>18.56</td>
</tr>
</tbody>
</table>

Overview

As found with untemplated samples, the change in pore volume with respect to that of hectorite KP was related to the silica content of the templated analogues. A 10% change in SiO₂ content led to an 18% change in pore volume for untemplated samples, whilst a 5% change was seen when the samples were templated. An increased silica content led to a maximum pore volume when templated with the surfactant CTMACl. However, the most significant relative difference was achieved on templating the sample with the lowest silica content; that sample nearly doubled its pore volume and increased its specific surface area by 200 m² g⁻¹ after templating with CTMACl.

Despite the porosity of hectorite KP being significantly greater than that of Laponite RD and the increase of silica content further improving its textural properties, templating of hectorite KP did not lead to similar improvements. The introduction of a surfactant during hectorite synthesis with an increase in silica content led to higher pore volumes after templating with CTMACl (0.60 cm³ g⁻¹), but this value was still lower than the analogous templating and restructuring of Laponite RD filtercake (0.65 cm³ g⁻¹).
5.5: Expanded Template Synthesis

Following on from the significant improvements achieved by addition of a template, the introduction of a pore swelling agent was considered. Mesitylene has been successfully introduced, as a pore-swelling agent, into many liquid templating systems during MCM synthesis\(^1\) leading to significantly enhanced textural properties.

5.5.1: Textural Studies

Our findings, in Table 5.5.1, were somewhat disappointing when considering previous research with surfactant modifiers\(^7\). Samples produced by restructuring Laponite RD filtercake with mesitylene and CTMACl showed no significant differences in specific surface area when compared to those templated with CTMACl alone. The modal mesopore diameter increased for a 1:1 surfactant:mesitylene mixture, but decreases for a 1:1.5 mixture. The total pore volume decreased on increasing the mesitylene content. For samples produced from the component salts (hectorite KP) changes were more noticeable; the specific surface area decreased only by a relatively small amount, whilst differences in pore volume and pore diameter distribution were more prominent. For the surfactant:mesitylene ratio of 1:1 the pore volume decreased, with a bimodal mesopore diameter profile observed.

Table 5.5.11 gives a more positive view of using a pore-swelling agent. Calcination in static air, as opposed to flowing oxygen, meant that increased specific surface area and total pore volume occurred. These results were still not as significant as the literature suggested was possible, but the modification results of Laponite RD filtercake are encouraging. The effects of the conditions of calcination are further discussed in Section 5.6.
### TABLE 5.5.I: Comparison of textural data for samples modified with a surfactant (CTMACl) and a pore swelling agent (mesitylene). Synthesized via (a) restructuring of Laponite RD filtercake and (b) from component salts (hectorite KP). All samples were calcined in flowing oxygen at 450°C.

<table>
<thead>
<tr>
<th>METHOD OF MODIFICATION</th>
<th>BET SPECIFIC SURFACE AREA / m² g⁻¹</th>
<th>TOTAL PORO VOLUME / cm³ g⁻¹</th>
<th>MODAL MESOPOR DIA METER / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CTMACl</td>
<td>460</td>
<td>0.65</td>
<td>39</td>
</tr>
<tr>
<td>CTMACl:Mesitylene = 1:1</td>
<td>440</td>
<td>0.63</td>
<td>43</td>
</tr>
<tr>
<td>CTMACl:Mesitylene = 1:1.5</td>
<td>420</td>
<td>0.50</td>
<td>31</td>
</tr>
<tr>
<td>b</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CTMACl</td>
<td>660</td>
<td>0.60</td>
<td>30</td>
</tr>
<tr>
<td>CTMACl:Mesitylene = 1:1</td>
<td>540</td>
<td>0.44</td>
<td>24/34*</td>
</tr>
<tr>
<td>CTMACl:Mesitylene = 1:1.5</td>
<td>660</td>
<td>0.61</td>
<td>34</td>
</tr>
</tbody>
</table>

# A bimodal pore size distribution was observed for this sample.

### TABLE 5.5.II: Comparison of textural data for samples modified with a surfactant (CTMACl) and a pore-swelling agent (mesitylene). Synthesized via (a) restructuring of Laponite RD filtercake and (b) from component salts (hectorite KP). All samples were calcined in static air at 450°C.

<table>
<thead>
<tr>
<th>METHOD OF MODIFICATION</th>
<th>BET SPECIFIC SURFACE AREA / m² g⁻¹</th>
<th>TOTAL PORO VOLUME / cm³ g⁻¹</th>
<th>MODAL MESOPOR DIA METER / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CTMACl</td>
<td>450</td>
<td>0.61</td>
<td>32</td>
</tr>
<tr>
<td>CTMACl:Mesitylene = 1:1</td>
<td>490</td>
<td>0.67</td>
<td>43</td>
</tr>
<tr>
<td>CTMACl:Mesitylene = 1:1.5</td>
<td>520</td>
<td>0.71</td>
<td>nd</td>
</tr>
<tr>
<td>b</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CTMACl</td>
<td>700</td>
<td>0.60</td>
<td>34</td>
</tr>
<tr>
<td>CTMACl:Mesitylene = 1:1</td>
<td>690</td>
<td>0.56</td>
<td>24/34*</td>
</tr>
<tr>
<td>CTMACl:Mesitylene = 1:1.5</td>
<td>720</td>
<td>0.64</td>
<td>29</td>
</tr>
</tbody>
</table>

# A bimodal pore size distribution was observed for this sample.

nd – no data recorded.
5.5.2: ELEMENTAL CHN ANALYSIS

The differences, observed in the porosity data indicate that the addition of mesitylene had only a minor effect on the templated system. This is supported by elemental CHN analysis data, which showed no significant change in carbon content for the new samples. Table 5.5.III shows that there appears to be negligible changes in carbon content for both modified Laponite RD samples and the analogous hectorite KP samples.

**TABLE 5.5.III:** Elemental CHN analysis data for hectorite samples modified with a surfactant (CTMACl) and pore swelling agent (mesitylene); synthesized via (a) restructuring of Laponite RD filtercake and (b) from component salts.

<table>
<thead>
<tr>
<th>METHOD OF MODIFICATION</th>
<th>DETERMINED MASS %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>CTMACl</td>
<td>29.98</td>
</tr>
<tr>
<td>CTMACl: Mesitylene = 1:1</td>
<td>29.39</td>
</tr>
<tr>
<td>CTMACl: Mesitylene = 1:1.5</td>
<td>29.13</td>
</tr>
<tr>
<td>CTMACl</td>
<td>20.36</td>
</tr>
<tr>
<td>CTMACl: Mesitylene = 1:1</td>
<td>19.70</td>
</tr>
<tr>
<td>CTMACl: Mesitylene = 1:1.5</td>
<td>21.00</td>
</tr>
</tbody>
</table>

5.5.3: SOLID STATE MAS-NMR

Non-incorporation of mesitylene into both the modified Laponite RD and hectorite KP systems was conclusively demonstrated using $^{13}$C solid state MAS-NMR. Analysis of these samples led to spectra similar to that of the templated samples, with no mesitylene in the synthesis method. Alkyl carbon signals, like those illustrated in Figure 5.3.D, relating to CTMACl were present, but no aromatic carbon signals were observed, as would be expected for mesitylene (1,3,5-trimethylbenzene) on incorporation into the clay system.
5.5.4: ALTERNATIVE SWELLING AGENTS

Alternative swelling agents such as straight chain alkanes have been previously investigated (5). The use of \( n \)-octane as a template enhancer had little impact on these systems. Both the surface area and the pore volume decreased, although the modal pore diameter distribution increased slightly, Table 5.5.IV.

**Table 5.5.IV:** Porosity data and carbon content of templated Laponite RD with and without \( n \)-octane. Porosity data was acquired after calcination in flowing oxygen at 450°C.

<table>
<thead>
<tr>
<th>Modification</th>
<th>CTMACl</th>
<th>CTMACl + ( n )-octane</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET Specific Surface Area / ( \text{m}^2 \text{ g}^{-1} )</td>
<td>460</td>
<td>340</td>
</tr>
<tr>
<td>Total Pore Volume / ( \text{cm}^3 \text{ g}^{-1} )</td>
<td>0.65</td>
<td>0.54</td>
</tr>
<tr>
<td>Modal Mesopore Diameter / ( \text{Å} )</td>
<td>39</td>
<td>42</td>
</tr>
<tr>
<td>Carbon Content / %</td>
<td>30.0</td>
<td>29.7</td>
</tr>
</tbody>
</table>

**OVERVIEW**

The use of template enhancers led to only slight improvements (if any) in porosity for both Laponite RD and hectorite KP based systems. The use of \( n \)-octane even had an adverse effect on the porosity of the clay system. Considering the advantages reported in the literature, these results were disappointing. \(^{13}\)C solid state MAS-NMR demonstrated the non-incorporation of the mesitylene pore swelling agent into the clay/surfactant system. Figure 1.4.D shows that mesitylene and the straight chain alkanes usually improve the porosity of a templated system by entering the surfactant micelles, causing them, and subsequently the inorganic framework, to swell (8). The possible reason for non-incorporation into this system is that the surfactant micelles were already fully expanded in the pores, leaving no room for further expansion by mesitylene.
CHAPTER 5: POROSITY ENHANCEMENT

5.6: TEMPLATE REMOVAL

Hand in hand with the use of templating methods in the production of large pore inorganic frameworks comes the process of template removal. In some cases this is not wholly necessary. The area of inorganic-organic nanocomposites, where organic functionalised groups are anchored to the inorganic framework for heightened catalytic and adsorptive activity, has expanded rapidly in recent years \(^{9-11}\). To achieve elimination of the organic moiety there is a wealth of suggestions in the literature, from straight-forward calcination \(^1, 2, 12\), to exotic oxidation routes utilising ozone \(^13\), extraction with supercritical carbon dioxide \(^14\) and microwave \(^15\) extraction for template removal. In this study, calcination of the samples was the method of choice for surfactant elimination. The use of various temperatures and gaseous environments were investigated. This process involved the heating of a templated sample to a temperature sufficient to eliminate the organic moiety without destroying the structure of the inorganic component.

5.6.1: DIFFERENT GASEOUS ENVIRONMENTS

During preliminary optimisation of calcination techniques, the use of three alternative methods were explored: (1) calcination in a tube furnace under flowing nitrogen gas, (2) calcination in a tube furnace under flowing oxygen gas, and (3) calcination in a muffle furnace in air (no forced flow), all at 450°C for at least 8 h. 450°C was chosen as a calcination temperature, because it is high enough to remove the organic moiety, low enough not to destroy the clay structure and is commonly used in the pillaring of clay samples.
Calcination both in flowing nitrogen gas and in static air exhibited partial removal of the template. Organic stretches and deformations were still observable in these FT-IR studies, but CHN elemental analysis, Table 5.6.I, proved that the organic content had been reduced. The combined use of FT-IR and CHN analysis provided evidence that complete surfactant elimination had occurred when using flowing oxygen gas, Figure 5.6.A and Table 5.6.I.

**TABLE 5.6.I:** Elemental CHN analysis data for as-synthesised and calcined templated Laponite RD samples to show the extent of template removal caused by using different calcination methods.

<table>
<thead>
<tr>
<th>METHOD OF CALCINATION</th>
<th>DETERMINED MASS %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>As-synthesised (uncalcined)</td>
<td>30.00</td>
</tr>
<tr>
<td>Flowing Nitrogen at 450°C</td>
<td>4.87</td>
</tr>
<tr>
<td>“Static air” at 450°C</td>
<td>2.00</td>
</tr>
<tr>
<td>Flowing Oxygen at 450°C</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Data in Table 5.6.I show that during partial removal of the template, nitrogen was completely eliminated, whilst small carbon deposits remained within the samples. Research suggests that this phenomenon is due to cleavage of the surfactant during calcination (16), those workers proposed that the surfactant splits into an alkyl group and an amine during the heating process.

Significant differences were observed when FT-IR spectra of as-synthesised and calcined templated materials were compared, Figure 5.6.A. The peaks (*) due to C-H stretching (−2900 cm⁻¹) and deformation (−1470 cm⁻¹) were lost following calcination, which confirmed template removal.


**Figure 5.6.A:** FT-IR spectra of an as-synthesised templated Laponite RD and the same sample calcined in static air at 450°C; the loss of peaks * indicates removal of the organic template.

**Table 5.6.II:** The main vibrations identified by FT-IR spectroscopy for a selection of templated Laponite RD samples, calcined in different gaseous environments.

<table>
<thead>
<tr>
<th>Method of Calcination</th>
<th>Wavenumber / cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3677 (SH/M)</td>
</tr>
<tr>
<td>Uncalcinated</td>
<td>3441 (M/B)</td>
</tr>
<tr>
<td></td>
<td>2920 (S)</td>
</tr>
<tr>
<td></td>
<td>2851 (S)</td>
</tr>
<tr>
<td></td>
<td>1637 (W)</td>
</tr>
<tr>
<td></td>
<td>1488 (M)</td>
</tr>
<tr>
<td></td>
<td>1384 (VW)</td>
</tr>
<tr>
<td></td>
<td>1070 (SH)</td>
</tr>
<tr>
<td></td>
<td>1004 (S)</td>
</tr>
<tr>
<td></td>
<td>655 (S)</td>
</tr>
<tr>
<td></td>
<td>444 (S)</td>
</tr>
<tr>
<td>Calcined in Nitrogen</td>
<td>3686 (SH)</td>
</tr>
<tr>
<td></td>
<td>3438 (S/B)</td>
</tr>
<tr>
<td></td>
<td>2928 (M)</td>
</tr>
<tr>
<td></td>
<td>2855 (M)</td>
</tr>
<tr>
<td></td>
<td>1635 (M)</td>
</tr>
<tr>
<td></td>
<td>1471 (W)</td>
</tr>
<tr>
<td></td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>1011 (S/B)</td>
</tr>
<tr>
<td></td>
<td>657 (S)</td>
</tr>
<tr>
<td></td>
<td>-</td>
</tr>
<tr>
<td>Calcined in Oxygen</td>
<td>3679 (SH)</td>
</tr>
<tr>
<td></td>
<td>3446 (M)</td>
</tr>
<tr>
<td></td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>1635 (M)</td>
</tr>
<tr>
<td></td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>1019 (S/B)</td>
</tr>
<tr>
<td></td>
<td>669 (S)</td>
</tr>
<tr>
<td></td>
<td>464 (S)</td>
</tr>
<tr>
<td>Calcined in Static Air</td>
<td>3677 (SH)</td>
</tr>
<tr>
<td></td>
<td>3437 (S/B)</td>
</tr>
<tr>
<td></td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>1635 (M)</td>
</tr>
<tr>
<td></td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>1016 (S/B)</td>
</tr>
<tr>
<td></td>
<td>659 (S)</td>
</tr>
<tr>
<td></td>
<td>466 (S)</td>
</tr>
</tbody>
</table>

FT-IR vibrational intensities: S = strong; M = medium; W = weak; VW = very weak; SH = shoulder; B = broad. X = removal of peak.
ASSIGNMENTS:

\[-3670 - 3630 \text{ cm}^{-1} \text{ O-H stretching of clay lattice (octahedral layer)}\]^{17, 18} 
\[-3620 - 3430 \text{ cm}^{-1} \text{ O-H stretching of water in interlayer region} \]^{17, 18} 
\[-2925 - 2850 \text{ cm}^{-1} \text{ CH}_2, \text{ CH stretching (template)}\]^{19} 
\[-1635 \text{ cm}^{-1} \text{ H-O-H deformation (scissoring)}\]^{17} 
\[-1460 \text{ cm}^{-1} \text{ R-CH}_2\text{-R bending (template)}\]^{20} 
\[-1400 - 1300 \text{ cm}^{-1} \text{ CH}_2, \text{ CH bending (template)}\]^{19} 
\[-1010 \text{ cm}^{-1} \text{ Si-O stretching}\]^{17} 
\[-660 - 650 \text{ cm}^{-1} \text{ O-H bend}\]^{17} 
\[-470 - 460 \text{ cm}^{-1} \text{ O-Si-O bend and deformation}\]^{17}

Porosity information for the samples was determined using \(\text{N}_2\) gas adsorption studies. This data showed that calcination in flowing oxygen gas not only achieved complete removal of the template, but also produced a modified Laponite RD sample with a greater specific surface area and pore volume, Table 5.6.III.

Table 5.6.III: Porosity data for restructured Laponite RD calcined in various gaseous environments at 450°C.

<table>
<thead>
<tr>
<th>METHOD OF CALCINATION</th>
<th>BET SPECIFIC SURFACE AREA / \text{m}^2\text{g}^{-1}</th>
<th>TOTAL PORE VOLUME / \text{cm}^3\text{g}^{-1}</th>
<th>MODAL MESOPORE DIAMETER / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flowing nitrogen</td>
<td>350</td>
<td>0.48</td>
<td>39</td>
</tr>
<tr>
<td>Flowing oxygen</td>
<td>460</td>
<td>0.65</td>
<td>39</td>
</tr>
<tr>
<td>Static air</td>
<td>450</td>
<td>0.61</td>
<td>32</td>
</tr>
</tbody>
</table>

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The use of flowing oxygen gas at 450°C was consequently adopted as the method of choice for template removal for subsequent samples. However, this method proved to be temperamental * and a number of samples produced later in the study became grey (sometimes even black) upon calcination. This indicated that complete elimination was not achieved. To verify this, and to rule out the possibility of impurities in the system, the sample was heated to 600°C. This returned the samples to the expected whiteness and combined with CHN analyses, this confirmed that the last of the organic moiety was removed, Table 5.6.IV. * Differences were particularly evident between templated Laponite and hectorite KP samples; calcination in flowing oxygen achieved complete template removal for templated Laponite RD but not for templated hectorite KP.

Surprisingly, heating to 600°C did not completely destroy the structure of the samples. Dehydration and the onset of dehydroxylation led to interlayer contraction, as highlighted by the $d_{001}$ peak moving to higher angles. The $hk0$ peaks were clearly visible and little or no shift in their position was apparent, Figure 5.6.B.

5.6.2: DIFFERENT CALCINATION TEMPERATURES

To define an optimum temperature for calcination of samples, several samples were subjected to heating over a range of temperatures between 450°C and 600°C in static air.
**Figure 5.6.B:** Powder XRD profiles of an as-synthesised templated Laponite RD sample and the same one calcined at 600°C in static air. NaCl was used as an internal standard.

**Table 5.6.IV:** Elemental CHN analysis data illustrating the extent of template removal achieved via various methods of calcination for hectorite KP samples synthesised with the template CTMACl and mesitylene (template:mesitylene ratio 1:1).

<table>
<thead>
<tr>
<th>Method of Calcination</th>
<th>Determined Mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Uncalcined</td>
<td>19.7</td>
</tr>
<tr>
<td>450°C in flowing oxygen</td>
<td>5.93</td>
</tr>
<tr>
<td>450°C in static air</td>
<td>0.00</td>
</tr>
<tr>
<td>500°C in static air</td>
<td>0.00</td>
</tr>
<tr>
<td>550°C in static air</td>
<td>0.00</td>
</tr>
<tr>
<td>600°C in static air</td>
<td>0.00</td>
</tr>
</tbody>
</table>
N\textsubscript{2} gas adsorption studies indicated that a slight increase in temperature was beneficial. However, the specific surface area decreased on heating at 600°C, Tables 5.6.V and 5.6.VI, indicating that the structure was prone to partial interlayer collapse at higher temperatures.

**Table 5.6.V:** Porosity data recorded after template removal by different methods of calcination for Laponite RD samples modified with the surfactant, CTMACl.

<table>
<thead>
<tr>
<th><strong>METHOD OF CALCINATION</strong></th>
<th><strong>BET SPECIFIC SURFACE AREA / m\textsuperscript{2} g\textsuperscript{-1}</strong></th>
<th><strong>TOTAL PORE VOLUME / cm\textsuperscript{3} g\textsuperscript{-1}</strong></th>
<th><strong>MODAL MESOPOROUS DIAMETER / Å</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>450°C in flowing O\textsubscript{2}</td>
<td>460</td>
<td>0.65</td>
<td>39</td>
</tr>
<tr>
<td>450°C in static air</td>
<td>450</td>
<td>0.61</td>
<td>32</td>
</tr>
<tr>
<td>500°C in static air</td>
<td>450</td>
<td>0.62</td>
<td>36</td>
</tr>
<tr>
<td>550°C in static air</td>
<td>450</td>
<td>0.70</td>
<td>45</td>
</tr>
<tr>
<td>600°C in static air</td>
<td>400</td>
<td>0.63</td>
<td>41</td>
</tr>
</tbody>
</table>

**Table 5.6.VI:** Porosity data recorded after template removal by different methods of calcination for hectorite KP samples modified with the surfactant, CTMACl.

<table>
<thead>
<tr>
<th><strong>METHOD OF CALCINATION</strong></th>
<th><strong>BET SPECIFIC SURFACE AREA / m\textsuperscript{2} g\textsuperscript{-1}</strong></th>
<th><strong>TOTAL PORE VOLUME / cm\textsuperscript{3} g\textsuperscript{-1}</strong></th>
<th><strong>MODAL MESOPOROUS DIAMETER / Å</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncalcined</td>
<td>78</td>
<td>0.12</td>
<td>Not type IV</td>
</tr>
<tr>
<td>450°C in flowing O\textsubscript{2}</td>
<td>660</td>
<td>0.60</td>
<td>30</td>
</tr>
<tr>
<td>450°C in static air</td>
<td>700</td>
<td>0.60</td>
<td>34</td>
</tr>
<tr>
<td>500°C in static air</td>
<td>640</td>
<td>0.54</td>
<td>43</td>
</tr>
<tr>
<td>550°C in static air</td>
<td>610</td>
<td>0.57</td>
<td>38</td>
</tr>
<tr>
<td>600°C in static air</td>
<td>620</td>
<td>0.57</td>
<td>34</td>
</tr>
</tbody>
</table>

In this latter part of the study calcination in static air appeared to be the better oxidation process. There was a difference in optimal temperature for template removal between Laponite RD and hectorite KP. However, Tables 5.6.V and VI show that this temperature was in the same region, 450 to 550°C.
5.6.3 "STAGGERED" REMOVAL

Calcination of templated samples in static air and flowing oxygen led to temperamental template removal. However, a two-step calcination process led to greater template removal in static air and hence increased porosity parameters. Data in Table 5.6.VII relates to unstaggered and staggered calcination in static air. The former was calcined at 450°C for at least 12h; whilst the latter was heated to 225°C and held there for at least 4h (preferably overnight) and then the temperature was raised to 450°C and held there for at least 12h.

| TABLE 5.6.VII: Porosity data recorded for Laponite RD samples modified with CTMACl. |
|----------------------------------------|----------------------------------------|----------------------------------------|----------------------------------------|
| **METHOD OF CALCINATION**             | **BET SPECIFIC SURFACE AREA / m²g⁻¹** | **TOTAL PORE VOLUME / cm³g⁻¹**          | **MODAL MESOPORE DIAMETER / Å**        |
| Unstaggered                           | 450                                    | 0.61                                   | 32                                     |
| Staggered                             | 510                                    | 0.66                                   | 36                                     |

OVERVIEW

Due to the similar porosity data and the greater availability of the muffle furnace, the majority of samples were calcined in static air at 450°C. Positioning of samples in the tube furnace led to problems with calcination in flowing O₂. This and the original lower porosity data achieved through calcination in static air were overcome by staggered removal in the muffle furnace. Best overall results were observed by calcination in static air at 225°C for at least 4h, preferably overnight and then at 450°C for at least 12h.
5.7: SUMMARY

The aim of this study was to enhance the textural properties of the synthetic hectorite clay Laponite RD, relative to samples provided by Rockwood Additives Ltd, without the introduction of aluminium into the system; in particular to increase the specific surface area, total pore volume and modal mesopore diameter. The appropriate choice of template, reagent concentrations, synthesis protocol and template removal strategy led to such increases.

The characteristics of these tailored materials were determined via nitrogen sorption porosimetry, X-ray powder diffraction, XRF analysis, FT-IR spectroscopy, elemental microanalysis, solid state MAS-NMR, TG analysis and SEM.

The production of hectorite KP led to improvements in porosity characteristics with respect to Laponite RD. However, the overall improvements in total pore volume were actually very similar for both samples, when templated with CTMACl and calcined under similar conditions. Modification of Laponite RD with this surfactant on an industrial scale would, therefore, depend upon ease of addition to the process i.e. during or post synthesis.

Templatimg of both Laponite RD and hectorite KP led to significant increases in textural parameters in comparison to parent and pillared materials. Both total pore volume and specific surface area increased through restructuring by globular quaternary ions, ionic surfactants and non-ionic PEG block co-polymer templates. Examples of the latter compounds (e.g. Tween 85) produced the most marked improvements. Total pore volume of Laponite RD increased from 0.27 cm$^3$ g$^{-1}$ to 0.95 cm$^3$ g$^{-1}$ for Laponite RD modified by templating with Tween 85, whilst the total pore volume of hectorite KP increased from 0.44 cm$^3$ g$^{-1}$ to 0.60 cm$^3$ g$^{-1}$ using CTMACl (both calcined in flowing oxygen at 450°C).
The use of pore-swelling agents such as mesitylene and n-octane made no significant difference to the porosity of these systems. This was due to non-incorporation of these compounds into the micellar system, as shown by $^{13}$C solid-state MAS-NMR analysis.

Process water analysis showed that ion exchange with interlayer Na$^+$ cations was the most likely method of template incorporation. Post templating with CTMACl, decanted water was shown to contain more than 100 fold the sodium ion content relative to water simply mixed with Laponite RD. This apparent exchange of bulky CTMA$^+$ ions for small Na$^+$ ions in the clay interlayer may have led to the increases in $d$-spacing and total pore volume found within these systems.

Increased silica content during the synthesis of hectorite KP led to increased total pore volume and specific surface area. These notable improvements were not, however, observed when combined with the templating process. A 10% increase in SiO$_2$ content led to an 18% increase in total pore volume for untemplated samples, whilst only a further 5% increase was seen when the samples were templated with the surfactant CTMACl. The introduction of a surfactant in modified hectorite synthesis led to higher pore volumes (0.60 cm$^3$ g$^{-1}$), but analogous templating of Laponite RD filtercake led to porosity improvements even greater than those achieved with a 10% increase in silica content (0.65 cm$^3$ g$^{-1}$).
Infrared spectroscopy and CHN analysis showed that the surfactant was not removed by simple heating of the compound. Flowing nitrogen gas was not aggressive enough to remove the template, whilst in some cases static air removed the majority of the surfactant rapidly but left a small percentage charred and persistent in the pores. A variety of calcination temperatures were explored, all led to increased porosity, although in the higher temperature region (600°C) partial interlayer collapse was apparent due to dehydration and the onset of dehydroxylation. Optimal conditions for template elimination were programmed heating to a temperature of 225°C for several hours and then raising the temperature to between 450 and 500°C in an air (no forced flow) environment.

The greatest improvement in porosity achieved within this study was through modification of Laponite RD with the block co-polymer Tween 85. The pore volume increased from 0.23 to 0.94 cm$^3$ g$^{-1}$. The specific surface area increased from 270 to 490 m$^2$ g$^{-1}$. The modal pore diameter increased from 37 to 52 Å.
REFERENCES


4. JCPDS file No. 77-2064 NaCl


CHAPTER 6

RESULTS AND DISCUSSION:
Sorption Studies
Many inorganic compounds, such as clays, have high internal surface areas and consequently have high adsorption capacities. These properties lead to extensive use as molecular sieves and ion-exchange materials in industrial processes \(^{(1-4)}\). Chapters 4 and 5 show that significant improvements in the textural properties of Laponite RD, particularly specific surface area and total pore volume, were achieved through templating this synthetic clay with an organic template. Investigations into the nature and efficiency of metal ion removal from aqueous solution by Laponite and other hectorite materials will now be discussed.

The removal of metal ions from aqueous solutions by clay samples was investigated through equilibrium batch testing of a selection of Laponite and hectorite materials with single and multi-element solutions. Atomic absorption spectrometry (AAS) was employed to determine the extent of metal ion removal from solutions, of known and unknown composition, achieved with unmodified and modified Laponite and hectorite materials. AAS was also used to determine whether sodium ions were released from clay materials during analysis and, if so, at what concentrations. Powder XRD was used to compare clay structure pre- and post- batch testing to illustrate any structural similarities, changes or damage caused during analysis.
6.1: Sorption Materials

Four hectorite samples were chosen for preliminary batch testing:

- Laponite RD (filtercake) (LP);
- Laponite RD modified with the surfactant CTMACl (LS);
- hectorite KP as-synthesised in the autoclave (KP) and
- hectorite KP modified with the surfactant CTMACl (KS).

The montmorillonite clay IKOMONT Ca-Weiss (IKO Minerals, Marl) (KCW) was also tested as a reference. The four hectorite samples were prepared in the same manner as those tested in Chapters 4 and 5 and all five clay materials were calcined at 450°C in a static air (no forced flow) environment. Table 6.1.I summarises the textural properties of these samples.

**Table 6.1.I: Textural properties of materials to be used in preliminary metal ion removal studies.**

<table>
<thead>
<tr>
<th>CHARACTERISTIC</th>
<th>CLAY MATERIAL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LP</td>
</tr>
<tr>
<td>Specific Surface Area / m² g⁻¹</td>
<td>270</td>
</tr>
<tr>
<td>Total Pore Volume / cm³ g⁻¹</td>
<td>0.23</td>
</tr>
<tr>
<td>Modal Pore Diameter / Å</td>
<td>41</td>
</tr>
<tr>
<td>Residual Carbon Content / %</td>
<td>NA</td>
</tr>
</tbody>
</table>

The use of these five materials demonstrated any difference between materials produced at the factory and those created in the laboratory. The effect of templating could also be observed by testing the two modified materials. The significant ion exchange capabilities of montmorillonite (which is a dioctahedral smectite) have previously been investigated \(^{5-7}\), and this clay was, therefore, analysed as a test of the batch testing methodology.
A selection of top row transition metals (manganese, iron, cobalt, nickel, copper, and zinc), plus lead and cadmium, were chosen for analysis to test sorption efficiency of Laponite and hectorite materials and any competition between these ions. As described in Section 1.5, the main sources of metal pollution in water are mining and the automobile industry. These chosen metals are known to exist at higher concentrations in areas exposed to high traffic volume (e.g. near the M25), than in regions with little traffic flow (e.g. the Channel Island of Alderney)\(^8\). Surprisingly, engine emissions account for less than 5% of traffic related pollution\(^9\); other contributors include road surface degradation, tyre wear, metal corrosion and wear, batteries and road de-icing\(^8\). Cadmium, copper, manganese and zinc pollution can be caused by tyre and brake pad wear, whilst nickel is used in metal plating and welding processes. Some iron in the environment occurs naturally because of the weathering of iron ores, but most is a result of automobile bodywork and other metal corrosion (rust), as well as from fertilizers, the inorganic chemicals industry, petrol refining and steel manufacture\(^10\). Copper, lead and zinc are also used in paint manufacture. Lead pollution in the environment has decreased significantly in the UK since the introduction of unleaded petrol.

**6.2: Batch Equilibrium Testing**

Having chosen five potential metal ion removal materials and eight elements (manganese, iron, cobalt, nickel, copper, zinc, lead and cadmium), to be tested, batch equilibrium testing was carried out to determine cation removal capabilities with solutions containing single elements. Subsequently, solutions containing a mixture of these metals were employed to investigate levels of competition between ions.
6.2.1: Ion Removal from Single Element Solutions

Batch equilibrium testing (parameters defined in Section 3.3.4) was carried out with eight 5 mg dm$^{-3}$ single element solutions prepared by dilution of Aristar™ stock solutions, as detailed in Table 3.3.1. This analysis established the percentage metal ion removal from aqueous solution after ten minutes of shaking with each clay sample, as reported in Table 6.2.1.

Table 6.2.1: Percentage metal ion removal from 5 mg dm$^{-3}$ single element solutions by Laponite and other smectite materials.

<table>
<thead>
<tr>
<th>Individual Metal in Solution</th>
<th>Metal Ion Removal / %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LP</td>
</tr>
<tr>
<td>Manganese</td>
<td>99</td>
</tr>
<tr>
<td>Iron</td>
<td>93</td>
</tr>
<tr>
<td>Cobalt</td>
<td>90</td>
</tr>
<tr>
<td>Nickel</td>
<td>100</td>
</tr>
<tr>
<td>Copper</td>
<td>96</td>
</tr>
<tr>
<td>Zinc</td>
<td>78</td>
</tr>
<tr>
<td>Cadmium</td>
<td>99</td>
</tr>
<tr>
<td>Lead</td>
<td>97</td>
</tr>
</tbody>
</table>

Therefore:

for Laponite RD filtercake (LP) the order of preference is

$$\text{Ni}^{2+} > \text{Cd}^{2+} = \text{Mn}^{2+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Fe}^{3+} > \text{Co}^{2+} > \text{Zn}^{2+},$$

with all ions removed at a level greater than 75%.
For Laponite RD filtercake modified with CTMACl (LS) the order of preference is

\[ \text{Cd}^{2+} = \text{Pb}^{2+} > \text{Zn}^{2+} > \text{Fe}^{3+} > \text{Cu}^{2+} > \text{Mn}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+}, \]

with all ions removed at a level greater than 20%.

For hectorite KP (KP) the order of preference is

\[ \text{Cd}^{2+} = \text{Cu}^{2+} = \text{Fe}^{3+} = \text{Mn}^{2+} = \text{Ni}^{2+} = \text{Zn}^{2+} > \text{Pb}^{2+} > \text{Co}^{2+}, \]

with all ions removed at a level greater than 60%.

For hectorite KP modified with CTMACl (KS) the order of preference is

\[ \text{Cd}^{2+} = \text{Co}^{2+} = \text{Cu}^{2+} = \text{Ni}^{2+} = \text{Zn}^{2+} > \text{Mn}^{2+} = \text{Pb}^{2+} > \text{Fe}^{3+}, \]

with all ions removed at a level greater than 95%.

For Ikomont Ca Weiss Montmorillonite (KCW) the order of preference is

\[ \text{Co}^{2+} = \text{Cd}^{2+} = \text{Cu}^{2+} = \text{Mn}^{2+} = \text{Ni}^{2+} = \text{Pb}^{2+} = \text{Zn}^{2+} > \text{Fe}^{3+} \]

with all ions removed at a level greater than 99%.

Ikomont Ca Weiss Montmorillonite demonstrated high ion removal efficiency; removing nearly all 5 mg dm\(^{-3}\) of all eight metals. This demonstrates that ion exchange may be achieved using the batch equilibrium testing parameters outlined in Section 3.3.4. The Laponite and other hectorite materials showed lower overall efficiency than the montmorillonite. The surfactant modified Laponite showed the best selectivity, with a range of removal efficiencies for individual metals. Laponite RD filtercake showed some selectivity with lower adsorption for cobalt and zinc, but had high removal efficiency for all other metals. Except for cobalt, both hectorite KP samples removed almost all the metal ions from each solution.
Unmodified Laponite RD filtercake removes greater than 75% of all eight ions in solution, whereas the modified analogue only removes five elements above this level. With double the specific surface area and nearly three times the pore volume, it might be expected that the modified Laponite would have a higher adsorption capacity. However, if ion exchange with clay interlayer ions is the mechanism of removal, the sample with a greater concentration of exchangeable ions would be expected to be more efficient. As reported in Section 5.1.2, the interlayer sodium ions from the modified Laponite sample were exchanged for CTMA\(^+\) ions during templating, and therefore less interlayer sodium ions are available for exchange with metal ions in solution (this is discussed further in Section 6.5).

### 6.2.2: ION REMOVAL FROM MULTI-ELEMENTAL SOLUTIONS

As shown in the previous section the chosen Laponite and hectorite materials can remove high levels of metal ions from solutions containing single elements. With the exception of cobalt and nickel removal by modified Laponite, at least 60% of each element, up to 100% in many cases, of all eight metals were removed by all five smectite materials. However, contaminated samples usually contain more than one element, so how will the clay materials interact with multi-elemental solutions? Competition of the elements was analysed by further batch equilibrium testing with solutions containing all eight metals at equal concentrations.
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Figure 6.2.A: Metal ion removal trends for different clay materials from a 5 mg dm$^{-3}$ multi-elemental solution. N.B. No data was collected for Fe removal by material KP due to insufficient volume of solution.

Batch equilibrium testing with 5 mg dm$^{-3}$ multi-element solutions, shows metal ion removal preferences are more pronounced than for single metal ion solutions, Figure 6.2.A. Laponite RD, modified Laponite and montmorillonite show similar trends of preference, with high removal efficiency for iron and nickel, and low removal of cadmium. Montmorillonite shows higher overall removal; whilst, unmodified Laponite is more efficient than the modified analogue, both for each individual metal and for overall ion content. Both unmodified and modified hectorite KP show similar sorption trends to each other but are different from the other three samples; with high (almost 100%) removal of copper, zinc and lead but lower sorption of nickel. The hectorite KP samples also removed more of the overall metal content of the solution than the Laponite materials; with KS removing greater than 75% of each metal and KP greater than 65%.
### Table 6.2.II: Percentage metal ion removal from multi-element solutions by Laponite and other smectite materials

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>INITIAL CONCENTRATION / mg dm⁻³</th>
<th>METAL ION REMOVAL / %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LP</td>
<td>LS</td>
</tr>
<tr>
<td>Manganese</td>
<td>5 A</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>5 B</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>9</td>
</tr>
<tr>
<td>Iron</td>
<td>5 A</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>5 B</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Cobalt</td>
<td>5 A</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>5 B</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>Nickel</td>
<td>5 A</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>5 B</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>Copper</td>
<td>5 A</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>5 B</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>Zinc</td>
<td>5 A</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>5 B</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>ndr</td>
</tr>
<tr>
<td>Cadmium</td>
<td>5 A</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>5 B</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>2</td>
</tr>
<tr>
<td>Lead</td>
<td>5 A</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>5 B</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0</td>
</tr>
</tbody>
</table>

ndr = no data recorded.

Mixtures contain 5, 10 or 20 mg dm⁻³ each of Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn, Cr, Hg, Sn, V; except 5A which only contains the first 8 metals.
Due to the high percentages of ions removed from 5 mg dm\textsuperscript{-3} mixed metal solutions, solutions with higher concentrations were investigated. Metal ion removal from mixed metal solutions containing 5, 10 and 20 mg dm\textsuperscript{-3} of each element was determined for each of the five clay materials, percentage removal is reported in Table 6.2.II. N.B. These solutions contain chromium, mercury, tin and vanadium as well as the eight metal ions originally tested as single element solutions (except 5A which is the original mixture whose results are shown in Figure 6.2.A).

Metal ion removal results for multi-element solutions were lower than expected. Table 6.2.II shows a drop in removal efficiency between 5 mg dm\textsuperscript{-3} solutions after the addition of four new elements. Only the montmorillonite sample showed a similar level of efficiency for the two solutions. Generally, the percentage of ions removed decreases as the overall concentration of ions increases, which is to be expected. However, many of the results for Laponite and hectorite materials are very low and inconsistent i.e. some removal percentages are higher at higher concentrations. These results may indicate that batch testing has had a detrimental effect on the potential metal ion removal materials.

6.3: CLAY STRUCTURAL STABILITY

In comparison to other studies (7, 11) sorption efficiency of Laponite and hectorite samples seemed quite low. In acidic media clay structure can be altered or even destroyed, through dealumination or in the case of hectorites delithiation (12). Although synthetic metal solutions were not deliberately acidified, the stock standards from which these solutions were made were acidic, Table 3.3.1. Determination of pH showed that the multi-element solutions were originally strongly acidic: 5 mg dm\textsuperscript{-3}: pH = 1.95; 10 mg dm\textsuperscript{-3}: pH = 1.73 and 20 mg dm\textsuperscript{-3}: pH = 1.37. Clay samples were, therefore, analysed by powder XRD after batch testing to assess if damage was caused by the acidic nature of the metal solutions.
Comparison of an as-synthesized sample of hectorite KP and samples which have been subject to batch equilibrium testing shows some notable similarities. The $hkk\theta$ peaks of $d_{020,110}$ and $d_{130,200}$ appear at $2\theta \approx 20^\circ$ and $2\theta \approx 35^\circ$ for all samples in Figure 6.3.A., clearly indicating that order remains within the layers. Movement in the lower angle region of the profiles shows that the compound’s stacking distance has been reduced. The acidic nature of the synthetic solutions has clearly affected the porous network within hectorite KP.
Figure 6.3.B: Powder XRD profiles of hectorite KP (a) acid soaked and (b) after batch testing with a multi-elemental mixture of 20 mg dm$^{-3}$ per metal. The acid soaked sample was spiked with NaCl (s) as an internal standard; the $d_{200}$ and $d_{220}$ peaks of this compound are present in profile (a).

Figure 6.3.A shows that exposure to acidic solutions reduced the interlayer spacing of hectorite KP. The clay layers themselves appeared not to be totally disrupted, as the $hk0$ peaks of $d_{020,110}$ and $d_{130,200}$ that appear at $2\theta \approx 20^\circ$ and $2\theta \approx 35^\circ$ were still present for all samples. The greatest change occurred for the 20 mg dm$^{-3}$ solution, with a significant shift to higher angles for $d_{100}$. When contrasted to an acid soaked sample of hectorite KP, Figure 6.3.B, however, the batch tested sample was not completely destroyed. XRD profile (a) in Figure 6.3.B represents the destruction of hectorite KP after being refluxed overnight in a 1M HCl in ethanol solution. The $hk0$ peak $d_{130,200}$ is not present, although a broad peak may be observed at $2\theta \approx 20^\circ$, suggesting $d_{020,110}$ is still present.
Comparison of XRD profiles in Figure 6.3.B indicates that partial destruction of the clay layers, probably through delithiation, has occurred for the acid soaked sample. The short contact time during batch testing has led to less extensive damage of hectorite KP. The layers of this sample are still intact but the porosity has been reduced.

Figure 6.3.C shows that Laponite RD filtercake also remains intact after batch testing. The \( hkl \) peaks are broader but have not been destroyed. Changes to the interlayer spacing of this compound, appear less significant than for hectorite KP. The apex of the \( d_{001} \) peak has not significantly shifted, although it is much broader than for the untreated sample.

**Figure 6.3.C**: Powder XRD profiles of Laponite RD filtercake (a) as-synthesized and (b) after batch testing with a multi-elemental mixture of 5 mg dm\(^{-3}\) per metal. The as-synthesized sample was spiked with NaCl \( (s) \) as an internal standard; the \( d_{200} \) and \( d_{220} \) peaks of this compound are present in profile (a).
Contrasting Laponite RD and hectorite KP after batch testing with a 5 mg dm$^{-3}$ multi-element solution, Figure 6.3.D, shows very little difference between the samples. In fact these powder XRD profiles show greater similarities between the two samples than those of untreated materials in Figure 4.2.B. In Chapter 4 as-synthesised hectorite KP was compared to Laponite RD, the powder XRD profiles of the two samples were similar for $hkl$ peaks but the $d_{001}$ peak was much clearer for Laponite RD.

**Figure 6.3.D:** Powder XRD profiles of (a) Laponite RD filtercake and (b) hectorite KP after batch testing with a multi-elemental mixture of 5 mg dm$^{-3}$ per metal.
6.4: Metal Ion Removal from Contaminated Water

Batch testing of materials with synthetic solutions containing known components at known concentrations has provided interesting results. Ion removal efficiencies from single element solutions were high, with the exception of cobalt and nickel removal by modified Laponite RD, in excess of 60% of each element was removed from solution by all five smectite clays. This efficiency decreased when overall metal ion concentrations were increased by introducing multi-element solutions. This decrease in efficiency has in some part been attributed to the acidic nature of the synthetic batch testing solutions, which has caused reductions in the clay samples' porosity. However, environmental applications for ion-exchangers and molecular sieves are not expected to have such low acidity levels.

Industrial and environmental applications are usually full of unknown species including organic compounds and even flora and fauna, which also interact with both the metal ions in solution and the adsorbents themselves. Therefore a variety of "natural" unknowns were introduced to a metal filled synthetic solution by the addition of water from the local University lake.

6.4.1: Solution Composition

As described in Section 3.3.3, solution L was created from a variety of scrap metal found in the laboratory, which was dissolved in acid and diluted with local lake water.
As can be seen in Table 6.4.1, the concentrations of some elements were high, many in excess of 100 mg dm$^{-3}$ for solution L. Due to the decrease in percentage removal of elements at concentrations lower than 20 mg dm$^{-3}$ it was felt that any removal of metal ions from this solution would be so low as to be negligible in comparison to overall elemental content. Therefore, solution LA was further diluted with more lake water, before batch testing was carried out.

Table 6.4.11 shows that the dilution of solution L reduced most of the metal ion concentrations below practical detection limits, cadmium, nickel and zinc have concentrations at high enough levels to determine removal efficiency from the synthetic metal ion solution LA II.
TABLE 6.4.II: Metal ion concentrations and pH of synthetically contaminated solutions.

<table>
<thead>
<tr>
<th>COMPOSITION</th>
<th>CONCENTRATION / mg dm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LA II</td>
</tr>
<tr>
<td>MANGANESE</td>
<td>0.60</td>
</tr>
<tr>
<td>IRON</td>
<td>&lt; 0.5</td>
</tr>
<tr>
<td>COBALT</td>
<td>0.14</td>
</tr>
<tr>
<td>NICKEL</td>
<td>2.13</td>
</tr>
<tr>
<td>COPPER</td>
<td>&lt; 0.5</td>
</tr>
<tr>
<td>ZINC</td>
<td>8.25</td>
</tr>
<tr>
<td>CADMIUM</td>
<td>5.04</td>
</tr>
<tr>
<td>LEAD</td>
<td>0.26</td>
</tr>
<tr>
<td>pH</td>
<td>7.13</td>
</tr>
</tbody>
</table>

6.4.2: BATCH TESTING WITH SYNTHETIC CONTAMINATED SOLUTION

Table 6.4.II shows that, cadmium, nickel and zinc are the only elements at concentrations high enough to determine removal efficiency from the synthetic metal ion solution LA II. Figure 6.4.A shows that greater than 50% of each of the three metals were removed from LA II by all five clay materials. All five materials preferentially absorbed zinc and cadmium to nickel. This follows the competition trend for KP and KS that was set in Figure 6.2.A, but is contrary to the preferences shown by the three other clays which absorbed a greater percentage of nickel from the equally concentrated solution (solution 5A).
The less acidic nature of solution LA II (pH ≈ 7), with respect to the synthetic multi-element solutions (pH < 2), has allowed all five clay materials to remove high levels of all three metals. Preferential removal of the metal ion with the highest concentration in this solution has occurred. The hectorite samples have once again shown a higher overall removal, with less than 15% of all three metals remaining in solution. Conversely, Laponite RD and modified Laponite have shown more selectivity, with higher removal efficiencies for zinc and cadmium than for nickel.
6.5: Nature of Metal Ion Removal

High levels of metal ion removal were achieved by all five clay materials when batch tested with "single" element solutions and low acidity multi-element solutions. If metal removal has occurred via ion-exchange with interlayer, Na\(^+\) or Ca\(^{2+}\), or clay surface ions, these ions should be present in the post batch testing solutions.

In Section 5.1.2 the possibility of interlayer sodium ions exchanging with the bulky CTMA\(^+\) ion was discussed. Analysis of water removed by centrifugation after templating of Laponite RD, but before washing and drying of the samples, revealed that 260 mg dm\(^{-3}\) of sodium was released from a templated sample, whilst only 20 mg dm\(^{-3}\) of sodium was present in the water of a non-templated Laponite RD sample. This apparent exchange of bulky CTMA\(^+\) ions for small Na\(^+\) ions in the clay interlayer, may explain the increases in d-spacing and total pore volume found within these systems.

The extent of sodium release from each of the clay materials was determined after batch equilibrium testing was carried out using single and multi-element solutions (5 mg dm\(^{-3}\)), Table 6.5.1. Clay materials were also shaken for ten minutes in deionized water; analysis of this blank reference solution indicated that some sodium ion release was due to hydrolysis rather than ion exchange with transition metal ions.

Hydrolysis is caused by the dissociation of water

\[
2\text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{OH}^-
\]

and the exchange of cations from the ion exchange material (underlined) with hydronium ions in solution

\[
\text{A}^+ + \text{H}_3\text{O}^+ \rightarrow \text{H}_2\text{O}^+ + \text{A}^+
\]
Hydrolysis causes interferences to ion-exchange in two ways. It leads to fewer exchange sites being available for the target ion to interact with and a change in the pH of the solution will occur. This latter effect can lead to degradation of the ion exchange material and precipitation of metal ions in solution.

**Table 6.5.1:** Concentration of sodium released into aqueous solution when materials were equilibrium batch tested with 5 mg dm$^{-3}$ mixed metal ion solution.

<table>
<thead>
<tr>
<th>5 mg dm$^{-3}$ SOLUTION OF:</th>
<th>CONCENTRATION OF Na$^+$ RELEASED / mg dm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LP</td>
</tr>
<tr>
<td>**BLANK ***</td>
<td>21.0</td>
</tr>
<tr>
<td><strong>MANGANESE</strong></td>
<td>18.1</td>
</tr>
<tr>
<td><strong>IRON</strong></td>
<td>24.6</td>
</tr>
<tr>
<td><strong>COBALT</strong></td>
<td>25.8</td>
</tr>
<tr>
<td><strong>NICKEL</strong></td>
<td>20.7</td>
</tr>
<tr>
<td><strong>COPPER</strong></td>
<td>23.0</td>
</tr>
<tr>
<td><strong>ZINC</strong></td>
<td>20.7</td>
</tr>
<tr>
<td><strong>CADMIUM</strong></td>
<td>21.6</td>
</tr>
<tr>
<td><strong>LEAD</strong></td>
<td>21.8</td>
</tr>
<tr>
<td><strong>MIX #</strong></td>
<td>50.6</td>
</tr>
</tbody>
</table>

* No metals present in solution.

# Mixture of 5 mg dm$^{-3}$ each of Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn.

ndr = no data recorded due to insufficient volume of solution.

Ion-exchange with interlayer sodium ions has previously occurred with CTMA$^+$ ions for surfactant modified Laponite and hectorite samples, therefore further exchange is unlikely with metal ions in solution. This is confirmed by Table 6.5.1 which shows very low release concentrations (< 1 mg dm$^{-3}$ for single element solutions) of sodium for the modified clay materials. XRF data, in Section 4.2.1, indicates that hectorite KP has low levels of sodium within its structure and therefore ion-exchange of this ion is also unlikely for this material.
A small amount of this ion is available for exchange in unmodified hectorite KP but it is very similar to the concentration released into a metal “free” solution as a result of hydrolysis. Further analysis of solutions post batch testing may determine whether ion-exchange has occurred with Mg$^{2+}$ or Li$^+$ from the surface or interior layers of the clay. Alternatively, the high metal ion removal levels observed for single element solutions may occur by surface complexation with OH$^-$ groups at the edges of the clay sheets\(^{(13)}\).

Unmodified Laponite RD and montmorillonite samples have released greater concentrations of sodium ions in the presence of multi-element solutions. Higher overall concentrations of metal ions (40 mg dm$^{-3}$ for a solution containing 5 mg dm$^{-3}$ of each of the eight elements) in mixed solutions have led to higher releases of sodium ions. This indicates that ion-exchange with interlayer clay ions has occurred within these samples.

**6.6: SUMMARY**

Five clay compounds were tested for cation removal efficiency with respect to 8 metal ions (manganese, iron, cobalt, nickel, copper, zinc, lead and cadmium) in solution:

- Laponite RD (filtercake) [LP];
- Laponite RD modified with the surfactant CTMACl [LS];
- hectorite KP as-synthesised in the autoclave [KP];
- hectorite KP modified with the surfactant CTMACl [KS] and
- montmorillonite clay IKOMONT Ca-Weiss (IKO Minerals, Marl) [KCW].
With the exception of cobalt and nickel removal by modified Laponite, all five samples were able to remove at least 60% of each element, up to 100% in many cases, of all eight metals from 5 mg dm$^{-3}$ single element solutions by all five clay materials. Montmorillonite and modified hectorite KP removed the majority (> 95%) of all eight metals from single element solutions. Unmodified hectorite KP, also removed the majority (> 98%) of all elements except cobalt (60%). Unmodified Laponite removed greater than 90% of all eight metals, except zinc (78%), from single element solutions. Whilst surfactant modified Laponite showed the best selectivity, with a range of removal efficiencies for individual metals. Cadmium, lead and zinc were favourably removed (> 90% removal of each metal) by this clay sample, whilst cobalt was least efficiently removed (< 25%). The high removal efficiency of hectorite KP, with respect to Laponite RD, may be due to the smaller particle size of hectorite KP. Malliou et al demonstrated that the uptake of lead and cadmium ions by the zeolite clinoptilolite was increased when the particle size of the natural zeolite was decreased (14).

Competition between metal ions was subsequently assessed, through batch testing with multi-element mixtures. Initial tests with 5 mg dm$^{-3}$ per metal mixed solutions showed that the Laponite materials appeared to be more selective than their hectorite KP analogues. Iron (> 60%) and nickel (> 50%) ions were favourably removed from solution by both unmodified and modified Laponite, with montmorillonite demonstrating a similar order of preference. Hectorite KP samples removed more of the overall metal content of the solution than their Laponite counterparts, with the modified sample removing greater than 75% of each metal and the unmodified hectorite removing greater than 65%.
Hectorite samples differed from Laponite ones by preferring not to remove nickel ions, however all five clay materials showed a low affinity for cadmium ions. In single element solutions, all five clay materials removed almost 100% of cadmium ions, but in a competitive solution it was the least favoured ion for unmodified and modified Laponite and montmorillonite materials whilst only nickel was less favoured by modified hectorite KP.

There are several reasons for competition between ions during exchange and the selectivity of an exchange material. The effect of counter ion charge; usually ions with higher charge are preferentially removed e.g. $\text{Fe}^{3+} > \text{Fe}^{2+}$. The extent of ionic solvation; ions with small solvation radii are preferred as less swelling within the porous network is caused within the exchange material. Size of ions without solvation may also lead to exclusion due to the porosity of an exchange material and its subsequent sieving properties. Ions may also be preferentially absorbed due to specific interactions with surface ion groups or less effectively removed due to interactions with other ions present in the equilibrium solution. The selectivity of one ion may also improve if another is removed from solution i.e. by precipitation. The removal of cadmium from aqueous solution has been reported in the literature $^{3, 15}$. In several studies cadmium was removed at high levels when not in competition, but lead and zinc were both preferentially removed from multi-element solutions $^{16-17}$.

Metal ion removal efficiencies from single element and initial 5 mg dm$^{-3}$ metal mixture solutions were compared for modified and unmodified samples, for both Laponite RD and hectorite KP. For hectorite KP there is only one notable difference between the metal ion removal efficiencies of modified and unmodified samples from single element solutions;
the modified clay removed all 5 mg dm$^{-3}$ of cobalt from solution whilst the unmodified hectorite KP only removed 60% of this ion. For the 5 mg dm$^{-3}$ multi-element solution, the modified hectorite material is the more efficient sample. With double the specific surface area and nearly three times the pore volume, it might be expected that the modified Laponite would have a higher adsorption capacity than the unmodified analogue. This was not the case. Unmodified Laponite RD filtercake removes greater than 75% of all eight ions in solution, whereas the modified analogue only removes five elements above this level. If, however, ion exchange with clay interlayer ions is the mechanism of removal, the sample with a greater concentration of exchangeable ions would be expected to be more efficient. As previously reported, the interlayer sodium ions from the modified Laponite sample were exchanged for CTMA$^+$ ions during templating, therefore less sodium interlayer ions are available for exchange with metal ions in solution. An alternative source of exchange is produced during calcination; the decomposition of templates leaves charge compensating proton species in the mesoporous calcined product (18). These protons are then available for ion exchange.

For multi-element solutions, at higher concentrations, the percentage of ions removed generally decreases as the overall concentration of ions increases, which is to be expected, due to greater competition between ions. However, some of the results for Laponite and hectorite materials were inconsistent i.e. some removal percentages are higher at higher concentrations. These results suggest that batch testing has had a detrimental effect on the potential ion-exchange materials, perhaps the clay structure was damaged in some way.
The acidic nature of the multi-element batch testing solutions (pH < 2) used in this study appears to have adversely affected the structure of the clay materials. Powder XRD analysis of hectorite KP samples pre- and post-batch testing shows that the \( hko \) peaks remain constant suggesting that clay layers have remained intact. Comparison with an acid soaked sample shows that short contact times with the synthetic solutions did not lead to extensive delithiation. Partial collapse of the interlayer space seems likely; \( d_{001} \) may still be observed, although it has shifted to higher angles and hence smaller \( d \)-spacings for hectorite KP samples. Powder XRD profiles of Laponite RD samples also show intact clay layers with damage restricted to interlayer spacings. Porosity analysis is required to confirm a reduction in porosity, but XRD results suggest that this is the likely cause of reduced sorption efficiency from the clay samples.

Batch testing of the removal of metal ions from a synthetic contaminated water solution by clay samples was also carried out. Solutions of unknown composition were created from metallic waste and diluted with lake water to introduce additional unknown species. Original solutions had very high metal ion concentrations, due to the decrease in percentage removal of elements at concentrations lower than 20 mg dm\(^{-3}\) it was felt that any removal of metal ions from these effluents would be so low as to be negligible in comparison to overall elemental content.
After further dilution, batch testing continued with the less concentrated, neutral, metal solution, LA II. This solution was used to determine metal ion removal efficiencies for cadmium, nickel and zinc by all five clay materials. Preferential sorption of the metal with the highest concentration in this solution occurred. Hectorite clays once again showed a higher overall sorption, removing over 85% of all three metals in solution. Conversely, Laponite RD and modified Laponite showed more selectivity than hectorite samples; cadmium and zinc ions were preferentially removed before nickel ions.

High levels of metal ion removal were achieved by all five clay materials when batch tested with “single” element solutions and low acidity multi-element solutions. If metal ion removal has occurred via ion-exchange with interlayer, Na\(^{+}\) or Ca\(^{2+}\), or clay surface ions, these ions should be present in the post batch testing solutions.

Ion-exchange with interlayer sodium ions has previously occurred with CTMA\(^{+}\) ions for surfactant modified Laponite and hectorite samples, therefore further exchange was unlikely between interlayer sodium ions and metal ions in solution. This was confirmed by AAS which showed very low release concentrations (< 1 mg dm\(^{-3}\) for single element solutions) of sodium for the modified clay materials. XRF data indicated that hectorite KP had low levels of sodium within its structure and therefore ion-exchange of this ion was unlikely for this material. A small amount of this ion is available for exchange in unmodified hectorite KP but it is very similar to the concentration released into a metal “free” solution as a result of hydrolysis. Further analysis of solutions post batch testing may determine whether ion exchange has occurred with Mg\(^{2+}\) or Li\(^{+}\) from the layers of the clay. Alternatively, the high metal ion removal levels observed for single element solutions may occur by surface complexation with OH\(^{-}\) groups at the edges of the clay sheets.\(^{(13)}\)
Unmodified Laponite RD and montmorillonite samples have released greater concentrations of sodium ions in the presence of multi-element solutions. Higher overall concentrations of metal ions (40 mg dm$^{-3}$ for a solution containing 5 mg dm$^{-3}$ of each of the eight elements) in mixed solutions have led to greater releases of sodium ions. This indicates that ion-exchange has occurred within these samples.
REFERENCES


CHAPTER 7

CONCLUSIONS AND FUTURE WORK
CHAPTER 7:

CONCLUSIONS AND FUTURE WORK

The aim of this study was to enhance the textural properties of the synthetic hectorite clay Laponite, relative to commercial Laponite RD samples provided by Rockwood Additives Ltd, without the introduction of aluminium into the system and in particular to increase the specific surface area, total pore volume and modal mesopore diameter. In 1992 Mobil Research and Development Corporation produced the first family of ordered mesoporous molecular sieves, M41S \(^{(1-2)}\). The basis of their synthesis was the liquid crystal templating of a silica source with an organic surfactant. As clay is primarily a substituted silicate the question arises "Why not apply the same principles to enhancing the textural properties of Laponite?"

For this study the appropriate choice of template, reagent concentrations, synthesis protocol and template removal strategy has led to increases in the targeted textural properties of Laponite-like materials. The characteristics of these tailored materials were determined via nitrogen sorption porosimetry, X-ray powder diffraction (XRD), X-ray fluorescence analysis (XRF), Fourier transform infrared spectroscopy (FT-IR), elemental microanalysis, thermogravimetry (TG), solid-state magic-angle-spinning nuclear magnetic resonance spectroscopy (MAS-NMR), and scanning electron microscopy (SEM).

In addition to porosity studies, the metal ion removal capabilities of a selection of Laponite-like materials were assessed. Atomic absorption spectrometry determined metal ion concentrations of solutions pre- and post- batch testing with the chosen clays. Powder XRD studies detected structural changes within the clays, caused by the acidic nature of the metal ion solutions.
7.1: Overall Conclusions

The greatest improvement in porosity achieved within this study was through modification of pre-synthesized Laponite RD filtercake with the block co-polymer Tween 85. The pore volume increased from 0.23 cm$^3$ g$^{-1}$ to 0.94 cm$^3$ g$^{-1}$; the specific surface area increased from 270 m$^2$ g$^{-1}$ to 490 m$^2$ g$^{-1}$; the modal pore diameter increased from 37 Å to 52 Å.

Initially, reference points were determined via characterization of parent materials. Analysis of Laponite RD, in both powdered and filtercake forms, was key in establishing the structure and nature of each sample. Once these reference points were established the nature and extent of modification through the tailoring of filtercake samples and the synthesis of new samples could be examined.

The synthesis of a Laponite-like hectorite, following the Rockwood in-house protocol, led to the production of a hectorite with decreased sodium and lithium contents (with respect to Laponite RD). Although no changes were made to the procedure, increased specific surface area and total pore volume were achieved. Powder XRD of dried and calcined samples showed that these samples were indeed synthetic hectorites. However, calcination at 1000°C highlighted differences between the chemistry, crystallinity and long-range order of these clays and the analogous Laponite RD. The hectorite synthesized in this study was designated hectorite KP.

The production of hectorite KP led to improvements in porosity characteristics with respect to Laponite RD; these changes are possibly due to scale-down changes between laboratory synthesis and Rockwood's multi-tonne manufacture of Laponite RD. A 70% increase in BET multipoint specific surface area was achieved; $S_{\text{BET}} = 360$ m$^2$ g$^{-1}$ for Laponite RD and $S_{\text{BET}} = 610$ m$^2$ g$^{-1}$ for hectorite KP, while the total pore volume rose from $0.27$ cm$^3$ g$^{-1}$ for Laponite RD to $0.44$ cm$^3$ g$^{-1}$ for hectorite KP.
Comparison with alternative methods of tailoring, such as pillaring of Laponite filtercake samples with the aluminium Keggin ion ([Al₁₃O₄(OH)₂₄(H₂O)₁₂]⁷⁺) were also carried out. 

²⁷Al solid state MAS-NMR confirmed that pillaring with the aluminium Keggin ion had been achieved. Compared to powdered Laponite RD, pillaring led to relatively minor changes in porosity. The main advantage of pillaring was the increased order of the porous network, as demonstrated by the more vertical H₂ hysteresis loop in the N₂ adsorption/desorption isotherm.

Templating of both Laponite RD and hectorite KP led to significant increases in textural values in comparison to parent and pillared materials. Both total pore volume and specific surface area increased through restructuring by globular quaternary ions, ionic surfactants and PEO block co-polymer templates. Examples of the latter compounds (i.e. Tween 85) produced the most marked improvements. Total pore volume increased from 0.23 cm³ g⁻¹ for Laponite RD to 0.94 cm³ g⁻¹ for Laponite filtercake modified by templating with Tween 85, whilst the total pore volume of hectorite KP was increased from 0.44 cm³ g⁻¹ to 0.60 cm³ g⁻¹ using CTMACl as a template. Both samples were calcined in flowing oxygen at 450°C.

Analysis of reaction water showed that ion exchange with interlayer Na⁺ cations was the most likely method of template incorporation. Post templating with CTMACl, decanted water was shown to contain more than 100 fold the sodium ion content than for water just mixed with Laponite RD. This apparent exchange of bulky CTMA⁺ ions for small Na⁺ ions in the clay interlayer, may explain the increases in d-spacing and total pore volume found within these systems.
In contrast to previous studies of mesoporous silicas\(^{(2-4)}\), the use of swelling agents such as mesitylene and \(n\)-octane made no significant difference to the porosity of these systems. This may be due to non-incorporation of these compounds into the micellar system: non-incorporation of mesitylene into both the modified Laponite RD and hectorite KP systems was conclusively demonstrated using \(^{13}\)C solid state MAS-NMR. Analysis of these samples led to spectra similar to that of the templated samples, with no mesitylene in the synthesis method. Alkyl carbon signals relating to CTMACl were present, but no aromatic carbon signals were observed, as would be expected for mesitylene (1,3,5-trimethylbenzene) on incorporation into the clay system.

Changes in the silica content of hectorite KP also led to changes in its porosity. A 25% change in the amount of silica introduced during synthesis of hectorite KP led to a 10% change in silica:magnesium oxide ratio of the product. Increased silica content during this synthesis led to increased total pore volume and specific surface area. A 10% increase in SiO\(_2\) content led to an 18% increase in pore volume for these samples; from 0.44 cm\(^3\) g\(^{-1}\) to 0.52 cm\(^3\) g\(^{-1}\), nearly double that of Laponite RD (0.27 cm\(^3\) g\(^{-1}\)). These notable improvements were not, however, observed when combined with the templating process. A 10% increase in SiO\(_2\) content led to an 18% increase in pore volume for untemplated samples, whilst only a further 5% increase was seen when the samples were templated with the surfactant CTMACl. The introduction of a surfactant in modified hectorite synthesis led to higher pore volumes, but analogous templating of Laponite RD filtercake led to even greater porosity improvements than those achieved with a 10% increase in silica content.
Infrared spectroscopy and CHN analysis showed that the surfactant was not removed by simple heating of the compound. Flowing nitrogen gas was not aggressive enough to remove the template, whilst in some cases static air removed the majority of the surfactant rapidly but left a small percentage of carbonaceous char persistent in the pores. A variety of calcination temperatures were explored, all led to increased porosity although in the higher temperature region (600°C) partial interlayer collapse was apparent for Laponite and hectorite KP samples. Optimal conditions for template elimination were heating to a temperature of 225°C for several hours and then raising the temperature to between 450°C and 500°C in a no forced flow air environment.

The removal of metal ions from aqueous solutions by clay samples was investigated through equilibrium batch testing of a selection of Laponite-like materials. Five clay compounds were tested for metal ion removal efficiency with respect to eight metal ions in single and multi-element solutions. The five chosen smectite clays were Laponite RD (filtercake) [LP]; Laponite RD modified with the surfactant CTMACl [LS]; hectorite KP as-synthesised in the autoclave [KP]; hectorite KP modified with the surfactant CTMACl [KS] and the montmorillonite clay IKOMONT Ca-Weiss [KCW], whilst the eight metals analysed were present as manganese, iron, cobalt, nickel, copper, zinc, cadmium and lead ions.
With the exception of cobalt and nickel removal by modified Laponite, all five samples were able to remove at least 60% of each element, up to 100% in many cases, of all eight metals from 5 mg dm\(^{-3}\) single element solutions. Montmorillonite and modified hectorite KP removed the majority (> 95% per element) of all eight metals from single element solutions. Unmodified hectorite KP, also removed the majority (> 98% per element) of all elements except cobalt (60%). Unmodified Laponite removed greater than 90% of each of the metals, except zinc (78%), from single element solutions. Whilst surfactant modified Laponite showed the best selectivity, with a range of removal efficiencies for individual metals. Cadmium, lead and zinc were favourably removed (> 90% removal of each metal) by this clay sample, whilst cobalt was least efficiently removed (< 25%). The high removal efficiency of hectorite KP, with respect to Laponite RD, may be due to the smaller particle size of hectorite KP. Malliou et al demonstrated that the uptake of lead and cadmium ions by the zeolite clinoptilolite was increased when the particle size of the natural zeolite was decreased (5).

Competition between metal ions was subsequently assessed, through batch testing with aqueous multi-element mixtures. Initial tests with 5 mg dm\(^{-3}\) per metal mixed solutions showed that the Laponite materials appeared to be more selective than their hectorite KP analogues. Iron (> 60%) and nickel (> 50%) ions were favourably removed from solution by both unmodified and modified Laponite, with montmorillonite demonstrating a similar order of preference, but with greater overall efficiency of removal. Hectorite KP samples removed more of the overall metal content of the solution than their Laponite counterparts, with the modified sample removing greater than 75% of each metal and the unmodified hectorite removing greater than 65%.
Hectorite samples differed from Laponite ones by a lower affinity for nickel ions, but all five clay materials showed a low affinity for cadmium ions. In single element solutions, all five clay materials removed almost 100% of cadmium ions, but in a competitive solution it was the least favoured ion for unmodified and modified Laponite and montmorillonite materials, whilst only nickel was less favoured by modified hectorite KP. In other studies cadmium was removed at high levels when not in competition, but lead and zinc were both preferentially removed from multi-element solutions \(^{(6-7)}\).

Metal ion removal efficiencies from single element and initial 5 mg dm\(^{-3}\) metal mixture solutions were compared for modified and unmodified samples, for both Laponite RD and hectorite KP. For hectorite KP there is only one notable difference between the metal ion removal efficiencies of modified and unmodified samples for single element solutions; the modified clay removed all 5 mg dm\(^{-3}\) of cobalt from solution whilst the unmodified hectorite KP only removed 60% of this ion. For the 5 mg dm\(^{-3}\) multi-element solution, the modified hectorite material remains the more efficient sample. With double the specific surface area and nearly three times the pore volume, it might be expected that the modified Laponite would have a higher adsorption capacity than the unmodified analogue. That was not the case. Unmodified Laponite RD filtercake removes greater than 75% of all eight ions in solution, whereas the modified analogue only removes five elements above this level. If, however, ion exchange with clay interlayer ions is the mechanism of removal, the sample with a greater concentration of exchangeable ions would be expected to be more efficient. As previously reported, the interlayer sodium ions from the modified Laponite sample were exchanged for CTMA\(^+\) ions during templating, therefore less interlayer sodium ions are available for exchange with metal ions in solution.
For multi-element solutions, at higher concentrations, the percentage of ions removed generally decreases as the overall concentration of ions increases, which is to be expected, due to greater competition between ions. However, some of the results for Laponite and hectorite materials were inconsistent i.e. some removal percentages are higher at higher concentrations. These results imply that batch testing had a detrimental effect on the potential ion-exchange materials, suggesting that the clay structure was damaged.

The acidic nature of the multi-element batch testing solutions (pH < 2) used in this study appears to have adversely affected the structure of the clay materials. Powder XRD analysis of hectorite KP samples pre- and post- batch testing shows that most of the hk0 peaks remain constant suggesting that clay layers have remained intact. Comparison with an acid soaked sample shows that short contact times with the synthetic solutions did not lead to extensive delithiation. Partial collapse of the interlayer space seems likely; d_{600} may still be observed, although it has shifted to higher angles and hence smaller d-spacings for hectorite KP samples. Powder XRD profiles of Laponite RD samples also show some intact clay layers with damage restricted to interlayer spacings. Porosity analysis would be required to confirm a reduction in porosity, but XRD results suggest that this is the likely cause of reduced sorption efficiency from the clay samples.

High levels of metal ion removal were achieved by all five clay materials when batch tested with "single" element solutions and low acidity multi-element solutions. If metal ion removal has occurred via ion-exchange with interlayer, Na^+ or Ca^{2+}, or clay surface ions, these ions should be present in the post batch testing solutions. Ion-exchange with interlayer sodium ions previously occurred with CTMA^+ ions for surfactant modified Laponite and hectorite samples, therefore further exchange was unlikely with metal ions in solution.
This was confirmed by AAS, which showed very low release concentrations (< 1 mg dm$^{-3}$ for single element solutions) of sodium for the modified clay materials. XRF data indicated that hectorite KP had low levels of sodium within its structure and therefore ion-exchange of this ion was unlikely for this material. A small amount of this ion is available for exchange in unmodified hectorite KP but it is very similar to the concentration released into a metal “free” solution as a result of hydrolysis. Further analysis of solutions post batch testing may determine whether ion exchange has occurred with Mg$^{2+}$ or Li$^+$ from the layers of the clay. An alternative source of exchange is produced during calcination; the decomposition of templates leaves charge compensating proton species in the mesoporous calcined product (8). These protons are then available for ion exchange. Alternatively, the high metal ion removal levels observed for single element solutions may occur by surface complexation with OH$^-$ groups at the edges of the clay sheets (9).

Unmodified Laponite RD and montmorillonite samples have released greater concentrations of sodium ions in the presence of multi-element solutions. Higher overall concentrations of metal ions (40 mg dm$^{-3}$ for a solution containing 5 mg dm$^{-3}$ of each of the eight elements) in mixed solutions have led to greater releases of sodium ions. This indicates that ion-exchange has occurred within these samples.

Batch testing of the removal of metal ions from a synthetic contaminated water solution by clay samples was also carried out. Solutions of unknown composition were created from metallic waste and diluted with lake water to introduce additional unknown species. Original solutions had very high metal ion concentrations, due to the decrease in percentage removal of elements at concentrations lower than 20 mg dm$^{-3}$; it was felt that any removal of metal ions from these effluents would be so low as to be negligible in comparison to overall elemental content.
After further dilution, batch testing continued with the less concentrated, neutral, metal solution LA II. This solution was used to determine metal ion removal efficiencies for cadmium, nickel and zinc by all five clay materials. Preferential sorption of the metal with the highest concentration in this solution occurred. Hectorite clays once again showed a higher overall sorption, removing over 85% of all three metals in solution. Conversely, Laponite RD and modified Laponite showed more selectivity than hectorite samples; cadmium and zinc ions were preferentially removed before nickel ions.

Studies by Pitcher (10) showed that, although clays have good sorption properties, their small particle size renders them impractical for applications such as sieves in detention ponds and industrial effluent treatment systems. However, the significant increases achieved for pore volume and surface area may make modified Laponite RD and hectorite KP suitable for other industrial applications such as catalyst supports or molecular sieves.

In summary, this study has shown that the porosity of Laponite RD and laponite-like hectorites may be enhanced with the use of organic templates. Cationic templates such as the surfactant CTMACl have increased the pore volume of both Laponte RD and hectorite KP, through ion-exchange with interlayer sodium ions. Larger non-ionic templates have led to even greater increases in porosity of these smectite materials, although the mechanism for this phenomenon is less clear.
7.2: Future Work

As with all research, future work may be undertaken to increase understanding of results already achieved.

❖ Studies with templates larger than Tween 85 could be carried out to determine the upper limit of increasing the textural properties of Laponite RD and other hectorites.

❖ Synthesis of hectorite KP with differing batch sizes could be carried out to investigate whether scaling down the procedure caused the observed differences in structure, composition and textural properties with respect to Laponite RD.

❖ Further characterization of clay materials after batch testing would determine the extent of destruction caused by acidic conditions. Powder XRD of unmodified Laponite RD and hectorite KP, post batch testing, indicated that clay layers were essentially still intact but that interlayer spaces had been affected by low pH solutions, thus reducing the porosity of the materials. To confirm that a reduction in porosity had occurred N₂ gas adsorption studies could be carried out to quantify any changes to textural properties. Powder XRD and N₂ gas adsorption studies should also be carried out for surfactant-modified clay materials to determine if these compounds are more or less stable in acidic conditions.

❖ Characterization of materials by SEM-EDAX, XRF and MAS-NMR could indicate whether ion-exchange has occurred. These analytical techniques could assess metal positions and percentage present in clay materials.
❖ The low pH of synthetic laboratory prepared metal ion solutions used in batch testing appears to have adversely affected the metal ion removal capabilities of Laponite-like materials. To determine whether the high ion removal efficiencies achieved for single element solutions can be repeated for higher ion concentrations and multi-elemental solutions, buffering of ion solutions at higher pH before batch testing could be carried out. This should reduce the effect of delithiation and magnesium loss and give a clearer idea of the nature of metal ion removal.

If buffering of solutions improves metal ion removal efficiencies for multi-element solutions with high concentrations, a suitable application for the samples should be identified. Factors which will effect the use of these synthetic clays in environmental clean up include particle size, reusability, and reactions with road salt.

❖ Atomic force microscopy could be employed to determine actual particle dimensions.
❖ Cyclic batch testing of clay compounds could be used to assess reusability; after ion-exchange has occurred, metal ions may be removed and then the exchange process repeated i.e. hydrotalcite may be repeatedly used for chromium removal; regeneration of the exchange material was achieved with the addition of sodium hydroxide[11].
❖ Batch equilibrium studies between clay compounds and metal ion solutions with added NaCl could be carried out to simulate the effect of road salt on metal ion removal efficiencies.
7.3: Error and Uncertainty within this Study

As with all experimental data, errors were inherent in this project. These errors may be due to synthesis inconsistencies or limits of detection of instrumentation. Table 7.1.1 shows the textural data for 5 batches of hectorite KP, all values are reported to 2 significant figures.

Table 7.1.1: Textural data for different synthesis batches of hectorite KP.

<table>
<thead>
<tr>
<th>Batch</th>
<th>BET Specific Surface Area / m² g⁻¹</th>
<th>Total Pore Volume / cm³ g⁻¹</th>
<th>Modal Mesopore Diameter / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>500</td>
<td>0.64</td>
<td>41</td>
</tr>
<tr>
<td>2</td>
<td>510</td>
<td>0.66</td>
<td>35</td>
</tr>
<tr>
<td>3</td>
<td>510</td>
<td>0.63</td>
<td>35</td>
</tr>
<tr>
<td>4</td>
<td>510</td>
<td>0.66</td>
<td>34</td>
</tr>
<tr>
<td>5</td>
<td>500</td>
<td>0.64</td>
<td>39</td>
</tr>
<tr>
<td>Average</td>
<td>510</td>
<td>0.65</td>
<td>37</td>
</tr>
</tbody>
</table>

From these data errors may be estimated for BET specific surface area as ± 10 m² g⁻¹; for total pore volume as ± 0.02 cm³ g⁻¹; and for modal mesopore diameter as ± 5 Å.

Original AAS data for single element solutions was run on a Perkin Elmer 5000 atomic adsorption spectrophotometer. Absorption data was collected in triplicate, averaged and then converted into concentration measurements. Each sample was carried out in duplicate, therefore data was averaged again for reporting. Absorption data was accurate to ± 0.005, therefore concentration data was dependant on the conversion factor but ranged between ± 0.07 ppm for zinc and ± 0.90 ppm for nickel. Later analyses were also carried out in triplicate by the Perkin Elmer Analyst 400 atomic adsorption spectrophotometer, but conversion to concentration was carried out directly by the software.
REFERENCES


APPENDIX I:

TEMPLATE FORMULAE
AND STRUCTURES
Template Formulae and Structures

Cetyltrimethylammonium chloride (CTMACl):

\[
\text{CH}_3 \quad \text{N} \quad \text{CH}_3
\]

Cetyltrimethylammonium bromide (CTMABr):

\[
\text{CH}_3 \quad \text{N} \quad \text{CH}_3
\]

Tetrabutylammonium bromide (TBABr):

\[
\text{C}_4\text{H}_9 \quad \text{N} \quad \text{C}_4\text{H}_9
\]

Tetramethylammonium bromide (TMABr):

\[
\text{CH}_3 \quad \text{N} \quad \text{CH}_3
\]

Methylammonium chloride (MACl):

\[
\text{H}_3\text{C} \quad \text{N} \quad \text{NH}_3
\]
Polyoxyethylene (4) lauryl ether (Brij 30):

\[ C_{12}H_{25}(OCH_2CH_2)_4OH \]

Polyoxyethylene (23) lauryl ether (Brij 35):

\[ C_{12}H_{25}(OCH_2CH_2)_{23}OH \]

Polyoxyethylene (20) stearyl ether (Brij 78):

\[ C_{18}H_{37}(OCH_2CH_2)_{20}OH \]

Polyoxyethylene (20) sorbitan monopalmitate (Tween 40):

\[ w + x + y + z = 20 \]

Polyoxyethylene (20) sorbitan trioleate (Tween 85):

\[ w + x + y + z = 20 \]
APPENDIX II:

SOLID STATE MAS-NMR ORIGINAL SPECTRA
**Figure II.A:** $^{29}\text{Si} \text{MAS-NMR of Laponite RD.}$

$(\text{CH}_3)_4\text{Si}$ as reference standard.
**Figure II.B:** $^{29}\text{Si}$ MAS-NMR of Laponite RD filtercake (dried at 70°C).

(CH$_3$)$_4$Si as reference standard.
**Figure II.C:** $^{29}\text{Si}$ MAS-NMR of Laponite RD filtercake (calcined at 450°C).

$(\text{CH}_3)_4\text{Si}$ as reference standard.
FIGURE II.D: $^{29}$Si MAS-NMR of Laponite RD filtercake ion-exchanged with "Al$_{13}^{7+}" Keggin ion. (CH$_3$)$_4$Si as reference standard.
\textbf{Figure II.E}: $^{29}\text{Si}$ MAS-NMR of Laponite RD filtercake pillared with $^{\text{Al}}_{13}^{7+}$ Keggin ion. (CH$_3$)$_4$Si as reference standard.
FIGURE II.F: $^{29}$Si MAS-NMR of hectorite KP (oven).

$(\text{CH}_3)_4\text{Si}$ as reference standard
**Figure II.G:** $^{29}$Si MAS-NMR of hectorite KP (autoclave).

$(\text{CH}_3)_4\text{Si}$ as reference standard
Figure II.H: $^{29}$Si MAS-NMR of Laponite RD filtercake templated with CTMACl (uncalcined). $(\text{CH}_3)_4\text{Si}$ as reference standard.
**Figure III:** $^{29}$Si MAS-NMR of Laponite RD filtercake templated with CTMACl (calcined at 450°C). (CH$_3$)$_4$Si as reference standard.
Figure II. J: $^{29}$Si MAS-NMR of hectorite KP templated with CTMACl (uncalcined).

(CH$_3$)$_4$Si as reference standard.
**Figure II.K:** $^{29}$Si MAS-NMR of hectorite KP templated with CTMACl (calcined at 450°C). $(\text{CH}_3)_4\text{Si}$ as reference standard.